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.
- $\sum$ 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
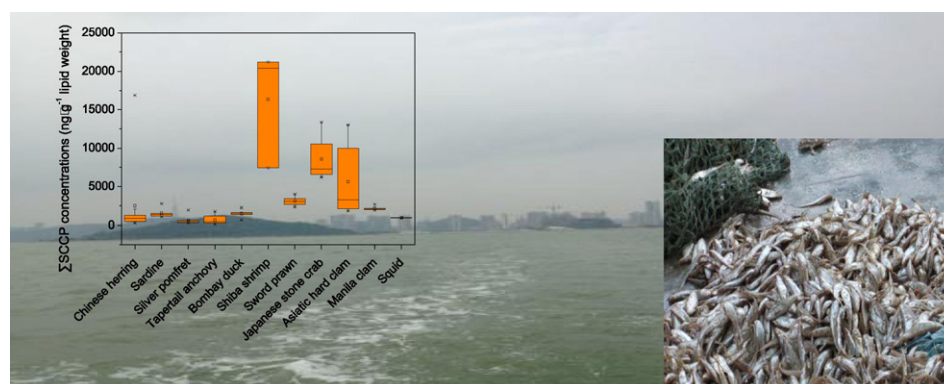
ARTICLE INFO

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.

© 2016 Published by Elsevier B.V.

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).

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·g^{-1} dry weight, dw), soil (18 ng·g^{-1} dw, average), and air samples (18 ng·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·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
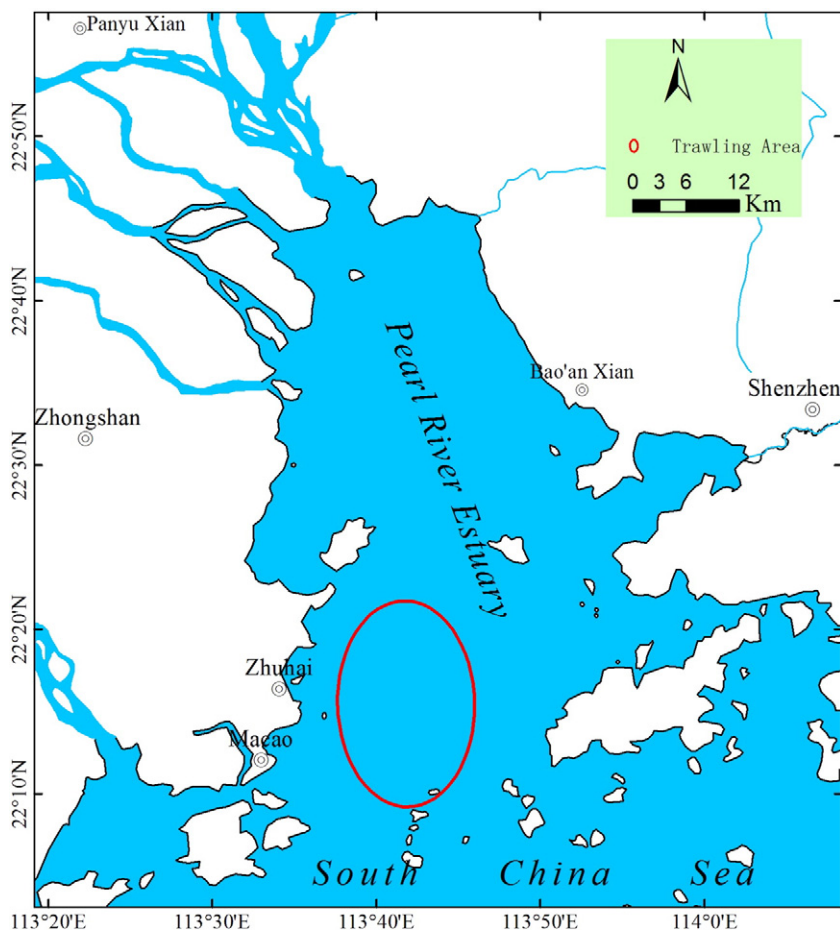
Fig. 1. Map of the sampling area.

were analyzed by four individual injections for each sample, based on a previous reported method (Zeng et al., 2011b). The total SCCP was quantified using the procedure described by Reth et al. (2005). The congener group abundance profiles in the standards and the samples were established from the actual relative integrated signals corrected by isotopic abundance and response factors (Tomy et al., 1997). The detailed chemical calculation method has been described by Reth et al. (2005) and Tomy et al. (1997).

2.4. Quality assurance and quality control (QA/QC)

Instrumental QC was done by regular injection of solvent blanks and standard solutions. The method QA/QC was performed by the spiking of surrogate standards into all the samples and analysis of procedural blanks, spiked blanks, spiked matrices, and triplicate samples. A procedural blank was run periodically for each batch of ten samples, and no SCCPs were detected in the procedural blanks. The recoveries of SCCP standards (51.5%, 55.5%, and 63.0% chlorine content) were 83–94% in the spiked blanks and 79–96% in the matrix-spiked samples, with relative standard deviations (RSDs) of <15% ($n = 3$). The surrogate recoveries of $^{13}C_{10}$-trans-chlordane in all samples were 71–94%. The method detection limits (MDLs) were defined as a signal-to-noise ratio of 3, and estimated at 20 ng·g^{-1} dry weight (dw) for total SCCPs.

