HEXABROMOCYCLODODECANE (HBCD) IN TWO MARINE FOOD WEBS FROM NORWAY.

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Introduction

Due to their environmental stability, persistence and high production volume 1,2,5,6,9,10-hexabromocyclododecan (HBCD) and polybrominated diphenyl ethers (PBDEs) are among the most abundant brominated flame retardants (BFRs) detected in the environment, wildlife and human tissue[1]. Over the last decades there has been an increasing interest in the determination of BFRs and especially the PBDEs. The use of pent- and octa-BDEs in all applications for the EU market is banned during this period. The demand for replacement BFRs, e.g. HBCD, has seen an increase. More recently HBCD has gained attention in the field of environmental monitoring[2]. The commercial product HBCD consist of three (α, β, and γ) isomers. Although γ-HBCD is the most dominant enantiomer in technical mixtures and sediments, α- HBCD is the primary congener detected in biota samples[2,3]. In the present study, we aim to examine the biomagnification and isomer pattern of HBCD in two food webs from Norway.

Material and Methods

All organisms sampled in the outer Oslofjord (Hvaler and Torbjørnskjær archipelago in south-eastern Norway) were collected during spring and/or summer 2003 and 2004. Plankton net, shovel fine-meshed beach seine, fishing rods and rifle was used to collect the samples. The polychaeta lugworm was held in a tank of seawater for 24 hrs to empty their intestine. Samples from Svalbard were collected during 2002-2003 as described in Sørmo et al. 2006[4]. For invertebrates and fish samples entire animals were stored. Blubber samples were collected from seals. All samples were kept frozen at -20° prior to analysis.

The HBCD are determined in different species from Svalbard and outer Oslofjord. From the outer Oslofjord polychaete lugworm (*Arenicola marina*), calanoid copepods (*Calanus spp*), glass shrimps (*Palaemon adspersus/P.elegans*), northern shrimp (*Pandalus borealis*), black goby (*Gobius niger*), sandeel (*Ammodytes spp*.), sand goby (*Pomatoschitus microps/P. minutus*), saithe (*Pollachius virens*), whiting (*Merlangus merlangus*), Atlantic cod (*Gadus morhua*) and harbour seals (*Phoca vitulina*) are analysed. From Svalbard we have analysed ice-amphipod (*Gammarus wilkitzkii*) polar cod (*Boreogadus saida*), ringed seal (*Phoca hispida)* and polar bear (*Ursus maritimus*).

For the polar bear, the seals and the Atlantic cod the fat, blubber and liver were analysed respectively. For the rest of the species the whole animals were homogenised and analysed. The bear, seal and cod were analysed individually while the rest of the species were analyzed by pools. The number of samples from each specie varied from 2-16.

Samples preparation and chemical analyses of HBCD were done in the Laboratory of Environmental Toxicology at the Norwegian School of Veterinary Science. The laboratory is accredited by Norwegian Accreditation for testing BFRs in biological material of animal origin according to the requirements of the NS-EN ISO/IEC 17025 (TEST 051). The method for total HBCD determination includes liquid extraction, clean up with sulphuric acid and GC-MS analysis and is further described in Sørmo et al. 2006[4]. For determination of α-, β- and γ-HBCD, the extracts were analysed using an API 3000 LC-MS-MS system (triple quadrupole) (Applied Biosystem, USA) connected to a C18 column (15 cm x 2.1 mm, 5 µm) (Supelco). As mobile phases Amoniumacetate in water (A) and Amoniumacetate in 99% acetonitrile and 1% water (B) were used with a flow of 0.2 ml/min and gradients of

70 % B to 100 % B in 10 min, hold 5 min at 100 %B. The detection was performed by MRM (multiple reaction monitoring) and the mass transition ion-pair was selected as m/z 640.7-m/z 80.8.

Results and Discussion

Our main results are that HBCD increase through two marine food webs from outer Oslofjord and Svalbard (Figure 1 and 2), thus showing high potential for biomagnification. In addition we found that α-HBCD dominate the isomer pattern (Figure 3). This is in line with results found in other studies[1,5].

