Brominated flame retardants in the Arctic – an overview of spatial and temporal trends

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Introduction

The Stockholm Convention on Persistent Organic Pollutants (POPs), which entered into force on May 17, 2004, includes wording that chemicals with the characteristics of POPs are those found in locations "distant from sources" and those for which "monitoring data showing that long-range environmental transport of the chemical … may have occurred". Thus, the Arctic has become an important indicator region for assessment of persistence and bioaccumulation. The Arctic environment is well suited as a region in which to evaluate POPs. Some regions of thee Arctic, particularly the Barents Sea area north of Norway and western Russia are relatively close to source regions of POPs. Cold conditions favor persistence of POPs relative to temperate or tropical environments. The presence of fourth level carnivores (e.g. polar bears and seabirds), and storage of lipid as an energy source, make Arctic food webs vulnerable to bioaccumulative chemicals. Indigenous people in the Arctic utilizing a traditional diet, which is high in nutritionally beneficial fat, results in their elevated exposure to some POPs [1].

The first indication that brominated flame retardants (BFRs) were reaching the Arctic was the detection by Jansson et al.[2] of lower molecular weight polybrominated diphenyl ethers (PBDEs) in Svalbard Brünnich's guillemots (130 ng/g lipid weight) and ringed seals (40 ng/g lw) collected in 1981. Whitefish collected from Lake Storvindeln in 1986, a pristine mountain lake in the Swedish mountains near Ammarnäs, had ΣPBDE levels of 26 ng/g lw [3]. Despite these early findings, only recently have the spatial and temporal trends of BFRs been studied in detail in the Arctic. The purpose of this paper is to review the new data on BFRs in the Arctic and assess whether this information supports the view that PBDEs and other BFRs of similar molecular weight are POPs and potential global pollutants. This review is based on a recent assessment of POPs in the Arctic [4] combined with newer data not available for that assessment. Unless otherwise noted, ΣPBDE denotes the sum of lower brominated congeners. If DecaBDE (BDE209) was quantified, this is indicated.

Results and discussion

Air: Using several global fate and transport models, Wania and Dugani [5] concluded that tetra- and penta- brominated PBDEs have comparable arctic accumulation potential to hexa- heptachloro PCBs. BFRs were analyzed in archived air samples (1994-95) from Alert and Tagish (Canadian Arctic) and Dunai (Russian Arctic) [6]. Mean ΣPBDEs (Di-HpBDEs) in air samples were 14 pg/m^3 at Dunai, 240 pg/m^3 at Alert and 424 pg/m^3 at Tagish. The concentrations at Alert and Tagish were

higher than those reported for the city of Chicago (52 pg/m^3) [7]. Mono-, di- and triBDEs were found in air samples from Alert, which may indicate photodegradation (debromination) of PBDEs during long-range atmospheric transport. The high PBDEs at Alert and Tagish, two sites that have been used for studies of PCBs, polyaromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) in air [8, 9, 10] illustrates a potential problem with measurements of PBDEs at background sites. Local burning, which is common in Arctic and sub-Arctic communities in Canada, because municipal waste is not recycled or incinerated and can't always be suitably landfilled, may cause local emissions of some chemicals in consumer products. Indeed, Halsall et al. [9] noted higher combustion related PAHs (phenanthrene, retene) during the summer months at Tagish and Alert which may be related to local burning. Farrar et al. [11] have recently demonstrated that PBDEs were elevated in air during "bonfire" events in the UK.

Preliminary analyses of some samples from Alert, Dunai, and Tagish site show HBCD and BDE209 concentrations below detection limits but tetrabromobisphenol-A (TBBPA) was detected on the filter of one Dunai sample at 70 pg/m^3 [6]. ΣPBDEs in air samples from Bjørnøya (Norway) taken in 1999-2000 ranged from 3 to 10 pg/m^3 [4]. Air samples were taken concurrently in 22 European countries including Iceland, Norway and on Svalbard using passive air samplers [12]. The ΣPBDE levels (Di-HxBDEs) in the samples from these sites were lower (1.65, 1.62 and 3.89 ng/sample, respectively) than at urban sites (up to 42 ng/sample) but were comparable to many rural or remote European sites. The major congeners observed at all Arctic sites were BDE47, 99, 100, 153 and 154 with BDE99 having the highest concentrations. Hexabromocyclododecane (HBCD) was measured in air and deposition samples from Pallas, northern Finland in 2000-01 [13]. Air concentrations were 2-3 pg/m^3 and deposition was 5.1 – 13 ng/m^2 day. An air sample collected in 1990-91 from Ammarnäs contained 8.3 pg/m^3 of Te-PeBDEs and 6.1 pg/m^3 of HBCD, indicating long-range transport [14].

