# Persistent halogenated compounds in fish from rivers in the Pearl River Delta, South China: Geographical pattern and implications for anthropogenic effects on the environment

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## ABSTRACT

Three fish species, mud carp (*Cirrhinus molitorella*), tilapia (*Tilapia nilotica*), and plecostomus (*Hypostomus plecostomus*), from rivers in the Pearl River Delta (PRD) were analyzed for dichlorodiphenyltrichloroethane and its metabolites (DDTs), hexachlorocyclohexanes (HCHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), decabromodiphenyl ethane (DBDPE), and Dechlorane Plus (DP). The concentrations of DDTs, HCHs, PCBs, PBDEs, DBDPE, and DP ranged from 380–57,000, 5.5–100, 30–4200, 6.9–690, 0.29–460, and 0.09–20 ng/g lipid weight, respectively. Congener profiles or chemical compositions of PBDEs, DPs, DDTs, and HCHs in plecostomus differed significantly from those in the other two fish species, which can be ascribed to species-specific metabolism. DDTs derived from historical residue and land erosion remained the predominant pollutants in the PRD, while industrial and urban activities resulted in elevated levels of PCBs and PBDEs in the metropolitan area. E-waste recycling activities have greatly impacted on the adjacent aquatic environment, and the potential point source for DBDPE was also revealed.

## 1. Introduction

Persistent halogenated compounds (PHCs), including organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs), are well-known for their persistence, bioaccumulation, long-range transport potential and toxicity. OCPs, particularly dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexanes (HCHs) have been widely used as insecticides in agriculture. PCBs were used primarily as dielectric and hydraulic fluids in capacitors, transformers and electric motors. PBDEs are widely used as additive flame retardant in textiles, paints, electronics, and plastics. DDTs, HCHs, PCBs, and the technical mixtures penta- and octa-BDE have been regulated by the Stockholm Convention on Persistent Organic Pollutants. Deca-BDE has been phased-out in Europe (EBFRIP, 2008), Canada, and the United States (EC, 2011; EPA, 2009). To meet stringent fire safety regulations, several non-regulated halogenated flame retardants (HFRs), such as decabromodiphenyl ethane (DBDPE), and

Dechlorane Plus (DP), are being used as alternatives for PBDEs in some applications (Covaci et al., 2011). Although information on the environmental effects of the alternative HFRs is limited, available data have revealed that these AHFRs could also be persistent, bioaccumulative, and subject to long-range transport on a global scale leading to their widespread presence in the environment (Gentes et al., 2012). The Pearl River Delta (PRD) is formed by the large river system that includes the Pearl, Xijiang, Beijiang, and Dongjiang Rivers. The PRD is comprised of 39,380 km$^2$ of land that is home to more than 65 million inhabitants, and in recent decades it has been one of the most rapidly developing regions in China. The PRD region has become known as one of the most significant manufacture and export bases for electronic/electrical products, textiles, and plastic products in the world. Furthermore, it is also one of the largest e-waste dismantling regions. The rapidly developing industrial, municipal, and agricultural activities have caused serious environmental pollution in the PRD. High levels of DDTs and HCHs have been detected in water and sediments from the PRD, and new input sources of DDTs may be present due to local use of dicofol and DDT-containing anti-fouling paints (Fu et al., 2003; Guo et al., 2009). Elevated levels of PCBs and PBDEs

have been frequently found in both biotic and abiotic matrices in the PRD (Mai et al., 2005a, 2005b; Luo et al., 2009). Meanwhile, DBDPE and DP have also been widely detected in local sediments (Chen et al., 2013). However, research on these halogenated compounds in wildlife from the PRD has traditionally mainly focused on the Pearl River Estuary and the highly contaminated areas such as the e-waste recycling region. Limited information is available on these contaminants in aquatic organisms from the rivers in this region (He et al., 2012, 2014). Therefore, there is currently a need for more detailed information on the geographical distribution, potential sources, fate and behavior of PHCs in freshwater organisms from rivers in the PRD to facilitate risk assessments of these compounds.

Fish have been widely used to monitor pollution in aquatic ecosystems (Pacini et al., 2013). In addition, fish are a critical link connecting the aquatic food web to the human life cycle, and consumption of contaminated fish is a major form of exposure to harmful chemicals by the general population (Fang et al., 2009). In the present study, various classes of PHCs, including DDTs, HCHs, PCBs, PBDEs, DBDPE, and DP, were determined in three fish species collected from the major river networks and a reference site, a pond of Qingyuan, a notorious e-waste recycling area, in the PRD, South China. The objectives of the study were to provide a comprehensive understanding of PHC pollution in the aquatic environment of the PRD, and to identify the potential sources of these contaminants in the study region. Differences in the accumulation of PHCs among the three fish species were also discussed.

## 2. Materials and methods

### 2.1. Sampling

Three fish species, including mud carp (*Cirrhinus molitorella*), tilapia (*Tilapia nilotica*), and plecostomus (*Hypostomus plecostomus*), were collected using gill nets between July and September 2014 along the main rivers (Xijiang, Beijiang, Dongjiang, and Pearl Rivers) in the PRD (Fig. S1, Supporting Information). Mud carp from a pond in the e-waste recycling area were also collected in December 2014 to be used as a reference for e-waste pollution. The three fish species were selected because they widely distributed in the river and are easily collected during sampling. Meanwhile, they are also the common edible fish for the resident in the PRD. The three fish species are all demersal fish and share similar feeding habits. Mud carp grazes on algae, phytoplankton and detritus; tilapia feeds on phytoplankton and small zooplankton; and plecostomus feeds on algae, aquatic plants, and small crustaceans. The samples were stored in an ice box and transported to the laboratory. Their body length and body mass were measured. Except for mud carp from the pond in the e-waste recycling area (five specimens), 2–12 fish were pooled to form a composite sample for each species from the same site to reduce labor intensity. The dorsal muscles of fish were dissected, freeze-dried, homogenized by a stainless steel blender, and then stored at −20 °C until chemical analysis was performed. A total of 120 samples (115 composite samples) were analyzed. Details of the samples are shown in Table S1.

