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Legacy and emerging halogenated organic pollutants in marine organisms from the Pearl River Estuary, South China

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HIGHLIGHTS

- Halogenated organic pollutants were investigated in marine organisms from the PRE.
- HOP concentrations in marine organisms were at global median levels.
- DDTs were the predominant contaminants in marine organisms.
- Biomagnification was observed between prey and predator fish.
- Seafood consumption is not expected to pose health risks to humans.

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ABSTRACT

A suite of legacy and emerging halogenated organic pollutants (HOPs) were measured in marine organisms (coastal fish and invertebrates) from the Pearl River Estuary, South China, to investigate the current contamination status after the Stockholm Convention was implemented in China. Dichlorodiphenyltrichloroethane and its metabolites (DDTs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) were detected in all samples at concentrations of 54–1500, 16–700, and 0.56–59 ng/g lipid weight, respectively. Dechlorane Plus (DP), decabromodiphenyl ethane (DBDPE), 2,3,5,6-tetrabromo-*p*-xylene (pTBX), and pentabromotoluene (PBT) were also found at concentrations of ND (non-detectable) to 37 ng/g lipid weight. The concentrations of these investigated contaminants in the present study were at moderate levels, as compared with those reported in other regions. Significant interspecies differences were found in the levels of DDTs, PCBs, PBDEs and the alternative halogenated flame retardants (AHFRs). DDTs were the predominant HOPs in those species and represented >50% of the total HOPs, followed by PCBs, PBDEs, and AHFRs. The total estimated daily intakes (EDIs) of DDTs, PCBs, PBDEs, and AHFRs were 28, 12, 1.0, and 0.18 (ng/kg)/d, respectively, via seafood consumption. These concentrations are not expected to pose health risks to humans.

1. Introduction

Halogenated organic pollutants (HOPs) such as dichlorodiphenyltrichloroethane (DDT) and its metabolites (DDTs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs), are extensively distributed in the environment and can pose serious risks to wildlife and humans due to their persistence, long-range transport, bioaccumulation, and toxicity. DDT has been widely used as an insecticide in agriculture, and PCBs were used historically in a variety of products such as lubricants and dielectric fluids. DDT and PCBs were banned in many countries in the 1970s and 1980s and are included in the list of the 12 initial persistent organic pollutants (POPs) by the Stockholm Convention (UNEP, 2001). PBDEs are a group of halogenated flame retardants (HFRs) that are used mainly in plastics, paints, textiles, and electronics. The penta-BDE and octa-BDE commercial formulations, which are two of the three major commercial PBDE mixtures, were withdrawn from the market in 2004 and added to the list of Stockholm Convention POPs in 2009 (Zhu et al., 2014). Following the phase-out of PBDE, the use of alternative halogenated flame retardants (AHFRs) increased, to continue to meet flammability standards. As a consequence, environmental levels of some unregulated alternative flame retardants have been on the rise around the world (Covaci et al., 2011).

As one of the fastest economically growing regions in China, the Pearl River Delta region has been subjected to serious ecological and environmental deterioration since the end of the 1970s. Many

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studies have revealed that the Pearl River Delta is one of the most DDT-polluted areas in the world, and new input sources of DDTs might be present in this region (Guo et al., 2009). PCBs and PBDEs are ubiquitous because of intensifying manufacturing, especially extensive e-waste recycling activities in the Pearl River Delta (Zhang et al., 2010).

The Pearl River Estuary, which was created by the inflow of fresh water from the large river system to the South China Sea, is a significant sink for HOPs derived from the Pearl River Delta. High levels of HOPs, including DDTs, PCBs, and PBDEs, were previously detected in both biotic and abiotic matrices in the Pearl River Estuary (Mai et al., 2005; Xiang et al., 2007; Guo et al., 2009). Several recent studies have revealed varying degrees of decreases in the levels of these chemicals in the biota from some areas of the world (Macgregor et al., 2010; Ross et al., 2013; Sericano et al., 2014). In addition, elevated levels of alternative halogenated flame retardants (AHFRs) were recently reported in marine mammals from the Pearl River Estuary due to the restrictions on the production and use of PBDE commercial mixtures (Zhu et al., 2014).

The accumulation of these HOPs in local marine organisms can have an adverse effect not only on marine organisms but also on human health via contaminated seafood. Previous investigations have demonstrated that seawater-farmed fish accumulated numerous DDTs, PCBs, and PBDEs, which reflected the high contaminant discharge from the Pearl River Delta loading in the coastal environment (Meng et al., 2007). Chinese people often prefer to consume fishery products from wild fishing rather than aquaculture. The Pearl River Estuary and its adjacent sea form an important fishing ground in China that produces tens of thousands of tons of seafood every year. Seafood consumption is one of the major routes of exposure to HOPs for humans (Binelli and Provini, 2003). However, few studies have focused on the dietary intake of HOPs via coastal wild fish and seafood consumption in this area. In particular, little information is available on the AHFR levels in marine organisms from this region.

Considering the above, various marine organisms, including coastal wild fish and invertebrates, were collected from the Pearl River Estuary, South China, and analyzed for DDTs, PCBs, PBDEs, and several of the currently used AHFRs. The aim of the present study was to investigate the current contamination status in marine organisms of this area after implementing the Stockholm Convention in China and to assess the potential health risks associated with seafood consumption by local residents of this region. Additionally, we discuss the species-specific bioaccumulation of HOPs in marine organisms.