2.5. Stable nitrogen isotope measurement and trophic level calculation

Stable isotope analysis and trophic-level calculation were done according to the method previously described (Sun et al., 2015b). Briefly, approximately 1 mg of freeze-dried and homogenized subsample was wrapped in a tin capsule, and then analyzed by a Flash EA 112 series elemental analyzer interfaced with a Finnigan MAT ConFlo III isotope ratio mass spectrometer. Stable isotope abundance was expressed as $\delta^{15}N$ (‰), with $\delta^{15}N = (^{15}N/^{14}N_{sample}/^{15}N/^{14}N_{standard} - 1) \times 1000$(‰). The $^{15}N/^{14}N_{standard}$ values were based on atmospheric N_2 (air). Stable isotope ratios of samples were assessed against the reference standards ammonium sulfate for $\delta^{15}N$. The precision of this technique was about ± 0.5‰ (2 SD) for $\delta^{15}N$. The trophic level (TL) was calculated for each sample according to the following equation $TL_{consumer} = [(\delta^{15}N_{consumer} - \delta^{15}N_{primary\ consumer})]/3.8 + 2$, where δ-$^{15}N_{primary\ consumer}$ is the stable nitrogen isotope value of the zooplankton with an average of 9.7‰, and 3.8 is the isotopic trophic enrichment factor (Yu et al., 2009).

2.6. Statistical analysis

All concentrations were presented on a lipid weight basis except where indicated. Data analysis was performed using SPSS 18.0 (SPSS Inc., Chicago, Illinois, USA). One-way analysis of variance (ANOVA) tests were used to evaluate the interspecies differences in the levels and congener distribution patterns of SCCPs. Concentration data were log-transformed when data did not follow a normal distribution. The p value below 0.05 was considered statistically significant.

3. Results and discussion

3.1. SCCPs levels in marine species

The concentrations of $\sum$ SCCPs in the sampled marine organisms from the Pearl River Estuary are listed in Table 1. $\sum$ SCCP concentrations in the marine species ranged from 210 to 21,000 ng·g^{-1} lw. The

Table 1
Biological parameters and concentrations of $\sum$ SCCPs in marine organisms from the Pearl River Estuary, South China.

Species	N[a]	Body length (cm)	Body mass (g)	Lipid (%)	Trophic level	Feeding habits	Habitat	$\sum$ SCCPs (ng·g^{-1} ww)	$\sum$ SCCPs (ng·g^{-1} dw)	$\sum$ SCCPs (ng·g^{-1} lw)
Fish										
Chinese herring (*Ilisha elongata*)	5 (25)	11–14	15–29	1.6 (1.4–3.4)[b]	3.5 (3.1–3.6)	Omnivorous	Pelagic	20 (16–57)	95 (79–240)	1200 (1200–1700)
Sardine (*Sardinella jussieu*)	5 (28)	10–13	13–29	2.3 (1.4–2.5)	3.1 (2.7–3.2)	Planktivorous	Pelagic	31 (20–42)	110 (73–160)	1400 (1200–2800)
Silver pomfret (*Pampus argenteus*)	8	12–18	64–190	5.3 (2.9–12)	3.3 (3.0–3.5)	Herbivorous	Mesopelagic	30 (25–58)	130 (101–270)	490 (330–2000)
Tapertail anchovy (*Coilia mystus*)	11 (105)	12–20	5–28	4.1 (1.2–11)	3.4 (3.1–3.6)	Omnivorous	Mesopelagic	22 (15–30)	89 (62–150)	460 (210–1900)
Bombay duck (*Harpadon nehereus*)	9 (57)	14–22	13–76	0.45 (0.34–1.5)	3.7 (3.2–4.1)	Carnivorous	Mesopelagic	6.4 (5.3–11)	73 (61–120)	1600 (770–2300)
Shrimp										
Shiba shrimp (*Metapenaeus joyneri*)	4 (120)	3–5	2–8	0.92 (0.88–0.96)	3.0 (2.8–3.2)	Omnivorous	Benthic	130 (67–190)	670 (390–930)	14,000 (7400–21,000)
Sword prawn (*Parapenaeopsis hardwickii*)	6 (180)	4–6	3–15	0.78 (0.70–0.91)	3.7 (3.7–3.9)	Carnivorous	Benthic	24 (20–28)	130 (100–140)	3100 (2400–4000)
Crab										
Japanese stone crab (*Charybdis japonica*)	4 (120)	–	8–19	0.49 (0.43–0.56)	3.2 (3.1–3.3)	Omnivorous	Benthic	39 (30–58)	130 (98–190)	7300 (6200–13,000)
Bivalve										
Asiatic hard clam (*Meretrix meretrix L.*)	6 (180)	–	18–35	0.85 (0.79–0.90)	2.2 (2.1–2.3)	Omnivorous	Benthic	27 (17–110)	200 (120–760)	3300 (1900–13,000)
Manila clam (*Ruditapes philippinarum*)	5 (150)	–	10–14	1.2 (1.0–1.2)	2.3 (2.2–2.3)	Omnivorous	Benthic	26 (23–28)	215 (190–230)	2100 (2000–2700)
Cephalopoda										
Squid (*Loligo tagoi*)	3 (60)	–	10–71	1.3 (1.1–1.4)	3.3 (3.1–3.7)	Carnivorous	Mesopelagic	13 (12–13)	90 (76–93)	1000 (990–1000)

[a] Number of composite samples analyzed. Figures in brackets indicate the number of individuals collected.
[b] Median (min–max).

levels of $\sum$ SCCPs in the marine species were significantly higher than previously detected levels of other halogenated organic pollutants including DDTs (54–1500 ng·g^{-1} lw), PCBs (16–700 ng·g^{-1} lw), PBDEs (0.56–59 ng·g^{-1} lw) and several of the currently used alternative halogenated flame retardants (AHFRs, non-detectable–37 ng·g^{-1} lw) in the same samples of the present study (Sun et al., 2015b). This result indicates that SCCPs might be the main halogenated organic pollutants in the study area.