### 2.2. Chemical analysis

Analysis of PHCs was performed following our previously established method (Sun et al., 2015a). Briefly, a homogenized sample of muscle tissue was 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) and then Soxhlet extracted with hexane/dichloromethane (1/1, v/v). An aliquot of the extract was used to determine the lipid content by gravimetrical method. The remainder of the extract used for chemical analysis was purified with concentrated sulfuric acid, and further clean-up using a multilayer column packed with Florisil, neutral silica, acid silica, and anhydrous sodium sulfate from bottom to top and eluted with 80 mL hexane and 60 mL dichloromethane. The eluate was concentrated to near dryness under gentle nitrogen and reconstituted in 200 μL isooctane. 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.

DDTs (4,4′-DDD; 2,4′-DDD; 4,4′-DDE; 2,4′-DDE; 4,4′-DDT; and 2,4′-DDT), HCHs (α-, β-, γ-, and δ-HCH), and 7 indicator PCBs (CBs 28, 52, 101, 118, 138, 153 and 180) were analyzed by an Agilent 7890 GC coupled to an Agilent 5975 MS using electron impact (EI) in the selective ion monitoring mode (SIM) and separated by a DB-5MS (60 m × 0.25 mm × 0.25 μm, J&W Scientific) capillary column. BDE 28, 47, 66, 99, 100, 153, 154, and 183, anti- and syn-DP, anti-Cl$_{11}$-DP were quantified by an Agilent 6890 GC equipped with 5975 MS with electron capture negative ionization (ECNI) in the SIM mode and separated by a DB-XLB (30 m × 0.25 mm × 0.25 μm, J&W Scientific) capillary column. BDE 209 and DBDPE were analyzed by a Shimadzu model QP2010 GC-MS using ECNI in the SIM mode and separated by a DB-5HT (15 m × 0.25 mm × 0.10 μm, J&W Scientific) capillary column. The detailed information of the GC conditions and monitored ions were given elsewhere (Luo et al., 2009).

### 2.3. Quality assurance (QA) and quality control (QC)

Instrumental QC included regular injection of solvent blanks and standard solutions. The method QA/QC was performed by the spiking of surrogate standards into all of the samples and regular analysis of procedural blanks, spiked blanks, spiked matrices, and triplicate samples. A procedural blank was processed in each batch of 11 samples, only traces of 4,4′-DDE, PCB 153, anti -DP, BDE 47, and 209 were detected. The final reported concentrations were blank-corrected. The average recoveries of surrogate standards were 91% ± 8% for CB 30, 90% ± 7% for CB 65, 85% ± 8% for CB 204, 98% ± 10% for BDE 77, 90% ± 8% for BDE 181, 90% ± 13% for BDE 205% and 73% ± 14% for $^{13}$C-BDE 209, respectively. The average recoveries were 88%-105%, 84%-102%, and 86%-102% in the spiked blanks, and 90%-110%, 96%-113%, and 92%-114% in matrix spiked samples for DDTs (4,4′-DDD; 4,4′-DDE; and 4,4′-DDT), 7 PCB congeners (CBs 28, 52, 101, 118, 138, 153 and 180), and 12 HFRs (BDEs 28, 47, 66, 100, 99, 154, 153, 183, and 209; syn-DP and anti-DP; DBDPE), respectively. The relative standard deviations were less than 15% ($n=3$) for all the target chemicals. The method detection limits (MDLs) were set as a signal-to-noise ratio of 10. Based on the average lipid weight (lw) of the samples, MDLs ranged from 0.02 to 0.31 ng/g lw, 0.05 to 0.62 ng/g lw, and 0.01 to 2.4 ng/g lw for DDTs, PCBs, and HFRs, respectively.

### 2.4. Data analysis

All concentrations were presented on a lipid weight (lw) basis unless specified. Data analysis was performed using SPSS 16.0 (SPSS Inc., Chicago, Illinois, USA). Concentrations data were log transformed when data did not follow a normal distribution. One-way analysis of variance (ANOVA) tests were used to evaluate the spatial and inter-species differences in contaminant concentrations. The level of significance was set at $p=0.05$. Chemical concentrations below LOQs were replaced with 1/2∗LOQ in statistical analysis. The principal component analysis (PCA) was performed to investigate the input source of pollutants. Factor scores and

loadings were determined and used to interpret principle component patterns.

## 3. Results and discussion

### 3.1. DDTs and HCHs

The concentrations of DDTs in mud carp, tilapia, and plecostomus from rivers in the PRD ranged from 580 to 2500, 380 to 57,000, and 500 to 5400 ng/g lipid weight (lw), respectively (Tables 1 and S2). Levels of DDTs in tilapia were two to three orders of magnitude greater than those (7.2–390 ng/g lw) detected in tilapia (*Oreochromis* sp.) from lakes in Africa (Adu-Kumi et al., 2010; Polder et al., 2014). The maximum DDT concentrations were found in sites from the Pearl River for all three fish species (P2 for mud carp, P3 for tilapia, and P3 for plecostomus), indicating that DDT pollution was heavier in the Pearl River than in the other watersheds in the PRD. The Pearl River runs through Guangzhou, the capital of Guangdong province with high level of urbanization and industrialization. Land erosion resulting from urbanization and a relatively higher use of DDT in the Pearl River catchment could contribute to the relatively high level of DDT pollution. Wei et al. (2015) found that higher concentrations of DDTs mainly occurred in soils from the central PRD where there is a higher level of urbanization and inhabited land that has experienced frequent land-use changes. An increasing trend was observed for the levels of DDTs from upstream to downstream of the Xijiang, Pearl, and Dongjiang Rivers. Two causes can be given for this spatial

distribution of DDTs. On one hand, the soil erosion is more serious in the lower reach than in the upper reach due to higher urbanization rates. On the other hand, the terrain in the upper reach is mountain while the lower reach is often plain and farmland with intense agricultural activities. A similar spatial concentration distribution of DDTs was previously found in sediments from the Xijiang River (Luo et al., 2005).

