LEVELS OF PCDD AND PCDF IN FISH EDIBLE TISSUES FROM POLISH COASTAL WATERES

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Introduction

Human exposure to polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) is a matter of great concern in many part of the world. In most countries, the bulk of the dietary intake of dioxins and related compounds is due to the contamination of food of animal origin1. According to Codex Alimentarius Commission 2–62% of dietary dioxin intake in Europe originates from fish and fish products.

In the past century he Baltic Sea has been exposed to heavy pollution, much of it from industry2. A lot of persistent toxic organohalogen compounds at high contaminant level can be found in tissues living in this area animals; eagles, seals and fish3. Baltic Sea is heavily loaded by dioxins, notable e.g. in high TEQs in herring, other fish and some humans. Dioxin content in fish caught in different north and east Baltic locations can be as high as four times the prescribed EU maximum level (4 pg WHO-TEQ PCDD/PCDF/g fresh weight). PCDD and PCDF content in fish from south part of Baltic - Polish coastal water is unknown.

The aim of the preliminary study on food dioxin contamination in Poland was to determine PCDD/PCDF level in tissues of Baltic consumption fish collected by local fishermen at the middle part of Polish Baltic coast (close to Kołobrzeg and Unieście, Koszalin voivodeship).

Materials and Methods

PCDD and PCDF congeners were analyzed in 40 samples of four fish species: wild salmon, herring, cod, and flounder. The fish were collected during trading season in November-December 2002 at non industrial part of Polish Baltic coast (Figure 1).

Figure 1: Sampling of Baltic fish from fishing grounds.

Each fish meat sample was extracted to obtain fat, which was cleaned-up on the semi permeable membranes (SPM) and the carbon column[4,5,6,7]. Dioxin congener standards, high purity solvents and the other chemicals were purchased from commercially available sources. Techniques of GC-MS/MS for dioxin determination was chosen, previously tested and verified for performance criteria[5]. Dioxin determination was performed using Thermo Quest GCQplus GC-MS/MS systems adjusted to double fragmentation mode. In this case, secondary ions which are formed by splitting out of COCl particle from PCDD/PCDF molecular ion M^+ resulting with $(M\text{-}COCl)^+$ ion were detected. For non-ortho-PCBs $(M\text{-}Cl)^+$ secondary ions were detected respectively. Gas chromatograph conditions are as follows: helium flow set to 1.0 ml/min. DB-5MS or DB-17 column temperature programs are as follows: 100°C for 1 minute, 20°C/min to 200°C, 2°C/min to 280°C and hold for 15 minutes. Transfer line temperature was adjusted to 270°C, because of different structures of cores of PCDDs and PCDFs molecules, optimum of collision energies with helium atoms in a MS/MS system differ[4,5,6,7]. The described procedure was validated using fish samples fortified with natural PCDDs/PCDFs mixture up to the concentrations of 1 – 10 pg WHO-TEQ/g f.w. These samples were analyzed using the same conditions, batch of solvents and reagents as well as calculation method. In this method the precision was better than 20% for concentration above 1 pg WHO-TEQ/g f.w. and better than 30% for lower concentrations. Limit of detection (LOD) was calculated at the level of 0.01 pg-TEQ/g of fresh fish muscle. For individual PCDD and PCDF congeners the LOD was in the range of 0.001 pg/g for TCDD/TCDF and 0.05 pg/g for H_7CDDs/Fs and OCDD/F. In the case, the concentration of the individual congener was below the detection limit, LOD value was used for TEQ calculation, however, it was necessary in some of the analyzed samples only. Recovery of each of 17 PCDD/F congeners was in the acceptable range of 65–120%. All samples were analyzed two times and average value was calculated.

Results and Discussion

The results of PCDD and PCDF analysis in forty fish meat samples (wild salmon, herrings, cod and flounder) expressed in pg WHO-TEQ/g fresh weight are showed in Table 1 and on Figure 2. PCDD/PCDF concentration in fish muscle tissues was in range from 0.82 to 4.82 pg WHO-TEQ/g of fresh weight (f.w.) and only in two tested wild salmon samples slightly exceeded permitted by EU level set by the European Commission Scientific Committee for Food (SCF)[8].

