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Legacy and emerging organohalogenated contaminants in wild edible aquatic organisms: Implications for bioaccumulation and human exposure

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HIGHLIGHTS

- High levels of OHCs were found in aquatic species from the Pearl and Dongjiang Rivers.
- The two rivers reside in an industrialized and urbanized region.
- Agrochemical inputs remained a considerable source of OHCs.
- Bioaccumulation of OHCs was biological species- and compound-specific.
- Exposure of PCBs via fish consumption is a potential health concern.

GRAPHICAL ABSTRACT

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ABSTRACT

Highly industrialized and urbanized watersheds may receive various contaminants from anthropogenic activities. In this study, legacy and emerging organohalogenated contaminants (OHCs) were measured in edible wild aquatic organisms sampled from the Pearl River and Dongjiang River in a representative industrial and urban region in China. High concentrations of target contaminants were observed. The Pearl River exhibited higher concentrations of OHCs than the Dongjiang River due to high industrialization and urbanization. Agrochemical inputs remained an important source of OHCs in industrialized and urbanized watershed in China, but vigilance is needed for recent inputs of polychlorinated biphenyls (PCBs) originated from e-waste recycling activities. Bioaccumulation of dichlorodiphenyltrichloroethane and its metabolites (DDTs), hexachlorocyclohexanes (HCHs), PCBs, polybrominated diphenyl ethers (PBDEs), and Dechlorane Plus (DP) was biological species- and compound-specific, which can be largely attributed to metabolic capability for xenobiotics. No health risk was related to the daily intake of DDTs, HCHs, and PBDEs via consumption of wild edible species investigated for local residents. However, the current exposure to PCBs through consuming fish is of potential health concern.

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1. Introduction

The occurrence of organohalogenated contaminants (OHCs) in the environment has been of international concern due to their high persistency, bioaccumulation and adverse effects on both wildlife and humans (Batt et al., 2017; Domingo, 2012; Zhang et al., 2013). Organochlorine pesticides (OCPs) have historically been widely used in agriculture on a global scale. For example, China applied 0.4 million tons of technical dichlorodiphenyltrichloroethane (DDT) and 4.9 million tons of hexachlorocyclohexanes (HCHs) between the 1950s and the 1980s. Polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) had a wide range of industrial applications as dielectric and hydraulic fluids and additive flame retardant, respectively. Considering evidence of negative impact on biota, DDTs, HCHs, PCBs, and PBDEs (including the technical mixtures penta-BDE, octa-BDEs, and deca-BDE) have been regulated by the Stockholm Convention on Persistent Organic Pollutants (POPs). Notwithstanding, those chemicals have been found in high concentrations in various environmental matrices, such as sediments and soil, and foodstuffs as well as in human samples (Zhang et al., 2013). In addition, the regulatory restrictions on PBDEs have led some nonregulated halogenated flame retardants, such as decabromodiphenyl ethane (DBDPE), Dechlorane Plus (DP) and 1, 2-bis (2, 4, 6-tribromophenoxy) ethane (BTBPE), to be used as replacements in some applications. Accordingly, these alternative halogenated flame retardants (AHFRs) are increasingly being detected in both biotic and abiotic matrices all over the world (Covaci et al., 2011).

Elevated levels of contaminants in the environment are caused by industrial, urban and agricultural activities (Wei et al., 2015; Zhang et al., 2013). The Pearl River Delta is one of the most agriculturally developed, industrially advanced, and urbanization-flourished regions in China. The region has long been characterized as a potential hotspot of high levels of contaminants due to rapid economic growth and intensifying manufacturing. A range of legacy and emerging OHCs are widespread in the local environment, especially near industrial and urban areas (Sun et al., 2016; Wei et al., 2015; Zhang et al., 2013). The Pearl River and Dongjiang River are two important freshwater rivers in the Pearl River Delta, and flow respectively through Guangzhou (the capital of Guangdong province, a metropolis of southern China and integrated industrial and manufacturing center) and Dongguan (an important city of Guangdong, and a global electronics and electrical manufacturing base). Contaminants from anthropogenic activities in the rivers are associated not only with the aquatic environment but also bioaccumulated into biota. Recent reports showed that the wildlife in local river ecosystems had been exposed to high levels of a variety of OHCs (He et al., 2012, 2014; Sun et al., 2016). Notably, many contaminants (e.g. DDTs, PCBs, PBDEs, and AHFRs) were detected in commonly consumed fish such as mud carp (*Cirrhinus molitorella*) and tilapia (*Tilapia nilotica*).

Dietary intake is the main route of human exposure to OHCs for the general population. The consumption of fish and fish products is the primary contributor to the total dietary intake of those contaminants (Domingo, 2012; Sun et al., 2015b). Fish and fish products are important for local food production in developing countries, since about 80% of the world's production of fish and fish products occurs in those regions (FAO, Food and Agriculture Organization, 2008). China is the world's largest producer and exporter of fish and fishery products. Guangdong province's fishery production has been among the largest in China (Zhang, 2015). In addition, Chinese are generally more passionate about consuming wild-caught fish than aquacultural products. Hence, general population, particularly those in highly industrialized and urbanized regions in China might be exposed to high levels of OHCs via the consumption of wild-caught fish. Numerous studies reported OHC contaminants in the wildlife in e-waste recycle sites and the Pearl River Estuary, and aquiculture products in the Pearl River Delta. Little information, however, is available about the bioaccumulation of those chemicals in wildlife and associated human exposure in local freshwater rivers.

In the present study, various wild aquatic organisms, including fish and invertebrates, were collected from the two main freshwater rivers, namely the Pearl River and Dongjiang River, in the Pearl River Delta. We analyzed a series of OHCs (OCPs, PCBs, PBDEs, and several of the currently used AHFRs). The objective was to investigate the contamination status of OHCs and to evaluate their bioaccumulation in the organisms collected from the highly industrialized and urbanized watershed. Daily intake for OHCs was estimated based on aquatic product consumption by local residents in this region.

