PCDD/FS IN BALTIC HERRING IN THE GULF OF FINLAND DURING THE 1990's

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Introduction

Fish products play a significant role in the Finnish dietary intake of polychlorinated dibenzo-*p*-dioxins, and dibenzofurans (PCDD/F). Of the PCDD/F intake, fish products accounted for 82%, and Baltic herring (*Clupea harengus* L.) alone 52% [1]. In November 2001, the EU Council set maximum levels for PCDD/Fs in foodstuffs [2]. For fish and fishery products, the limit was set at 4 pg toxic equivalents ($WHO_{PCDD/F}$-TEq) per gram of fresh weight (fw).

Baltic herring population in the Gulf of Finland has suffered from diminished growth since the 1980's [3], which might affect the prevailing concentrations of PCDD/Fs. An explanation for diminished growth of herring in the Gulf of Finland might be the changes in the water salinity which affect the amount, composition and availability of zooplankton suitable for herring [4].

Continuous decline of several organochlorines, including polychlorinated biphenyls (PCBs), in Baltic herring from 1978 to 1995 has been reported [5]. The declining trends were most intensive during the late 1970's and during the 1980's, but have started to level off at the beginning of the 1990's. Consistent data for PCDD/Fs is currently missing.

In this study of PCDD/Fs in Baltic herring, the following main tasks were undertaken: a) to determine the age correlation of $WHO_{PCDD/F}$-TEq concentrations; b) to evaluate the time trend of concentrations during the 1990's.

Materials and Methods

Baltic herring were collected from the Gulf of Finland during most vigorous spawning season (beginning of May to mid-June) in 1993-94 and 1999. Weight (w) and length (l) of individual fish were measured. Otoliths of herring were taken for age determination in 1993-94, but age was not determined in 1999. Herring from 1993-94 were pooled into age groups (2, 3, 4, 5, 6, 7 years of age). Pooling of herring, caught in 1999, was based on length. Number of individual herring in pools varied from 20 to 337.

Fats from cleaned (head, fins and gut removed), pooled, freeze-dried, and homogenized herring were extracted with toluene and the fat contents were determined gravimetrically. A previously described method was used for purification and analysis of samples [6]. Toxic equivalents ($WHO_{PCDD/F}$-TEq) were calculated with the toxic equivalency factors (TEF) recommended by WHO in 1998 [7]. Limits of determination (LOD) for PCDD/Fs were isomer dependent, and varied between 0.005-0.05 pg/g fw. The laboratory is an accredited testing laboratory (No. T077) in Finland (current standard: EN ISO/IEC 17025).

Results and discussion

The age correlation of $WHO_{PCDD/F}$-TEq was obtained from concentrations of 1993-94 collected herring samples (Fig. 1). A rule of thumb was created: every year of a herring's life lead a rise of one $WHO_{PCDD/F}$-TEq unit.

Figure 1. Age correlation of $WHO_{PCDD/F}$-TEq of Baltic herring caught in 1993-94.

To obtain time-trends of PCDD/F concentrations in herring in the 1990's, age groups 5 and 6 were extracted from the data in 1993-94. The basis for selection of these age groups was similarity of weights and lengths between these groups and herring caught in 1999. PCDD/F concentrations (Table 1) in herring in the Gulf of Finland in 1993-94 and 1999 indicated that concentrations did not decrease during this time period. Since herring age was not determined in 1999 samples, there is a possibility that herring in 1999 were older than 1993-94 herring. Possible difference in herring age between 1993-94 and 1999 might obscure the possible downward trend in herring exposure to PCDD/Fs.

PCDD/F profiles in herring were similar during the 1990's. In Figure 2 median percentage profiles of PCDD/F congeners from the sum of PCDD/Fs and from toxic equivalents are shown. The dominating congener in both profiles was 2,3,4,7,8-PeCDF followed by 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 1,2,3,7,8-PeCDD, 1,2,3,6,7,8-HxCDD and OCDD in the sum of PCDD/Fs profile, and 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD in the toxic equivalent profiles. Similar profiles of Baltic herring, and herring caught from the North Sea have been reported by Rappe et al.[8]. The PCDD/F profiles in Baltic herring were similar to those measured from seafood, in particular anchovy and mackerel, in the Adriatic Sea [9].

In conclusion, concentrations in herring measured in 1993-94 in the Gulf of Finland showed a clear age dependency of PCDD/Fs. A rule of thumb was that there was one unit increase of $WHO_{PCDD/F}$-TEq concentration for every year of a herring's life. The time trend of PCDD/Fs in herring in the Gulf of Finland did not reveal any clear decline between 1993-94 and 1999.

Assessment of the exposure of Finns to PCDD/Fs via herring is quite difficult since there is no reliable information about the size or age distribution of consumed herring, and data on concentrations of harmful substances in herring in seasons other than spring are missing. The age of herring for human consumption usually is 3 years or older, and the fish used for human consumption are usually 3-6 years. Hence, according to the rule of thumb created in this study, concentrations in a major fraction of the herring used by Finns as food, will exceed the limit value of 4 pg $WHO_{PCDD/F}$-TEq/g set by EU.