A more recent study of SCCPs in Indo-Pacific humpback dolphin (*Sousa chinensis*) was conducted by Zeng et al. (2015) in the Pearl River Estuary, and the measured $\sum$ SCCP concentrations in blubber samples ranged from 920 and 24,000 ng·g^{-1} lw with a mean value of 5500 ng·g^{-1} lw, which were higher than those detected in this study (210–21,000 ng·g^{-1}). The levels of $\sum$ SCCPs in the dorsal muscle of fish species (210–2800 ng·g^{-1} lw and 5.3–58 ng·g^{-1} wet weight, ww) from the Pearl River Estuary were higher than the concentrations reported for top predatory fish (2–10 ng·g^{-1} ww in the whole body homogenates) in Canada (Basconcillo et al., 2015), but lower than those in the muscles of marine fish from Liaodong Bay of North China (9700–33,000 ng·g^{-1} lw) (Ma et al., 2014b), and marine fish (33–140 ng·g^{-1} ww) from Ebro River Delta in Spain (Parera et al., 2013). The concentrations of $\sum$ SCCPs in bivalves in the present study varied from 120 to 760 ng·g^{-1} dw, which were in the range of 65–5500 ng·g^{-1} dw in the bivalves from the Bohai Sea in China (Yuan et al., 2012; Ma et al., 2014a). The median concentrations of $\sum$ SCCPs in Asiatic hard clam and Manila calm from the Chinese Bohai Sea were 2600 ng·g^{-1} dw (Yuan et al., 2012) and 54,000 ng·g^{-1} lw (Ma et al., 2014b), which were one order of magnitude higher than those observed in the same bivalve species in the present study.

3.2. Species-specific difference in bioaccumulation of SCCPs and potential influence factors

Significant interspecies differences were observed in the levels of $\sum$ SCCPs in the present study ($p < 0.05$). The lowest concentration was found in tapertail anchovy (median of 460 ng·g^{-1} lw), and the highest was detected in shiba shrimp (median of 14,000 ng·g^{-1} lw) (Table 1). Overall, shrimps, crabs, and bivalves exhibited higher $\sum$ SCCP levels than did fish and cephalopods. Of the five fish species, $\sum$ SCCP levels in Chinese herring (1200 ng·g^{-1} lw), sardine (1400 ng·g^{-1}) and Bombay duck (1600 ng·g^{-1} lw) were higher than those in silver pomfret (490 ng·g^{-1} lw) and tapertail anchovy (460 ng·g^{-1}).

Differences in habitat between fish and other marine species in the present study were a possible explanation for the observed interspecies variation. SCCPs are hydrophobic compounds, and the octanol–water partition coefficient (log K_{OW}) values of a series of commercial and synthesized SCCPs were reported in a range from 4.01 to 8.67 (Hilger et al., 2011), implying they tend to be reserved by sediments. Shrimp, crabs, and bivalves are generally exposed more frequently to the sediment than fish species and squid, which can result in a higher body burden for SCCPs. Additionally, metabolic capability for SCCPs may influenced the SCCP body burden of marine species. Large number of studies had shown that bivalves have high accumulation capacity and slow elimination of heavy metals, organometallic compounds, and persistent organic pollutants (Sudaryanto et al., 2002; Monirith et al., 2003; Tanabe et al., 2008; Rouane-Hacene et al., 2015). A lower metabolic debromination capacity for PBDEs was also observed in bivalve species than in the fish species in the Pearl River Estuary (Sun et al., 2015b). Thus, the metabolism rate of SCCPs in shrimp and bivalves might be lower than that occurring in fish species. To date, little is known about the metabolism of SCCPs in marine organisms. Thus, more studies on metabolism of SCCPs in marine organisms are needed to validate the above hypothesis.

Regarding the species-specific accumulation of SCCPs among fish, the lipid content could play an important role in the determination of the SCCP burden (Yuan et al., 2012; Ma et al., 2014b). Significant linear

relationship was observed between the lipid content and the concentrations of $\sum$ SCCPs of marine species in the Chinese Bohai Sea when expressed on the wet weight or dry weight basis (Yuan et al., 2012; Ma et al., 2014b). In the present study, the lipid contents were significantly lower in three of the fish species (2.3% for Chinese herring, 1.6% for sardine, and 0.45% for Bombay duck), which also exhibited relatively high $\sum$ SCCP lipid normalized concentrations compared to the other two fish species which had higher lipid contents (5.3% for silver pomfret and 4.1% for tapertail anchovy) (Table 1). A simple correlation analysis between $\sum$ SCCP level based on wet weight and lipid content, however, revealed that the $\sum$ SCCP levels in fish did not significantly correlate with lipid content in silver pomfret and tapertail ($p > 0.05$). Thus, the high tissue lipid content in these two fish species caused pollutant dilution when the concentration was expressed on a lipid basis. Similarly, metabolism was also a potential factor affecting the SCCP burden in fish species.

The different growth periods of the studied marine species may be a complicating factor for SCCP bioaccumulation. We took two of the fish species, the tapertail anchovy and Bombay duck, for example to explore the relationship between the body size and the SCCPs body burden, because of their large sample number and wide range of body size. 105 tapertail anchovies and 57 Bombay ducks were divided into 11 and 9 groups, respectively based on the body length. The concentrations of SCCPs decreased significantly with the increasing body length for the two fish species ($p < 0.001$) (Fig. 2). Growth dilution, spawning at a certain age, and movement could be possible causes for this phenomenon (Daley et al., 2014; Huertas et al., 2016).

