Contamination of Russian Baltic fish by polychlorinated dibenzo-p-dioxins, dibenzofurans and dioxin-like biphenyls

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Introduction

The high level of industrialization in the Baltic countries has led to the water area of the sea being the most polluted in the world. At the same time the Baltic remains an important fishing region. Recently it was found that the dioxin level (TEQ) in the blood of Finnish fishermen consuming much Baltic fatty fish can reach the levels of exposure seen in Seveso in 1976 [1]. The present work is a next step of our research which has been presented in the previous Dioxin symposiums [2,3]. In this paper we summarise the data and report new results.

Experimental Methods

All fishes were caught by fishermen or during scientific marine expeditions in the Russian economic zone of the Baltic Sea. Analytical samples were the edible portions of fresh and smoked fishes, and in the case of the canned fish, these were analysed without the oil sauce. Samples have been prepared for analysis as described earlier [3,4]. Each analytical run contained a method blank. All solvents, solutes and reusable glassware were tested to ensure the absence of contaminants and interference. The analyses were performed on mass spectrometer Finnigan MAT 95XL at resolution 10000 equipped with Hewlett Packard HP 6890 Plus gas chromatograph.In the calculations of TEQs, concentrations below detection limits were considered as zero; all concentrations are given on a fresh weight (f.w.) basis.

Results and Discussion

Freshwater fishes - bream (*Abramis brama*) and pike-perch (*Stizostedion lucioperca*) are caught in Pregolya Riveror Kaliningrad gulf, the part of Vistula gulf where the river runs. A pulp and paper plant ("Zeprus" using chloric bleaching) is situated in the mouth of Pregolya River. The pike (*Esox lucius*) lives in the river Neman where there is also a pulp and paper plant with chloric bleaching technology. Despite the vicinity of the large factories, bream, pike-perch and even big predator fish such as pike have significantly smaller TEQ, than the sea fish (table 1). Even considering WHO-PCBs, the total toxicity of pike at 2.81 ng/kg WHO-$TEQ_{PCDD/F,\ PCB}$, is less than that established by the EC Council maximum level for PCDD/F in fish and fishery products of 4 ng/kg WHO-$TEQ_{PCDD/F}$.

The data show a high level of pollution for almost all wild saltwater fishes. Only the cod fillet TEQ level (0.15 ng/kg WHO-$TEQ_{PCDD/F}$) was comparable with values for the freshwater fishes. Cod (*Gadus morhua callaria)* is a greedy predator, and only its low fat content can explain the low TEQ of its muscle tissue compared to other sea fish. However accumulation of dioxin-like compounds occurs in the cod liver, where contamination was found to be high (16.6 ng/kg WHO-$TEQ_{PCDD/F}$ and 142.2 ng/kg WHO-$TEQ_{PCDD/F,PCB}$), in contrast with the other fish, so required separate analysis.

Baltic herring *(Clupea harengus membras)* and sprat *(Sprattus sprattus balticus)* are the primary fish in natural feeding webs and the fisheries industry. Four samples of pooled fresh fish, canned and smoked Baltic herring were analysed. The ratio of WHO-TEQ_{PCB}/WHO-$TEQ_{PCDD/F}$ were higher than that found for herring caught in 1993-1994 and 1999 in the Gulfs of Finland Bothnia[5], and in that study, the PCDD/F levels were greater than those reported here, while WHO-TEQ_{PCB} were in same range. More recent data has shown more close values for the PCDD/PCDFs contents in "background polluted" populations, with wide deviations in the PCB results [6,7,8].

