PCDDs, PCDFs, AND DL-PCBs LEVELS IN BALTIC SALMON, SPRAT AND HERRING CAUGHT IN POLISH FISHING AREA – IS THERE A HEALTH RISK?

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Introduction

Among 75 PCDDs, 135 PCDFs and 209 PCBs, namely 7 PCDDs, 10 PCDFs, and 12 so-called dioxin-like PCBs (DL-PCBs) congeners are of special toxicological concern. Multiple effects are possible as a consequence of the diverse biochemical and cellular changes activated by a chronic exposure to low doses of dioxins and dioxin-like compounds. It is commonly known from the results of recently published studies that the dietary intake of dioxins for some parts of European populations or subpopulations exceeds internationally accepted "safe" levels as TDI, TWI or PTMI[1-3]. For many years the Baltic Sea, which is an ecologically vulnerable inner sea of the EU, has been contaminated by emissions of dioxins and PCBs. Most of them released over the years are still present in the environment and thus are accessible to the marine organisms. This problem applies particularly to fatty fish species. The elevated concentration of above mentioned contaminants in some fish species, namely salmon, herring and sprat caught in the Baltic Sea, has been evidenced in several studies, including surveys carried out in Member States according to Commission Recommendations 2004/705 and 2006/794 EC. The UE maximum limits are exceeded in substantial percentage of those fish, this applies particularly to salmon[4-8]. This means that people who regularly consume these fish species may be at risk as they are chronically exposed to doses exceeding the TWI (and even PTMI) for dioxins. The risk associated with an increased exposure to dioxins also refers to a particularly vulnerable sub-populations such as pregnant women or breastfeeding women.

The subject of research was to evaluate the potential health risk associated with dioxin intake, expressed as % of Tolerable Weekly Intake (TWI), consumed in one portion of fish by an adult and a child. The evaluation was based on results of Polish dioxin Baltic fish study in 2007-2010[4].

Materials and methods

Fish samples. 48 salmon (*Salmo trutta*), 42 sprat (*Sprattus sprattus balticus*) and 42 herring (*Clupea harengus membrus*) samples have been collected in 2007-2010 by the Veterinary Inspection. The Baltic fish were caught in four regions of the Baltic: ICES zones 24, 25, 26 and 27. Sampling procedure was in accordance with provisions of the Regulation 1883/2006. The quantification of the analyzed compounds (7 PCDDs, 10 PCDFs and 12 DL-PCBs) was based isotope dilution technique.

Instrumental analysis. Dioxins, furans and DL-PCBs were determined in the National Research Veterinary Institute in Pulawy by high resolution gas chromatography coupled with high resolution mass spectrometry (HRGC-HRMS): MAT 95XP (Thermo Scientific, Germany) with an Ultra Trace GC (Thermo Scientific, Italy) with GC PAL and auto sampler (CTC Analytics AG, Switzerland). Chromatographic separation was achieved by splitless injection of 1µL on a DB5-MS (60 m, id 0.25 mm, 0.1 µm, J&W Scientific, USA). The MS was operated in SIM mode at a resolution equal or superior to 10000. Two the most intense ions were monitored for native and labeled compounds. The method was validated, and uncertainty of measurement was estimated. The recoveries of the internal standards ranged between 60 and 120% for PCDD/Fs and 40-150% for PCBs.

Calculation of TEQs. Toxic equivalents (TEQs) for PCDD/Fs and DL-PCBs were calculated according to toxic equivalency factors (TEFs) adopted by the WHO in 1998, in accordance with the Regulation 1881/2006. The concentrations below LOQs for the particular congeners were equated as the LOQ (upperbound concentrations). The results are expressed as pg WHO_{1998}-TEQ/g of wet weight (w.w.).

Quality Assurance/Quality control. All QA/QC measures necessary for such analysis have been applied. PCDD/Fs and DL-PCBs data were assessed for compliance with published acceptance criteria, and the method performance requirements laid down in the Regulation 1883/2006/EC. The laboratory successfully participates in proficiency testing organized by the EURL for Dioxins and PCBs in Feed and Food (Freiburg, Germany).

