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 (PPCB).The concentrations of these compounds are most often measured in the Baltic herring (*Clupea harengus membras 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 (PPCB) in Baltic herring 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 were 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 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 and homogenized before being extracted using 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 aluminium oxide and florisil. Identification and quantification was achieved using ^{13}C-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 (Table1) 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 described in Roots and Zitko.[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 and co-workers[2, 4] and in this work.

				This			This
		[3]	[2;4]	work	[3]	[2;4]	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	.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	7.11	3.68	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	1.653	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		4176	850.16		31723
	114			1916			1455
	118	130		103271	74.1		78434
	123			10129			7693
	156	18		1389	510.26		10553
	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.[3] partly because of a high lipid content in the former. After the spawning, organochlorine compound levels decreased, probably partially excreted during this process. Comparing the results, it appears that total organochlorine compound levels in fish with maturity levels VI-II (when the 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, then in those reported in Kiviranta et al.[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 Roots and Zitko.[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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