Brominated Flame Retardants in the Arctic Environment – Trends and New Candidates

Cynthia A. de Wit[1], Dorte Herzke[2] and Katrin Vorkamp[3]

[1]Department of Applied Environmental Science (ITM), Stockholm University, SE-10691, Stockholm, Sweden
[2]Norwegian Institute of Air Research (NILU), N-9296, Tromsø, Norway
[3]National Environmental Research Institute (NERI), Box 358, DK-4000, Roskilde, Denmark

Introduction

In a previous review of this topic, results from studies up to mid-2005 showed that several brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs, including BDE-209), hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA) were reaching the Arctic (de Wit et al. 2006). Spatial trends of PBDEs and HBCD in top predators such as polar bears were similar to those seen for polychlorinated biphenyls (PCBs) indicating western Europe and eastern North America as source regions. Temporal trends indicated increasing concentrations of tetra-decaBDEs in several Arctic species and the tetra-hexaBDEs were found to biomagnify. The concentrations of the various BFRs were generally lower in the Arctic compared to more southerly regions and were lower than concentrations of legacy chemicals such as PCBs. The results indicated that most of these BFRs undergo long range transport to the Arctic.

The Stockholm Convention on Persistent Organic Pollutants (POPs), which went into force in May, 2004, states that chemicals may qualify as POPs if they are found far from sources and show evidence of long range transport. This has made the Arctic an important indicator region for assessing persistence and bioaccumulation properties of POPs and for identifying potential new POPs. Based on the previous review, several of the BFRs were considered to have characteristics that qualify them as POPs according to the Stockholm Convention. As part of the Arctic Monitoring and Assessment Programme's (AMAP) ongoing work with updates on POPs in the Arctic, we update the previous review of this topic and also consider new candidate BFRs that may have potential for long range transport to the Arctic (de Wit et al. 2010 and references therein). These include decabromodiphenyl ethane (DBDPE), polybrominated biphenyls (PBBs), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), hexabromobenzene (HxBBz), pentabromoethylbenzene (PBEB), pentabromotoluene (PBT), and 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECH). Unless otherwise noted, ΣPBDE denotes the sum of lower brominated congeners.

Results and discussion

PBDEs: As in the previous review, most new data for brominated compounds in the Arctic have been generated for the PBDEs, particularly the components of the PentaBDE technical product, although more data are now available also for the higher brominated BDEs including several octa- and nonaBDEs and BDE-209. The di-heptaBDEs are found in numerous abiotic (air, soil, moss, freshwater and marine sediments) and biotic matrices (zooplankton, invertebrates, fish, terrestrial birds, seabirds, terrestrial and marine mammals) from Alaska to the Barents Sea and the number of species studied has increased. There are some indications of elevated concentrations near emission sources, such as much higher PBDE concentrations in seabirds from the coast of the Gulf of Alaska, which is more populated, compared to

seabirds from the Bering Sea (Fig. 1). Higher concentrations of PBDEs are seen in some freshwater lake sediments on Svalbard as well as in Lake Ellasjøen on Bjørnøya, which may be due to inputs of seabird guano. Spatial trends of ΣPBDEs in several species sampled away from emission sources indicate that the European Arctic is more contaminated than the North American Arctic (Fig. 1), implicating similar atmospheric transport pathways for PBDEs as for organochlorines, i.e. from highly populated eastern North America and western and central Europe. Lowest ΣPBDE concentrations are generally seen in the terrestrial ecosystem, exemplified by soils, moss, moose and grouse, and highest concentrations are seen in marine seabirds and marine mammals at high trophic levels in the food web. The highest ΣPBDE concentrations are seen in Alaskan offshore killer whales (3300 ng/g lw), which are similar to what has previously been seen in long-finned pilot whales from the Faroe Islands (up to 3200 ng/g lw). Alaskan transient killer whales and northern Norwegian killer whales had somewhat lower concentrations (76-790 ng/g lw) but were still considerably higher than has been seen in other Arctic biota, including polar bears (range 40-90 ng/g lw). High PBDE concentrations were also seen in landlocked Arctic char from Lake Ellasjøen on Bjørnøya, which is due to the input of seabird guano from colonies on a nearby cliff. ΣPBDE concentrations in Arctic biota are lower than in biota from more southerly latitudes, and are generally lower than organochlorine compounds.

