CONTAMINATION OF RUSSIAN BALTIC FISH BY PCDD/F

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Introduction

Baltic Sea is well known as the most polluted sea in the world. Baltic waters received contaminates (including polychlorinated compound) over a long period. Organic chlorinated compounds typically contain polychlorinated dibenzo-p-dioxins and furans. Although many hazardous manufactures were banned, emission from others were decreased, the results of their activity will have long-reaching environmental consequences. Fish products have a significant role in diet of Baltic countries habitants; the fish is also used in chicken feed. Although contamination of different path of Baltic Sea essentially varied, 2,3,7,8-TCDD, 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF as usual observed in seafood. Other 2,3,7,8-substituted PCDDs and PCDFs are also often present. But a single congener does not absolute dominate among the contaminant. It is necessary to note considerably lower contents of highly chlorinated dioxin and furans were found in fish as compared to ones found in sediments [1,2]. In this study we have analyzed eight Baltic region fish species including two types of canned fish, caught by Russian fisherman for market.

Materials and Methods

Kaliningrad Sanitation Service collected the samples. 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 fish was placed into a 500 ml flask and spiked with ^{13}C-labeled PCDD/F standard mixture. 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. Consolidated extract was cleared by carbon, acid-basic multilayer and alumina column as described previously[3]. Canned fishes samples (without sauce) were extracted by the same procedure. The analyses were performed on 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

Profile of PCDD/Fs congeners in fish tissue are presented in Figure 1. In general, all profiles were rather similar except the cod where PCDDs dominated; and large subspecies of sprat showed increased level of 2,3,7,8-TCDD. Among the most probable sources of fish pollution we can name: chloric bleaching, outflow of PCBs and incineration. There are no serious arguments to assume that fish contamination were affected fungicide Ky-5 or similar chlorophenol mixtures [5].

The quantitative results of the study are presented in Table 1 and 2. The first two samples belonged to the same biological species of sprat (*Sprattus sprattus balticus)*, fresh and canned. Both analyses gave close values, although canned fish contained more HpCDDs and OCDD and decreased level of others congeners. It could be caused by smoking and redistribution between the fish and oily sauce. Bigger species of sprat (*Clupea harengus membras*) had significantly higher concentration of 2,3,7,8-TCDD; the levels of HxCDDs in oil blanched sample are remarkable differ from fresh fish.

Due to a large size (>4.5 kg) of Baltic Salmon (*Salmo salar)* essential bioaccumulation of toxicants was expected. Analysis has shown the highest dioxin level in salmon's fat compared with the rest fish specimens (Table 2). The congener profile was close to one found in smaller fishes. (Figure 1).

Flounder (*Platichthys flesus flesus)* living at sea bottom reflects the pollution of sediments better than other fish. Large specimens (530-700 g) were selected for study. Indeed, the flounder's fat contained elevated levels of PCDFs, which could indicate sediments pollution by PCBs. But concentrations of highly chlorinated dioxins were lower than expected.

Each selected cod (*Gadus morhua callaria)* weighted more then 600 g. Cod is a greedy predator, but the low fat content resulted in the lowest TEQ in fresh fish tissue.

Relative small eels (*Anguilla anguilla)* (300-380g) were presented to the analysis. Eels had atypical behavior for fish, but it was not reflected in PCDD/PCDFs profile.

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

Fish species	Fresh Sprat	Smoked Sprat in oil sauce	Fresh Sprat	Blanched Sprat in oil	Baltic salmon	Flounder	Eel	Cod
	small subspecies		big subspecies					
	Sprattus sprattus balticus		*Clupea harengus membras*		*Salmo salar*	*Platichthys flesus flesus*	*Anguilla anguilla*	*Gadus morhua callarias*
2,3,7,8-TCDD	0,12	0,10	7,89	0,24	0,46	0,37	0,08	0,02
1,2,3,7,8-PeCDD	0,30	0,20	0,64	0,61	0,74	0,77	0,18	0,07
1,2,3,4,7,8-HxCDD	0,20	<d.l.*	0,25	2,8	<d.l.	0,15	0,08	0,06
1,2,3,6,7,8-HxCDD	0,37	<d.l.	0,99	14,2	0,74	0,43	0,35	0,08
1,2,3,7,8,9-HxCDD	0,10	<d.l.	0,23	0,18	<d.l.	0,1	0,05	0,07
1,2,3,4,6,7,8-HpCDD	0,22	2,41	<d.l.	0,13	<d.l.	0,52	0,15	0,13
OCDD	0,78	3,81	<d.l.	1,08	0,27	0,37	0,25	0,31
2,3,7,8-TCDF	3,94	2,7	3,59	1,51	3,71	7,77	0,17	0,14
1,2,3,7,8-PeCDF	0,99	0,46	1,08	3,26	1,22	1,36	<d.l.	0,04
2,3,4,7,8-PeCDF	3,81	1,2	4,93	3,27	5,52	1,52	2,25	0,06
1,2,3,4,7,8-HxCDF	0,46	<d.l.	0,95	0,36	0,37	0,5	0,26	<d.l.
1,2,3,6,7,8-HxCDF	0,36	<d.l.	0,89	0,36	0,04	0,33	0,08	<d.l.
1,2,3,7,8,9-HxCDF	0,39	<d.l.	0,4	0,26	0,28	0,33	0,08	<d.l.
2,3,4,6,7,8-HxCDF	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	0,04	<d.l.	<d.l.
1,2,3,4,6,7,8-HpCDF	<d.l.	<d.l.	<d.l.	0,06	<d.l.	0,2	0,05	0,08
1,2,3,4,7,8,9-HpCDF	<d.l.	<d.l.	<d.l.	<d.l.	0,08	0,07	<d.l.	<d.l.
OCDF	<d.l.	<d.l.	<d.l.	0,32	<d.l.	0,09	<d.l.	<d.l.
I-TEQ	**2,81**	**1,12**	**11,46**	**4,31**	**4,17**	**2,56**	**1,40**	**0,12**

