Environmental Pollution 206 (2015) 611–618

Contents lists available at ScienceDirect

Environmental Pollution

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

Hexabromocyclododecane flame retardant in Antarctica: Research stations as sources

Da Chen [a, *], Robert C. Hale [b], Mark J. La Guardia [b], Drew Luellen [b], Stacy Kim [c], Heidi N. Geisz [b]

[a] Cooperative Wildlife Research Laboratory and Department of Zoology, Southern Illinois University, Carbondale, IL 62901, USA
[b] Virginia Institute of Marine Science, The College of William and Mary, Gloucester Point, VA 23062, USA
[c] Moss Landing Marine Laboratories, Moss Landing, CA 95039, USA

ARTICLE INFO

Article history:
Received 24 May 2015
Received in revised form
12 August 2015
Accepted 15 August 2015
Available online 25 August 2015

Keywords:
Hexabromocyclododecane
Flame retardant
Antarctica
Research station

ABSTRACT

Historical persistent organic pollutants (POPs) are banned from Antarctica under international treaty; but contemporary-use POPs can enter as additives within polymer and textile products. Over their useful lives these products may release additives in-situ. Indeed, we observed 226 and 109 ng/g dry weight (dw) of the total concentrations of α-, β- and γ-hexabromocyclododecane (HBCD) in indoor dust from McMurdo Station (U.S.) and Scott Station (New Zealand), respectively. Sewage sludge collected from wastewater treatment facilities at these stations exhibited ∑HBCD of 45 and 69 ng/g dw, respectively. Contaminants originally within the bases may exit to the local outdoor environment via wastewaters. Near McMurdo, maximum ∑HBCD levels in surficial marine sediments and aquatic biota (invertebrates and fish) were 2350 ng/g (total organic carbon basis) and 554 ng/g lipid weight, respectively. Levels declined with distance from McMurdo. Our results illustrate that Antarctic research stations serve as local HBCD sources to the pristine Antarctic environment.

1. Introduction

Hexabromocyclododecane (HBCD) is a widely used additive brominated flame retardant (BFR). The dominant application of HBCD is in polystyrene insulation used in construction, with lower amounts used for backcoating textiles and in thermoplastics (WHO, 1997). Like the less brominated polybrominated diphenyl ether (PBDE) congeners such as BDE-47 or -99, HBCD is bioaccumulative (Covaci et al., 2006). In 2001 global demand for HBCD (16,700 MT) exceeded the combined total for commercial PentaBDE and OctaBDE mixtures (11,290 MT) (de Wit et al., 2010). European usage of HBCD surpassed that of DecaBDE prior to the restriction of the use of HBCD (VECAP, 2009). On 2 May 2013, the Conference of the Parties (COP) of the United Nation Environmental Programme (UNEP) Stockholm Convention on Persistent Organic Pollutants (POPs) agreed to list HBCD as a POP for elimination in Annex A of the Convention (www.pops.int). However, time-limited exemptions were given to production for use in expanded and extruded polystyrene insulation foams in buildings, in order to give countries time to phase-in safer substitutes. In addition, existing HBCD-added products that are in use, or remain in discarded materials, will continue to serve as environmental sources.

While HBCD has been used intensively, its environmental distribution has received far less attention than the PBDEs, particularly in polar regions. Long-range transport of HBCD from developed zones of the northern hemisphere to the Arctic has been reported (Covaci et al., 2006; Letcher et al., 2010). Interestingly, a 2010 study indicated that HBCD was the dominant BFR in the upper layers of a Svalbard (Norway) ice core (Hermanson et al., 2010). Contamination pathways likely also exist from developed areas of the southern hemisphere to Antarctica. In addition, polar ice can trap POPs, which may be released to ecosystems during thawing events (Chiuchiolo et al., 2004).