The metabolites of DDT, dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD), were the dominant components of DDTs in all samples (Fig. S2). 4,4′-DDT accounted for only 4%, 15%, and 3% of total 4,4′-DDTs (summation of 4,4′-DDE, 4,4′-DDD, and 4,4′-DDT) in mud carp, tilapia, and plecostomus, respectively, and 2,4′-DDT accounted for 13%, 32%, and 12% of total 2,4′-DDTs in the three fish species. These results indicated that DDTs in the PRD region could mainly originate from historical discharge instead of from recent inputs (Hitch and Day, 1992). The average ratios of 2,4′-DDT/4,4′-DDT in mud carp, tilapia, and plecostomus were 0.26, 0.08, and 0.21, respectively, which were similar to or lower than those in technical DDTs (85% 4,4′-DDT and 15% 2,4′-DDT), but were remarkably lower than the value observed in dicofol (ratio of 2,4′-DDT/4,4′-DDT about 7) that was reported recently as a relatively more important source of DDTs (Guo et al., 2009). This result suggested that dicofol had little impact on the environment in the study area.

Significant interspecies differences were observed in the chemical composition of DDTs ($p < 0.05$). Tilapia exhibited the highest abundance of 4,4′ or 2,4′-DDT, suggesting a lower metabolic capacity for DDTs than those of the other two fish species. The ratios of DDE/DDD in the plecostomus (25 for 4,4′-substituted and 1.8 for

**Table 1**
Biological parameters and concentrations of persistent halogenated compounds (ng/g lipid weight) in wild freshwater fish from the Pearl River Delta, South China.

