Concentrations and profiles of brominated diphenyl ethers (BDEs) in Baltic and Atlantic herring*

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Abstract

The total concentrations of BDEs in Baltic herring, caught in different years (2002–08) from various areas of the Baltic, and in Atlantic herring (2006) can be reasonably well described by a single concentration vs weight relationship. Samples collected a few years earlier and analysed by others show a slightly different relationship. This indicates that the weight of the fish is an important factor determining the level of contamination and that the contamination apparently did not increase between 1999 and 2008. However, two Baltic herring samples collected in 2007 contained, for reasons unknown, very high concentrations of BDE 209. The BDE profiles (concentrations scaled to a sum of 100) varied a great deal. It is impossible to determine how much of this variation is real and how much is caused by errors in the analyses. The concentration of the BDE 75 was much higher in the Atlantic than in the Baltic herring. Even after taking this into consideration, however, the BDE profile in Atlantic herring is different from the BDE profiles in Baltic herring.

1. Introduction

The action plan of the Helsinki Commission (HELCOM) to reduce pollution in the Baltic Sea and to restore its good ecological status by 2020 was approved on 15 November 2007 by representatives of Estonia, Finland, Germany, Latvia, Lithuania, Poland, Russia, Sweden and the European Community. The ecological objectives related to this goal are to reduce concentrations of hazardous substances (including BDEs) to close to natural levels, to ensure that all fish are safe to eat, to have a healthy wildlife and to attain pre-Chernobyl levels of radioactivity (HELCOM 2007).

Once released into the Baltic Sea, hazardous substances can remain in the marine environment for very long periods and can accumulate in the marine food web up to levels that are toxic to marine organisms. Levels of some hazardous substances in the Baltic Sea exceed concentrations, found for example in the north-east Atlantic, by more than 20 times. Hazardous substances cause adverse effects on the ecosystem, such as

– impaired general health status of animals;
– impaired reproduction of animals, especially top predators;
– increased pollutant levels in fish for human food.

As far as BDEs are concerned, more information on their occurrence in the Baltic marine environment and in discharges (e.g. from sewage treatment plants and landfills) and air emissions from HELCOM countries is very much needed (HELCOM 2007).

At present, BDE levels in Estonian air (Jaward et al. 2003, Gioia et al. 2007, Roots & Sweetman 2007), food (Jaward et al. 2004, Roots et al. 2007, 2008) and soil (Kumar et al. 2009) are generally low.

Among the Baltic fish, herring (*Clupea harengus membras* L.) is the species of choice for monitoring BDE levels and trends in the Baltic. Herring are an important commercial species, available in all parts of the Baltic; in addition, they are easy to catch and of a size suitable for sample treatment, and their biology is fairly well known.

Available BDE data indicate that the age and weight of the fish are a more important determinant of BDE concentrations than the area of the Baltic they come from.

In comparison with the amount of data on BDEs in Baltic herring, there is a scarcity of data on BDEs in herring from the north-west Atlantic (*Clupea harengus* L.); to our knowledge, only one report has been published (Shaw et al. 2009).

It was therefore of interest to incorporate these data into the Baltic herring data set and to examine the profiles in terms of individual BDE congeners as well as by Principal Component Analysis (PCA) of the whole profiles.

2. Material and methods

Herring (*Clupea harengus membras* L.) were obtained from commercial fisheries. The herring analysed in 2006–08 were caught in the open Baltic Sea (2006), Gulf of Finland, and Gulf of Riga (2007, 2008). The fish samples were frozen immediately after examination and selection. The length, gender, weight, and gonad maturity of the fish were determined. Otoliths were removed to determine the age of the fish. The head, tail fin and viscera were also removed.

Fifteen polybrominated diphenyl ethers (BDE 28, 75, 71, 47, 66, 77, 100, 119, 99, 85, 154, 153, 138, 183 and 209) were measured in whole-body samples of Baltic Sea herring during 2006–08. The samples were extracted, defatted, fractionated and purified, and then analysed for BDEs by HRGC/HRMS as described earlier (Kiviranta et al. 2004). The laboratory is an accredited testing laboratory (No. T077) in Finland (current standard: EN ISO/IEC 17025). The scope of accreditation includes PCDD/Fs, non-ortho-, mono-ortho- and other PCBs, and BDEs in environmental samples.

The limit of quantitation (LOQ) of BDEs ranged from 0.035 to 13 pg g^{-1} fresh weight, depending on individual congeners. Fresh weight concentrations were calculated with lower, medium and upper bound methods. In the lower bound method, the results of congeners with concentrations below LOQ were designated as nil, while in the upper bound method they were denoted as the LOQ. Fish oil was used as an internal quality control sample in the laboratory, and the random error within the laboratory for $\sum$BDE was 4.3% (Kiviranta et al. 2004).

