Levels and trends of brominated flame retardants in the Arctic

Cynthia A. de Wit[1] and Derek C.G. Muir[2]

[1]Institute of Applied Environmental Research, Stockholm University, Stockholm, Sweden
[2]National Water Research Institute, Environment Canada, Burlington, ON, Canada

The first indication that brominated flame retardants (BFRs) were reaching the Arctic was the detection of lower brominated PBDEs in Svalbard Brünnich's guillemots (130 ng/g lipid weight) and ringed seals (40 ng/g lw) collected in 1981[1]. 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 [2] and 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 [3]. New data on brominated flame retardants in the Arctic are summarized here. ΣPBDE denotes the sum of lower brominated congeners. If DecaBDE (BDE209) was quantified, this is indicated.

Air: BFRs were analyzed in archived air samples (1994-95) from Alert and Tagish (Canadian Arctic) and Dunai (Russian Arctic)[4]. 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. Concentrations at Alert and Tagish were higher than those reported for the city of Chicago (52 pg/m^3)[5] and may be due to waste burning. Mono-, di- and triBDEs were found in Alert air samples, which may indicate photodegradation (debromination) during long-range atmospheric transport. Preliminary analyses of some samples from each site show HBCD and BDE209 concentrations below detection limits but TBBPA was detected on the filter of one Dunai sample at 70 pg/m^3. ΣPBDEs in air samples from Bjørnøya (Norway) taken in 1999-2000 ranged from 3 to 10 pg/m^3 [6]. Air samples were taken concurrently in 22 European countries including Iceland, Norway and on Svalbard using passive air samplers[7]. 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. Air and deposition samples from Pallas, northern Finland from 2000-01 had HBCD concentrations of 2-3 pg/m^3 and 5.1 – 13 ng/m^2 day, respectively [8].

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[6]. 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)[9]. 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[10]. Slices at different depths were analyzed for PBDEs including BDE209. BDE209 was detected in recent slices of most 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 have much lower fluxes than more southerly lakes with somewhat later appearance of BDE209. This is consistent with BDE209 having lower mobility due to being sorbed to and transported on particles. The fluxes in the cores indicate increasing inputs with time. Dated sediment cores from seven lakes in West Greenland had BDE47 levels of 0.007-0.051 ng/g dw in the top layer and showed increasing concentrations in recent layers[11]. 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)[12]. BDE47 was the major 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 BDE209, 1.24 ng/g dw TBBPA and no detectable HBCD[13]. Sediments from three sites in northwest Russia were analyzed for Te-HxBDEs[14]. 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[15]. 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 Ammarnäs frogs. 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[6]. The congener pattern in all three species is evenly distributed between BDE47 and 99, and resembles the PeBDE technical product. ΣPBDE levels in Arctic char from Lake Fergusson on southern Greenland were 23 ng/g lw in liver and 41 ng/g lw in muscle[16]. 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[6]. For marine fish, Atlantic cod and tusk liver from Norway had ΣPBDE levels ranging from 24-109 and 60-300 ng/g lw, respectively[6]. 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[13]. 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[13]. Atlantic cod and Greenland halibut from Greenland had liver ΣPBDE levels of 8.9 and 7.5 ng/g lw[6]. Polar cod from Svalbard had a ΣPBDE level of 3.6 ng/g lw[17]. ΣPBDEs 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)[6]. 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 and Norway[6,18]. 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. PBDEs in peregrine falcons may be linked to their migratory

habits. PBDEs were measured in thick-billed murres, northern fulmars and black-legged kittiwakes collected in 1993 from Prince Leopold Island in Lancaster Sound (Canada)[6]. ΣPBDE levels in egg and liver samples from kittiwakes were 60-70 ng/g lw, and 14 and 15 ng/g lw in 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[19]. PBDEs were measured in the liver and intestinal contents of glaucous gulls collected on Bjørnøya in 1999[6]. 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[6] and black guillemot livers and eggs from East and West Greenland in 2000[20]. 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[6]. BDE 47 dominates the congener pattern in seabirds.

Marine mammals: ΣPBDE concentrations in blubber of ringed seals from northeastern Greenland (58 ng/g lw)[6] and on Svalbard (18 ng/g lw)[17] 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)[6]. BDE209 was analyzed for but not detected in the western Canadian ringed seals[6]. Concentrations of ΣPBDE were 29-161 ng/g lw in Svalbard beluga blubber from adults collected in 1998[17] and were higher, compared to concentrations of 17 ng/g lw in beluga from the western Canadian Arctic and 1.6-3.0 ng/g lw from the eastern Canadian Arctic[6]. 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)[6], have shown rapidly increasing concentrations of these compounds. Harbor porpoises from Icelandic waters had ΣPBDE levels of 25-95 ng/g lw[21]. 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[6]. The greatest concentrations of PBDEs measured in the Arctic are those observed in Faroe Island long-finned pilot whales (82-3200 ng/g lw)[6]. 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. ΣPBDE concentrations in polar bears from Svalbard were 14-144 ng/g lw in one study[6] and 13-70 ng/g lw in a more recent study[17]. A spatial study of PBDEs included polar bears from East Greenland, six locations in the Canadian arctic (Amundsen Gulf, Lancaster Sound, Foxe Basin/Boothia Peninsula, Northeast- and Southeast Baffin Island, Western Hudson Bay), Svalbard as well as western Beaufort Sea/Chukchi/Bering Sea regions of Alaska[22]. 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)[17]. Polar bears seem to readily metabolize PBDEs so little biomagnification is seen. BDE47 dominates the congener pattern in marine mammals.