2. Materials and methods

2.1. Sample collection

Wild aquatic organisms were caught with nets and electric fishing by commercial fishermen from the Pearl River (Guangzhou section) and Dongjiang River (Dongguan section) in August 2014 (Fig. 1). Twelve target species were selected based on their wide geographic distribution, high abundance, and wide consumption in the study region. After collection, samples were preserved in a refrigerator box and transferred to the laboratory immediately. The body length and body mass of each individual were measured and edible parts were sampled. Two to 30 individuals of a similar body size were pooled to form a composite sample for each species from the same site for analyses. All samples were lyophilized, ground, and stored in glass bottles at −20 °C until analysis. Detailed information of the samples is shown in Table 1. There were a total of 78 composite samples pooled from a total of 803 specimens including seven fish species and five invertebrate species.

2.2. Sample extraction, clean-up, and instrumental analysis

OHCs were analyzed according to the method previously established (Sun et al., 2015b). In brief, a lyophilized and homogenized sample (3 g dry weight) was spiked with surrogate standards (PCBs 30, 65, and 204 for OCPs and PCBs; BDEs 77, 181, 205, and ^{13}C-BDE 209 for halogenated flame retardants). The samples were Soxhlet extracted with 200 mL of hexane/dichloromethane (1/1, v/v) for 48 h. After gravimetrical lipid determination, the extracts were treated with concentrated sulphuric acid to remove the fat, and then purified by a multilayer Florisil-silica gel column fractionation. The fraction containing OHCs was eluted with 80 mL of hexane and 60 mL of dichloromethane from the multilayer column. The clean extract was concentrated to near dryness and reconstituted with isooctane to a final volume of 100 μL. Known amounts of recovery standards (PCBs 24, 82, and 198 for OCPs and PCBs; BDE 118, BDE 128, 4-F-BDE 67, and 3-F-BDE 153 for HFRs) were added to all final extracts prior to instrumental analysis.

OCPs (4,4′-DDD; 2,4′-DDD; 4,4′-DDE; 2,4′-DDE; 4,4′-DDT; and 2,4′-DDT; α-, β-, γ-, and δ-HCH) and PCBs (7 indicator PCBs, CBs 28, 52, 101, 118, 138, 153 and 180) were analyzed on an Agilent 7890 GC-5975 MS at electron impact (EI) and separated on a DB-5MS (60 m × 0.25 mm × 0.25 μm, J&W Scientific) capillary column. Tri- to hepta-BDE congeners (BDEs 28, 47, 66, 99, 100, 153, 154, 138 and 183), DP, 2,3,5,6-tetrabromo-p-xylene (pTBX), and pentabromotoluene (PBT) were analyzed by an Agilent 6890 GC-5975 MS at electron capture negative ionization (ECNI) and separated on a DB-XLB (30 m × 0.25 mm × 0.25 μm, J&W Scientific) capillary column. BDE 209, decabromodiphenyl ethane (DBDPE) and 1,2-bis (2,4,6-tribromophenoxy) ethane (BTBPE) were analyzed with a Shimadzu Model QP2010 GC–MS using ECNI and separated by a DB-5HT (15 m × 0.25 mm × 0.10 μm, J&W Scientific) capillary column. Selected ion monitoring (SIM) mode was used for all target chemicals with two ions monitored for each one. Details of the instrument conditions and monitored ions were given elsewhere (Luo et al., 2009).

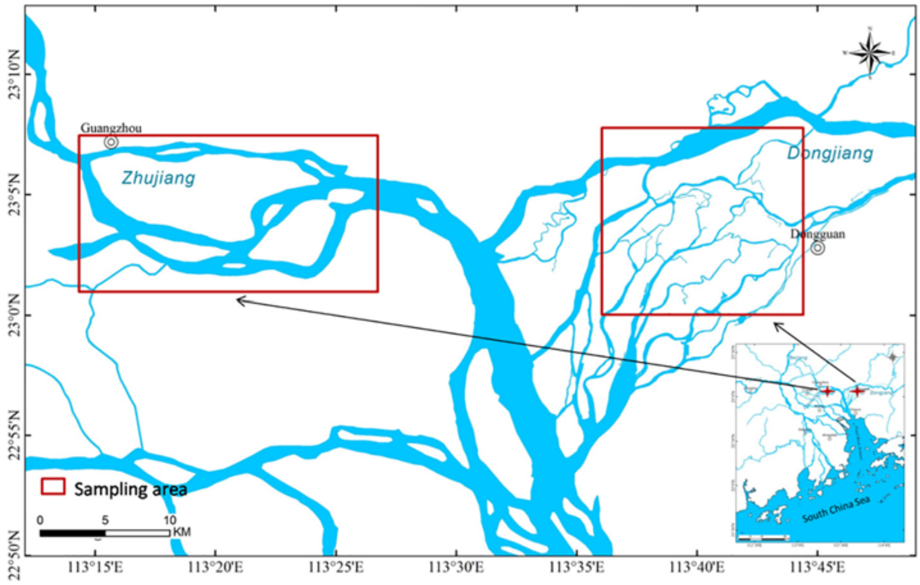

Fig. 1. Map of the sampling region.

2.3. Quality assurance and quality control

Field blanks (clean baked $NaSO_4$) and method blanks (clean baked $NaSO_4$) were treated identically to the actual samples. Only trace amounts of CB 153, and BDE 209 were detected in blanks. The concentrations in the actual samples were corrected for blank concentrations. The surrogate recoveries were 98% ± 12% for CB 30, 110% ± 10% for CB 65, 115% ± 15% for CB 204, 94% ± 11% for BDE 77, 103% ± 11% for BDE 181, 97% ± 15% for BDE 205 and 116% ± 17% for ^{13}C-BDE 209 in all samples, respectively. The mean recoveries of target analytes in spiked blanks and matrix spikes were 86%–117% and 80%–121%, respectively. The relative standard deviations (RSDs) were <20% for all target analytes in the triplicate samples. The method detection limits (MDLs), defined as a signal to noise ratio of 3, were 0.01–0.62 ng/g lipid weight (lw) for OCPs, 0.005–0.21 ng/g lw for PCBs, and 0.01–6.1 ng/g lw for HFRs. The recoveries, RSDs and MDLs of the target analytes are given in Table S1 in the Supplementary material.

