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BROMINATED FLAME RETARDANTS IN THE ANTARCTIC

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Introduction

Like the chlorinated persistent organic pollutants (POPs), brominated diphenyl ethers (BDEs) are another class of persistent, lipophilic, bioaccumulative organic chemicals that have been found to travel through the atmosphere, and have an environmental dispersion similar to that of PCBs and DDT[1]. BDEs have been produced for use as flame retardant in plastics, textiles, electronic circuitry and other materials since the early 1970's[1,2]. These compounds are similar in structure to the PCBs and are speculated to exhibit a number of harmful effects in humans and animals at low-level exposures. Although the toxological impacts of BDEs are still being assessed, effects of BDEs on thyroid function in animals appear to be similar to adverse effects reported for PCBs[3]. Evidence also suggests BDE mediated production of pseudoestrogens in humans, neurotoxic effects in animals, liver toxicity and a reduction in spawning success in fish, and endocrine disruption[1,4].

While there are 209 BDE congeners, three general BDE-based flame retardant technical products are produced. Though not the most abundant of the technical products, pentaBDE (PeBDE), containing tetra- through hexa- BDEs, has the highest potential for toxicological effects, based on the degree of bromination of its congeners. PeBDEs are easily bioaccumulated, and are frequently found in biological and environmental samples. PeBDE products contain a number of lower brominated BDE congeners, including BDE-47 (2,2',4,4',-TeBDE), BDE-99 (2,2',4,4',5-PeBDE), and BDE-100 (2,2',4,4',6-PeBDE), which are the BDEs of focus in this study. Unlike the organochlorine (OC) pesticides in the "Dirty Dozen," BDEs are not targeted for elimination by international treaty. Not only are they in current use today, but they are being commercially produced in large quantities.

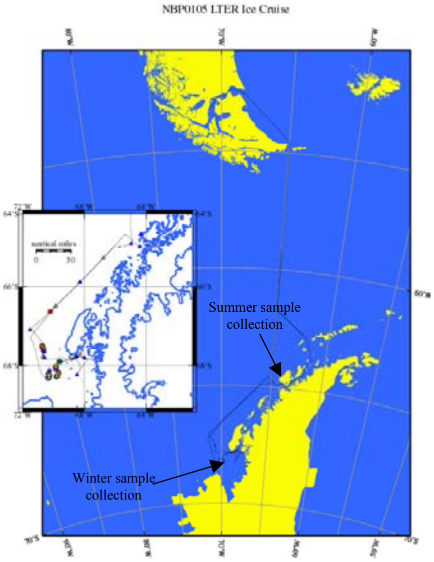
Like many POPs, BDEs have a tendency for atmospheric travel. This characteristic has led to their existence in ecosystems far from areas of release. In the Arctic, contaminants have been measured not only in high trophic level seals and polar bears[5-7], but in breast milk of northern inhabitants, who have traditionally lived and hunted marine mammals within the Arctic[7]. Likewise, organochlorine contamination in Antarctica was reported in the 1960's with the discovery of DDT and PCBs in Antarctic regions[8]. Since that time, a number of studies on Antarctic organochlorine contamination have been conducted, particularly in high trophic level predators. OC pesticides have been detected in Antarctic fish[9], seabirds[10], penguins[11], Weddell seals[12], in the eggs of both penguins and skuas[13], and in Minke whales from Antarctic regions[14]. OC pesticides have also been detected in Antartic air, water, snow, ice, aquatic sediments, soils, mosses, and lichens[15-17].

Although studies on BDEs in the environment, particularly in polar regions, are far fewer and relatively recent compared to those on OC pesticides, BDEs have been detected in a number of samples in ecosystems far from areas of release. BDEs were first discovered in the Arctic and hypothesized to be global contaminants in 1987, when they were found in tissue samples of fish-eating birds and the Ringed seal from the Arctic Ocean[3,18]. Since then, BDEs have been detected in the Ringed seal in a number of studies[4,19-20], in Beluga whales[20], and in Arctic air samples[1]. However, no studies have been published on the presence of BDEs in Antarctica.

Methods and Materials

Air, snow, sea ice, sea ice microbial community (SIMCO), and juvenile krill samples were collected in Austral late winter/early spring during the 2001 LTER Ice Cruise (September 7 – October 26) aboard the R/V Nathaniel B. Palmer. Samples were collected at ice stations located west of the Antarctic Peninsula, southwest of Adelaide Island (Figure 1). Summer sampling took place between January 7 and March 14, 2002, at Palmer Station, located in the southwest region of Anvers Island (Figure 1). Samples of air, snow, glacier ice and runoff, surface water, phytoplankton and adult krill were collected at various time intervals within 2 miles of Palmer Station.

Figure 1. Cruise track for the 2001 LTER Ice Cruise Sept. 7 – Oct. 26 along the western Antarctic Peninsula aboard the R/V Nathaniel B. Palmer. Also shown is the location for summer sampling.



