Environment International 94 (2016) 408–414

Contents lists available at ScienceDirect

Environment International

journal homepage: www.elsevier.com/locate/envint

Occurrence, bioaccumulation and long-range transport of short-chain chlorinated paraffins on the Fildes Peninsula at King George Island, Antarctica

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ARTICLE INFO

Article history:
Received 24 September 2015
Received in revised form 12 April 2016
Accepted 4 May 2016
Available online 21 July 2016

Keywords:
Short-chain chlorinated paraffins (SCCPs)
Antarctica
Biomagnification
Long-range transport

ABSTRACT

As a candidate persistent organic pollutant of the Stockholm Convention, short-chain chlorinated paraffins (SCCPs) have recently received particular attention. In this study, we investigated, for the first time, the concentrations of SCCPs in biota samples collected from the Fildes Peninsula at King George Island and Ardley Island, Antarctica. The concentrations of SCCPs ranged from 3.5 to 256.6 ng/g (dry weight, dw), with a mean of 76.6 ± 61.8 ng/g dw, which was lower than those detected in mid- and low-latitude regions. The long-range transport behaviour of SCCPs was confirmed by both the detection of SCCPs in Antarctic remote areas and their special congener profiles. Short carbon chain (C_{10}) congeners predominated in the Antarctic samples, which accounted for 56.1% of the total SCCP contamination. Such enrichment of C_{10} congeners indicated the high potential for the long-range transport of shorter chain congeners. In addition, SCCPs tended to be enriched in the species with high lipid contents. The biomagnification potential of SCCPs was found between *Archeogastropoda* (*Agas*) and *Neogastropoda* (*Ngas*), and the biomagnification factors of shorter chain congeners of SCCPs were higher than that of the longer chain ones. Considering that the endemic species in polar regions may be sensitive and vulnerable to the adverse effects of environmental contaminants, more attention should be paid on the bioaccumulation and toxicological risks of SCCPs in polar environments.

1. Introduction

Chlorinated paraffins (CPs) have 10–30 carbon atoms and chlorine content that ranges from 30% to 70% by weight (Bayen et al., 2006). The variety of carbon chain lengths and chlorine contents of CPs results in diverse properties and extensive applications, including lubricant additives, plasticizers in rubbers, metal-working fluids, flame retardants, paints and sealants (Campbell and McConnell, 1980). Short-chain chlorinated paraffins (SCCPs, C_{10}–C_{13}) can affect the liver, thyroid hormone system, and kidneys, e.g., by inducing hepatic enzymes and hyperactivity in the thyroid, which can lead to both acute and chronic toxic effects with long-term exposure (UNEP/POPS/POPRC.8/6, 2012). Because of their potential for environmental persistence (Iozza et al., 2008), toxicity (Geng et al., 2015), bioaccumulation (Fisk et al., 1996; Houde et al., 2008; Ma et al., 2014b; Zeng et al., 2011b) and long-range atmospheric transport (Ma et al., 2014c; Vulykh et al., 2007), SCCPs have received widespread public attention. SCCPs were even included in Annex E of the Stockholm Convention by the persistent organic pollutants (POPs) Review Committee as a POP candidate in 2008 (UNEP/POPS/POPRC.3/20, 2008) since these properties are quite similar to those of legacy POPs (Poremski et al., 2001). However, with the scarcity of current monitoring data, including for the occurrence, capacity for accumulation, and long-range transport, the listing of SCCPs as POPs into the Stockholm Convention remains controversial (Wang et al., 2013).

