Papers

Polychlorinated dibenzo-*p*-dioxin, dibenzofuran and biophenyl content in selected groups of Baltic herring and sprat from Estonian coastal waters in 2006

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Abstract

The concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (DL-PCB) were determined in samples of Baltic herring (*Clupea harengus membras*) and sprat (*Sprattus sprattus balticus*) in 2006 from commercial catches in Estonian coastal waters, Baltic Sea. The dioxin content of the fish sampled in 2006 did not exceed the European Union's maximum permissible level for PCDD/Fs (4.0 pg WHO -TEQ/g fresh weight) and for the sum of PCDD/Fs and DL-PCBs (8.0 pg WHO -TEQ/g fresh weight). PCDD/Fs and the sum of PCDD/Fs and DL-PCBs content in herring were 2.12 and 3.84 pg WHO-TEQ/g of fresh weight respectively; the corresponding figures for sprat were 1.94 and 3.82 pg WHO-TEQ/g of fresh weight. Comparable with our earlier data on the content of dioxins in three to four year old herring and two to three year old sprat, these data show that two servings of fish per week are not at all harmful to the health of the Estonian people; indeed, the opposite is more likely to be the case.

1. Introduction

At a time when we are seemingly provided with abundant resources of everything, there is, however, one area that is dominated by an ever-growing shortage: this is the inadequate amount of safe food. National authorities have the responsibility and obligation to ensure that toxic chemicals are not present in food at levels that may adversely affect the health of consumers (Roots 2006).

Dioxins, as referred to in the Commission Regulation 2006/199/EC, cover a group of 75 polychlorinated dibenzo-*p*-dioxin congeners (PCDDs) and 135 polychlorinated dibenzofuran congeners (PCDFs), 17 of which are of toxicological concern. Polychlorinated biphenyls (PCBs) are a group of 209 different congeners that can be divided into two groups according to their toxicological properties: a small number (12 congeners) exhibit toxicological properties similar to those of dioxins and are therefore termed 'dioxin-like PCBs' (DL-PCBs). Commission Regulation 2006/199/EC sets maximum levels for dioxins and dioxin-like PCBs in foodstuffs. For muscle meat of fish and fishery products the limits are 4.0 pg WHO-TEQ/g fresh weight for PCDD/Fs and 8.0 pg WHO-TEQ/g fresh weight for the sum of PCDD/Fs and DL-PCBs.

When collecting fish and food product samples, the Estonian Marine Institute biologist followed European Union legislation: Council directive 91/493/EEC, which sets out the health requirements for the production and the marketing of fishery products; Commission recommendation 2004/705/EC on the monitoring of background levels of dioxins and dioxin-like PCBs in foodstuffs; Commission directive 2002/69/EC, which stipulates the sampling and analytical methods for the official control of dioxins and the determination of dioxin-like PCBs in foodstuffs.

In our earlier measurements (Roots et al. 2003, 2005, Roots & Zitko 2004, Simm et al. 2006), the PCDD and PCDF profiles in sprat (*Sprattus sprattus balticus*) were much higher than the variability of the corresponding profiles in Baltic herring (*Clupea harengus membras*). PCDD/F toxic equivalent concentrations (WHO-TEQ) increased with the age of sprat and herring, and limits higher than the EU maximum are expected for fish older than five years (Kiviranta et al. 2003, Roots et al. 2003, Roots & Zitko 2004, Parmanne et al. 2006, Roots et al. 2006, Simm et al. 2006).

The aim of this study is to determine the contents of PCDD/Fs and DL-PCBs in Baltic herring and sprat from Estonian coastal areas in 2006 and to estimate how much fish we can eat without being exposed to risk.

2. Material and methods

Baltic herring and sprat were selected for this study as the most important commercial fish species in Estonia. To determine the dioxin content in the fish, a total of seven samples from commercial catches in Estonian coastal waters, Baltic Sea, were collected during spring 2006.