Exposure/risk assessment. This part of a study was performed by the members of Risk Assessment Team from the National Institute of Public Health – National Institute of Hygiene in Warsaw. A number of assumptions and default values are usually applied at the various steps of the exposure/risk assessment process. For the needs of this study an estimated doses of the sum of PCDD/Fs and DL-PCBs taken in one serving of fish of each species by adults and children were expressed as % of TWI (equal to 14 pg TEQ/kg b.w.). This assumption, apparently similar to the methodology for the acute risk assessment, refers to a scenario where the consumer is regularly eating fatty Baltic fish species. According to the EFSA Guidance[9], the default body weight 23.1 kg was adopted for a child and 70 kg for an adult. The assumed default portion size of fish was 100 g for children and 200 g for an adult, respectively.

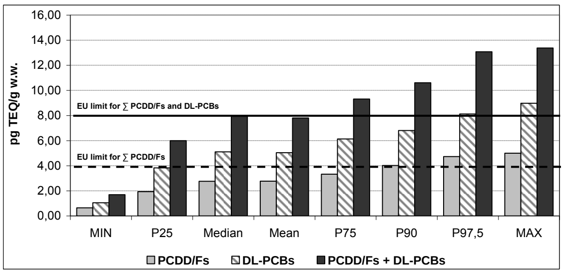
Results and discussion

Summaries of chemical analysis of PCDD/Fs and DL-PCBs levels in fatty Baltic fish species surveyed in 2007-2010 are presented in Figures 1A-1C. The highest mean concentrations of PCDD/Fs and sum of PCDD/Fs and DL-PCBs were found in salmon: 2.77 ± 0.95 and 7.80 ± 2.50 pg TEQ/g w.w. with median value for the sum of PCDD/Fs and DL-PCBs equal to 7.93 pg TEQ/g w.w. Indeed, almost 50% of the salmon samples (23/48) were above the EU limit value of 8 pg TEQ/g w.w. For PCDD/Fs the number of samples above the limit of 4 pg TEQ/g w.w. was 5. It is worthy to note that number of official non-compliances was smaller as the measurement uncertainty has to be taken into account when the results are compared to the limit. DL-PCBs accounted for about 65% of the total TEQ. Levels of dioxins and DL-PCBs in remaining fish species were lower. For sprat the mean concentrations of PCDD/Fs and sum of PCDD/Fs and DL-PCBs were: 1.96 ± 0.73 and 4.51 ± 1.36 pg TEQ/g w.w. with median value for the sum of PCDD/Fs and DL-PCBs equal to 4.61 pg TEQ/g w.w. Only one sample had level of sum of PCDD/Fs and DL-PCBs equal to the EU limit value. DL-PCBs accounted for about 55% of the total TEQ. For herring the mean concentrations of PCDD/Fs and sum of PCDD/Fs and DL-PCBs were: 1.61 ± 0.76 and 3.29 ± 1.36 pg TEQ/g w.w. with median value for the sum of PCDD/Fs and DL-PCBs equal to 3.19 pg TEQ/g w.w. The number of samples with PCDD/Fs and sum of PCDD/Fs and DL-PCBs above the EU limit value were 2 and 1, respectively. DL-PCBs accounted for about 50% of the total TEQ.

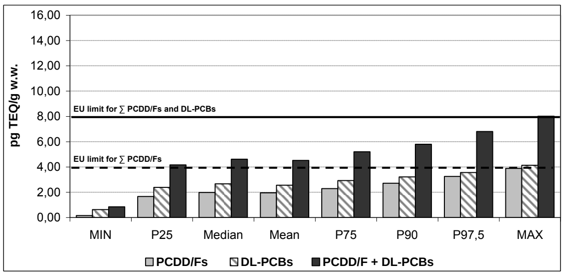
The human dietary intake of dioxins (sum of PCDD/Fs and DL-PCBs) from seafood consumption is different in various countries and depends mostly on dietary habits. In two Baltic countries – Finland and Sweden, input of fish and fishery products in total dioxins intake is over 50% due to high consumption of Baltic fish[2,10]. An average fish consumption in Poland is estimated at 18.9 g/person/day[11] (with P50 = 0 g) which is among the lowest in the EU (3 time less than EU average, 9 time less than in Portugal). This value covers consumption of all fish and fishery products. Such value suggests that the dietary intake of dioxin with fish and fishery products in Polish population will be low but there is no rationale to apply this value to estimate dioxins intake with Baltic fish. As no data exists on detailed consumption of single fish species, it was decided to calculate dose of the sum of PCDD/Fs and DL-PCBs (expressed as % of TWI) taken in one serving of fish by adults and children. The results are presented in Figures 2A-2C. The dioxins intake in children and adults ranges from 52.3 and 34.5% TWI, respectively for one portion of the least contaminated salmon up to 413.7 and 273.1% TWI for the most contaminated one. The intake around 100% of TWI would be achieved by the level of a 5th percentile of results. It means that in 95% of cases, consumption of one portion of Baltic salmon causes dioxins intake over TWI. As the dioxins concentration in sprats and herring are lower, the dioxin intake with one portion of these fish species is proportionally lower, but not fully within in safe limits. For sprats, the dioxins intake in children and adults ranges from 26.3 and 17.3% TWI, respectively for the least contaminated fish up to 247.7 and 163.5% TWI for the most contaminated one. The intake around 100% of TWI would be achieved by the level of a 25th percentile of results. It means that in 75% of cases, consumption of one portion Baltic sprats causes dioxins intake over TWI. For herring, the dioxins intake in children and adults ranges from 42.1 and 27.8% TWI, respectively for the least contaminated fish up to 280.5 and 185.1% TWI for the most contaminated one. The intake around 100% of TWI would be achieved by the level of a 50th percentile of results for children and 95th percentile for adults. It means that in 50%, and 5% of cases, consumption of one portion Baltic sprats causes dioxins intake over TWI for children and adults, respectively.

