DECHLORANE PLUS IN ANTARCTIC BIOTA IN KING GEORGE ISLAND, ANTARCTICA

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Introduction

Dechlorane plus (DP, $C_{18}H_{12}Cl_{12}$) is a chlorinated flame retardant which was manufactured as a substitute for Dechlorane (also called Mirex, $C_{10}Cl_{12}$) by Hooker Chemical (now known as OxyChem, Niagara Falls, NY) in the mid-1960s[1]. The flame retardant has been used for at least 40 years, with annual production being estimated to be as high as 10 million pounds, and has been sold worldwide including North America, Europe, and Asia[2]. In addition, recently, Wang et al. identified another DP production facility in China[3].

Hoh et al. first reported in 2006 on the environmental occurrence of DP in air, fish, and sediment samples within the North American Great Lake Basin[1]. Since then, other researchers measured DP in other regions of the world in various environmental matrix, including air, water, sewage sludge, indoor dust, soil, sediment, tree bark, fish, birds, and human serum and hair. Moreover, the recent occurrence of DP in air sampled along an oceanic transect from Greenland to Antarctica suggests that DP is susceptible to long-range atmospheric transport[4, 5]. The DP isomers have been detected in biota samples, which indicated that DP can be bioaccumulated and biomagnified regardless of its high molecular weight and very high log K_{ow} value. The bioaccumulation of DP in birds has been reported by a few studies[6, 7]. Gauthier et al. reported that several flame retardants including DP were accumulated in maternal herring gull via their aquatic environment and food web, and transferred during ovogenesis to their eggs[8, 9]. However, biotic monitoring data of the DP isomers were limited. Moreover, no data is available on the bioaccumulation of DP in biota samples from the very remote regions.

In the present suty, we used several Antarctic biota samples to evaluate DP exposure in the remote ecosystems of Antarctica. The aim of this study is to evaluate the bioaccumulation of DP isomers in Antarctic biota samples collected from King George Island, Antarctica.

Materials and methods

Sampling: Three Brown skuas (Catharacta antarctica lonnbergi) were collected from near King Sejong Station, King George Island in 2008 (Fig. 1). Two Gentoo penguin (Pygoscelis papua) were collected from the site, Narebski Point (Antarctic Specially Protected Area no. 171) and one Adelie penguin (Pygoscelis adeliae) was collected from Narebski Point in 2009 (Fig. 1). Map of sampling sites are shown in Figure 1. All samples were collected from carcasses, and the specific tissues were removed from the carcass and transferred to a pre-cleaned Teflon-lined capped glass jar, and frozen until analysis.

Sample analysis: Approximately 15 g of tissue samples were spiked with a surrogate standard and extracted with dichloromethane:hexane (1:1) using a soxhlet extration for 24 hours. Lipid was removed using gel permeation chromatography packed with 60 g of Biobead SX-3 (Bio-Rad Laboratories, USA). Further purification was achieved on a column of silica gel (Merck, Germany) and Florisil (Aldrich, USA). Before the analysis, the samples were reconstituted with the isotopically labeled recovery standard. DP in the samples was analyzed by gas chromatography-high resolution mass spectrometry (GC-HRMS) on an Agilent 6890 N gas chromatography coupled to a JEOL 800D mass spectrometry with the electron impact (EI) mode.

Chemicals: Technical grade DP, syn-DP, and anti-DP (100 μg/mL, in nonane) was supplied by Cambridge Isotope Laboratories (Cambridge, MA, USA). The mass labeled $^{13}C_{12}$-mirex and $^{13}C_{12}$-PCB 70 were purchased from Cambridge Isotope Laboratories (Cambridge, MA, USA), and were used as internal surrogate standard and recovery standard, respectively. The solvents and chromatographic materials were all of pesticide-analysis grade.