The four herring and three sprat samples were obtained from the 'Lipton' in the port of Veere. The fish had been caught with a mid-water trawl in the open waters of the Baltic Sea to the west of Hiiumaa and Saaremaa (ICES rectangles 46H0 and 45H0). Samples for chemical analysis were prepared from the largest-sized (length, weight) male and female fish. The head, caudal fin and viscera of the fish were removed. The dioxin content was therefore determined from the sum of all the parts of the fish typically used for human food: the muscle, skin, fins (excluding the caudal fin) and bones.

The sampled fish were subjected to biological analysis in that their length, weight, sex and age were determined. Then, the samples were arranged according to the different size/age of the fish (the number of fish was such that the weight of one sample would be c. 300 g). The chemical analysis of samples took place at an accredited laboratory in Finland (National Public Health Institute, Department of Environmental Health, Laboratory of Chemistry, Neulaniementie 4, FI-70 210 Kuopio, Finland). The method included ASE (accelerated solvent extractor) or Soxhlet extraction of solid matrices and liquid-liquid extraction of liquid matrices, sample purification with column chromatography, and finally, HRGC-HRMS analyses of the samples. The analytical methods were the same as those used by Kiviranta et al. (2003, 2004), Parmanne et al. (2006), and Isosaari et al. (2006).

Toxic equivalents (TEQ) for PCDD/Fs and DL-PCBs were calculated using the toxic equivalency factors (TEF) adopted by WHO (Van den Berg et al. 1998). The concentrations were calculated as 'upper bound' concentrations (non-detected congeners are set as their limits of detection). In the herring samples all the analysed compounds were above the detection limit; therefore, the 'upper bound' and 'lower bound' values are equal. In the sprat samples, some of the PCDD/Fs were below the detection limit: in sample 5, two PCDDs and three PCDFs; in sample 6, OCDD and 2,3,4,6,7,8-HxCDF; and in sample 7, 2,3,4,6,7,8-HxCDF. Even though there were practically no differences in the results between the 'upper bound' and 'lower bound' values, it is the 'upper bound' values that are presented.

3. Results and discussion

3.1. Baltic herring (*Clupea harengus membras*)

Table 1 gives the results of the biological analysis of all the herring sampled (length, mass, age), together with source data.

Table 1. Baltic herring: length, mass and age (average ± SE and limits) in samples

Sample number	Number of fish	Length [cm]	Mass [g]	Age [years]
1	28	14.1 ± 0.2 12.3–15.5	16.0 ± 0.6 9.2–23.1	3.9 ± 0.2 3–6
2	24	14.7 ± 0.2 13.2–17.0	19.2 ± 0.8 11.2–27.6	4.3 ± 0.2 3–7
3	26	14.4 ±0.2 13.1–16.5	17.2 ±0.6 11.5–22.6	3.5 ± 0.2 2–6
4	24	14.5 ± 0.2 12.4–16.2	12.8–23.9	3–6

The average length of the herring was 14.4 ± 0.1 cm (range: 12.3 –17.0 cm); the average mass was 17.6 ± 3.4 g (range: 9.2–27.6 g). In different samples, the length and mass of fish did not vary significantly, even though the herring in sample 2 (Table 1) were somewhat longer and heavier. There were more female than male herring – 56.9% and 43.1% respectively, and the age range was from two to seven years (av. = 3.9 ± 1.0 years). Again, the fish in sample 2 were somewhat older.

On the basis of all the average concentration data of the herring analysed (pg/g fresh weight), the dominant PCDD/F congeners were found to be 2,3,4,7,8-PeCDF (39%) and 2,3,7,8-TCDF (28%).

