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THE BIOACCUMULATION OF SCCPS IN AN AQUATIC FOOD CHAIN FROM AN POND CONTAMINATED BY E-WASTE IN SOUTH CHINA

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Introduction:
Short-chain chlorinated paraffins (SCCPs) have attracted increasing attention in the last decade due to their persistence, bioaccumulation, toxicity to organisms. SCCPs are currently reviewed as potential persistent organic pollutants by the Stockholm Convention. Studies indicate that SCCPs have become ubiquitous in the environment and are routinely detected in both biotic and abiotic compartments [1]. However, the understanding on the bioaccumulation and trophic transfer of SCCP in food web is still limited by far [2, 3]. In the present study, aquatic organisms, including fish and invertebrates, were collected from a pond contaminated by e-waste in South China. The aims of this study were to investigate the tissue distribution and trophic dynamic behavior of SCCPs in aquatic organisms.

Material and method
Fish and invertebrates were caught by net and electric fishing in a pond located in Longtang Town, Qingyuan County, Guangdong province in October 2015. The discarding e-wastes were stacked in the bottom of the pond which resulted in a high e-waste related pollutant exposure for organisms. The species included oriental river prawn (Macrobrachium nipponense, 50 individuals to 5 pooled samples), Chinese mitten crab (Eriocheir sinensis, 18 individuals to 9 samples), crucian carp (Carassius auratus, 16 individuals to 5 samples), mud carp (Cirrhinus molitorella, n=5 for larger group and 60 individuals to 5 samples for small group), catfish (Clarias batrachus, n=2), and snakehead (Ophicephalus argus, n=5). Three water samples and three sediment samples were also collected. Mud carp was divided into two groups according to the body weight (larger group, average body weight 1800 g, small group, average body weight 5 g). The larger group was used for tissue distribution investigation and the small group was used for trohpic transfer study. The dorsal muscles of the fish and the edible part of the invertebrates were taken. Skin, gill, liver, kidney, and muscle were taken from lager group of mud carp and snakehead respectively to perform tissue distribution study.
The extraction and cleanup method for SCCPs in organisms were same as that in the previous study[4]. Briefly, after being spiked with surrogate standards (5 ng of ε-hexachlorocyclohexane, ε-HCH), the samples were Soxhlet extracted with 200 mL of n-hexane/dichloromethane (1:1, v:v) for 48 h. 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 and further cleaned on a complex column packed with Florisil. The fraction contained SCCPs was concentrated to near dryness under a gentle nitrogen flow, and solvent exchanged to isooctane to a final volume of 200 μL.10 ng of 13C10-trans-chlordane was added as a recovery standard for GC/MS analysis.
Water was filter using 45 μm glass fiber filter then liquid-liquid extracted three times using DCM. Sediment was extracted with 200 mL of n-hexane/dichloromethane (1:1, v:v) for 48 h. The extracts for water and sediment were cleaned on the same Florisil column as that for organism analysis.
SCCPs were analyzed using a Shimadzu model 2010 gas chromatograph equipped with a model QP-2010 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). SCCP congeners having 10–13 carbon atoms and 5–10 chlorine atoms were analyzed. The mass-to-charge ratios used for quantification and confirmation were published elsewhere [5]. The most and second-most abundant isotope ions were used for quantification and confirmation, respectively. The total SCCP was quantified using the procedure described by Reth et al.[6]. 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 [5] Stable nitrogen isotope of muscle were determined by a Flash EA 112 series elemental analyzer interfaced with a Finnigan MAT ConFlo III isotope ratio mass spectrometer.

Results and discussions
Concentrations of SCCPs:

The concentrations of SCCPs in muscle of organisms ranged from 1700-95000 ng/g lw and the highest and lowest concentrations (median of 22000 ng/g lw and median of 2100 ng/g lw) were found in the Chinese mitten crab and large mud carp group, respectively. The SCCP levels in the large mud carp group were significantly lower than those in the small mud carp group (median of 3400 ng/g lw, $p<0.01$). Similarity, the large catfish (1340 g) show lower SCCP concentration (2600 ng/g lw) than the small catfish (177g with SCCP level of 13000 ng/g lw). These results indicated a growth dilution of SCCPs in fish.
The SCCP level in water was 61 ± 5.5 ng/L while it covered several orders magnitude in sediment from 82 – 350000 ng/g dw. When we check TOC content of sediment, we found two sediments have extraordinary high TOC content (13% and 40%). These sediments are mainly composited with discarded e-waste particle. Thus, the SCCP levels (82 ng/g dw) in sediment with normal TOC content (1.5%) was adopted.
The levels of SCCPs in the present study were comparable with those (11000 ng/g lw in catfish and 25000 ng/g in crucian carp) in fish collected in Gaobeidian lake which received influents of WWPT [3] and those in marine organisms in Liaodong Bay (9700 – 33000 ng/g lw)[7]. However, the levels of SCCPs in the present study was remarkable higher than those (4.6-34 ng/glw) in fish in Lake Ontario and Lake Michigan [2] and those (12-288 ng/glw) in top predatory fish across Canada.[8]
The homologue profiles of SCCPs varied among aquatic organisms. The homologue profiles of SCCP can be divided into three groups. Crucian carp and mud carp share similar homologur profiles with low abundance of C10 but high abundance of C12 and C13. On the contrary, prawn and crab exhibited similar homologue profile with relative high abundance of C10. Snakehead and catfish have similar homologue profile with C11 as the highest abundance chemicals. Differences in feeding habit and habitat could contribute to the observed homologue profile differences.