Plankton, krill, SIMCO, and snow/ice/runoff particulate samples were thoroughly mixed with pre-cleaned (4 hrs @ 450 °C) hydromatrix to remove water, and extracted with 65%:35% dichloromethane:methanol via accelerated solvent extraction (2000 psi; 100 C; Dionex ASE 200 Accelerated Solvent Extractor) following addition of a surrogate standard containing deuterated α-HCH and PCB-204. For each sample, the extract was brought to 1:1:0.9 DCM:methanol:water by addition of methanol and 20% NaCl in hexane-extracted water, and back extracted 3 times into hexane via agitation for 3 minutes. The hexane fraction was reduced in volume to 5 ml by turbo- and/or roto-evaporation, followed by blow down with purified N_2. The remaining ca. 5 ml fraction was vortexed with 1 ml H_2SO_4 to remove lipids, and the hexane layer removed after settling. Ca. 2 ml hexane were added to the remaining extract/acid mixture and the procedure repeated 3 times. A second H_2SO_4 clean-up was done on the biological samples. The hexane fraction was then blown down under N_2 to 1 ml and passed through a column containing 10 g pre-cleaned (Soxhlet extraction with DCM for 24 hrs) deactivated silicic acid (mesh size 100-200), topped with 1 inch pre-cleaned (4 hrs @ 450 °C) $NaSO_4$, for further removal of interfering substances. Both 25 ml hexane and 40:10 ml DCM:hexane eluents were collected and reduced by roto-evaporation followed by nitrogen blow down to 1 ml. An internal standard containing deuterated lindane was added, and the extract further reduced to 100 µl under N_2 for analysis.

Samples were analyzed via gas chromatography/negative chemical ionization mass spectrometry (Hewlett Packard 6890 Series GC system/Hewlett Packard 5973 Mass Selective Detector) using a J&W DB-35MS wide bore capillary column (30 m length, 0.25 mm diameter, 0.25 µm film thickness) and selective ion monitoring.

Results and Discussion

To date, we have detected BDEs associated with snow and glacier ice particulate matter and in SIMCO, phytoplankton, and krill (adult and juvenile) from the western Antarctic Peninsula. Antarctic air samples (gas and particulate) are currently being analyzed for BDEs. In general, levels of BDEs exceeded levels of OC pesticides (hexachlorobenzene, hexachlorocyclohexanes, heptachlor, and ΣDDT) for most samples analyzed.

Table 1. Range of POP concentrations in Antarctic marine biota samples.

	HCB	ΣHCH	heptachlor	ΣDDT	ΣBDE
SIMCO	.007 - .032 $\mu g/g_{lipid}$	nd - nq	nd - .01 $\mu g/g_{lipid}$	nd - nq	2.4 - 46 $\mu g/g_{lipid}$
phytoplankton	nq - .009 $\mu g/g_{lipid}$	nd - .007 $\mu g/g_{lipid}$	nd - .011 $\mu g/g_{lipid}$	nd - .047 $\mu g/g_{lipid}$	0.01 – 0.14 $\mu g/g_{lipid}$
Juvenile krill	.009 - .01 $\mu g/g_{lipid}$	.001 - .002 $\mu g/g_{lipid}$	.001 - .027 $\mu g/g_{lipid}$	nd - nq	0.8 - 1.8 $\mu g/g_{lipid}$
Adult krill	3 - 4 ng/g_{lipid}	0.1 – 0.22 ng/g_{lipid}	nd - nq	nd - nq	2.6 – 6.6 ng/g_{lipid}

HCB – hexachlorobenzene; ΣHCH – sum α, β, γ - hexachlorocyclohexanes, ΣDDT – sum o,p-DDT, DDE, DDD and p,p'- DDT, DDE, DDD; ΣBDE – sum BDEs 47, 99, 100.
nd – not detected; nq – not quantifiable.

The majority of BDEs in Antarctic snow, ice, and water were associated with particulate matter. Moreover, in SIMCO and phytoplankton BDE-47 ≈ BDE-99 ≈ 4 x BDE-100 (Figure 2), with similar, but slightly lower levels of BDE-47 observed in krill. However, BDE-47 was largely depleted in glacier ice particulate matter, but enriched in glacier runoff (dissolved phase) indicating preferential weathering of BDE-47 (Figure 2).

Our results indicate that BDEs are currently entering the Antarctic presumably by atmospheric transport and are deposited onto glacier and sea ice. BDEs are subsequently transferred into SIMCO, phytoplankton, and krill at the base of the Antarctic marine food web. Therefore it is likely that BDEs may be accumulating in and potentially adversely impacting higher trophic level animals in the Antarctic marine ecosystem.

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Figure 2. BDEs in sea ice (SIMCO) – left, glacier ice particulate matter – center, and glacier runoff (dissolved) – right.