The toxic equivalent concentration (pg WHO-TEQ/g fresh weight) was also dominated by 2,3,4,7,8-PeCDF (61%), followed by 1,2,3,7,8 -PeCDD (16%). Therefore, the dominant compounds were PCDDs with respect to concentration and PCDFs with respect to toxic equivalent concentration (86 and 75% respectively; see Table 2). In the case of DL -PCBs, the concentrations of congeners CB-118 (58%) and CB-105 (20%) were dominant, whereas CB-126 (70%) and CB-118 (12%) were dominant on the basis of the toxic equivalent concentration. On a concentration basis, therefore, mono-*ortho* PCBs (99%) were dominant, but on a toxic equivalent concentration, non-*ortho* PCBs (72%) were dominant. Based on concentration (Table 2), DL-PCBs (totalling an average of 99%) were overwhelmingly dominant in herring samples, whereas based on toxic

Table 2. Content (pg/g fresh weight) and toxic equivalent concentration (pg WHO-TEQ/g fresh weight) of PCDD/Fs and DL-PCBs in 2006 herring samples

Compound	Sample number			
	1	2	3	4
pg/g fresh weight				
PCDDs	1.1	1.1	0.8	0.8
PCDFs	6.5	6.3	5.2	5.2
Sum of PCDD/Fs	**7.6**	**7.4**	**6.0**	**6.0**
Non-*ortho* PCBs	50	52	39	42
Mono-*ortho* PCBs	3718	3859	2921	3052
Sum of DL-PCBs	3768	3911	2960	3094
Sum of PCDD/Fs and DL-PCBs	**3775**	**3919**	**2966**	**3100**
pg WHO-TEQ/g fresh weight				
PCDDs	0.63	0.61	0.43	0.48
PCDFs	1.78	1.75	1.38	1.43
Sum of PCDD/Fs	**2.40**	**2.36**	**1.81**	**1.91**
Non-*ortho* PCBs	1.40	1.41	1.03	1.12
Mono-*ortho* PCBs	0.52	0.55	0.41	0.43
Sum of DL-PCBs	1.92	1.96	1.44	1.55
Sum of PCDD/Fs and DL-PCBs	**4.33**	**4.32**	**3.25**	**3.46**

equivalent concentration the percentage of PCDD/Fs was somewhat higher than that of DL-PCBs (55% and 45% respectively). In none of the analysed samples did the content of PCDD/Fs and DL-PCBs exceed EU limits (Table 2).

Based on the average data, the PCDD/F and DL-PCB content in herring was 2.12 and 1.72 pg WHO-TEQ/g of fresh weight, which yields a total dioxin content of 3.84 pg WHO-TEQ/g of fresh weight. The results were in agreement with our earlier data on the content of dioxins in three to four year old herring.

The total content of dioxins (sum of PCDD/F and DL-PCB) in herring increases with the age of the fish analysed. According to our earlier data (Roots et al. 2003), the PCDD/F content was already hazardous (containing >4 pg TEQ/g of fresh weight) in 5–6 year old herring.

3.2. Sprat (*Sprattus sprattus balticus*)

The length of the sprat ranged from 7.4 to 12.6 cm (av. $= 10.2 \pm 0.1$ cm; the average mass was 6.2 ± 0.1 g (range: 1.9–11.3 g). The length and mass of the fish in different samples did not differ significantly (Table 3). There

Table 3. Average (av. ±SE and limits) length, mass and age of sprat in samples

Sample number	Number of fish	Length [cm]	Mass [g]	Age [years]
5	65	10.2 ± 0.1 7.4–12.6	64.0 ± 0.2 2.2–11.3	2.3 ± 0.1 1–5
6	72	10.4 ± 0.1 8.6–12.5	6.5 ± 0.1 3.5–9.8	2.3 ± 0.1 1–4
7	76	9.9 ±0.1 7.5–12.2	5.8 ±0.2 1.9–10.3	2.1 ± 0.1 1–4

were practically equal percentages of the sexes in the samples: females – 46.2%, males – 53.2%, and the average age of the sprat was 2.2 ± 0.1 years (range: 1–5 years).

