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An eight year (2005–2013) temporal trend of halogenated organic pollutants in fish from the Pearl River Estuary, South China

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ABSTRACT

Dichlorodiphenyltrichloroethane and its metabolites (DDTs), hexachlorocyclohexanes (HCHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), dechlorane plus (DP), 2,3,5,6-tetrabromo-p-xylene (pTBX) and pentabromotoluene (PBT) were measured in baby croaker (*Collichthys lucidus*) and mullet (*Osteomugil ophuyseni*) collected in 2005 and 2013 from the Pearl River Estuary. DDTs, HCHs, PCBs, and PBDEs were detected in two fish species at concentrations of 150–8100, 1.4–120, 22–560, 2.2–280 ng/g lipid wt., respectively. The levels of these chemicals were significantly lower in 2013 than in 2005. The compositions for DDTs, HCHs, and PBDEs in 2013 differed from those in 2005, indicating source changes between the two sampling periods. DP, pTBX and PBT were detected at concentrations of ND–130 ng/g lipid wt. No clear temporal trends were found for these contaminants. Overall, these results indicated the effectiveness of regulations and source controls in substantively reducing inputs of these contaminants to the Pearl River Estuary.

1. Introduction

Halogenated organic pollutants (HOPs) such as organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and halogenated flame retardants (HFRs) have been a matter of serious concern around the world for several decades because of their persistence, bioaccumulation, and potential adverse effects on humans and wildlife. OCPs, particularly dichlorodiphenyl trichloroethane (DDT) and hexachlorocyclohexanes (HCHs) have been among the most widely used chemicals for pest and insect control for more than half a century due to their low cost and exceptional insecticidal properties (Guo et al., 2008). The production and use of DDTs and HCHs were forbidden in the early 1970s in developed countries and in 1983 in China. The amount of DDTs and HCHs produced and applied between the 1950s and the 1980s in China is 0.4 and 4.9 million tons, respectively, accounting for 20% and 33% of the total world production (Zhou et al., 2013). PCBs were used primarily as dielectric and hydraulic fluids in transformers, capacitors, and electric motors before they were banned in the late 1970s. Polybrominated diphenyl ethers (PBDEs) are a class of additive brominated flame retardants widely applied in electronics, furniture, paints, plastics, textiles and other materials (Cordner et al., 2013). The technical mixtures penta- and octa-BDE have been prohibited and were included in the list of controlled persistent organic pollutants under the Stockholm Convention in 2009. Deca-BDE was also banned in 2008 in Europe (EBFRIP, 2008), and the decamix product has been phased-out in Canada and the United States since 2013 (EC, 2011; EPA, 2009). In order to meet flammability standards, alternative flame retardants are being developed and used in consumer products. Previous researches have confirmed that several current-use alternative HFRs (AHFRs), including BTBPE, HBB, and PBEB, showed bioaccumulation and biomagnification behaviors and undertake long-range atmospheric transport leading to their widespread occurrence in the environment (Gentes et al., 2012; Wu et al., 2010).

The Pearl River Estuary, created by the inflow of freshwater from the large river system including the Pearl River, Xi Jiang (West River), Bei Jiang (North River), and Dong Jiang (East River) to the South China Sea, is located in the Pearl River Delta region of southern China, one of the most agriculturally developed, fishery-flourished, and industrially advanced regions in China. During the last decades, environmental pollution has become an important issue with the rapid socioeconomic development and population growth. Elevated levels of OCPs, PCBs, and PBDEs have been reported in both biotic and abiotic compartments from the Pearl River Estuary in many previous publications (Luo et al., 2004; Mai et al., 2005; Xiang et al., 2007). AHFRs such as PBT,

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PBEB, BTBPE, and DP have also been widely detected in local sediments (Chen et al., 2013). However, several recent studies revealed reductions to various degrees in the levels of HOPs, including OCPs, PCBs, and PBDEs in other regions of the world (Macgregor et al., 2010; Ross et al., 2013; Sericano et al., 2014). In addition, a significant increase in the shift from PBDEs to AHFRs was observed in marine mammals from the Pearl River Estuary and the adjacent South China Sea due to the ban on PBDEs (Zhu et al., 2014). In our latest study in the Pearl River Estuary, we also found that PBDE concentrations in surface sediments collected in 2010 were lower than those observed in 2002 (Chen et al., 2013). The results of that study indicate that it is necessary to examine the temporal variation of halogenated organic pollutants in this area.