Soil: Surface soil was collected from four regions of the Russian Arctic: Chukotka (Kanchalan and Laurentiya); Kola Peninsula; Pechora Basin; and, Taymir Peninsula (Dudinka), in 2000-2001 [4]. Detectable concentrations (0.16 to 0.23 ng/g dw) of ΣPBDEs (detection limits approximately 0.5 ng/g in soil) were observed in 3 soil samples from the two Chukotka sites. In soils collected on a latitudinal transect of UK and Norway, median ΣPBDE concentration (Te-HpBDEs) for Norwegian soils was 0.71 ng/g dw (1.1 ng/g organic matter) [15]. Latitudinal fractionation was seen with higher relative contribution of BDE47 to ΣPBDE going northwards.

Sediments: Dated sediment cores were collected from Canadian lakes on a north-south transect from southern Ontario to Ellesmere Island [16]. Slices at different depths were analyzed for PBDEs including BDE209. BDE209 was detected in recent slices of most of the cores and concentrations in the three Arctic lakes were 0.075 (AX-AJ Lake), <0.1 (Romulus Lake) and 0.042 (Char Lake) ng/g dw. The Arctic lakes had much lower fluxes than more southerly lakes with somewhat later appearance of BDE209. This is consistent with BDE209 having lower long range transport potential due to being transported on atmospheric aerosols [5]. The fluxes in the cores indicate increasing inputs with time. ΣPBDEs in three marine sediments from High Arctic Canada were 0.107 (Barrow Strait), 0.122 (Penny Strait) and 0.297 ng/g dw (Nanisivik) [17]. BDE47 was the most abundant congener. Marine sediments from Tromsø harbor (northern Norway) had concentrations of 0.06-0.25 ng/g dw ΣPBDE, 0.42-0.43 ng/g dw of BDE209, 1.24 ng/g dw of TBBPA and no detectable HBCD [18]. Sediments from three sites along Kola Bay (northwest Russia) were analyzed for Te-HxBDEs [19]. ΣPBDEs for Kola Bay and Guba Zapadnaya Litsa were 0.14-0.16 ng/g dw, but

at Polyarnyy, a closed city with a navy base, they were 241 ng/g dw, with BDE99 dominating the congener profile.

Frogs and fish: Common frogs were collected in Sweden along a latitudinal gradient and livers analyzed for BDE47 and 99 [20]. BDE47 concentrations were 2.3 and 0.93 ng/g lw in frogs from Ammarnäs and Kiruna, respectively, but BDE99 (5.6 ng/g lw) was only found in the Ammarnäs sample. In northern Norwegian lakes, ΣPBDE in burbot liver was 175 ng/g lw in trout muscle, 8-14 ng/g lw, and for Arctic char from Lake Ellasjøen on Bjørnøya, 1250 ng/g lw [4]. The congener pattern in all three species is evenly distributed between BDE47 and 99, and resembles the PeBDE technical product. ΣPBDE levels (Tri-HxBDEs) in Arctic char from Lake Fergusson on southern Greenland were 23 ng/g lw in liver and 41 ng/g lw in muscle[21]. In the Mackenzie River (Canada), ΣPBDE levels in the burbot liver collected in 1999 and 2000 were 4.2 and 3.7 ng/g lw, respectively [4]. For marine fish, Atlantic cod and tusk liver from Norway had ΣPBDE levels ranging from 24-109 and 60-300 ng/g lw, respectively [4]. Blue mussels from Lofoten and Varanger (northern Norway) had ΣPBDE levels of 5.9-19 and 1.5 ng/g lw, and HBCD levels of 9-11 and 3.6 ng/g lw, respectively [18]. Atlantic cod liver from the same two sites had ΣPBDE levels of 13.4-16.3 and 16.1-25.7 ng/g lw, HBCD levels of 6.6 and 7.7 ng/g lw and TBBPA levels of 0.5 and 2.5 ng/g lw, respectively [18]. Atlantic cod and Greenland halibut from Greenland had liver ΣPBDE levels of 8.9 and 7.5 ng/g lw [4]. Polar cod from Svalbard had a ΣPBDE level of 3.6 ng/g lw [22]. ΣPBDEs (4 congeners) were studied in shorthorn sculpin, cod, spotted wolfish, starry ray and blue mussels during 2000 near the western Greenland villages of Quaqortoq (3500 inhabitants), Igaliko (30 inhabitants) and Usuk (background site 3-5 km from Igaliko) [4]. Concentrations were low in mussels (5.5 ng/g lw). A spatial trend in sculpins was apparent with the highest concentrations observed in samples from Quaqortoq (43 ng/g lw) followed by Igaliko (19 ng/g lw) and Usuk (11 ng/g lw). The concentrations in the other fish species ranged from 3.3-34 ng/g lw. The results suggest that villages are sources of PBDEs to the nearby marine environment.