SCCPs are primarily released into the environment from anthropogenic sources as a type of high production volume chemical and are detected in the different environmental matrices, including air, water, sediments and biota (Barber et al., 2005; Bayen et al., 2006; Coelhan, 2010; Fridén et al., 2011; Marvin et al., 2003; Thomas et al., 2006; Zeng et al., 2015). The SCCPs travel to polar regions in a three-step process: release, transport and deposition (Wania, 2003). The vapour pressure of SCCPs is very low and varies from 2.8×10^{-7} to 0.066 Pa (Feo et al., 2009), which make them easily volatilize into the atmosphere. Most pollutants migrate to higher latitudes in a series of relatively short jumps called the "grasshopper effect" (Wania and Mackay, 1996). SCCPs can also be transported through the atmosphere and ultimately deposited in remote areas such as the polar regions (Wania, 2003; Wania and Mackay, 1993). The detection of SCCPs in the polar regions would provide direct evidence for their long-range transport, but SCCPs have been observed in polar regions in only a few studies. The concentrations of SCCPs were studied in the biota and sediment samples from Arctic and sub-Arctic environments (Reth et al., 2006; Strid et al., 2013; Tomy et al., 2000; Tomy et al., 1999). For Antarctica, the only data for SCCPs are from the air samples collected on the Fildes Peninsula (Ma et al., 2014c).

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http://dx.doi.org/10.1016/j.envint.2016.05.005
0160-4120/

Antarctica is far from industrial regions and is less affected by global anthropogenic activities. Most species found in Antarctica are endemics and may be more sensitive and vulnerable to the adverse effects of persistent contaminants than those of the industrialized regions. Low levels of pollutants can have significant effects on local fragile ecosystems (Bargagli, 2008). Moreover, biomagnification through food chains can lead to relatively high contaminant concentrations in biota, which potentially threaten the health of wildlife at higher trophic levels. In several studies, SCCPs biomagnified through the food web in aquatic ecosystems (Ma et al., 2014b; Zeng et al., 2011b). As an additional factor, the temperature in Antarctica is lower than that in other regions, and based on previous studies, low temperatures may decrease the growth rate more than the uptake rate, which results in a net accumulation of POPs in the tissues of biota (Honkanen and Kukkonen, 2006; Muijs and Jonker, 2009). Therefore, relatively high levels of bioaccumulation are expected for Antarctic species.

In this study, we systematically collected soil, vegetation, and animal samples on the Fildes Peninsula at King George Island and Ardley Island, Antarctica. The primary purpose was to investigate the occurrence and congener profiles of SCCPs in Antarctic samples to demonstrate the long-range transport behaviour of SCCPs. The spatial distribution of SCCPs was also examined to determine the effect of human activities on the local Antarctic environment. Finally, the bioaccumulation behaviour of SCCPs was investigated to study the effects on the Antarctic ecosystem. The results of our study will provide valuable information on the environmental behaviour of SCCPs on a global scale.

2. Materials and methods

2.1. Sampling

The samples were all collected during the 29th Chinese Antarctic Expedition between December 2012 and January 2013. Eight soil, six algae (*Halymenia floresia*), six moss (*Sanionia uncinata*), three fish (*Notothenia coriiceps*), five neogastropoda (*Trophon geversianus*, *Ngas*) and sixteen archeogastropoda samples (*Nacella concinna*, *Agas*) were collected on the Fildes Peninsula at King George Island and Ardley Island, Antarctica (Fig. 1). The samples were immediately freeze-dried and homogenized at the Chinese Great Wall Station and were then transported to the laboratory in Beijing, China, and preserved at −20 °C in a specialized refrigerator for polar samples until analyses. Detailed information on sampling and transportation is in the Supplementary Data.

Of the sampled species, the species of *Agas* was the most widely distributed on the Fildes Peninsula and therefore was the sentinel species used to investigate the spatial distribution of SCCPs. Moreover, the predator-prey relationship was confirmed for *Agas* and *Ngas* (*Ngas* preys on *Agas*; Fig. S1), and therefore, paired samples of *Agas* and *Ngas* were collected from sites 5, 7, 9, 12 and 18 (Fig. 1) to study the biomagnification behaviour of SCCPs.

