PCDD/Fs AND PCBs IN BALTIC SEA HERRING AND SALMON – CONCENTRATION CHANGES BETWEEN 2002-2009

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Introduction

Finland and Sweden have a derogation to the Commission regulation No 1881/2006, allowing them to place on their markets certain Baltic Sea fish species that exceed the current maximum levels of dioxins and dioxin-like PCBs. Of the five fish species included in the derogation, Baltic herring (*Clupea harengus membras*) and salmon (*Salmo salar*) are the most important species from both public health and economic perspective in Finland. The derogation expires in 31 December 2011. For the continuance of the derogation, an updated view on the concentrations of these environmental pollutants in Baltic fish was needed.

To obtain information on current levels of polychlorinated dibenzo-*p*-dioxins (PCDD/F) and polychlorinated biphenyls (PCB) in fish, the EU Fish II project was launched in 2009. The EU Fish II project was coordinated by the Finnish Food Safety Authority, as well as the first EU Fish project conducted in 2002–2003. The new project provided new information about the levels of PCDD/Fs and PCBs, as well as several other groups of organic pollutants in various fish species across the Baltic Sea and Finnish freshwater and farmed fish. The project also provided information on the concentration changes between this study and the previous project.

Based on the results of the EU Fish II project, the exposure to these hazardous substances through fish consumption will be estimated. Finally, the project will provide data for dietary advice regarding the potential risks associated with the consumption of contaminated fish. In this paper, we report the levels of dioxins and dioxin-like PCBs in Baltic herring and salmon and discuss the change in concentrations between 2002 and 2009.

Materials and methods

Sampling and preparation of fish samples

Between April and June 2009, composite samples of Baltic herring (n=6) and salmon (n=5) were collected from several sites in the Northern Baltic Sea (Fig. 1). In addition, 69 individual Baltic herring were collected from Southern Bothnian Sea.

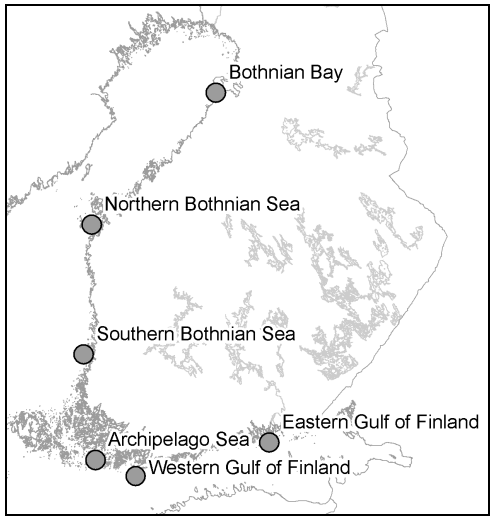

Figure 1. Sampling sites.

The Finnish Game and Fisheries Research Institute collected the samples by random sampling and documented the length, weight, sex, and age of the fish. The age determination of Baltic herring and salmon was based on microscopic examination of otoliths and scales, respectively. The samples were frozen and sent to the laboratory of the National Institute for Health and Welfare.

The Baltic herring samples were analysed as whole, and for the salmon samples, a 50–150 g medallion was cut from behind the dorsal fin. The head and gut was removed and the samples were halved in order to get material for other chemical analyses besides PCDD/Fs and PCBs. Composite samples were based on the length of the fish, and included 10 and 5 individuals for Baltic herring and salmon, respectively. The skin was not removed from the fish in order to replicate the analyses done in 2002 and to fulfill the regulation 1883/2006 of the EU.

Chemical analysis and quality control

Extraction, clean-up, and HRMS analyses of 17 2,3,7,8-chlorine-substituted PCDD/Fs and 12 dioxin-like PCBs followed a previously published method with slight modifications[1]. In brief, samples were homogenised and freeze dried. Analytes were extracted with an Accelerated Solvent Extractor and after extraction the fat content was determined gravimetrically. The fat was removed from the sample in a silica gel column containing adidic silica. Finally a clean-up and fractionation of the analytes were done with an aluminum oxide column and with a carbon column, respectively.