In addition to long-range transport, local human activities in Antarctica may serve as contaminant sources (Hale et al., 2008). Although Antarctica has no permanent indigenous human inhabitants, approximately 30 nations operate over 80 full- or part-time research stations and field camps across the continent (Gröndahl et al., 2009). The number of scientists and support staff in residence ranges from 1000 in winter to over 4000 in summer

* Corresponding author.
E-mail address: dachen@siu.edu (D. Chen).

http://dx.doi.org/10.1016/j.envpol.2015.08.024
0269-7491/

(Gröndahl et al., 2009). The Antarctic Treaty's Protocol on Environmental Protection, enacted in 1998, prohibited the importation and release of specific POPs (Consultative Parties to the Antarctic Treaty, 1991). The Protocol requires that sewage from coastal research stations that house more than 30 people be treated before disposal. However, the Protocol only requires research stations to macerate prior to discharge based on the assumption that domestic wastewaters are free of POPs and wastes therein are biodegradable (Hale et al., 2008). This has resulted in stations discharging substantial quantities of total suspended solids (TSS) and associated organic contaminants to the Antarctic environment. A recent survey of water disposal practices indicated that approximately 46% of permanent Antarctic stations and 68% of summer stations lack any sewage treatment or use simple maceration (Gröndahl et al., 2009). Stations that employ sophisticated treatment techniques generally implemented these within the last decade.

Among Antarctic research stations, the U.S.-run McMurdo Station is the largest, supporting up to 1200 residents (Gröndahl et al., 2009). Due to their remoteness and the extremely dry and cold climate, fires are a great concern at such research stations. Hence, insulative building materials containing flame retardants may be abundant on-site, along with many thermoplastics and electronic equipment that contain BFRs. These additives may escape from such materials and enter or become associated with indoor air, dust, clothes, or other materials (Harrad et al., 2010; Stapleton et al., 2005). A portion may end up in wastewater via cleaning, washing, voiding of human wastes, or other pathways (Stapleton et al., 2005; Schecter et al., 2009). We hypothesized that HBCD may contaminate indoor dust in Antarctic stations and be released to outside environment via wastewater discharges. To evaluate these hypotheses, we investigated the presence of HBCD in: (1) indoor dust and sewage sludge collected from the McMurdo (U.S.) and Scott (New Zealand) research stations; (2) surface sediments and aquatic organisms collected at varying distances from the McMurdo Station wastewater treatment plant (WTP) outfall; and (3) Adélie penguin (*Pygoscelis adeliae*) fat and eggs obtained 30 km from the McMurdo and 5 km from the Palmer (U.S.) Station, respectively.

2. Materials and methods

2.1. Sampling

Dust from indoor room surfaces was obtained from the McMurdo Station in 2005, along with wastewater sludge from the station's wastewater treatment plant (WTP). Dust was collected with household vacuums from living quarters. Dust and sludge were also collected in 2006 from the Scott Station, located 3 km away from McMurdo Station. Both stations are located on Ross Island, Antarctica (Fig. 1). A composite sample of dust (approximately 10 g (g)), as well as a composite of sludge (approximately 50 g), was collected from each station. Surface sediments and marine organism composites were collected from 11 sites at varying distances from the McMurdo Station WTP outfall from October to December 2003 (Fig. 1). A composition of sediments (approximately 250–300 g) was collected from each site. Organisms included proboscis worm (*Parborlasia corrugatus*), sponge (*Haliclona* sp. *and Homaxinella balfourensis*), sea urchin (*Sterechinus neumayeri*), sea star (*Odontaster validus*), clam (*Laternula elliptica*), and rock cod (*Trematomus bernacchii*). Multiple (2–5) individuals from each species were subject to opportunistic catch and then pooled into a composite for chemical analysis. No macro-organisms were available from the immediate vicinity of the outfall (i.e. the Outfall site). These samples were previously analyzed for PBDEs (Hale et al., 2008). Adélie penguin adipose tissues (n = 4) from dead adults and egg content homogenates (n = 5) were collected in 2003–2005