Chemical body burdens in bivalves, in particular mussels, have long been utilized to monitor coastal pollution levels (e.g., Asia-Pacific Mussel Watch Progress). However, stocks of mussels in the majority of China's waterways are dangerously low due to overfishing and the destruction of their habitats. Many fish, which may occupy high trophic levels in the aquatic food webs and have long life spans, tend to accumulate and concentrate numerous contaminants; thus they represent the general pollution in an aquatic system (Fang et al., 2009). Furthermore, fish are a critical link connecting the aquatic food web to the humans and contaminated fish consumption is one of the major routes of halogenated organic pollutants into the human body (Binelli and Provini, 2003; Pacini et al., 2013). Hence, fish have been used with increasing frequency for contaminant monitoring, and these applications have received widespread success (Schmitt et al., 1990). Baby croaker (*Collichthys lucidus*) are typically benthic carnivores, feeding on invertebrates and smaller fish. Mullet (*Osteomugil ophuyseni*), a pelagic fish rich in lipids, feed on detritus and plankton. These two fish species are relatively abundant and widely distributed in the coastal areas of China. All of these ecological and physiological traits allow them to be considered ideal biomonitor species for halogenated organic pollutants in aquatic environments.

In the present study, two fish species, baby croaker and mullet, were collected from the Pearl River Estuary in 2005 and 2013, and analyzed for DDT and its metabolites (DDTs), HCHs, PCBs, PBDEs, and several AHFRs, including dechlorane plus (DP), 2,3,5,6-tetrabromo-p-xylene (pTBX), and pentabromotoluene (PBT). We assessed the current contamination levels of these chemicals in the Pearl River Estuary, and examined the changes in their composition profiles in the fish after the Stockholm Convention was implemented in China. To the best of our knowledge, this is the first study to investigate the temporal variations in concentrations of a wide range of halogenated organic pollutants and congener patterns in wild fish in the Pearl River Estuary.

2. Materials and methods

2.1. Sample collection

Two fish species, baby croaker and mullet, were collected from the Pearl River Estuary (Fig. 1) in October 2005 and October 2013 using fish trawls on a commercial fishing vessel. After being transported to the laboratory on ice, fish were immediately identified, and their length and weight were measured. Four to thirty individuals of a similar body size of each fish species in the same year were pooled to provide a composite sample. A total of 24 composite samples ($n = 5$ in 2005 and $n = 9$ in 2013 for baby croaker; $n = 5$ for mullet in 2005 and 2009) were analyzed. The samples were dissected, and muscle tissue was freeze-dried, homogenized by a stainless steel blender, and then stored at −20 °C until analysis. Detailed information on the fish samples used in the present study is given in Table 1 and Table S1.

2.2. Sample extraction and cleanup

Approximately 3 g of the lyophilized samples were spiked with surrogate standards (PCB30, 65, and 204; BDE77, 181, and 205; $^{13}C_{12}$-BDE209) and Soxhlet extracted with 200 mL of dichloromethane/hexane (1:1,v:v) for 48 h. The extract was concentrated to 1 mL using a rotary evaporator, solvent exchanged to hexane (10 mL), and then divided into two subsamples. An aliquot of the extract (1/10) was used to determine lipids by gravimetric measurement. The remainder extract was treated with concentrated sulfuric acid (10 mL) to remove lipids and further purified by passing through a complex column filled with Florisil (14 g, 3% water deactivated), neutral silica (2 g, 3% water deactivated), acid silica (7 g, 44% sulfuric acid), and anhydrous sodium sulfate (2 g) from the bottom to top. The column was eluted with 80 mL of hexane followed by 60 mL of dichloromethane, and the collected eluate was concentrated to near dryness and then reconstituted in 100 μL of isooctane. Known amounts of recovery standards (PCB24, 82, and 198 for PCBs and OCPs; BDE118, 128, 4-F-BDE 67, and 3-F-BDE 153 for HFRs) were added to the final extracts before instrumental analysis.