2. Materials and methods

2.1. Sample collection

Marine organisms were caught by commercial fishers in the Pearl River Estuary (Fig. S1; "S" designates the figure in the Supplementary Materials) in October 2013. After the samples were transferred to the laboratory on ice, they were identified, and the body length and body mass were measured immediately. The designated species were selected because they are widely distributed and relatively abundant in the Pearl River Estuary and are a common food in the South China diet. The selected organisms comprised the following: Chinese herring (*Ilisha elongata*), sardine (*Sardinella jussieu*), silver pomfret (*Pampus argenteus*), tapertail anchovy (*Coilia mystus*), Bombay duck (*Harpadon nehereus*), shiba shrimp (*Metapenaeus joyneri*), sword prawn (*Parapenaeopsis hardwickii*), Japanese stone crab (*Charybdis japonica*), Asiatic hard clam (*Meretrix meretrix L.*), Manila clam (*Ruditapes philippinarum*), and squid (*Loligo tagoi*). Four to 30 individuals were pooled as a composite sample for each species, except for silver pomfret. A total of 58 composite samples and 8 silver pomfrets were obtained. Muscle tissues were freeze-dried, homogenized by a stainless steel blender, and then stored at −20 °C until analysis. Detailed information is given in Table 1.

2.2. Sample preparation and analysis

After being spiked with surrogate standards (PCBs 30, 65, and 204 for PCBs and DDTs; BDEs 77, 181, 205, and ^{13}C-BDE 209 for halogenated flame retardants), approximately 3 g (dry weight) of the samples was extracted with 200 mL hexane/dichloromethane (1/1, v/v) for 48 h. An aliquot of the extract was used to determine the lipid content by gravimetric analysis. The rest of the extract was purified with concentrated sulfuric acid (10 mL) and further cleaned on a multilayer Florisil-silica gel column (length, 30 cm; inner diameter, 10 mm) packed from bottom to top with Florisil (14 g, 3% deactivated), neutral silica (2 g, 3% deactivated), acid silica (7 g, 44% sulfuric acid), and anhydrous sodium sulfate (2 g). The extracts were eluted with 80 mL hexane followed by 60 mL dichloromethane and were further concentrated to near dryness under a gentle nitrogen flow before finally being reconstituted in 100 μL isooctane for analysis. Prior to instrumental analysis, the extract was spiked with known amounts of the recovery standards (PCBs 24, 82, and 198; BDE 118, BDE 128, 4-F-BDE 67, and 3-F-BDE 153).

The concentrations of DDTs and PCBs were determined by an Agilent 7890 GC coupled to an Agilent 5975 MS using electron ionization in the selected ion monitoring mode. HFRs, PBDEs, Dechlorane Plus (DP), decabromodiphenyl ethane (DBDPE), 2,3,5,6-tetrabromo-*p*-xylene (pTBX), and pentabromotoluene (PBT) were analyzed by an Agilent 6890 gas chromatograph equipped with an Agilent 5975 mass spectrometer in the electron capture negative ionization mode. Detailed information for the instrumental analysis is given elsewhere (Zhang et al., 2010).

2.3. Quality assurance and quality control

A procedural blank was run periodically for each batch of 10 samples; only traces of target chemicals were detected, but the levels were less than 1% of the analyzed concentration in most of the samples. Reported analyte concentrations were blank-corrected. The average recoveries were 89–97%, 76–101%, and 88–106% in the spiked blanks and 84–96%, 70–92%, and 86–110% in the matrix spiked samples for DDTs (4,4′-DDD; 4,4′-DDE; and 4,4′-DDT), 19 PCB congeners (PCB 8 to PCB 206), and 13 HFRs (BDE 28, 47, 100, 99, 154, 153, 183, and 209; syn-DP and anti-DP; DBDPE), respectively, with relative standard deviations (RSDs) < 15% ($n = 3$) for all of the target chemicals. The average recoveries of surrogate standards were 109 ± 11%, 99 ± 9%, 88 ± 9%, 90 ± 4%, 80 ± 7%, 79 ± 13%, and 87 ± 15% for PCBs 30, 65, and 204, BDEs 77, 181, and 205, and ^{13}C-BDE 209, respectively. The method detection limits (MDLs), which were set as a signal-to-noise ratio of 10, ranged from 0.002–3.0 ng/g lipid weight (lw), 0.01–0.63 ng/g lw, and 0.005–2.1 ng/g lw for DDTs, PCBs, and BFRs, respectively.

2.4. Nitrogen isotope measurement and trophic level calculation

Stable isotope analysis and trophic level calculation were done according to the method described by Yu et al. (2009). Briefly, approximately 1 mg of freeze-dried and homogenized subsample for nitrogen stable isotope analysis was wrapped in a tin capsule and then analyzed using a Flash EA 112 series elemental analyzer coupled with a Finnigan MAT ConFlo III isotope ratio mass spectrometer. Stable isotope abundance was expressed as $\delta^{15}N$ (‰), with $\delta^{15}N = (R_{sample}/R_{standard} - 1) \times 1000$, where R is the ratio

Table 1
Details of samples from the Pearl River Estuary, South China.