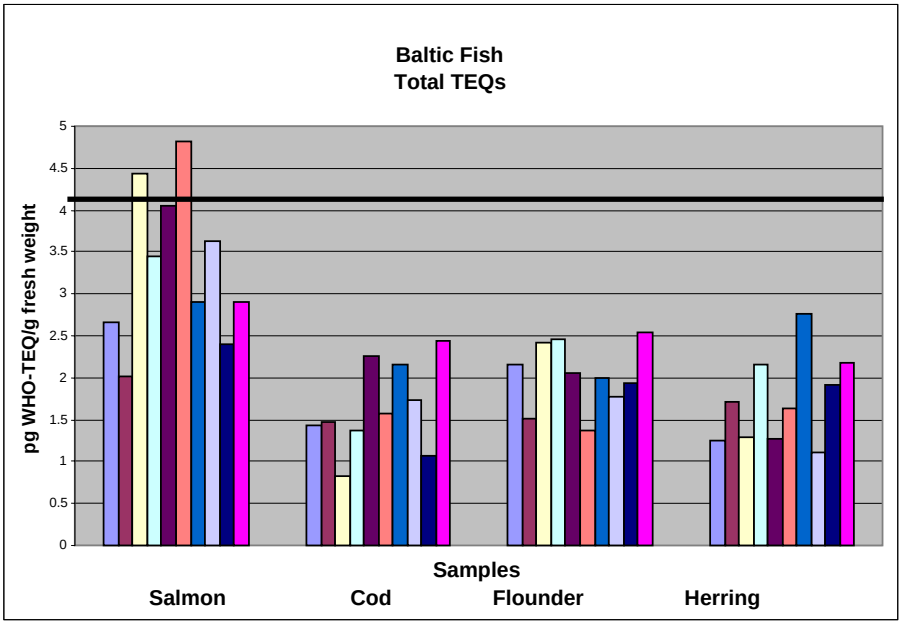

Figure 2: Dioxin content in muscles of individual fish from Polish Baltic coast.

Received data on the 40 samples allow some preliminary observations on the dioxin distribution among tested fish species. Wild salmon samples with the average fat content of 8.5 % generally showed the highest dioxin concentration (2.01–4.82 pg WHO-TEQ/g f.w.). Other fish species, with average fat contents 4.6–8.2 % shown dioxins concentration of 0.82–2.76 pg WHO-TEQ/g f.w. The results are an average value from two independent analyses of each sample.

The presence of 2,3,7,8-TCDF was found in the most Baltic fish samples. 2,3,7,8-TCDF is the most abundant congener among the other TCDFs. The elevated concentration of 2,3,7,8-chlorosubstituted PCDDs and PCDFs congeners is probably caused by higher bioaccumulation of these compounds in fish adipose tissue. Generally, the results of the present study on dioxins and dibenzofurans contamination of Baltic fish catches from Polish coast indicate that dioxins level was rather low and that in 95 % of samples concentration of PCDD/F congeners was below the maximum level permitted by EU.

Table 1: PCCD and PCDF concentration in Baltic Sea fish from Polish coast.

Species	Number of samples tested	Fat content average / range (%)	PCDD/PCDF pg WHO-TEQ/g f.w.	
			(x±SD)	Range
Salmon	10	8.46±2.15 6.0–11.9	3.2±1.2	2.01–4.82
Cod	10	6.43±1.05 4.5–7.9	1.6±0.5	0.82–2.43
Flounder	10	6.46±1.15 4.7–8.2	2.0±0.4	1.52–2.55
Herring	10	5.58±1.33 4.9v7.5	1.7±0.5	1.10–2.76

Dioxins are environmental contaminants which find their way in very low concentrations into many food sources[9]. They are readily soluble in fats and oils and as a result, they accumulate in the tissues of living organism and multiply in concentrations as they move up the food chain. PCDD and PCDF are particularly found in fatty foods, including fish. Although PCDD and PCDF are usually present in aquatic system only at very low level, bioaccumulation can result in significant concentrations.

It is known, that dioxin and PCB concentrations in fish depend on their fat contents, the extent to which fish migrate, the number of times they spawn, their ages, feeding habits, species, tissue and organs as well as contamination of water. Certain fish species – herring and wild salmon originating from Baltic region are recognized as containing a high dioxin concentration[10].

