

LEVELS OF PCDD/F IN BALTIC FISH IN DIFFERENT AGE GROUPS

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Introduction

High levels of polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), polychlorinated biphenyls (PCB) have been analyzed in the central part of the Baltic Sea and southern Bothnian Sea^{1,2,3,4}. A chemical mass balance model was developed and used to identify sources of PCDDs and PCDFs in sediment samples from the Baltic Sea⁵. As possible sources various combustion sources and manufacturing processes were considered, such as municipal waste incineration, coal and wood burning, and pentachlorophenol, bleaching of pulp and paper using free chlorine⁶. The environmental contaminants such as PCDDs, PCDFs and PCBs accumulate in tissues of living organisms⁷. They are particularly often found in fatty foods. The dioxin content of fatty fish from the Baltic Sea often exceeds the prescribed maximum limits^{8,9}. Dioxin concentrations in a population that frequently eat fish from the Baltic Sea are comparable to those seen in inhabitants of Seveso, Italy, after the accident release of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)¹⁰. At the same time, fish and fish products play an important role in dietary intake for the people living in nine countries close to the Baltic Sea. A monitored study assesses a high breast cancer incidence and cardiovascular mortality among women with a high dietary intake of fatty fish from the Baltic Sea (on the Swedish east coast), contaminated with persistent organochlorine compounds¹¹. Investigations of PCDD/F and PCB concentrations in adipose tissue of 420 Finns living in southern Finland during 1997-1999 present fairly good correlation with ages¹². In November 2001, the EU Council set a maximum limit value for PCDD/Fs in fish¹³ of 4 pg toxic equivalent (WHO-TEQ) per gram of fresh weight (fw). Finland and Sweden got an exemption order until the end of 2006 for the Baltic Sea fish market within their own countries¹⁴. Recently, strong correlation was found between some PCDD/F congeners and the age of herring¹⁵. As a consequence it was found that the concentrations of organohalogens in older Baltic herring were higher than in the younger age groups. Furthermore another investigation manifest that the median PCDD/F (WHO-TEQ) content increase with the age due to the higher lipid content and the measured values for the more than 5 year old fish are larger than the EU limit¹⁶. Here a concise summary of persistent organic pollutions detected in Baltic Sea fish is presented. Age, area of collection and fish species are characterised as predictors of dioxin contamination. Recent tendency of PCDD/F toxic equivalent (TEQ) contents in young Baltic fish, less than 5 year old and further investigations are also integrated.

Materials and Methods

In 2002-2004 dioxin concentrations in the Baltic Sea fish from four areas of the Estonian coastal waters were determined. Baltic herring (*Clupea harengus membras*) and sprat (*Sprattus sprattus balticus*) were caught from the eastern and central parts of the Gulf of Finland and Open Baltic Sea (Central Baltic) in the beginning of October 2002, May-June 2003 and April-May 2004^{2,17}. In addition PCDD/F concentrations were determined for herring collected from the Gulf of Riga during these periods. Further six perch (*Perca fluviatilis*) samples were collected from the Gulf of Riga (Pärnu Bay) in June 2003 and three perch samples from the Lake Peipsi in May 2004¹⁵. Three flounder (*Platichthys flesus trachurus*) fish samples were collected as well from the western coast of the Open Baltic Sea in April 2004. Before the analysis, each sample was determined for their length, weight, gender, and the maturity of gonads. The head, tail fin and viscera were removed from the analysed fish. Therefore, the summarized dioxin level in all the parts of fish, used for human consumption, was determined. In case of perch and flounder, the dioxin level was determined in muscle tissue including skin and scales. Only younger than five years old Baltic herring and sprat were analysed. Flounder and perch collected in 2003 and

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2004, in range of 3 and 6 years old fish were used to find a correlation between the organohalogenic compound concentration and the fish age.

The fish samples have been freeze-dried and homogenized before being extracted by employing accelerated solvent extraction¹⁸. Clean up encompasses sandwich, alumina and florisil chromatography columns and further HRGC/HRMS measurement was processed. Identification and quantification of the most toxic 2,3,7,8-substituted PCDD/F congeners was achieved by ¹³C-labeled standards of PCDD/F^{19, 20}. The resulting values are presented in pg WHO-TEQ/g fresh weight (fw).

Results and Discussion

In older Baltic fish the concentrations of PCDD/F were higher than in the younger age groups (Table 1). The almost six years old flounder and perch became more than 2-fold dioxin contaminated compared with the approximately three years old ones. The highest PCDD/F values were detected for perch caught from the Gulf of Riga in 2003. However, the perch residence in fresh lake waters shows much lower concentrations of PCDD/F.

