

Comparison of spatial and temporal trends of methoxylated PBDEs, PBDEs, and hexabromocyclododecane in herring along the Swedish coast

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Introduction

Some brominated flame retardants, for example poly brominated diphenyl ethers (PBDEs) have been identified as ubiquitous environmental contaminants ¹. The use of the technical PentaBDE product in the European Union has been drastically reduced in the last years and is banned from 2004, while another brominated flame retardant, hexabromocyclododecane (HBCD), continues to be used. In addition to the commercial BFR products, methoxylated PBDEs (MeO-PBDEs) have been identified in biota in the aquatic environment ^{2, 3, 4, 5, 6}. The origin of the MeO-PBDEs is under discussion. To our knowledge, neither OH-PBDEs nor MeO-PBDEs are commercially produced, nor have they been reported as impurities in brominated technical products or formed as by-products in any industrial process. However, MeO-PBDEs has been reported to be natural products formed in the marine environment ⁷. As regards MeO-PBDEs detected in Baltic fish several factors points in the direction of a natural origin ⁵. On the other hand, certain MeO-PBDEs detected in environmental samples could also be metabolites/environmental transformation products of PBDEs ^{8, 5}.

Knowledge of the spatial and temporal trends of the flame retardants in biota can be very useful in identifying sources of emission to the environment and in evaluating the impacts of voluntary restrictions / bans (PBDEs) and ongoing use (HBCD) on environmental contamination. In addition, this knowledge could provide valuable help in identifying the origin of the MeO-PBDEs. To this end, the Swedish Environmental Monitoring Programme on Contaminants in Biota (SEMP) has incorporated these 3 substance groups into its monitoring of organic contaminants in herring (*Clupea harengus*). In this contribution we report on the results of the first 4 years.

Materials and Methods

Between 1999 and 2002 specimens of herring were collected from six different sites located along the Swedish coast (see Table 1). All sites were reference sites within SEMPC with no known local sources of pollutants and are thus believed to be representative of a larger area. Sampling was conducted in the autumn of each year between 1999 and 2002. All specimens were females: 2-3 years old from the two sites (Fladen and Väderöarna) on the west coast (Kattegatt/North Sea), and 3-4 years old from the rest of the sites (Baltic Sea).

The PBDE standards were purchased from Cambridge Isotope Laboratories (MA, USA) and MeO-PBDE standards were kind gifts from Göran Marsh (Stockholm University) and were synthesized as described elsewhere ⁹. Dechlorane 603 (Hooker Chemical Corp) was used as internal standard. Herring muscle samples were extracted and cleaned up according to the method described by Jensen et al. ¹⁰. The samples were analyzed by GC/MS using chemical ionization with ammonia as the reaction gas (MS-ECNI). The mass fragments monitored were m/z 79 and 81 for PBDEs and MeO-PBDEs, and m/z 237 and 239 for the internal standard dechlorane. The PBDE congeners BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154 were quantified as were HBCD and 6-methoxy-2,2',4,4'-tetraBDE (6-MeO-BDE-47) and 2'-methoxy-2,3',4,5'-tetraBDE (2'-MeO-BDE68). The laboratory has successfully taken part in intercalibration exercises for the analysis of PBDEs in fish muscle.

BROMINATED COMPOUNDS: BIOTIC LEVELS, TRENDS, EFFECTS

Results and Discussion

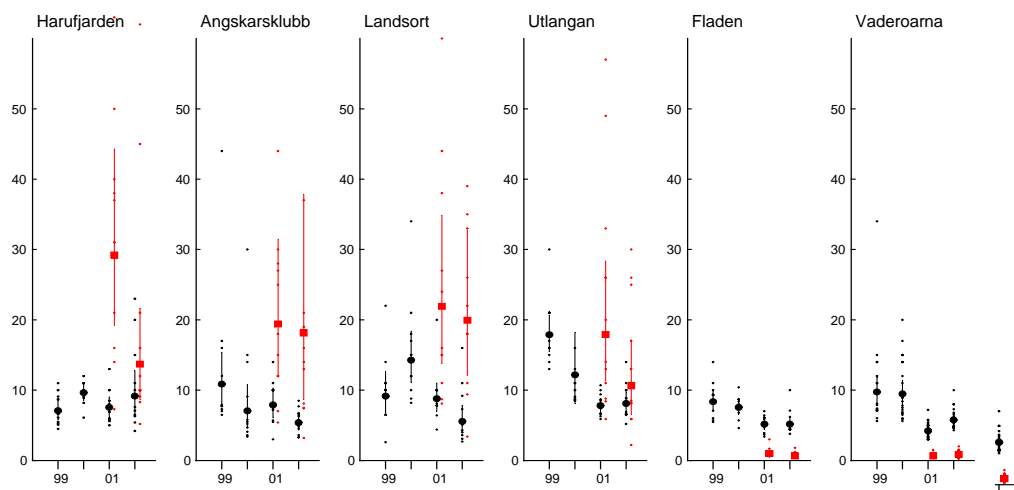
The results from year 2002 are shown in Table 1.

Table 1: Geometric mean concentrations (ng/g lipid w) and ranges for year 2002 at the various sampling sites.