Based on the concentration data of all the sprat analysed, the dominant PCDD/F compounds were 2,3,7,8-TCDF (40%) and 2,3,4,7,8-PeCDF (30%). The toxic equivalent concentration was also dominated by 2,3,4,7,8 -PeCDF (55%), followed by 1,2,3,7,8-PeCDD (16%) and 2,3,7,8-TCDF (15%). Therefore, the dominant compounds were PCDDs with respect to concentration (86%) and PCDFs with respect to toxic equivalent concentration (74%) (see Table 4). In the case of DL-PCBs, the congeners CB-118 (58%) and CB-105 (20%) were dominant with respect to concentration, whereas CB-126 (74%) and CB-118 (10%) were dominant with respect to toxic equivalent concentration. Based on concentration the dominant DL-PCB compounds were mono-*ortho* PCBs (98%), but based on toxic equivalent concentration the non-*ortho* PCBs (75%) were dominant. Based on average concentration data, DL-PCBs were overwhelmingly dominant in sprat (totalling 99.8% on average), while based on toxic equivalent concentration PCDD/Fs were somewhat higher than DL-PCBs (51% and 49% respectively).

In none of the analysed sprat did the PCDD/F and DL-PCB content exceed EU limits (Table 4). Based on the average data of all analysed samples, the respective PCDD/F and DL-PCB contents were 1.94 and 1.87 pg WHO-TEQ/g of fresh weight, which gives a total dioxin content of 3.82 pg WHO-TEQ/g of fresh weight. The results are in agreement with our earlier data on the content of dioxins in two to three year old sprat (Pandelova et al. 2006, Roots et al. 2006, Simm et al. 2006).

The total content of dioxins (sum of PCDD/Fs and DL-PCBs) in sprat increases with the age of the fish analysed. With the aid of data from previous years, it was determined that the content exceeded established

Table 4. Content (pg/g fresh weight) and toxic equivalent concentration (pg WHO-TEQ/g fresh weight) of PCDD/Fs and DL-PCBs in 2006 sprat samples

Compound	Sample number		
	5	6	7
pg/g fresh weight			
PCDDs	1.2	0.9	0.9
PCDFs	7.0	6.2	5.9
Sum of PCDD/Fs	**8.2**	**7.1**	**6.7**
Non-*ortho* PCBs	76	73	66
Mono-*ortho* PCBs	3501	3389	3008
Sum of DL-PCBs	3577	3462	3074
Sum of PCDD/Fs and DL-PCBs	**3586**	**3469**	**3081**
pg WHO-TEQ/g fresh weight			
PCDDs	0.50	0.52	0.46
PCDFs	1.52	1.44	1.37
Sum of PCDD/Fs	**2.02**	**1.96**	**1.83**
Non-*ortho* PCBs	1.49	1.43	1.32
Mono-*ortho* PCBs	0.49	0.47	0.42
Sum of DL-PCBs	1.98	1.90	1.74
Sum of PCDD/Fs and DL-PCBs	**4.0**	**3.86**	**3.57**

limits (8.0 pg WHO-TEQ/g of fresh weight) in 5.3 year old fish. According to our earlier data, the PCDD/F content is already hazardous (over 4 pg WHO-TEQ/g of fresh weight) in sprat over five years old. Therefore, the total content of dioxins does not change the acceptable age of sprat for human consumption.

3.3. How much and what can we eat without being exposed to risk?

Thanks to the assistance of the Estonian Ministry of Agriculture it has been possible to study persistent organic pollutants in the fish of the Baltic Sea and to a smaller degree in the fish of Lake Peipus as well. Fish and fish products play a significant role in the dietary intake of PCDD/Fs. In Finland, Baltic herring alone accounted for 52% of the total intake of PCDD/Fs (Kiviranta et al. 2003).

On 30 May 2001 the Scientific Committee for Food (SCF) adopted an Opinion on the Risk Assessment of Dioxins and Dioxin-like PCBs in Food, updating its Opinion of 22 November 2000 on this subject on the basis of fresh scientific evidence that had become available since the latter's adoption. The SCF fixed a tolerable weekly intake (TWI) of 14 pg WHO -TEQ/kg body weight for PCDD/Fs and DL-PCBs. Data from surveys conducted in Baltic Countries in the summer of 1997 were used (Pomerleau et al. 2001). Information was collected using a 24 h recall of dietary intake and an interviewer-administered questionnaire. Representative national samples of adults were selected. All the information from the dietary recall has been included in this study (Table 5). The proportion of men and women were similar to those found in the general adult population of Estonia. Respondents tended to be slightly younger than the general adult population of Estonia (Pomerleau et al. 2001).

