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Short-chain chlorinated paraffins in marine organisms from the Pearl River Estuary in South China: Residue levels and interspecies differences

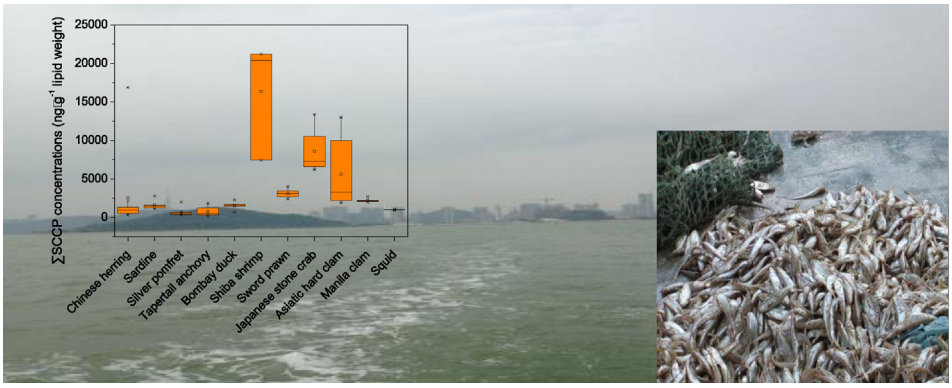
Runxia Sun [a,b], Xiaojun Luo [a,*], Bin Tang [a,b], Zongrui Li [a,b], Liqian Huang [a,b], Tao Wang [a,b], Bixian Mai [a]

[a] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, People's Republic of China
[b] University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

HIGHLIGHTS

- SCCPs were measured in marine organisms from the Pearl River Estuary, South China.
- ∑SCCP levels in the marine species were in the medial level of world figures.
- Biomagnification was found between prey fish (tapertail anchovy) and predator fish (Bombay duck).
- Interspecies difference was found in the level and composition of SCCPs.

GRAPHICAL ABSTRACT



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ABSTRACT

There is limited information available on the bioaccumulation of short-chain chlorinated paraffins (SCCPs), a complicated group of persistent organic pollutants (POPs) candidates listed in the Stockholm Convention, in estuarine ecosystem. This study analyzed SCCPs in marine organisms (five fish and six invertebrates) from the Pearl River Estuary in South China. The concentrations of total SCCPs ranged from 210 to 21,000 ng·g^{-1} lipid weight, with relatively higher levels in benthic invertebrates (shrimp, crabs and bivalves) than in non-benthic species (pelagic and mesopelagic fish and squid). SCCPs were biomagnified from prey fish (tapertail anchovy, *Coilia mystus*) to predator fish (Bombay duck, *Harpadon nehereus*), and the biomagnification factors (BMFs) of SCCP congeners ranged from 1.1 ($C_{10}H_{16}Cl_6$) to 3.4 ($C_{13}H_{18}Cl_{10}$). Species-specific homologue group patterns were also observed, with significantly lower proportions of C_{10} congeners in the shrimp, bivalves and Bombay duck than in the other species.

1. Introduction

Chlorinated paraffins (CPs) are industrial chemicals extensively used as additives in metalworking fluids, paints, and extreme-pressure lubricants, and as secondary plasticizers and flame retardants in plastics, sealants, and leather (Bayen et al., 2006). The CP commercial mixtures are manufactured by direct chlorination of n-alkane feedstocks with carbon chain lengths 10–30 (Tomy et al., 1998). In general, CPs are divided into three groups according to their carbon chain length: short chain CPs ($C_{10–13}$, SCCPs), medium chain CPs ($C_{14–17}$, MCCPs) and long chain CPs ($C_{18–30}$, LCCPs) (Feo et al., 2009). Among different

* Corresponding author.
E-mail address: luoxiaoj@gig.ac.cn (X. Luo).

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CP groups, SCCPs have attracted increasing attention in the last decade due to their persistence (Iozza et al., 2008), bioaccumulation (Houde et al., 2008; Zeng et al., 2011a; Basconcillo et al., 2015), toxicity to organisms (Warnasuriya et al., 2010; Geng et al., 2015, 2016), and high potential for long-distance atmospheric transport (Reth et al., 2006; Strid et al., 2013). SCCPs have been placed on the toxic release inventory in the European Union, Japan, Canada, and the United States, and are classified as priority toxic substances in the United States (UNEP, 2015a). Furthermore, SCCPs are currently reviewed as potential persistent organic pollutants (POPs) by the Stockholm Convention (UNEP, 2015b).

China is the largest producer of CPs in the world, and the production volume has rapidly increased from 24.2 kt/year in 1990 to about 1000 kt/year in 2009 (Chen et al., 2011; Zeng et al., 2011a). As high production volume chemicals, CPs can be inevitably released into the environment during the production, storage, transportation, usage, and disposal or recycling of CPs and CP-based products. Limited studies indicate SCCPs have become ubiquitous in the environment and are routinely detected in both biotic and abiotic compartments in China (Gao et al., 2012; Ma et al., 2014a, 2014b). In addition, higher dietary exposure to SCCPs was reported in China, than that in Japan and South Korea (Harada et al., 2011). Thus, it is important to investigate the environmental fate, behavior, and ecological and health effects of SCCPs in China.