| | | | $N^a$ | DDTs | HCHs | PCBs | PBDEs | DBDPE | DP |
|---|---|---|---|---|---|---|---|---|---|
| Mud carp | Xijiang River | X1 | 3 (10) | $920 \pm 48^b$ | $36 \pm 0.76$ | $100 \pm 47$ | $77 \pm 26$ | $36 \pm 16$ | $0.53 \pm 0.07$ |
| | | X2 | 3 (9) | $1100 \pm 604$ | $12 \pm 1.6$ | $150 \pm 28$ | $20 \pm 3.2$ | $1.3 \pm 0.86$ | $0.22 \pm 0.17$ |
| | | X3 | 3 (7) | $2000 \pm 430$ | $13 \pm 0.68$ | $84 \pm 37$ | $32 \pm 20$ | $1.5 \pm 0.56$ | $0.13 \pm 0.07$ |
| | Beijiang River | B1 | 3 (8) | $590 \pm 150$ | $18 \pm 2.0$ | $830 \pm 220$ | $77 \pm 16$ | $0.29 \pm 0.18$ | $0.84 \pm 0.12$ |
| | | B2 | 3 (6) | $1200 \pm 160$ | $9.1 \pm 2.9$ | $570 \pm 420$ | $100 \pm 61$ | $5.0 \pm 3.8$ | $0.53 \pm 0.51$ |
| | | B3 | 3 (10) | $580 \pm 120$ | $10 \pm 1.9$ | $370 \pm 200$ | $40 \pm 21$ | $0.59 \pm 0.35$ | $0.58 \pm 0.32$ |
| | | B4 | 6 (12) | $1500 \pm 1000$ | $12 \pm 2.2$ | $300 \pm 240$ | $61 \pm 49$ | $0.64 \pm 0.53$ | $0.57 \pm 0.17$ |
| | | B5 | 3 (6) | $1260 \pm 26$ | $15 \pm 1.7$ | $57 \pm 2.1$ | $9.3 \pm 3.5$ | $1.9 \pm 1.8$ | $0.09 \pm 0.07$ |
| | Pearl River | P1 | 5 (25) | $2500 \pm 64$ | $46 \pm 2.5$ | $1900 \pm 130$ | $170 \pm 10$ | $2.2 \pm 1.2$ | $0.51 \pm 0.08$ |
| | Dongjiang River | D1 | 3 (7) | $740 \pm 110$ | $6.8 \pm 0.08$ | $180 \pm 45$ | $130 \pm 49$ | $11 \pm 14$ | $1.3 \pm 1.1$ |
| | | D2 | 5 (10) | $990 \pm 190$ | $15 \pm 0.75$ | $340 \pm 21$ | $130 \pm 18$ | $22 \pm 5.5$ | $0.69 \pm 0.30$ |
| | E-waste site | Ew | 5 | $890 \pm 170$ | $35 \pm 8.7$ | $120,000 \pm 48,000$ | $18,000 \pm 2600$ | $11 \pm 8.7$ | $82 \pm 27$ |
| Tilapia | Xijiang River | X2 | 3 (7) | $380 \pm 120$ | $5.5 \pm 0.76$ | $37 \pm 6.1$ | $8.2 \pm 1.9$ | $1.6 \pm 0.10$ | $0.67 \pm 0.16$ |
| | | X3 | 3 (6) | $15,000 \pm 500$ | $8.8 \pm 0.45$ | $30 \pm 2.0$ | $6.9 \pm 0.62$ | $3.4 \pm 3.8$ | $0.59 \pm 0.02$ |
| | Beijiang River | B1 | 3 (6) | $1000 \pm 720$ | $8.1 \pm 3.8$ | $2300 \pm 2200$ | $290 \pm 240$ | $2.5 \pm 1.9$ | $27 \pm 22$ |
| | | B3 | 3 (6) | $740 \pm 53$ | $8.3 \pm 0.12$ | $380 \pm 24$ | $41 \pm 3.5$ | $2.1 \pm 0.94$ | $2.7 \pm 0.26$ |
| | | B5 | 3 (6) | $810 \pm 43$ | $11 \pm 0.82$ | $65 \pm 0.58$ | $15 \pm 0.58$ | $1.2 \pm 0.65$ | $1.5 \pm 0.09$ |
| | Pearl River | P2 | 5 (10) | $2500 \pm 820$ | $41 \pm 5.4$ | $1300 \pm 460$ | $140 \pm 48$ | $2.2 \pm 1.9$ | $4.6 \pm 2.2$ |
| | | P3 | 3 (7) | $57,000 \pm 26,000$ | $44 \pm 3.2$ | $420 \pm 85$ | $78 \pm 27$ | $3.1 \pm 4.0$ | $2.2 \pm 0.30$ |
| | Dongjiang River | D2 | 5 (10) | $1700 \pm 290$ | $30 \pm 5.0$ | $410 \pm 110$ | $160 \pm 51$ | $16 \pm 7.8$ | $5.2 \pm 4.0$ |
| | | D6 | 3 (6) | $1700 \pm 360$ | $29 \pm 6.2$ | $570 \pm 140$ | $110 \pm 28$ | $2.3 \pm 0.87$ | $5.3 \pm 1.8$ |
| | | D7 | 3 (6) | $7600 \pm 2000$ | $23 \pm 1.1$ | $460 \pm 170$ | $89 \pm 32$ | $1.2 \pm 0.09$ | $1.7 \pm 0.71$ |
| Plecostomus | Xijiang River | X1 | 3 (6) | $790 \pm 93$ | $100 \pm 3.8$ | $130 \pm 25$ | $95 \pm 5.7$ | $460 \pm 25$ | $2.7 \pm 0.50$ |
| | | X2 | 3 (6) | $1700 \pm 320$ | $38 \pm 1.8$ | $250 \pm 51$ | $190 \pm 8.7$ | $3.5 \pm 2.4$ | $5.0 \pm 0.87$ |
| | Beijiang River | B3 | 3 (6) | $1300 \pm 57$ | $94 \pm 6.8$ | $880 \pm 35$ | $350 \pm 23$ | $2.5 \pm 0.54$ | $12 \pm 0.64$ |
| | Pearl River | P1 | 3 (30) | $1500 \pm 940$ | $31 \pm 1.8$ | $4200 \pm 800$ | $690 \pm 150$ | $3.5 \pm 0.86$ | $10 \pm 3.4$ |
| | | P2 | 3 (6) | $2900 \pm 560$ | $51 \pm 18$ | $3200 \pm 4200$ | $690 \pm 200$ | $19 \pm 3.2$ | $20 \pm 1.6$ |
| | | P3 | 3 (6) | $5400 \pm 3800$ | $32 \pm 6.7$ | $1200 \pm 160$ | $210 \pm 21$ | $2.6 \pm 0.27$ | $7.0 \pm 2.3$ |
| | Dongjiang River | D1 | 3 (6) | $600 \pm 55$ | $12 \pm 1.7$ | $290 \pm 128$ | $200 \pm 71$ | $0.78 \pm 0.18$ | $3.6 \pm 1.2$ |
| | | D2 | 5 (10) | $960 \pm 250$ | $29 \pm 14$ | $550 \pm 140$ | $350 \pm 70$ | $8.3 \pm 5.6$ | $3.7 \pm 2.5$ |
| | | D3 | 3 (6) | $510 \pm 49$ | $11 \pm 0.56$ | $640 \pm 180$ | $280 \pm 31$ | $5.0 \pm 0.70$ | $2.5 \pm 0.28$ |
| | | D4 | 3 (6) | $940 \pm 120$ | $30 \pm 8.5$ | $530 \pm 55$ | $310 \pm 83$ | $5.1 \pm 2.6$ | $3.1 \pm 0.48$ |
| | | D5 | 3 (6) | $1300 \pm 410$ | $16 \pm 2.1$ | $440 \pm 69$ | $160 \pm 15$ | $1.6 \pm 0.64$ | $2.5 \pm 0.62$ |
| | | D6 | 3 (6) | $1300 \pm 180$ | $26 \pm 2.7$ | $470 \pm 81$ | $180 \pm 14$ | $4.0 \pm 2.0$ | $3.8 \pm 0.55$ |
| | | D7 | 3 (6) | $2400 \pm 420$ | $23 \pm 1.7$ | $390 \pm 82$ | $180 \pm 59$ | $2.6 \pm 3.5$ | $2.8 \pm 1.0$ |

[a] Number of composite samples analyzed. Figures in brackets indicate the number of individuals collected.
[b] Mean $\pm$ SD.

2,4′-substituted) were significantly higher than those in mud carp (3.1 and 0.39 for 4,4′-substituted and 2,4′-substituted) and tilapia (2.1 and 0.62 for 4,4′- and 2,4′-substituted), implying a higher oxidative metabolic capacity for DDT in plecostomus than in the other two species. DDE/DDD ratios for 2,4′-substituted were both less than 1 in mud carp and tilapia, and were all one order of magnitude lower than those for 4,4′-substituted in the three fish species. This suggested that 2,4′-DDT were more resistant to oxidative metabolism than were 4,4′-DDT.

The levels of HCHs were one to three orders of magnitude lower than those of DDTs (Table 1), and were also slightly lower than those in gibel carp (*Carasius auratus gibelio*) from Romania (150–320 ng/g lw) (Covaci et al., 2006), but higher than the concentrations detected in tilapia (*Oreochromis* sp.) from Tanzania ($<$ not detected-2.1 ng/g lw) (Polder et al., 2014). The lowest (5.5 ng/g lw) and the highest (100 ng/g lw) HCH concentrations were detected in tilapia from site X2 and plecostomus from site X1 of the Xijiang River. No clear geographic distribution was found for HCHs in the PRD. Relatively higher HCH levels were detected in fish from site P2 and site X1, which suggested HCH emission sources in adjacent areas. Noticeably, the plecostomus in sampling site B3 contained a substantially higher concentration of HCHs (94 ng/g lw) while the other two fish species showed lower HCH levels (10 ng/g lw and 8.3 ng/g lw). The significantly low lipid content (0.41%) in plecostomus from site B3 resulted in the high HCH normalized-lipid concentration.