3.3. Biomagnification factor (BMF) of SCCPs

The Bombay duck, a piscivorous fish, exhibited the highest level of $\sum$ SCCPs among the five fish species. The higher trophic position occupied by the Bombay duck in the marine food web may play an important role in SCCP accumulation. It is impossible, however, to assess the influence of trophic levels on the SCCP burden in the studied species, because most of the species collected for the study had similar trophic levels (2.2–3.7) (Table 1). Fortunately, tapertail anchovy were frequently observed in the stomach contents of Bombay duck during the dissection. This indicated clearly that there was an actual predator-and-prey relationship between the Bombay duck and the tapertail anchovy. The biomagnification factors (BMFs), defined as the ratio of the average SCCP congener lipid-normalized concentration between the Bombay duck (predator) and the tapertail anchovy (prey) were obtained. The calculated BMFs for SCCP homologues ranged from 1.1 ($C_{10}H_{16}Cl_6$) to 3.4 ($C_{13}H_{18}Cl_{10}$) (Fig. 3), which were comparable to the reported values from alewife to lake trout in Lake Ontario and from rainbow smelt to lake trout in Lake Michigan (Houde et al., 2008).

The BMFs higher than 1 confirmed that SCCPs had potential biomagnification through the food chain. Biomagnification of DDTs, PCBs, and PBDEs in the same predator/prey relationship have also been observed in our previous study (Sun et al., 2015b). The observed BMFs for the SCCP homologues were generally higher than those reported for DDT, PCB, and PBDE congeners (Sun et al., 2015b). Significant positive correlations were observed between BMFs and carbon-chain length ($r = 0.54$, $p < 0.05$) and between BMFs and chlorine atom number ($r = 0.67$, $p < 0.05$) in the SCCP homologues (Fig. 3). Similar results were also reported previously between bioaccumulation factors (BAFs) and the carbon and chlorine atoms in many other studies (Houde et al., 2008; Zeng et al., 2011a; Ma et al., 2014b). These results implied a high biomagnification potential for the SCCP formula groups with the longer carbon chain and higher chlorine content, which may be partly attributed to their higher log K_{OW} and the elimination potential of the shorter chained CPs. The K_{OW} values generally increased with the number of carbon and chlorine atoms for these chemicals (Hilger et al., 2011). Additionally, the exposure experiments in rats in the laboratory have revealed a relative increase of Cl_5-SCCP in blood and urine and a higher accumulation of $Cl_{8–10}$-SCCPs in feces in the elimination stage (Geng et al., 2016).

3.4. Homologue patterns in marine species

Homologue group abundance profiles of SCCPs in marine species were presented in Fig. 4. The relative abundance of SCCPs with different carbon atoms (C_{10}–C_{13}) were similar in the marine species sampled from the Pearl River Estuary. An increase trend was observed for SCCP homologue group abundance with the increasing carbon atoms (19%, 23%, 27%, and 30% for C_{10}, C_{11}, C_{12}, and C_{13}, respectively) when the average percentages were calculated for all species. Regarding the chlorine content, Cl_7 and Cl_8 were the dominant congeners with the average percentages ranging from 25%–30% (27%, average) and from 21%–33% (26%, average) of the total SCCPs, respectively. This patterns of SCCPs were generally consistent with those in Indo-Pacific humpback dolphins from the study region in recent years (2012–2014) (Zeng et al., 2015); but different from those reported in the surface sediment samples with higher abundance of short carbon chain (C_{10} and C_{11}) in the Pearl River Estuary, although homologue groups with 7–8 chlorines dominated in the sediments (Chen et al., 2011). However, it was not clear whether this finding suggested selective accumulation of longer carbon chain SCCPs in these organisms; because Zeng et al. (2015) found a more significant temporal shift trend in the SCCP homologue pattern from shorter- to longer-chain groups in dolphin from the Pearl River Estuary between 2004 and 2014. The temporal shift trends in mammals may reflect a change of SCCP homologues group pattern in the environment. Meanwhile, Ma et al. (2014b) reported a similar
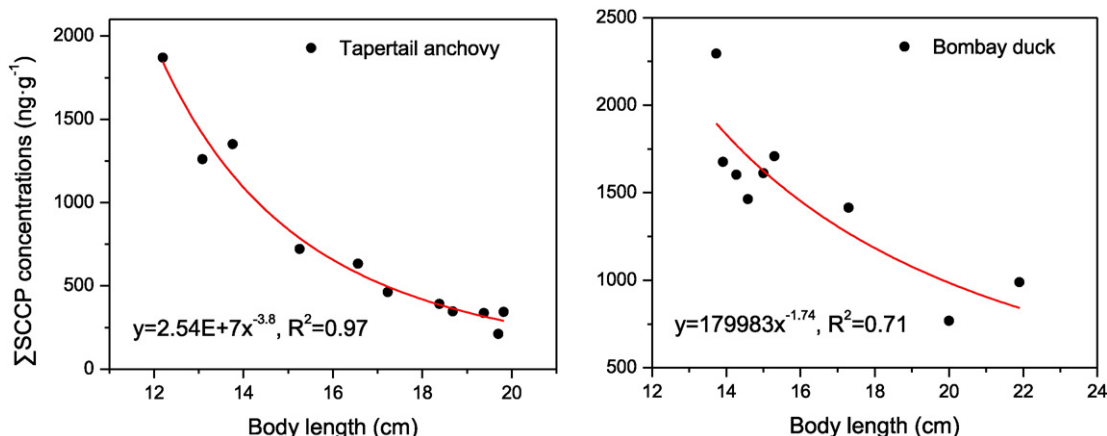