3. Results and discussion

3.1. Contaminant levels and comparison with other studies

Fig. 2 and Table S2 shows concentrations of OHCs in the investigated wild aquatic species collected from the Pearl River and Dongjiang River in China. DDTs, HCHs, PCBs, and PBDEs were detected in all samples. The detection frequency of AHFRs was >60%, indicating the widespread accumulation of the contaminants in the aquatic organisms. The median concentrations of DDTs, HCHs, PCBs, PBDEs and AHFRs (the concentrations given here are the sum of those of DP, DBDPE, pTBX, PBT and BTBPE) in aquatic species ranged from 601 to 5550, 14.3 to 102, 82.1 to 3610, 46.2 to 890, and 2.47 to 122 ng/g lw in organisms from the rivers, respectively. Samples from the Pearl River generally exhibited higher contaminant levels than those from the Dongjiang River (Fig. 1, and Table S2). This may be attributed to the higher degree of urbanization and industrial activity in the Pearl River watershed. The Pearl River

Table 1
General information of samples from the Pearl River and Dongjiang River in China.

Species	N[a]	Feeding habits	Habitat	Body length (cm)	Body mass (g)	Water content (%, ww)	Lipid (%, ww)
Pearl River							
Mud Carp (*Cirrhinus molitorella*)	5 (25)	Omnivorous	Benthopelagic	16.4 (13.9–19.5)[b]	86.2 (47.8–150.6)	76.1 (75.1–76.4)	3.2 (2.8–3.8)
Tilapia (*Tilapia nilotica*)	5 (10)	Omnivorous	Benthopelagic	22.4 (21.4–24.2)	222.6 (196.8–283)	76.0 (75.1–77.5)	2.2 (1.5–3.4)
Plecostomus (*Hypostomus plecostomus*)	5 (10)	Omnivorous	Benthic	27.6 (24.0–36.6)	298.6 (252.6–553)	75.5 (75.4–75.8)	0.67 (0.56–0.82)
Snakehead (*Ophicephalus argus*)	3 (6)	Carnivorous	Benthic	28.4 (25.7–28.4)	217.1 (201.6–217.1)	74.7 (74.2–74.9)	4.3 (4.0–4.4)
Snakehead mullet (*Channa asiatica*)	2 (4)	Carnivorous	Benthic	19.5 (18.7–21.5)	79.2 (69.8–91.6)	71.5 (70.8–72.3)	6.3 (6.0–6.5)
Mud eel (*Monopterus albus*)	4 (8)	Carnivorous	Benthic	46.0 (45.2–48.9)	117.5 (115.1–126.7)	77.7 (77.6–77.9)	1.8 (1.1–2.7)
Oriental river prawn (*Macrobrachium nipponense*)	5 (150)	Omnivorous	Benthic	2.3 (1.8–3.1)	1.7 (1.2–2.6)	80.0 (79.8–80.1)	0.83 (0.79–0.96)
Chinese mitten crab (*Eriocheir sinensis*)	6 (120)	Omnivorous	Benthic	–	17.1 (16.4–17.7)	70.6 (70.3–70.8)	0.47 (0.43–0.49)
Mud snail (*Cipangopaludina cahayensis*)	3 (90)	Herbivorous	Benthic	–	2.6 (2.2–2.8)	80.9 (80.4–90.1)	1.2 (1.1–1.3)
Dongjiang River							
Mud Carp (*Cirrhinus molitorella*)	5 (10)	Omnivorous	Benthopelagic	21.0 (18.3–22.2)	223.6 (118.8–248.1)	77.1 (75.6–77.4)	2.3 (2.0–3.8)
Tilapia (*Tilapia nilotica*)	5 (10)	Omnivorous	Benthopelagic	21.7 (17–24)	230.1 (110.1–310.4)	74.7 (73.4–75.8)	1.9 (1.7–1.9)
Plecostomus (*Hypostomus plecostomus*)	5 (10)	Omnivorous	Benthic	27.0 (23.5–31.2)	281.2 (151.2–311.8)	75.9 (75.3–76.8)	1.1 (0.90–2.2)
Snakehead (*Ophicephalus argus*)	5 (10)	Carnivorous	Benthic	35.0 (34–36)	370.2 (350–407.5)	77.0 (76.6–77.3)	2.5 (1.2–2.8)
Catifish (*Clarias batrachus*)	5 (10)	Carnivorous	Benthic	27.4 (23.4–44)	170.4 (113–623.4)	77.3 (76.7–77.7)	3.0 (2.7–3.5)
Oriental river prawn (*Macrobrachium nipponense*)	5 (150)	Omnivorous	Benthic	2.1 (1.7–2.5)	3.4 (2.7–3.8)	76.5 (76.1–76.8)	1.2 (1.2–1.3)
Stone snail (*Bellamya quadrata*)	5 (150)	Herbivorous	Benthic	–	2.3 (1.6–2.3)	80.2 (79.6–80.2)	1.0 (0.95–1.1)
Clam (*Anodonta woodiana*)	5 (30)	Omnivorous	Benthic	–	428.1 (260.4–606.7)	80.4 (80.0–81.6)	1.1 (0.94–1.2)

[a] Number of composite samples analyzed, number of individuals collected.
[b] Median (min–max).