The quantification was performed by gas chromatography - high resolution mass spectrometry (GC-HRMS) in SIR mode and with a resolution of 10000.

The Chemical Exposure Unit of the National Institute for Health and Welfare is an accredited testing laboratory (Centre for Metrology and Accreditation code T077, EN ISO/IEC 17025). The scope of accreditation covers the determination of PCDD/Fs and PCBs from fish samples. In each sample batch, blank samples treated exactly as the real samples were determined along with a control fish sample. Average recovery of PCDD/Fs and PCBs from the control fish sample as WHO-TEQ_{05}s was 93% (RSD 6.3%) and 88% (RSD 4.6%), respectively.

Results and discussion

Table 1 summarizes the concentrations of PCDD/Fs and PCBs as sum TEQs in composite samples of Baltic herring by size group. TEQs calculated using both toxic equivalency factors (TEFs) set by WHO in 1998 and 2005 are reported. In order to describe the change in the concentrations and ratios of PCDD/Fs and PCBs since 2002, the results from the previous EU Fish project are also included in Table 1.

The current maximum level (ML) for the sum of PCDD/Fs and PCBs set by the European Commission is 8 pg/g fresh weight (f.w.). The concentrations in herring in the Gulf of Finland were below the ML in all but one sample, regardless of size group. The change since 2002 was greatest in the herring samples from the Gulf of Finland, where the average decrease in concentrations was 47%. The average decrease in the Archipelago Sea and in the Gulf of Bothnia was 29 and 13%, respectively. When considering the ratio of PCDD/Fs and PCBs in the Gulf of Finland, it was observed that among the larger size groups (> 17 cm), and among the older herring, PCDD/F concentration has decreased more than PCB concentration. Since sexually mature herring migrate from the Gulf of Finland to as far as the southern Baltic Sea, one might conclude that the environmental pressure of PCDD/Fs towards herring has been less pronounced in the southern Baltic Sea, especially when compared with the Gulf of Bothnia in the north. In the north, the herring stocks are more stationary, and the ratio of PCDD/Fs to PCBs has stayed stable between 2002–2009 despite of the overall decline in concentrations.

In all three sampling sites in the Gulf of Bothnia, the TEQ concentrations in herring larger than 17 cm exceeded the ML values and the situation in this respect has not changed between 2002–2009. Studies of the Swedish Museum of Natural History have shown that the concentrations of PCDD/Fs and PCBs in herring can vary a lot between years in the Baltic Sea, and in 2002, the concentrations of PCDD/Fs in herring peaked for some unknown reason[2]. Since in the original EU Fish project the samples were collected in 2002, the observed decrease between 2002–2009 might be at least partly explained by the presumed extreme concentrations in 2002 compared with other years. Therefore, with only two points of sampling in time, it is difficult to make conclusions about the direction of the change in concentrations.

Using the new 2005 TEFs when calculating the TEQs instead of 1998 TEFs decreased the WHO-TEQ concentrations in herring on average by 26%. However, if the new suggested ML of 6.5 pg/g f.w. will come into force, the situation with herring will stay almost stable in the sense that herring ≥17 cm will still exceed the ML in the Gulf of Bothnia.

Correlations between concentrations of PCDD/Fs and PCBs as WHO-TEQ_{98} and length in individual herring in the Gulf of Bothnia in 2002[3] and 2009 are described in Figure 2. In both data sets, the concentrations were less scattered among the herring smaller than 17 cm. Among the small herring, the current and also future ML will most probably not be exceeded. The concentrations were more scattered among the larger herring, which is probably due to growth-related change feeding habits. As the herring mature, they change from feeding on zooplankton to higher trophic level in their prey, feeding on crustaceans and small fish. The total decrease in concentrations among individual herring in the southern Bothnian Sea was 38%, being more pronounced in larger herring, 41%.

