CHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS PATTERNS IN THE BALTIC HERRING AND SPRAT

O.Roots[1], V. Zitko[2] and I. Holoubek[3]

[1] Estonian Environmental Research Centre, 10 617 Tallinn Marja 4D, Estonia (e-mail:ott@klab.envir.ee)
[2] Marine Environmental Science (Consultant), 114 Reed Ave, St.Andrews, NB, E5B 1A1,Canada
[3] RECETOX-TOCOEN & Associates, 625 00 Brno, Kamenice 126/3, Czech Republic

Introduction

Contents of persistent organic pollutants in the sea organisms have been studied in Estonia since the early seventies [1]. In our earlier work the profile of polychlorinated biphenyls in grey seals from the Baltic, Eastern and Northern-Eastern England, and the St. Lawrence Estuary (Canada), were examined by Principal Component Analysis (PCA). The patterns differ between juveniles and adult animals, but the gender of adults and geography do not appear to play a role [2]. The objective of this paper is to examine the patterns of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in the Baltic herring (Clupea harengus) and sprat (Sprattus sprattus).

Methods and Materials

In the end of September – beginning of October, 2002, fish samples were taken for testing the dioxin level were collected from four areas of Estonian coastal sea. The analysis of fish samples was done at the Institute of Ecological Chemistry of the National Research Centre for Environment and Health in Neuhenberg (Germany). The concentrations of PCDDs/Fs in herring and sprat (Table 1) are in Table 2. Table 3 contains the description of an abbreviated coding of the positions of chlorine atoms in the PCDDs/Fs. The concentrations were centered by subtracting means, and scaled by dividing by standard deviations. For an examination of the CDDF 'profiles', the concentrations were adjusted to a sum of 100 (%) before centering and scaling (Table 4). The data were analyzed by Principal Component Analysis (PCA).

Results and Discussion

In the 1980s-90s the feeding of pelagic fishes, changed due to altered hydrological conditions. The feeding intensity of herring decreased and its food spectrum shifted towards the energetically less valuable zooplankton. As a result, the mean body weight of herring and sprat decreased significantly. Increase in the percentage rate of empty stomachs of Baltic herring and sprat in the beginning of 1990s may turn out to be one of the reasons for the decrease of persistent organic pollutants concentration in Baltic fish and seals.

Table 1: Size, age and maturity distribution of the fish

			Mean cm	Median cm	Mean g	Median g	Median age	I	II	II-III	III	III-IV	F	M
Central Baltic	Herring	B1	17.6	17.6	37.4	37.7	5		1	2	5	1	7	3
		B2	16.1	16	29.3	28.55	4.5			7	5		10	3
		B3	15.5	15.65	27.4	27.05	3			5	7		8	4
Western Gulf of Finland	Herring	T1	15.1	14.95	23.3	23	3		8	2	4		7	7
		T2	14	14.1	18.2	17.95	2		17		3		15	5

		T3	13.6	13.6	17.3	17.2	1.5		16		4		9	10
Middle Gulf of Finland	Herring	K1	15.4	15.05	23.6	23.1	4		3	7	4		2	12
		K2	14.4	14.55	20.1	20.15	3		5	3	12		7	13
		K3	14.3	13.95	19.3	17.85	2.5		7	2	9	2	4	10
Gulf of Riga	Herring	R1	16.2	16.1	28.9	28.15	4		5	2	5		8	4
		R2	14.5	14.4	21.3	21.7	2		2	5	10	1	8	10
		R3	14.3	14.45	20.4	20.85	2		5	2	11		7	11
Central Baltic	Sprat	B4	12	12	11.2	11.15	2		1	22	7		19	11
		B5	12	11.95	10.9	10.65	2.5			18	12		11	19
Western Gulf of Finland	Sprat	T4	12.6	12.55	12.8	12.7	3		24	2			21	5
		T5	12	12	11.7	11.7	3		24		2		14	12
		T6	12.1	12	11.8	11.8	3		29				18	11
		T7	11.8	11.8	11.2	11	3	1	34				19	16
Middle Gulf of Finland	Sprat	K4	11.8	11.7	11	10.9	2		16	17	2		19	16
		K5	11.6	11.5	10.3	10.1	2		27	7	1		8	27