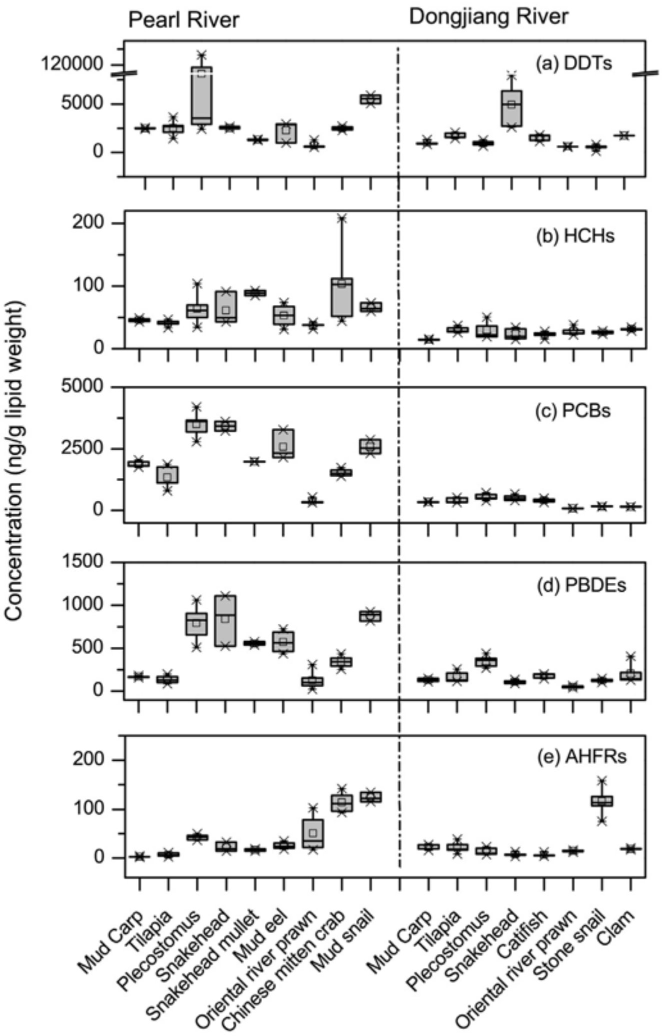

Fig. 2. Boxplots of concentrations of DDTs (a), HCHs (b), PCBs (c), PBDEs (d), and AHFRs (e) in aquatic organisms.

running through Guangzhou city, an old and highly urbanized megacity with well-developed industries. Consequently, it receives greater contamination from various point and nonpoint sources (e.g., industrial and household discharges) than the emerging industrialized and urbanized watershed (Dongjiang River) does. Higher concentrations of insecticides (i.e., OCPs and organophosphates) were also found in the soils from the area with high urbanization level in the Pearl River Delta (Wei et al., 2015).

The Pearl and Dongjiang Rivers winding their way through the Pearl River Delta flow into the Pearl River Estuary, and then enter the South China Sea. The concentrations of the studied contaminants in aquatic organisms from these two rivers were generally up to 1–2 orders of magnitude greater than those in marine organisms from the Pearl River Estuary (Sun et al., 2015b). One possible explanation for these observations is that the water exchange of the Pearl River Estuary as a semi-enclosed sea facilitates the dilution and diffusion of pollutants besides far from sources of human pollution. The lower levels of legacy and emerging organohalogenated contaminants such as DDTs, PCBs, and PBDEs were found in open sea, e.g., Yongxing Island waters (median range of 37–265 ng/g lw for DDTs, 11–89 ng/g lw for PCBs, and 5.8–11 ng/g lw for PBDEs) farther from the Pearl River Estuary in the South China Sea (Sun et al., 2014). The concentrations of PCBs and PBDEs in the fish in the present study were also much greater than those in fish from major coastal cities in China (20.1–304 ng/g lw for PCBs and 1.11–5.28 ng/g lw for PBDEs, respectively) (Pan et al., 2016; Xia et al., 2011), but the levels of DDTs and HCHs in the studied freshwater catchment stayed within the range of concentrations in fish along coastal fisheries in China (80.6–9460 ng/g lw for DDTs, and 9.20–121 ng/g lw for HCHs) (Pan et al., 2016). Meanwhile, He et al. (2012, 2014) investigated halogenated flame retardant contamination in the same three-fish species (mud carp, tilapia, and *Plecostomus*) collected from the same sampling site in the Dongjiang River as the present study in 2010. The comparable concentrations of PBDEs were found for fish samples in both studies, although PBDE technical mixtures were restricted and declining concentrations of PBDEs have been observed in a range of marine species in the Pearl River Estuary (Sun et al., 2015a, 2015b). However, the levels of DBDPE and DP reported by He et al. (2012, 2014) were higher than those observed in the present study, which may reflect the change in the industrial structure or the decreasing production of these chemicals. Previously reported concentrations of PBDEs in fish collected in European river basins varied between 42.4 and 135 ng/g lw (Giulivo et al., 2017), which were significantly lower than the data detected in the present study. The concentrations of PBDEs, DP, DBDPE, BTBPE, and pTBX observed in the present study were all much higher than those reported previously in Great Lakes fish (Guo et al., 2017). Comparison with previous studies indicates that the overall levels of industrial chemicals such as PBDEs and other AHFRs in the investigated industrialized and urbanized catchment were at the median and higher end of the global range.

