LEVELS OF SOME POLYBROMINATED DIPHENYL ETHER (PBDE) FLAME-RETARDANTS IN ANIMALS OF DIFFERENT TROPHIC LEVELS OF THE NORTH SEA FOOD WEB

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Introduction

Many plastics in household equipment, car interiors and textiles contain brominated flame-retardants for fire safety reasons. The most frequently used PBDE mixture (30,000 tons in 1992) is currently decabromodiphenylether (deca-BDE); other PBDE flame-retardants are pentabromodiphenyl ether (penta-mix; e.g. Bromkal 70-5DE), and octabromodiphenyl ether (Octa-mix). The main use of the penta-mix is flame-retarded flexible polyurethane foam.
Like related organochlorines, the PBDEs are very hydrophobic ($\log K_{ow}$ values 4-10) and resistant to degradation[1]. The water solubility and vapour pressure of the PBDEs decrease with increasing degree of bromination. Thus, these parameters have the lowest values for BDE209.
Three components of the penta-mix, i.e. the BDE congeners 47, 99 and 153 (numbering according to the IUPAC nomenclature for PCBs) showed even higher bioaccumulation factors as the comparably chlorinated PCBs in blue mussels, despite their larger molecular size[1]. These congeners, and BDE100, are also widespread in biota [2-5]. The presence of tetra, penta- and hexa-brominated diphenylether congeners in deep-sea foraging animals as sperm whales indicates that these PBDEs can be regarded as globally occurring chemicals[6].
Measurements of the levels of anthropogenic compounds in biota are often used for identifying geographical and temporal trends, and to obtain information about the availability of such compounds to humans. Because of their possible environmental spread, the inclusion of certain PBDE congeners in monitoring programmes is appropriate. The present study focussed on their determination in a number of animal species from the North Sea representing different trophic levels of the food web. Since the production figures of especially penta-mixtures are momentarily decreasing, whereas that of deca-BDE remains similar, the bioaccumulation potential of the fully brominated congener BDE209 (> 97% of deca-BDE) is of special interest.

Methods and materials

Invertebrates and fish: The majority of the samples were taken during a cruise with the RV Pelagia in August-September 1999. The herring samples were caught at 51°34' N and 2°47' E by the fishing vessel TX 37. The following tissues were analysed: starfish: pyloric caeca; hermit crab: abdomen; whelk: whole body except the shell; fish: liver and filet. All samples were pooled from 5 individuals, no differentiation was made between the sexes. The levels of the PBDEs are expressed on the basis of extractable lipids[7,8].
Marine mammals: Samples of blubber and liver were analysed. The cetacean samples were obtained from Dr. Chris Smeenk. The samples of harbour seals were obtained from Dr. Ursula

Siebert and originated from Wadden Sea area of Schleswig-Holstein (Germany). All samples came from beach-stranded animals, or animals drowned in fishing nets.

Extraction: Tissue amounts corresponding to approximately 50 mg lipid were extracted, using an ultra-Turrax method. After extraction with pentane and acetone, the sample was treated with sulphuric acid and a silica clean-up was performed.

Analysis: The levels of 15 individual PBDEs were determined by GC/MS. The GC was a Hewlett Packard 6890; the mass-selective detector a Hewlett Packard 5973. GC specifications: split-splitless injection, split valve closed for 1.5 min. $T_{injector}$ 270°C. Column: stationary phase CP Sil-8, 25 m * 0.25 mm * 0.25 µm (Chrompack, NL). Carrier gas He; linear gas velocity 74 cm s^{-1}, constant flow programmed. Oven temperature program: 90°C (1.5') / 20°C min^{-1} / 190°C (0') / 4.5°C min^{-1} / 270°C (5') / 10°C min^{-1} / 320°C (10'). MSD specifications: negative chemical ionisation (NCI) in the SIM mode at the m/z ratios of both bromine isotopes (79 and 81) and m/z=487 (for BDE 209 only). Ionisation gas CH_4. $T_{ion\ source}$ 210°C; $T_{transferline}$ 320°C; $T_{quadrupole}$ 160°C.