WHO-TEQ$_{human}$	**2,96**	**1,22**	**11,78**	**4,62**	**4,54**	**2,94**	**1,49**	**0,16**
Others TCDD	*0,29*	*0,03*	*0,11*	*0,03*	*0,28*	*0,74*	*0,17*	*0,12*
Others PeCDD	*<d.l.*	*0,4*	*<d.l.*	*0,4*	*<d.l.*	*0,25*	*<d.l.*	*<d.l.*
Others HxCDD	*0,1*	*<d.l.*	*0,07*	*<d.l.*	*<d.l.*	*0,53*	*0,1*	*0,2*
Other HpCDD	*<d.l.*	*0,3*	*<d.l.*	*0,3*	*0,14*	*0,19*	*<d.l.*	*0,12*
Others TCDF	*0,25*	*<d.l.*	*0,14*	*<d.l.*	*<d.l.*	*4,84*	*0,42*	*0,03*
Others PeCDF	*0,43*	*<d.l.*	*0,37*	*<d.l.*	*0,4*	*5,41*	*0,12*	*0,12*
Others HxCDF	*0,22*	*<d.l.*	*<d.l.*	*<d.l.*	*<d.l.*	*0,82*	*0,08*	*0,06*
Others HpCDF	*<d.l.*	*<d.l.*	*<d.l.*	*<d.l.*	*<d.l.*	*<d.l.*	*<d.l.*	*<d.l.*

*) Average detection limit (0,01-0,10 ng/kg).

Table 2. PCDDs and PCDFs content in Baltic fish (ng/kg fat)

Fish species	Baltic salmon	Flounder	Eel	Cod
	Salmo salar	*Platichthys flesus flesus*	*Anguilla anguilla*	*Gadus morhua callarias*
2,3,7,8-TCDD	3,43	4,11	0,24	2,50
1,2,3,7,8-PeCDD	5,52	8,56	0,53	8,75
1,2,3,4,7,8-HxCDD	<d.l.	1,67	0,24	7,50
1,2,3,6,7,8-HxCDD	5,52	4,78	1,03	10,00
1,2,3,7,8,9-HxCDD	<d.l.	1,11	0,15	8,75
1,2,3,4,6,7,8-HpCDD	<d.l.	5,78	0,44	16,25
OCDD	2,01	4,11	0,74	38,75
2,3,7,8-TCDF	27,67	86,33	0,50	17,50
1,2,3,7,8-PeCDF	9,10	15,11	<d.l.	5,00
2,3,4,7,8-PeCDF	41,16	16,89	6,62	7,50
1,2,3,4,7,8-HxCDF	2,76	5,56	0,76	<d.l.
1,2,3,6,7,8-HxCDF	0,30	3,67	0,24	<d.l.
1,2,3,7,8,9-HxCDF	2,09	3,67	0,24	<d.l.
2,3,4,6,7,8-HxCDF	<d.l.	0,44	<d.l.	<d.l.
1,2,3,4,6,7,8-HpCDF	<d.l.	2,22	0,15	10,00
1,2,3,4,7,8,9-HpCDF	0,60	0,78	<d.l.	<d.l.
OCDF	<d.l.	1,00	<d.l.	<d.l.
I-TEQ	**31,07**	**28,40**	**4,13**	**15,55**
WHO-TEQ	**33,82**	**32,68**	**4,39**	**19,89**
Others TCDD	2,09	8,22	0,50	15,00
Others PeCDD	<d.l.	2,78	<d.l.	<d.l.
Others HxCDD	<d.l.	5,89	0,29	25,00
Other HpCDD	1,04	2,11	<d.l.	15,00
Others TCDF	<d.l.	53,78	1,24	3,75
Others PeCDF	2,98	60,11	0,35	15,00
Others HxCDF	<d.l.	9,11	0,24	7,50
Others HpCDF	<d.l.	<d.l.	<d.l.	<d.l.

