EVOLUTION STUDY OF CONTAMINATION RUSSIAN BALTIC FISH BY PCDD/F AND WHO-PCB

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Introduction

Baltic Sea is well known as the most polluted sea in the world, but its fish products have a significant role in diet of Baltic countries habitants. In Dioxin 2003 meeting we have present first results of analysis of Baltic fishes caught by Russian fisherman for market[1]. The results confirmed a rather high level of pollution in the Baltic seafood by PCDD/Fs and have shown necessity of the further researches. Although PCDD/Fs profile in fisher's body is not consist unsteady and was formed under affection of various factors, it was obvious that essential path comes with PCB; also previously were found that WHO-TEQ$_{PCB}$ in seafood could exceed WHO-TEQ$_{PCDD/F}$ level [2,3].
In given works we present results of the analysis of two freshwater species of fishes and updating research of former analyzed kinds, included of WHO-PCBs determination.

Materials and Methods

Kaliningrad Sanitation Service collected the samples from among caught in Russian economic zone. Whole fish was frozen until analysis at -25ºC; canned fish was stored at room temperature. A sub-sample (300-500 g) was ground in mincing machine. A 100 g (fresh weight) of minced sample was placed into a 500 ml flask and spiked with ^{13}C-labeled PCDD/Fs and WHO-PCBs standard mixture (Wellington Laboratories). A 150 ml of acetone was added, and mixture was homogenized for 5 min. Next 150 ml of hexane was added into the mix and homogenized after 5 min followed by addition of 60 g of ammonium sulfate. The final sample was mixed by a homogenizer for 30 minutes and let settle. After 1-2 hours the top fraction was decanted and filtered. The residue was washed twice by

30-50 ml of hexane. Canned fishes samples (without sauce) were extracted by the same procedure.
For simultaneously determination PCDD/Fs and WHO-PCBs we have modified sample clean-up method used earlier[4]. Initially (for fat removing) extract have been passed through the column with sulfuric acid on porous quartz (60%) and through common multilayer column. Next solution was rotary evaporated to 2 ml and transferred to the pre-eluted with 10 ml of hexane alumina column (4g basic alumina, activated overnight at 600-650°C) and wash column with 20 ml of hexane. All hexane fractions are discharged. The fraction, containing mono-ortho PCBs was eluted with 20 ml hexane:dichloromethane (95:5 v:v). Next PCDD/Fs and cPCB fraction was eluted with 50 ml hexane:dichloromethane mixture (40:60 v:v); this fraction was cleaned by carbon column (20 mg AX-21 on 180 mg Celite 545). Additional both fractions passed through Pasteur pipette filled with acid silica gel (44%) before final evaporation to 10 µl.
The analyses were performed by GC-MS (Hewlett Packard HP 6890 Plus, Finnigan MAT 95XL) at resolution 10000, column DB5-MS, J&W Scientific (20 m length, 0.18 mm id, 0,18 µm film thickness).

Results and Discussion

Bream *(Abramis brama)* and Pike-perch *(Stizostedion lucioperca)* are freshwater fishes, they are caught in Kaliningrad gulf, the part of Vistula gulf where runs the Pregolya river in which mouth there is pulp and paper plant – "Zeprus".
Eel *(Anguilla anguilla)* is a passing fish also caught in the Kaliningrad gulf.
Baltic herring *(Clupea harengus membras)* were caught in November 2003 in 26 square of Baltic sea (Russian economic area). Fresh fish and products of its processing most likely belong to one of two existing populations coming into this area. Individuals analyzed earlier were belonged to other population[1].
The quantitative results of the study are presented in Table 1. Profiles of WHO-PCBs in fish tissue are presented in Figure 1. In general, all profiles were rather similar, only minor congeners PCB-81 and PCB 169 in eel are outstanding. Currently we have not data on PCBs level on fresh eel, but due to smoking and canning of sprat does not cause serious changing in PCBs profile, therefore it is possible to assume, that fresh eel could also have increased WHO-PCBs level.