Results and discussion

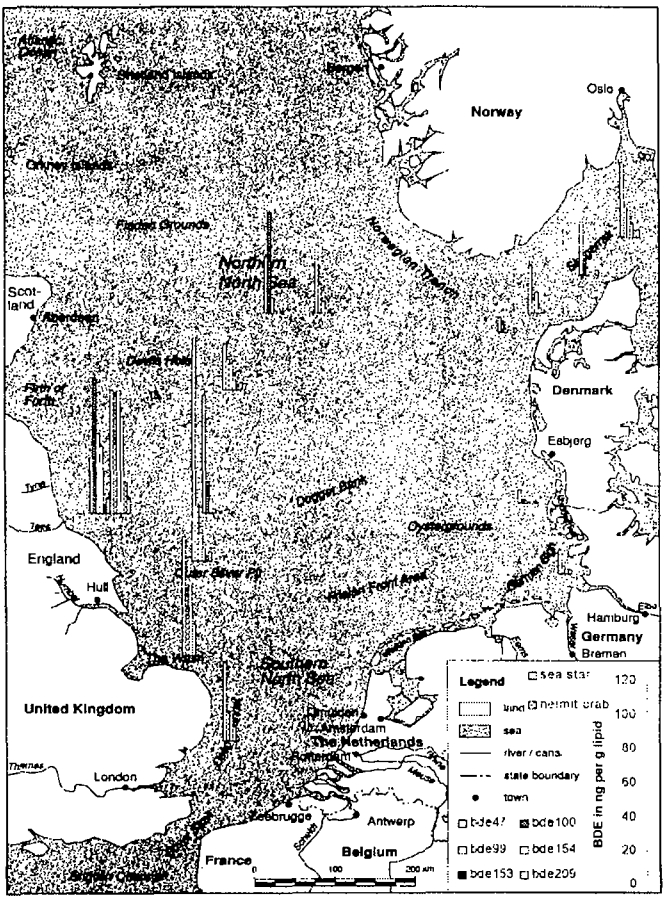

Figure 1. *The concentrations of BDE congeners in starfish and hermit crabs from the North Sea.*

The results for starfish, *Asterias rubens,* and the hermit crab, *Pagurus bernhardus,* are shown in fig. 1. In general the geographical trend is highly similar in both species, the concentrations of BDEs in the abdomens of hermit crabs being slightly above those in the pyloric caeca of sea stars. BDE47 is usually present in the highest concentrations, followed by the penta-BDEs 99 and 100, and the hexa-BDEs 153 and 154. The other congeners determined were below limit of detection. BDE209 was sometimes present just above the detection limit. However, when the samples contain parts of the digestive system, the presence of BDE209 above the detection limit cannot be interpreted as unambiguous proof for uptake by the organism. Instead, these levels may represent remainders of food present in the digestive system. Other studies have confirmed that the bioaccumulative properties of BDE209 are much lower than those of the dominant congeners of the penta-mix[9]; some studies have reported a complete lack of proof of uptake from river sediment[1], whereas others have reported a low, but measurable uptake efficiency[10].

The highest levels of PBDEs in these invertebrates occurred near the English coast, especially at the latitude of the estuaries of the rivers Tyne and Tees, but also further south. Low levels of PBDEs were found along the coasts of continental Europe, showing that the major rivers there (Rhine, Meuse, Elbe) do not appear to be major sources for the North Sea ecosystem. In the Skagerrak, the levels seem to increase from west to east, representing an increase influence of the Baltic, which is known to contain elevated levels of PBDEs[11; 12]. Since these invertebrates do not migrate over large distances, they are more representative for the site of capture than fish and marine mammals.