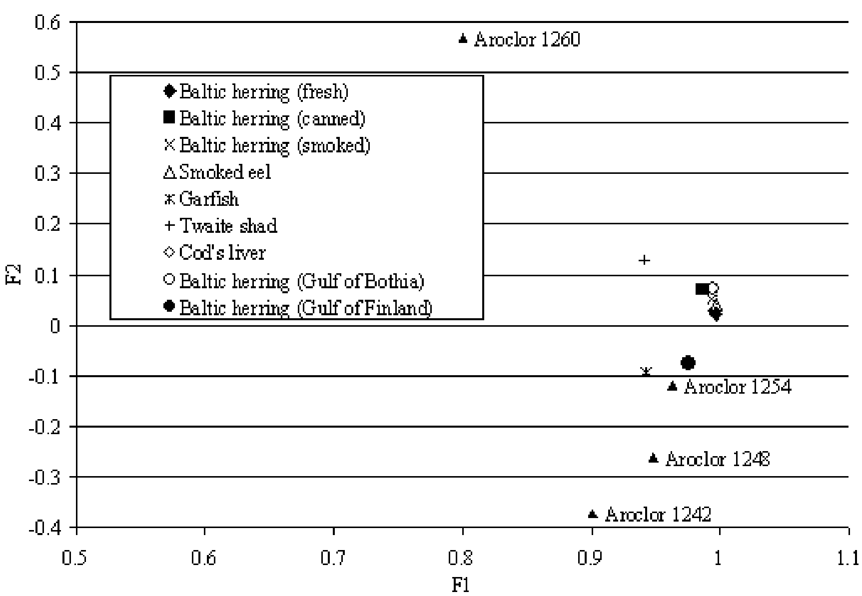
Atlantic salmon (*Salmo salar)* is the largest fish at the top of the food chain of the Baltic Sea, and bioaccumulation of toxicants was expected. However in spite of this, and a moderate fat content, PCDD/PCDFs concentrations in the salmon were 4.54 ng/kg WHO-TEQ, exceeding the level in sprats or Baltic herrings less than twice. This value corresponds well with the data for salmon caught along the Swedish coast (3.1-7.8 ng/kg WHO-TEQ)[6]; but dramatically exceeds the levels we detected for Norwegian farmed salmon – 0.72 ng/kg, in this study and that in the literature - 0.5-0.7 ng/kg WHO-TEQ [10,11]. With inclusion of WHO-PCBs, the $\text{WHO-TEQ}_{PCDD/F,PCB}$ of farmed salmon was 2.97 ng/kg.

Eel (*Anguilla anguilla*) is a passing fish with a very extensive and complex circuit of migration. PCDD/F and PCB levels in the European eel have been reported previously [6,12]. Data from these papers are highly variable, ranging from 2.6 in the UK to 119 in Germany (in I-TEQ ng/kg lipid). The PCB proportion in the total TEQ is also highly variable, ranging from 14% in Greenland to 92 % in the UK. Our results of PCDD/F analyses are close to the lower border of the given range – 1.4 (4.3) ng/kg I-TEQ f.w. (lipid). Dioxin-like PCBs were measured only in a smoked sample, where the contribution of WHO-PCBs to the total TEQ was 94.8%.

The garfish *(Belone Belone),* a typical inhabitant of the North Sea, has in the last two years been more frequently found in the Baltic Sea. Dioxin concentration of the fillets was 1.11 ng/kg WHO-TEQ f.w., less than that typically found in Baltic fatty fishes, but with a high level of PCBs (7.09 ng/kg WHO-TEQ). Garfish muscular tissue is not less toxic than traditional Baltic fish.

The twaite shad is a large fatty fish usually caught together with other fishes. Shad are rare in the Baltic Sea, spawning in the Neman, but the basic dwelling area is located near Bornholm. To the knowledge of the authors,there are no data available on the contamination of twaite shad by PCDD/Fs or dioxin-like PCBs. However a high level of dioxin-like compounds dominated by PCBs in the total TEQ, is specific for Bornholm region, where fishing of herring and salmon was recently banned by the Danish ministry of Food and Agriculture[7].

Fig. 1. Factor scores of dioxin-like PCBs in fish samples and Aroclors (À-1242 – À-1260).



The data set with addition of results for herring caught in Finland[5] and industrial Aroclor 1242-1264 mixtures analysis[18] has been assessed utilising principal component analysis (fig. 1). Two factors account for approximately 95% of the total variance, and the first factor falls at 92 %. The first factor has the main loading on PCB-118, the second - on PCBs-77, 105, 167 and 156. The points corresponding to our samples, and herring from the Gulf of Finland, are close to these points. Points corresponding to Aroclor 1254 are within this cluster (similar to the main

Russian PCB mixture ‘Sovol’).In general, all the PCDD/Fs profiles (fig. 2) were rather similar and most differences are within standard deviation, the most probable sources of fish pollution we can name: chloric bleaching and outflow of PCBs [14,15,16,17]. Relative contributions of each dioxin-like PCBs to the total TEQ in fish tissue are presented in figure 3.