Additionally the theoretical portion size of Baltic salmon, sprat, and herring that provides dose of sum of PCDD/Fs and DL-PCBs equal to TWI (14 pg TEQ/kg b.w.) for several contamination levels have been calculated (Figures 3A-3C). For the 50th percentile of results such portion size for child and adult consumer would be 41.5, and 125.6 g, respectively for salmon, 70.2, and 212.6 g for sprat, and for herring 101.4, and 307.2 g.

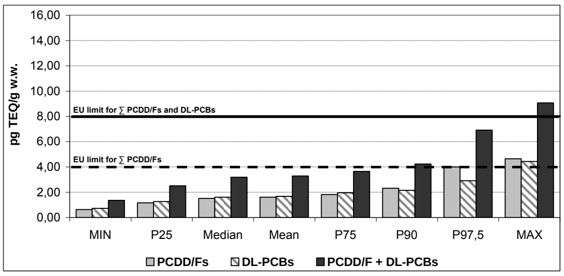
1A)



1B)

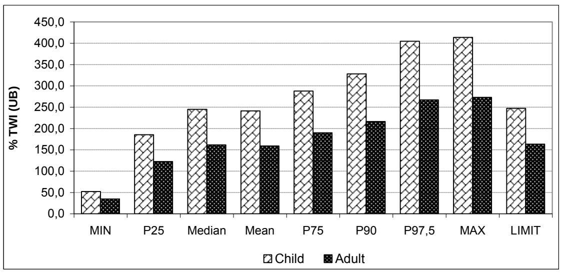


1C)

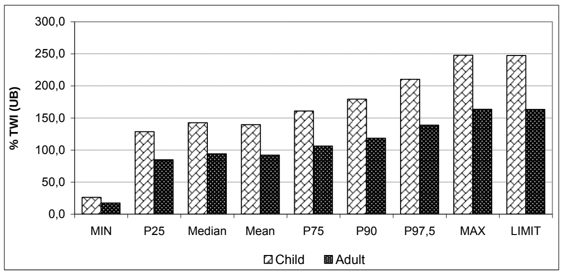


Figures 1A-1C. PCDD/Fs and DL-PCBs in (A) Baltic salmon, (B) Baltic sprat, and (C) Baltic herring caught in Polish fishing areas in 2007-2010, upperbound concentrations (pg TEQ/g w.w., TEFs 1998).

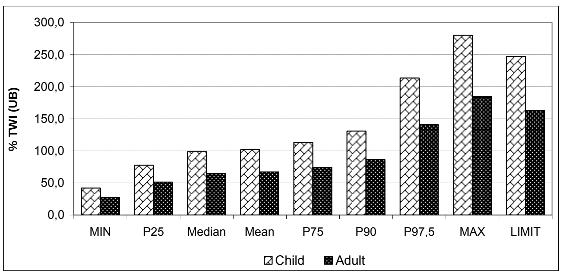
2A)



2B)

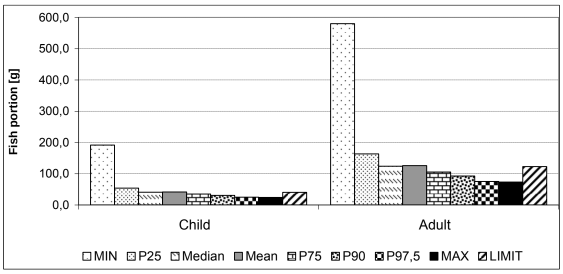


2C)