Species	N[a]	Body length (cm)	Body mass (g)	Lipid (%)	Trophic level	Feeding habits	Habitat
Fish							
Chinese herring (*Ilisha elongata*)	5 (25)	11–14	15–29	1.6 (1.4–3.4) [b]	3.5 (3.1–3.6)	Omnivorous	Pelagic
Sardine (*Sardinella jussieu*)	5 (28)	10–13	13–29	2.3 (1.4–2.5)	3.1 (2.7–3.2)	Planktivorous	Pelagic
Silver pomfret (*Pampus argenteus*)	8	12–18	64–190	5.3 (2.9–12)	3.3 (3.0–3.5)	Herbivorous	Mesopelagic
Tapertail anchovy (*Coilia mystus*)	11 (105)	12–20	5–28	4.1 (1.2–11)	3.4 (3.1–3.6)	Omnivorous	Mesopelagic
Bombay duck (*Harpadon nehereus*)	9 (57)	14–22	13–76	0.45 (0.34–1.5)	3.7 (3.2–4.1)	Carnivorous	Mesopelagic
Shrimp							
Shiba shrimp (*Metapenaeus joyneri*)	4 (120)	3–5	2–8	0.92 (0.88–0.96)	3.0 (2.8–3.2)	Omnivorous	Benthic
Sword prawn (*Parapenaeopsis hardwickii*)	6 (180)	4–6	3–15	0.78 (0.70–0.91)	3.7 (3.7–3.9)	Carnivorous	Benthic
Crab							
Japanese stone crab (*Charybdis japonica*)	4 (120)	–	8–19	0.49 (0.43–0.56)	3.2 (3.1–3.3)	Omnivorous	Benthic
Bivalve							
Asiatic hard clam (*Meretrix meretrix L.*)	6 (180)	–	18–35	0.85 (0.79–0.90)	2.2 (2.1–2.3)	Omnivorous	Benthic
Manila clam (*Ruditapes philippinarum*)	5 (150)	–	10–14	1.2 (1.0–1.2)	2.3 (2.2–2.3)	Omnivorous	Benthic
Cephalopoda							
Squid (*Loligo tagoi*)	3 (60)	–	10–71	1.3 (1.1–1.4)	3.3 (3.1–3.7)	Carnivorous	Mesopelagic

[a] Number of composite samples analyzed. Figures in brackets indicate the number of individuals collected.
[b] Median (min–max).

Table 2
Concentrations of DDTs, PCBs, PBDEs, and AHFRs (median and range, ng/g lipid weight) in marine organisms from the Pearl River Estuary, South China.

Species	DDTs[a]	PCBs[b]	PBDEs[c]	DP[d]	DBDPE	PBT	pTBX
Fish							
Chinese herring (*Ilisha elongata*)	400 (250–500)[e]	130 (100–170)	19 (5.4–45)	0.16 (0.01–11)	0.61 (0.24–2.8)	ND[f]	0.02 (0.01–0.04)
Sardine (*Sardinella jussieu*)	710 (440–1000)	570 (220–700)	38 (35–45)	1.0 (ND-1.7)	0.58 (0.21–1.2)	0.36 (0.02–0.67)	0.18 (0.11–0.45)
Silver pomfret (*Pampus argenteus*)	410 (220–1000)	190 (80–490)	8.0 (3.3–20)	0.29 (ND-3.7)	ND (ND-0.21)	2.9 (1.2–5.1)	0.32 (0.18–0.53)
Tapertail anchovy (*Coilia mystus*)	300 (150–760)	130 (62–350)	8.1 (3.1–39)	0.57 (ND-5.5)	0.04 (ND-0.34)	0.04 (0.01–0.08)	0.06 (ND-0.10)
Bombay duck (*Harpadon nehereus*)	360 (260–650)	220 (70–400)	18 (13–59)	0.93 (ND-3.18)	0.41 (0.07–2.5)	0.01 (ND-0.10)	0.06 (0.04–0.08)
Shrimp							
Shiba shrimp (*Metapenaeus joyneri*)	63 (54–72)	44 (41–49)	2.7 (1.4–9.0)	ND (ND-1.7)	3.6 (0.75–5.9)	ND	0.01 (ND-0.03)
Sword prawn (*Parapenaeopsis hardwickii*)	97 (82–130)	58 (47–78)	2.3 (1.1–4.2)	ND (ND-0.31)	3.7 (2.4–7.1)	ND	0.02 (ND-0.03)
Crab							
Japanese stone crab (*Charybdis japonica*)	910 (560–1500)	170 (140–200)	13 (11–14)	0.35 (ND-1.0)	2.3 (0.80–7.0)	0.18 (ND-0.38)	0.07 (0.03–0.09)
Bivalve							
Asiatic hard clam (*Meretrix meretrix L.*)	340 (320–360)	55 (41–60)	38 (24–43)	2.0 (0.39–13)	6.9 (5.5–15)	0.01 (ND-0.05)	0.02 (ND-0.05)
Manila clam (*Ruditapes philippinarum*)	260 (150–290)	27 (16–30)	2.5 (0.56–22)	0.95 (0.12–37)	0.78 (0.34–1.1)	0.32 (0.21–0.34)	0.03 (ND-0.07)
Cephalopoda							
Squid (*Loligo tagoi*)	120 (110–250)	94 (78–190)	16 (12–56)	5.4 (0.35–21)	0.28 (0.17–1.9)	0.01 (ND-0.11)	0.04 (0.03–0.09)

