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

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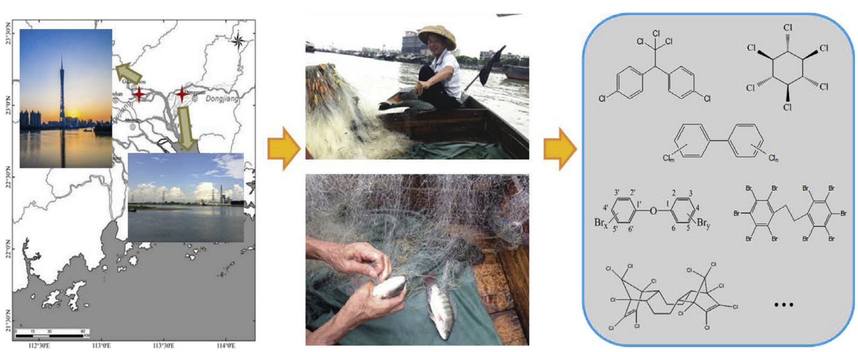
HIGHLIGHTS

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

GRAPHICAL ABSTRACT



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ABSTRACT

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

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1. Introduction

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

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

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

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

2. Materials and methods

2.1. Sample collection

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

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

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

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