Table 2: Concentrations of chlorinated PCDDs/Fs. The chlorine substitution patters of the individual congeners (column 1) are coded according to Table 3.

	b1	b2	b3	b4	b5	k1	k2	k3	k4	k5	t1	t2	t3	t4	t5	t6	t7	r1	r2	r3
66d	2.4	2.2	2.3	1.6	1.1	0.82	2.1	1.2	0.61	1.5	2.5	0.57	1.1	0.6	1.5	0.86	0.89	1.8	1.5	0.97
76d	7.1	5	4.1	2.7	2.9	5.8	2.2	2.7	1.3	3.3	5.5	2	1.5	3.4	2.6	3.4	2.2	2.6	1.5	1.2
F6d	1.3	0.61	0.07	0.38	0.45	0.15	0.11	0.08	0.31	2.3	0.94	0.11	0.11	0.48	0.055	0.51	0.36	0.73	0.28	0.05
77d	4.2	3	2.6	2.6	2.6	4.2	2	1.7	1.6	5.4	3.6	2.9	2	2.8	2.5	3.1	2.6	1.1	1.1	0.6
7Ed	0.36	0.44	0.42	0.38	0.07	0.15	0.1	0.08	0.06	2.4	0.1	0.095	0.11	0.23	0.05	0.23	0.13	0.08	0.065	0.05
F7d	2.1	1.2	1.7	1.7	3.3	0.17	0.47	1.2	0.88	7.6	1.6	2.3	1.7	2.1	1.3	3.1	2.1	0.91	1.1	0.92
FFd	10.1	6.1	6.3	5.1	20.8	2.2	2.6	5.1	2.6	60	8.5	11.3	7.9	6.5	2.6	10.5	3.3	2.4	3.2	1.9
66f	32.2	33.7	30.2	20.1	21.2	24.3	21.8	23	16.3	20.4	21.9	19.2	16	21.6	21.8	18.8	18.9	22.6	19.1	18.6
76f	7.1	6.4	4.9	4.7	4.4	2.9	1.8	1.9	1.6	2.8	2.7	1.8	1.1	3.9	4.6	3.7	3	3.8	2.2	1.9
E6f	45.1	31.6	25.5	17.2	19.4	38.1	18.3	19	13.1	13.6	29.4	17.4	10.6	22.7	18.4	17.7	14.2	30.9	15.2	16.8
F6f	2.1	2.1	1.1	1.3	2.6	0.91	0.49	0.55	0.35	2.4	0.9	0.83	0.35	0.95	1	1.2	0.83	0.75	0.84	0.58
77f	3.3	2.6	1.6	2.2	2.2	1.6	0.56	0.45	0.83	2.4	1.6	0.7	0.82	1.8	1	2.1	1.2	0.95	0.54	0.74
7Ef	0.015	0.03	0.02	0.02	0.05	0.04	0.04	0.04	0.03	1.8	0.035	0.035	0.025	0.015	0.025	0.03	0.025	0.02	0.025	0.02
E7f	2.9	2.1	1.8	2.1	4.8	1.8	1.2	1.2	0.94	2.8	1.8	1.7	1.1	2.5	1.9	1.9	1.9	1.1	0.93	0.91
F7f	2.1	1.3	0.66	1	10.2	0.82	1.1	2.6	1.5	9.6	1.3	1.8	1.6	1.4	1	1.4	1.1	0.53	0.55	0.49
FEf	0.06	0.05	0.11	0.07	0.3	0.14	0.22	0.13	0.11	4.9	0.075	0.08	0.07	0.045	0.045	0.07	0.05	0.05	0.045	0.04
FFf	8.5	3.1	0.46	0.37	46	0.6	0.85	10	0.32	128	4.3	3.2	5.2	2.5	2.2	2.5	1	1.6	1.7	1.4

Table 3 Coding of substitution patterns [7].

