BIOMAGNIFICATION QUANTIFICATION OF PBDEs IN FISH USING STABLE NITROGEN ISOTOPES

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Introduction

Polybrominated diphenyl ethers (PBDEs) are used as flame retardants in textiles and plastics in large amounts. PBDEs are highly hydrophobic halogenated aromatic compounds why there is a risk that they may turn out to be environmental pollutants like other such substance groups, e.g. polychlorinated biphenyls (PCBs). Earlier, it has been shown that some PBDE congeners are efficiently absorbed from food in fish (Burreau, et al., 1997). It is necessary to establish if there occurs biomagnification of PBDEs, i.e. if they are enriched in food chains, leading to high concentrations at high trophic levels. In nature, nitrogen occurs as the two stable isotopes, ^{14}N and ^{15}N. Among a vast number of applications, measures of the ratio of these two isotopes can be used to characterise food web dynamics and trophic level interactions. The isotopic composition of nitrogen in a sample is often expressed as $\delta^{15}N$ in parts per thousand (ppt) which is calculated according to Equation 1.

$$\delta^{15}N(ppt) = \frac{\left(\frac{^{15}N}{^{14}N}\right)_{sample} - \left(\frac{^{15}N}{^{14}N}\right)_{air}}{\left(\frac{^{15}N}{^{14}N}\right)_{air}} \cdot 1000 \qquad \text{Eq. 1}$$

It has been shown that ^{15}N is enriched compared to ^{14}N with increasing trophic position of an organism. Hence, the difference in $\delta^{15}N$-value between organisms at two successive "classical" trophic levels, e.g. "producer" and "1st consumer" is 3-5 ppt (Peterson and Fry, 1987). With this measure, the trophic position of organisms is expressed with a continuos parameter which is ecologically relevant since it is an exception that an organism feeds on exclusively one trophic level. Using this instrument for determination of trophic position together with analyses of pollutants, it is possible to describe the biomagnification of a substance according to Equation 2, where c is the concentrations of a certain substance measured in organisms in which the $\delta^{15}N$ value is also measured (Rolff et al., 1993). The term A in Equation 2 is a constant depending concentration at the base of the food chain and the B value describes the biomagnification potential of a certain substance.

$$c = A \cdot e^{(B \cdot \delta^{15}N)} \qquad \text{Eq. 2}$$

A positive B value means that the concentration of a certain substance is higher at higher trophic levels, i.e. biomagnification has occurred. A negative B value means that the concentration is lower at higher trophic levels, indicating for example biotransformation at the higher trophic level. Earlier, the biomagnification potential has been calculated for PCDDs and PCDFs (Broman et al. 1992, Rolff et al., 1993). It was in these studies shown that the most toxic PCDD/Fs (i.e. 2,3,7,8-TCDD, 2,3,4,7,8-PnCDF and 1,2,3,7,8-PnCDD) had a common B value = 0,21, whereas the less toxic PCDD/Fs, e.g. OCDD, had a B value = –0,34. In the present study, we present B-values of some PBDEs measured in three fish species from the Baltic Sea.

Material and Methods

Sprat (*Sprattus sprattus*) (n=6, weight: 7,0-9,8g), herring (*Clupea harengus*) (n=6, weight: 9,7-24,3g) and salmon (*Salmo salar*) (n=10, weight 7,70-13,94kg) were caught in the central and northern part of the Baltic proper in the summer and autumn 1998. The samples were whole body homogenised and two samples were taken out from each fish: one for determination of the isotopic nitrogen composition and one for analysis of content of PBDEs. For determination of the isotopic composition of nitrogen, the samples were dried at 60°C and powdered. Approximately 1 mg of the samples was analysed for $\delta^{15}N$ using a Carlo Erba elemental analyser (E1108 CHNS-O) connected to an Optima isotopic ratio mass spectrometer. For analysing of PBDEs, extraction, clean up and lipid determination was performed according to Jensen et al. (1972). Before extraction, 13C-labelled PCB #180 was added as internal standard. Analyses of PBDEs were performed using a HP 6890 GC coupled to a Micromass AutoSpec Ultima mass spectrometer (EI, 32 eV). A 30m, 0,25mm Supelco PTE-5 column with 0,25 μm film thickness was used and the samples were splitless injected. Quantification of the PBDEs were done after calculating the relative response factors of the individual congeners relative to the internal standard. The individual PBDE congeners were synthesised by Åke Bergmans group at the department of Environmental Chemistry at Stockholm University.

Result and Discussion

The averages of the $\delta^{15}N$-values of the three different fish species is presented in Figure 1.

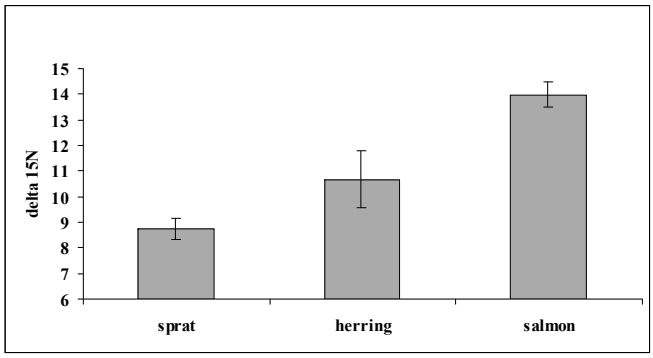

Fig. 1: Mean $\delta^{15}N$-values of the three species. Bars represent s.d.