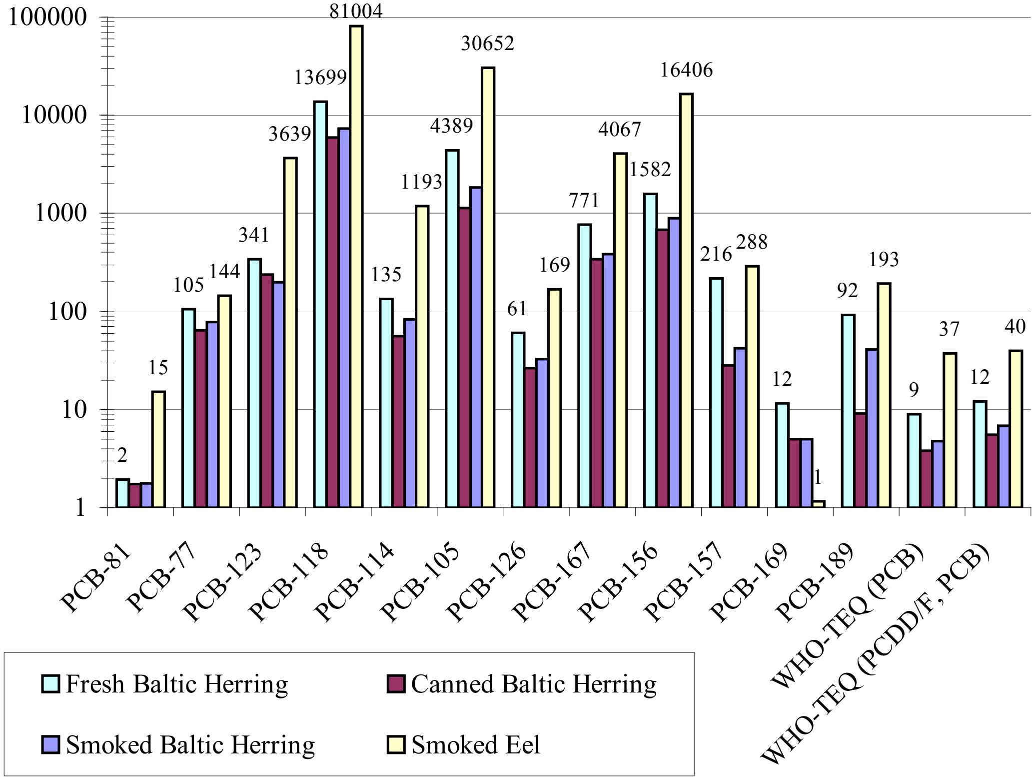

Fig.1. Concentration of WHO-PCBs (pg/g) in Baltic seafood samples.

The data set with addition of results for herring contamination in Finland [2] and industrial Aroclor mixtures analysis[7] has been processed by principal component analysis (fig. 2). Two factors take about 97% of the total variance. All points lay on one smooth curve, extreme points on which are Aroclor 1242 and Aroclor 1260. The points corresponding to our samples and herring, caught in Gulf of Finland are almost identical; point of herring caught in Gulf of Bothnia is located more nearer to Aroclor 1254 (main Russian PCB mixture Sovol alike to it). Thus it is possible to count, that profile of PCBs contained in fishes are practically identical and close to Aroclor 1254; pollution rather fresh, i.e. there was not time enough to change the profile.

Fresh-water fishes (Bream and Pike-perch) had significant smaller TEQ, than sea fishes. The lowest value among the investigated fishes has Pike-perch, a little bit greater value, probable due to the greater fat content was is found in a bream. It is difficult to compare PCDD/Fs profile in sea and freshwater fishes due to in last ones most of congeners were below detection limit. But on the other hand, detectable congeners in Bream and Pike-perch were also most intensive in sea fishes; it is glance indicates that could have at least one similar source of contamination.

In samples of Baltic herring WHO-TEQ$_{PCBs}$ on 2-3 times higher then WHO-TEQ$_{PCDD/Fs}$, this ratio is higher than found earlier for herring caught in 1993-1994 and 1999 in Finland and Bothnia gulfs, but concentration on PCBs are in the same range, and generally data are not in contradiction[2]. In contrast with it the analysis of smoked eel has shown, that PCBs are brought the basic contribution to the total toxicity. Most likely it is connected with eel's high ability to bioaccumulation of PCBs contained in sediments as has been shown previously[5].

The results of our research have shown necessity of determination in all Baltic fish not only PCDD/Fs but also dioxin-like PCBs and an urgency of corrective action for regulation. Now in Russia the maximum concentration limit for fish is 11 ng/kg I-TEQ fresh weight or 88 ng/kg fat; European - 4 ng/kg WHO-TEQ$_{PCDD/F}$ of fresh weight [6], toxicity of dioxin-like PCBs are leave out of account.

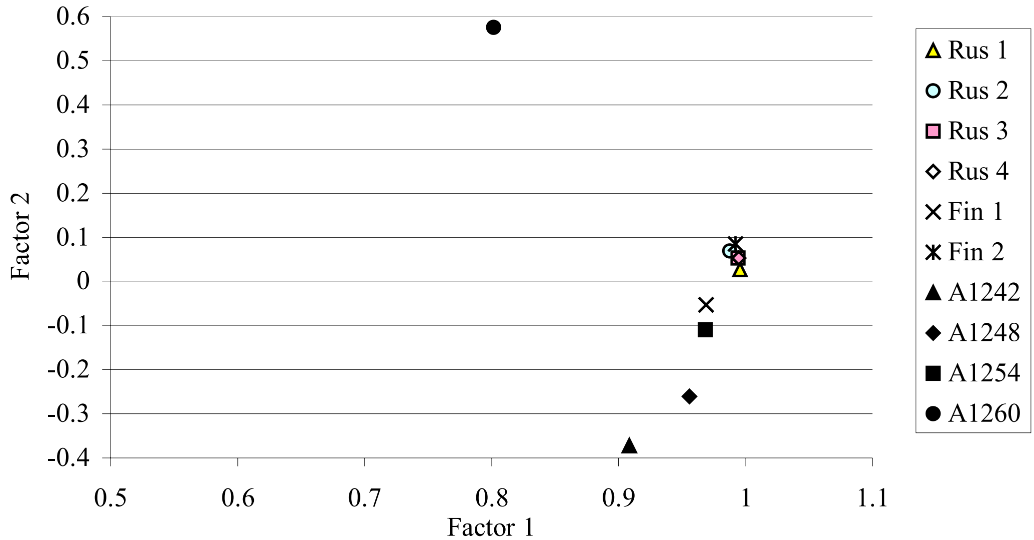

Fig. 2 Factor scores of WHO-PCBs in Russian (Rus 1-4) and Finnish Baltic fish [2] and Aroclors (A-1242 – A-1260) [7].

