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Bioaccumulation of short chain chlorinated paraffins in a typical freshwater food web contaminated by e-waste in south china: Bioaccumulation factors, tissue distribution, and trophic transfer☆

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ABSTRACT

Short chain chlorinated paraffins (SCCPs) are under review for inclusion into the Stockholm Convention on Persistent Organic Pollutants. However, limited information is available on their bioaccumulation and biomagnification in ecosystems, which is hindering evaluation of their ecological and health risks. In the present study, wild aquatic organisms (fish and invertebrates), water, and sediment collected from an enclosed freshwater pond contaminated by electronic waste (e-waste) were analyzed to investigate the bioaccumulation, distribution, and trophic transfer of SCCPs in the aquatic ecosystem. SCCPs were detected in all of the investigated aquatic species at concentrations of 1700–95,000 ng/g lipid weight. The calculated bioaccumulation factors (BAFs) varied from 2.46 to 3.49. The relationship between log BAF and the octanol/water partition coefficient (log K_{OW}) for benthopelagic omnivorous fish species followed the empirical model of bioconcentration, indicating that bioconcentration plays an important role in accumulation of SCCPs. In contrast, the relationship for the benthic carnivorous fish and invertebrates was not consistent with the empirical model of bioconcentration, implying that the bioaccumulation of SCCPs in these species could be more influenced by other complex factors (e.g., habitat and feeding habit). Preferential distribution in the liver rather than in other tissues (e.g., muscle, gills, skin, and kidneys) was noted for the SCCP congeners with higher log K_{OW}, and bioaccumulation pathway (i.e. water or sediment) can affect the tissue distribution of SCCP congeners. SCCPs underwent trophic dilution in the aquatic food web, and the trophic magnification factor (TMF) values of SCCP congener groups significantly correlated with their corresponding log K_{OW} values ($p < 0.0001$). The present study results improved our understanding on the environmental behavior and fate of SCCPs in aquatic ecosystem.

1. Introduction

Short chain chlorinated paraffins (SCCPs) are a synthetic complex mixture of chlorinated *n*-alkanes ranging from C_{10} to C_{13} with degrees of chlorination of 40–50% by mass weight (Fiedler, 2010). They are used as flame retardants and plasticizers in rubber compounds and polymers, additives in metal working fluids, paints, sealants, and leather treatment agents, as well as in extreme-pressure lubricants. SCCPs have generated worldwide concern in the last decade owing to their persistence in the environment, high potential for long-range transport, bioaccumulation, and toxicity to organisms (Basconcillo et al., 2015; Geng et al., 2015; Ma et al., 2014a, 2014c; Zeng et al., 2011b; Zhang et al., 2016). The manufacture and use of SCCPs is restricted or banned in the European Union, Japan, Canada, and the United States (UNEP, 2015b). Furthermore, SCCPs are currently candidates for classification as persistent organic pollutants (POPs) under the Stockholm Convention (UNEP, 2015a).

SCCPs are high production volume chemicals, and have been produced in many countries, especially China, which is the largest producer and consumer of chlorinated paraffins in the world

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(Sverko et al., 2012; van Mourik et al., 2016). In 2013, China's annual production of chlorinated paraffins was equal to 1.05 million tons (WCC, 2014), which accounted for 15% of the total global chlorinated paraffins production (van Mourik et al., 2016), although specific information on the production volumes of SCCPs are limited. The release of SCCPs into the environment can occur during production, storage, transportation, usage, and disposal or recycling of SCCPs and SCCP-containing products. Even in countries where SCCPs are prohibited, discharge into ecosystems continues to occur by means of old materials that are still in use or during disposal of these materials (van Mourik et al., 2016). Studies indicate that SCCPs are ubiquitous in the environment and are routinely detected in the air, soil, water, sediment, and in aquatic and terrestrial wildlife (Chen et al., 2011; Huang et al., 2016; Luo et al., 2015; Ma et al., 2014b; van Mourik et al., 2016; Wang et al., 2013). Notably, concentrations of SCCPs are generally present in higher levels than are other organohalogen compounds such as polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), and dichlorodiphenyltrichloroethanes (DDTs) in biotic and abiotic compartments (Bytingsvik, 2015; Li et al., 2014; Strid et al., 2013; Sun et al., 2016; Tan et al., 2016). Thus, it is important to improve our understanding of the environmental fate, behavior, and potential risks posed by SCCPs.

