Differences in PCDD/F concentrations and patterns in herring (Clupea harengus) from southern and northern Baltic Sea

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Introduction

The Baltic Sea is a shallow (mean depth 57 m) brackish-water sea with a wide drainage area and a long residence time. It is surrounded by 9 countries with *ca*. 90 million inhabitants. Thus the Baltic Sea is heavily loaded by domestic and industrial effluents and also through long-range transport, although the loading from surrounding countries has considerably reduced during the last decades. Quite high concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) have been measured in Baltic fish species[1], and concentrations of organochlorines have been demonstrated to increase according to age of Baltic herring (*Clupea harengus*)[2,3].

In July 2002 the decision of the European Commission set a new maximum allowable concentration in fish edible part to 4 pg WHO-TEQ g^{-1} (fresh weight) for human consumption. Finland and Sweden got an exemption order until end of 2006 for commercial exploitation of Baltic fish within their own markets. However, they were ordered to monitor the concentrations of those toxicants in fish and to advice their consumers.

In Finland a large project was performed during 2002–2003 to study PCDD/F and PCB concentrations in fish, which were commercially most important species and caught from three most important Baltic Sea and inland fishing areas. The present paper investigates PCDD/F concentrations and congener profiles in Baltic herring of different size caught from southern and northern Baltic Sea in order to map differences and find out causes for them. Such a knowledge is important for setting regulations for fisheries, advising consumers and finding means to further reduce emissions of these toxicants.

Methods and Materials

Baltic herring (*Clupea harengus*) were obtained from catches of professional fishermen from the southern Main Basin of the Baltic Sea in March 2002 and from the Bothnian Bay in May 2002 (Fig. 1). Herring of total body length of 12-14.9, 15-16.9, 17-18.4, 18.5-20.9, and >21 cm from the Bothnian Bay and 15-17.9, 18-20.9, and >21 cm from the Main Basin were collected. The total length of individual fish was measured and otoliths were removed for age determination. Fish were frozen and transported to the laboratory, where they were kept frozen (-20 ºC) until analysed. On the basis of length of fish, pools of ten fish were formed for chemical analysis. The mean lengths and ages of the fish in the pools were: 13.5, 16.0, 17.8, 19.8, and 30.0 cm and 2.3, 3.0, 6.5, 7.7, and 8.5 years from the Bothnian Bay and 16.5, 19.5, and 22.0 cm and 2.1, 3.4, and 7.0 years from the Main Basin, respectively.

The pools of ten herring with heads and internal organs removed were thoroughly homogenised, freeze-dried and extracted with toluene in a Soxhlet apparatus. Determination of concentrations of PCDD and PCDF was performed as described earlier[4]. Toxic equivalent concentrations (WHO-TEQ, pg g^{-1} fresh weight) were calculated according to Van den Berg et al.[5].

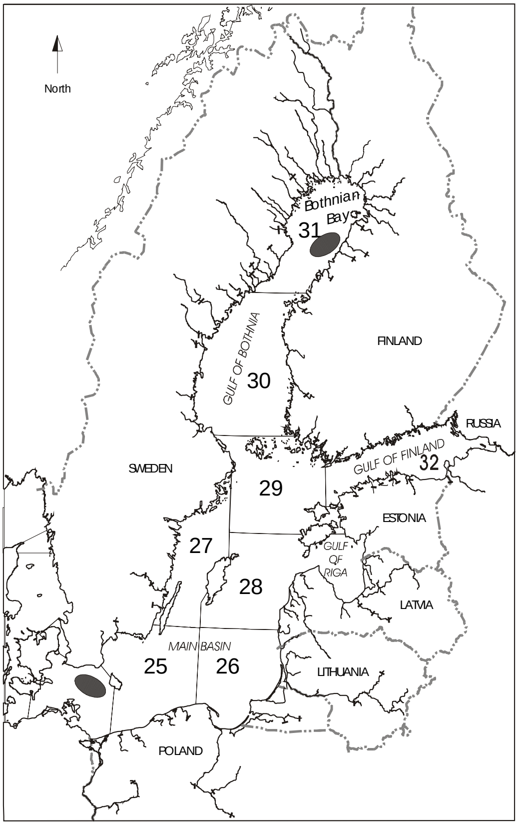

Figure 1: The sampling areas of Baltic herring for the study are indicated by dark grey ellipses.