Fig. 2. Relationships between the body length and concentrations of $\sum$ SCCPs (ng/g lipid weight) in tapertail anchovy and Bombay duck.
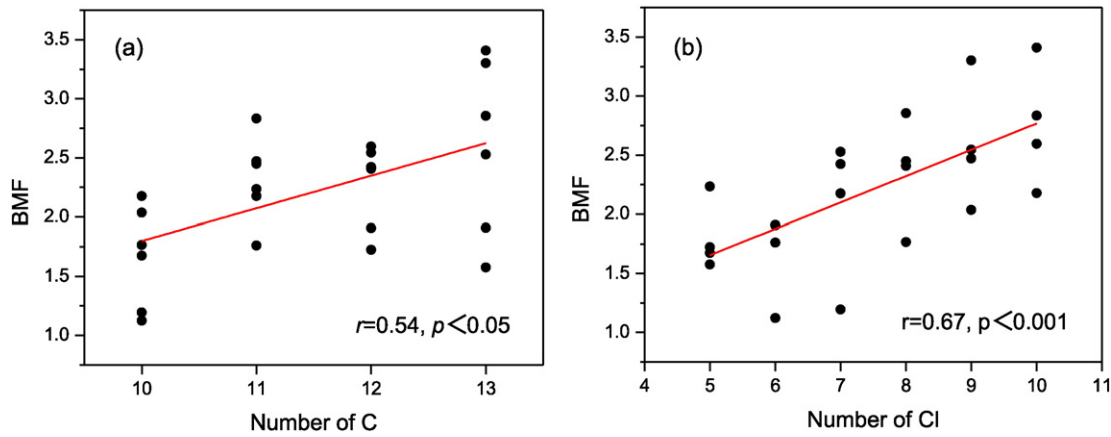
Fig. 3. Relationships between BMF for tapertail anchovy—Bombay duck and the number of carbon atoms (a) and chlorine atoms (b) in the SCCP congeners.

homologue group abundance profiles of SCCPs (C_{10-11}, Cl_{5-7} SCCPs dominating) in seawater, sediments and marine species from Liaodong Bay in China. A similar congener distribution of SCCPs was also observed between organisms and the habitat in an aquatic ecosystem receiving effluents from a sewage treatment plant (Zeng et al., 2011a). Hence, more comprehensive sampling including environmental samples is necessary for further evaluating the fate and bioaccumulation of SCCPs. In addition, the SCCP homologue group pattern in the present

study was also different from the pattern observed in the fish (C_{11-12} dominating) from Canada (Basconcillo et al., 2015), and marine species (C_{10-11} dominated in fish and invertebrates) from Bohai Sea in China (Yuan et al., 2012; Ma et al., 2014a, 2014b); indicating different contaminant sources or spatial distribution in usage of CP formulations.

Interspecies differences were observed in homologue group pattern of SCCPs in the present study. The average proportions of C_{10} congeners in shrimps and bivalves (15–17%, average range) were significantly
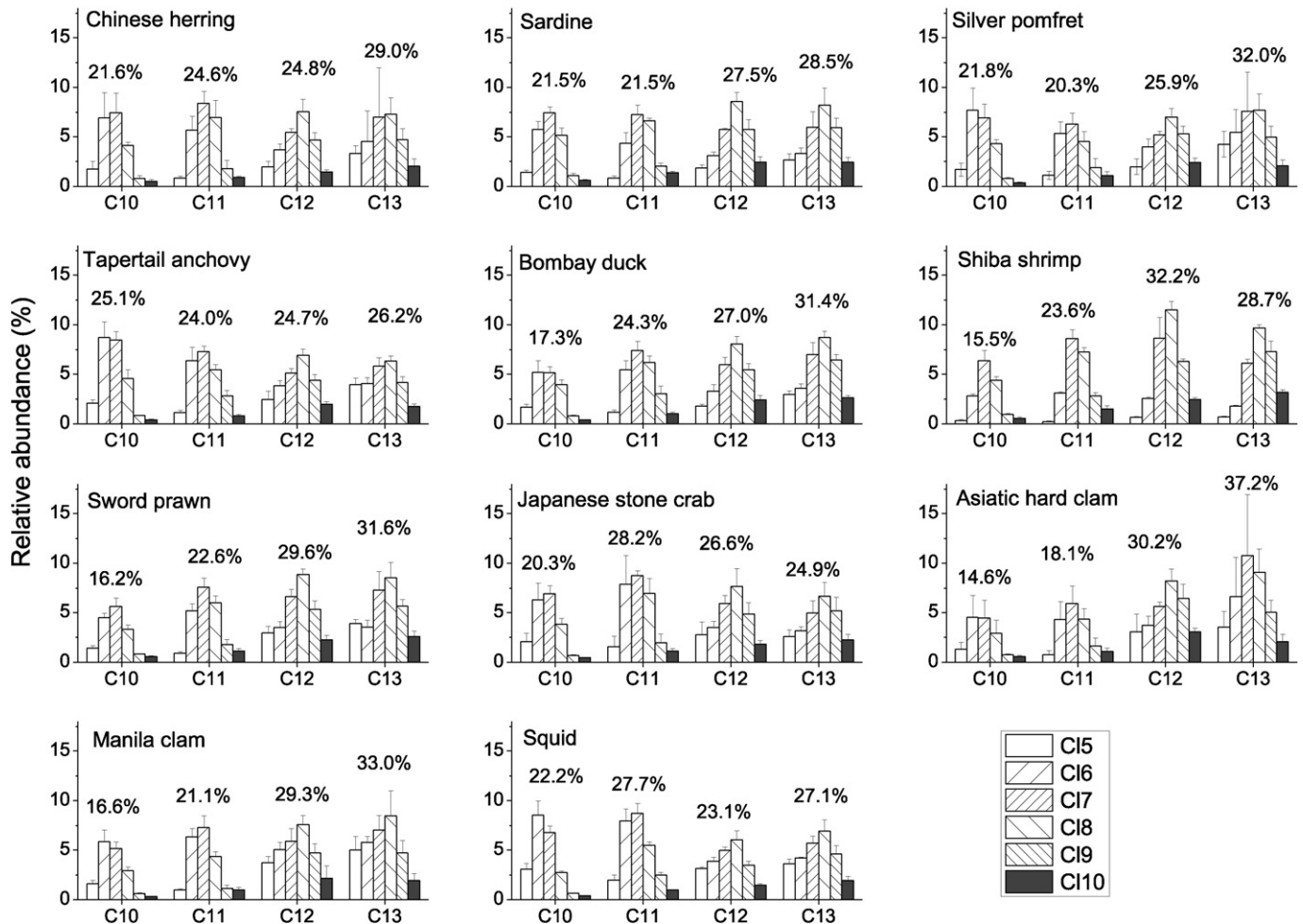