Table 5. Mean (standard deviation) daily intake [g] of food items by sex and age group in Estonia (Pomerleau et al. 2001)

Age	All ages		19–34		35–49		50 +	
Sex	Men	Women	Men	Women	Men	Women	Men	Women
				No. of humans analysed				
	900	1115	396	459	319	376	185	280
				Milk & milk products				
Mean	328	296	331	301	304	284	360	306
(s.d.)	(383)	(296)	(389)	(296)	(386)	(258)	(365)	(263)
Median	233	250	244	250	200	243	264	250
				Milk & meat products				
Mean	198	123	223	134	188	126	163	102
(s.d)	(172)	(123)	(184)	(119)	(168)	(115)	(140)	(98)
Median	166	100	188	104	150	100	150	81
				Fish				
Mean	24	22	21	21	21	19	37	30
(s.d.)	(72)	(22)	(65)	(55)	(61)	(66)	(96)	(74)
Median	0	0	0	0	0	0	0	0

The dioxin content in fish has been fairly exhaustively studied in Estonia (Roots & Zitko 2004, 2006, Roots et al. 2006, Simm et al. 2006). No risk is incurred by perch, pike-perch or flounder. The Atlantic salmon, the sea trout and the eels caught in the Baltic Sea have not been adequately examined so far, because these fish species are caught (eaten) in Estonia to a relatively small extent and their proportion in human consumption is inconsiderable. People should be also moderate in their consumption of the river lamprey. In general, however, two servings of fish per week are not at all harmful to the health of the Estonian people; indeed, the opposite is more likely to be the case (Roots et al. 2004, Roots 2006, Roots & Simm 2006).

As far as the Baltic herring is concerned, the consumption of 'large Baltic herring' longer than 17 cm and five years old should be avoided or at least restricted (especially by pregnant women). At the present time, the Baltic herring in Estonian coastal waters are mostly 2–4 years old (Roots & Simm 2006).

The surveys should be continued for a number of years and the results presented and evaluated in terms of both TEQs and weight concentrations.

The concentrations of PCDD and PCDF congeners in four-year-old trout from Lake Ontario have not changed much over a period of 16 years. This may mean that the PCDD and PCDF concentration in fish from the Baltic could also remain fairly constant over a number of years (Huestis et al. 1997). Since year-on-year concentrations do not appear to change very much, it would be better to carry out surveys only every 3–4 years, to stratify the sampling according to the age and sex of the fish, and to analyse replicate extracts by replicate measurements (Roots & Zitko 2004).

4. Conclusion

The dioxin content in Baltic herring and sprat sampled in 2006 did not exceed established EU limits (8.0 pg WHO-TEQ/g fresh weight). The PCDD/F and total (sum of PCDD/Fs and DL-PCBs) dioxin content in herring were 2.12 and 3.84 pg WHO-TEQ/g fresh weight respectively; the corresponding figures for sprat were and 1.94 and 3.82 pg WHO-TEQ/g fresh weight. These results are comparable with our earlier data concerning the content of dioxins in three to four year old herring and in two to three year old sprat: two servings of fish per week are not at all harmful to the health of the Estonian people; indeed, the opposite is more likely to be the case.

The total dioxin content in herring and sprat increases with the age of the fish. The EU maximum permissible level of 8.0 pg WHO-TEQ/g fresh weight is exceeded by the total dioxin content in 7.5-year-old herring and 5.3-year-old sprat. Based on PCDD/F content, only five-year-old and older herring and sprat are hazardous (containing > 4 pg WHO-TEQ/g fresh weight). Apparently, the established limit for the total dioxin content does not reduce the age of herring and sprat suitable for human consumption. As far as the fish are concerned, the investigation of industrial fish – herring and sprat – should be continued in 2007.

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