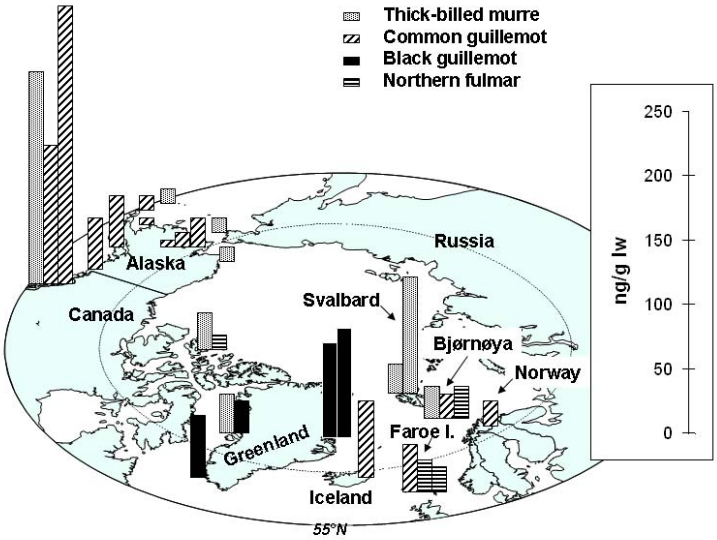

Fig. 1. ΣPBDE concentrations in eggs from common guillemot, thick-billed murre, black guillemot and northern fulmar (plasma for Bjørnøya) (ng/g lw).

Temporal trends for the lower brominated BDEs indicate continued increases (air, freshwater sediment, land-locked char, lake trout, burbot, ivory gull, West Greenland ringed seal, East Canada beluga) or a tendency to leveling off or possible declines (land-locked char, lake trout, Atlantic cod, thick-billed murres, northern fulmars, East Greenland and western Canada ringed seal, western Canada beluga),

depending on the matrix studied and the geographic location. Many of the lower brominated BDEs bioaccumulate and biomagnify, particularly BDE-47 and -153.

BDE-209 is present in high volume air samples (filters – particle bound) from the High Arctic (Bering Sea, Alert) at concentrations of 0.09-9.8 pg/m^3, as compared to ΣPBDE concentrations of 0.40-47 pg/m^3. These findings and modelling results indicate that periods of stable air conditions and high winds, such as during Arctic haze events, will lead to episodes of long range transport for particulate-bound contaminants, are strong indications that BDE-209 undergoes long-range transport to the Arctic. This is further supported by the findings of BDE-209 as the predominant BDE congener in soils and mosses, probably due to deposition, as well as its presence in biotic samples, including a number of higher trophic level organisms such as glaucous gulls, ringed seals and polar bears. Although it is found in high trophic level biota, BDE-209 appears to undergo trophic dilution instead of accumulation in the marine food web, leading to decreasing concentrations at higher trophic levels. There is an increasing temporal trend in air samples from Alert, Canada. Otherwise, there are no new studies presenting spatial or temporal trends for BDE-209 and therefore such studies should be undertaken.

HBCD: Considerably more data have been generated for the Arctic since the previous review, including more isomer-specific data. HBCD has been found in high volume air samples, freshwater sediments, freshwater fish, marine sediments, zooplankton, marine invertebrates, marine fish, seabirds, ringed seals, beluga, minke whale, long-finned pilot whale and polar bears. Where isomer-specific analysis was done, γ-HBCD was the predominant isomer in air, α-HBCD predominates in biota, and for marine sediments, similar concentrations of α-, β- and γ-HBCD were found. As for PBDEs, it is now clear that HBCD is ubiquitous in the Arctic, undergoes long range atmospheric transport, bioaccumulates and the α-isomer biomagnifies, whereas the γ-isomer undergoes trophic dilution. Very few temporal trends are available, and indicate no change (eastern and western Canadian beluga, Canadian burbot, Brünnich's guillemot from Svalbard and Bjørnøya) or possibly increasing concentrations (ivory gull, northern fulmars and ringed seals from Canada) of HBCD with time, but more data are needed before any conclusive statements can be made. Spatial trends seem to indicate a similar pattern as for organochlorines and for PBDEs, with higher concentrations in the European Arctic.

