INSIGHTS TO BIOACCUMULATION OF CHLORINATED PARAFFINS IN WILDLIFE

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Introduction

Chlorinated paraffins (CPs) refer to extremely complex mixtures of polychlorinated *n*-alkane congeners, where *n* = 6–38 with a relative chlorine content of 35-70%. They are abundant industrial products, commonly categorized into short-chain ($C_{10\text{-}13}$, SCCPs), medium-chain ($C_{14\text{-}17}$, MCCPs), and long-chain ($C_{18\text{-}}$, LCCPs) products[1]. The U.S. EPA further categorized wax-like $C_{>20}$ CPs as very long-chain CPs (vLCCPs)[2]. $C_{6\text{-}9}$ CPs are potentially impurities or by-products formed during the CP manufacturing process[3]. Here we denote $C_{6\text{-}9}$ CPs as very short-chain CPs (vSCCPs).

Due to recent addition of SCCPs to the Stockholm Convention on persistent organic pollutants (POPs), MCCPs and LCCPs are expected to be manufactured in increasing quantities as replacements[4]. Research efforts on MCCPs have been increasing while in contrast vSCCPs and LCCPs have received only limited attention. It has become clear that certain CP products are not solely SCCP or MCCP but rather looks like chlorination products of a wider span of alkane chain lengths, like C_{10}-C_{20}[5]. Our studies revealed that CPs of all chain lengths have been used and emitted into the envrionment[6,7] and are bioaccumulative[8]. Consequently, more insights into all CP categories is warranted for understanding their environmental fate and their potential threats to living organisms.

There has been a long lasting desire to accomplish CP exposure assessments among wildlife and humans even though the analytical methodology was less well developed[9]. Still some early work reported wildlife data on CPs in the early 1990's[10]. With the significant methodological developments in CP analysis[11,12] it has been possible, in recent time, to investigate all CPs, from vSCCPs to LCCPs. Data has been reported in wildlife from China, Sweden, and Denmark[5,13]. The studies have updated our knowledge on bioaccumulation of CPs in wildlife including: *i*) CPs from vSCCPs to vLCCPs do bioaccumulate in a wide range of species, *ii*) CPs of different chain-length categories have different bioaccumulation potentials, and *iii*) bioaccumulation of CPs seems to differ between tissues.

Materials and methods

Chemicals and environmental samples: Commercial SCCP, MCCP, and LCCP mixtures were used for quantifying the corresponding CP classes in wildlife. A Chinese CP-52 mixture containing $C_{6\text{-}9}$ CPs was used for quantifying vSCCPs. A wide range of terrestrial and aquatic wildlife species were collected between 2006 and 2017 from the Yangtze River Delta (YRD), China, as well as from Sweden and Denmark[5,13].

Instrumental analysis and CP quantification: The instrument APCI-QTOF-MS (QTOF Premier, Waters, Manchester, UK) was operated in full scan (*m/z* 250 – 1000), negative ion mode at a resolution of 8000-9000. We measured congener groups from vSCCPs to vLCCPs (C_nCl_m, where $n \geq 6$, m = 2-12). S/M/LCCPs in these

samples were quantified by corresponding commercial mixtures using a C_nCl_m-pattern-reconstruction algorithm developed by Bogdal et al.[11]. vSCCPs were quantified using CP-52. Detailed information on the instrumental analysis of CPs are available elsewhere[6].

Results and discussion

Widespread findings of chlorinated paraffins: We found that SCCPs, MCCPs, and LCCPs are widespread in wildlife from the YRD, China[5], which is the largest CP producer worldwide. SCCP, MCCP, and LCCP concentrations ranged from <91–43 000, 96–33 000, and 14–10 000 ng/g lipid, respectively. Principal component analysis (PCA) and carbon stable isotope analysis suggest that habitat and feeding habits were key factors driving CP accumulation and C_nCl_m fingerprints in wildlife.

The occurrence of SCCPs, MCCPs, and LCCPs have also been confirmed in wildlife collected from Sweden and Denmark[13], where CPs are not produced but imported, primarily in products and goods. SCCP, MCCP, and LCCP concentrations were generally lower than those in China, ranging from 26–1500, 30–1600, 6.0–1200 ng/g lipid, respectively. It is still notable that the concentrations are reaching above the ppm level. LCCP concentrations in terrestrial birds from Sweden were generally higher than the corresponding median values for Chinese birds on which analyses have been performed. For example, LCCP concentrations in peregrine falcons (*Falco peregrinus*) from Sweden was 1200 ng/g lipid, while the median value in the same species in China was 690 ng/g lipid. Differences in CP concentrations may reflect that CPs imported and use in Sweden[7] were different from CPs produced and used in China[5]. Different local use/emissions of CPs can also be indicated by C_nCl_m fingerprints in peregrine falcons from Sweden and China, respectively (Figure 1).