The Pearl River Delta region, one of the fastest developing regions in China in recent decades, is being subjected to accelerated ecological and environmental deterioration. Many studies demonstrate that the Pearl River Delta region have become a hotspot area for persistent halogenated compound contamination due to rapid industrialization and urbanization, and intensive e-waste recycling activities (Fu et al., 2003; Mai et al., 2005a, 2005b). High levels of $\sum$SCCPs were observed in various environmental matrices such as sediment (320–6600 $ng \cdot g^{-1}$ dry weight, dw), soil (18 $ng \cdot g^{-1}$ dw, average), and air samples (18 $ng \cdot m^{-3}$, average) obtained from this region (Chen et al., 2011; Wang et al., 2013). Luo et al. (2015) reported that $\sum$SCCP concentrations in terrestrial bird species inhabiting an e-waste recycling site in the Pearl River Delta, South China ranged from 620 to 17,000 $ng \cdot g^{-1}$ lipid weight (lw).

The Pearl River Estuary, located in the Pearl River Delta region, is created by freshwater inflow from a complicated river system including the Pearl River, West River, North River, and East River to the South China Sea. The Pearl River Estuary has been acting as an important reservoir for persistent halogenated compounds derived from the Pearl River Delta, which may pose negative impacts to local coastal ecosystems (Fu et al., 2003; Mai et al., 2005a, 2005b). High levels of persistent halogenated compounds, including Dichlorodiphenyltrichloroethane and its metabolites (DDTs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), have been detected in biota from the Pearl River Estuary (Sun et al., 2015a,b). Limited information, however, is available on the occurrence of SCCPs in marine species in this region (Zeng et al., 2015).

In this study, various marine organisms, including fish and invertebrates, were collected from the Pearl River Estuary in South China in order to analyze the presence of SCCPs. The objectives of this study were to investigate the residual levels and congener distribution patterns of SCCPs in marine species of the area. Furthermore, species-specific bioaccumulation of SCCPs in marine organisms was explored. It is hoped that the corresponding results in this study can provide valuable information to better understand the contamination of SCCPs in marine ecosystems.

2. Materials and methods

2.1. Sampling

Marine organisms were caught with a bottom trawl by commercial fishers in the Pearl River Estuary in October 2013 and the sampling area is shown in Fig. 1. The samples were wrapped in aluminum foil, and stored in an insulated cooler with sufficient ice. These species were identified after they were transferred to the laboratory. The collected species included 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*). Next, the body length and body mass of these specimens were measured. Four to 30 individuals were pooled to form a composite sample for each species, except for silver pomfret (*Pampus argenteus*) (Table 1). The dorsal muscles of the fish and the edible part of the invertebrates were taken, freeze-dried, and ground into fine powders using a stainless steel blender. A total of 58 composite samples and 8 silver pomfrets were obtained, and then stored at −20 °C until chemical analysis. Details of the samples are provided in Table 1.

2.2. Sample extraction and cleanup

Analysis of SCCPs was performed following our previously established method with minor modification (Sun et al., 2015a,b). Briefly, after being spiked with surrogate standards (5 ng of ε-hexachlorocyclohexane, ε-HCH), approximately 3 g of the lyophilized samples were Soxhlet extracted with 200 mL of n-hexane/dichloromethane (1:1, v:v) for 48 h. The extract was concentrated to 1 mL by a rotary evaporator, solvent exchanged to n-hexane (10 mL), and then divided into two subsamples. An aliquot of the extract (1/10) was used for the gravimetric determination of the lipid content. The remainder extract was purified with concentrated sulfuric acid (10 mL) to remove lipids, and further cleaned on a complex column packed with Florisil (14 g, 3% water deactivated), neutral silica gel (2 g, 3% water deactivated), acid silica gel (7 g, 44% sulfuric acid), and anhydrous sodium sulfate (2 g) from the bottom to top. The column was eluted with 80 mL of n-hexane (first fraction, containing PCBs, PBDEs, and most of organochlorine pesticides including DDTs) followed by 60 mL of dichloromethane (second fraction, containing CPs and several organochlorine pesticides). The second fraction was collected, concentrated to near dryness under a gentle nitrogen flow, and solvent exchanged to isooctane to a final volume of 100 μL. 5 ng of $^{13}C_{10}$-trans-chlordane was added as a recovery standard for GC/MS analysis.

2.3. Instrumental analysis

SCCPs were analyzed using a Shimadzu model 2010 gas chromatograph equipped with a model QP-2010 low resolution mass spectrometer (Shimadzu, Japan) with electron capture negative ionization in the selective ion monitoring mode. The separation was achieved with a DB-5HT capillary column (15 m × 250 μm i.d. × 0.10 μm film thickness, J&W Scientific). The oven temperature was initially isothermal 100 °C for 2 min, further increased to 280 °C at a rate of 40 °C/min, held for 2 min, and finally increased to 320 °C at 70 °C/min, keeping the final temperature for 6 min. The temperatures of the injector, interface and ion sources were set to 250, 280 and 200 °C, respectively. The carrier gas was helium with a constant flow rate of 1.3 mL/min, and the reagent gas was methane at a flow rate of 2 mL/min.

SCCP congeners having 10–13 carbon atoms and 5–10 chlorine atoms on the main chain were analyzed for all biota samples. The mass-to-charge ratios used for quantification and confirmation were published elsewhere (Tomy et al., 1997). The most and second-most abundant isotope ions were used for quantification and confirmation, respectively. In addition, the CP congener groups were also identified by comparing retention time, signal shape, and correcting isotope ratio between samples and standards. To enhance instrument sensitivity and to minimize the interference of MCCP congeners, all monitored SCCPs ions were divided into four groups (C_{10}, C_{11}, C_{12}, and C_{13}) and