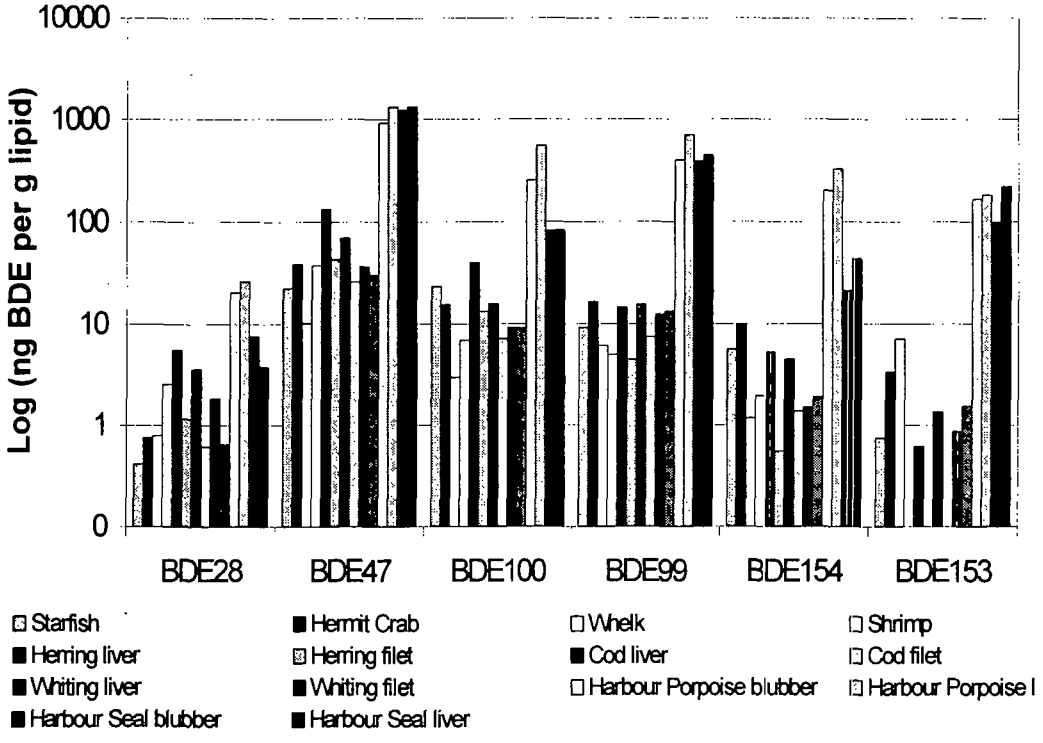

Figure 2. Amount of BDE in all biota measured.

The levels in fish are measured in liver and filet. The geographical trends in concentrations do not correspond with the trends in the invertebrates. The levels in whiting varied from 20 to 200 ng per g lipid. (ΣBDEs). This variation is larger than for cod, where only one station was twice as high as the others. The major biomagnification step in the food-chain occurred from fish to marine mammals; the levels in blubber and liver were an order of magnitude higher. The concentrations of ΣBDE in most porpoises is around 1500 ng per g lipid, but there are two exceptions: a foetus with very low levels and an immature female with a total level of about 10 μg per g lipid in her liver. Two harbour seals showed rather high levels of about 4 and 10 μg BDE per g lipid; the other animals showed levels of about 750 ng.

The general order of importance of the different congeners is BDE 47> BDE99, BDE100 > BDE 153, BDE 154. In fish and most of the marine mammals the concentrations for BDE209 are below detection limits, only in the immature female porpoise mentioned above low levels of BDE209 were detected. In the invertebrates, the amount of BDE 47 is generally less than 50 percent of ΣBDE except for the shrimps, whereas in fish it is always higher than 50 percent. In the harbour porpoise the level for BDE 47 is less than 50 percent and for the harbour seal it is higher than 50 percent. In the starfish BDE 100 is higher than BDE47 and BDE99. In contrast, BDE100 is remarkably low in the harbour seal tissues; this might indicate the occurrence of a low biotransformation capacity.

Acknowledgement:

We wish to express our gratitude to the crew of the R.V. Pelagia and the cruise-leader Dr. C.C. ten Hallers-Tjabbes for allowing us to take samples for this project during a cruise organised for the EU-LIFE project 'Harmfull impact of TBT communicated' (HIC-TBT). This project was financed by the Bromine Science and Environmental Forum (BSEF, Brussels, Belgium). This is NIOZ publ. No. 3592.

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