2.3. Instrumental analysis

OCPs and PCBs were analyzed by an Agilent 7890A gas chromatograph (GC) coupled to an Agilent 5975C mass spectrometer (MS) using electron ionization (EI) in the selected ion monitoring mode (SIM), and separated using a DB-5 ms capillary column (60 m × 0.25 mm i.d., 0.25 μm film thickness; J&W Scientific, CA). All of the HFRs were analyzed by an Agilent 6890N/5975B GC–MS in electron capture negative ionization mode (ECNI). A DB-XLB capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness; J&W Scientific, CA) was used to separate the tri- to hepta-BDEs (BDE 28, 47, 66, 85, 99, 100, 138, 153, 154 and 183), dechlorane plus (anti- and syn-DP), 2,3,5,6-tetrabromo-p-xylene (pTBX), and pentabromotoluene (PBT). For deca-BDEs (BDE 209), a DB-5HT capillary column (15 m × 250 μm i.d. × 0.10 μm film thickness; J&W Scientific, CA) was used. Details of the instrumental conditions and monitored ions were published elsewhere (Sun et al., 2013).

2.4. Quality assurance (QA) and quality control (QC)

The method quality assurance (QA) and quality control (QC) were performed by the spiking of surrogate standards into all of the samples and analysis of procedural blanks, blank spikes, matrix spikes, and sample duplicates. Instrumental QC included regular injection of solvent blanks and standard solutions. Procedural blanks were processed consistently for each batch of 10 samples. Only trace levels of PCB153, BDE47, and 209 were detected in the procedural blanks ($n = 3$), and they were subtracted from the samples. The average recoveries of OCPs (α-,β-,γ-, and δ-HCH; 4, 4′-DDD; 2, 4′-DDD; 4, 4′-DDE; 2, 4′-DDE; 4, 4′-DDT; and 2, 4′-DDT), 19 PCB congeners (PCB 8 to PCB 206) and 10 PBDE congeners (BDE 28, 47, 100, 99, 154, 153, 183, and 209) had ranges of 76–99%, 67–95%, and 94–123% in the spiked blanks, and 68–88%, 65–90%, and 68–114% in matrix spiked samples, respectively. The relative standard deviations ($n = 3$) of all targets were less than 20% for all targets except for BDE209, which was 27%. The recoveries of surrogate standards were 88 ± 4%, 97 ± 3%, 95 ± 3%, 92 ± 6%, 81 ± 6%, 70 ± 14%, and 89 ± 18% for CB30, CB65, CB204, BDE77, BDE181, BDE205, and ^{13}C-BDE209, respectively. The method detection limit (MDL), defined as a signal to noise ratio of 10 ($S/N = 10$), ranged from 0.03 to 1.6 ng/g lipid weight for OCPs, 0.02–0.4 ng/g for PCBs, and 0.01–15 ng/g for HFRs, respectively.