[a] Sum of 4,4′-DDD; 2,4′-DDD; 4,4′-DDE; 2,4′-DDE; 4,4′-DDT; and 2,4′-DDT.
[b] Sum of 69 selected PCB congeners (CB 20/33, 22, 28/31, 29, 32, 40, 42, 44, 52, 56, 66, 70, 71, 74, 83, 84, 87,92, 95, 99, 101,103, 105, 107, 110, 115/87, 118, 119, 128, 135, 136, 138, 141, 144, 146, 147, 149, 151, 153/132, 156, 158, 164, 170/190, 171, 172, 173, 174, 177, 178, 180/193, 183, 187, 191, 194, 195, 196, 197, 199, 203, 205, 206, 207, 208, and 209.
[c] Sum of 9 PBDE congeners (BDE 28, 47, 66, 99, 100, 153, 154, 183, and 209).
[d] Sum of concentrations of syn-DP and anti-DP.
[e] Median (min–max).
[f] Not detected.

of $^{15}N/^{14}N$. The $R_{standard}$ was based on an ammonium sulfate standard. The precision of the analytical method and instrument was approximately 0.5‰ (two standard deviations). The trophic level (TL) was calculated for each sample according to the following equation $TL_{consumer} = [(\delta^{15}N_{consumer} - \delta^{15}N_{primary\ consumer})]/3.8 + 2$, where 3.8 is the isotopic trophic enrichment factor.

2.5. Data analysis

Statistical analysis was performed with SPSS 16.0 software for windows (SPSS Inc., Chicago, IL, USA). The level of significance was set at $p = 0.05$ throughout the present study. The data were transformed using the logarithm function to obtain normal distribution. One-way analysis of variance (ANOVA) tests were used to evaluate the interspecific differences of contaminant levels.

3. Results and discussion

3.1. Residue levels

The concentrations of DDTs (sum of 4,4′-DDD; 2,4′-DDD; 4,4′-DDE; 2,4′-DDE; 4,4′-DDT; and 2,4′-DDT) in organisms ranged from 54 to 1500 ng/g lw (Table 2 and Tables S1 and S2). DDT levels varied largely among organism species, and the descending concentrations followed the order of crabs (910 ng/g lw) > fish (300–710 ng/g lw) > bivalves (260–340 ng/g lw) > cephalopods (120 ng/g lw) > shrimps (63–97 ng/g lw). The levels of DDTs in fish observed in the present study were much higher than those in fish from the marine island waters far from the inland of the South China Sea such as Yongxing Island (median range of 37–270 ng/g lw) (Sun et al., 2013) and Natuna Island, which is further afield (mean range of 8–40 ng/g lw) (Hao et al., 2014). Compared with data from other waters around the world, DDT concentrations in the present study were similar to those in fish from Negro River basin, Argentinean Patagonia (240–1400 ng/g lw) (Ondarza et al., 2014) but lower than the DDT concentrations in fish from Maggiore Lake, Northern Italy (300–4200 ng/g lw) (Bettinetti et al., 2012). In addition, the concentrations of DDTs in the bivalves considered in this study were higher than those in oysters (*Crassostrea virginica*) collected in the Gulf of Mexico (54–100 ng/g lw) (Castañeda-Chávez et al., 2011).

The PCB concentrations in marine organisms from the Pearl River Estuary ranged from 16 to 700 ng/g lw, and the highest median concentration was found in sardines, at a level 2–12 times higher than the PCB concentration in the other species (Table 2 and Tables S1 and S2). The PCB levels in the fish in this study were higher than those in fish from major coastal cities in China (13–78 ng/g lw) (Xia et al., 2012) but were one to two orders of magnitude lower than the PCB levels in fish collected in North America and Europe in recent studies, where the PCB concentrations generally ranged up to several or tens of thousands of ng/g (Bettinetti et al., 2012; Greenfield and Allen, 2013; Bodin et al., 2014). These results may indicate the overall PCB levels in this study area were at the lower end of the global range but were at the higher end of the Chinese range. One possible explanation for this observation was the limited historical usage of PCBs in China (approximately 10,000 tons between 1965 and 1974) (Xing et al., 2005). The relatively high concentrations of PCBs in marine species from the Pearl River Estuary compared with other coastal region in China may be related to the continuous release of PCBs from varieties of PCB-containing electric equipment, especially through the disposal of electronic waste (e-waste) in the region. In fact, elevated levels of PCBs have been found in a wide range of aquatic organisms from electronic waste (e-waste) recycling sites in South China (Zhang et al., 2010).