β-HCH was the predominant isomer of HCHs, accounting for 86%, 80%, and 71% of the total HCHs in mud carp, tilapia, and plecostomus, respectively (Fig. S3), which may be ascribed to its high resistance to biodegradation. In addition, the α- and γ-HCHs can be transformed to β-HCH in the environment (Walker et al., 1999). The ratio of α-HCH/γ-HCH is often used to identify whether the source of HCHs in the samples is from the technical HCH (a ratio of 4–7) or from lindane (containing $>$ 99% γ-HCH, with a ratio of nearly 0). In the present study, γ-HCH was detected in all the tilapia and plecostomus samples, with the ratio of α-HCH/γ-HCH ranging from 0.04 to 0.82 and nearly 0 to 0.39, respectively. These values were significantly lower than the ratio of technical HCH, indicating lindane was the main source. In our previous study, the contribution of lindane (γ-HCH) in fish from the Pearl River Estuary in 2013 was higher than in fish in 2005. These results indicated that lindane had become a more important source of HCHs in the study area.

### 3.2. PCBs

The concentrations of seven indicator PCB congeners varied from 57 to 1900 ng/g lw in mud carp, 30 to 2300 ng/g lw in tilapia, and 130 to 4200 ng/g lw in plecostomus from the rivers (Table 1). The levels of PCBs in the fish from the rivers were two orders of magnitude lower than in fish from the pond in the e-waste recycling area (120,000 ng/g lw), but higher than in gibel carp from Romania (81–250 ng/g lw) (Covaci et al., 2006) and in tilapia from Tanzania (not detected-68 ng/g lw) (Polder et al., 2014). Fish at site B1, located downstream of the e-waste recycling area, also exhibited remarkably high PCB concentrations, which revealed that the pollutants resulting from e-waste had an impact on the local river ecosystems. Fish from the Pearl River showed the highest PCB concentrations whereas fish in the Xijiang River had the lowest PCB levels. This was consistent with previous studies that reported the highest and lowest PCB concentrations in the sediments from the Pearl River and Xijiang River, respectively (Mai et al., 2002). The low PCB concentrations observed in the Xijiang River may be primarily ascribed to the limited historical use of PCBs in the watershed. Alternatively, the fairly large water flow ($8.84 \times 10^{10}$ m³/yr, larger than those of the other rivers) could also

result in low PCB levels, as the water flow can dilute the concentration of PCBs in the water body. PCB concentrations in the Pearl River were significantly higher than those in the other watersheds in the study, and gradually decreased from upstream to downstream, which implied the existence of potential emission sources of PCBs in the Pearl River watershed, especially the upper reach of the river. E-waste could contribute to PCB levels in this watershed, as several e-waste distribution centres and recycling areas are located in this region. Previous studies have demonstrated that e-wastes were the main source of PCBs in the e-waste recycling area (Luo et al., 2009; Sun et al., 2012). However, the spatial distribution of PCBs was uniform in the Xijiang and Dongjiang Rivers, implying the absence of point sources for PCBs in these two catchments.

PCB 153, 138, and 118 were predominant in all samples and collectively contributed 55–82% to total PCBs (Fig. S4). This can be ascribed to their high persistence due to the presence of chlorine at adjacent *meta* and *para* positions on the phenyl rings (Drouillard et al., 2001). Plecostomus had a lower abundance of less chlorinated congeners (CB28 and 52) than did the other two fish species in the same sampling site ($p < 0.05$), which can be attributed to the difference in metabolism for PCBs among fish species. Generally, high trophic level organisms accumulate more penta- to hepta-PCB congeners than lower trophic level organisms due to a high metabolism capacity (Walters et al., 2008; Zeng et al., 2013). The proportion of less chlorinated congeners (CB28 and CB52) in fish from the rivers (17%, 18%, and 12% for mud carp, tilapia, and plecostomus, respectively) was significantly higher than that (7%) in mud carp from the e-waste recycling site ($p < 0.05$). The difference may be attributed to the higher transfer ability of the less chlorinated PCBs due to their higher volatility and higher water solubility.

### 3.3. Halogenated flame retardants

PBDE levels in the fish samples from the rivers ranged from 6.9 to 690 ng/g lw (Table 1), which were much higher than the concentrations detected in gibel carp from Romania (0.8–4.4 ng/g lw) (Covaci et al., 2006) and in tilapia from Tanzania (not detected-34 ng/g lw) (Polder et al., 2014). The PBDE levels in plecostomus (94–690 ng/g lw) were significantly higher than those in mud carp (9.3–170 ng/g lw) and tilapia (6.9–290 ng/g lw). The highest PBDE level was also found in mud carp from the pond in the e-waste recycling region (18,000 ng/g lw). Fish in the site B1 also exhibited higher PBDE levels than did those of other investigated sites of the rivers. This result further demonstrated that e-waste recycling activities had an obvious influence on halogenated organic chemicals such as PCBs and PBDEs in the local river. This was in accordance with previous studies that characterized the e-waste recycling area as highly contaminated by PBDEs (Luo et al., 2009; Zhang et al., 2010; Sun et al., 2012).