2.2. Analytical procedures

Approximately 5 g of soil and 2 g of biological samples were spiked with surrogate standards (1 ng of $^{13}C_{10}$-*trans*-chlordane), mixed with 15 g of anhydrous sodium sulphate and extracted with dichloromethane and hexane (1:1, v/v) using accelerated solvent extraction (Dionex ASE 350). The extract was cleaned by a multilayer Silica-Florisil column that contained 3 g of Florisil, 2 g of activated silica gel, 5 g of acid silica gel (30%, w/w) and 4 g of anhydrous sodium sulphate from the bottom to the top. The cleanup procedure for the SCCPs was based on our previously reported methods (Zeng et al., 2011a).

The SCCPs were analysed on a 7890A high-resolution gas chromatograph (HRGC) in electron capture negative ion (ECNI) mode coupled with a 7000B triple quadruple mass spectrometer in single quad mode (Agilent, USA). 1 μL of extract 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).

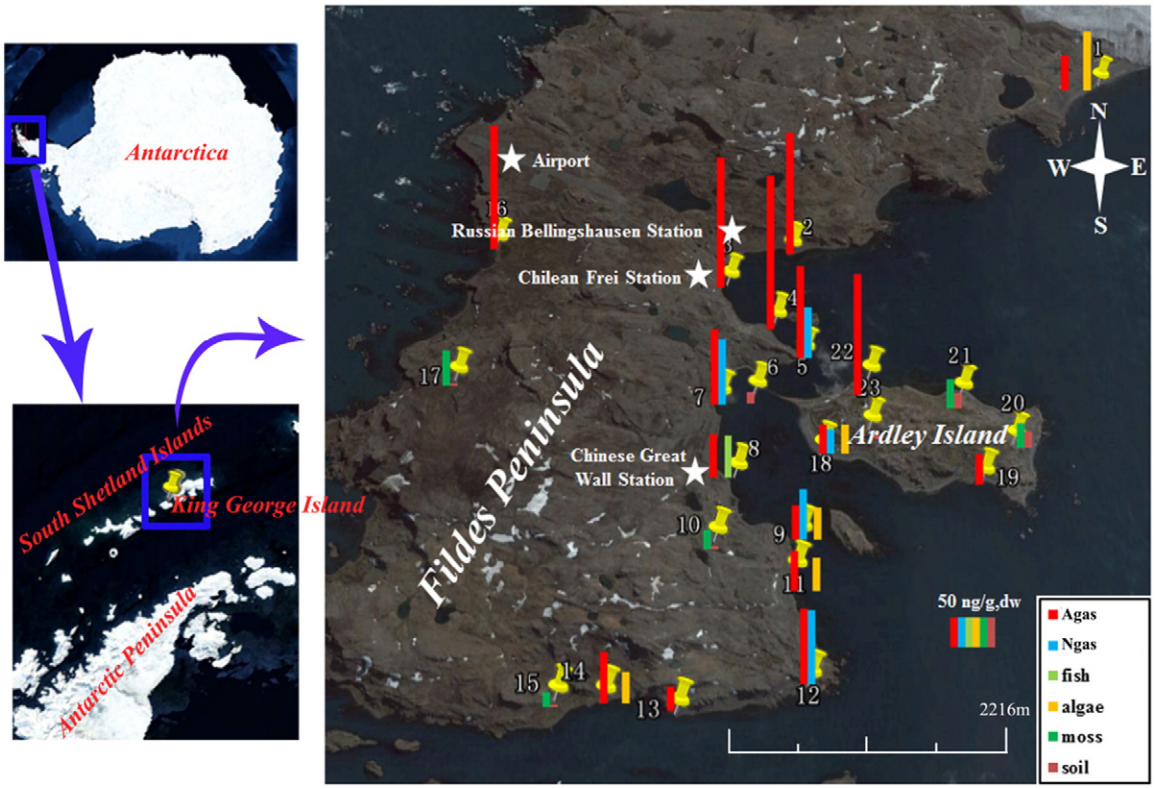

Fig. 1. Distribution of the sample sites and the concentrations of SCCPs in Antarctic samples. Numbers 1–23 are the different locations; detailed information is provided in Table S1.