Levels of PCDD/Fs and \"dioxin like\" PCBs in the perch from the north-eastern part of the Baltic Sea

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Introduction

From point of view of the health of human the most interesting persistent organic pollutants (POP) are the polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in the nutrition, in the case of the Baltic Sea, first and foremost in the fish. It is expected that the people living clouse to the Baltic Sea receive 63-83% of the total PCDD/Fs from the fish (1). The concentrations of dioxins in the samples of herring (*Clupea harengus membras*) and sprat (*Sprattus sprattus*), analyzed in the year 2002, did not exceed the limits, established by the European Union, as a rule. The only exception was herring older than six years, caught from the open part of the Baltic Sea. In this sample the dioxin level was 4.5 pg TEQ/g wet weight (2). As there is limited information, concerning the dioxin and “dioxin like PCBs” level in the perch (*Perca fluviatilis*), in 2003 the aforementioned fish was caught for analysis and a spatial evaluation in the Gulf of Riga (Pärnu Bay).

Materials and Methods

Perch is one of the most abundant fish species in Estonian coastal waters. The Estonian total annual catch (from the sea) in the years 1994-1997 was from 300 to 600 t and has a decreasing trend. The main coastal fishing areas are Matsalu Bay, the Väinameri (Moonsund) Archipelago, and Pärnu Bay in the Gulf of Riga (3). The samples of perch, in total six (marked from A1203 to A1703), were collected from the Gulf of Riga (Pärnu Bay) on June 2 and 11, 2003. The length of the fish, included in the samples, was between 15 to 28 cm while the weight was, respectively, from 30.0 to 245.6 g (Table 1). The age of the perch in the samples analyzed remains between two to six years (Table 2). Samples A1203 to A1503 consists only of male and, respectively, sample A1603 of female fish. In samples A1703 the ratio of gender was – female/male – 2/1. As a rule, the gonads of all the fish analyzed had reached the maturity level V-VI.

Table 1. Length and weight of perch, collected from the Gulf of Riga (Pärnu Bay) in 2003

Sample	n	Length (cm)		Weight (g)	
		avg ± SE	Limits	avg ± SE	Limits
A1203	9	15.8 ± 0.2	15.0 – 16.6	38.7 ± 2.3	30.0 – 50.0
A1303	6	18.1 ± 0.2	17.6 – 18.6	57.5 ± 2.0	50.0 – 62.0
A1403	5	20.1 ± 0.1	19.8 – 20.4	81.2 ± 3.8	69.0 – 93.0
A1503	4	21.7 ± 0.2	21.2 – 22.0	94.8 ± 1.9	90.3 – 101.0
A1603	4	23.8 ± 0.2	23.1 – 24.3	146.5 ± 10.3	117.4 – 175.3
A1703	3	26.7 ± 0.7	25.1 – 28.0	207.4 ± 19.7	162.9 – 245.6

Table 2. Age of perch and level of lipids in samples collected from the Gulf of Riga (Pärnu Bay) in 2003

Sample	n	Lipids	Age (years)	
		(% for wet weight)	avg ± SE	limits
A1203	9	0.8	2.6 ± 0.2	2 – 3
A1303	6	0.8	3.5 ± 0.2	3 – 4
A1403	5	0.8	4.2 ± 0.2	4 – 5
A1503	4	0.6	5.0 ± 0.0	5
A1603	4	0.8	5.0 ± 0.0	5
A1703	3	0.8	5.7 ± 0.3	5 – 6

The analysis of fish samples was done at the Institute of Ecological Chemistry of the National Research Centre for Environment and Health in Neuherberg (Germany). The Centre has been accreditated in Germany for determination of dioxins and polychlorinated biphenyls (accreditation licence No. DAC-P-0141-01-00 valid through 21.11.2006). In brief the fish were freeze dried, homogenized before being extracted by employing accelerated solvent extraction. Cleanup encompassed a silica column coated with layers of H_2SO_4 and NaOH followed by column chromatography on a column filled with aluminiumoxide and florisil each. Identification and quantification was achieved by ^{13}C-labelled standards and HRGC-HRMS measurements.

Results and Discussion

The terms of reference, concerning the collection of fish samples and biological and chemical analysis, have been met. The results of the analysis allow to assess the size/age dynamics of the level of PCDD/Fs and “dioxin like PCBs” in the perch, living in the coastal waters of Estonia.

In all the samples of perch analyzed, the dioxin level remained well below the limits established by the EU. According to the average data (Table 3), the level of PCDD/Fs and PCB compounds, "dioxin like PCBs", is practically equal, amounting to, respectively 46.2 and 53.8 %. As it was the case with the herring and sprat, the PCDFs concentration exceeds the PCDDs content. The concentration of non-ortho-PCBs, differently from sprats and herrings, exceeds the level of mono-ortho-PCBs by half. The dominant isomers in the perch are PCB 126 (31.0%) and 2,3,4,7,8-PeCDF (24.9%).

*Table 3.*Average dioxin content (avg ± SE) in samples of perch, collected in 2003

Dioxin	pg TEQ/g for wet weight	pg TEQ/g for lipids
PCDDs	0.25 ± 0.03	33.6 ± 4.6
PCDFs	0.42 ± 0.05	56.6 ± 9.2
PCDD/Fs	0.67 ± 0.08	90.2 ± 13.6
non-ortho-PCBs	0.50 ± 0.07	67.9 ± 13.1
mono-ortho-PCBs	0.27 ± 0.05	37.3 ± 9.3
PCBs	0.77 ± 0.12	105.2 ± 22.4
Sum of PCDD/Fs and PCBs	1.45 ± 0.19	195.3 ± 35.5

The dioxin level in younger fish, aged from two to five years, is somewhat lower than that in the older fish, where the age exceeds five years. The respective average indicators have been given in table 4.

*Table 4.*Average dioxin concentration (pg TEQ/g for wet weight) in perch of different age

Age of fish	Less than five years	More than five years
PCDDs	0.20 ± 0.02	0.30 ± 0.04
PCDFs	0.33 ± 0.02	0.51 ± 0.08
PCDD/Fs	0.54 ± 0.01	0.81 ± 0.11
non-ortho-PCBs	0.38 ± 0.01	0.62 ± 0.09
mono-ortho-PCBs	0.19 ± 0.01	0.36 ± 0.08
PCBs	0.56 ± 0.02	0.98 ± 0.16
Sum of PCDD/Fs and PCBs	1.10 ± 0.01	1.79 ± 0.26

None of the perch samples, collected in 2003, exceeded the limit for the concentration of dioxin, established by the EU. The analysis of six samples of fish should be provisionally satisfying both for testing of dioxin and "dioxin like PCBs" level in perch and informing the consumers of the amount of toxicants consumed when eating perch.

Acknowledgments

The project was financially supported by the Ministry of the Agriculture (Contract No. 133).

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