The PBDE concentrations in marine organisms from the Pearl River Estuary ranged from 0.56 ng/g lw in the Manila clam to 59 ng/g lw in Bombay duck (Table 2 and Tables S1 and S2). The median concentrations of PBDEs were the highest in the sardine (38 ng/g lw) and Asiatic hard clam (38 ng/g lw), followed by Chinese herring (19 ng/g lw), Bombay duck (18 ng/g lw), squid (16 ng/g lw), Japanese stone crab (13 ng/g lw), tapertail anchovy (8.1 ng/g lw) and silver pomfret (8.0 ng/g lw). Shiba shrimp, Manila clam, and sword prawn exhibited relatively low PBDE concentrations, with medians of 2.7 ng/g lw, 2.5 ng/g lw, and 2.3 ng/g lw, respectively. A median PBDE concentration of 148 ng/g lw was reported for silver pomfret collected from this region in 2004 (Xiang et al., 2007), which was one to two orders of magnitude higher than the PBDE concentration observed in the same species in the present study. The levels of PBDEs detected in crab in the present study were also slightly lower than the levels of PBDEs in two crabs (*Portunidae*) that were examined (median of 19 and 21 ng/g lw) from the Pearl River Estuary during 2005 and 2007 (Yu et al., 2009). These results suggested a declining trend in PBDEs in marine organisms in the area studied, which is consistent with our findings in a previous study (Sun et al., 2015). The levels of PBDEs in marine fish in the present study were higher than the levels of PBDEs from coastal cities along the eastern China coastline (1.1–5.3 ng/g lw, for 9 congeners) (Xia et al., 2011) but lower than the levels of PBDEs in fish from the Negro River basin, Argentinean Patagonia (22–870 ng/g lw, for 9 congeners) (Ondarza et al., 2014).

DP, DBDPE, PBT, and pTBX were detected in more than 50% of the samples, with median concentrations of ND-5.4 ng/g lw, ND-6.9 ng/g lw, ND-2.9 ng/g lw, and 0.01–0.32 ng/g lw, respectively (Table 2). The levels of several AHFRs were all significantly lower than the levels of PBDEs ($p < 0.05$). DP and DBDPE were generally the most dominant chemicals among AHFRs, except in the silver pomfret, and collectively accounted for more than 75% of the AHFRs investigated. To date, limited data are available on the AHFRs in wild marine species. DP concentrations in the present study were comparable to the DP concentrations in organisms collected in Lake Winnipeg and Lake Ontario, Canada (0.03–0.82 ng/g and 0.02–4.4 ng/g lw, respectively, in invertebrates and fish) (Tomy et al., 2007), but the levels of DBDPE observed in the present study were slightly higher than the reported values for DBDPE levels in fish and mussels (<MLD-1.0 ng/g lw) from Lake Winnipeg (Law et al., 2006).

3.2. Interspecies variations

Significant interspecies differences were observed in the levels of DDTs, PCBs, PBDEs and the AHFRs in the present study ($p < 0.05$). Overall, the fish species exhibited relatively higher DDT and PCB levels than shrimp, bivalves, and cephalopoda. PBDE levels in fish were in the same range as the PBDE levels in bivalves and squid but were significantly higher than the PBDE levels in shrimp. Regarding the AHFRs, relatively high concentrations of DP were found in bivalves (0.12–37 ng/g lw) and the carnivorous predator squid (0.35–21 ng/g lw). The bentonic organisms such as bivalves, crab, and shrimp also exhibited higher DBDPE levels (0.34–15 ng/g lw). Of the five fish spices, sardine had the highest body burden for DDTs, PCBs and PBDEs (Table 2 and Tables S1 and S2). Japanese stone crab showed relatively higher concentrations of DDTs (560–1500 ng/g lw, with median of 910 ng/g lw) and PCBs (140–200 ng/g lw, with median of 170 ng/g lw).

It is difficult to provide actual reasons for the above inter-species differences in HOP levels. Various factors such as habitat, feeding habit, trophic level occupied, metabolic capability for xenobiotics, and physical and chemical properties of pollutants can contribute to these species differences (Law et al., 2006; Yu et al., 2009). During the dissection, tapertail anchovy was often found in the stomach contents of Bombay duck. Thus, an actual predator/prey relationship was expected. The calculated biomagnification factors (BMFs; the ratio of average lipid-normalized concentrations between Bombay duck and tapertail anchovy) indicated that most of the PCB congeners, BDE 28, 47, 100 and 154, and DDE show biomagnification from tapertail anchovy to Bombay duck (Fig. S2). The BMFs for PCBs increased with increasing K_{OW} at $\log K_{OW} < 7.7$, and subsequently decreased with a further increase of $\log K_{OW}$. However, a negative relationship was found for PBDEs. The trophic levels occupied by the species in the present study varied from 2.2 to 3.7, and most species had similar trophic levels. Therefore, it is impossible to assess the influence of trophic level on the body burden of HOPs in different species. Additionally, the different period of growth of fish when they were collected is a confounding factor. Taking the tapertail anchovy as an example, the 105 individual samples can be divided into 11 groups based on the body length. A simple linear regression analysis indicated that the body burden of DDTs, PCBs and PBDEs (an outlier was removed) was negatively correlated with the body length ($p < 0.001$) (Fig. S3), which may be attributed to many factors such as growth dilution, spawning at a certain age and movement.