In addition, BDE concentrations in Baltic herring analysed by Parmanne et al. (2006) (obtained in 2002 in the eastern part of the Bothnian Sea), herring analysed by Koistinen et al. (2008) (landed in 1999 off the west and south coast of Finland and in the Gulf of Finland), and Atlantic herring analysed by Shaw et al. (2009) (caught in the Gulf of Maine (U.S.A.) in 2006), were included in the data analysis.

The concentrations of total BDEs at different weights of herring were taken from Table 2 of Parmanne et al. (2006).

The concentrations of total BDEs as a function of weight of the herring landed in 2006–08 was expressed by the empirical equation:

$$\text{total BDEs, ng g}^{-1}\text{ fw} = \text{weight}/(15.65 + 0.342 \times \text{weight}).$$

The constants in this equation were obtained by linear regression of the relationship (weight/total BDEs) vs weight.

The concentrations of the individual BDE congeners were calculated from the parameters of the fitted curves in Table 7 of Parmanne et al. (2006) and converted to profiles. After the age-based calculations, weight instead of age was used from Table 2 of Parmanne et al. (2006); these data are referred to as the 'Parmanne model'.

The BDE profiles were examined by PCA. The PLS_ Toolbox 2 (Eigenvector Research, Inc., www.eigenvector.com) in Matlab 5.0 (The Mathworks, Inc., www.mathworks.com) and profiles of the congeners 28, 47, 66, 99, 100, 153 were used (the level of BDE 75 was much higher in the Atlantic herring than in the Baltic herring).

3. Results and discussion

Figure 1 shows the total BDE concentrations reported by Parmanne et al. (2006), Koistinen et al. (2008), Shaw et al. (2009), and Roots et al. (2009 submitted), plotted against the weight of the herring. The total concentrations are the sums of the main congeners reported in these papers (28, 47, 66, 75, 99, 100, 153 and 154), as well as a few other congeners reported in some other papers.

The total BDE concentrations are highest in two herring samples, obtained in 2007 in the Gulf of Riga and in the mouth of the Gulf of Finland. These samples contain very high concentrations of BDE 209. The reasons for this are not known. Total BDE levels in the herring of Koistinen et al. (2008) are reasonably close to the values obtained by Parmanne et al. (2006). The concentrations found in herring 4 to 6 years later by Roots et al. (2009 submitted) appear to be higher in smaller, and lower in large, herring.

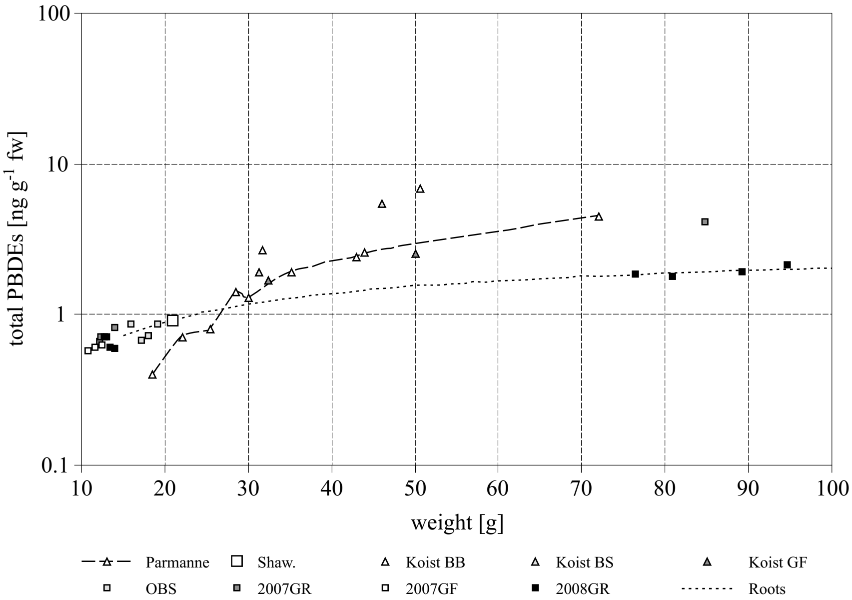

Figure 1. Total BDE concentration [ng g^{-1} fw] in herring from the Baltic (Kiviranta et al. 2004, Parmanne et al. 2006, and Roots et al. 2009 submitted) as well as in herring from the north-west Atlantic (Shaw et al. 2009)

Clearly, additional monitoring is required, but it appears that the concentration of BDEs in Baltic herring did not change considerably between 1999 and 2008. Interestingly, the concentration of BDEs in Atlantic herring fits the empirical relationship derived for the 2006–08 Baltic herring.