Among all the investigated target chemicals, DDTs were the predominant contaminants (average, 61%) in aquatic biota from both rivers, especially the Dongjiang River with higher DDT proportion of the total OHC concentrations. The finding suggested that agrochemical sources remained an important source of OHC contaminants in the highly industrialized and urbanized watershed in China. The contributions of PCBs to total OHCs were the second highest in the samples (average, 28%) followed by PBDEs (9%). The dominance of DDTs in total OHCs was also found in fish collected from the coastal and marine areas of China (Pan et al., 2016; Sun et al., 2015b; Sun et al., 2014), the Vistula River estuary in Poland (Waszak et al., 2014), and Negro River basin in Argentinean Patagonia (Ondarza et al., 2014), which is different from the results of fish from U.S. Rivers (Batt et al., 2017), the Douro River estuary in Portugal (Waszak et al., 2014), and the Norwegian Coast (Bustnes et al., 2012), where PCBs were the most abundant pollutants. In addition, it is noteworthy that the contributions of PCBs to total OHCs were equivalent to or even higher than those of DDTs in several species (e.g. *Plecostomus*, northern snakehead, and snakehead mullet) from the Pearl River, indicating the existence of a local PCB pollution source in this catchment. *E*-waste is the most likely contributor of higher PCBs levels because of the limited production and usage of PCBs in China. E-waste recycling activities have been conducted in the studied region for many years. Dali town in Foshan City, one of the largest e-waste dismantling and recycling sites in China, is located on the upper reaches of the Pearl River. High concentrations of PCBs were previously reported in the local e-waste recycling area (Luo et al., 2009). The finding highlights the need to watch for the harmful effects of e-waste recycling activities for urban environment. The contributions of AHFRs to total OHCs were minimal in all the samples (average proportion of 1.5% to OHCs). DBDPE was the AHFR with the highest detection frequency (100%), followed by DP (94%). DP and DBDPE were the dominant AHFRs in the samples with the collective contribution of over 80% to the total concentrations of the AHFRs investigated, which is similar to the result in the Pearl River Estuary (Sun et al., 2015b).

3.2. Biological species- and compound-specific bioaccumulation characteristics of OHCs

Bioaccumulation of OHCs investigated in aquatic organisms varied among different species and chemicals. The lowest concentrations of DDTs, PCBs, PBDEs, and DP were all detected in the shrimp (Fig. 2, Table S2). One-way analysis of variance (ANOVA) with Tukey's post hoc test revealed that the levels of aforementioned chemicals in shrimp were significantly lower than those in fish in both rivers ($p < 0.05$). Similarly, the significantly low concentrations were observed for DDTs, PCBs, and PBDEs in seawater shrimp from the Pearl River Estuary (Sun et al., 2015b). These results indicated that shrimp had a lower bioaccumulation potential compared to the other aquatic species. Shrimp occupy lower trophic position in the ecosystem, which is a probable cause of lower bioaccumulation potential in shrimp. Previous studies have reported biomagnification of these chemicals (e.g., DDTs, PCBs, PBDEs, etc.) in the food web (Zhang et al., 2013). In addition, the PBDE concentrations had significant correlations with PCB and DP concentrations in all aquatic organisms from the Pearl and Dongjiang Rivers, respectively ($p < 0.05$) (Fig. S1), which was in line with the results in several other studies (Sun et al., 2014). This was ascribed to similar contaminant sources and/or environmental behaviors.

Among the DDTs, all analyzed DDTs metabolites (i.e., *p,p′*-DDE, *p,p′*-DDD, *o,p′*-DDE, and *o,p′*-DDD) were detected in all samples. *p,p′*-DDE was the predominant component of DDTs in all of the aquatic species, contributing over 50% of the overall contamination burden (Fig. 3). The composition profiles of DDTs exhibited significant interspecies differences ($p < 0.05$). The abundance of *p,p′*-DDE was significantly higher in *Plecostomus*, shrimp, and crabs than in other species, implying the higher oxidative metabolic capacity for DDT in these species. The high biotransformation capacity for DDT was also reported for Japanese stone crab (*Charybdis japonica*) among marine species from the Pearl River Estuary in China (Sun et al., 2015b). Additionally, the ratios of *p,p′*-DDE/*p,p′*-DDD ranged from 1.6 to 29, and were 1–2 orders of magnitude than those of *o,p′*-DDE/*o,p′*-DDD (0.10–3.9) in organisms, suggesting that *p,p′*-DDT was more sensitive to oxidative metabolic activity compared to *o,p′*-DDT in the studied aquatic species. The ratios of *o,p′*-DDT/*p,p′*-DDT were in the range of 0.02–0.78 with an average value of 0.21, which were similar to the value in technical DDTs (ratio of *o,p′*-DDT/*p,p′*-DDT ranging from 0.2 to 0.3), but were far below that in dicofol (ratio of *o,p′*-DDT/*p,p′*-DDT ranging from 1.3 to 9.3 or higher) (Pan et al., 2016). This observation together with the higher proportion of *p,p′*-DDE to the total DDTs is a strong indication that historical residue from technical DDTs was the main contaminant source of DDTs in the Pearl and Dongjiang Rivers, a highly industrialized and urbanized watershed in China.

HCH contamination profiles were dominated by β-HCH (constituting > 50% of the total HCHs) in all samples (Fig. 3), which differed from the composition profiles of HCH products (including two types: technical HCH containing 55–80% α-HCH, 5–14% β-HCH, 8–15% γ-HCH and 2–16% δ-HCH, and lindane containing > 99% γ-HCH) used worldwide. The dominance of β-HCH can probably be attributed to its high resistance to degradation and the isomerization from α- and γ-HCHs to β-HCH in the environment (Walker et al., 1999). The ratios of α/γ-ratios of HCHs ranged from 0 to 1.65, which were similar to those detected in fish along coastal fisheries in China (0.662–1.281) (Pan et al., 2016). This result indicated that the HCHs originated from both HCH technical (a ratio of 4–7) and lindane (a ratio of nearly 0) residues. HCHs have been banned for decades in the study region. α-HCH and δ-HCH had higher contributions to total HCHs in samples from the Pearl River than those from the Dongjiang River, which implied that HCHs were discarded later in the Dongjiang River than the Pearl River. The Dongjiang River flows through the newly-emerging industrialized city, Dongguan, whose economy was historically dominated by agriculture. γ-HCH exhibits the highest degradation and bioconversion rates among the HCHs. The lowest mean proportion of γ-HCH to the total HCHs (<1%) was observed in mud carp, suggesting a highest metabolic capability for HCHs among all aquatic species studied.