Birds: High ΣPBDE concentrations have been found in predatory birds feeding on terrestrial mammals and birds, particularly peregrine falcons in northern Sweden [4] and Norway [4, 23]. The mean ΣPBDE (Te-HxBDEs) in the two populations are 4500 and 4700 ng/g lw, respectively, with levels ranging from 680-39 000 ng/g lw in the Swedish population. The Swedish and Norwegian peregrine falcons also had measurable levels of BDE183 and BDE209. HBCD concentrations ranged from 34-2400 ng/g lw in the Swedish peregrine falcons. The ΣPBDE levels in Norwegian golden eagles, gyrfalcons and merlins were approximately 140, 360 and 720 ng/g lw and BDE183 and 209 were also present. The congener pattern in these bird species is dominated by BDE 153 and 99. The burden of PBDEs in peregrine falcons may be linked to their migratory habits as the northern population in Sweden overwinters along the coast and estuaries of central and southern Europe. In addition, many of the birds they prey on in the Arctic are also migratory and may have PBDE burdens from their overwintering sites further south. PBDEs were measured in thick-billed murres, northern fulmars and black-legged kittiwakes collected in 1993 from Prince Leopold Island in Lancaster Sound (Canada)[4]. ΣPBDE levels in egg and liver samples from kittiwakes were 60-70 ng/g lw, and 14 and 15 ng/g lw in the murre and fulmar samples. PBDEs in thick-billed murres and northern fulmars collected in 1975, 1988, 1993 and 1998 from Prince Leopold Island, Canada, show rapidly increasing trends, from 2-4 ng/g lw to 18-20 ng/g lw [24]. PBDEs were measured in the liver and intestinal contents of fifteen glaucous gulls collected on Bjørnøya in 1999 [4]. Only BDE47

and 99 were detected at concentrations between 27-450 ng/g lw. ΣPBDE levels were determined in the liver of thick-billed murre and black guillemot collected from southwestern Greenland in 1999 [4] and in black guillemot livers and eggs from East and West Greenland in 2000 [25]. Concentrations of ΣPBDE were 32 ng/g lw in the thick-billed murre and 46 ng/g lw in black guillemot from southwestern Greenland. ΣPBDE levels in West Greenland black guillemot liver and eggs were both 25 ng/g lw, and for liver from East Greenland, 73 ng/g lw. PBDEs in herring and great black-backed gull eggs collected in 2001 from northern Norway contained approximately 500-800 ng/g lw [4]. BDE 47 dominates the congener pattern in seabirds.

