DISPERSION OF POLYBROMINATED DIPHENYL ETHER AND HEXABROMOCYCLODODECANE FLAME RETARDANTS IN THE POLAR BEAR FOOD CHAIN IN SVALBARD, NORWAY

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Introduction

Due to their environmental stability, persistence and high production volume, polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) are among the most abundant brominated flame retardants (BFRs) detected in the environment and wildlife and human tissues.[1,2] Three PBDE technical products have been used commercially; penta-, octa and deca-BDE technical mixtures. Currently, there are no laws prohibiting the use of PBDEs in Asia and the USA, but the European Union banned the use of penta- and octa-BDEs commencing in 2004. Deca-BDE, consisting mostly of BDE-209, is thought to be less threatening to the environment because of the larger molecular size of this congener is assumed to limit its global transport potential and its bioavailability over biological membranes[2]. There are currently no restrictions on the use of technical deca-BDE products or HBCD.

Bioaccumulation and biomagnification potentials of persistent organic pollutants have conclusively been linked to the lipophilicity of the various compounds. Highly lipophilic or hydrophobic compounds such as PBDEs and HBCD tend to adhere into particles in the water column, or to sediments, and are bioavailable to aquatic organism trough dietary intake of particulate matter, phytoplankton, prey or detritus.[3] There are few local sources of POPs, such as BFRs, polychlorinated biphenyls (PCB) and organochlorine pesticides in the Arctic, and the dominant route for these chemicals in the region is believed to be long-range transport by the atmosphere, ocean currents, river inputs and sea-ice-drift. There are numerous reports on organochlorine uptake and biomagnification in arctic biota, but at present there are few studies of transport and biomagnification of BFRs in arctic ecosystems. The main aim of the present study was to investigate food web transfer of PBDE and HBCD flame retardants in the marine ecosystem around Svalbard, Norway, with samples ranging across the trophic web from pelagic zooplankton to polar bears. These data have also been presented elsewhere.[4]

Material and Methods

Sample collection: Samples were collected during 2002 and 2003 as describe in Sørmo et al.[4] Lower trophic sampling of the marine food web included four invertebrate groups: herbivorous pelagic calanoid copepods (predominately *Calanus glacialis*) and the herbivorous pelagic krill *Thysanoessa inermis* both grazing on phytoplankton; the omnivorous pelagic amphipod *Themisto libellula*), and the ice-associated omnivorous amphipod *Gammarus wilkitzkii*. Both amphipods include calanoid copepods in their diet. Higher trophic sampling included polar cod (*Boreogadus saida*) (*n*=7) that feeds predominately on pelagic-, but also sympagic (= ice associated) invertebrates, adult male ringed seals (*n*=6) (*Pusa hispida*) that feeds predominately on polar cod, but also consumes pelagic and sympagic invertebrates, and the polar bear (*Ursus maritimus*) (n=4) which is the apex predator of the marine food chain of the Arctic, predominately preying on ringed seals, but also other seal species. Invertebrates, polar cod and ringed seals were sampled north of 78°N.

Brominated flame retardant and statistical analyses: Levels of BFRs were analysed according to methods described previously.[4] The invertebrate data are represented by one observation for each species, which is the mean value of two replicates for pelagic invertebrates and five replicates for the sympagic *G. wilkitzkii*. One observation from each species did not allow for statistical analyses between invertebrate species. Pelagic zooplankton or invertebrates (i.e., calanoid copepods, *T. inermis* and *T. libellula*) were therefore merged into one group and compared to higher trophic levels (Table 1). Data are presented as whole body concentrations (ng g^{-1})

as these gave the more realistic dispersion and biomagnification potentials of BFRs compared to lipid based concentrations which were biased by the large variability in lipid content of the investigated species.[4]

Results and Discussion

BDE-47 and -99 were detected in all four species of invertebrates (Table 1). BDE-100 was also observed in both pelagic- (*T. libellula*) and sympagic- (*G. wilkitzkii*) amphipods. Levels of these PBDEs were ~10 times higher in sympagic compared to pelagic invertebrates. In invertebrates, BDE-209 was only analysed in *G. wilkitzkii*, where it was found to be the most abundant compounds, constituting about 50% of the total PBDE load. The high PBDE levels (particularly of deca-BDE) in the ice-amphipod which permanently inhabit the subsurface of the Arctic sea ice may relate to that PBDEs concentrate in sea-ice as shown in Antarctica[5], thereby possible being particularly bioavailable to the sympagic organisms.