Table 1: Total WHO-TEQ$_{98/05}$ concentrations of PCDD/Fs and PCBs in composite samples of Baltic herring, PCDD/F:PCB-ratio, and change between 2002–2009.

Sampling site	Size, cm	WHO-TEQ$_{98}$, pg/g fw		WHO-TEQ$_{05}$, pg/g fw	PCDD/F:PCB ratio		Decrease, %
		2002	2009	2009	*2002*	2009	
Eastern Gulf of Finland	12-14.9	*3.9*	**2.5**	1.8	*1.1*	**1.1**	-36
	15-16.9	*7.7*	**4.1**	3	*1.5*	**1.1**	-47
	17-18.4	*11*	**9.2**	6.6	*1.9*	**1.2**	-18
	18.5-20.9	*7.8*	**4.2**	3	*1.8*	**1.3**	-46
	> 21	*14*	**2.3**	1.6	*1.3*	**1.1**	-83
Western Gulf of Finland	12-14.9	*2.5*	**1.6**	1.3	*1.3*	**1.2**	-36
	15-16.9	*5.5*	**2.4**	1.8	*1.4*	**1.2**	-56
	17-18.4	*7.7*	**3.2**	2.4	*1.4*	**1.3**	-58
	18.5-20.9	*10*	**3.7**	2.8	*1.8*	**1.1**	-64
	> 21	*6.2*	**4.6**	3.4	*1*	**0.9**	-26
Archipelago Sea	12-14.9	*3.1*	**2.1**	1.6	*1.8*	**1.2**	-32
	15-16.9	*3.9*	**4.4**	3.3	*1.8*	**1.8**	13
	17-18.4	*9.4*	**8.1**	6.1	*2.3*	**2.2**	-14
	18.5-20.9	*19*	**15**	11	*2.5*	**2.4**	-21
	> 21	*25*	**8.2**	6	*2.4*	**1.5**	-67
Southern Bothnian Sea	12-14.9	*3.2*	**-**	-	*1.7*	**-**	-
	15-16.9	*4*	**5.4**	4.1	*1.7*	**2.4**	38
	17-18.4	*12*	**9.3**	7	*2.4*	**2.2**	-21
	18.5-20.9	*22*	**14**	9.9	*2.5*	**2.3**	-39
	> 21	*23*	**21**	15	*2.6*	**2.3**	-8
Northern Bothnian Sea	12-14.9	-	**1.6**	1.2	-	**1.7**	-
	15-16.9	-	**3.5**	2.7	-	**1.6**	-
	17-18.4	-	**8.4**	6.2	-	**2.3**	-
	18.5-20.9	-	**14**	10	-	**2.5**	-
	> 21	-	**17**	12	-	**2.7**	-
Bothnian Bay	12-14.9	*3.6*	**2.3**	1.8	*1.8*	**1.7**	-36
	15-16.9	*5.8*	**6.5**	4.9	*1.7*	**2.2**	12
	17-18.4	*16*	**8.9**	6.6	*2.1*	**2.4**	-45
	18.5-20.9	*16*	**15**	11	*2.4*	**2.7**	-8
	> 21	*24*	**-**	-	*2.7*	**-**	-