3.3. Composition profiles of HOPs

DDTs were the predominant contaminants (50–83%) in all of the marine species studied, especially in crabs and bivalves (where DDTs were >77% of the measured contaminants) (Fig. 1). PCBs also showed relatively high proportions, with contributions of 9–43% of the total HOPs investigated. The relative proportions of PBDEs were less than 10% and were higher than the relative proportions of the AHFRs in the marine species studied, except for shrimp. The

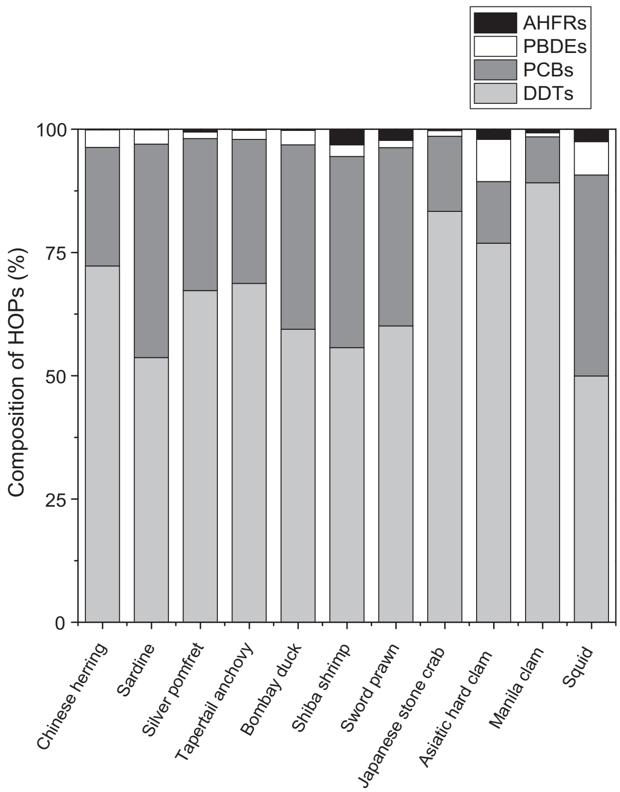

Fig. 1. Compositional pattern of HOPs in marine organisms from the Pearl River Estuary.

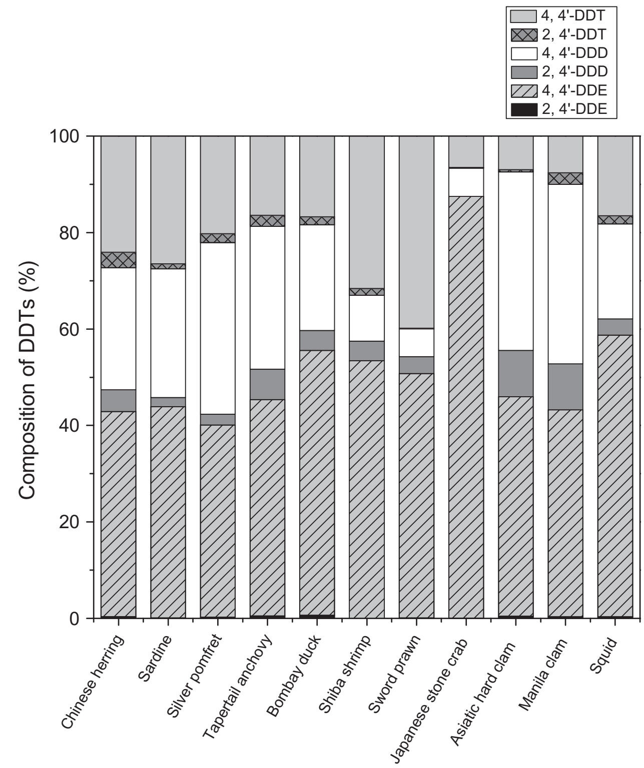

Fig. 2. Composition of DDTs in marine organisms from the Pearl River Estuary.

pattern of legacy HOPs was similar to a previous study of fish consumed in this region (Meng et al., 2007) but different from the present contaminant pattern of the PCB- and PBDE-dominant HOPs in aquatic organisms from the e-waste recycling site near the Pearl River Estuary (Zhang et al., 2010), which suggests that various contaminant sources play an important role in this region and that agrochemical sources might be more important than industrial sources.

Among the DDTs, 4,4′-DDT, 4,4′-DDD, and 4,4′-DDE were detected in all samples. Overall, 4,4′-DDE was the predominant component (at >40% of the total DDTs) in all of the marine species (Fig. 2). Five fish species and squid showed a similar DDT composition. Two bivalve species showed a higher DDD abundance (sum 2,4-DDD and 4,4-DDD) than did the other species, which can be attributed to their benthic filter feeding habits. DDTs tend to degrade to DDD under the reducing conditions in the sediment. The abundance of DDTs was significantly higher in two shrimp than in other species, which indicated that the shrimp have a lower metabolic capacity for DDT than do other species. Japanese stone crab exhibited the lowest abundance of DDT but the highest abundance of DDE among all of the marine species, which indicated that the biotransformation capacities of Japanese stone crab for DDT might be the highest among all species studied. The ratios of (DDE + DDD)/DDTs are often used to identify a recent input of DDTs; a ratio of <0.5 suggests new DDT input in the region studied (Sun et al., 2013). The ratios of (DDE + DDD)/DDTs (0.57–0.96) were >0.5 in all of the samples from the Pearl River Estuary, thus indicating that the DDTs in this region might derive mainly from historical residues instead of recent inputs, although higher residue levels were found in marine organisms. These results are consistent with the results from a previous study at an e-waste recycling site in this region (Zhang et al., 2010).

