

Polychlorinated dibenzo-p-dioxins, dibenzofurans and dioxin-like polychlorinated biphenyl patterns in Estonian food.

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Introduction

The Baltic Sea is highly contaminated with polychlorinated dibenzo-p-dioxins (CDD), polychlorinated dibenzofurans (CDF) and dioxin-like (planar) polychlorinated biphenyls (PCPB). The concentrations of these compounds are most often measured in the Baltic herring (*Clupeaharengusmembras L.*). The Baltic herring are a very good species for monitoring purposes since they can be caught in all parts of the Baltic, their biology is fairly well known [1-2], and they are of suitable size for pre-analytical sample treatment. Baltic herring and sprat are also the most important fish species in the Baltic and are of considerable importance for the Estonian fish-processing industry. This paper reports the concentrations of polychlorinated dibenzo-p-dioxins (CDD), polychlorinated dibenzofurans (CDF), and dioxin-like (planar) polychlorinated biphenyls (PCPB) in Baltic herring (*Clupeaharengusmembras L.*), caught in 2003. The concentrations are compared with those found in fish landed in 2002 in fish landed in 2002 [2] and in the 1990s [3].

Methods and Materials

Baltic herring was caught between May 2003 and June 2003 by industrial trawlers along the Estonian coast [4]. The fish were immediately frozen. Before the analysis, their length, weight, gender, and the maturity of gonads were determined. Samples of muscle were submitted for chemical analysis.

Because there are no facilities for analysing dioxins and furans in Estonia the analysis of the Baltic herring and sprat samples was done at the Institute of Ecological Chemistry of the National Research Centre for Environment and Health in Neuherberg (Germany). The laboratory has been accredited 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 H₂SO₄ and NaOH followed by column chromatography on a column filled with aluminiumoxide and florisil each. Identification and quantification was achieved by ¹³C-labelled standards and HRGC-HRMS measurements.

Results and Discussion

A previous study [2] suggested that age of the fish is a major factor affecting the levels, and, to some extent also the congener profiles of CDD and CDF in herring. This paper reports the results of a similar study, performed a year later, and compares them with results obtained by another laboratory on herring collected in the 1990s [3]. Baltic herring (Table 1) were collected in the Central Baltic, in the western Gulf of Finland and in the Gulf of Riga. In comparison with the samples collected in 2002 and in the 1990s, the codes of the former are as in the reference [2].

Table 1. A comparison of the median CDD, CDF, and PCB concentrations (pg/g lipid and pg/ fish) in herring, reported in Kiviranta et al. [3], Roots et al. [2;4] and in this work.

	[3]	[2;4]	This work	[3]	[2;4]	This work
Lipids (%)	1.9	9.5	3.1			
Length, cm	17.4	14.75	16.05			
Weight, g	30	22.35	24.5			
Age, years	5.5	3	4.5			
Code	pg/g lipid		pg/fish			
66d 2378D	15	1.65	5.9	8.55	3.50	4.48
76d 12378D	64	2.65	14.6	36.5	5.63	11.1
F6d 123478D	4.1	0.13	3.25	2.34	0.28	2.47
77d 123678D	66	2.3	9.3	37.6	4.88	7.06
7Ed 123789D	5.80	0.0975	0.74	3.31	0.21	0.56
F7d 1234678D	11	1.2	3.5	6.27	2.55	2.66
FFd OCDD	34	5.6	4.35	19.4	11.89	3.30
66f 2378F	76	22.3	86.4	43.3	47.24	65.6
76f 12378F	52	2.45	17.9	29.6	5.20	13.6
E6f 23478F	390	22.3	107	222	47.24	81.3
F6f 123478F	20	0.835	4.75	11.4	1.77	3.61
77f 123678F	23	0.885	6.85	13.11	1.88	5.20
7Ef 123789F		0.0275	0.82	0	0.06	0.62
E7f 234678F	24	1.45	7.1	13.68	3.08	5.39
F7f 1234678F	11	1.20	2.45	6.27	2.55	1.86
FEf 1234789F		0.0725	0.68	0	0.15	0.52
FFf OCDF	2.9	2.4	2.95	1.65	5.10	2.24
CDD/F						
TEQ	271	18.1	79.6	155	38.5	60.4
77	1200		1507	684		1145
81			28.0			21.2
126	1040		431.5	593		328
169	480		378.5	274		287
105	88		417	685	0.16	317
114			1916			1455
118	130		103	271	74.1	784
123			10129			7693
156	18		138	951	0.26	105
157			3251			2469
167			7030			5339
189			1097			833
PPCB						
TEQ	109		72.3	62.1		54.9
Total						
TEQ	380		153	217		116

The concentrations in fish of the same age do not differ noticeably between 2002 and 2003. The concentrations (pg/g lipid) of CDD and CDF in herring from 2002 and 2003 are lower than the concentrations reported by Kiviranta et al. 2003 [3] partly because of a high lipid content in the former.

After the spawning, chlororganic compounds levels decreased, probably partially excreted during this process.

Comparing the results, it appears that total chlororganic compounds levels in fish with maturity levels VI-II (fish's organism rests from spawning) is significantly lower than in maturity level III and IV specimens [5]. Surprisingly, the concentrations of the chlorobiphenyls 105, 118, and 156 are much higher in the fish studied in this work, than in those reported in [3]. Unfortunately, a more detailed evaluation of complete chlorobiphenyl profiles cannot be carried out, because concentrations of nonplanar chlorobiphenyls are not available for herring in the work [2].

An important factor for the concentration of CDD, CDF, and PPCB is the age of the fish. Monitoring programs should be using fish samples of well-defined age [2;4;6].

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References

1. Lankov A. & Kukk H. 2002. Feeding of herring in the Gulf of Finland in the 1970s-90s. Proc. Estonian Acad. Sci. Biol. Ecol., 51:277-293.
2. Roots O. & Zitko V. 2004. Chlorinated Dibenzo-p-dioxins and Dibenzofurans in the Baltic Herring and Sprat of Estonian Coastal Waters. Environmental Science & Pollution Research, 11:186-193.
3. Kiviranta H., Vartiainen T., Parmanne R., Hallikainen A. & Koistinen J. 2003. PCDD/Fs and PCBs in Baltic herring during the 1990s. Chemosphere: 50:1201-1216.
4. Otsa E., Roots O. & Simm M. 2003. Level of dioxins and polychlorinated biphenyls, similar to dioxins, in the fish in the coastal sea of Estonia in the year 2003. Estonian Environmental Research Centre. Contract No.133, <http://www.agri.ee/eng>.
5. Roots, O., Järv, L. & Simm, M. 2004. DDT and PCB concentrations dependency on the biology and domicile of fish: an example of perch (*Perca fluviatilis* L.) in Estonian coastal sea. FEB., 13, No. 7, 620-625.
6. Balodis, M. 2003. Monitoring of dioxins levels in the fish of Baltic Sea and Gulf of Riga. Integrated dioxin and PCB monitoring in the Baltic region. Brussel, May 5, 2003 (Latvian presentation).