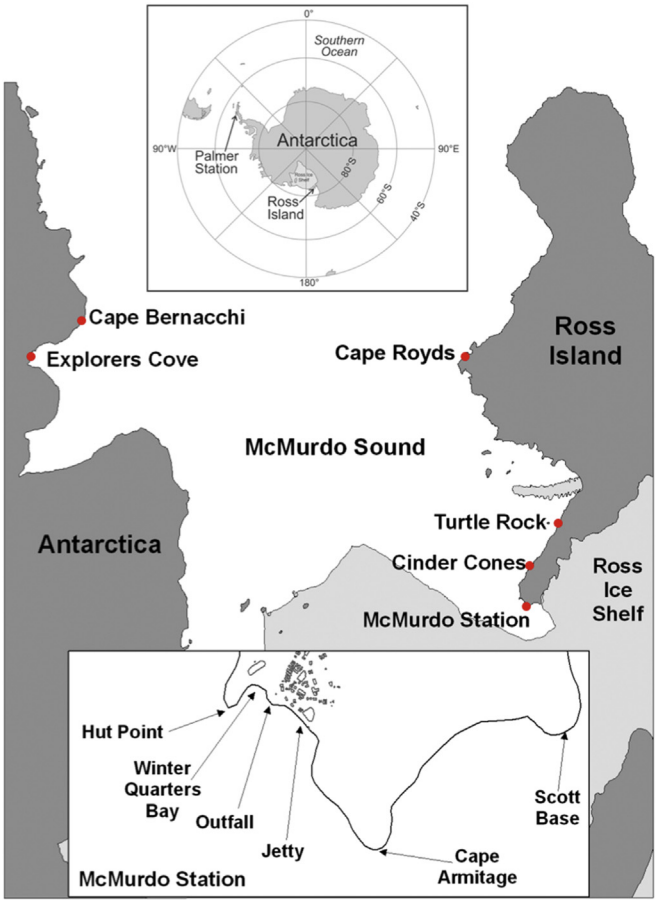

Fig. 1. Sediments, invertebrates and fish were collected at varying distances from the McMurdo Station wastewater treatment plant outfall, i.e., Winter Quarters Bay (WQB) middle and inner (0.1 km), Outfall South A (0.1 km), Hut Point (0.5 km), Jetty (0.5 km), Cape Armitage (1 km), Cinder Cones (13 km), Turtle Rock (25 km), Explorer's Cove (77 km) and Cape Bernacchi (80 km). Scott Station is located 3 km away from McMurdo and is not shown on the map. Adélie penguin eggs and adipose were obtained at Cape Royds (Ross Island) and nearby Palmer Station (Anvers Island) (site not shown).

at Cape Royds (Fig. 1). Four additional eggs and five adult adipose samples were collected at an Anvers Island site (64°46′30″S, 64°03′04″W) 5 km from Palmer Station in 2004. At the time of sampling, Palmer station macerated and then directly discharged its wastewater to the ocean. All samples were stored at −20 °C prior to chemical analysis.

2.2. Analysis

Sample extraction and purification methodologies have been reported previously (Chen et al., 2011) and are described in detail in the Supplemental Material. Briefly, samples and method blanks (sodium sulfate) were freeze-dried and spiked with a ^{13}C-labeled α-HBCD surrogate standard (Wellington Laboratories, Ontario, Canada). Samples were then subjected to accelerated solvent extraction (Dionex ASE 200, Sunnyvale, CA). After gravimetric determination of extractable lipids, the remainder of each extract was purified by size exclusion and silica gel chromatography (2-g, silica gel, solid-phase extraction column; Isolute, Biotage, U.S.). The fraction containing HBCD was collected, reduced in volume under a purified nitrogen stream and spiked with the internal quantification standard d_{18}-labeled α-HBCD (Wellington Laboratories, Ontario, Canada). Dust and sludge samples were also analyzed for the total