Table 1

Mean (*standard deviation*) whole body concentration (ng g^{-1}) in pelagic and sympagic (=ice associated) invertebrates, polar cod (*n*=7), ringed seals (*n*=6) and polar bears (*n*=4) in Svalbard, Norway. Unequal letters indicate significant differences ($p<0.05$) in contaminant concentrations between pelagic invertebrates (as a group of three species), polar cod, ringed seals and polar bears. Data from Sørmo et al.[4]

	BDE-28	-47	-99	-100	-153	-154	-209	ΣPBDEs	ΣHBCD
Pelagic invertebrates									
Calanoid copepods	n.d	0.008	0.008	n.d	n.a	n.a	n.a	0.016	n.a
Thysanoessa inermis	n.d	0.018	0.011	n.d	n.a	n.a	n.a	0.032	n.a
Themisto libellula	n.d	0.030	0.010	0.005	n.a	n.a	n.a	0.045	n.a
Mean	n.a	0.019^{A}	0.010^{A}	n.a	n.a	n.a	n.a	0.031^{A}	n.a
Sympagic invertebrates									
Gammarus wilkitzkii	n.d	0.091	0.152	0.034	n.a	0.010	0.278	0.565	n.d
Vertebrates									
Polar cod	0.008	0.072^{B}	0.013^{A}	0.014^{A}	n.a	0.008^{A}	0.021^{A}	0.130^{B}	0.151^{A}
	(*0.001*)	(*0.02*)	(*0.012*)	(*0.007*)		(*0.004*)	(*0.01*)	(*0.05*)	(*0.03*)
Ringed seals	0.355	14.10^{C}	0.667^{B}	1.338^{B}	0.195^{A}	0.195^{B}	0.006*	16.88^{C}	5.544^{B}
	(*0.23*)	(*4.24*)	(*0.41*)	(*0.73*)	(*0.09*)	(*0.128*)		(*5.72*)	(*1.99*)
Polar bears	0.047	5.593^{D}	0.197^{C}	0.312^{C}	1.307^{B}	0.042^{C}	0.022^{B}	7.501^{D}	2.883^{C}
	(*0.02*)	(*1.84*)	(*0.06*)	(*0.14*)	(*0.68*)	(*0.01*)	(*0.01*)^{A}	(*2.59*)	(*1.32*)

* =BDE-209 only detected in one ringed seal

A greater range of BFRs (i.e., BDE-28, -47, -99, -100, -154, and 209 and HBCD) were analysed and detected in the polar cod samples (Table 1). Levels of BDE-47 were 3-4 times higher in polar cod than in its pelagic invertebrate prey (*p*=0.017), but there were no statistical difference between pelagic invertebrates and polar cod for BDE-99 (Table 1). Lack of trophic increase of BDE-99 from zooplankton to their fish predator is consistent with findings of lower assimilation of BDE-99 compared to BDE-47 in other teleosts experimentally exposed to PBDEs[6], probably as a consequence of intestinal or tissue debromination of BDE-99 to BDE-47 or other compounds. Levels of BDE-209 were 10 times higher in the ice-amphipod compared to polar cod. Unfortunately in this study, BDE-209 was not analysed in the key pelagic prey species (calanoid copepods, krill and *T. libellula*) of the polar cod. Thus, the presence of deca-BDE (accounting for ~10% of the total PBDE load in polar cod) may present novel uptake at the level of this species or alternately deca-BDE may bioaccumulate from sympagic prey such as *G. wilkitzkii*. This as polar cod at Svalbard also feed on sympagic macrofauna typically constituting up to 25% their diet. It should however be noted that since the samples of the invertebrates and fish were homogenates of whole organisms, BDE-209 could be located within their digestive system or even stuck onto their body surfaces and thus not subject to real uptake. Moreover, the lack of biomagnification of BDE-209 in polar cod may also relate to that deca-BDE are readily debrominated to lower brominated congeners in teleosts.[7]

In contrast to the ice-amphipod where BDE-209 dominated, BDE-47 accounted for ~55% of the total PBDE load in the polar cod. This great difference in PBDE profiles may relate to that profiles of POPs in surface water, either dissolved in water phases or absorbed to phytoplankton reflect those found in gas-phases in the above air.[8] Most PBDEs are transported both in gas- and in particulate phases the atmosphere, and although temperature dependent, BDE-47 and -99 are essentially the dominating PBDEs in gas-phase in air.[9] This may explain the greater relative importance of lower brominated BDE congeners in the pelagic community (pelagic zooplankton and polar cod). In contrast, although BDE-209 is by far the dominant PBDE congener in air, its atmospheric transport differs from lower brominated congeners by being predominately particle-controlled.[9,10] This suggests that atmospheric particle deposition onto the sea-ice may be the main source for contamination of PBDEs to the sympagic ecosystem (e.g., *G. wilkitzkii*) of the Arctic.