Seals and whales: ΣPBDE concentrations in the blubber of ringed seals from northeastern Greenland (58 ng/g lw) [4]and on Svalbard (18 ng/g lw) [22] were up to an order of magnitude higher than levels reported from western Greenland (4 ng/g lw), the eastern (1 ng/g lw) and the western Canadian Arctic (5 ng/g lw) [4]. BDE209 was analyzed for but not detected in the western Canadian ringed seals [4]. Concentrations of ΣPBDE were 29-161 ng/g lw in Svalbard beluga blubber from adults collected in 1998 [22] and were higher, compared to concentrations of 17 ng/g lw in beluga from the western Canadian Arctic [4] and 1.6-3.0 ng/g lw from the eastern Canadian Arctic [4]. Svalbard juveniles and calves had even higher concentrations (174-314 ng/g lw). Temporal trend studies of ΣPBDEs in Canadian Arctic beluga (1982-1997) and ringed seals (1981-2000) [4]), have shown rapidly increasing concentrations of these compounds with doubling times of about 4 years. Harbor porpoises from Icelandic waters had ΣPBDE levels of 25-95 ng/g lw [26]. Minke whales (from the Barents Sea had ΣPBDE levels of 32-44 ng/g lw in muscle, while minke whales from the Norwegian Sea had higher levels at 400-440 ng/g lw in muscle [4]. The greatest concentrations of PBDEs measured in the Arctic are those observed in Faroe Island long-finned pilot whales (82-3200 ng/g lw) [4]. Concentrations are an order of magnitude greater than in any other Arctic marine mammal examined to date. As with belugas, highest levels were found in juveniles.

Polar bears: ΣPBDE concentrations in polar bears from Svalbard were 14-144 ng/g lw in one study [4] and 13-70 ng/g lw in a more recent study [22]. A spatial study of PBDEs included polar bears from Svalbard, East Greenland, six locations in the Canadian arctic (Amundsen Gulf, Lancaster Sound, Foxe Basin/Boothia Peninsula, Northeast- and Southeast Baffin Island, Western Hudson Bay), as well as western Beaufort Sea/Chukchi/Bering Sea regions of Alaska[27]. Highest mean ΣPBDE concentrations were found in Svalbard, East Greenland, Southeast Baffin, and Western Hudson Bay (36-73 ng/g lw). Lowest concentrations were found in northwest Alaska, Amundsen Gulf and Lancaster Sound (11-17 ng/g lw). Biomagnification of lower brominated PBDEs is seen from polar cod to ringed seal (BMF=5) and polar cod to beluga (BMF=8-45) [22]. BDE47 dominates the congener pattern in marine mammals. Low biomagnification of BDE47 and BDE 99 was seen in polar bears suggesting these congeners are readily metabolized. However, Muir et al. [27] found the BDE153 was biomagnified to the same extent as PCB 153. Muir et al. [27] also detected HBCD in polar bears. HBCD was present at similar concentrations to BDE47. Highest levels were found in polar bears from east Greenland and Svalbard.

Humans: There is currently only a limited amount of information on BFRs in humans in the Arctic, however, given the wide use of marine mammals in the traditional diet of the Inuit of eastern Siberia, North America and Greenland, their presence in humans is expected. The ΣPBDE

level in human milk from Arctic Quebec was 6.2 ng/g lw in 1996-2000 [28]. This is a three-fold increase since 1989-91.

Conclusions

ΣPBDEs (Br_2-Br_7) are detectable in all environmental samples from the Arctic and there is evidence for the presence of BDE 209 and HBCD. However, ΣPBDE concentrations in all sample types from the Arctic are one or more orders of magnitude lower than total PCB concentrations except for some results for air. PBDE concentrations in Arctic samples are also lower than in similar sample types than PBDEs from more southerly regions. However, doubling times for PBDEs in the North American Arctic biota parallel those seen further south. There are large regional variations in concentrations in top predators with highest PBDEs and HBCD in biota from regions influenced by atmospheric transport from western Europe and eastern North America. The air and harbour sediment results for PBDEs indicate that there are local sources near highly populated areas within the Arctic. Further work is needed to evaluate the influence of local sources. The presence of some high values also underscores the need to collect samples using clean techniques that avoid contamination from BFRs in consumer products if results are to be accepted as evidence for presence in remote environments. While the tetra- and pentabrominated BDEs are ubiquitous in the Arctic, the presence of BDE209 in remote Arctic lake sediments indicates that even this congener is subject to long range transport. Very little data is presently available for HBCD and TBBPA however, in principal, they too could be transported by the same pathways as the Br_2-Br_{10}-PBDEs.

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