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

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HIGHLIGHTS

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

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ABSTRACT

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

1. Introduction

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

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

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

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

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

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

2. Materials and methods

2.1. Sample collection

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

2.2. Sample preparation and analysis

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

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

2.3. Quality assurance and quality control

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

2.4. Nitrogen isotope measurement and trophic level calculation

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