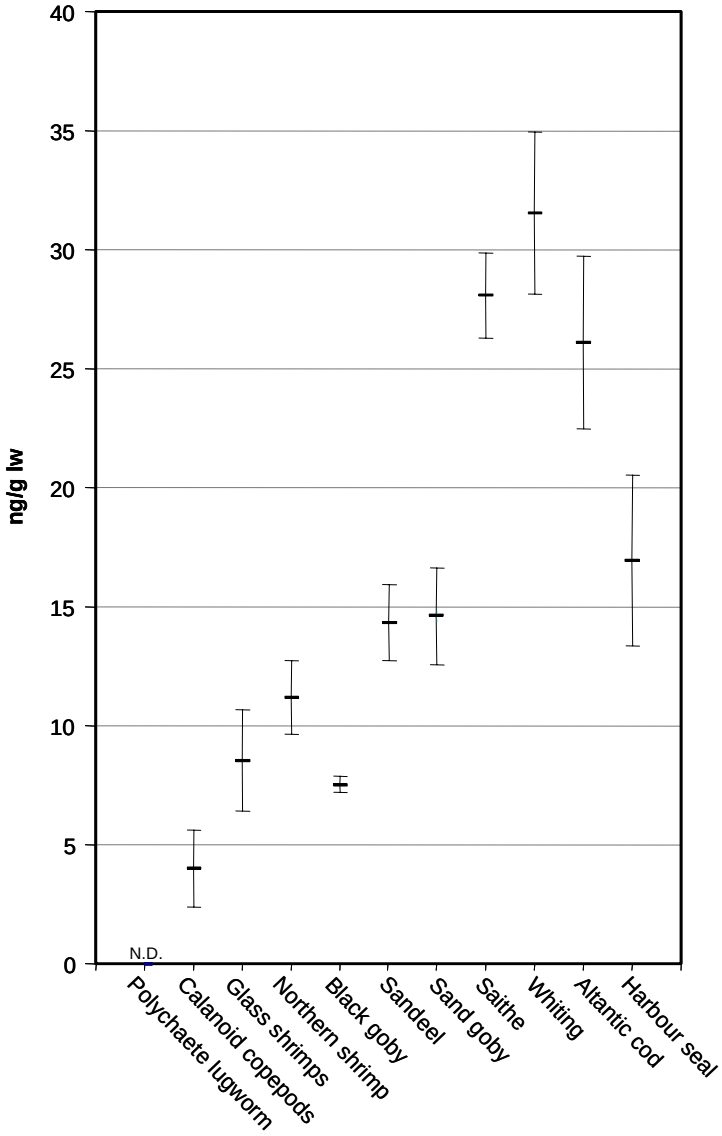


Figure 1. Mean (std. error) lipid weight concentrations (ng/g lw) of HBCD in different species from outer Oslofjord, Norway. N.D = not detected.