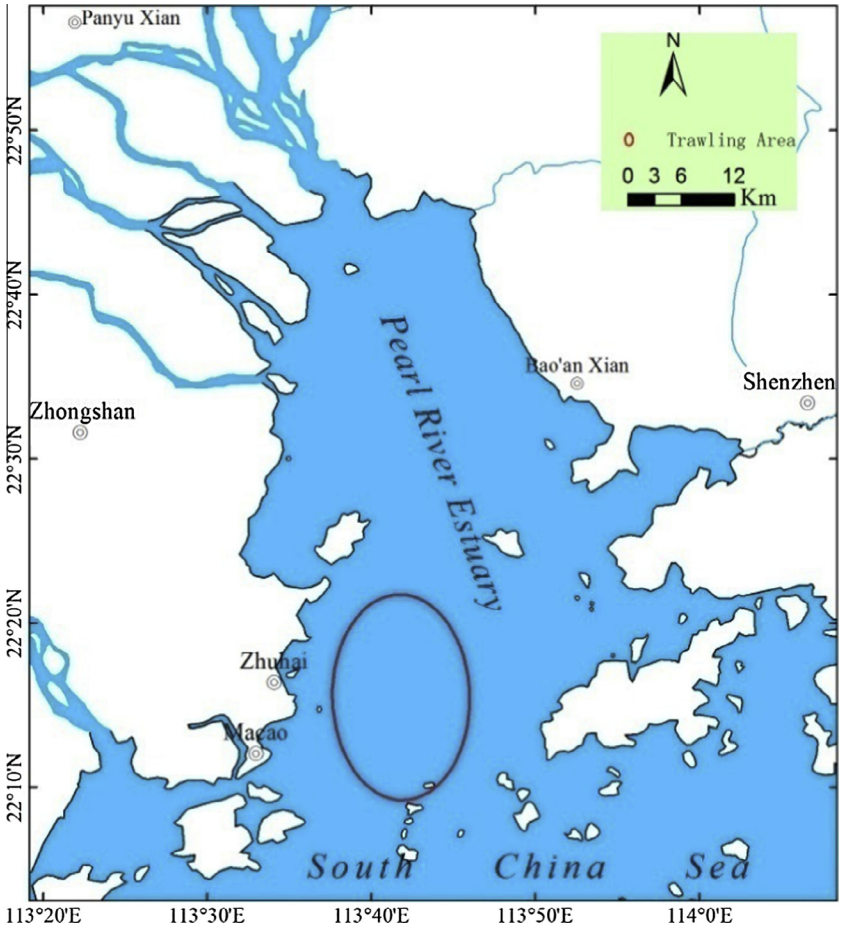

Fig. 1. Map of the sampling area.

Table 1
Concentrations of DDTs, HCHs, PBDEs, and AHFRs (median and range, ng/g lipid wt.) in baby croaker (*Collichthys lucidus*) and mullet (*Osteomugil ophuyseni*) from the Pearl River Estuary, South China.

	Baby croaker		Mullet	
	2005 (n = 5, 74)[a]	2013 (n = 9, 40)	2005 (n = 5, 56)	2013 (n = 5, 30)
Lipid (%)	0.34 (0.32–2.0)	5.0 (3.6–6.3)	1.8 (1.2–3.8)	4.2 (2.0–7.6)
Length (cm)	6.7 (5.6–9.7)	10.5 (8.7–15.0)	10.3 (8.5–11.6)	10.5 (8.5–11.5)
Weight (g)	6.2 (3.2–18.2)	28.8 (16.7–65.3)	14.3 (9.5–24.2)	13.4 (8.7–25.3)
DDTs[b]	1800 (1300–3000) [c]	200 (150–370)	5800 (4300–8100)	820 (450–5000)
HCHs[d]	72 (35–120)	8.0 (1.4–11)	33 (32–42)	9.7 (6.8–12)
PCBs[e]	460 (430–560)	92 (83–230)	160 (140–240)	64 (22 –74)
PBDEs[f]	90 (71–280)	3.8 (2.2–6.7)	96 (60–220)	3.9 (3.1–14)
DP[g]	ND(ND[h]–130)	0.17 (ND–4.2)	ND	0.02 (ND–0.81)
pTBX	ND (ND–0.21)	0.01 (0.01–0.02)	0.02 (ND–0.03)	0.06 (0.05–0.09)
PBT	0.05 (ND–1.7)	ND (ND–0.03)	0.03 (ND–0.06)	0.01 (ND–0.04)

[a] Number of composite samples analyzed, number of fish collected.
[b] Sum of 4, 4′-DDD; 2, 4′-DDD; 4, 4′-DDE; 2, 4′-DDE; 4, 4′-DDT; and 2, 4′-DDT.
[c] Median (min–max).
[d] Sum of α-,β-,γ-, and δ-HCH.
[e] 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).
[f] Sum of 9 PBDE congeners (BDE 28, 47, 66, 99, 100, 153, 154, 183, and 209).
[g] Sum of concentrations of syn-DP and anti-DP.
[h] Not detected.

2.5. Statistical analysis

All concentrations were presented on a lipid weight basis except where indicated. Statistical analysis was performed using SPSS 16.0 (SPSS Inc., Chicago, Illinois, USA). Statistical significance was accepted at $p < 0.05$ throughout the present study. For samples with concentrations below MDLs, a value of 1/2 MDLs was used for statistical analysis. Concentration data that did not follow a normal

distribution were log normalized. One-way analysis of variance (ANOVA) tests accompanied by Tukey's tests were used to evaluate the temporal and interspecific differences in contaminant levels of both studied fish species.

3. Results and discussion

3.1. Physiological parameters

Physiological parameters, such as body length, body weight, and lipid content, are important factors in determining the body burden of contaminants in fish. During whole life histories, biodilution or bioamplification can occur when an animal experiences a rapid weight increase or loss event, respectively (Daley et al., 2014). For lipophilic chemicals, tissue lipid content is a key factor in bioaccumulation. In the present study, the lipid content increased with the increasing body size (length and weight) for baby croaker and mullet (Table S2), which might be correlated with the feeding and other activities during the life history. In addition, the correlations were also examined between lipid content of the fish and the concentrations of the analyzed contaminants except for AHFRs due to their low detection frequencies. Most compounds showed positive correlations with the lipid contents (Table S2). Thus, when a comparison of the level of contaminants between different sampling periods is performed, the differences in physiological parameters should be borne in mind.