CBs 153, 118, 138, and 101 exhibited higher contributions to the total PCB congeners among the studied species except for a benthic mollusc, stone snail (*Bellamya quadrata*) which exhibited the highest contribution of CB 52 (33%, average) (Fig. 3). Predominance of hexa-CBs (PCB 153 and 138) and penta-CBs (PCB 118 and 101) was consistently observed in aquatic fish and birds (Luo et al., 2009; Pan et al., 2016), which may be attributed to their higher accumulation and persistence. The higher abundance of less chlorinated PCBs (CB28 and 52) in the stone snail is in line with the PCB congener profile of the sediments in the study area (Mai et al., 2005). A similar phenomenon was reported previously for in a benthic mollusca species in the Pearl River Estuary (Sun et al., 2015b), and the benthic habitat be a plausible the explanation.

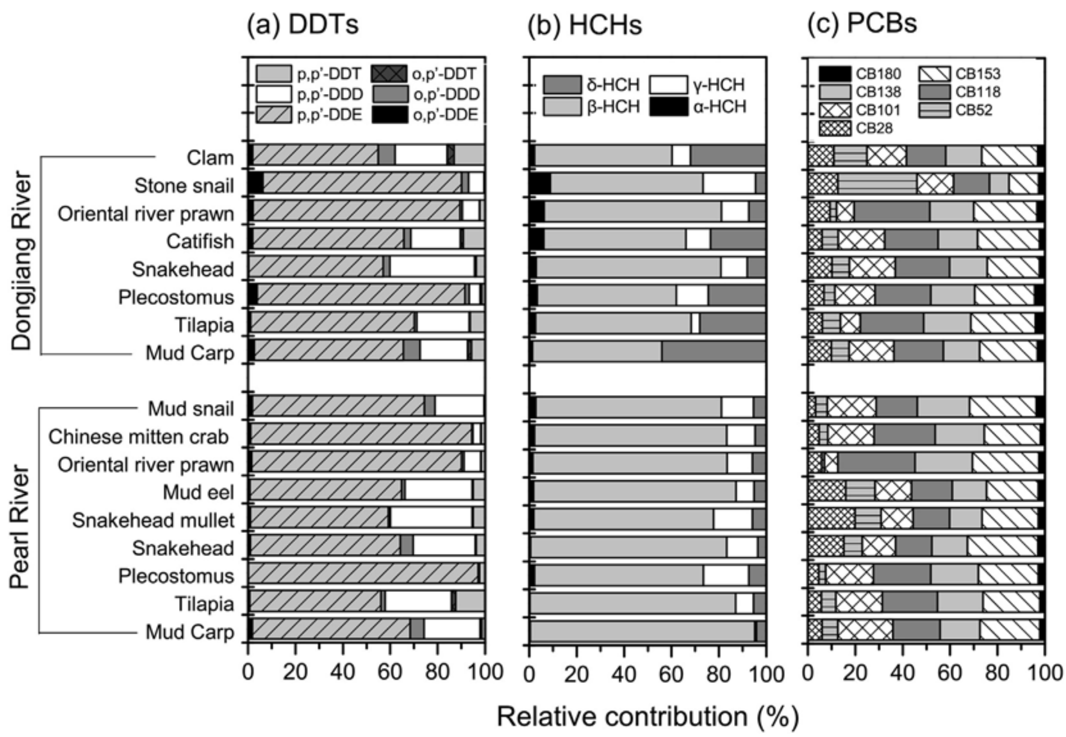

Fig. 3. Accumulation profiles of DDTs (a), HCHs (b), and PCBs (c) in aquatic organisms.

Different PBDE congener profiles were observed among aquatic species (Fig. 4). BDE 209 was predominant in almost all invertebrate species (excluding the oriental river prawn in Dongjiang River) and one fish species (*Plecostomus*) in both rivers. The dominance of BDE 209 in aquatic organisms reflected the heavy use of deca-BDE flame retardant in the catchment. Deca-BDE commercial formulation rapidly raised to become one of major BFRs in China since penta-, and octa-BDE mixtures were withdrawn from the market. Previous studies documented that BDE 209 dominated in the sediments from the study area (Chen et al., 2013). The aquatic species mentioned above are all benthic species. They are exposed to the sediment and can obtain BDE 209 in the sediment. However, BDE 47 was the most abundant congener in a benthic carnivorous fish species catfish, and two benthopelagic omnivorous fish species the mud carp and tilapia. In particular, the percentage contribution of BDE 47 in the cyprinid fish, mud carp from both rivers was up to 80%. The observation may be linked to differences in metabolic debromination, although the differences in feeding habit and habitat are also possible reasons. Laboratory exposure experiments have demonstrated that cyprinid fish can efficiently debrominate higher brominated congeners to substantial BDE 47 (Roberts et al., 2011; Tang et al., 2017). BDE 99/BDE 100, a ratio related to metabolic debromination, was 1–2 orders of magnitude lower in mud carp (0–0.059) than in the other species (0.063–7.13) in the present study. This supported a higher debromination rate of PBDEs in the cyprinid fish. The PCA analysis further revealed differing physicochemical properties of PBDE congeners resulted in their different bioaccumulation behaviors in aquatic organisms. Two components were extracted and accounted for 78% of the variance in total. The principal component 1 (PC1) was characterized by PBDE congeners which are resistant to debromination (BDE 28, BDE 47, BDE 100, and BDE 154). PC2 was highly associated with easily debrominated congeners, BDE 153, BDE 99, BDE 183, and BDE 209.