							Substitution	Value
Position in right ring	1	2	3	4			2,3 or 7,8	2+4=6
Position in left ring	6	7	8	9			1,2,3 or 6,7,8	1+2+4=7
Value	**1**	**2**	**4**	**8**			2,3,4 or 7,8,9	2+4+8=14=E
Code for sums >9	10	11	12	13	14	15	1,2,3,4 or 6,7,8,9	1+2+4+8=15=F
	A	B	C	D	E	F	For CDD ‘d’’, for CDF ‘f’ are added	

As can be seen from the projection of the concentrations on the plane of the principal components 1 & 2 (Fig. 1), the sample K5 is an ‘outlier’ and so are, to some extent also the samples B1, B2 and, particularly. B5.

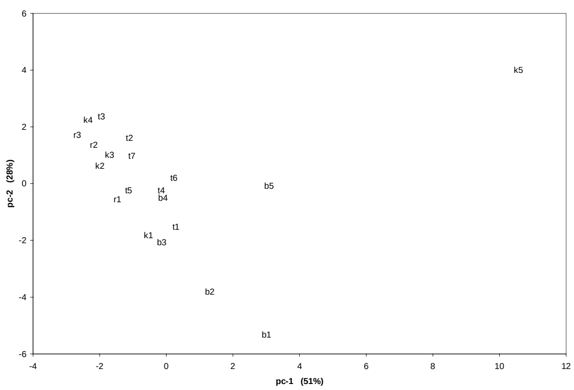

Figure 1: Projection of the samples on the plane of the principal components 1 & 2. Fractions of original variance, accounted for, are indicated on the axes. For sample codes see Table 1.

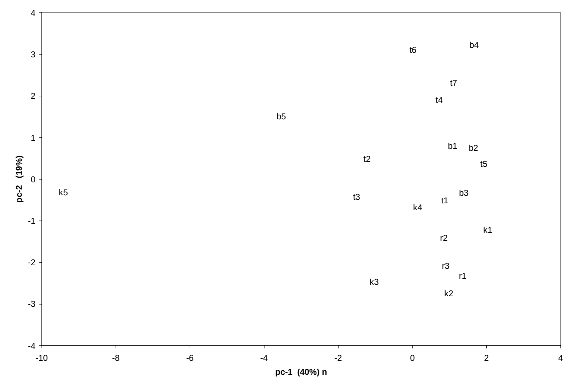

Figure 2: Projection of adjusted PCDDs/Fs concentrations on the plane of the principal components 1 & 2. Fractions of original variance accounted for are indicated on the axes. For sample codes see Table 1.

The Principal component 1, pc-1 separates the samples primarily according to increasing concentrations of PCDDs/Fs. The second principal component, pc-2, is also affected to some extent by the total PCDDs/Fs concentration, however, the projection on the plane of these two principal components shows the overall patterns of the data. The PCDDs/Fs concentrations in Central Baltic herring decrease from B1 to B3. This decreasing could be age-related (Table 1). The PCDDs/Fs profiles are very similar, as indicated by the tight ‘cluster’ of the adjusted concentration, projected on the planes of the principal components pc-1 & pc-2 (Fig. 2) and pc1 & pc-3 (Fig. 3). Sprats from the same area (B4, B5) are smaller and younger than the herring. This could account for the lower PCDDs/Fs concentrations in the sample B4. The sample B5 is an ‘outlier’, primarily because of the unusually high concentrations of FFd and F7f (Table 2). The PCDDs/Fs pattern in this sprat is very different from that in the herring (Figs. 2, 3).

PCDDs/Fs concentrations in herring form the Western Gulf of Finland (T1, T2, T3) show a pattern similar to that of the B1-B3 herring. Concentrations of PCDDs/Fs in sprat from this area form a cluster between the Samples T1 and T2 (Fig. 1). The PCDDs/Fs profile in the sample T1 is similar to that in the herring from the central Baltic and differs from that in the samples T2 and T3. This difference may again be caused by the age of the fish (Table 1). The

PCDDs/Fs profiles in sprat T4, T6, and T7 form a cluster (Figs. 2, 3) and differ from that in the sample T5, for no obvious reason.