The body length and body weight of mullet in 2005 were similar to those of mullet collected in 2013 (Table 1), so the mullet in the two sampling periods were in the same period of growth when they were collected. Feeding habits and habitat cannot be major factors affecting the body burden of contaminants. However, the lipid contents in 2013 mullet were twice those in 2005 mullet, which might be attributed to the temporal variation in food supply in the ecosystem. Hence, when the concentration was expressed on a lipid basis, it will be double the wet weight normalized concentration. Regarding baby croaker, the body length and body weight in 2013 were significantly higher than in 2005 ($p < 0.05$), and the lipid contents in 2005 were approximately one-tenth of those in 2013 (Table 1). This could be cause by different growth stage of fish between two sampling years. Of five composite samples in 2005, only one (6 specimens pooled) had a similar body length and weight to those in 2013, and its lipid content was slightly lower than in the 2013 samples. Thus, the conclusions derived from baby croaker should be treated cautiously.

3.2. DDTs and HCHs

The concentrations of DDTs (sum of DDT and its metabolites DDD and DDE) in mullet were significantly higher than those in baby croaker for both sampling periods (Table 1). This may be attributed to the habitat differences between the fish species; mullet are pelagic fish, while baby croaker are benthic fish. Earlier studies suggested that concentrations of DDTs in the water column decreased with increasing depth in the Pearl River Estuary due to the influence of a main input source from the upper river inflow (Luo et al., 2004). As a consequence, the pelagic mullet was prone to accumulate more DDTs than the benthic baby croaker.

The concentration of DDTs in mullet was significantly lower in 2013 than in 2005 ($p < 0.01$) on both a lipid and weight basis (Table 1, Table S3). The DDT concentrations in baby croaker were one order of magnitude higher in 2005 than in 2013 when expressed on a lipid weight basis. However, comparable concentrations between 2005 and 2013 were observed when expressed on a wet weight basis. This could have been caused by the fish being in different periods of growth when samples were collected in the two sampling periods. The small bodies of baby croaker in 2005 implied short exposure times. In fact, when comparing only the samples with a similar body length and weight to those in 2013, the DDT concentrations in 2005 were higher than those in 2013 regardless of how the concentration was expressed. The results of the present study show decreased pollution of DDTs in the Pearl River Estuary.

DDE and DDD, the highly environmentally persistent metabolites of DDT, were the predominant components of DDTs, collectively accounting for more than 59% of all DDTs in both fish species (Fig. 2). The proportions of DDE in baby croaker were higher than those of DDD, while the opposite occurred in mullet, although no significance was observed ($p > 0.05$). Fish can acquire the metabolites together with their food after the degradation of DDT in some of the early stages of the food chains. Meanwhile, fish can also degrade DDT to DDE. Thus, the difference in the ratio of DDE/DDD between the fish species could be because of their different food sources and/or because DDT endured more aerobic transformation in baby croaker than in mullet. The (DDE + DDD)/DDTs ratio is commonly used to assess the chronology of DDT input into the ecosystems. In general, a ratio of (DDE + DDD)/DDTs of more than 0.5 indicates long-term biotransformation of DDT to DDE and DDD, while a ratio of less than 0.5 may indicate recent input of DDT (Hitch and Day, 1992). The ratios of (DDE + DDD)/DDTs

