Environmental Pollution 235 (2018) 302–311

Contents lists available at ScienceDirect

Environmental Pollution

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

Occurrence and distribution of old and new halogenated flame retardants in mosses and lichens from the South Shetland Islands, Antarctica☆

Jun-Tae Kim [a, b, 1], Yun-Jeong Choi [a, 1], Mandana Barghi [a], Young-Jun Yoon [b], Jeong-Hoon Kim [b], Ji Hee Kim [b], Yoon-Seok Chang [a, *]

[a] Pohang University of Science and Technology (POSTECH), San 31, Hyoja-dong, Nam-gu, Pohang, 37673, Republic of Korea
[b] Korea Polar Research Institute (KOPRI), 26 Songdomirae-ro, Yeonsu-gu, Incheon, 21990, Republic of Korea

ARTICLE INFO

Article history:
Received 24 May 2017
Received in revised form
21 December 2017
Accepted 22 December 2017

Keywords:
Halogenated flame retardants
Antarctica
Hexabromocyclododecanes
Dechloranes
Long-range transport

ABSTRACT

The spatial distribution of old and new halogenated flame retardants (HFRs), including polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs), and Dechlorane Plus (DPs) and related compounds (Dechloranes), were investigated in the South Shetland Islands of Antarctica, employing mosses (*Andreaea depressinervis* and *Sanionia uncinata*) and lichens (*Himantormia lugubris* and *Usnea antarctica*) as bioindicators. The levels of PBDEs, HBCDs, and Dechloranes ranged from 3.2 to 71.5, 0.63–960, and 2.04–2400 pg/g dw (dry weight) in the mosses, and from 1.5 to 188, 0.1–21.1, and 1.0–83.8 pg/g dw in the lichens, respectively. HFRs were detected in all of the collected samples, even in those from the remote regions. The dominance of high brominated-BDE, *anti*-DP fraction, and HBCD diastereomeric ratio in the samples from remote regions suggested the long-range atmospheric transport (LRAT) of the HFRs. The relatively high HBCDs and Dechloranes contamination and their similar chemical profile with commercial products in the vicinity of Antarctic research stations indicated that human activities might act as local sources, while PBDEs appeared to be more influenced by LRAT and bioaccumulation rather than local emission. Lastly, the relatively high HFR levels and dominance of more brominated BDEs at the Narębski Point and in the wet lowlands suggested that penguin colonies and melting glacier water could be secondary HFR sources in Antarctica. The HFR levels differed by sample species, suggesting that further research on the factors associated with the HFR accumulation in the different species is necessary. This study firstly reports the alternative HFR levels in a wide area of the Antarctica, which could improve our understanding of the source, transport, and fate of the HFRs.

1. Introduction

Halogenated flame retardants (HFRs) are a group of chlorinated or brominated chemicals that have been employed to retard the combustion of flammable products such as plastic and wood products, furniture, electronic products, and interior and exterior building materials (Alaee et al., 2003). The chlorine and bromine atoms in the HFR molecules produce radicals upon heating, and they prohibit the propagation of the combustion process by reacting with reactive radical species produced from combusting products (Laoutid et al., 2009). The halogen atoms, however, give side effects to the HFR molecules, which are persistent, bioaccumulative, lipophilic, and long-range transportable characteristics (Muir and Howard, 2006). For that reason, the Stockholm Convention on Persistent Organic Pollutants (POPs) has banned the production and use of the most commonly used HFR, polybrominated diphenyl ethers (PBDEs), in 2009 (UNEP, 2001). Since then, the alternative HFRs, such as hexabromocyclododecanes (HBCDs) and Dechlorane Plus (DPs) and related compounds (Dechloranes), have replaced PBDEs. As they also have halogen atoms and stable carbon backbone, it has been speculated that these alternative HFRs could have POP-like properties (Alaee et al., 2003; Covaci et al., 2006).

Antarctica is one of the most pristine regions, which has few

☆ This paper has been recommended for acceptance by Eddy Y. Zeng.

* Corresponding author.
E-mail address: yschang@postech.ac.kr (Y.-S. Chang).

[1] These authors (Yun-Jeong Choi and Jun-Tae Kim) contributed equally as first authors.

https://doi.org/10.1016/j.envpol.2017.12.080
0269-7491/

chemical sources and is located far from industrialized regions. Therefore, the detection of an anthropogenic chemical in Antarctica demonstrates the possibility of long-range atmospheric transport (LRAT) of the chemical (Kim et al., 2015). Although the detection of PBDEs in Antarctica has been reported for the last decade in the samples of atmosphere, soil, animals, and plants (Dickhut et al., 2012; Mwangi et al., 2016), few studies have reported the occurrences of the alternative HFRs in the Antarctic environment. For example, HBCDs, even though they were listed on the Stockholm Convention on 2015, were only detected in marine surface sediment and aquatic biota samples (Chen et al., 2015), and Dechloranes were detected in the Antarctic atmosphere and the sea water (Möller et al., 2010). Our previous study also reported the detection of PBDEs, HBCDs, and Dechloranes in the Antarctic avian tissues (Kim et al., 2015), and suggested the LRAT and bioaccumulation of the HFRs. To verify POP-like property of HFRs and their influences on the Antarctic ecosystem, however, the environmental behavior of HFRs should be first investigated, as the source, distribution, and fate of the HFRs in the Antarctic environment have been hardly identified.