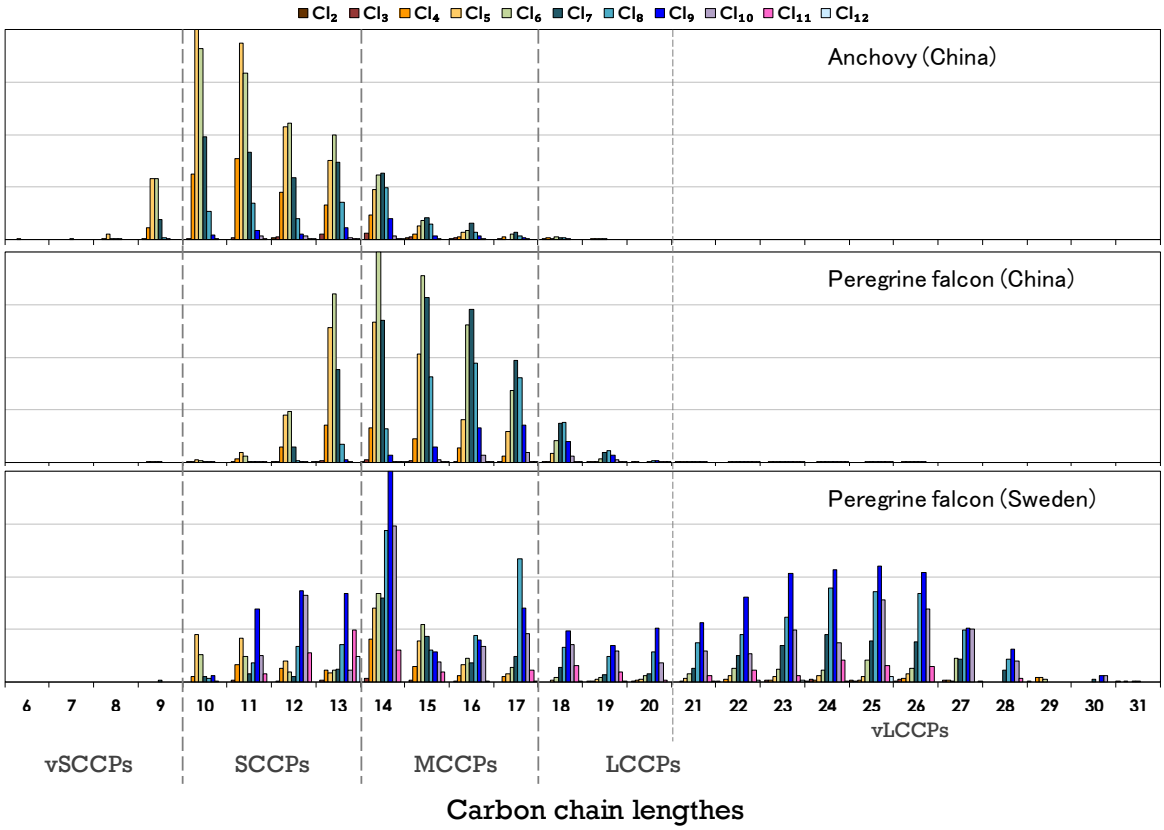

Figure 1. Carbon chain lengths and chlorination (C_nCl_m) fingerprints in the wildlife samples. X-axis represents carbon chain lengths. Y-axis represents relative abundances of the chlorine number within each chain length.

Bioaccumulation of LCCPs: Most notably, LCCP concentrations predominated (55% of total CPs) in peregrine falcons from Sweden[13], which is the first case in which LCCP concentrations surpass those of SCCPs and MCCPs in wildlife. The most abundant chain length was $C_{24/25}$, which are defined as CPs with very long alkane chain lengths. Meanwhile, LCCP concentrations in terrestrial species were generally higher than those in aquatic species from Sweden. This species difference may be explained by bioaccumulation models for POP-like chemicals [14,15] that predict that air-respiring organisms (especially terrestrial species) have a greater ability to absorb high log K_{OW} chemicals from the environment.

Tissue Differences: In wildlife samples from Sweden and Denmark, lipid-normalized concentrations of SCCPs, MCCPs, and LCCPs were somewhat higher in liver than in muscle/blubber tissues. This may indicate different hepatic metabolic efficiencies and/or different sequestration in tissues for the different CP groups. The indication of tissue-specific accumulation was soon echoed by our study on CPs in black-spotted frogs (*Pelophylax nigromaculatus*), an amphibian species prevalent in the YRD, China[16].

Bioaccumulation of vSCCPs: We identified occurrences of vSCCPs in 94% of the wildlife from the YRD, China. Quantification of vSCCPs using a commercial mixture CP-52 showed similar vSCCP fingerprints (R^2 >0.50) in CP-52 compared to those of wildlife (Figure 1). vSCCP concentrations contribute 0.65 – 38% of total CP concentrations in wildlife from the YRD, and were significantly correlated to the SCCP concentrations (p<0.05). Species-specific bioaccumulation of vSCCPs was identified in two benthic species from the YRD.

Perspectives

Our results confirm bioaccumulation of CPs from vSCCPs to LCCPs in wildlife. Given the high production volume and shifting use patterns of CPs[17], comprehensive investigations covering all the CP categories are needed. CPs (in particular the in-use products) found in peregrine falcons are alarming, given that the species has previously been shown to be particularly vulnerable to a variety of chemical pollutants[18]. Findings of vSCCPs in biota necessitates research on their risks to the ecosystem, given that the toxicity of CPs is not well understood[19]. Additionally, SCCPs, MCCPs, and LCCPs seem to biomagnify[13] and thus in-depth studies on specific food chains/webs are warranted to further assess environmental risk from such a large group of contaminants.

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