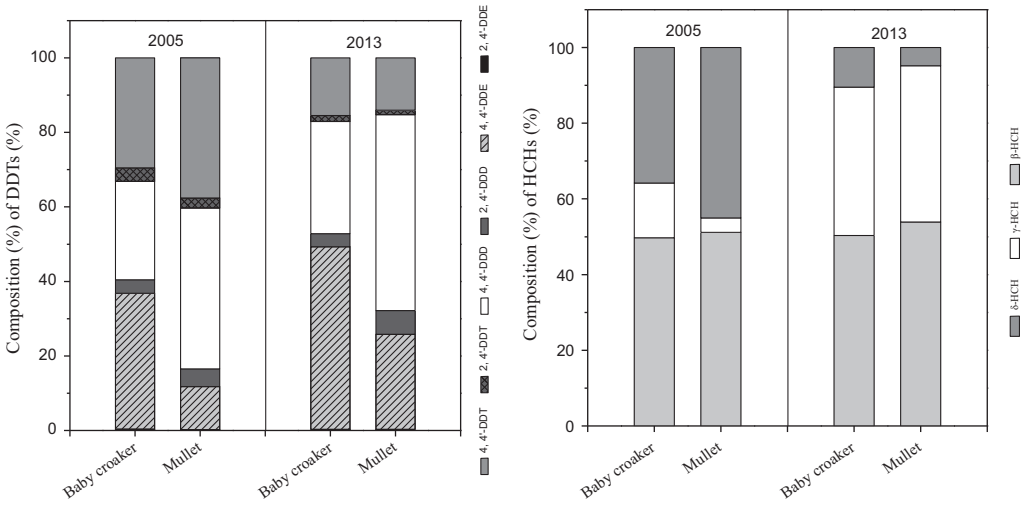

Fig. 2. Compositions (%) of DDTs and HCHs in fish species from the Pearl River Estuary, South China.

were 0.83 and 0.80 (average) in baby croaker and mullet, respectively, collected in 2013. These values were significantly higher than those (0.68 for baby croaker and 0.60 for mullet) in fish collected in 2005 ($p < 0.05$), implying that there has been no recent input of technical DDT and that historical residues are the major source of DDTs in this region (Zhang et al., 2010).

The concentrations of HCHs were lower by 1–2 orders of magnitude than those of DDTs (Table 1). The HCH levels in baby croaker (median value of 8.0 ng/g, lipid wt) were comparable to those in mullet (median value of 9.7 ng/g, lipid wt) in 2013, while the median HCH value in baby croaker (72 ng/g, lipid wt) was twice that in mullet (33 ng/g, lipid wt) in 2005, which was caused by the significant difference in lipid content between the fish species in 2005. When the concentration was expressed on a wet weight basis, no significant difference was observed in HCHs between the fish species in 2005 ($p > 0.05$).

The HCHs followed the same temporal trend as that described for DDTs in the Pearl River Estuary (Table 1). The median HCH concentration in baby croaker had declined by 89% and that in mullet by 71%. In a previous study, a significant downturn was also reported in levels of HCHs in finless porpoises (*Neophocaena phocaenoides*) from the South China Sea, from 2001 onward (Ramu et al., 2006), which is in line with the findings in the present study.

β-HCH, γ-HCH, and δ-HCH were detected in all fish samples, but α-HCH was below detection limits. β-HCH was the most abundant component of HCHs (more than 49%) in both fish species in both sampling periods (Fig. 2), which can be attributed to its resistance to degradation (Gan et al., 2009). A significant increase was observed for the percentage of γ-HCH in total HCHs from 8.2% in 2005 (average value of two fish species) to 40% in 2013, whereas the proportions of δ-HCH to total HCHs decreased sharply from 41% to 7.7% ($p < 0.05$). Among the HCHs, γ-HCH is the least persistent owing to its high degradation and bioconversion rates. In general, the longer HCHs exist in the environment, the lower the ratio of γ-HCH/HCHs becomes (Gan et al., 2009). The significant increase in the contribution of γ-HCH in 2013 suggested that a shift from technical HCHs to lindane, a pesticide containing >99% γ-HCH, occurred for the source of HCHs in the Pearl River Estuary in recent years, although the total contamination of HCHs decreased.

3.3. PCBs

The concentrations of PCBs ranged from 140 to 560 ng/g lipid wt in 2005 and from 22 to 230 ng/g lipid wt in 2013 (Table 1), which were generally 1–3 orders of magnitude lower than those in fish from industrial regions of Europe (Bodin et al., 2014; Macgregor et al., 2010; Stephansen et al., 2012) and North America (Chang et al., 2012; Rasmussen et al., 2014). Contrary to DDTs, the concentrations of PCBs in baby croaker were 1–2 times higher than those in mullet. Baby croaker, which are carnivorous benthic fish, occupied a higher trophic position and were exposed more frequently to the sediment. Their feeding habits and living habitats might result in their higher PCB burdens. Meanwhile, the interspecies differences in the concentrations of PCBs, contrary to DDTs, probably signaled different pollutant source input structures, and PCB input from the upper river inflow was at least not the only important input source.