For the monitoring of POPs in the remote region, the use of bioinidicators has some advantages. Although the passive air sampler (PAS) and the high-volume sampler (HVS), employing resins and polyurethane foams, can provide atmospheric POP concentrations directly (Wania and Mackay, 1996; Choi et al., 2008), the instruments require additional structures, such as supporting poles and wires for PAS and power sources for HVS, which might influence the natural ecosystem. The bioindicators, such as tree bark or pine needles, have been developed for the alternative passive sampling without installation of the additional equipment in the remote region (Ratola et al., 2011; Salamova and Hites, 2013). As Antarctica is a frigid and arid continent with extreme sunlight, precipitation, and UV radiation, its vegetation has few vascular plant species and is dominated by mosses and lichens which have adapted to extreme environmental conditions (Kim et al., 2007; Olech, 2002). Fortunately, it has been suggested to use the mosses and lichens as bioindicators for the atmospheric monitoring of POPs and heavy metals (Van der Wat and Forbes, 2015; Wu et al., 2014).

In this study, we investigated the spatial distribution of HFRs with mosses and lichens from the South Shetland Islands, an archipelago ranged over a distance of 200 km. We collected two species of mosses and lichens samples each from 16 sites in the South Shetland Islands and analyzed for PBDEs, HBCDs, and Dechloranes with high-resolution mass spectrometry. The concentrations and chemical profiles of the HFRs were assessed, and their altitudinal and latitudinal distributions, potential sources, and species dependence were investigated.

2. Materials and methods

2.1. Sampling and study region

The moss and lichen samples were collected in the South Shetland Islands from December 2013 to January 2014. Fig. 1 and Table 1 present the study area and samples collected at the sampling sites. Of 16 sampling sites (T1-T16), T1-T10 were located on King George Island, T11-T15 were located along the South Shetland Islands, and T16 was located on Anvers Island in the Palmer Islands; the sampling sites were distributed over a distance of 200 km. This area is a part of maritime Antarctica and is relatively warmer than continental Antarctica; the monthly mean temperature varies from −6.7 °C in August to 1.6 °C in February. In summer (December to March), the snow covering the islands partly melted, and the land and the

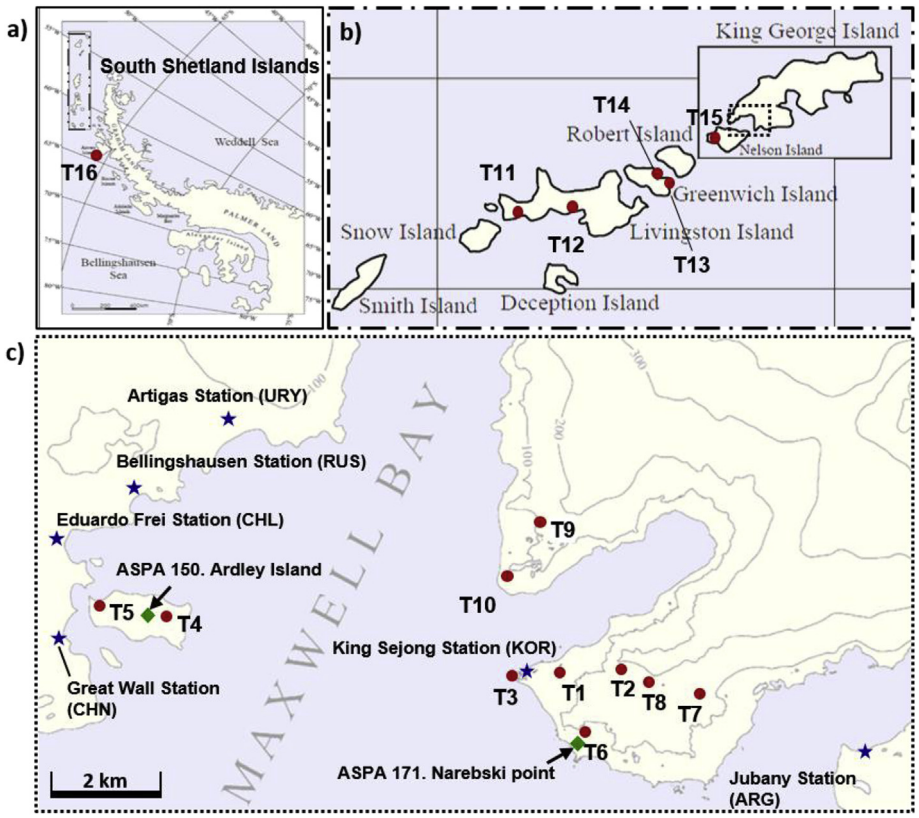

Fig. 1. Map of the sampling area in the South Shetland Islands, Antarctica. a) site T16 in the South Shetland Island and Antarctic Peninsula; b) site T11-T16 in the South Shetland Islands; c) site T1-T10 in King George Island. (★: Antarctic research station; ◆: Antarctic specially protected area (ASPA)).