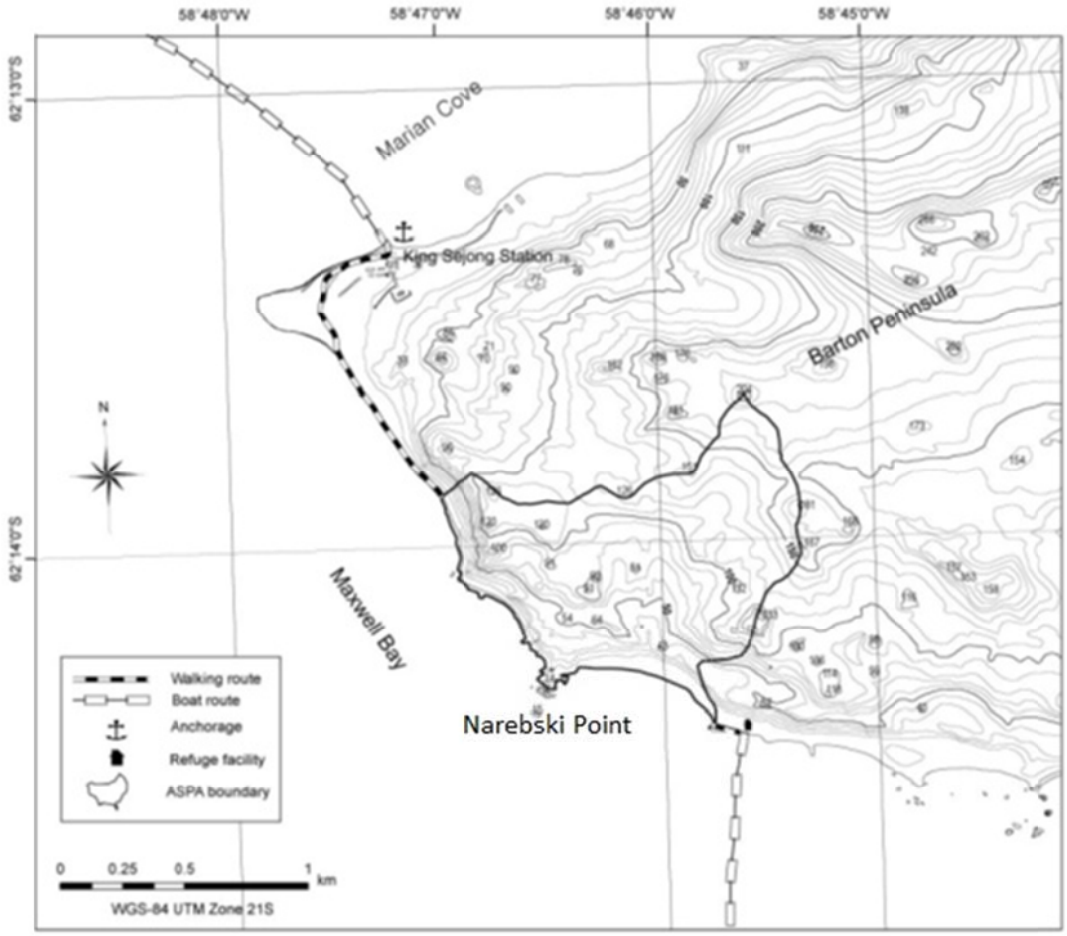

Fig. 1. Map of the samling sites (King Sejong Station and Narebski Point) in King George Island, Antarctica

Results and discussion

Concentrations of *syn*- and *anti*-DP in Antarctic biota

Concentrations of DP isomers in several Antarctic biota samples, brown skua (n=3), gentoo penguin (n=2), and adelie penguin (n=1), are given in Table 1. The DP isomers were detected in all samples (n=6) collected in King George Island, Antarctica. Concentrations of DP isomers ranged from 0.25 to 11.1 ng g^{-1} lipid. The results indicated that DP was accumulated in several species of Antarctic biota with relatively high concentrations, even though DP was designed to minimize bioavailability by increasing molecular size.

Species-specific accumulation

The DP concentrations of brown skua showed relatively high concentrations compared to those of gentoo penguin and adelie penguin. The mean concentrations of DP in brown skua (n=3) were 4.55 ng g^{-1} lipid, but the mean concentrations of DP in gentoo and adelie penguin (n=3) were 0.28 ng g^{-1} lipid. Relatively low concentrations of DP were measured in penguin species, but the DP concentrations of two penguin species were similar to each other. The number of samples was too small to evaluate the difference of DP bioaccumulation between gentoo penguin and adelie penguin. The samples consisted of brown skua, gentoo penguin and adelie penguin collected from King George Island in Antarctica. Brown skua, gentoo penguin, and adelie penguin are top predators in the Antarctic ecosystem. Of the species, a brown skua, which attack and eat the penguins, is upper-level top predator in the food web of the Antarctic ecosystem. The skua feed on a wide variety of items,

including eggs and chicks of penguins, flying birds, small mammals, fish, marine invertebrates, and barbage. Even the garbage from the people who visit and work at the Antarctic station could be another food source for the brown skua. It could be explained that exceedingly high concentrations of DP were observed in a brown skua sample showed a high concentration of 11.1 ng/g lipid. On the other hands, the penguins are known to feed mainly on Antarctic krill, which explained that relatively low concentrations of DP in the penguins. It was suggested that DP exposure to Antarctic biota is related to their food source and diet behavior.

Tissue-specific accumulation

Within individual adelie penguin, the lipid-base concentration of DP did not differ between muscle and intestines tissues. However, the wet-base concentrtions of DP between muscle (0.005 ng g^{-1} wet) and intestines tissues (0.228 ng g^{-1} wet) were significantly different.

Isomeric Profiles

In all samples, concentrations of *anti*-DP were consistently greater than that of *syn*-isomer. The technical DP has two isomers: syn- and anti-DP. The fractional abundance of the anti-isomer (f_{anti}) is calculated by dividing the concentration of the anti-DP isomer by the sum of the concentrations of *syn*- and *anti*-DP isomers. The mean f_{anti} was calculated to be 0.75 (n=3) of the technical DP standard (CIL) in our laboratory[10]. The f_{anti} value for the our samples in this study ranged from 0.69 to 0.88. The mean f_{anti} value for the samples (0.76 ± 0.07) did not showed significant difference from the value of the technical DP. Even the f_{anti} value of a brown skua sample was 0.69, relatively low f_{anti} value was observed in our biological samples, which suggests that the bioavailability or biodegradation of the two isomers could be different[11]. Stereoselective enrichment or biodegradation of DP in the Antarctic biota should be more researched.

Table 1. Concentrations of DP isomers in Brown Skua, Gentoo Penguin, and Adelie Penguin (ng g^{-1} lipid)

samples	*syn*-DP	*anti*-DP	ΣDP	f_{anti}
Brown Skua 1	2.71	8.34	11.1	0.75
Brown Skua 2	0.67	1.45	2.12	0.69
Brown Skua 3	0.05	0.37	0.42	0.88
Gentoo Penguin 1	0.08	0.25	0.33	0.77
Gentoo Penguin 2	0.07	0.18	0.25	0.71
Adelie Penguin 1	0.06	0.21	0.26	0.78
Adelie Penguin 1-I	0.09	0.21	0.30	0.71

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