In the ringed seal, the biomagnification of BDE-47 from polar cod to ringed seal was ~200 times, whereas concentrations of BDE-28, -99, -100, 154 and HBCD showed more modest 20 to 85 times biomagnification from polar cod. BDE-209 showed no biomagnification in the seals, and was also only detected in one seal. Thus, in contrast to the modest biomagnification of BFRs in the lower parts of the Arctic marine food web (from invertebrates to fish), there was a more than two orders of magnitude biomagnification of many BFRs from pelagic zooplankton and polar cod to the ringed seal (Table 1). This is consistent with the much greater energetic demand and food intake of homeotherms (mammals) compared to poikilotherms (zooplankton and fish), predicting that the steps in the marine food chain with highest biomagnification should be where homeotherms eat poikilotherms or other homeotherms. However, despite the 1-2 orders of magnitude higher loads of most BFRs in the diet of the polar bear (ringed seals) compared to the diet of ringed seals (zooplankton and polar cod), most BFRs were found in lower concentrations in the polar bear as compared to its seal prey (Table 1). This suggests a marked difference in biotransformation and biodegradation rates of BFRs in these two mammalian species. This is in accordance with previous findings of higher oxidative biotransformation and biodegradation capacities for other POPs such as PCBs in polar bears compared to seals. This difference may relate to species-specific traits or it may be the result of enhanced induction of detoxifying enzymes in the polar bear due to their much higher exposure to POPs. Moreover, the apparently high biotransformation rate of BFRs in polar bears raises concern about syntheses of potentially toxic BFR metabolites in this species.[11] BDE-153 was the only BFR observed to biomagnify from ringed seal to polar bears (Table 1) indicating that this congener, relative to other BFRs might be more resistant to biotransformation. Thus, the most bioaccumulative PBDEs seem to be those that have halogen substation pattern similar to the most bioaccumulative PCBs (e.g., PCB 153), at least when oxidative detoxifying processes are highly involved for the fate and degradation of these compounds in the organisms.

Reports on HBCD in marine ecosystems are scarce. The finding of no biomagnification from ringed seals to polar bears, indicate that HBCD like most of the investigated PBDEs are biodegradable in the polar bears (Table 1). However, the substantial biomagnification of HBCD from polar cod to ringed seal indicates its high bioaccumulation potential in other species, emphasizing that there might be cause of concern and need of risk assessment studies at the ecosystem level. For instance, complementary studies are needed to assess the bioaccumulative potential of the different HBCD diastereomers at various trophic levels of the polar bear food chain. Our ongoing studies seem to indicate that α-HBCD was the most abundant of the HBCD diastereomers in the higher trophic levels of the polar food chain. To conclude, this study demonstrates that PBDEs and HBCD have reached measurable concentrations even in the lower trophic levels (invertebrates and fish) in the Arctic and that they generally are biomagnified in the polar food chain. Deca-BDE was particularly abundant in the sympagic section of the food web.

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References

1. Alaee M, Arias P, Sjödin A, Bergman Å. *Environ Int* 2003;29:683-689.
2. de Wit CA. *Chemosphere* 2002;46:583-624.
3. Borgå K, Fisk AT, Hoekstra PF, Muir DGC. *Environ Toxicol Chem* 2004;23:2367-2385.
4. Sørmo EG, Salmer MP, Jenssen BM, Hop H, Bæk K, Kovacs KM, Lydersen C, Falk-Petersen S, Gabrielsen GW, Lie E, Skaare JU. *Environ Toxicol Chem* 2006;25: *in press*.
5. Dickhut R, Cincinelli A, Cochran M, Geisz H, Ducklow H. Transport and Fate of Persistent Organic Pollutants (POPs) in Antarctic Coastal Seas (Abstract). SETAC 26th Annual meeting in North America, Baltimore, Maryland, USA, 13-17 November 2005.
6. Stapleton HM, Letcher RJ, Li J, Baker JE. *Environ Toxicol Chem* 2004;23:1939-1946.
7. Stapleton HM, Alaee M, Letcher RJ, Baker JE. *Environ Sci Technol* 2004;38:112-119.
8. Dachs J, Eisenreich SJ, Hoff RM. *Environ Sci Technol* 2000;34:1095-1102.
9. Chen L-G, Mai B-X, Bi X-M, Chen S-J, Wang X-M, Ran Y, Luo X-J, Sheng G-Y, Fu J-M, Zeng EY. *Environ Sci Technol* 2006;40:1190-1196.
10. ter Schure AFH, Larsson P, Agrell C, Boon JP. *Environ Sci Technol* 2004;38:1282-1287.
11. Verreault, Gabrielsen GW, Shaogang C, Muir DCG, Andersen M, Hamaed A, Letcher J. *Environ Sci Technol* 2005; 29:6021-6028.