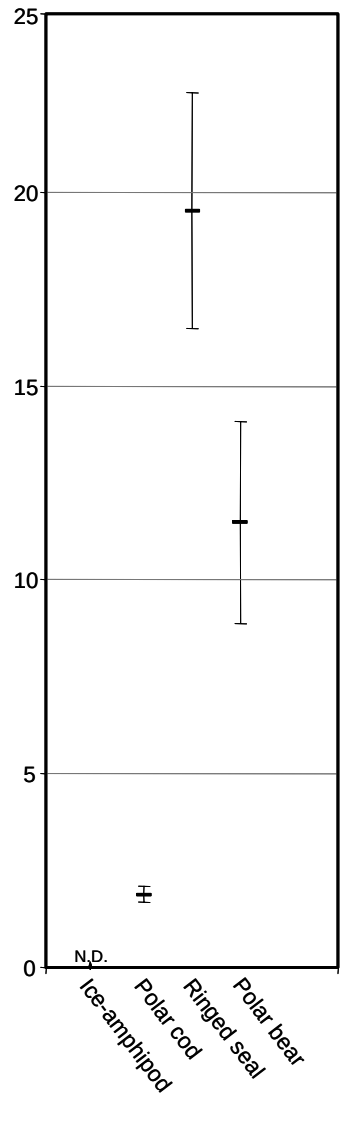
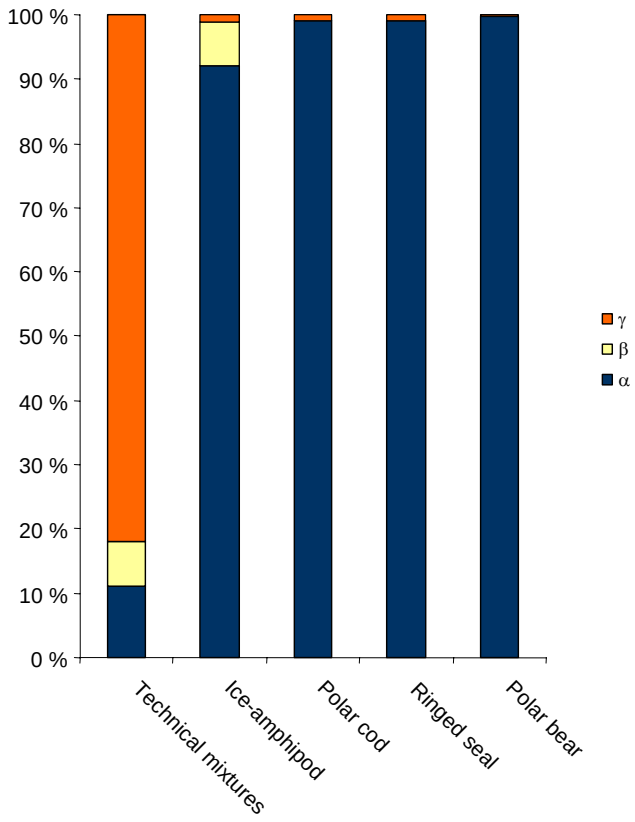


Figure 2. Mean (std. error) lipid weight concentrations (ng/g lw) of HBCD in different species from Svalbard, Norway[4]. N.D = not detected.

All species sampled from outer Oslofjord (Figure 1) are presented with expected increasing trophic levels from lugworm to harbour seal[6]. Due to large diversity and complexity of the North Sea food web, the study will not present the complete picture of exposure to and bioaccumulation of HBCD. However, our results cover some of the main pelagic and benthic links in the food web. We see that the levels increases from invertebrates to small fish and further to piscivorous fish (saithe and whitting), but there was seen no biomagnification in harbour seals. The relative low levels of HBCD in the harbour seals compared to saithe, whiting and Atlantic cod can mainly bee explained by the fact that three of the four seals where young (< 2 years) and lower levels have to be expected. Additionally reasons will be discussed elsewhere[6].

The results from Svalbard (Figure 2) have been presented and discussed elsewhere[4]. The main findings were that HBCD biomagnifies in the food chain up to ringed seal. However, we found no biomagnifications from ringed seal to polar bear. This result indicates that HBCD are biodegradable in the polar bears. The same has also been observed for PBDEs[4]. Total HBCD for the ice-amphipod is not detected in the GC-MS analysis, but due to a lover detection limit in the LC-MS system, it was possible to determinate the isomers.

The spatial trends show that the highest levels are found at outer Oslofjord compared to Svalbard. We can see that the polar cod at Svalbard only contains 10% of the levels found in the Atlantic cod in the outer Oslofjord. However the difference between the sites is smaller compared to the PBDE levels[7].



Figur 3. The contribution of the different diastereomers of HBCD in a technical mixture and in the different species analyzed at Svalbard.

The α-, β-, and γ- isomers of HBCD were determined in samples of ice-amphipod, polar cod, seal and bears. α-HBCD was the dominating isomers in all species (more than 90%), whereas γ-HBCD dominates in the technical mixtures. We can observe a trend that the α-isomer is more dominating in the top-predator (polar bear) compared to a lower level (ice amphipod) in the food chain. The results are in line with other studies[2,3,5].

This project also includes the analysis of the HBCD isomers in species from the outer Oslofjord, but the results are not finished at this point.

In conclusion, we have found that HBCD biomagnify in different food chains and that α-HBCD is the dominating isomer in all the species studied. Due to low sample size, different biological matrices, and the reports of increased levels of HBCD the last decades[5] there is a need for further research on HCBD in environmental samples.

Acknowledgements
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