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Environmental behaviour of short-chain chlorinated paraffins in aquatic and terrestrial ecosystems of Ny-Ålesund and London Island, Svalbard, in the Arctic

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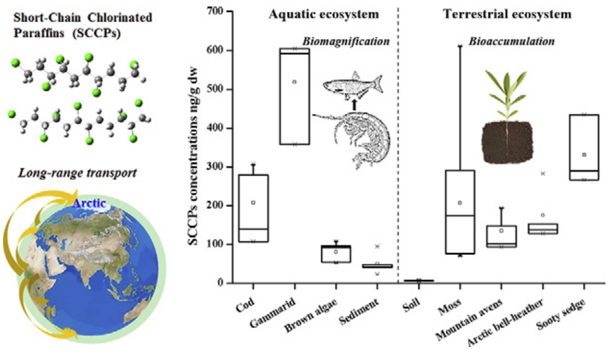
HIGHLIGHTS

- Environmental behaviour of SCCPs was investigated in both aquatic and terrestrial ecosystems in the Arctic.
- No biomagnification of SCCPs was found between cod and gammarid species.
- SCCPs were bio-accumulated in vegetation samples in the terrestrial ecosystems.
- The number of carbon atoms had a greater influence on the BAFs of SCCPs in terrestrial species than that of the number of chlorine atoms.

GRAPHICAL ABSTRACT



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ABSTRACT

The environmental behaviour of short-chain chlorinated paraffins (SCCPs) was investigated in both aquatic and terrestrial ecosystems in the Arctic. The mean concentrations of SCCPs in the aquatic and terrestrial samples were 178.9 ng/g dry weight (dw) and 157.2 ng/g dw, respectively. Short carbon chain (C_{10}) and less-chlorinated (Cl_6) congener groups were predominant in the Arctic samples, accounting for 48.6% and 34.8% of the total SCCPs, respectively. The enrichment of lighter SCCP congener groups (i.e., fewer chlorine atoms with shorter carbon chain lengths) indicated that the fractionation process occurred during long-range transport. The biomagnification factor (BMF) was 0.46 from gammarid to cod, which indicated that the SCCPs did not biomagnify between these two species. The soil–vegetation bioaccumulation factor (BAF) of SCCPs was 29.9, and C_{13} and $Cl_{7,\,8}$ congener groups tended to accumulate in the terrestrial vegetation. Regression analysis ($BAFs = 10.9 \times \#C + 5.6 \times \#Cl - 125.2$, $R = 0.53$, $P < 0.01$) showed that the number of carbon and chlorine atoms influenced the bioaccumulative behaviour of SCCPs and suggested that the number of carbon atoms had a greater influence on the BAFs of SCCPs in the terrestrial ecosystem than did the number of chlorine atoms.

1. Introduction

Chlorinated paraffins (CPs) are produced industrially by direct free radical chlorination of straight-chain paraffin fractions with molecular

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chlorine (Fiedler, 2010; van Mourik et al., 2016). CPs usually contain 10–30 carbon atoms and a chlorine content ranging from 30% to 70% by weight (Feo et al., 2009); C_{10}-CPs have a total of 42,720 constitutional compounds (Sun et al., 2016). This variety of complex mixtures results in the CPs having diverse properties and extensive applications, such as in metalworking fluids, plasticizers in plastics, flame retardants, additives in paints, leather fatliquors, sealants, and PVC (Fiedler, 2010). Anthropogenic releases of short-chain chlorinated paraffins (SCCPs, C_{10}–C_{13}) into the environment may occur during the production, storage, and use of SCCP-containing products, as well as during the disposal of waste and from landfill products (Bayen et al., 2006; Fiedler, 2010; Glüge et al., 2016). SCCPs have gained wide public attention because of their similar physicochemical properties to legacy persistent organic pollutants (POPs). Many previous studies have described the persistence (Iozza et al., 2008; Zeng et al., 2013a), bioaccumulation (Houde et al., 2008; Ma et al., 2014a; Zeng et al., 2011), potential for long-range environmental transport (Li et al., 2016; Ma et al., 2014b; Tomy et al., 1999), and toxicity (Geng et al., 2015; Zhang et al., 2016) of SCCPs. Recently, in the twelfth meeting of the POPs review committee, the Conference of the Parties considered listing and specifying related control measures for SCCPs in Annex A to the Stockholm Convention (UNEP, 2016).

SCCPs are found ubiquitously in diverse environments and matrices, including industrialized regions as well as remote areas (Bayen et al., 2006; Feo et al., 2009; Fridén et al., 2011; Li et al., 2016; Thomas et al., 2006; Wei et al., 2016; Zeng et al., 2013b). The different carbon chain lengths and chlorine contents of SCCPs lead to a wide range in solubility and vapour pressure values (Feo et al., 2009), indicating that SCCP congeners could be transported via both atmospheric and oceanic pathways to remote environments to ultimately accumulate in terrestrial and aquatic organisms (Li et al., 2016; Ma et al., 2014b; Tomy et al., 1999). SCCPs rarely originate from local production and usage in the Arctic; thus, long-range transport from middle and low latitude sources is regarded as the predominant input pathway for SCCPs to the Arctic (Reth et al., 2006; Tomy et al., 2000). Previous studies found evidence of fractionation processes of less-halogenated congeners (Galbán-Malagón et al., 2012; Sobek and Gustafsson, 2004) and low concentrations of POPs (Ma et al., 2014b; Tomy et al., 1999) at high latitudes and in the polar regions. Our previous study also found that lighter SCCP congeners were predominant in Antarctic samples and that the concentration of SCCPs was lower than that in other regions (Li et al., 2016).

