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Trophic magnification of Dechlorane Plus in the marine food webs of Fildes Peninsula in Antarctica

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ABSTRACT

The food web composition, assimilation efficiency of Dechlorane Plus (DP) in food web components, and even extrinsic conditions can affect the trophic biomagnification potentials of DP isomers in food webs. Antarctica ecological system is characterized by the presence of few consumers and simple trophic levels (TLs), which are crucial in discussing the behavior of contaminants. To assess the biomagnification potential of DP in the Antarctic food web, nine representative species were sampled and analyzed from the Fildes Peninsula. Results showed the DP concentrations ranged from 0.25 ng g^{-1} to 6.81 ng g^{-1} lipid weight in Antarctic biota and the concentrations of *anti*-DP and *syn*-DP showed significantly positive correlations with TLs ($p < 0.05$, $r_a = 0.85$; $r_s = 0.81$, respectively), suggesting that *syn*-DP and *anti*-DP underwent biomagnification and the biomagnification ability of *anti*-DP was higher than that of *syn*-DP. The *anti*-DP fraction (*anti*-DP/$\sum$DP) ($f_{anti} = 0.23–0.53$) of the organisms was lower than that of commercial products ($f_{anti} = 0.68$), demonstrating f_{anti} was changed during long-range atmospheric transport or stereoselection enrichment through the food web. Furthermore, based on food web magnification factors (FWMF) comparison between DP and polychlorinated biphenyls (PCBs), the biomagnification potential of DP was found to be similar to that of highly chlorinated PCBs.

1. Introduction

As a chlorinated flame retardant additive, Dechlorane Plus (DP) is widely used in electrical wirings, computer and television connectors, cable coatings, plastic roofing materials, and other polymeric systems. Commercial-grade DP is synthesized via the Diels–Alder reaction and has two stereo isomers, *syn*-DP (1, 4:7,10-dimethanodibenzo[*a*,*e*]cyclooctene,1,2,3,4,7,8,9,10,13,13,14,14-dodecachloro-1,4,4a,5,6,6a,7,10,10a,11,12,12a–dodecahydro-,(1R,4S,4aS,6aR,7R,10S,10aS,12aR)-rel-) and *anti*-DP (4:7,10-dimethanodibenzo[*a*,*e*]cyclooctene,1,2,3,4,7,8,9,10,13,13,14,14-dodecachloro-1,4,4a,5,6,6a,7,10,10a,11,12,12a–dodecahydro-,(1R,4S,4aS,6aR,7S,10R,10aR,12aR)-rel-), with a ratio of approximately 1:3 (Garcia and McLaughlin, 1991; Hoh et al., 2006). DP shares similar properties to those of persistent organic pollutants (POPs), including high lipophilicity, bioaccumulation potential, and potential for long-range transport, and has become ubiquitous in the environment. Hoh et al. (2006) analyzed air, sediment, and fish samples collected from the Great Lakes, including in Niagara Falls, NY, located in close proximity to the OxyChem facility, which manufactured DP, and reported the presence of DP in the environment. Other publications also focused on regions close to DP manufacturing facilities, such as Huai'an in China (Wang et al., 2010) and the Great Lake (Salamova and Hites, 2011; Shen et al., 2011) showing varying concentrations of DP, indicating manufacturing facilities as possible environmental sources of DP. Several studies have also focused on the concentration and bioaccumulation of DP in organisms, such as in eels (Sühring et al., 2013), peregrine falcon (Guerra et al., 2011), and aquatic invertebrates (Jia et al., 2011; Schlabach et al., 2011). High concentrations of DP were also found in fishes from urban-industrial rivers in Korea (Kang et al., 2010).

DP isomers are expected to have low bioaccumulation potentials due to their high molecular mass and octanol-water partition coefficients (Log $K_{OW} = 9.3$). However, several studies have indicated that DP isomers have a different bioaccumulation potential than expected in various food webs (Tomy et al., 2007; Wu et al., 2010; Zhang et al., 2011), including a freshwater ecosystem or relatively simple ocean food webs (Jia et al., 2011; Wang et al., 2015). Uptake of *syn*-DP and *anti*-DP metabolites was also observed in freshwater organisms (Wu et al., 2010), while *anti*-DP is reportedly enriched in all organisms in

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Lake Winnipeg and Lake Ontario food webs (Tomy et al., 2007). Further, the trophic magnification potential of *syn*-DP is similar to that of polychlorinated biphenyls (PCBs) and greater relative to polybrominated diphenyl ethers (PBDEs) in biota (Wu et al., 2010), which indicates that DP and PCBs may have similar environmental behaviors especially on biomagnification. Antarctica features low consume of DP products. Since DP is a class of chemical compounds with high molecular mass and low vapor pressure may be transported great distances by air masses where they will undergo global fractionation processes along temperature gradients, favouring deposition in colder climates such as high altitude or latitude environments (Cropp et al., 2011). Evidence of DP in Antarctica suggests DP is a global pollutant that is susceptible to long-range atmospheric transport and may impact the fragile ecosystems of Antarctic (Möller et al., 2010). In addition, the Antarctic ecosystem is relatively isolated from most other ecosystems, and the gradation of chemical levels in the food chain there clearly reflects the bioaccumulation of chemicals through the transfer from prey to predators (Kim et al., 2015) and the biomagnification of chemicals with trophic levels (TLs). However, research on the biomagnification behavior of DP in the Antarctic is lacking and most studies of DP isomers in the environment only focused on individual organisms (Kim et al., 2015). Only few integrated studies have illustrated the bioaccumulation potential of DP isomers in food webs of the ocean. Based on these reasons, we seek to study the magnification of DP isomers in marine food webs of Antarctica, where background levels due to human contribution is low.