PCDDs/Fs concentrations in herring from the Middle Gulf of Finland (K1-K3) again follow the same pattern (Fig. 1), except that, in this case, the samples K2 and K3 are very similar, probably because of the similar size, age and sex ratio in these two samples. The profile cluster of the K samples is not very tight (Figs. 2, 3). It is strange that one sample of sprat from this area (K5) is so different. This should be further investigated. As a first step, a replicate analysis of the sample, if it still exists, would be in order.

The PCDDs/Fs concentration in herring from the Gulf of Riga (R1-R3) follows the pattern of the other herring samples (Fig.1). The profiles also form a relatively tight cluster (Figs.2, 3), below those of the B and T herring.

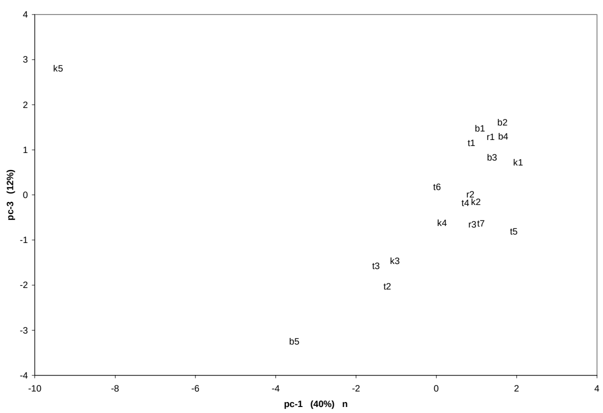

Figure 3: Projection of the adjusted PCDDs/Fs concentrations on the plane of the principal components 2 & 3. Fractions of original variance accounted for are indicated on the axes. For sample codes see Table 1.

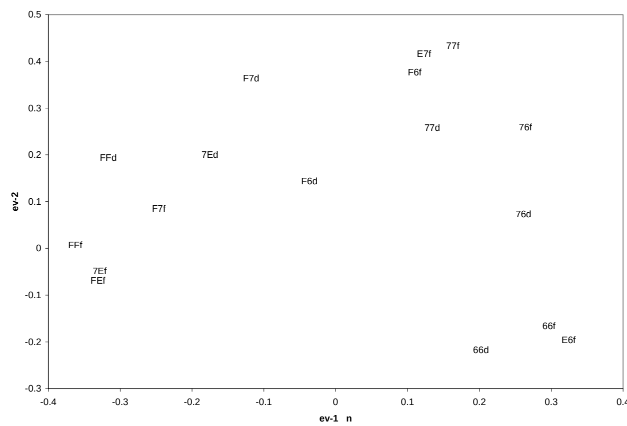

Figure 4: Loading plot of the adjusted PCDDs/Fs concentrations on the principal components pc-1 and pc-2 of Fig. 2. For variable symbols see Table 3.

To save space, only one loading plot (plot showing the effect of the original variables, PCDDs/Fs concentrations, on the principal components) is included. This plot (Fig. 4) shows the loading of the adjusted to 100 (%) concentrations on the principal components pc1 & pc-2 and corresponds to the score plot in Fig. 2. As Fig. 4 shows, the principal component pc-1 (ev-1) separates the highly chlorinated PCDDs/Fs on the left-hand side, form the less chlorinated PCDDs/Fs on the right-hand side. The principal component pc-2 (ev-2) separates the 66d, 66f, and E6F PCDDs/Fs from 77f, E7f and F6f.

References:

[1] Roots,O. (1996): Toxic chlororganic compounds in the ecosystem of the Baltic Sea. Ministry of the Environment, Tallinn, 144p., ISBN 9985-9072-0-5.

[2] Roots, O. and Zitko,V. (2002): Polychlorinated biphenyls patterns in grey seals (Halichoerus Grypus). Ecological Chemistry, Thesa, St.Petersburg, 11(1):68-71.