	Harufjärden	Ängskärsklubb	Landsort	Utlången	Fladen	Väderöarna
	(1)	(2)	(3)	(4)	(5)	(6)
MeO-47	13.7 (5.2-62)	18.1 (3.2-200)	19.9 (3.4-67)	10.6 (2.2-30)	0.66 (0.4-1.8)	0.86 (0.3-2.0)
MeO-68	5.82 (1.5-26)	2.84 (0.53-23)	3.12 (0.7-13)	2.06 (0.41-12)	0.35 (0.2-0.6)	0.20 (0.0-1.0)
BDE-47	9.16 (4.2-23)	5.38 (3.3-8.5)	5.57 (2.7-16)	8.11 (5.2-14)	5.18 (3.8-10)	5.78 (4.3-10)
BDE-99	2.75 (1.4-5.3)	1.08 (0.6-2.4)	1.32 (0.7-3.5)	3.17 (1.8-6.7)	1.18 (0.8-2.5)	1.67 (1.1-4.6)
BDE-100	1.85 (0.9-6.0)	1.30 (0.8-2.1)	1.14 (0.5-3.5)	1.51 (0.9-2.6)	0.99 (0.7-1.8)	1.21 (0.8-2.3)
BDE-153	0.43 (0.2-1.0)	0.20 (0.1-0.3)	0.23 (0.1-0.6)	0.43 (0.3-0.6)	0.24 (0.1-0.5)	0.29 (0.2-0.6)
BDE-154	0.62 (0.3-1.3)	0.28 (0.2-0.5)	0.36 (0.2-0.8)	0.58 (0.4-0.8)	0.30 (0.2-0.5)	0.39 (0.2-0.7)
HB CD	7.85 (3.7-12)	3.98 (1.5-6.1)	13.7 (7.4-31)	18.3 (14-26)	10.3 (7.3-18)	7.94 (5.6-12)
CB-153	59 (31-191)	94 (61-173)	57 (26-234)	59 (31-100)	49 (32-83)	37 (18-67)

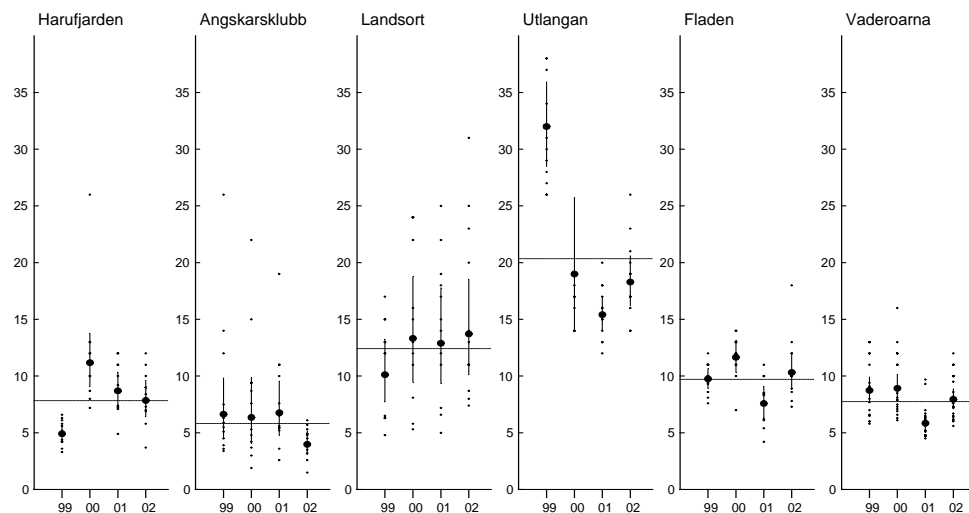
The results from the period 1999 to 2002 are illustrated in Figure 1. In the upper panels the concentrations of the BDE-47 and 6-MeO-BDE47 are shown, while the lower panels show the results for HB CD. Important features of the results include:

MeO-47, BDE-47 ng/g lipid w., herring muscle



pia - 04.04.06 17:17, MeO47c

HBCD, ng/g lipid w., herring muscle



pia - 04.04.06 14:56, hbcde

Figure 1: Chemical concentrations plotted as a function of time for 5 of the stations studied. The individual data points are shown along with the median (large dot). The upper panel shows the results for the BDE-47 and the MeO-BDE-47, which are slightly offset to the right. The lower panel shows HBCD.

The concentrations of BDE-47 is very homogenous among the 4 stations in the Baltic Sea and only slightly lower in the North Sea. This stands in contrast to the polychlorinated biphenyls (PCBs), for which the concentrations are about 5 times higher in the Baltic ¹¹. This suggests that historically the inputs of PCBs and PBDEs to the region have been quite different.

HBCD shows a stronger regional differentiation, with higher levels in the southern Baltic. This may be an indication of ongoing inputs to the southern part of the Baltic Sea.

The levels of 6-MeO-BDE-47 are quite similar at the 4 stations in the Baltic Sea, but they are approximately 20 times lower in herring from the Kattegatt/North Sea, confirming the results of a preliminary study ⁶. This may indicate a specific MeO-PBDEs source in the Baltic Sea or that the marine environment of the North Sea is less favorable for the accumulation of these substances. This could possibly be a result of lower formation rates or greater dilution.

The ratio of 6-MeO-BDE-47 to BDE-47 is about 10 times lower in herring from the Swedish west coast compared to the east coast. Consequently, metabolism in herring is not a likely source of 6-MeO-BDE-47.

Several arguments point in the direction of a biogenic source for the MeO-PBDEs. For example OH- and MeO-BDE have been isolated from red algae species collected in the Baltic Sea ¹². However, other possible sources have to be investigated before any clear conclusion about the origin of the MeO-BDEs in the Baltic Sea can be drawn.

No significant time trends are yet apparent for any of the chemicals. However, there are indications that the time trends of PBDEs and MeO-PBDEs are not congruent, which would suggest that the sources are not directly coupled.

The herring monitoring data from SEMPC provide useful clues about the sources and fate of brominated flame retardants and related compound in the environment.

Acknowledgements

We thank Michael McLachlan for assistance in preparing the abstract. Göran Marsh is gratefully acknowledged for the gifts of the MeO-PBDE standards. The Swedish Environmental Monitoring Programme on Contaminants in Biota is financed by the Swedish Environmental Protection Agency.

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