The PCB concentrations on lipid weight in the samples collected in 2013 were significantly lower than those in 2005 (Table 1, $p < 0.05$). Declines of 80% and 61% were observed in baby croaker and mullet, respectively, during the 8-year period. As discussed above, lipid content might play a more important role in the observation, especially for baby croaker, which showed a significant difference in lipid content between 2005 and 2013 ($p < 0.05$). When the concentrations were expressed on wet weight, the PCB levels in mullet still declined by 47% over the past 8 years and a decrease

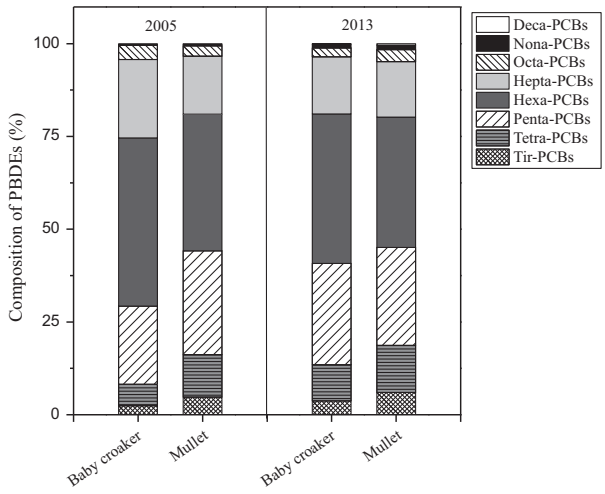

Fig. 3. The halogenated profiles of PCBs in baby croaker (*Collichthys lucidus*) and mullet (*Osteomugil ophuyseni*) from the Pearl River Estuary, South China.

by 43% for PCBs was observed if only the sample with similar body length to those in 2013 was used. Hence, the findings in the present study indicated that reduction in PCB pollution might have occurred in the Pearl River Estuary. A similar declining trend in PCBs levels has also recently been reported in Indo-Pacific humpback dolphins (*Sousa chinensis*), a representative biomonitor for contaminants in aquatic ecosystems, in this region (Wu et al., 2013).

However, the rate of decrease of PCBs was lower than those of DDTs (89% and 86% in baby croaker and mullet, respectively) and HCHs (89% and 71% in baby croaker and mullet, respectively). This is consistent with POPs in the Great Lakes region of North America, where PCBs in fish had longer-half lives than polycyclic aromatic hydrocarbons, DDTs, and other OCPs (Chang et al., 2012; Rasmussen et al., 2014; Venier and Hites, 2010). A previous study had confirmed that the production and usage of PCBs in the Pearl River Estuary and adjacent sea area were of minor importance on a global scale (Breivik et al., 2002). The disposal of electronic waste, such as old transformers and capacitors, in recent years (Zhang et al., 2010), could have contributed to the lower rate of decreased rate of PCBs observed in the present study.

No significant changes were found in the halogenated patterns of PCBs in the two fish species between the two sampling periods

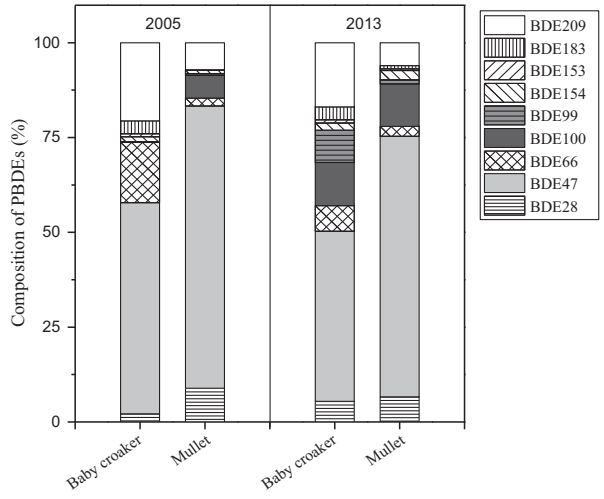

Fig. 4. The congener profiles of PBDEs in baby croaker (*C. lucidus*) and mullet (*O. ophuyseni*) from the Pearl River Estuary, South China.

($p > 0.05$), although a slight upward trend for less chlorinated homologue groups (tri- and tetra-PCBs) was observed (Fig. 3). Hexa-PCBs were the dominant PCB compounds, followed by penta-PCBs and hepta-PCBs, collectively constituting 77–88% of total PCBs in the studied fish species during both periods. The minor pattern variations in PCBs indicated that the main sources of PCBs in 2013 were the same as those in 2005 in the study area.

