Brominated Flame Retardants in the Arctic – Trends, Pathways and New Candidates

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Introduction

The presence of brominated flame retardants (BFRs) in the Arctic has been known since the 1980s (Jansson et al. 1987,Sellstrom et al. 1993) although most measurements have been made since 2000 (de Wit et al. 2006). Here we update our previous review of this topic which was based on published and some unpublished results up to mid-2005 (de Wit et al. 2006) and also consider new candidate chemicals that may have potential for long range transport to the Arctic.

Results and Discussion

Air: Shen et al. (2006) reported PBDEs (mainly BDE 47) in XAD-based passive samplers (PAS) deployed for 1 year at 6 locations in the Canadian arctic in 2000-01. Total PBDE (ΣPBDE) concentrations ranged from 0.3 to 68 pg/m^3 based on an estimated sampling rate of 0.52 m^{3}d^{-1}. A ΣPBDE concentration of 4 pg/m^3 was found at Alert, the long term atmospheric monitoring site in Northern Ellesmere Island. Pozo et al. (2006) reported ΣPBDE concentration of 2 pg/m^3 at Alert using Polyurethane (PUF) based PAS deployed for 4 months (Dec 2004-Mar 2005) at Alert, 5 pg/m^3 at Barrow AK and 5.3 pg/m^3 at Ny Alesund (Svalbard). Hung (2006) recently reported PBDEs in high volume air samples collected weekly at Alert in 2002. Twelve PBDEs (congeners 17, 28/33, 47, 66, 85, 99, 100, 153, 154, 183 and 209) were above detection limits (gas+particle phase) and concentrations ranged from 0.3-16 pg/m^3 (mean 3.7 pg/m^3). The ΣPBDE concentrations were thus in the range of PAS measurements. However, BDE-209 was not detected using PAS, probably because these devices sample mainly gas phase chemical. BDE-209 detected with high vol sampling was presumably on particles but this has yet to be confirmed since the initial samples were combined filter and PUF extracts (Hung 2006). Excluding BDE-209, which has not been previously determined in arctic air, the results for PBDEs were in good agreement with previous measurements by PAS in northern Norway and Iceland (Jaward et al. 2004). Wang et al. (2005) measured PBDEs collected on quartz-fibre filters along a transect from the Bohai Sea to the Beaufort Sea in the high Arctic (37 °N to 80 °N). Concentrations of ΣPBDE averaged 17 pg/m^3 in the Beaufort/Chukchi Sea but were lower than found for 9 samples collected during the cruise along the eastern coast of the Pacific Ocean near China, Korea, Russia and Japan.

Long-range transport (LRT) behaviour: Breivik et al. (2006) examined the long range transport behavior of BDE-209 and other PBDEs using a multi-media transport and fate model and results from dated sediments cores along a latitudinal transect in North America. The decline in BDE-209 flux with latitude based on 7 lakes translated to an empirical half-distance (EHD) of 566 ± 101 km. BDE-47 flux also declined with latitude (although the trend was not statistically significant), which translated into an EHD (± SE) of 1168 ± 942 km. EHDs for PCB congeners 138/163, 153, and 180 based on the same lakes were significantly greater (P= 0.10) than those for BDE-209 based on paired t-tests of the slopes. Calculations using the CoZMo-POP model (Wania et al. 2006) overestimate the observed atmospheric mobility of BDE-209 relative to that of the PCBs. This may be caused by processes of potential significance in limiting LRT that are so far not included in the CoZMo-POP model due to lack of quantitative understanding, notably (i) direct or indirect photolytic degradation of BDE-209 sorbed to atmospheric particles and (ii) snow scavenging of particles, which could be more efficient than rain scavenging.

