# PCDDs and PCDFs in Biota from the Southern Part of the Baltic Sea

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## Abstract

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) were determined in plankton, mussel, crab, fishes, aquatic birds, birds of prey and marine mammals collected in 1991-1993 from the southern part of the Baltic Sea. The biota examined seem to be only slightly contaminated with PCDDs and PCDFs. The toxic equivalents (international model) due to PCDDs and PCDFs were 18 pg/g lipid in plankton, from 23 to 590 in mussel, 42 pg/g in crab, from 3.8 to 67 pg/g in fishes, 5.6 pg/g in blubber of harbour porpoise, and 110 in the breast muscles and 420 pg/g in liver of black cormorant, while for an adult white-tailed sea eagles in the breast muscles and liver were from 470 to 870 pg/g, and for the juveniles from 13 to 77 pg/g .

*Key words: Plankton, molluscs, crustaceans, fishes, marine mammals, marine birds, polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans*

## Introduction

Despite of nearly two decades of world-wide interest and intensive studies on PCDDs and PCDFs, practically till now there are no data available on this compounds in environmental matrices in Poland. The knowledge on sources of environmental pollution and emission rates of PCDDs and PCDFs in Poland is also extremely limited[1]. In the past some chemical products potentially contaminated with dioxins were used. For example a popular wood preservative of the Xylamit series contained technical pentachlorophenol, and Maść grzybobójcza (Fungicidal ointment) contained the waste products of the distillation of technical chlorophenols and was used for technical purposes. A technical pentachlorophenol (*e.g.* Antox), and herbicides such as 2,4-D, 2,4-DP, MCPA, MCPP and Dicamba were also used in the past in Poland. Some efforts have been undertaken to elucidate the status of PCDDs and PCDFs in some of those formulations [2-4], nevertheless, due to a non-specific analytical method used (GC-ECD), a detailed composition and concentrations of contaminating dioxin residues remain unknown. Some other potential sources of the emission of PCDDs and PCDFs in Poland can be related to usage of chlorine, leaded gasoline, refining of the metals, paper mills, and less of municipal and industrial waste incineration.

This paper present data on PCDDs and PCDFs in organisms of different marine food webs from the Polish coast of the Baltic Sea.

### Experimental Methods

Plankton (mixed phyto- and zooplankton), mussel, crab, fishes (11 species), harbour porpoise, black cormorant and white-tailed sea eagles were collected from the Gulf of Gdańsk and some other sites in the southern part of the Baltic Sea in 1991-1993. A whole fishes and crab, soft tissue of mussel, blubber of harbour porpoise, and the breast muscles, liver and adipose tissue of birds, respectively, were analysed (Table 1).

After homogenisation of the sample (77-378 g) with anhydrous sodium sulphate, which was baked at 550°C for 2 days, a powdered mixture was packed into a wide bore open glass column (1-1.5 m x 4 cm i.d.), spiked with an internal standard ([$^{13}C_{12}$]-2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD, 2,3,7,8-TCDF, 2,3,4,7,8-PeCDF, 1,2,3,7,8,9-HxCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,4,7,8,9-HpCDF and OCDF), extracted with a 500 ml mixture of acetone and *n*-hexane (2.5:1) and 500 ml of *n*-hexane and diethyl ether (9:1) to obtain a fat extract. Bulk lipid removal was performed by means of polyethylene film dialysis method[5]). The remaining fat (1-20% of the original lipids) was removed on a combined silica column (20 cm x 38 mm i.d.) packed as follows from the bottom: glass wool, potasium silicate (10 ml), a layer of neutral silica gel, 40% sulfuric acid silica gel (20 ml), and a layer of anhydrous sodium sulphate on the top. The gravimetric elution of planar organochlorines was done with 200 ml of *n*-hexane, and 40 $\mu$l of tetradecane was added as a keeper before evaporation of the solvent. The extract was then fractionated on HPLC using an activated carbon column (Amoco PX-2; 2-10 $\mu$m., dispersed on LiChrospher RP-18; 15-25 $\mu$m). Between the carbon column and the precolumn, a filter valve (Valco Instruments Co., Inc., TX) was mounted, enabling backflush of the column. The elution from the HPLC carbon column was performed with 1% methylene chloride in *n*-hexane for 7.5 min, solvent 1, and then gradient elution up to 10% toluene for 32.5 min, solvent 2 (Budrick and Jackson, Muskegon, MI), degassed with argon. Fraction one, containing organochlorine pesticides and 2-4 *ortho* PCBs, is collected during the first 15 min, and fraction two, containing mono-*ortho* PCBs, is collected between 15 and 40 min. The total volume of the solvents used was 160 ml, and the flow rate was 4 ml/min. PCDDs and PCDFs together with PCNs, and non-*ortho* planar PCBs were reverse eluted in fraction three with 80 ml of toluene. The eluate was microconcentrated and spiked with ([$^{13}C_{12}$]-1,2,3,7,8-PeCDF and 1,2,3,4,6,7,8-HpCDF) as a recovery standard and evaporated to a final volume of 30 $\mu$l with tetradecane added as a keeper.