Of the four main rivers, the Pearl River exhibited the highest PBDE levels, followed by the Dongjiang and Beijiang Rivers, with the lowest PBDE levels found in the Xijiang River. PBDE pollution has been linked to urbanization and industrialization; thus, it is not surprising that high PBDE levels were found in the Pearl and Dongjiang Rivers, which run through Guangzhou (a metropolis of Southern China) and Dongguan (a global electronics manufacturing hotspot), respectively. The industrial, commercial, and domestic human activities in Guangzhou were the main causes of the high occurrence of PBDEs in the Pearl River, and emissions from usage and disposal of PBDEs in industries such as electronics and electrical manufacturing in Dongguan were the major source of PBDEs to the Dongjiang River (Mai et al., 2005a; Chen et al., 2013). The Xijiang and Beijiang Rivers run through areas of low industrialization in the PRD, and they showed relatively lower levels
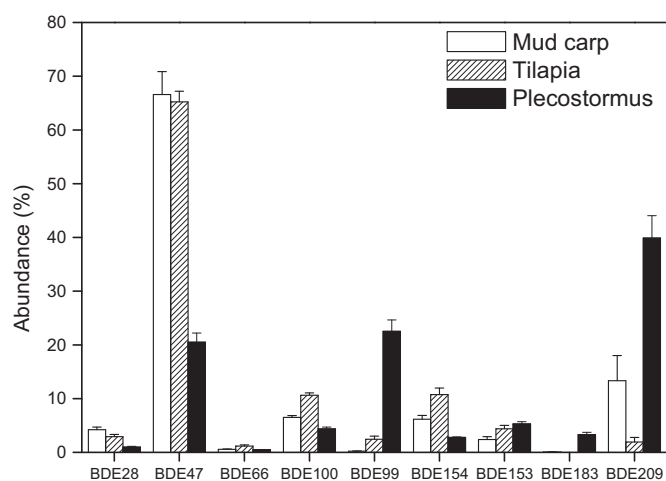
Fig. 1. Congener profile of PBDEs in three fish species from rivers in the Pearl River Delta.



Fig. 2. The $f_{anti}$ values in three fish species in rivers from the Pearl River Delta.

of PBDE contamination.

Two distinct PBDE congener profiles were found among the three fish species. BDE 47 was the most abundant congener in mud carp and tilapia, while BDE 209 was the predominant compound in plecostomus, followed by BDE 99 and 47 (Fig. 1). This result was similar to our previous study on PBDE in fish from Dongjiang River, in which BDE 99 and BDE 209 exhibited significantly higher abundance in plecostomus than in mud carp and tilapia (He et al., 2012). The difference in diet among the three fish species is a possible explanation for this observation, but differences in metabolic debromination among different fish species may play a more important role, considering the three fish species share similar feeding habit but different metabolism debromination of PBDEs. The exposure experiments in the laboratory revealed cyprinidae (common carp and tiger fish) and cichlidae (oscar fish) can debrominate some congeners with specific structures, for example BDE 99 and congeners with at least one meta- or para- doubly flanked bromine atom, to form low bromiated congeners while no debromination occurred in catfish (redtail catfish, *Phractocephalus hemiliopterus*) (Zeng et al., 2012; Luo et al., 2013). The catfish (*Clarias batrachus*) collected in the e-waste recycling area, as in the present study, also exhibited a high BDE 99 abundance (Zhang et al., 2010). Plecostomus is a member of the catfish family; little or no debromination occurs in this fish species. Therefore, BDE 209 and BDE 99 showed a high abundance in plecostomus. However, mud carp and tilapia belong to cyprinidae and cichlidae, respectively. Debromination of BDE 99 to BDE 47 led to the highest abundance of BDE 47 in these two fish species.

DBDPE was detected in all samples at concentrations ranging from 0.29 to 460 ng/g lw, which were two orders of magnitude lower than those of PBDEs (Table 1). The geographic distribution of DBDPE differed from that of PBDEs, and the highest DBDPE concentrations were observed in mud carp and plecostomus at site X1 rather than in the pond in the e-waste region or the sites in the Pearl River, although these sites also showed relatively higher levels of DBDPE. Besides site X1, high levels of DBDPE were also found in site P2 in the Pearl River and sites D1 and D2 in the Dongjiang River. DBDPE is an alternative of PBDEs, and previous studies have confirmed that local industrial activity was the main source of DBDPE in the PRD (Sun et al., 2012). The elevated DBDPE levels in the aforementioned sites indicated that there could be unknown industrial sources of DBDPE pollution, and further investigation is needed to better understand the potential sources, fate, and behavior of DBDPE in the study area. Additionally, the DBDPE concentrations in the e-waste area were higher than those
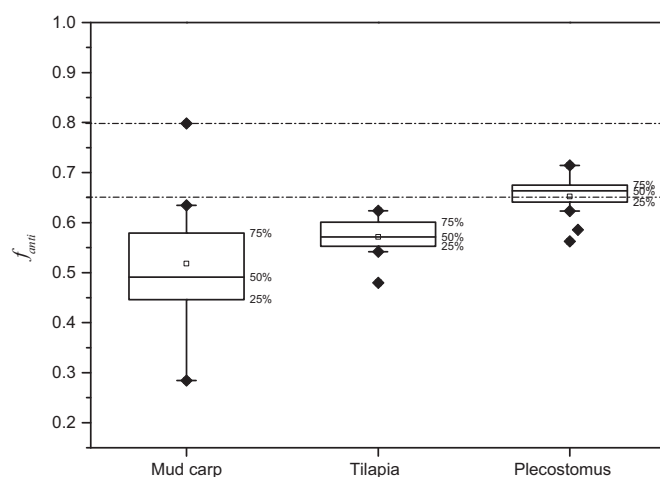
in most sampling sites of the rivers, implying that e-waste remained another important source of DBDPE.

The concentrations of DP in the fish from the rivers ranged from 0.09 to 27 ng/g lw (Table 1). The highest concentration was detected in the mud carp from the pond in the e-waste recycling area (82 ng/g lw). Meanwhile, the second highest DP concentration was found in the tilapia from site B1 of the Beijiang River. This indicated that e-waste recycling was a primary source of DP in the study area, and it had a significant impact on DP levels in the local wild freshwater fish. The fish samples, especially plecostomus, from site P2 of the Pearl River near Guangzhou, also exhibited relatively higher DP levels, which implied that the emissions from industrial, commercial, and domestic human activities were another important source of DP in the PRD. DP is an additive chlorinated flame retardant that has been used in electrical wires and cable coatings, furniture, and hard connectors in computers and televisions for more than 40 years (Sverko et al., 2011).