The general pattern is expected: the planktivorous sprat shows the lowest values, herring, that both eat zoo plankton and zoo planktivores (Arrhenius and Hansson, 1993), intermediate values and the piscivorous salmon the highest $\delta^{15}N$ values. Salmon in the Baltic sea has been reported to mainly

feed on sprat and to some extent herring (Karlsson et al., 1999) and the difference in $\delta^{15}N$ between sprat and salmon of 5,2 is somewhat higher than what would be expected if salmon fed exclusively on sprat or other planktivorous fish. The larger spread in the $\delta^{15}N$-values in herring compared to the two other investigated species indicates a more variable diet in this species.

Tri- tetra- penta- and hexa-BDE were detected in all species. The retention times of PBDE 28 and 49 indicates that these peaks are distorted and the quantification is uncertain. The concentrations of the PBDEs are shown in Table 1. The highest concentrations of PBDEs were found in salmon. Asplund et al. (1999) reported considerably higher lipid weight based concentrations of PBDEs in Baltic salmon muscle tissue. The difference between the two studies might be explained by the obvious different metabolic status of the animals. Asplund et al. (1999) reported the lipid content in salmon muscle to be 4,7%. During consumption of lipid reserves, lipid weight based concentrations of pollutants increase. In the present study, the lipid content of the salmon is 14,7%. However, in cannot be excluded that the difference in PBDE concentration is tissue dependent since we, in contrast to Asplund et al (1999), analyse whole body homogenate.

Table 1: Concentrations (ng/g lipid) of PBDEs in the three fish species

	17+25	**35**	**28**	**49**	**47**	**66**	**100**	**99**	**155**	**154**	**153**
No of Br	3	3	3	4	4	4	5	5	6	6	6
sprat	0,18	0,22	0,60	1,85	4,32	0,18	0,80	0,71	0	0,12	0
herring	0,04	0,12	0,85	2,18	6,21	0,22	0,81	0,62	0,06	0,47	0
salmon	0,79	0,52	4,39	15,19	46,29	1,42	6,37	7,27	0,33	1,98	0,95

Of the hexa-BDE, only PBDE 154 occurred in detectable amounts in herring and sprat, with the exception of PBDE #155 which was detected in one herring. In salmon, PBDE 153, 154 and 155 were detected in most individuals. The pattern with higher concentrations of PBDEs in salmon compared to sprat and herring indicate that these substances are biomagnified, which is apparent in Figure 2.

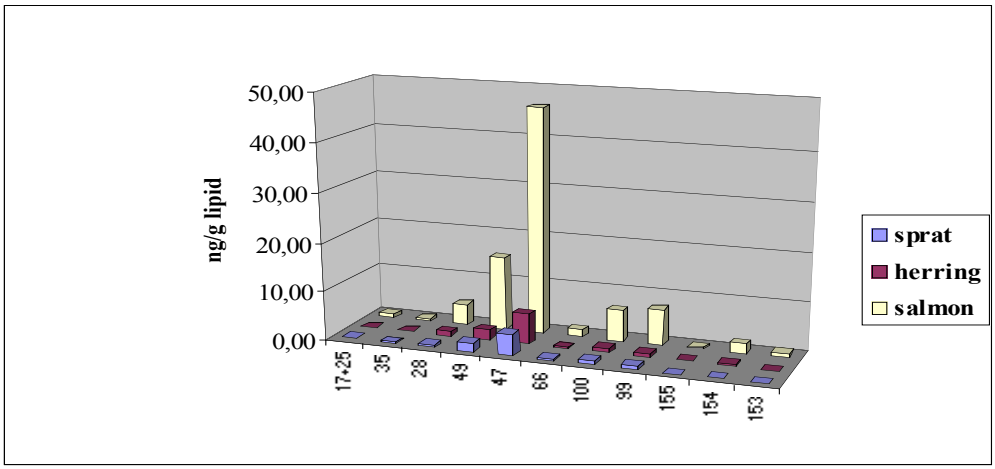

Fig. 2: Mean concentrations of PBDEs in the three fish species

The calculation of the biomagnification potentials (B-values) gives a numeric measure on the biomagnification potential of the PBDEs (Table 2). For the calculations of the B values, only the congeners are chosen that are present in all species.

Table 2: Biomagnification potentials (B value) of PBDEs

	17+25	**35**	**28**	**49**	**47**	**66**	**100**	**99**	**154**
No of Br	3	3	3	4	4	4	5	5	6
B value	0,35	0,33	0,38	0,41	0,43	0,46	0,40	0,44	0,14

All PBDE congeners analysed are biomagnified. The tetra- and penta-BDEs are biomagnified to approximately the same degree, the tri-BDEs slightly less and the hexa-BDEs considerably less. If biomagnification was dependent on hydrophobicity only, one would have expected that the B values would be higher for higher brominated congeners. The low B value of the hexa-BDE indicates that this substance either is absorbed with low efficiency and/or is biotransformed in the salmon. It has earlier been shown that the dietary uptake efficiency is negatively correlated with the number of bromine atoms in PBDEs (Burreau et al., 1997). Preliminary B-values of PCBs indicate that tri, tetra- and penta-PBDEs are more efficiently biomagnified than all PCBs.

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