The conditions used for separation, identification and quantification of PCDDs and PCDFs were described in detail in the works by Lindström *et al.*[6]) and Bergqvist *et al* [7]. A gas chromatograph (Hewlett Packard 5890 GC) coupled to high-resolution electron impact mass spectrometry with selected ion recording. A VG-11-250-J (Altrichnam, UK) double focusing (EB geometry) mass spectrometer was utilized, tuned to a resolution (m/Δm, 10% valley) of approximately 7000 in the EI+ mode (35 eV electron energy) on m/z 330.9792 from the calibrant perfluorokersone. Sample introduction was achieved by autosampler (Hewlett Packard 7676A, 5890 GC, USA) using splitless injection at 250°C. Carier gas (99.996% helium, Aga Gas, Sweden) column head pressure was adjusted for a linear velocity of 30 cm per sec. The capillary column (Supleco SP-2330, 60 m x 0.32 mm i.d., USA) was temperature programmed as follows: 180°C initial for 2 min, increased at 3°C per min to an isothermal condition at 260°C. The ion source was maintained at 250°C and the mass spectrometer was operated by a progressive selected ion recording program on the two most abundant ions in the chlorine cluster of the

molecular ion for the native PCDD/F congeners. One ion was recorded for the [$^{13}C_{12}$]- labelled internal and recovery standards. Tetra- through octa-chlorinated homologue groups were monitored according to their known GC elution times for the chromatographic conditions employed, with one appropriate calibrant lock mass chosen in each mass range of interest. The identification of all PCDDs and PCDFs congeners is based on the GC retention time of the authentic standard made of 17 native 2,3,7,8-chloro substituted PCDD/Fs. [$^{13}C_{12}$]- labelled PCDDs and PCDFs (internal and recovery standards) were used for compensation of possible losses during the enrichment procedure. To eliminate the background contamination a procedural blank was performed with every set of the real samples analysed. The concentrations of PCDD/Fs were corrected for possible losses during the enrichment procedure.

**Results and Discussion**

The concentrations of PCDDs, PCDFs and PCDD/Fs in each species were calculated using an international/EPA TEQs TCDD model [8] (Table 1). For a lower marine food web animals such as plankton and crab the PCDD/Fs concentrations were similar, and in the case of the two pooled samples of mussel differed widely (23 and 590 pg/g on a lipid weight basis). One of the mussel samples was taken at a distance of *ca.* 1 km north-east to the seaport/shipyard complex of the city of Gdynia and the other in a site away *ca.* 10 km south-east in the Gulf of Gdańsk.

The concentrations of PCDD/Fs in a whole fishes collected from the south-western and western parts of the Gulf of Gdańsk were between 2.7 and 16 pg/g lipid weight in most of the samples, and 67 pg/g lipid weight was found in herring.