The fractional abundance of the *anti*-DP (f_{anti}), defined as the concentration ratio of *anti*-DP to the sum of *syn*-DP and *anti*-DP, was calculated to evaluate the DP isomeric profiles. The average f_{anti} values in the investigated aquatic species ranged from 0.50 to 0.72 (Fig. 5), which were lower than those of the technical mixture (0.65–0.80) and riverine sediments (0.65–0.80) in the region (Chen et al., 2013). Results of one way analysis of variance (ANOVA) revealed that mussel showed significantly lower f_{anti} values than tilapia and *Plecostomus* ($p < 0.05$), implying species-specific DP isomer accumulation in aquatic organisms. The preferential enrichment of *syn*-DP in aquatic organisms can be attributed to its higher assimilation efficiency and lower depuration rate compared to *anti*-DP (Tomy et al., 2008). In the present study, *anti*-Cl_{11}-DP, *mono*-dechlorination product of anti-DP, was detected in 54% of the samples. Correlation analysis indicated that *anti*-Cl_{11}-DP had a significant positive relationship with *anti*-DP in all the detectable aquatic biota samples (Fig. 5, $r = 0.88$, $p < 0.001$). Hepatic dechlorination of *anti*-DP in northern snakehead was reported previously based on significantly higher concentration ratios of *anti*-Cl_{11}-DP to *anti*-DP in liver than in muscle (Zhang et al., 2011). However, it is unclear whether *anti*-Cl_{11}-DP in organisms was derived from the biotransformation of *anti*-DP in vivo and/or bioaccumulation from the environment, due to the occurrence of *anti*-Cl_{11}-DP in sediment (Sverko et al., 2007; Zhang et al., 2011).

3.3. Daily intake exposure of OHCs to human

OHCs (i.e., DDTs, HCHs, PCBs, PBDEs, and AHFRs) intakes from wild edible aquatic species for local residents were estimated by the equation as follows: the estimated daily intake (EDI; (ng/kg)/d) = contaminant concentration (ng/g)/body mass (kg) × daily consumption (g/d). The aquatic products are divided into four categories: fish, shrimp, crab, and molluscs (Table 2). For the general population, the consumption data of aquatic products were obtained from a questionnaire-based dietary survey conducted in the Chinese cities (Guo et al., 2010). The daily consumption levels of fish, shrimp, crab, and molluscs are 63.6, 6.2, 2.5, and 24.5 g/d, respectively. Fishermen eat more aquatic produce than the general population. Due to limited data, a default aquatic produce consumption rate of 142.4 g/d for fishermen recommended by U.S. EPA was used in the present study (USEPA, U.S. Environmental Protection Agency, 2000). An adult consumer was assumed to have a mean body mass of 60 kg.

Average total daily dietary intakes of DDTs, HCHs, PCBs, PBDEs and AHFRs were 71.5 (ng/kg)/d, 3.92 (ng/kg)/d, 51.2 (ng/kg)/d, 13.1 (ng/kg)/d, and 0.84 (ng/kg)/d for the general population and 100 (ng/kg)/d, 5.69 (ng/kg)/d, 72.9 (ng/kg)/d, 18.5 (ng/kg)/d, and 1.12 (ng/kg)/d for the fishermen, respectively. The EDIs of legacy organohalogenated contaminants, DDTs and PCBs were up to 3 orders of magnitude larger than those of emerging contaminants, indicating a concern of these legacy contaminants cannot be neglected. Fish was the food group with the highest contribution to the total daily dietary intakes of OHCs (>80%), due to its higher consumption amounts and contaminant concentration than the other three products (i.e., shrimp, crab, and molluscs).

The EDIs of these investigated OHCs (e.g., DDTs, PCBs, PBDEs, etc.) in the present study were far higher than those in aquatic products from the adjacent area with lower level of urbanization and industrialization in China (e.g., the Pearl River Estuary, Yongxing Island, and Zhoushan) (Shang et al., 2016; Sun et al., 2015b; Sun et al., 2014). Compared with

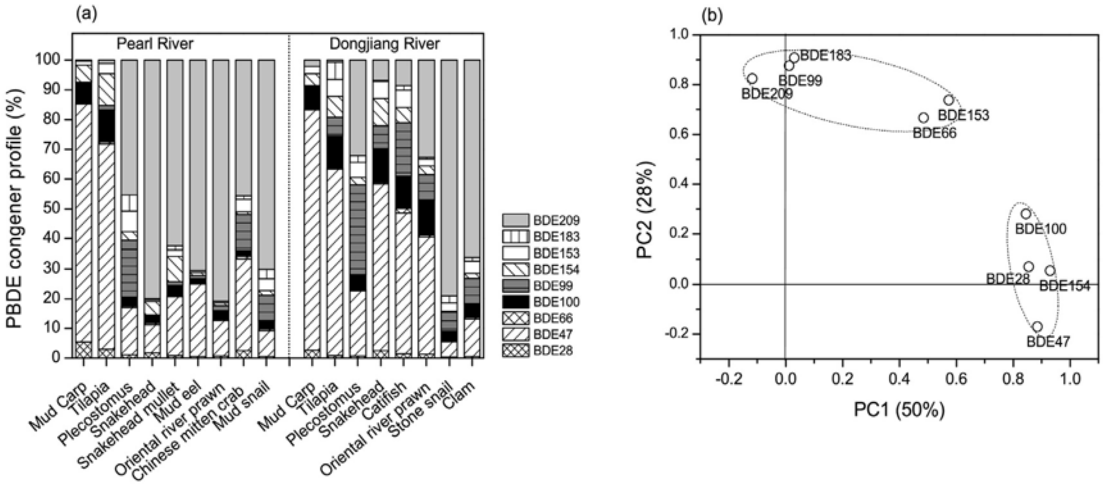

Fig. 4. Accumulation profiles of PBDEs in aquatic organisms. (a) relative abundances of individual PBDE congeners in aquatic species; (b) PCA factor loading based on the log10-transformed concentrations of PBDE congeners in aquatic organisms.