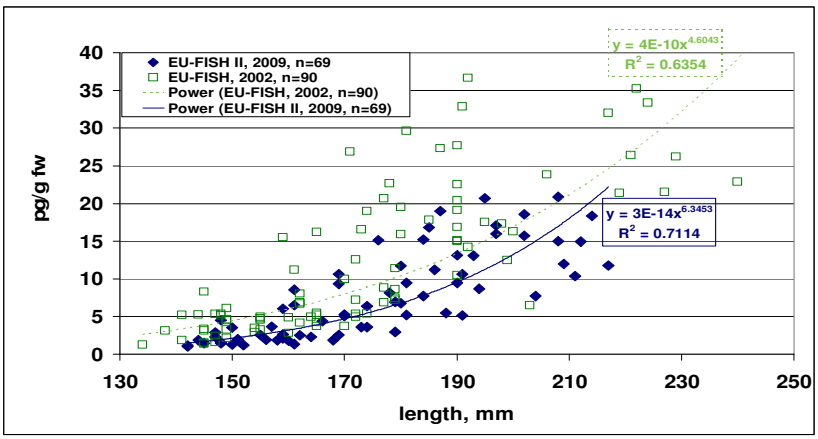

Figure 2. Total WHO-TEQ$_{98}$ concentrations of PCDD/Fs and PCBs in individual Baltic herring samples from the Bothnian Sea in 2002 and in 2009.

In Table 2, WHO-TEQs for Baltic salmon measured in 2002 and 2009 are described. The concentrations in all samples still exceed the current MLs, although the decrease in concentrations has been significant since 2002, 47% on average. The ratio of PCDD/Fs and PCBs in salmon was different from the ratio in herring. PCBs tend to accumulate in salmon more effectively than PCDD/Fs. The ratio of PCDD/Fs and PCBs was similar between sampling sites, ranging from 0.6 to 0.8. This suggests that all sampled salmon have been migrating in the Baltic Sea in a similar manner. In 2002, the salmon in the Gulf of Bothnia had a slightly higher contribution from PCDD/Fs than in the other sampling sites, which was also seen as higher concentrations. In 2002, it was concluded that those salmon had not migrated outside the Gulf of Bothnia for some reason, and had been exposed to higher concentrations of PCDD/Fs when feeding on herring in that area.

Using the new 2005 TEFs when calculating the TEQs instead of 1998 TEFs, the decrease in concentrations (22%) was slightly smaller than in Baltic herring (26%).

Table 2: Total WHO-$TEQ_{98/05}$ concentrations of PCDD/Fs and PCBs in composite samples of Baltic salmon, PCDD/F:PCB-ratio, and change between 2002–2009.

Sampling site	Size, cm	WHO-TEQ_{98}, pg/g fw		WHO-TEQ_{05}, pg/g fw	PCDD/F:PCB ratio		Decrease, %
		2002	2009	2009	2002	2009	
Eastern Gulf of Finland	76-91		16	13		0.7	
Western Gulf of Finland	80		11	8.7		0.7	
	77-102	23			0.7		-53
Archipelago Sea	82-93		13	10		0.6	
	80-101	23			0.7		-44
Southern Bothnian Sea	82-93		15	11		0.8	
	81-97	30			1.1		-51
Bothnian Bay	83-94		15	12		0.7	
	80-100	26			1.1		-41

The results of Baltic herring and salmon in the EU Fish II –project confirm that the situation with respect to EU maximum levels of PCDD/Fs and PCBs has not changed since 2002, although the levels of these contaminants have decreased. The concentrations still exceed the MLs in large herring, especially in the Gulf of Bothnia, and in all salmon sampled. In order to ensure the beneficial health effects of consuming fish, it is crucial for economic perspective and public health point of view that Finland will be granted a new derogation for placing on markets these fish species originating in the Baltic region. Dietary advice on fish consumption will protect consumers, even though Baltic herring and salmon exceed the current maximum levels of dioxins and dioxin-like PCBs.

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References:

1. Isosaari P, Hallikainen A, Kiviranta H, Vuorinen PJ, Parmanne R, Koistinen J, Vartiainen T (2006). *Environmental Pollution* 141 : 213-225
2. Bignert A, Danielsson S, Nyberg E, Asplund L, Eriksson U, Nylund K, Berger U. (2010). *Report nr 1:2010. Swedish Museum of Natural History.*
3. Parmanne R, Hallikainen A, Isosaari P, Kiviranta H, Koistinen J, Laine O, Rantakokko P, Vuorinen P and Vartiainen T (2006). *Marine Pollution Bulletin* 52 : 149-161