Species-specific accumulation and biotransformation of polybrominated diphenyl ethers and hexabromocyclododecane in two Dutch food chains

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Introduction

The European project FIRE is a multi- and interdisciplinary project that focus on the improvement of risk assessment of brominated flame retardants (BFRs) for human health and wildlife. BFRs, such as the high production volume chemicals polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol-A (TBBPA) and hexabromocyclododecane (HBCD) have been identified as potential endocrine disrupters. One of the main aims of the FIRE project is to identify and characterize the presence of the major BFRs (PBDEs, TBBPA and HBCD) in abiotic and biotic samples from the EU environment, and to determine the food chain transfer of BFRs from water, sediment to invertebrates to predators (fish) and fish-eating top-predators (tern, harbour seals, and polar bear). This paper focuses on the transfer of PBDEs and HBCD in two food chains (common tern and harbour seal) from the Dutch marine environment.

Materials and methods

Sample collection and preparation

Samples of sediment, suspended particulate matter (SPM), invertebrates (e.g. bivalves, shrimps, worms), and fish (e.g. sandeel, flounder, sole, goby, herring, whiting) were collected in the spring of 2003 in the feeding habitats of the tern (Western Scheldt estuary) and seals (Wadden Sea). Tern eggs were collected, in the same period, from the Terneuzen colony. Blubber samples of adult male harbour seals were collected from stranded animals from the Wadden Sea population. The invertebrates were placed, after collection, for one day in surface water to remove most of the sediment particles from the intestine. Whole animals were homogenized using a blender.

Chemical analysis

The samples were analysed for 15 PBDE congeners (BDE 28, BDE47, BDE49, BDE66, BDE71, BDE75, BDE77, BDE85, BDE99, BDE100, BDE119, BDE138, BDE153, BDE154, BDE183, BDE190, BDE209), HBCD and TBBP-A. Briefly, samples were dried with sodium sulphate, followed by a Soxhlet extraction (hexane:acetone). Internal standards BDE116, 13C-BDE209, and 13C-TBBP-A were added. The Soxhlet extract was acidified, and the organic layer was cleaned with gel permeation chromatography (GPC).

The GPC extract was further purified with sulphuric acid, followed by silica chromatography. The final extract was analysed for PBDEs and HBCD with GC-MS in the negative chemical ionisation mode, and with LC-MS using electrospray ionisation for the analysis of TBBP-A and the isomeric composition of HBCD.

Results and discussion

Concentrations

In sediment and SPM the dominant BFRs for both the Wadden Sea and the Western Scheldt were BDE209 and HBCD. In biota the dominant BFRs were BDE47 and HBCD, followed by BDE49, BDE99, BDE100, and BDE154. In other studies, also BDEs 47, 99 100 and HBCD have been found to be the dominant congeners in biota (e.g. de Boer et al.[1]; Sellstrom et al.[2]), and BDE209 in sediment and SPM[1]. For the common tern food chain the PBDEs levels, on a lipid weight basis, increased from invertebrates to fish (sandeel) to tern, see Figure 1. On the contrary, HBCD levels increased from invertebrates to fish but decreased from fish to tern egg. This may imply that tern metabolises HBCD. In the tern egg and fish samples the alpha-HBCD diastereomer dominates, and the gamma-HBCD diastereomer dominates in the sediment and SPM samples. This is consistent with earlier reported results for the three (alpha, beta- and gamma) diastereomers of HBCD for sediment[3] and biota[3,4,5]. It is, however, unknown if this is a result of selective uptake between the three diastereomers, conversion of the gamma to the alpha diastereomer, or a result of selective metabolism.

BDE209 has not only been found in the abiotic compartment but also in 24% of the fish samples analysed. The BDE209 levels of the positive samples varied from 1.9 to 17 ng/g lw, and are in general at the low site compared to the other PBDEs. It is remarkable that this compound has been found in biota, because of the large molecular size of the compound, which makes it difficult to pass cell membranes, and the low water solubility of the compound. On the other hand, recently BDE209 have been found in terrestrial birds[6,7]. A number of possible explanations can be given for the presence of BDE209 in fish:

i) Sediment particles present in the intestine of the fish contribute to 'whole' fish levels, as BDE209 was the dominant congener in sediment
ii) BDE209 is bound to the outside skin of the fish
iii) BDE209 is stored into a target organ(s) (e.g. liver)

If we assume that 5% of the body weight in fish are sediment particles, we can explain only <9% to a maximum of 50% of the BDE209 levels found in fish by the levels found in sediment. This indicates that the sediment theory can be rejected. Until now BDE209 has not been found in muscle tissue above the limit of detection. Analysing organs and skin will test the other two hypotheses.