The penta-, hexa-, and hepta-PCBs were predominant in all marine species except the Manila clam, collectively constituting >60% of the total PCBs (Fig. 3). The high lipophilicity, stability, and persistence of these congeners may be responsible for their high proportions in marine organisms. However, PCB fingerprints showed the dominance of tri- and tetra-PCBs in the Manila clam (54%), consistent with the homolog profile of PCBs found in sediment from the Pearl River Estuary (Mai et al., 2005). The increasing contribution of less-chlorinated PCBs in the Manila clam may, in large part, be due to their benthic habitat. In the present study, the benthic organisms all showed higher contributions from tri- and tetra-PCBs (17–54%) than did the other species (11–16%), thus further confirming the above hypothesis that habitat is a significant factor.

Different PBDE congener patterns were observed among marine organisms (Fig. 4). In the sardine, silver pomfret, tapertail anchovy, and Japanese stone crab, BDE47 was dominant, ranging from 41% to 58% of the total PBDEs. However, BDE209 was the predominant congener (constituting >42% of the total PBDEs) in Chinese herring, Bombay duck, shiba shrimp, sword prawn, Asiatic hard clam, and squid. In the Manila clam, the most abundant component was BDE99, followed by BDE209, BDE47 and BDE183, significantly different from the other species studied. In addition, bivalves exhibited a higher ability to accumulate the highly brominated PBDE congeners: for example, BDE209 constituted 88% of the PBDE congeners in the Asiatic hard clam, and BDE183 constituted 17% of the congeners in the Manila clam. A possible explanation for this observation was that the living and feeding habits render bivalves more easily exposed to particle-bound, highly brominated congeners. Further, the metabolic abilities of species might be an important contributor to their species-specific PBDE profiles. The ratio of BDE99/BDE100 is related to debromination in organisms because BDE99 can debrominate to BDE47, whereas BDE100 is not easily debrominated (Xiang et al., 2007). The BDE99/BDE100 ratios in the Manila clam and the Asiatic hard clam were 3.9 and 2.5, which were higher than those in the other species, especially in fish (0.36–0.97), thus implying a lower debromination rate of

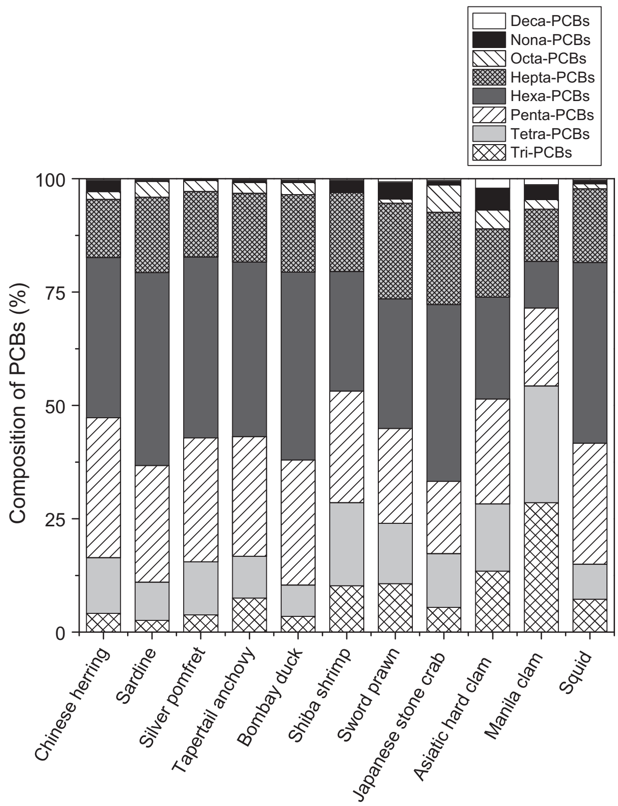

Fig. 3. Composition of PCBs in marine organisms from the Pearl River Estuary.

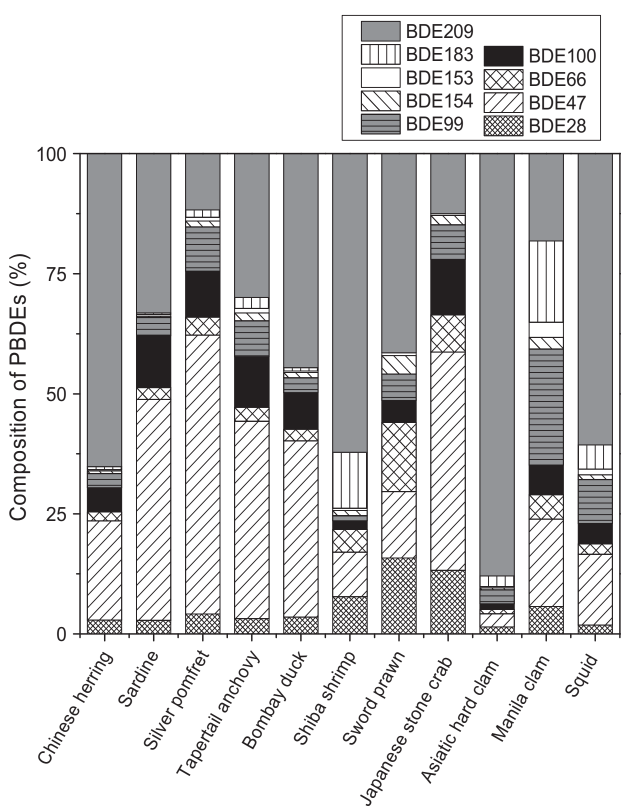

Fig. 4. Congener profile of PBDEs in marine organisms from the Pearl River Estuary.