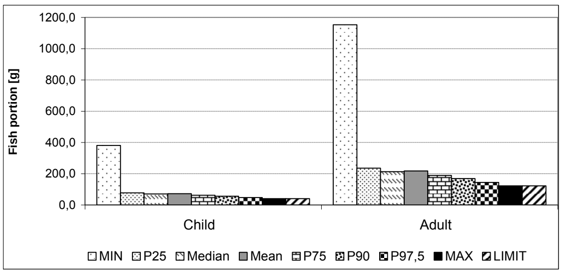


Figures 2A-2C. Estimated intake of PCDD/Fs and DL-PCBs with one portion of (A) Baltic salmon, (B) Baltic sprat, and (C) Baltic herring expressed as % of TWI, based on Polish monitoring results from 2007-2010.

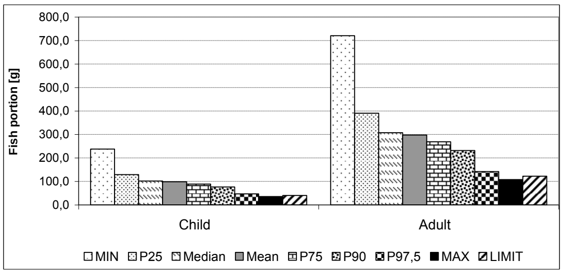
3A)



3B)



3C)



Figures 3A-3C. Estimated portion of (A) Baltic salmon, (B) Baltic sprat, and (C) Baltic herring that provides dose of sum of PCDD/Fs and DL-PCBs equal to TWI (14 pg TEQ/kg b.w.), based on Polish monitoring results from 2007-2010.

Taking into account low fish consumption in Poland and low percentage of Baltic fish consumption in the total consumption of marine fish, despite such alarming results it seems that the problem does not apply to general population. Occasionally elevated dioxins intakes above TWI (or even PTMI) are not necessarily related to health risk because of uncertainty factors embedded in these reference values. However, those who regularly consume fatty fish originated from Baltic may be at elevated health risk relating to potential consequences of chronic exposure to dioxins. This also applies to vulnerable groups of consumers such as pregnant and lactating women, as well as persons of reproductive age. On the other hand the multiple nutritional benefits of fish consumption, including protective effects of n-3 PUFAs on coronary heart disease, reducing arrhythmias and thrombosis, are well known. Therefore, careful risk-benefit analysis should accompany the development of dietary recommendations warning vulnerable groups of consumers of the risks associated with elevated dioxins levels in certain species of fish from the Baltic Sea[12].

References:

1. Bilau M, Matthys C, Baeyens W, Bruckers L, De Backer G et al. (2008) *Chemosphere* 70: 584-592
2. Bergkvist C, Öberg M, Appelgren M, Becker W, Aune M et al. (2008) *Food Chem Toxicol* 46: 3360-367
3. Fattore E, Fanelli R, Turrini A, di Domenico A. (2006) *Mol Nutr Food Res* 50: 915-921
4. Piskorska-Pliszczynska J, Maszewski S, Warenik-Bany M, Mikolajczyk S, Goraj L. (2012) *The Sci World J* doi:10.1100/2012/973292
5. Isosaari P, Hallikainen A, Kiviranta H, Vuorinen PJ, Parmanne R. (2006) *Environ Pollut* 141: 213-225
6. Szlinder-Richert J, Barska I, Usydus Z, Ruczyńska W, Grabic R. (2009) *Chemosphere* 74: 1509-1515
7. Vuorinen PJ, Keinänen M, Kiviranta H, Koistinen J et al. (2012) *Sci Total Environ* 421-422: 129-143
8. Shelepchikov AA, Shenderyuk VV, Brodsky ES et al. (2008) *Environ Toxicol Pharmacol* 25: 136-143
9. EFSA (2012) Guidance on selected default values to be used by the EFSA Scientific Committee, Scientific Panels and Units in the absence of actual measured data, *EFSA Journal* (3): 2579
10. Kiviranta H, Ovaskainen M-L, Vartiainen T. (2004) *Environ Int* 30: 923-932
11. EFSA (2008) Concise European Food Consumption Database
12. Domingo JL, Bocio A, Falcó G, Llobet JM. (2007) *Toxicology* 230: 219-226