Freshwater biota: PBDEs have been detected in Arctic freshwater fish and invertebrates but generally at very low concentrations. Evenset et al. (2005) detected ΣPBDEs in landlocked arctic char (*Salvelinus alpinus*) from lakes Ellasjøen and Øyangen on Bjørnøya with highest concentrations in large char from Ellasjøen (17.5±7.4 ng/g ww). In Lake Øyangen, ΣPBDE concentrations in char ranged from <0.03-1.6

ng/g ww. Concentrations in zooplankton were generally near or below detection limits (0.05-0.30 ng/g ww). The differences between lakes were attributed to inputs from seabird guano which has elevated the trophic status of Lake Ellasjøen, and also may bring in greater PBDEs from seabird excreta. Gandhi et al. (2006) used the data from the study by Evenset et al. to model the biomagnification of PBDEs in Lake Ellasjøen. They concluded that biotransformation was a significant factor in explaining PBDE concentraitions in the food web i.e. elevated BDE-47 was best explained by debromination of more highly brominated congeners. In contrast to the relatively high PBDEs in char from Lake Ellasjøen, concentrations similar to those in Lake Øyangen have been reported in landlocked char from Resolute, Char and Amituk Lakes on Cornwallis Island. ΣPBDEs concentrations range from <0.3 to 9.3 ng/g ww in char muscle (+skin) (Muir, unpublished data 2006; Muir et al. (2005)). ΣPBDEs increased in landlocked char from Resolute Lake (Cornwallis Is) over the period 1997 to 2004 with doubling time of 3.3±0.8 yrs (Muir, unpublished data 2006). Hexabromocyclododecane (HBCD) was also detected at concentrations ranging from <0.02 – 0.25 ng/g ww (Muir, unpublished data 2006). In anadromous char collected from 5 communities in the Canadian arctic in 2005, ΣPBDEs ranged from 0.04 to 8.2 ng/g ww (Evans, M, unpublished data 2006; (Evans et al. 2006)). HBCD as well as bis(tribromo-phenoxy)ethane (BTBPE), decabromodiphenyl ether (BDE-209) and decabromodiphenyl ethane (DBDPE) were undetectable in char muscle.

Marine mammals and their food webs: Sørmo et al. (2006) examined biomagnification of PBDEs and HBCD in the polar bear food chain at Svalbard. Highest ΣPBDE concentrations were found in polar bear adipose tissue (21-45 ng/g lw) and ringed seal blubber 42-94 ng/g lw. Sub-ng/g (lw) concentrations were found in calanoid copepods, *Thysanoessa inermis*, and *Themisto libellula* (0.16-0.53 ng/g lw). Polar cod (*Boreogadus saida*) had higher concentrations than most invertebrates (0.49-3.59 ng/g lw). Very low concentrations of BDE-209 were found in polar bear fat (0.03-0.16 ng/g lw) while greater BDE-209 concentrations were found in polar cod. HBCD was detected only in polar cod, seals and polar bears. BDE-153 had the highest biomagnification factor (BMF=7.5) between seals and polar bear, while HBCD biomagnified from cod to seals (BMF=11) but not from seals to bears (Sørmo et al. 2006). Muir et al. (2006a) also observed higher BMFs for BDE-153 based on reported concentrations in ringed seal blubber and polar bear fat from the same regions. Dietz et al. (2006) examined the effects of age and seasonal variability of PBDEs in East Greenland polar bears. Mean ΣPBDE concentrations were 69.5 ng/g lw (range: 21.7-192 ng/g lw) and showed no relationship with age or sex. However, the proportion of BDE-47 to ΣPBDE decreased while BDE-153/ΣPBDE increased with age. A unique observation was that PBDEs and other organohalogens were found to vary seasonally with concentrations in March to July being 1.2 to 1.8 times higher than the rest of the year. Kannan et al. (2005) compared the concentrations of BDE-47 in livers of polar bears from the Alaskan Beaufort Sea and Chukchi Sea sub-populations. Only BDE-47 could be detected in polar bear liver and concentrations ranged from <0.2 to 2.7 ng/g ww and levels decreased with age. Verreault et al. (2005) determined PBDEs in plasma of Svalbard polar bears. ΣPBDE concentrations ranged from 2.7 to 9.7 ng/g ww and consisted predominately of BDE-47 although BDE-209 was detected in 7% of samples. Wolkers et al. (2006a) reported BDE-47 and 99 in beluga (*Dephinapterus leucas*) and narwhal (*Monodon monoceros*) blubber as well as in their prey, polar cod and Greenland halibut (*Reinhardtius hippoglossoides*). Highest concentrations were found in narwhal blubber (ΣPBDE=195 ng/g lw) while concentrations in halibut were about 100-fold lower assuming a lipid content of 10%. McKinney et al. (2006) compared concentrations of ΣPBDEs in St. Lawrence River estuary and Western Hudson Bay beluga liver and found 42-times higher concentrations in the St. Lawrence animals. Hydroxy-PBDEs were also detectable in liver but at concentrations near detection limits. Methoxy-BDEs, 6-MeO-BDE-47 and 2-MeO-BDE-68, which are thought to be of natural origin (Teuten et al. 2005) were also detected. Wolkers et al. (2004) have also reported methoxy-BDEs in Svalbard beluga. Tomy et al. (2006) found highest concentrations of ΣPBDEs in beluga blubber from Hudson Bay and the Southeastern Beaufort Sea, and lowest from eastern Canadian Arctic stocks (Baffin Island). HBCD was found to have increased between 1993 and 2001 in the SE Beaufort Sea while ΣPBDEs showed no significant trend from 1993 to 2005 (4 sampling years). Wolkers et al. (2006b) found relatively low concentrations of ΣPBDEs in blubber of walrus (*Odobenus rosmarus*) from Svalbard. Concentrations of ΣPBDEs ranged from 2.1-75.9