The 'Parmanne model' predicts an increase in the percentage of BDEs 47 and 100, and a decrease in the percentages of the other BDEs. Considering the substantial noise in the data, the predictions are reasonable (Figures 2 and 3). A notable exception is the much larger than predicted proportion of BDE 75 (Figure 3) in the Atlantic herring; this was also recorded in Baltic herring.

An examination of whole profiles by PCA shows the same pattern: an increase in the proportion of BDEs 47 and 100, and a decrease in the proportion of the other BDEs (Figure 4 – a loading plot). In addition, the correlation of BDEs 153 and 28 can be seen from the loading plot.

According to the score plot (Figure 5) there is considerable variation among the samples. The north-west Atlantic sample remains an 'outlier' in spite of the removal of the unusually high proportion of BDE 75 from the PCA, and the proportions of congeners 47 and 100 do not increase as fast as predicted by the 'Parmanne model'.

The profiles in herring from the open Baltic (OBS 2006) form a separate cluster. The other samples also show some less pronounced clustering.

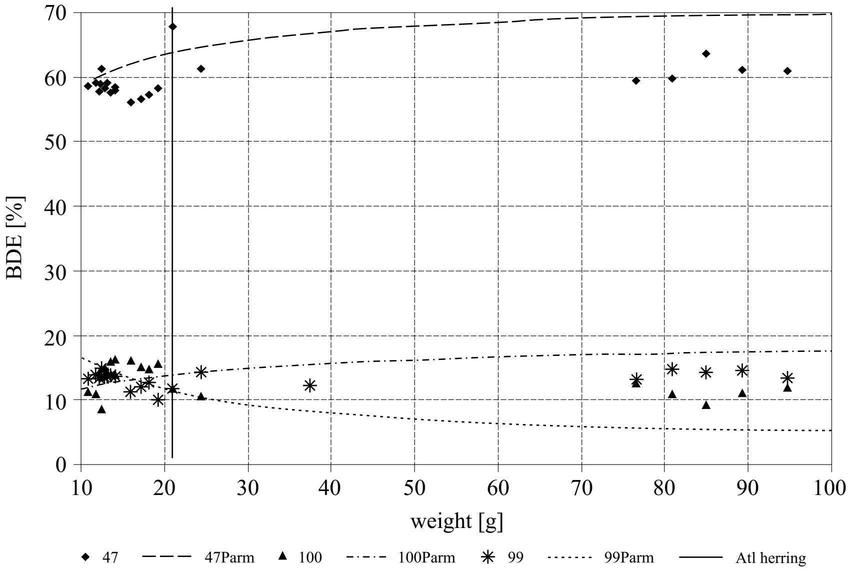

Figure 2. Predicted (Parmanne at al. 2006) (lines) and reported (symbols) proportions of BDEs 47, 99, and 100 in Baltic herring. The weight of herring from the Northwest Atlantic (Shaw et al. 2009) is 21 g (see vertical line)

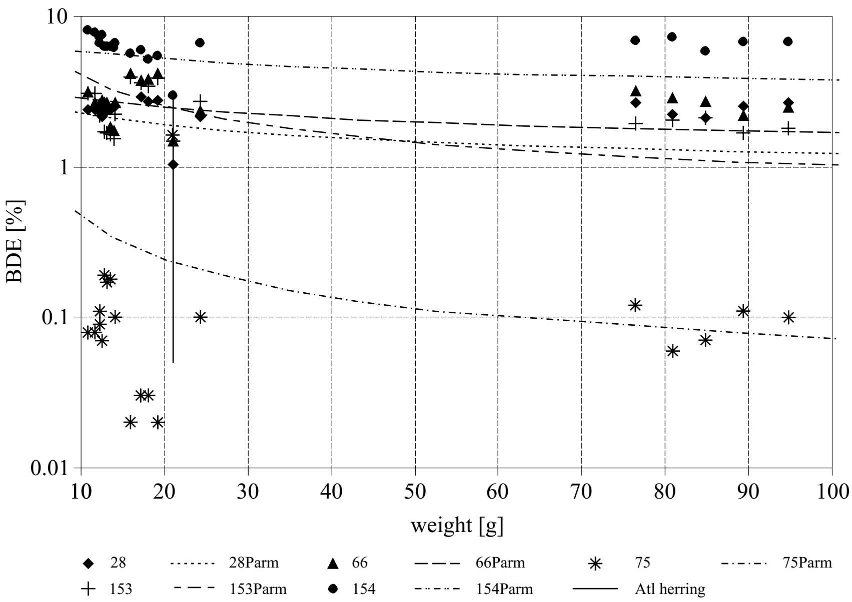

Figure 3. Predicted (Parmanne et al. 2006) (lines) and reported (symbols) proportions of BDEs 28, 66, 75, 153, and 154 in Baltic herring. The weight of herring from the Northwest Atlantic (Shaw et al. 2009) is 21 g (see vertical line). Note the much higher proportion of BDE 75 in herring from the Northwest Atlantic