Rus 1 – Fresh Baltic herring
Rus 2 – Baltic herring canned in oil
Rus 3 - Smoked Baltic herring
Rus 4 - Smoked Eel
Fin 1 - Herring caught in Gulf of Finland
Fin 2 - Herring caught in Gulf of Bothnia

Table 1. PCDD/PCDFs and PCBs content in Baltic region fish (ng/kg fresh weight)

Fish species / Congener *	Baltic herring			Eel		Bream	Pike-perch
	Fresh	Canned in oil	Smoked	Smoked	Fresh [1]		
	Clupea harengus membras			*Anguilla anguilla*		*Abramis brama*	*Stizostedion lucioperca*
Total fat, %	*3,2*	*13,8*	*11,0*	*37,2*	*34*	*7,0*	*1,49*
2,3,7,8-TCDD	0,38	0,26	0,29	0,24	0,08	*<d.l.* **	*<d.l.*
1,2,3,7,8-PeCDD	0,22	0,48	0,47	0,23	0,18	0,06	*<d.l.*
1,2,3,4,7,8-HxCDD	0,48	<d.l.	<d.l.	0,49	0,08	<d.l.	*<d.l.*
1,2,3,6,7,8-HxCDD	0,39	0,88	0,37	0,33	0,35	<d.l.	*<d.l.*
1,2,3,7,8,9-HxCDD	<d.l.	<d.l.	<d.l.	<d.l.	0,05	<d.l.	*<d.l.*
1,2,3,4,6,7,8-HpCDD	0,25	<d.l.	<d.l.	0,66	0,15	<d.l.	*<d.l.*
OCDD	9,39	1,91	1,29	10,18	0,25	<d.l.	*<d.l.*
2,3,7,8-TCDF	1,72	1,72	2,9	0,46	0,17	2,69	0,22
1,2,3,7,8-PeCDF	1,37	0,54	0,62	0,27	<d.l.	<d.l.	*<d.l.*
2,3,4,7,8-PeCDF	3,98	1,17	1,84	2,73	2,25	0,48	0,07
1,2,3,4,7,8-HxCDF	0,62	0,23	0,13	0,26	0,26	<d.l.	*<d.l.*
1,2,3,6,7,8-HxCDF	0,14	0,13	0,12	0,13	0,08	<d.l.	*<d.l.*
1,2,3,7,8,9-HxCDF	0,14	0,07	0,11	0,21	0,08	<d.l.	*<d.l.*
2,3,4,6,7,8-HxCDF	0,27	0,25	0,14	0,1	<d.l.	<d.l.	*<d.l.*
I-TEQ	**2,94**	**1,44**	**1,85**	**1,95**	**1,40**	**0,54**	**0,06**
WHO-TEQ$_{D,F\ (human)}$	**3,04**	**1,68**	**2,09**	**2,05**	**1,49**	**0,57**	**0,06**
Others TCDDs	0,17	0,37	0,39	0,87	*0,17*	0,65	0,07
Others PeCDDs	<d.l.	<d.l.	<d.l.	0,37	*<d.l.*	*<d.l*	0,04
Others TCDFs	1,5	0,81	0,96	1,6	*0,42*	1,57	*<d.l.*
Others PeCDFs	0,63	<d.l.	<d.l.	<d.l.	*0,12*	*<d.l*	*<d.l.*
Others HpCDFs	<d.l.	<d.l.	<d.l.	0,33	*<d.l.*	0,07	*<d.l.*
PCB-81	1,95	1,74	1,76	15,23			
PCB-77	104,8	64,72	78	144,1			
PCB-123	340,5	237,0	199,0	3639			
PCB-118	13699	5965	7279	81004			
PCB-114	134,8	56,53	83,3	1193			
PCB-105	4389	1133	1835	30652			
PCB-126	60,54	26,56	32,69	169,3			
PCB-167	770,9	343,2	383,3	4067			
PCB-156	1582	684,9	897,7	16406			
PCB-157	216,0	28,28	41,91	288,5			
PCB-169	11,62	5,01	5,01	1,16			
PCB-189	92,09	9,17	41,14	193,5			
WHO-TEQ$_{PCB}$	***9,01***	***3,84***	***4,78***	***37,49***			
WHO-TEQ$_{D,F,PCB}$	***12,04***	***5,52***	***6,87***	***39,55***			

*) Concentration of omitted 2,3,7,8 – substituted congeners or sum of isomers were below detection limits.
**) Average detection limit (d.l.) were 0,05-0,30 ng/kg.

References

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