The contribution of dioxin-like PCBs to the WHO-TEQ usually considerably exceeds the contribution of PCDD/Fs. Hence, including consideration of WHO-PCBs, the WHO-TEQ level in all the Baltic saltwater fishes and products studied here exceed the established EC Council maximum level – 4 ng/kg WHO-$TEQ_{PCDD/F}$. While if dioxin-like PCBs are left out of the WHO-TEQ calculations, only cods liver does not exceed the Russian regulations (11 ng/kg I-TEQ), and Atlantic salmon and large Baltic herring slightly exceed the EU limit. This shows the necessity of reviewing the environmental legislation to include WHO-PCBs for calculations of the total TEQ in food and fodder, to ensure the quality assurance of forages and foodstuffs as a priority tool for the protection of human health.

Table 1. PCDD/PCDFs and PCBs content in the Baltic fishes and fish products in 2004-2005.

ng/kg	Pike *Esox lucius*	Baltic herring *Clupea harengus membras* *2005*		Garfish *Belone belone*	Twaite shad *Alosa fallax*	Baltic salmon *(farmed)* *Salmo salar*	Cod *Gadus morhua callarias*		
		<15cm	*>15cm*				fillet	liver	canned liver
Lipids, %	*1.8*	*2.95*	*2.4*	*4.1*	*10.2*	*4.7*	*0.8*	*56*	
2,3,7,8-TCDD	0.08	0.14	0.23	0.15	0.32	0.13	0.02	2.89	1.21
1,2,3,7,8-PeCDD	0.06	0.37	0.94	0.71	1.52	0.21	0.07	2.39	1.32
1,2,3,4,7,8-HxCDD	<0.05	0.05	0.08	<0.10	<0.10	<0.03	0.06	<0.10	0.17
1,2,3,6,7,8-HxCDD	<0.05	0.21	0.49	<0.10	0.15	0.09	0.08	2.70	1.73
1,2,3,7,8,9-HxCDD	<0.05	0.04	0.06	<0.10	<0.10	0.04	0.07	0.23	0.29
1,2,3,4,6,7,8-HpCDD	<0.10	0.05	0.10	<0.20	<0.20	0.10	0.13	0.48	0.68
OCDD	0.51	9.64	0.32	0.32	0.49	0.33	0.31	3.58	2.59
2,3,7,8-TCDF	0.66	1.21	1.23	2.04	2.76	1.53	0.14	37.16	11.59
1,2,3,7,8-PeCDF	0.06	0.56	0.79	0.55	0.74	0.18	0.04	9.53	5.22
2,3,4,7,8-PeCDF	0.09	2.44	6.23	<0.05	2.53	0.39	0.06	15.31	9.37
1,2,3,4,7,8-HxCDF	<0.05	0.15	0.30	<0.10	0.22	<0.03	<0.05	2.49	0.86
1,2,3,6,7,8-HxCDF	<0.05	0.21	0.56	<0.10	0.20	0.04	<0.05	0.14	2.33
1,2,3,7,8,9-HxCDF	<0.05	<0.03	<0.03	<0.10	0.11	<0.03	<0.05	<0.10	<0.10
2,3,4,6,7,8-HxCDF	<0.05	0.17	0.40	0.14	0.22	0.05	<0.05	1.32	1.05
1,2,3,4,6,7,8-HpCDF	<0.10	<0.05	0.06	<0.20	0.06	<0.05	<0.10	0.22	0.39
1,2,3,4,7,8,9-HpCDF	<0.10	<0.05	<0.05	<0.20	<0.20	<0.05	<0.10	<0.20	<0.20
OCDF	0.42	1.34	<0.1	<0.40	<0.40	<0.1	<0.20	<0.40	0.91
I-TEQ	**0.22**	**1.79**	**4.17**	**0.75**	**2.75**	**0.62**	**0.12**	**16.63**	**8.63**

WHO-TEQ$_{PCDD/F}$	**0.25**	**1.96**	**4.64**	**1.11**	**3.51**	**0.72**	**0.16**	**17.82**	**9.29**
WHO-TEQ$_{PCB}$	**2.56**	**4.86**	**7.11**	**7.09**	**15.86**	**2.25**	**NA**	**124.40**	**NA**
including non-ortho-	*2.21*	*3.11*	*4.11*	*4.95*	*11.37*	*1.01*		*87.96*	
WHO-TEQ$_{PCDD/F, PCB}$	**2.81**	**6.83**	**11.75**	**8.19**	**19.37**	**2.97**		**142.22**	
%PCB of total WHO-TEQ	91.1	71.2	60.5	86.6	81.9	75.8		87.5	