Fig. 4. Average individual SCCP congener group abundance profiles in marine species from the Pearl River Estuary in South China. Values are mean ± standard error.

lower than those in cephalopods (22%) and fish (21%–25%) except for the Bombay duck (17%) ($p < 0.05$). The relatively low proportions of C_{10} congeners in shrimps and bivalves may be attributed to their benthic habitat. It was demonstrated that the log K_{OW} of SCCPs is linearly positively related to the number of carbon atoms (Hilger et al., 2011). Consequently, the congeners with more carbon atoms are more prone to be absorbed to suspended particulate matter and to be subsequently deposited to sediments, while the short chain congeners are more easily distributed in the water. The fact that the relative abundance of C_{10}-SCCPs was higher in water than in sediment has been reported in many aquatic environments, such as Liaodong Bay in North China (Ma et al., 2014b) and Gaobeidian Lake, a freshwater lake receiving effluents from a sewage treatment plant (Zeng et al., 2011a). Benthic invertebrates, such as shrimp and bivalves are exposed more frequently to the sediment than the fish inhabiting in the pelagic and mesopelagic layer, which could cause a lower abundance of C_{10} congeners.

An exception among the fish species, however, was the Bombay duck, which showed a similar SCCP homologue pattern to that of shrimp and bivalves (Fig. 4). The difference in the species' feeding habit may be an important reason for this observation. Among the five studied fish species, Bombay duck is the only carnivorous fish, feeding on benthic invertebrates and smaller fish; which may facilitate the accumulation of C_{10} congeners from benthic organisms. In addition, the metabolic capacity for the SCCP congeners may play an important role in the congener distribution pattern. Actually, congener group-specific elimination and excretion process for SCCPs were found in Sprague–Dawley rats following single oral administration (Geng et al., 2016). As a carnivorous fish, Bombay duck was expected having higher SCCP metabolic capacity than other fish species. However, limited information is available for aquatic biota, and more research should be conducted in the future.

For the benthic invertebrates, Japanese stone crab exhibited a higher proportion of C_{10} congeners and a lower abundance of C_{13} congeners than the other four benthic invertebrate species. Similar to the case of the Bombay duck, feeding habits and metabolism of SCCPs can be responsible for the observation made with the Japanese stone crab. Among the investigated species, the Japanese stone crab is the only scavenger. Accumulation of SCCP direct from sediment was less than other benthic invertebrates. Besides, the highest biotransformation capacity for DDT also occurred in this crab among the studied marine species, as reported in our previous study (Sun et al., 2015b).

4. Conclusion

SCCP contamination was examined in marine organisms collected from the Pearl River Estuary in South China. The results demonstrated that the levels of $\sum$ SCCPs in the marine species in the study area were in the medial level of world figures. The concentrations and congener group abundance profiles of SCCPs exhibited interspecies difference, which could be attributed to the differences in habitat, feeding habits, trophic levels and metabolic capacity among the marine species. Biomagnification was found between prey and predator, and the BMFs for SCCP congeners were generally higher than those for DDT, PCB and PBDE congeners. Furthermore, the BMFs increased significantly with the number of carbon and chlorine atoms. These findings indicated higher biomagnification potential for the SCCP formula groups with the longer carbon chain and higher chlorine atom numbers. This is the first report on the accumulation of SCCPs in marine species in the Pearl River Estuary.

Acknowledgments

References

Basconcillo, L.S., Backus, S.M., McGoldrick, D.J., Zaruk, D., Sverko, E., Muir, D.C., 2015. Current status of short- and medium chain polychlorinated n-alkanes in top predatory fish across Canada. Chemosphere 127, 93–100.

Bayen, S., Obbard, J.P., Thomas, G.O., 2006. Chlorinated paraffins: a review of analysis and environmental occurrence. Environ. Int. 32, 915–929.