Hilger et al. (2011) reported that the log K_{OW} values (octanol-water partition coefficient) of a series of synthesized and technical mixtures of SCCPs ranged from 4.01 to 8.67, which fell in the range of bioaccumulative compounds (Kelly et al., 2007). However, in field studies, the enrichment capability of SCCPs remained disputable due to their diverse bioaccumulative behaviour in different ecosystems. In several studies, SCCPs were reported to biomagnify through the food web in aquatic ecosystems (Ma et al., 2014a; Zeng et al., 2011). A dramatic increase in the concentration of SCCPs in top predators such as marine mammals (Zeng et al., 2015), sharks (Strid et al., 2013) and seabirds (Reth et al., 2006) was found, leading to an increasing concern to investigate their bioaccumulation potential. In contrast, no trophic magnification of SCCPs was found in mollusks from the Chinese Bohai Sea (Yuan et al., 2012). More research is needed to investigate the bioaccumulative behaviour of SCCPs in different food webs.

The bioaccumulative mechanism of certain compounds might be different between aquatic and terrestrial ecosystems. Kelly et al. (2007) reported that hexachlorocyclohexanes (HCHs), tetrachlorobenzenes (TeCBz) and endosulfans did not biomagnify in the piscivorous food web, but showed a high degree of biomagnification in the lichen-caribou-wolf food chain. In that study, bioaccumulation in the aquatic food webs mainly relied on the lipid-water partitioning process and was controlled by the K_{OW} of the target compounds. However, in terrestrial food webs, K_{OA} (lipid-air partition coefficient) also played an important role in the bioaccumulative behaviour (Kelly et al., 2007). To date, no study has been performed that focused simultaneously on the environmental behaviour of SCCPs in both aquatic and terrestrial ecosystems. In addition, the comprehensive effect of different carbon chains and chlorine contents on the bioaccumulative behaviour of SCCPs has not been the focus of any studies.

In the present study, we collected both aquatic and terrestrial samples from Ny-Ålesund and London Island, Svalbard, in the Arctic. Both the levels and congener profiles of SCCPs in these different environmental media and biota samples were investigated to reveal the bioaccumulation and long-range transport behaviour of SCCPs. In addition, the relationships between bioaccumulation factors (BAFs) and the number of carbon/chlorine atoms were studied to explore the principal factor(s) that influence(s) the accumulation of SCCPs. The bioaccumulation and trophic transfer of SCCPs in the Arctic ecosystems reported in this study may help elucidate the environmental behaviour of SCCPs in cold high-latitude environments.

2. Materials and methods

2.1. Sampling

Ny-Ålesund is situated in northwest Spitsbergen, which is the largest island of the Svalbard archipelago in the Arctic Ocean. Ny-Ålesund is surrounded by a variety of high Arctic ecosystems, making it an ideal base for conducting Arctic research (Fig. 1). In September 2011 and September 2012, a total of 46 samples, including 5 brown algae (*Fucus evanescens*), 4 cod (*Gadus morhua*), 3 gammarid (*Gammarus setosus*), 5 sediment, 4 mountain avens (*Dryas octopetala*), 3 sooty sedge (*Carex misandra*), 11 moss (*Drepanocladus aduncus*), 4 arctic bell-heather (*Cassiope tetragona*), and 7 soil samples were collected from aquatic and terrestrial ecosystems in the study area. Detailed longitude and latitude information for the sample sites is provided in Table S1. All samples were freeze dried and homogenized immediately at the Chinese Arctic Yellow River Station and then wrapped in aluminium foil; transported to the laboratory in Beijing, China; and preserved at −20 °C prior to extraction.

2.2. Sample pretreatment, instrumental analysis, and quantification

Sample pretreatment and instrumental analysis of SCCPs were based on our previous work with minor modifications (Zeng et al., 2013b). Briefly, approximately 5 g soil/sediment samples and 2 g biological samples were spiked with surrogate standards (1 ng of $^{13}C_{10}$-*trans*-chlordane) and extracted with dichloromethane and hexane (1:1, V/V) using accelerated solvent extraction (Dionex ASE 350). The extract was cleaned using a multilayer Silica-Florisil column containing 3 g Florisil, 2 g activated silica gel, 5 g acid silica gel (30%, w/w), and 4 g anhydrous sodium sulfate from the bottom to the top. Before instrumental analysis, 10 ng ε-HCH was added. The SCCPs were analysed using a 7890A high-resolution gas chromatograph in electron capture negative ion (ECNI) mode coupled with a 7000B triple quadruple mass spectrometer in single quad mode (Agilent, USA). The extract (1 μL) was injected with a 7683B series injector (Agilent, USA) in splitless mode into a DB-5MS capillary column (30 m length, 0.25 mm i.d., 0.25 μm film thickness; Agilent, CA).

To ensure the validity of the analytical identifications and quantifications, strict quality assurance and control measures were employed (detailed in the Supplementary data). The concentrations of SCCPs detected in anhydrous sodium sulfate (blank controls throughout the treatment process) ranged from 0.56 ng/g to 2.17 ng/g with an average of 1.33 ng/g, which was <5% of the average sample concentrations (165.2 ng/g dw). The recovery of $^{13}C_{10}$-*trans*-chlordane was between 66% and 96%. The spiked recoveries for the three SCCP references with chlorine contents of 51.5%, 55.5%, and 63.0% were between 81% and