Table 1.

Age and PCDD/F concentrations (pg WHO-TEQ/g lipid) of founder and perch in the Baltic Sea in 2003 and 2004; in parentheses: lipid content based on fresh weight

| Flounder caught from the Open Baltic Sea in 2004 | | Perch caught from the Lake Peipsi in 2004 | | Perch caught from the Gulf of Riga in 2003 | |
|--|-----------------------------|---|-----------------------------|--|-----------------------------|
| Age (year) | PCDD/F (pg WHO-TEQ/g lipid) | Age (year) | PCDD/F (pg WHO-TEQ/g lipid) | Age (year) | PCDD/F (pg WHO-TEQ/g lipid) |
| 3.5 | 19.9 (1.1%) | 2.8 | 12 (0.5%) | 2.6 | 65.1 (0.8%) |
| 5 | 45.8 (1.2%) | 4 | 22.7 (0.5%) | 4.2 | 66.5 (0.8%) |
| 6.8 | 55.6 (0.9%) | 5 | 31.5 (0.5%) | 5 | 140 (0.6%) |
| | | | | 5.7 | 124 (0.8%) |

It already has been reported that the dioxin level of older fish is often higher than that in the younger^{12, 14}. For fish older than five years the limit value of 4 pg (WHO-TEQ)/g (fw) can be met or exceeded¹⁶. In this point of view the dioxin level in younger fish (less than five years) is important to be monitored and investigated. Table 2 shows the PCDD/F concentrations of herring and sprat in relation to the area of collection, sampling period and the age of the fish. The herring data collected in 2002 from the Gulf of Finland provide a good example to manifest the correlation between the PCDD/F content and the age of the fish. As we already concluded from Table 1, the juvenile fish result in the lower PCDD/F concentrations. Despite the lack of sufficient comparable data it is indicated that the herring and sprat have relatively similar dioxin levels.

Table 2.

Area of collection, sampling date, age and PCDD/F concentrations (pg WHO-TEQ/g fw) of herring and sprat

| Area of collection | Time of collection | Age of herring (year) | | | | | | |
|--------------------------|--------------------|-----------------------|---------|---------|---------|---------|---------|---------|
| | | 1.5-2.0 | 2.0-2.5 | 2.5-3.0 | 3.0-3.5 | 3.5-4.0 | 4.0-4.5 | 4.5-5.0 |
| PCDD/F (pg WHO-TEQ/g fw) | | | | | | | | |
| Gulf of Riga | 2002 | | 1.39 | | | 2.37 | | |
| | 2003 | | | | 2.02 | 1.92 | | |
| | 2004 | | 2.86 | | | | | |
| Gulf of Finland | 2002 | 0.81 | 0.99 | 1.32 | 1.39 | | | 1.95 |
| | 2003 | | | | | | | 4.09 |
| | 2004 | | 1.47 | 1.69 | | | | |
| Open Baltic Sea | 2002 | | | | | 2.81 | 3.39 | |
| | 2003 | | | | | | 2.76 | |
| | 2004 | 1.63 | 1.51 | | | | | |

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| Area of collection | Time of collection | Age of sprat (year) | | | | | | |
|--------------------|--------------------|--------------------------|---------|---------|---------|---------|---------|---------|
| | | 1.5-2.0 | 2.0-2.5 | 2.5-3.0 | 3.0-3.5 | 3.5-4.0 | 4.0-4.5 | 4.5-5.0 |
| | | PCDD/F (pg WHO-TEQ/g fw) | | | | | | |
| Gulf of Finland | 2002 | 2.51 | | 1.64 | 1.98 | 2.14 | | |
| | 2003 | | | | 3.28 | | 3.38 | 4.53 |
| | 2004 | 0.99 | | 2.09 | 2.47 | 2.18 | | |
| Open Baltic Sea | 2002 | | 2.43 | 2.55 | | | | |
| | 2003 | | | | | | | |
| | 2004 | | 1.55 | | 2.67 | 3.51 | | |

Fortunately in all samples except herring and sprat older than 4.5-5 years old collected from the Gulf of Finland the PCDD/F concentrations remained below the limit value of 4 pg (WHO-TEQ) / g (fw) established by EU. In conclusion fish caught in the Open Baltic Sea of age less than five years seem to comply with the toxicologically derived limit values of EU.

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