Chen, M.Y., Luo, X.J., Zhang, X.L., He, M.J., Chen, S.J., Mai, B.X., 2011. Chlorinated paraffins in sediments from the Pearl River Delta, South China: spatial and temporal distributions and implication for processes. Environ. Sci. Technol. 45, 9936–9943.

Daley, J.M., Paterson, G., Drouillard, K.G., 2014. Bioamplification as a bioaccumulation mechanism for persistent organic pollutants (POPs) in wildlife. Rev. Environ. Contam. Toxicol. 227, 107–155.

Feo, M., Eljarrat, E., Barcelo, D., Barceló, D., 2009. Occurrence, fate and analysis of polychlorinated n-alkanes in the environment. Trends Anal. Chem. 28, 778–791.

Fu, J., Mai, B., Sheng, G., Zhang, G., Wang, X., Peng, P.a., Xiao, X., Ran, R., Cheng, F., Peng, X., 2003. Persistent organic pollutants in environment of the Pearl River Delta, China: an overview. Chemosphere 52, 1411–1422.

Gao, Y., Zhang, H., Su, F., Tian, Y., Chen, J., 2012. Environmental occurrence and distribution of short chain chlorinated paraffins in sediments and soils from the Liaohe River Basin, PR China. Environ. Sci. Technol. 46, 3771–3778.

Geng, N., Zhang, H., Xing, L., Gao, Y., Zhang, B., Wang, F., Ren, X., Chen, J., 2016. Toxicokinetics of short-chain chlorinated paraffins in Sprague–Dawley rats following single oral administration. Chemosphere 145, 106–111.

Geng, N., Zhang, H., Zhang, B., Wu, P., Wang, F., Yu, Z., Chen, J., 2015. Effects of short-chain chlorinated paraffins exposure on the viability and metabolism of human hepatoma HepG2 cells. Environ. Sci. Technol. 49, 3076–3083.

Harada, K.H., Takasuga, T., Hitomi, T., Wang, P., Matsukami, H., Koizumi, A., 2011. Dietary exposure to short-chain chlorinated paraffins has increased in Beijing, China. Environ. Sci. Technol. 45, 7019–7027.

Hilger, B., Fromme, H., Völkel, W., Coelhan, M., 2011. Effects of chain length, chlorination degree, and structure on the octanol–water partition coefficients of polychlorinated n-alkanes. Environ. Sci. Technol. 45, 2842–2849.

Houde, M., Muir, D.C., Tomy, G.T., Whittle, D.M., Teixeira, C., Moore, S., 2008. Bioaccumulation and trophic magnification of short-and medium-chain chlorinated paraffins in food webs from Lake Ontario and Lake Michigan. Environ. Sci. Technol. 42, 3893–3899.

Huertas, D., Grimalt, J.O., Benito, J., Benejam, L., García-Berthou, E., 2016. Organochlorine compounds in European catfish (Silurus glanis) living in river areas under the influence of a chlor-alkali plant (Ebro River basin). Sci. Total Environ. 540, 221–230.

Iozza, S., Müller, C.E., Schmid, P., Bogdal, C., Oehme, M., 2008. Historical profiles of chlorinated paraffins and polychlorinated biphenyls in a dated sediment core from Lake Thun (Switzerland). Environ. Sci. Technol. 42, 1045–1050.

Luo, X.J., Sun, Y.X., Wu, J.P., Chen, S.J., Mai, B.X., 2015. Short-chain chlorinated paraffins in terrestrial bird species inhabiting an e-waste recycling site in South China. Environ. Pollut. 198, 41–46.

Ma, X., Chen, C., Zhang, H., Gao, Y., Wang, Z., Yao, Z., Chen, J., Chen, J., 2014a. Congener-specific distribution and bioaccumulation of short-chain chlorinated paraffins in sediments and bivalves of the Bohai Sea, China. Mar. Pollut. Bull. 79, 299–304.

Ma, X., Zhang, H., Wang, Z., Yao, Z., Chen, J., Chen, J., 2014b. Bioaccumulation and trophic transfer of short chain chlorinated paraffins in a marine food web from the Liaodong Bay, North China. Environ. Sci. Technol. 48, 5964–5971.

Mai, B., Chen, S., Chen, S., Luo, X., Chen, L., Chen, L., Yang, Q., Sheng, G., Peng, P., Fu, J., 2005a. Distribution of polybrominated diphenyl ethers in sediments of the Pearl River Delta and adjacent South China Sea. Environ. Sci. Technol. 39, 3521–3527.

Mai, B., Zeng, E.Y., Luo, X., Yang, Q., Zhang, G., Li, X., Sheng, G., Fu, J., 2005b. Abundances, depositional fluxes, and homologue patterns of polychlorinated biphenyls in dated sediment cores from the Pearl River Delta, China. Environ. Sci. Technol. 39, 49–56.

Monirith, I., Ueno, D., Takahashi, S., Nakata, H., Sudaryanto, A., Subramanian, A., Karuppiah, S., Ismail, A., Muchtar, M., Zheng, J., Richardson, B.J., Prudente, M., Hue, N.D., Tana, T.S., Tkalin, A.V., Tanabe, S., 2003. Asia-Pacific mussel watch: monitoring contamination of persistent organochlorine compounds in coastal waters of Asian countries. Mar. Pollut. Bull. 46, 281–300.

Parera, J., Ábalos, M., Santos, F., Galceran, M., Abad, E., 2013. Polychlorinated dibenzo-p-dioxins, dibenzofurans, biphenyls, paraffins and polybrominated diphenyl ethers in marine fish species from Ebro River Delta (Spain). Chemosphere 93, 499–505.