In the present study, we analyzed nine species in the Antarctic, representing different TLs to investigate the trophic magnification of DP in the Antarctic food web: red algae (*Palmaria decipien*), limpet (*Mutulus*), starfish (*Protoreaster nodosus*), gammarid (*Gammarid*), krill (*Euhausia superba*), cod (*Dissostichuseleginoides*), penguin (*Spheniscidae*), seal (*Hydrurga leptonx*), and stercorarius (*Stercorarius maccormicki*). The different biomagnification behaviors of two DP isomers in the food web were observed by calculating the food web magnification factors (FWMFs). To reveal the relationships to other POPs, the biomagnification factors of the DP isomers were compared with PCBs.

2. Materials and methods

2.1. Biota sampling

Samples of Antarctic biota were collected in 2013 from the Fildes Peninsula, which is located in King George Island, southwest of the Antarctic (Fig. 1). There are several scientific stations on the Fildes Peninsula, and the marine ecosystem has been shown to be influenced slightly by human activities (Martins et al., 2010; Dauner et al., 2015). Samples of red algae ($n = 6$) were collected at least 30 cm beneath the water surface. Limpet ($n = 7$), starfish ($n = 5$), gammarid ($n = 6$), krill ($n = 6$), and cod ($n = 3$) were sampled at the bottom and midwater trawls during several cruises. The immobilized penguins ($n = 3$), seals ($n = 3$) and injured stercorarius were obtained in January 2013. All samples were wrapped with aluminum foil, sealed in clean plastic bags, freeze-dried and homogenized until analysis.

2.2. Chemical analysis

The lipid content of the samples was determined using the chloroform–methanol extraction method from a previous publication (Wang et al., 1993). Each sample (2.0 g, dry weight) was spiked with 1.0 mL of 100 ng mL^{-1} PCB-209 as a surrogate standard prior to extraction for analysis of DP isomers and PCBs (PCBs: 18, 28, 66, 77, 118, 126, 138, 153, 169, 189, 195, and 200) In brief, biota samples were extracted with accelerated solvent extraction (Dionex ASE 350, USA) using 50 mL of n-hexane and acetone (1:1 v/v) at 120 °C and 10.3 MPa for three cycles. The extracts were combined and concentrated to 5 mL with a turbo evaporator (RE-2000, Shanghai, China). Acidified silica was used to remove the lipids in the concentrated solution and the extract was cleaned up using a multilayer silica/alumina column (2.0 g activated silica gel, 4.0 g neutral alumina, and 1 cm anhydrous Na_2SO_4) with 20 mL of n-hexane and 70 mL of n-hexane/dichloromethane (7:3) for solvents. Elution solvent was evaporated to near dryness and reconstituted in 200 μL of n-hexane. S*yn*-DP and *anti*-DP were analyzed using an Agilent 6890 N gas chromatography (GC) coupled to an Agilent 5973I mass-selected (MS) detector, in electron capture negative ionization mode. A DB-5HT capillary column (15 m × 0.25 mm i.d., 0.1 μm film) was used for separation. Initial GC oven was set to temperature of 80 °C, then ramped to 180 °C at a rate of 20 °C min^{-1}, ramped to 250 °C at 5 °C min^{-1} and held for 2 min, and finally ramped to 310 °C at 30 °C min^{-1} and held for 5 min. The injection port temperature was set at 280 °C. Helium was used as carrier gas at a flow rate of 1.0 mL min^{-1}. The extract,(1 μL) was injected in pressure-pulsed splitless mode. Selected ion monitoring mode was used with mass to charge (m/z) ions of 653.5/651.5/655.5 for *syn*- and *anti*-DP.

PCB congeners were quantified using a GC equipped with an electric capture detector (GC–ECD, Aligent 7890A, USA) and confirmed with GC coupled to a tandem mass spectrometer (MS/MS, Aligent 7000B, USA) (Zhang et al., 2014; Yuan et al., 2015). The GC was equipped with an HP-5MS capillary column (30 m in length, 0.25 mm i.d., 0.25 μm film in thickness). The temperature program for PCBs was as follows: initial GC oven temperature was set to 75 °C and held for 3 min, then increased to 150 °C at 15 °C min^{-1} rate and then increased further to 260 °C at 6 °C min^{-1} rate; finally, the temperature increased up to 300 °C at 20 °C min^{-1} rate and held for 5 min. The temperatures of the injector port and ECD detector were 220 and 300 °C, respectively. Sample

Fig. 1. Sampling area of the Antarctica.

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