Table 1. Medians (range) of fat%, weights, lengths, concentrations (pg/g fw) of PCDD/Fs and $WHO_{PCDD/F}$-TEq in Baltic herring, caught in 1993-94 and 1999 in the Gulf of Finland.

	Herring in the Gulf of Finland 1993-94	1999
Number of pools	20	4
Fat%	1.8 (0.99-3.5)	2.0 (1.5-2.9)
Weight, g	29 (23-35)	32 (27-33)
Length, cm	17.2 (16.7-18.3)	17.6 (17.1-17.9)
2378-TCDD	0.32 (0.15-0.76)	0.3 (0.23-0.38)
12378-PeCDD	1.3 (0.71-2.5)	1.2 (0.86-1.4)
123478-HxCDD	0.082 (0.013-0.14)	0.14 (0.13-0.15)
123678-HxCDD	1.4 (0.47-3.8)	1.5 (0.89-2.0)
123789-HxCDD	0.099 (ND-0.25)	0.15 (0.14-0.18)
1234678-HpCDD	0.28 (0.11-1.2)	0.11 (0.094-0.13)
OCDD	0.78 (0.25-7.2)	0.15 (0.086-0.19)
Dioxins	4.6 (1.9-12)	3.6 (2.5-4.3)
2378-TCDF	1.4 (0.59-3.1)	1.7 (0.84-2.5)
12378-PeCDF	1.0 (0.62-1.9)	1.3 (0.89-1.6)
23478-PeCDF	7.4 (4.4-9.7)	10 (7.3-12)
123478-HxCDF	0.33 (0.17-2.0)	0.39 (0.32-0.52)
123678-HxCDF	0.42 (0.075-2.6)	0.6 (0.44-0.79)
234678-HxCDF	0.75 (0.35-1.3)	0.49 (0.32-0.56)
123789-HxCDF	ND	0.024 (ND-0.034)
1234678-HpCDF	0.28 (0.11-0.78)	0.1 (0.057-0.16)
1234789-HpCDF	ND	0.006 (ND-0.03)
OCDF	0.066 (0.015-0.27)	ND
Furans	12 (6.6-20)	15 (10-18)
Sum of PCDD/Fs	18 (8. 6-26)	19 (13-21)
$WHO_{PCDD/F}$-TEq	5.7 (3.3-8.9)	7.2 (5.1-8.2)

ND = concentration below LOD

Congeners: 1D: 2,3,7,8-TCDD; 2D: 1,2,3,7,8-PeCDD; 3D: 1,2,3,4,7,8-HxCDD; 4D: 1,2,3,6,7,8-HxCDD; 5D: 1,2,3,7,8,9-HxCDD; 6D: 1,2,3,4,6,7,8-HpCDD; 7D: OCDD; 1F: 2,3,7,8-TCDF; 2F: 1,2,3,7,8-PeCDF; 3F: 2,3,4,7,8-PeCDF; 4F: 1,2,3,4,7,8-HxCDF; 5F: 1,2,3,6,7,8-HxCDF; 6F: 2,3,4,6,7,8-HxCDF; 7F: 1,2,3,7,8,9-HxCDF; 8F: 1,2,3,4,6,7,8-HpCDF; 9F: 1,2,3,4,7,8,9-HpCDF; 10F: OCDF.

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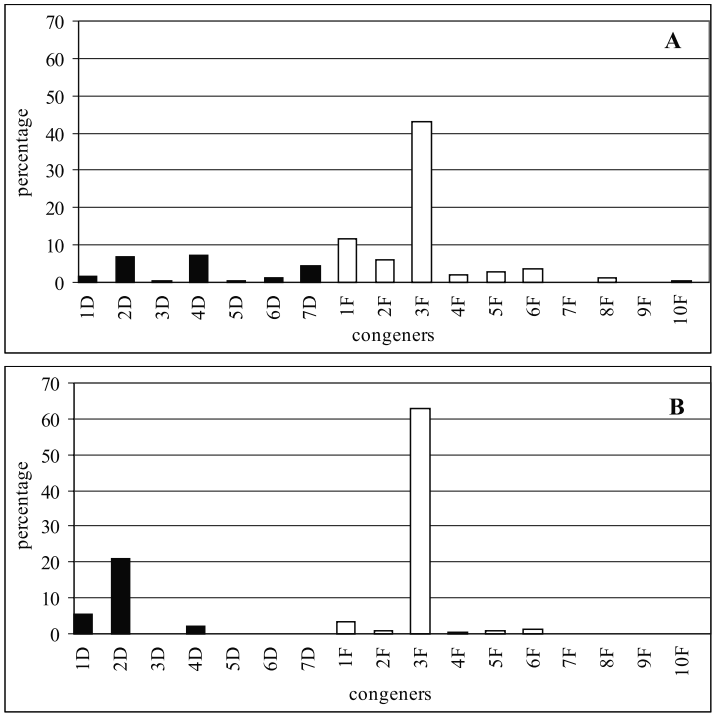

Figure 2. Median percentages of PCDD/F congeners in Baltic herring in the 1990's. A: percentages from sum of PCDDs (black bars) and PCDFs (white bars), and B: percentages from $WHO_{PCDD/F}$-TEq.

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