Reth, M., Ciric, A., Christensen, G.N., Heimstad, E.S., Oehme, M., 2006. Short-and medium-chain chlorinated paraffins in biota from the European Arctic—differences in homologue group patterns. Sci. Total Environ. 367, 252–260.

Reth, M., Zencak, Z., Oehme, M., 2005. New quantification procedure for the analysis of chlorinated paraffins using electron capture negative ionization mass spectrometry. J. Chromatogr. A 1081, 225–231.

Rouane-Hacene, O., Boutiba, Z., Belhaouari, B., Guibbolini-Sabatier, M.E., Francour, P., Risso-de Faverney, C., 2015. Seasonal assessment of biological indices, bioaccumulation and bioavailability of heavy metals in mussels Mytilus galloprovincialis from Algerian west coast, applied to environmental monitoring. Oceanologia 57, 362–374.

Strid, A., Bruhn, C., Sverko, E., Svavarsson, J., Tomy, G., Bergman, Å., 2013. Brominated and chlorinated flame retardants in liver of Greenland shark (Somniosus microcephalus). Chemosphere 91, 222–228.

Sudaryanto, A., Takahashi, S., Monirith, I., Ismail, A., Muchtar, M., Zheng, J., Richardson, B.J., Subramanian, A., Prudente, M., Hue, N.D., 2002. Asia-Pacific mussel watch: monitoring of butyltin contamination in coastal waters of Asian developing countries. Environ. Toxicol. Chem. 21, 2119–2130.

Sun, R.X., Luo, X.J., Tan, X.X., Tang, B., Li, Z.R., Mai, B.X., 2015a. An eight year (2005–2013) temporal trend of halogenated organic pollutants in fish from the Pearl River Estuary, South China. Mar. Pollut. Bull. 93, 61–67.

Sun, R.X., Luo, X.J., Tan, X.X., Tang, B., Li, Z.R., Mai, B.X., 2015b. Legacy and emerging halogenated organic pollutants in marine organisms from the Pearl River Estuary, South China. Chemosphere 139, 565–571.

Tanabe, S., Ramu, K., Isobe, T., Takahashi, S., 2008. Brominated flame retardants in the environment of Asia-Pacific: an overview of spatial and temporal trends. J. Environ. Monit. 10, 188–197.

Tomy, G., Fisk, A., Westmore, J., Muir, D., 1998. Environmental chemistry and toxicology of polychlorinated n-alkanes. Rev. Environ. Contam. Toxicol. 158, 53–128.

Tomy, G.T., Stern, G.A., Muir, D.C., Fisk, A.T., Cymbalisty, C.D., Westmore, J.B., 1997. Quantifying C10-C13 polychloroalkanes in environmental samples by high-resolution gas chromatography/electron capture negative ion high-resolution mass spectrometry. Anal. Chem. 69, 2762–2771.

UNEP, 2015a. Short-chained chlorinated paraffins: risk profile UNEP/POPS/POPRC.11/10/Add.2. United Nations Stockholm Convention on Persistent Organic Pollutants, Rome.

UNEP, 2015b. Report of the Persistent Organic Pollutants Review Committee UNEP/POPS/POPRC. 11/10. United Nations Environmental Programme Stockholm Convention on Persistent Organic Pollutants, Rome.

Wang, Y., Li, J., Cheng, Z., Li, Q., Pan, X., Zhang, R., Liu, D., Luo, C., Liu, X., Katsoyiannis, A., 2013. Short-and medium-chain chlorinated paraffins in air and soil of subtropical terrestrial environment in the Pearl River Delta, South China: distribution, composition, atmospheric deposition fluxes, and environmental fate. Environ. Sci. Technol. 47, 2679–2687.

Warnasuriya, G.D., Elcombe, B.M., Foster, J.R., Elcombe, C.R., 2010. A mechanism for the induction of renal tumours in male Fischer 344 rats by short-chain chlorinated paraffins. Arch. Toxicol. 84, 233–243.

Yu, M., Luo, X.J., Wu, J.P., Chen, S.J., Mai, B.X., 2009. Bioaccumulation and trophic transfer of polybrominated diphenyl ethers (PBDEs) in biota from the Pearl River Estuary, South China. Environ. Int. 35, 1090–1095.

Yuan, B., Wang, T., Zhu, N., Zhang, K., Zeng, L., Fu, J., Wang, Y., Jiang, G., 2012. Short chain chlorinated paraffins in mollusks from coastal waters in the Chinese Bohai Sea. Environ. Sci. Technol. 46, 6489–6496.

Zeng, L., Wang, T., Han, W., Yuan, B., Liu, Q., Wang, Y., Jiang, G., 2011b. Spatial and vertical distribution of short chain chlorinated paraffins in soils from wastewater irrigated farmlands. Environ. Sci. Technol. 45, 2100–2106.

Zeng, L., Wang, T., Wang, P., Liu, Q., Han, S., Yuan, B., Zhu, N., Wang, Y., Jiang, G., 2011a. Distribution and trophic transfer of short-chain chlorinated paraffins in an aquatic ecosystem receiving effluents from a sewage treatment plant. Environ. Sci. Technol. 45, 5529–5535.

Zeng, L., Lam, J.C., Wang, Y., Jiang, G., Lam, P.K., 2015. Temporal trends and pattern changes of short-and medium-chain chlorinated paraffins in marine mammals from the South China Sea over the past decade. Environ. Sci. Technol. 49, 11348–11355.