Humans: ΣPBDE level in human milk from Arctic Quebec was 6.2 ng/g lw in 1996-2000[23]. This is a three-fold increase since 1989-91.

Conclusions: ΣPBDE concentrations in all sample types except for air are one or more orders of magnitude lower than PCB concentrations. Except for air, PBDE concentrations in Arctic samples are lower than in similar sample types from more southerly regions. Lower brominated BDEs are ubiquitous in the Arctic and the presence of BDE209 in remote Arctic lake sediments indicates that even this congener is subject to long range transport. Temporal trends for PBDEs in the North American Arctic parallel those seen further south. Very little data is available for HBCD and TBBPA.

References

1. Jansson, B., Asplund, L., Olsson, M. Chemosphere, 1987, 16: 2343-2349.
2. Sellström, U., Jansson, B., Kierkegaard, A., de Wit, C., Odsjö, T., Olsson, M. Chemosphere, 1993, 26:1703-1718.
3. de Wit, C.A.. Chemosphere, 2002, 46:583-624.
4. Alaee, M., Muir, D., Cannon, C., Helm, P., Harner, T., Bidleman, T. Sources, Occurrence, Trends and Pathways in the Physical Environment, Canadian Arctic Contaminants Assessment Report II, 2003, pp. 116-124.
5. Strandberg, B., Dodder, N.G., Basu, I., Hites, R.A. Environ. Sci. Technol. 2001, 35: 1078-1083.
6. de Wit, C.A., Fisk, A.T., Hobbs, K.E., Muir, D.C.G., Gabrielsen, G.W., Kallenborn, R., Krahn, M.M., Norstrom, R.J. and Skaare, J.U. *AMAP Assessment 2002: Persistent Organic Pollutants in the Arctic*. Arctic Monitoring and Assessment Programme, Oslo, Norway, 2004 and references therein.
7. Jaward, F., Farrar, N., Harner, T., Sweetman, A.J., Jones, K.C. Environ. Sci. Technol. 2004, 38: 34-41.
8. Remberger, M., Sternbeck, J., Palm, A., Kaj, L., Strömberg, K., Brorström-Lundén, E. Chemosphere 2004, 54: 9-21.
9. Hassanin, A., Breivik, K., Meijer, S.N., Steinnes, E., Thomas, G.O., Jones, K.C. Environ. Sci. Technol. 2004, 38: 738-745.
10. Muir, D., Teixeira, C., Chigak, M., Yang, F., D'Sa, I., Cannon, C., Pacepavicius, G., Alaee, M. Organohal. Cmpds. 2003, 61: 77-80.
11. Malmquist, C., Bindler, R., Renberg, I., van Bavel, B., Karlsson, E., Anderson, N.J., Tysklind, M. Environ. Sci. Technol. 2003, 37: 4319-4324.
12. Stern, G., Evans, M. Sources, Occurrence, Trends and Pathways in the Physical Environment, Canadian Arctic Contaminants Assessment Report II, 2003, pp. 100-115.
13. Fjeld, E., Schlabach, M., Berge, J.A., Eggen, T., Snilsberg, P., Källberg, G., Rognerud, S., Enge, E.K., Borgen, A., Gundersen, H. Norsk institutt för vannforskning (NIVA), Oslo, Norway, Rapport 4809-2004 (in Norwegian).
14. Chernyak, S.M., Savinova, T.N., Dahle, S., Matishov, G.G., Hickey, J.P., Begnoche, L.J., Quintal, R.T. Levels and distribution of PBDEs in sediments from the Barents Sea and the Sea of Azov, SETAC 24th Annual Meeting, Austin, Texas, 9-13 November 2003.
15. ter Schure, A.F.H., Larsson, P., Merilä, J., Jönsson, K.I. Environ. Sci. Technol. 2002, 36: 5057-5061.
16. Vives, I., Grimalt, J.O., Lacorte, S., Guillamon, M., Barcelo, D., Rosseland, B.O. Environ. Sci. Technol. 2004, in press.
17. Wolkers, H., van Bavel, B., Derocher, A.E., Wiig, Ø., Kovacs, K.M., Lydersen, C., Lindström, G. Environ. Sci. Technol. 2004, 38: 1667-1674.
18. Herzke, D., Berger, U., Nygård, T., Vetter, W. Organohal. Cmpds. 2003, 61: 466-469.
19. Braune, B., Simon, M., Donaldson, G.M. Organohal. Cmpds. 2003, 61: 317-320.
20. Vorkamp, K., Christensen, J.H., Glasius, M., Riget, F.F. 2004. Mar. Poll. Bull. 2004, 48: 111-121.
21. Thron, K.U., Bruhn, R., McLachlan, M.S. Fresenius Environ. Bull. 2004, 13: 146-155.
22. Muir, D.C.G., Letcher, R., Fisk, A.., Backus, S., Born, E., Dietz, R., Evans, T., Gabrielsen, G., Norstrom, R., Riget, F., Sonne, C. Geographical trends of brominated diphenyl ethers in polar bear adipose tissue from the North American and European Arctic. SETAC-Europe, Prague, Czech Republic, 18-22 April 2004.
23. Pereg, D., Ryan, J.J., Ayotte, P., Muckle, G., Patry, B., Dewailly, E. Organohal. Cmpds. 2003, 61: 127-130.