Limited data is available on the bioaccumulation and trophic transfer of SCCPs, which are the key criteria for assessing their potential risk. To our knowledge, the trophic magnification factors (TMFs) for SCCPs have only been reported in three freshwater food webs from Gaobeidian Lake (China) (Zeng et al., 2011b), and Lake Ontario and Lake Michigan (Canada) (Houde et al., 2008), and two marine food webs from the Bohai Bay (China) (Ma et al., 2014b; Yuan et al., 2012) and the Arctic (Herzke, 2013). The results on the bioaccumulation potential and trophic transfer of SCCPs in the organisms from these studies are inconsistent. Houde et al. (2008) reported that the biomagnification for SCCPs was found between *Diporeia* (prey) and sculpin (*Cottus cognatus*) (predator) in Lake Ontario and Lake Michigan, while lake trout (*Salvelinus namaycush*), a top predatory fish, in both lakes had lower SCCP concentrations than did several of their prey based on lipid content. SCCPs exhibited trophic dilution in shelled benthic species (bivalves, gastropods, and crustaceans) in the Bohai Sea in China, but showed biomagnification in trophic transfer from zooplankton-shrimp-fish in this region (Ma et al., 2014b; Yuan et al., 2012). These complex results indicate that further research is necessary to provide understanding on the bioaccumulation potential of SCCPs in different food webs. Additionally, limited information is available on tissue-specific accumulation and the pathways for aquatic organisms to accumulate SCCPs.

Electronic waste (e-waste) recycling sites have been demonstrated as hot spots for SCCP contamination (Chen et al., 2011; Luo et al., 2015). In comparison to large volume water bodies, e.g., oceans and lakes, a pond is a small-enclosed water body that can minimize interruption from activities such as the migration of organisms, which may make interpretation of food web magnification of chemicals problematic. In our previous study, a food web model from a pond contaminated by e-waste in South China has been created and successfully used to characterize trophic transfer of PCBs, PBDEs, and other flame-retardants (Wu et al., 2010a, 2009, 2010b). In the present study, aquatic organisms, including fish and invertebrates, water, and sediment were collected from the same pond as in the above previous studies. The aims of the present study were to investigate the bioaccumulation, tissue distribution, and trophic dynamic behavior of SCCPs in aquatic organisms.

2. Materials and methods

2.1. Sample collection

Wild fish and invertebrates were caught by net and electric fishing in an enclosed natural freshwater pond located in Longtang Town, Qingyuan County, Guangdong province, South China (23.60° N, 113.08° E) in December 2014. The pond covers 5000 square meters and reaches a depth of 2 m in summer. The discarded e-wastes were stacked at the bottom of the pond, which resulted in high e-waste related pollutant exposure for organisms inhabiting in this pond (Chen et al., 2011). Detailed information regarding this pond can be found in a previous publication (Wu et al., 2008). The species collected included oriental river prawn (*Macrobrachium nipponense*, 50 individuals divided up into 5 pooled samples), Chinese mitten crab (*Eriocheir sinensis,* 16 individuals divided up into 5 pooled samples), crucian carp (*Carassius auratus*, 16 individuals divided up into 5 pooled samples), mud carp (*Cirrhinus molitorella,* $n = 5$ for large group and 60 individuals divided up into 5 pooled samples for small group), catfish (*Clarias batrachus*, $n = 2$), and snakehead (*Ophiocephalus argus,* $n = 5$). Three water samples and four surface sediment samples were also collected. Mud carp was divided into two groups according to body size (large group: average body length and weight were 49 ± 3.0 cm and 1800 ± 230 g, respectively, and small group: average body length and weight were 8.2 ± 1.1 cm and 5.3 ± 1.5 g, respectively). The large group was used for the investigation of tissue distribution and the small group was used for the study of trophic transfer. The muscles of fish and invertebrates were sampled. Skin, gill, liver, kidney, and muscle were taken from the large group of mud carp and snakehead to perform the tissue distribution study.

2.2. Sample preparation and instrumental analysis

The extraction and cleanup method for SCCPs in organisms were the same as that used in a previous study (Sun et al., 2016). Briefly, after being spiked with a surrogate standard (10 ng of epsilon-hexachlorocyclohexane, ε-HCH), the lyophilized 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 of the extract was purified with concentrated sulfuric acid and further cleaned on a complex column packed with Florisil and silica gel. The column was eluted with 80 mL of *n*-hexane (first fraction, containing PCBs, PBDEs, and most of dichlorodiphenyltrichloroethane and its metabolites) followed by 60 mL of dichloromethane (second fraction, containing short -chain and medium-chain CPs, HCHs, and a few of dichlorodiphenyltrichloroethane and its metabolites) (Fig. S1 in the Supporting Information, SI). The second fraction was concentrated to near dryness under a gentle nitrogen flow, and solvent exchanged with isooctane to a final volume of 200 μL. A total of 10 ng of $^{13}C_{10}$-trans-chlordane was added as a recovery standard for gas chromatography − mass spectrometry analysis.

The water filtered through glass fiber filter (Whatman 0.7 μm pore size, 47 mm diameter), and then dissolved SCCPs in water were liquid-liquid extracted three times using dichloromethane. Sediment samples were freeze-dried, passed through an 80-mesh sieve, and 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 complex column as that for the organism analysis.

SCCP congeners having 10–13 carbon atoms and 5–10 chlorine atoms were analyzed by a Shimadzu model 2010 gas chromatograph coupled with a model QP-2010 mass spectrometer

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