In a study by Bergqvist *et al.* [9] PCDD/Fs concentrations in pooled Baltic herring samples collected in 1987 ranged between 1.8 to 9 pg/g on a wet weight basis. Herring collected from the southern part of the Baltic Sea contained 8.1 pg PCDD/Fs/g wet weight, and lipid (10 %) weight adjusted concentration is 81 pg/g, what is very similar to the value of 67 pg/g in 1992 noted in this study.

For the four harbour porpoises stranded on the Polish coast the PCDD/Fs concentration in the blubber was 5.6 pg/g lipid weight, what is much less then in herring, their staple food in the Baltic Sea. Van Scheppingen *et al.* [10] determined PCDD/Fs in the blubber of four harbour porpoises, which were stranded on the Dutch coast between 1990 and 1993, and have indicated on a lack of bioaccumulation of those substances (TEQs between 1.1 and 1.8 pg/g lipid weight).

An adult black cormorants breeding at the coast of the Gulf of Gdańsk and adult white-tailed sea eagles breeding in the north-western part of Poland (Woliński National Park, the Isle of Wolin and the Szczecin Lagoon area) were the environmental matrices most contaminated with PCDD/Fs in this study (Table 1).

The observed concentrations of PCDD/Fs in biota from the Polish coast of the Baltic Sea are a consequence of the background contamination of the coastal marine environment probably from atmospheric input and do not indicate on an existence of the important local sources of emission at least in the western part of the Gulf of Gdańsk. A relatively higher concentrations of PCDD/Fs found in the breast muscles and liver of adult black cormorants as well as white-tailed sea eagles indicate on biomagnification potential of those substances in a particular marine food webs.

Table 1

TEQ[a] values for PCDDs and PCDFs in biota from the Polish coast of the Baltic Sea (pg/g lipid weight)

| Sample | n | PCDDs | PCDFs | PCDD/Fs |
|---|---|---|---|---|
| Plankton | 4 | 12 | 7.9 | 20 |
| Mussel *Mytilus trossulus* | 2 (700)[b] | 170 | 140 | 310 |
| Crab *Carcinus means* | 1 (3) | 10 | 32 | 42 |
| Stickleback *Gasterosteus aculeatus* | 4 (120) | 3.4 | 15 | 18 |
| Sand eel *Heperoplus lanceolatus* | 1 (20) | 1.0 | 1.7 | 2.7 |
| Lesser sand eel *Amodytes tobianus* | 1 (20) | 2.1 | 1.7 | 3.8 |
| Eelpout *Zoarces viviparus* | 1 (3) | 5.3 | 11 | 16 |
| Round goby *Neogobius melanostomus* | 1 (6) | 5.8 | 8.0 | 14 |
| Herring *Clupea harengus* | 1 (3) | 38 | 29 | 67 |
| Cod *Gadus morhua* | 1 (3) | 3.6 | 4.2 | 7.8 |
| Flounder *Platychthis flesus* | 3 (15) | 3.7 | 4.7 | 8.4 |
| Pike perch *Stizostedion lucioperca* | 1 (3) | 8.5 | 7.3 | 16 |
| Perch *Perca fluviatilis* | 2 (16) | 3.4 | 6.3 | 9.7 |
| Lamprey *Lampetra fluviatilis* | 2 (6) | 4.1 | 5.4 | 9.5 |
| Harbour porpoise *Phocoena phocoena*† | 4 | 3.2 | 2.4 | 5.6 |
| Black cormorant *Phalacrocorax carbo* | | | | |
| *Breast muscles* | 3 | 50 | 58 | 110 |
| *Liver* | 3 | 89 | 330 | 420 |
| White-tailed sea eagle *Haliaeetus albicilla* | | | | |
| *Breast muscles*; juvenile | 1 | 42 | 34 | 77 |
| *Liver*; juvenile | 2 | 7.0 | 6.2 | 13 |
| *Adipose fat*; juvenile | 2 | 7.0 | 7.9 | 15 |
| *Breast muscles*; adult | 3 | 230 | 240 | 470 |
| *Liver*; adult | 3 | 370 | 500 | 870 |

[a]Calculated basing on an international model
[b]Number of the samples and number of animals (in parentheses)
†Blubber

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