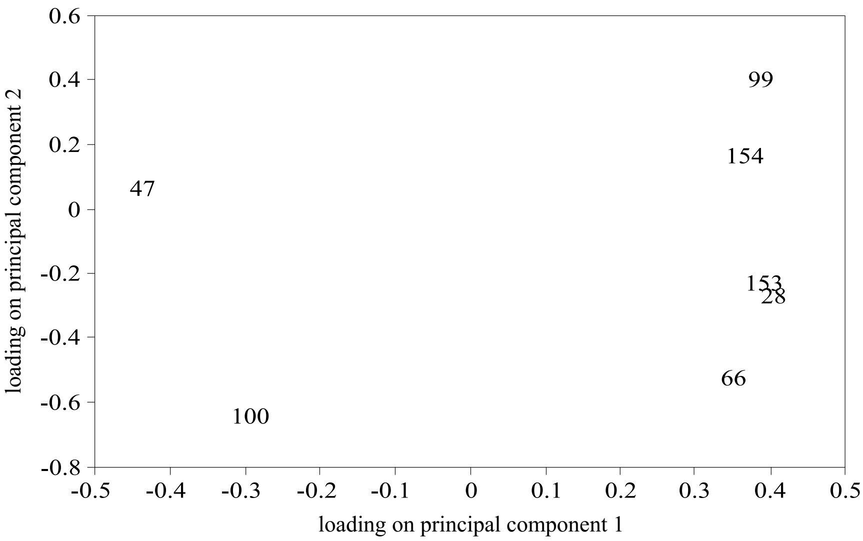

Figure 4. Loading plot of the PCA analysis of the whole profiles. The numbers indicate the loadings of the individual BDEs on the first two principal components

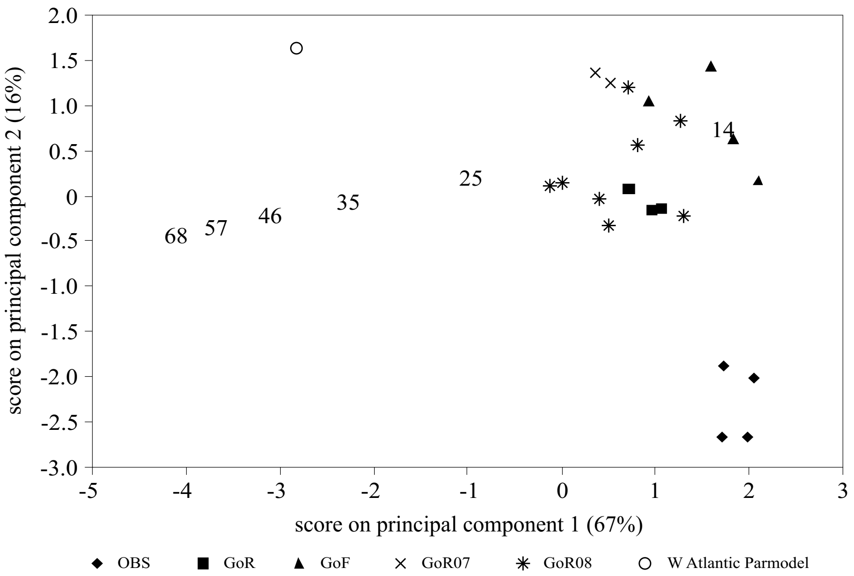

Figure 5. Differences and similarities in the whole BDE profiles are shown on this score plot. The positions of samples are indicated by symbols. Fish weight is shown for the 'Parmanne model'. OBS, GoR, GoF stand for 'Open Baltic Sea', 'Gulf of Riga', and 'Gulf of Finland', respectively. The proportions of the total variance, captured by the principal components, are shown on the axes

4. Conclusion

It appears that contamination of Baltic herring by BDEs is not increasing and is similar in different geographical areas. The high concentration of BDE 209 in some samples requires further study. In any case, yearly monitoring of age/weight-stratified samples is needed. It would also be interesting to have samples stratified by gender and maturity.

There are large differences in the BDE profiles. It is impossible to determine to what extent they are 'real' and to what extent they are analytical artefacts. A much more thorough intercalibration of the reporting laboratories is needed to settle this question.

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