Results and Discussion

In herring both from the Main Basin and the Bothnian Bay the WHO-TEQ concentration correlated positively and significantly with age and length (Fig. 2) as has also been earlier reported for chlorinated pesticides and PCBs as well as PCDD/Fs in herring[2,3]. In the present study the Pearson correlation coefficients were 0.954–1.000. The WHO-TEQ concentration was higher in herring from the Bothnian Bay than from the Main Basin when comparing concentrations in fish of similar length and age (Fig. 2). However, testing by covariance analysis the fat content as a covariate resulted in significant difference between the fishing areas and the age of fish (Table 1). The fat content did not contribute significantly to the areal differences as did length neither. The fact that length did not have an effect in the covariance analysis was due to correlation of age and length of fish: Age = -3.70 + 0.36Length, $p = 0.029$ for the Main Basin and Age = -8.87 + 0.81Length, $p = 0.011$ for the Bothnian Bay. The cause for the difference in WHO-TEQ between the fishing areas is the different growth of herring in these areas. In the southern parts of the Main Basin the herring growth is much faster than in the Bothnian Bay (Fig. 2), the mean yearly length increase, calculated from the age–length regressions was 2.80 and 1.23 cm per year, respectively. In the Bothnian Bay the salinity is very low, approximately 0.2%, whereas in the Main Basin it is more than 1%. Herring have to use much more energy to ion regulation in the Bothnian Bay than in the Main Basin and thus they have less energy for growth. Apparently the feed abundance is also lower in northern than in southern Baltic Sea.

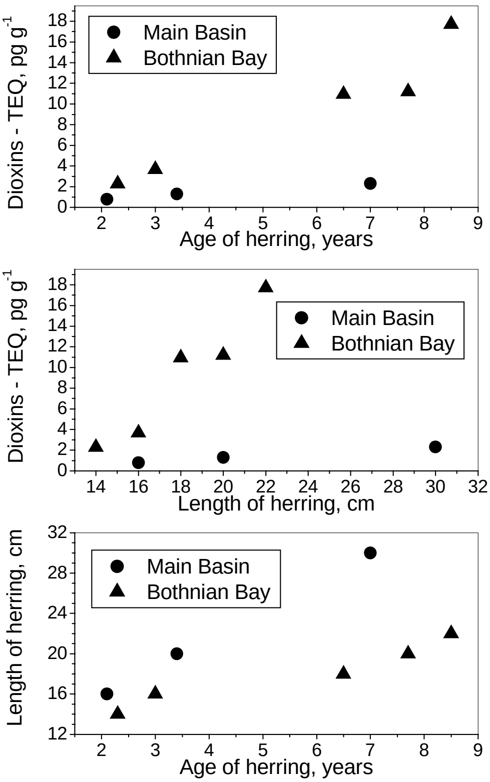

Figure 2: The concentration of WHO-TEQ of Baltic herring from the Main Basin and the Bothnian Bay as a function of age (top) and length (middle) and the relationship of age and length of herring (bottom).

Table 1: The results of covariance analysis (fat content as a covariate) of WHO-TEQ concentrations in Baltic herring of different ages from the Main Basin and Bothnian Bay of the Baltic Sea.

Source of variation	Type III sum Of squares	d.f.	F	*p*
Area	0.071990	1	16.45	0.0270
Fat	0.015628	1	3.57	0.1552
Age	0.058292	1	13.32	0.0355
Length	0.000011	1	0.00	0.9629

The congener profiles of PCDD/F in herring of different ages from the Main Basin were quite similar whereas herring from the Bothnian Bay demonstrated variable profiles (Fig. 3). In herring of different ages from the Main Basin 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF were the dominant congeners as was the case in 2 and 3 years old herring from the Bothnian Bay. These two congeners were also the dominant ones in herring and sprat (*Sprattus sprattus*) caught from the Gulf of Finland and south-west from the Åland Islands and in Baltic salmon (*Salmo salar*)[6,7]. However, in herring from the Bothnian Bay the proportion of 2,3,4,7,8-PeCDF increased steadily along the age increase (Fig. 3). This contradicts the suggestion that fish have more limited capability to metabolise lower than higher chlorinated PCDD/Fs[8]. Apparently the congener 2,3,4,7,8-PeCDF is the most persistent one as well as being the most toxic of the PCDF congeners[5].

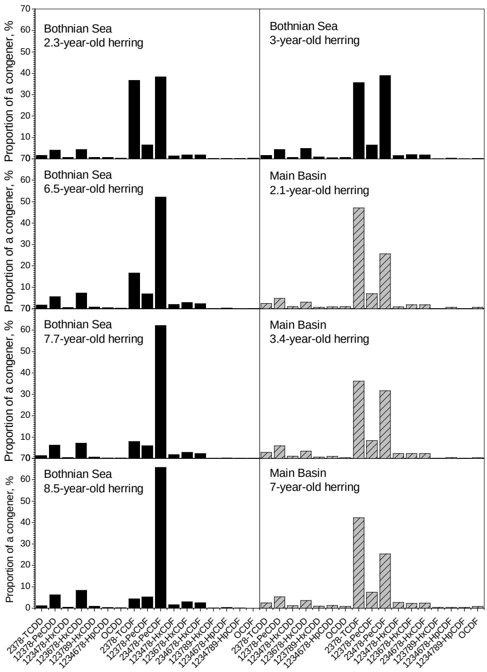

Figure 3: The congener profiles as proportions (%) of PCDD/F in Baltic herring of different ages from the Main Basin and Bothnian Bay of the Baltic Sea.

It can be concluded that Baltic herring from the Bothnian Bay contain higher levels of PCDD/F due to slower growth. The lipid content did not affect the differences.

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