Tissue distribution
The tissue distribution of SCCPs in two fish species follow same order when levels was expressed as wet weight, that is: liver > gill > kidney > skin > muscle. The wet weight normalized SCCP levels were found to positive correlate with the content of lipid in tissues. Thus, lipid play an important role in deposition of SCCP in tissues. No significant differences were found among tissues in mud carp when levels was expressed as lipid weight. However, kidney was found having significant higher SCCP levels than muscle and liver in snakehead, which means other factors beside the lipid content could also affect the SCCP deposition in organs.
To investigate whether different homologue have different tissue distribution, a ratio of M/(M+L) was calculated. The ratios of total SCCP don't significant different from 0.5 in both fish species, meaning no significant differences. However, the ratios of different homologue varied from 0.40 to 0.80 for mud carp and 0.40 to 0.83 for snakehead. Simple linear regress analysis between ratio and log KOW indicated that ratio negative related to log KOW (Fig 1), which means liver prefer accumulated high lipophilic chemicals.

Bioaccumulation factor and Bio-sediment accumulation factor
The levels of SCCPs in muscle (lipid normalized concentration) of fish were used to calculate BAF and the levels of SCCPs in invertebrates were used to calculate BSAF. The log BAF ranged from 2.21 to 3.99, which in the low end of log BAF for PCB congeners (1.2-8.3) and PBDE congeners (2.9-5.3) in the same pond. For two omnivorous fish species, a positive correlation between log BAF and log KOW was found (Fig 2). However, this correlation was not found in two carnivorous fish species (Fig 2). SCCPs mainly derived from diet for two carnivorous fish but mainly derived from water for two omnivorous species is a possible reason for this observation.

The BSAF varied from 0.37-33 for crab and from 0.2-12 for prawn. Generally, C12 and C13 homologue have lower BSAF than C10 and C11 homologue and the BSAF decreased with increasing chlorinated content in a given homologue. An exponential decay with increasing log KOW was found for BSAF in both two invertebrates (Fig 3). When log KOW > 6, BSAF was about 1, indicating equilibration between sediment and invertebrates, while homologue having low Log KOW prefer to accumulate in organisms.

Trophic transfer
The log transferred SCCP concentration in organisms was negative correlated with the δ15N (Fig 4), indicating a trophic dilution of SCCP along food chain, which is different from two previous studies [2,3] which all reported trophic magnification of SCCP in aquatic food web. The reason for this difference

is very complex. Food chain composition, the size of organisms, and the concentration of SCCP could all contributed to this differences.

The TMF of homologue positive correlated with the log KOW, (Fig 5) indicating long chain and high chlorinated homologues are relative easily accumulated in high trophic level organisms.

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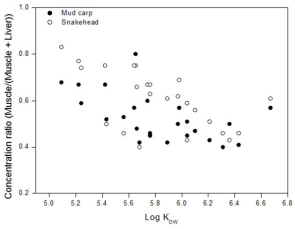

Figure 1: correlation between ratio of M/(M+L) and Log *Kow*.

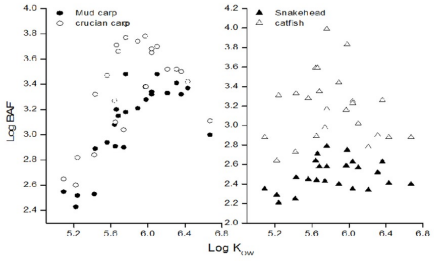

Figure 2: Correlation between log BAF and log Kow

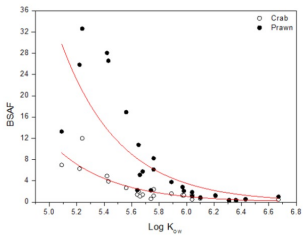

Figure 3: correlation between BSAF and log Kow.

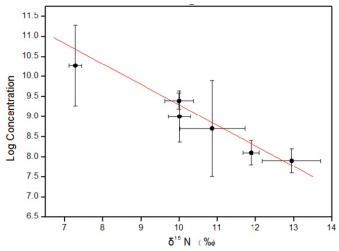

Figure 4: Trophic transfer of SCCP in food chain.

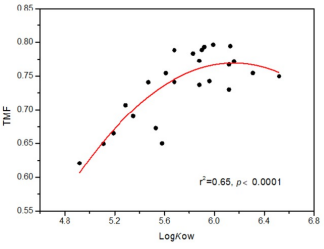

Figure 5: Correlation between TMF and log KOW.