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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.