Mullet had a higher accumulation of less chlorinated homologue groups (tri- and tetra-PCBs, accounting for 17%) than did baby croaker (10%), which can be attributed to the differences in habitat between the fish. The benthic baby croaker is more prone to accumulating highly chlorinated congeners from the sediment than the pelagic mullet. In addition, baby croaker's diet of fishes, crustaceans, and mollusks might also contribute to the accumulation of highly chlorinated PCBs. Many studies have reported that higher trophic level fish tend to accumulate more high-chlorinated PCBs (Nie et al., 2005; Zhang et al., 2010).

3.4. PBDEs and AHFRs

In the present study, PBDEs were predominant among all of the HFRs detected (Table 1). PBDEs were in the same concentration ranges as HCHs in the studied fish species, with concentrations of 60–280 ng/g lipid wt in 2005 and 2.2–14 ng/g lipid wt in 2013. No significant difference was found in PBDE concentrations on a lipid weight basis between the fish species in the two sampling periods.

Over the course of the 8 years between 2005 and 2013, PBDE concentrations had declined by up to 96% in both fish species when expressed on a lipid weight basis. Even when expressed on a wet weight basis, the declines were up to 48% for baby croaker and 85% for mullet (Table S3). The rate of decrease of PBDEs was highest among all of the contaminants analyzed. The temporal trend of PBDEs in the present study was consistent with that previously reported in fish collected in this region between 2005 and 2007(Yu et al., 2009). The concentrations of PBDEs in the present study were also lower than those (median range 114–250 ng/g, lipid wt) in fish collected from the Pearl River Estuary in 2004 (Xiang et al., 2007). These results may reflect the decreased use of PBDEs due to the effectiveness of regulations and controls. The commercial penta- and octa-formulations were restricted in China in 2006, while DDT, HCHs, and PCBs had been banned for more than three decades. A sharp drop in pollution levels often occurs shortly after contaminants are banned, with consequent reductions in their release into the environment.

Similar to PCBs, the proportions of higher brominated congeners, including BDE183 and 209, were higher in baby croaker (22%) than in mullet (7%) (Fig. 4). Because of their benthic habit, baby croaker have more exposure to highly brominated congeners in sediments than mullet, which may explain this observation. However, differences in the metabolism of PBDEs between the fish species might play a more important role than habitat differences. The BDE100/BDE99 ratio is linked to debromination in fish because BDE99 can be debrominated to BDE47, while BDE100 is not easily debrominated (Roberts et al., 2011). The ratio of BDE100/BDE99 in baby croaker was between 0.80 and 1.7, which is significantly lower than that in mullet (4.8–15) ($p < 0.05$). This shows that baby croaker had a lower debromination rate than mullet, which could result in higher percentages of BDE209, and BDE183 in baby croaker.

DP, pTBX, and PBT were detected in the studied fish species from the Pearl River Estuary, with median concentrations ranging from ND–0.17, ND–0.06, and ND–0.05 ng/g lipid wt, respectively (Table 1). No significant trends were observed for these AHFRs due to their low detection frequencies and low levels. Data on these AHFRs in wild aquatic species are extremely limited. The concentrations of DP (19–9630 ng/g lipid wt) and PBT (mean concentrations ranging from 1.20 to 3.60 ng/g lipid wt) detected in a freshwater food web from a highly contaminated site in South China were substantially higher than most values, especially DP, in the present study. However, Zhang et al. (2010) reported that the concentrations of DP and PBT ranged from ND to 12.5 ng/g lipid wt (median value of ND) and from ND to 1.80 ng/g lipid wt (median value of ND) in fish species from an e-waste recycling region in South China, which were similar to the levels obtained in this study. Comparable levels of DP (range of ND–0.47 ng/g lipid wt, median value 0.22 ng/g lipid wt) were also reported in freshwater fish from Liaohe River, Northeast China (Ren et al., 2013).

4. Conclusions

This is the first study to investigate the temporal variation of a wide range of halogenated organic pollutants in wild fish in the Pearl River Estuary. DDTs, HCHs, PCBs, and PBDEs all showed sharp decreases, with more than 60% drops between 2005 and 2013, despite legacy DDTs remaining the most abundant contaminants in fish (DDTs > PCBs > PBDEs ≈ HCHs > AHFRs) during both time periods. No significant difference was found in AHFR levels between the two sampling periods because of low detection rates and low concentrations. However, new inputs from diverse sources still exist in the Pearl River Estuary. More comprehensive sampling is necessary for further monitoring of these compounds.

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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.marpolbul.2015.02.014.

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