The fraction of the *anti*-DP to the total DP concentration ($f_{anti}$) in the fish samples from the rivers were $0.52 \pm 0.13$ in mud carp, $0.57 \pm 0.04$ in tilapia and $0.65 \pm 0.04$ in plecostomus, respectively (Fig. 2). The $f_{anti}$ values in the riverine sediment were similar to that of the technical DP products (0.65–0.80) (Chen et al., 2013), which were higher than those in the present study, indicating a stereoselective enrichment of *syn*-DP in the studied fish species. Similar results have been widely reported in fish species from many regions (Tomy et al., 2007; Wu et al., 2009), and the higher assimilative efficiency and lower metabolic rate of *syn*-DP have been demonstrated to be the main factor in the lower $f_{anti}$ values in fish (Tomy et al., 2008). Plecostomus had higher $f_{anti}$ values than the other two fish species, which was consistent with the results of a previous study in Dongjiang River (He et al., 2014) and also indicated the species-specific stereoselective accumulation of DPs.

### 3.4. Contaminant patterns of PHCs

Generally, the PHCs in the three fish species were dominated by DDTs in all sites with the exception of sites B1, P1, P2, and D3 (Fig. 3). The contributions of DDTs to total PHCs were greater than 50% for most fish samples, indicating DDTs was still the main PHCs in the PRD, although it has been banned for more than 30 years. This result was also consistent with the composition profiles of PHCs in fish from the Pearl River Estuary (Sun et al., 2015b). Moreover, the proportions of DDTs exhibited an increasing trend from upstream to downstream in all the rivers in the PRD. As discussed in Section 3.1, soil erosion caused by recent rapid urbanization has resulted in the DDT emissions from terrestrial soil
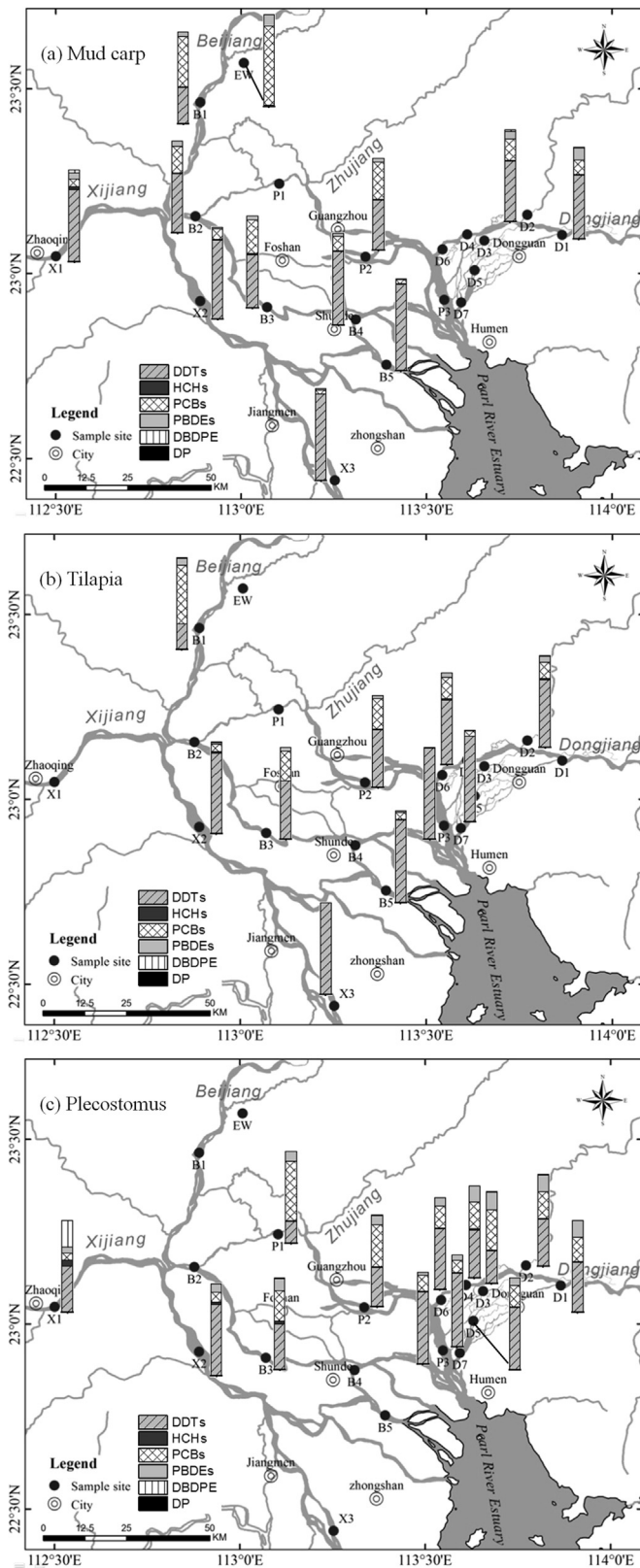
**Fig. 3.** Compositional pattern of PHCs in fish from the Pearl River Delta.

to rivers through runoff. These results indicated that agrochemical sources remained an important source of PHC contaminants in the PRD region and they must not be overlooked.

PCBs rather than DDTs became the dominant contaminants at site B1, located downstream of the e-waste recycling area. The contributions of PCBs to total PHCs were 55% for mud carp and 65% for tilapia in site B1, respectively. In the mud carp from the pond in the e-waste recycling area, PCBs were the predominant contaminants accounting for 86.7% of total PHCs, followed by PBDEs (12.6%), while DDTs were less than 1% of total PHCs. That PHCs such as PCBs and PBDEs derived from industrial sources outnumbered PHCs derived from agrochemical sources was also observed in several aquatic organisms and water birds collected from the same e-waste recycling site (Luo et al., 2009; Zhang et al., 2010). Thus, the contaminant pattern at site B1 shifting from DDT-dominant to PCB-dominant can be ascribed to the influence of e-waste activities in the upper reach.