TBBPA: TBBPA was screened for in marine sediments in one study, and TBBPA and methyl-TBBPA were screened for in shorthorn sculpin, several seabird and marine mammal species in another study but these were below detection limits in all sample types. No other studies included the analysis of TBBPA or Me-TBBPA. TBBPA is a high volume chemical and in the previous review, some studies did show its presence in moss, marine sediments, fish liver and Norwegian peregrine falcon and golden eagle eggs and Me-TBBPA was found in Greenland peregrine falcon eggs. More data are needed to understand possible long-range transport of TBBPA to the Arctic, how prevalent it is in Arctic abiotic and biotic samples, and if there are temporal and spatial trends.

PBBs: PBBs were only included in a few studies. BB-153 was found in air samples from Svalbard, land-locked Arctic char and northern fulmars from Bjørnøya, northern fulmars from the Faroe Islands and polar bears from Canada and BB-101 was found in glaucous gulls from Svalbard and ivory gulls from Canada. In the GC-MS analysis, BB-153 often co-elutes with BDE-154, which may mask the presence of BB-153,

as was seen in studies of ivory gull and Arctic fox. Thus, BB-153 may be more prevalent in the Arctic, but methods to separate it from the BDEs are needed to confirm this.

Other BFRs: A range of new BFRs have been screened for and in many cases detected in Arctic biota including BTBPE, DBDPE, HxBBz, PBEB, PBT and TBECH. BTBPE was detected in northern fulmars (Faroe Islands), glaucous gulls (Bjørnøya), beluga (Canada), and ringed seals (Canada). HxBBz, PBEB and PBT were detected in glaucous gulls (Bjørnøya) and HxBBz was detected in East Greenland polar bears. TBECH was detected in beluga (Canada). DBDPE was analyzed for but not detected in ringed seals from Canada. The results for these new BFRs indicate that several are reaching the Arctic and can accumulate in higher trophic level organisms. As many of these are being used as replacements for PBDEs that have been banned or discontinued, their presence in the Arctic is a warning sign that these compounds may also undergo long-range atmospheric transport, are potentially bioaccumulative and that increasing use will lead to increasing concentrations in the environment with time. There is thus a need to increase our knowledge of the prevalence of these compounds in Arctic abiotic and biotic samples, spatial and temporal trends and confirmation from air sampling that they are undergoing long-range transport.

Conclusions

Studies published since mid-2005 have contributed substantial additional information on current 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 air, soil and in lake sediments and a variety of organisms including polar bear, illustrates that even very non-volatile chemicals can reach the Arctic and accumulate. Overall, concentrations of BFRs measured to date have been low compared with legacy organochlorines. However, the number of BFRs determined has been rather limited compared to the number in commerce. There are a number of semi-volatile BFRs including but not limited to tetra-hexaBDE, HBCD, TBECH, (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. Recently, Brown and Wania (2008) have used an extensive screening method specifically designed to select chemicals with high likelihood of becoming Arctic contaminants. The method combines models predicting long-range atmospheric transport, accumulation in Arctic marine food webs and bioaccumulation in humans. Besides the PBDEs, they identify a number of brominated flame retardants that would be good candidates for further screening in Arctic samples. The fact that a wide range of BFRs are now being detected in the Arctic illustrates the need for more information on these compounds and others predicted to reach the Arctic.

Acknowledgements

The authors wish to thank the community councils and Hunters and Trappers Organizations in many circumpolar regions e.g. Alaska, Canada, Greenland, Scandinavia, and Russia. Their cooperation and active participation in the collection of biological samples made much of this work possible.

References

Brown TN, Wania F. 2008 Environ Sci Technol 42: 5202-5209.
de Wit CA, Alaee M, Muir DCG. 2006. Chemosphere 64: 209-233.
de Wit CA, Herzke D, Vorkamp K. 2010. Sci Tot Environ, ASAP.
Muir DCG, Howard PH. 2006. Environ Sci Technol 40: 7157-7166.