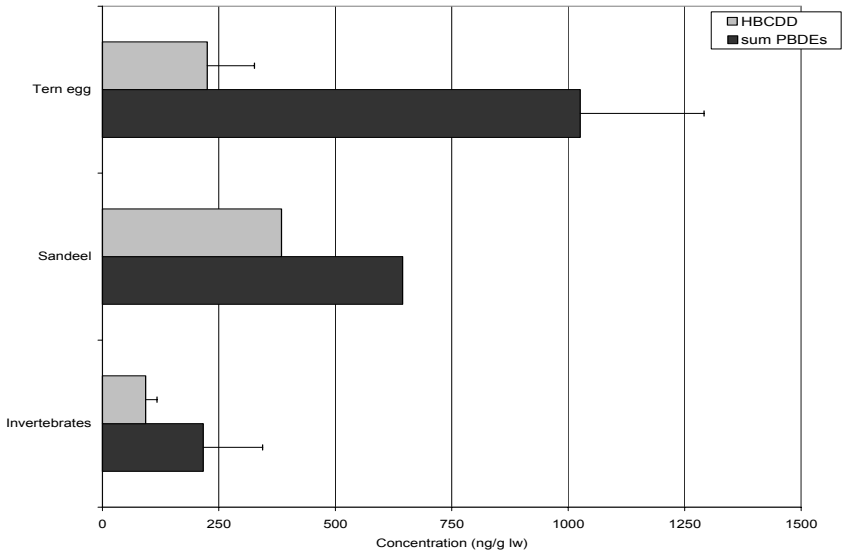

Figure 1: Levels (ng/g lipid weight) of the sum of PBDEs (14 congeners, excluding BDE209) and HBCD in invertebrates, fish, and tern eggs from the Western Scheldt estuary. Sandeel is the dominant food source for terns.

PBDE patterns in tern and seal food chain

The PBDE patterns in prey, tern egg and seal blubber are presented in Figure 2. The PBDE pattern for fish from the seal food chain is an average pattern found in various fish species. If the relative concentration of a BDE in prey (fish) is much lower than the relative concentration in the top-predator (tern or seal) it is assumed that tern or seal metabolises this BDE. Tern probably metabolises BDE49, which has vicinal H-atoms at the meta-para position. Tern does not metabolise BDEs that have vicinal H-atoms at the ortho-meta position, such as BDEs 28, 66, and 75. This is consistent with the biotransformation rules of PCBs for birds. It is know that birds are able to metabolise PCBs that have vicinal H-atoms at the meta-para position, but are unable to metabolise PCBs that have vicinal H-atoms at the ortho-meta position.

Seals were able to metabolise both groups (vicinal H-atoms at meta-para and ortho-meta position) of BDEs. This is similar to what has been found for PCBs[8]. The metabolic capacity for seals is higher than for terns.

Acknowledgment

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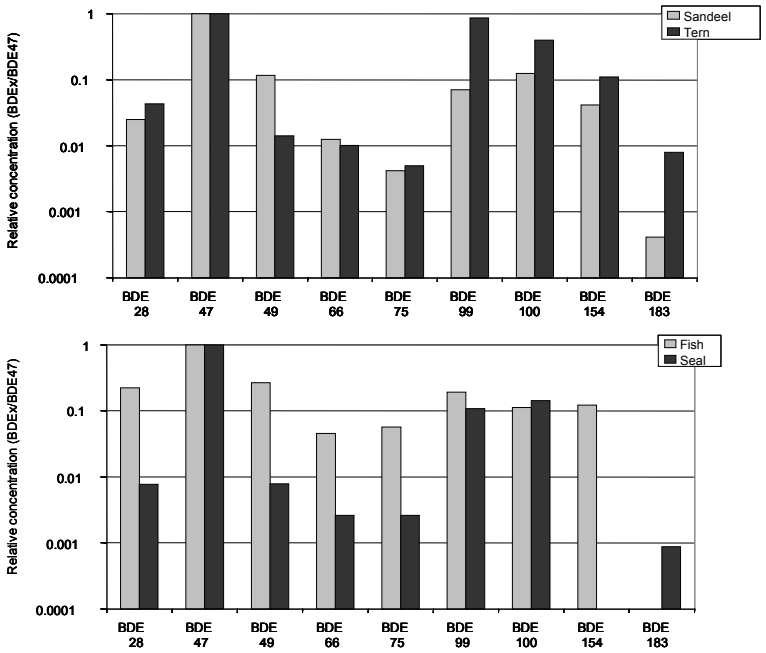

Figure 2: PBDE pattern, relative concentration of BDEs to BDE47, in sandeel, tern egg and harbour seal. Note that the concentration scale is on logarithmic basis. BDE154 in seal and BDE183 in fish were below the limit of detection.

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