PBDEs in these bivalve species. Thus, the weak ability to metabolize PBDEs might have resulted in higher proportions of BDE209 in the Asiatic hard clam and BDE99 and BDE183 in the Manila clam. BDE209 is the main component of deca-BDE, a commercial flame retardant with a high level of usage in the Pearl River Delta; a previous investigation indicated that BDE209 has been the dominant congener in sediments from this region (Chen et al., 2013). The relatively higher proportions of BDE209 in the present study imply that BDE209 can accumulate in wild marine organisms and that more comprehensive studies are needed on BDE209 in this region.

3.4. Human dietary exposure

The concentrations of DDTs, PCBs, PBDEs, and several AHFRs, including DP, PBT, and pTBX, based on wet weight in seafood from the Pearl River Estuary, South China, are summarized in Tables S3 and S4. Currently, China has recommended a maximum residual level (MRL) of 500 ng/g ww for DDTs and PCBs in fishery products to mitigate the health risks for human consumption (China, 2012, 2014), but no MRLs have been established for PBDEs or AHFRs. The concentrations of DDTs and PCBs in the seafood samples in the present study were all well below the MRLs set by China.

The estimated daily intake of HOPs via seafood, including DDTs, PCBs, PBDEs, and AHFRs, was calculated using the following equation: estimated daily intake (EDI; (ng/kg)/d) = daily consumption (g/d) × contaminant concentration (ng/g)/body mass (kg). The daily consumption levels of five different products (fish, shrimp, crabs, bivalves, and cephalopods) were obtained from a questionnaire-based dietary survey conducted in a Chinese coastal city (Jiang et al., 2007), and 60 kg was assumed as the average adult body mass. The average EDIs of DDTs, PCBs, PBDEs, and the AHFRs via seafood consumption were estimated to be 28 (ng/kg)/d, 12 (ng/kg)/d, 1.0 (ng/kg)/d, and 0.18 (ng/kg)/d, respectively (Table 3). The dietary intake of AHFRs via seafood has rarely been reported in the previous literature. Although the EDIs of AHFRs were low in the present study, more attention should be paid to the AHFR intake by coastal residents. Because only DP, PBT, and pTBX have been measured traditionally, a larger class of AHFRs should be investigated, over a larger region, and with a longer sampling campaign.

The EDIs of DDTs and PCBs were up to 3 orders of magnitude higher than those of other chemicals, although DDTs and PCBs have been banned for three decades. Among five biota groups, fish (over 50%) was the largest contributor to the intake of DDTs, PCBs, PBDEs and AHFRs (Table 3), which resulted from the relatively high contaminant levels and greater consumption of fish than the other biota groups (shrimp, crabs, bivalves, and cephalopods). Overall, the EDIs of these contaminants in the present study were higher than or comparable to the EDIs reported for fishery products purchased from local markets in China in previous studies (Meng et al., 2007; Guo et al., 2010; Su et al., 2012).

The EDIs of the DDTs obtained through the consumption of the studied seafood were far below the oral reference dose (RfD) of 500 (ng/kg)/d proposed by the United States Environmental Protection Agency (USEPA, 2000), and the acceptable daily intake (ADI) of 10 000 (ng/kg)/d set by the Food and Agriculture Organization and World Health Organization (FAO/WHO, 2009). The EDIs of PCBs in the present study were also below the RfD (20 (ng/kg)/d for total PCBs) proposed by the U.S. EPA (USEPA, 2000). No RfDs or ADIs

Table 3
Estimated dietary intakes of contaminants ((ng/kg)/d) in fishery products.

	Fish	Shrimp	Crab	Bivalve	Cephalopoda	Total
DDTs	20	2.4	1.3	3.7	0.09	28
PCBs	11.0	0.57	0.23	0.49	0.07	12
PBDEs	0.76	0.04	0.02	0.22	0.01	1.0
AHFRs	0.09	0.02	0.004	0.06	0.004	0.18

were available for PBDEs and AHFRs. These results indicate that seafood intake would not pose a health risk to humans, but more concern should be paid to fish consumption.

4. Conclusion

Legacy and emerging halogenated organic pollutants were determined in marine organisms from the Pearl River Estuary, South China. DDTs were found to be the predominant contaminants, followed by PCBs, PBDEs and AHFRs. The concentrations of these contaminants in the present study were at global median levels. The concentration and contaminant pattern exhibited species-specific values in marine organism, and various factors such as habitat, feeding habit, trophic level occupied, and metabolic capability for xenobiotics can contribute to these species differences. The EDIs of DDTs, PCBs, PBDEs, and AHFRs through seafood consumption suggested that consuming seafood in the Pearl River Estuary might not pose a significant health risk to local residents in China. This is the first report on the AHFR levels in marine species in the Pearl River Estuary, and more AHFRs should be investigated in a comprehensive sampling campaign in the future to update the data for effective environmental management in the region.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2015.07.044.

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