The results of our research confirmed a rather high level of pollution in the Baltic seafood by PCDD/Fs. But PCDD/Fs concentration in only one sample has exceeded Russian limit for fish product (11 ng/kg I-TEQ fresh weight or 88 ng/kg fat) and TEQ in more two samples have slightly exceed EU regulation. (4 ng/kg WHO-$TEQ_{PCDD/F}$ of fresh weight) [5]. However the environmental regulations in Sweden, Finland, Germany and other Baltic countries allow reducing PCDD/Fs discharge to the Baltic Sea; and due to the fish pollution are predominantly reflected contamination of the water, it is possible to expect decrease of fish products toxicity.

References

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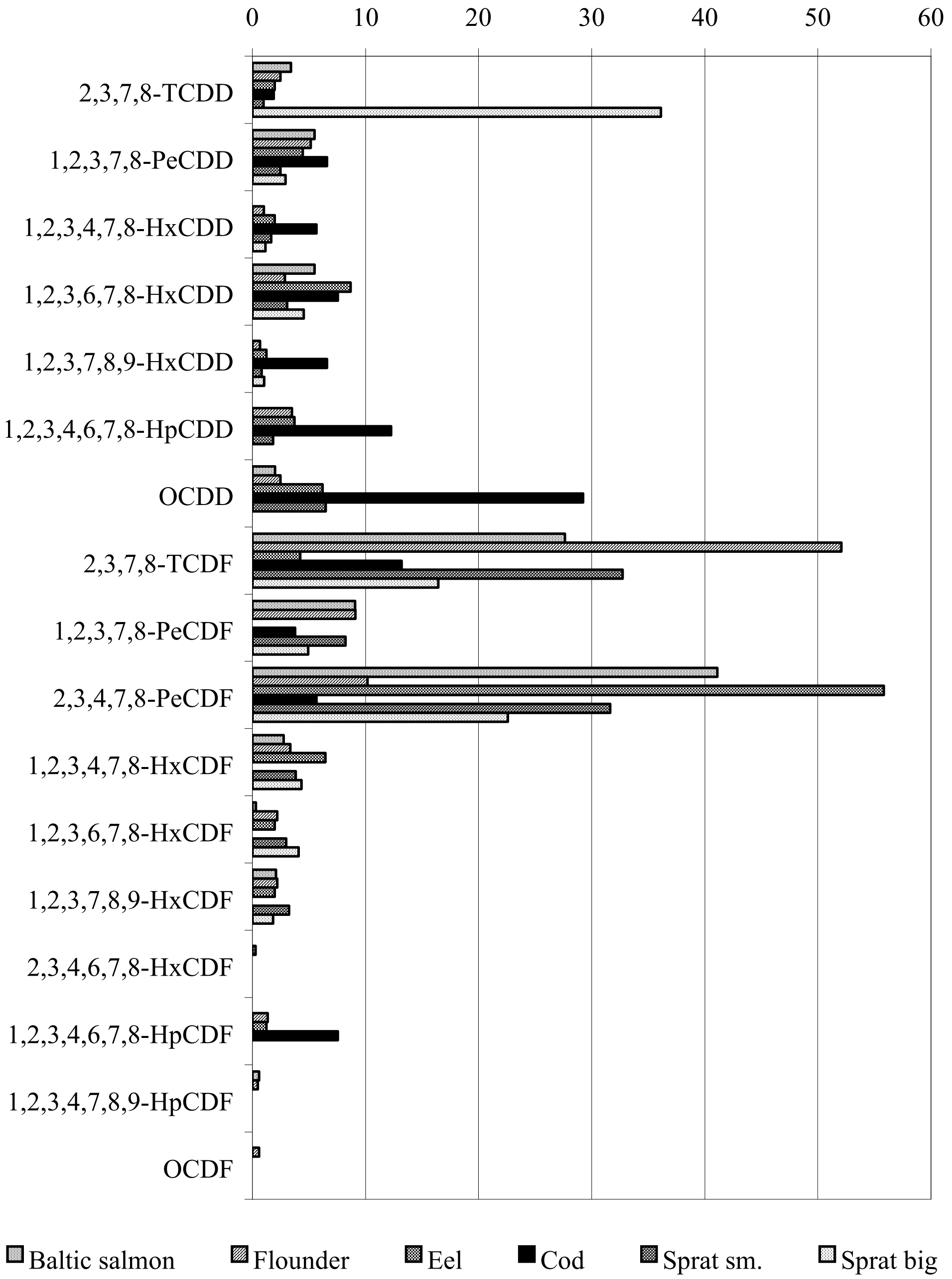

Fig.1. The percentage contribution of each 2,3,7,8-substituted PCDD/Fs congener to the total sum.