In fish from sites in the Pearl and Dongjiang Rivers, PCBs and PBDEs also showed higher contributions to total PHCs. For example, PCBs accounted for 65%, 46%, and 18% of total PHCs in plecostomus from sites P1, P2, and P3 of the Pearl River, respectively. In plecostomus from sites in the Dongjiang River, the contributions of PCBs were higher than 20% except for site D7, where the percentage of PCBs was 13%. PCB and PBDE contaminants are always linked to urbanization and industrial activities, and the elevated proportion of PCBs and PBDEs indicated that the contaminant pattern has gradually shifted from the traditional pattern dominated by pesticides to a pattern dominated by industrial sources in the highly urbanized and industrialized areas of the PRD.

### 3.5. Pollution pattern and sources of PHCs derived by PCA

To better understand the pollution pattern and sources of PHCs in the fish from the rivers in the PRD, principal component analysis (PCA) was conducted using the raw data, excluding mud carp from the pond in the e-waste region. The first four factors identified in PCA accounted for 47%, 17%, 12%, and 6% of the total variance (Table S3). PC1 was heavily weighted by all PCB congeners and BDEs 28, 47, 66, 100, and 154, indicating industrial chemical sources. PC2 was heavily weighted by chemicals from DDTs, reflecting agrochemical sources, which have been banned for several decades. PC3 was heavily weighted by BDE 153, BDE 99, BDE 183, and BDE 209. This factor may be related to the species-specific metabolic debromination for PBDEs. A number of studies have indicated that these four congeners in fish can be debrominated to less brominated congeners (Stapleton et al., 2004, 2006; Roberts et al., 2011; Zeng et al., 2012). However, BDE 28, 47, 100, and 154 have been identified as resistant to debromination (Roberts et al., 2011; Zeng et al., 2012). This statement can be further supported by PCA using only plecostomus, in which all BDE congeners except for BDE 209 belonged to PC1 (Table S4). PC4 was heavily loaded with chemicals from HCH isomers and DBDPE. This factor is a reflection of point sources of currently used agrochemicals and industrial chemicals. The PCA loading plot with the first two factors clearly illustrated the source of PHCs in the study region (Fig. 4a). The factor score plot indicated that downstream of Xijiang River (X3) and Pearl River (P3) had high a score in PC2, indicating heavier DDT pollution (Fig. 4b). The sites P1, P2, and B1 had high PC1 scores, suggesting more contributions from PCBs and PBDEs than at other sites. These chemicals could originate from e-waste and from domestic electronic and electrical products in which PCBs and PBDEs have been added.

## 4. Conclusion

A comprehensive investigation of PHC pollution in the aquatic environment in the PRD was conducted by analysis of residues of DDTs, HCHs, PCBs, PBDEs, DBDPE, and DP in three fish species from different rivers in the PRD. The results of the present study clearly
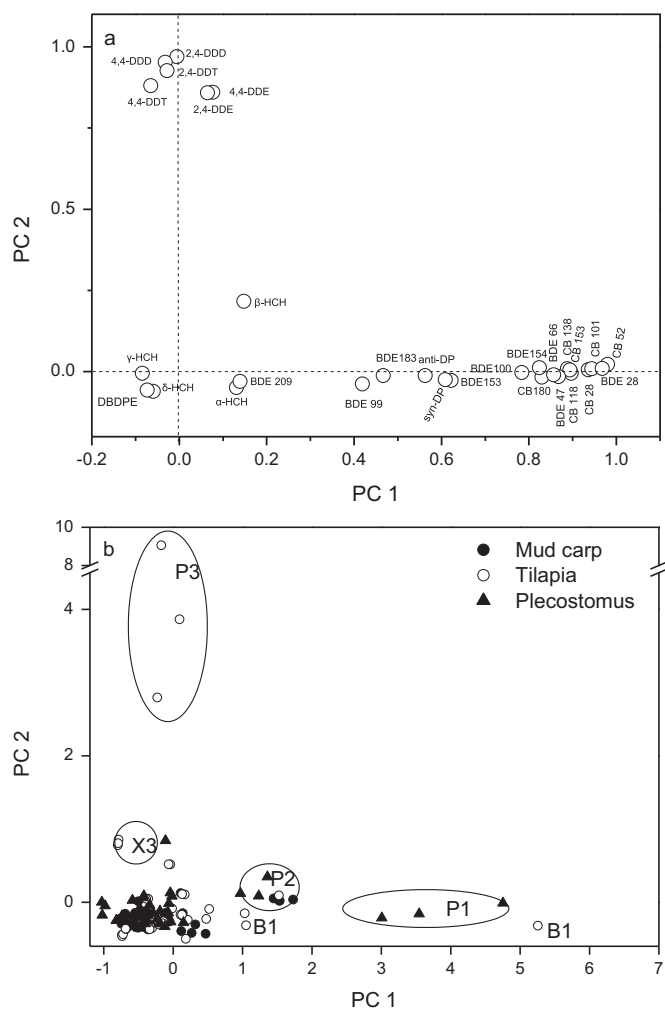
**Fig. 4.** Principal component analysis results based on the concentrations of DDTs, HCHs, PCBs, PBDEs, DBDPE, and DPs. (a) Factor loadings (b) factor scores.

demonstrated the geographical distribution and potential sources of PHCs in the PRD. Anthropogenic activities had a great impact on the environment and PHC concentrations were relatively high in the region with intense anthropogenic practice. Furthermore, e-waste recycling activities, urbanization, and industrialization in the study area influenced the contaminant pattern of PHCs in the fish studied. Species-specific levels and composition patterns observed in the present study suggested that the species difference in accumulation and metabolism of xenobiotics should be taken into consideration if fish are to be used to monitor PHC pollution.

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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.envres.2016.01.021.

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