Table 2. PCDD/PCDFs and PCBs content in the Baltic fishes and fish products in 2002-2004.

ng/kg	Sprat *Sprattus sprattus balticus*		Baltic salmon *(wild)* *Salmo salar*	European flounder *Platichthys flesus flesus*	Bream *Abramis brama*	Pike-perch *Stizostedion lucioperca*
	fresh	canned				
I-TEQ	**2.81**	**1.12**	**4.17**	**2.56**	**0.54**	**0.06**
WHO-TEQ$_{PCDD/F}$	**2.96**	**1.22**	**4.54**	**2.94**	**0.57**	**0.06**

ng/kg	Baltic herring (2003-2004) *Clupea harengus membras*				Eel *Anguilla anguilla*		
	fresh 1	fresh 2	smoked	canned in jelly	fresh	canned	smoked
I-TEQ	**2.99**	**1.40**	**1.95**	**0.85**	**2.94**	**1.44**	**1.85**
WHO-TEQ$_{PCDD/F}$	**3.44**	**1.49**	**2.05**	**0.91**	**3.04**	**1.68**	**2.09**
WHO-TEQ$_{PCB}$	**4.84**	**NA**	**37.49**	**NA**	**9.01**	**3.84**	**4.78**
including non-ortho-	3.41		16.96		6.18	2.71	3.32
WHO-TEQ$_{PCDD/F, PCB}$	**8.28**		**39.55**		**12.04**	**5.52**	**6.87**
% PCB of total WHO-TEQ	**58.5**		**94.8**		**74.8**	**69.6**	**69.6**

Fig. 2.

The percentage contribution of each 2,3,7,8-substituted PCDD/Fs congener to the total sum.

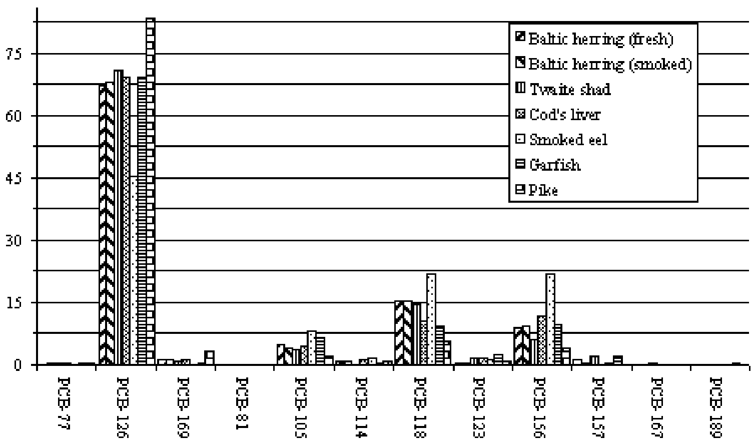
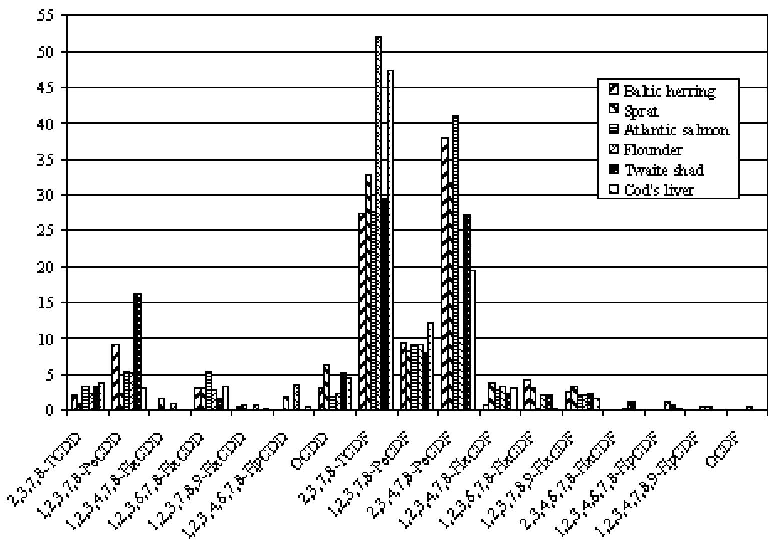


Fig. 3. The percentage contribution of each dioxin-like PCBs congener to the total WHO-TEQ$_{PCB}$



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