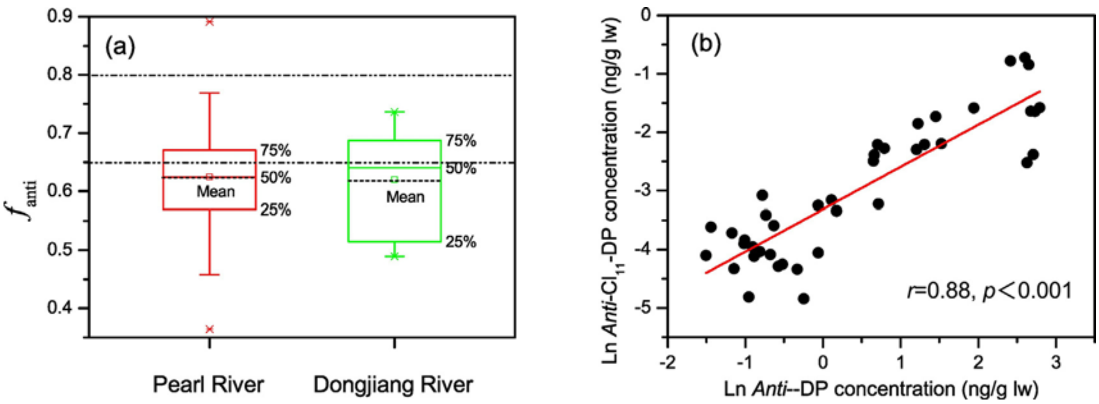

Fig. 5. Fractions of anti-DP (f_{anti}) (a) and correlations between concentrations (Ln transformed) of *anti*-DP and *anti*-Cl_{11}-DP (b) in aquatic species.

data from other areas, the EDI of PBDEs in the present study was also one order of magnitude higher than those recently reported in commercial seafood species available in Europe (Aznar-Alemany et al., 2017). The EDI of seven indicator PCBs for fishermen was in the range of 18.4–237.6 (ng/kg)/d via eel consumption in European, while the EDI for the general population in Europe (4.3 (ng/kg)/d) was lower than those in the present study (Bilau et al., 2007). The sum of six indicator PCBs (CBs 28, 52, 101, 138, 153 and 180) represents about 50% of the total non-dioxin like PCBs (NDL-PCBs) in food (Bilau et al., 2007). The EDI of six NDL-PCBs for the general population in the present study was 41.3 (ng/kg)/d, which was eight times higher than that for the adult population through consumption of fish and seafood in Catalonia, Spain (Perelló et al., 2015).

The Food and Agriculture Organization and World Health Organization (WHO, World Health Organization, 2009) recommend the acceptable daily intake (ADI) of 1000 (ng/kg)/d for DDTs to evaluate the risk for the considered population groups. The United States Environmental Protection Agency (USEPA, U.S. Environmental Protection Agency, 2000) proposes the oral reference doses (RfDs) of 500 (ng/kg)/d, 500 (ng/kg)/d, and 20 (ng/kg)/d for DDTs, HCHs, and PCBs, respectively, when assessing risk of fish consumption. EDIs of DDTs and HCHs in the present study were also far below these recommended values. Remarkably, the EDIs of PCBs via the studied fish consumption were greater than twice the RfD proposed by U.S. EPA. This indicated that consuming these contaminated fish could induce potential adverse health effects on humans.

No health based guidance value (e.g. ADI and RfD) is available for PBDEs and AHFRs. Instead, the European Food Safety Agency (EFSA) proposes to assess the associated health risk of halogenated flame retardants intake via fish consumption by a margin of exposure (MOE) approach (EFSA, European Food Safety Authority, 2011). The MOE is calculated as the ratio of benchmarked dose lower confidence limit 10% ($BMDL_{10}$) to the estimated dietary intake of halogenated flame retardants. Due to limited data on the human toxicity of halogenated flame retardants, only several BDE congeners (i.e. BDE 47, 99, 153, and 209) were assessed the potential risk in the present study. The $BMDL_{10}$ values of 309,000 (ng/kg)/d, 12,000 (ng/kg)/d, 83,000 (ng/kg)/d and 1,700,000 (ng/kg)/d were used for BDE 47, 99, 153, and 209, respectively (EFSA, European Food Safety Authority, 2011). The MOE larger than 2.5 suggests no health risk related to the exposure to PBDEs. In the current study, the calculated MOE of BDE 47, 99, 153, and 209 were 85,617, 20,772, 267,028, and 242,115 for the general population and 59,202, 15,200, 194,964, 174,462 for fishermen, respectively. Therefore, no health risk was associated to the intake of PBDEs through wild edible aquatic species consumption.

Table 2
Estimated daily intakes of OHCs (EDI, (ng/kg)/d) via fish diets consumption.

Compound	General population					Fishermen
	Fish	Shrimp	Crab	Molluscs	Total	Total
DDTs	58.1	0.65	0.48	12.3	71.5	100
HCHs	3.68	0.03	0.02	0.19	3.92	5.69
PCBs	46.1	0.20	0.30	4.60	51.2	72.9
NDL-PCBs	37.2	0.14	0.22	3.80	41.3	58.9
PBDEs	11.1	0.073	0.067	1.83	13.1	18.5
AHFRs	0.40	0.024	0.022	0.39	0.84	1.12

4. Conclusion

High levels of OHCs were widely detected in wild edible aquatic species collected from highly industrialized and urbanized watersheds in China. The past agricultural usage of DDTs remained a considerable source of OHC contaminants in the study area. Bioaccumulation of OHCs investigated in aquatic species exhibited biological species- and compound-specific characteristics due to various factors including habitat, feeding habit, metabolic capability of organisms and physicochemical property of chemicals. The EDIs of DDTs, HCHs, and PBDEs indicate that consuming wild edible aquatic organisms in the present study does not pose a health risk to local residents in China. However, a significant health risk may be associated to the intake of PCBs via the fish consumption.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2017.10.296.

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