Numerous surveys of dioxins in Baltic Sea fish have revealed considerable variation in PCDD/F concentration[11,12,13]. The dioxin content in Baltic herring caught in Finnish waters in the Archipelago Sea and the Gulf of Bothnia was as much as four times the prescribed by EU maximum (4 pg WHO-TEQ /g f.w.). The large amounts of dioxin previously released from Swedish and Finnish pulp industries seem to be the explanation, why the dioxin levels in fish still are especially high in the northern part of the Baltic Sea, and exceed the EU limit. In German studies, PCDD/PCDF concentration of the herring fillets ranged from 0.317 to 3.163 pg/g f.w. showing a clear dependency on the fishing area (13). Elevated concentration were also observed for dioxins and dioxin-like PCBs in Baltic herring (*Clupea harengus*) collected in 1999 by German fishery from nine different fishing ground of the Baltic Sea. Concentration range was from 0.5 to 7 ng/kg f.w. with the highest value at Bornholm and Latvia coast[13]. In another study the average level in Baltic herring was 2,6 pg WHO-TEQ/g f.w. and was much lower than expected. Only the salmon caught from the northern Baltic Sea contained PCDD/F levels that exceeded the EU's maximum permissible limit[14]. According to Estonian data for herring samples from coast waters only one sample had dioxin level above the internationally permitted threshold[15].

Presented in this paper results on dioxin contamination of Polish Baltic coast fish has revealed rather low dioxin concentrations which do not cause significant toxicological risk for consumers. It can be concluded that the PCDD/PCDF levels in most of the Polish coast fish species

remain below the maximum permissible limits. Neither the age nor the lipid content of the fish species tested was sufficient predictor of the PCDD/F concentration in the investigated fish.

Although the industrial sources of dioxins are in many countries strictly controlled, this group of chemicals will remain in the environment for many more years due to their persistence. Toxic effects of dioxin may cause the long term health consequences and will need to be monitored and followed up. Food safety is essentials public health issues for all countries.

References

1. Roeder R.A., Garber M.J., Schelling G.T. (1998) J Anim Sci, 76, 142.
2. Jensen S., Jensen A.G., Olsson M., Otterlind G. (1969) Nature 224, 247.
3. Falandysz J., Florek A., Bergqvist P-A., Stranberg L., Rappech, Mizera T. (1996) Bromatol. Chem. Toksykol, 29, 40.
4. Grochowalski A., Chrząszcz R. (2000) Organohalogen Comp. 2000, 47, 310.
5. Grochowalski A. (2000) Monografia nr 272, Zesz. Nauk Politechniki Krakowskiej, Kraków, ISSN 0860-097X.
6. Holcomb J., Ferrario J.,Byrne CH. (1999) Organohalogen Comp. 40, 137.
7. Strandberg B., Bergqvist P.-A., Rappe C. (1998) Anal Chem, 70, 526.
8. Council Regulation (EC) No 2375/2001 of 29 November 2001 amending Commission Regulation (EC) No 466/2001.
9. Safe S.H. (1990) CRC Crit. Rev. Toxicol. 1990, 21, 51-88.
10. Svanson B.G., Nilsson A., Hansson M., Rappe C., Akesson B., Skerfving S. (1991) N Engl J Med, 324, 8.
11. Kiviranta H., Hallikainen A., Ovaskainen M.L., Kunpulainen J., Vartiainen T. (2001) Food Addit Contam, 18, 945.
12. Aune M., Bjerselius R., Atuma S., Larsson L., Bergh A., Darnerud P., Andersson A., Arrhenius F., Bergek S., Tysklind M., Glynn A. (2003) Organohalogen Comp, 64, 378.
13. Karl H., Ruoff U., Bluthgen A. (2002) Chemosphere 49, 764.
14. Isosaari P., Kiviranta H., Hallikainem A., Parmanne R., Vourinen P.J., Vartiainen T. (2003) Organohalogen Comp, 62, 41.
15. Roots O., Lahne R., Simm M., Schramm K-W. (2003) Organohalogen Comp, 62, 207.