ng/g lw. The wide range of concentrations (which was also seen for PCBs and other OCs) was attributed to higher trophic level feeding by some walrus, possibly on ringed seals. Muir et al.(2006c) found increasing concentrations of ΣPBDEs and HBCD in ringed seal blubber from Arviat (western Hudson Bay) and Resolute (central Canadian archipelago) over the period 1992 to 2005. Mean concentrations of ΣPBDEs from 5 locations in the Canadian arctic ranged from 4.9 to 28 ng/g lw with highest levels in samples from Nain on the Labrador coast (Muir et al. 2006c).

Seabirds: HexaBDEs 153 and 154 were the most abundant congeners, representing ~50% of ΣPBDEs in Eggs from Northern fulmars sampled in the Faroe Islands (Karlsson et al. 2006). BTBPE was detected in 8 of 9 samples, however, mean levels werer 0.11 ng/g lw, about 150 times lower than the average ΣBDE concentrations. Murvoll et al. (2006) determined PBDEs and HBCD in yolk sacs of kittiwake (Rissa tridactyla) hatchlings from Kongsfjorden at Svalbard (Norwegian Arctic; 79°N) and from Runde, an island on the coast of Norway (62°N). Mean concentrations of ΣPBDEs and HBCD were slightly higher at Runde (528 and 260 ng/g lw, respectively) than at Kongsfjorden (461 and 118 ng/g lw, respectively). A local source near Runde may have contributed to higher levels there. Verreault et al.(2005) analysed BFRs in glaucous gull (*Larus hyperboreus*) plasma and found HBCD (0.07-1.24 ng/g wet wt) and brominated biphenyls (BB-101) (<0.13-0.72 ng/g wet wt) as well as hepta- and decabromo-BDEs. Hydroxy- and methoxy-PBDEs were also detected in glaucous gulls (ΣOH-PBDE up to 1.05 ng/g ww; ΣMeO-PBDE: 0.30 – 4.30 ng/g ww) suggesting natural sources as well as metabolism of BDE-47 may be important. Muir et al. (2006b) compared temporal trends of PBDEs in ringed seals and seabirds from Lancaster Sound in the Canadian arctic. Increasing concentrations were seen in all species but doubling times for ΣPBDEs were faster in seals (5 y) compared to northern fulmar (*Fulmaris glacialis*) (10 y) and thickbilled murres (*Uria lomvia*) (8 y).

Conclusions

Studies published since mid-2005 have contributed substantial additional information on levels, trends and biomagnification of BFRs in the Arctic, particularly for marine biota. The presence of BDE-209 at low but readily detectable levels in a variety of organisms, and in lake sediments, illustrates that even very non-volatile chemicals can reach the Arctic. Overall, concentrations of BFRs measured to date have been low compared with legacy OCs. However, the number of BFRs determined has been rather limited compared to the number in commerce. There are a number of semi-volatile BFRs, e.g. see Muir and Howard (2006), with relatively long predicted atmospheric oxidation half-lives which could be atmospherically transported, and would be good candidates for future surveys of spatial and temporal trends.

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