# DIOXINS AND DIOXIN-LIKE PCBS IN FISH IN GENERAL AND IN PARTICULAR FROM BALTIC SEA

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**Introduction**

Commission Regulation No 466/2001 establishes maximum levels for dioxins in foodstuffs, foreseeing to review the maximum levels by 31 December 2006 and to include dioxin-like PCBs in the levels to be set. Fish is known to accumulate dioxins and dioxin related compounds in the lipid phase of their tissue. To collect information of the actual contamination levels in fish species on the German market, samples were taken from fishing grounds important for the supply and in particular from the Baltic Sea. Sampling concentrates on fish species with higher fat content like mackerel (*Scomber scombrus*), salmon (*Salmo salar*), trout (*Oncorhynchus mykiss*), red fish (*Sebastes sp*.) and herring (*Clupea harengus*), because lean fish species are known to be less contaminated.

Herring is the most important fat fish species for the German fish processing industry with a market share of 19 % in 2001. The annual demand is approximately 149.000 t.

Today North Sea herring and other Atlantic herring stocks are mainly used as raw material but the demand of the western Baltic Sea herring is increasing. High levels of polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs) and biphenyls (PCBs) have been repeatedly reported in herring and other fatty fish from the eastern Baltic Sea [1, 2)], which very recently led to a ban on fishing and landing of herring and salmon in waters east of Bornholm by the Danish ministry of Food and Agriculture. Herring and other fish species accumulate PCDD/Fs with increasing age and dioxin levels in the edible part of eastern Baltic herring exceeds the maximum limit of 4 ng WHO-PCDD/F-TEQ/kg wet weight (w.w.) at ages of 4 - 6 years, corresponding to sizes of approximately 17 – 18 cm and a weight of 40 g, respectively [3,4,5)]. Hence Isosaari [4)] recommended to use preferably young fish from this area for human consumption. However, the German herring industry is based on the processing of large herring with a minimum weight of > 85g up to 250g. Therefore our interest focused on herring sizes of potential interest for the German processing industry [6)]. Samples were collected in September 1999 within two weeks covering an area from the Skagerrak to the Coast of Latvia.

Additionally the contamination levels in sprat (*Sprattus sprattus*), flounder, brown trout (*Salmo trutta)* and in spring spawning herring from commercial landings around the area of Rügen have been analysed.

## Methods and Materials

**Sample preparation**
Each sample consisted of 20 individuals. Length of each fish was measured, the fish was manually filleted and the skin was removed. In case of herring the skin was peeled off by hands being typical for the production of Maatjes fillets and for marinated herring pieces intended to be used in salads. Applying this procedure only the upper skin is removed and the subcutaneous fat layer remains on the fillet. All fillets were combined, homogenised and deep frozen until analysis.

**Analytical methods**
The analysis of dioxin-like PCBs was done by GC/MS (mono-ortho) and GC/MS-MS (non-ortho) (Ion trap) after addition of $^{13}C$ – labelled standard mixture, fat extraction, GPC and fractionating on ENVI-CARB-SPE tubes. Dioxin residues were analysed according to the method described in detail by Karl et al. [7]. Briefly, after fat extraktion, removal of fat by GPC and further clean up with different adsorbents the PCDD/Fs were determined and quantified by GC/HRMS.
Determination included 17 toxic PCDD/Fs, for which toxic equivalency factors (WHO-TEF) have been laid down by the WHO in 1998, 4 non-ortho-PCB congeners (77, 81, 126 and 169) and 8 mono-ortho PCB congeners (105, 114, 118, 123, 156, 157, 167, and 189). TEQs for dioxin-like PCBs were calculated with TEF factors by WHO (WHO-PCB-TEQ).
All results are given as sum of the WHO-PCDD/F-TEQ and WHO-PCB-TEQ, respectively using full LOQ.

## Results

Contaminant levels in fishes on the German market

Fig. 1: Average content of dioxin and dioxin-like PCBs in seafood on the German market (marked line = EU limit for dioxins)

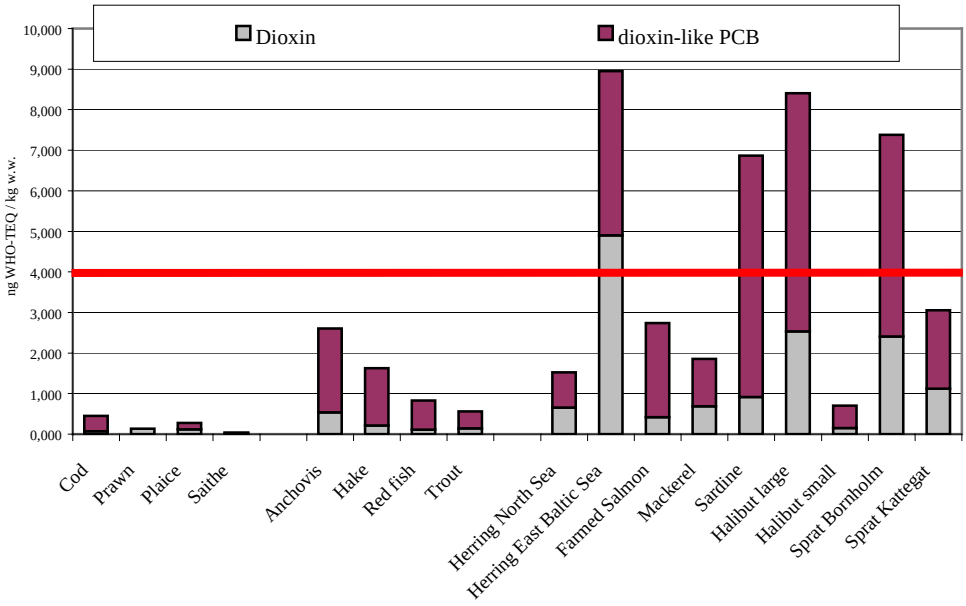



Figure 1 shows, that only same fat fish species (fat content > 10 %) and fishes from the Baltic area had elevated contaminant levels. Lean seafood like cod, saithe , plaice and prawns (fat content appr. 1%) and fishes with moderate fat content like hake and red fish (fat content 5%) were relatively low contaminated as well as the edible part of farmed trout and farmed salmon.

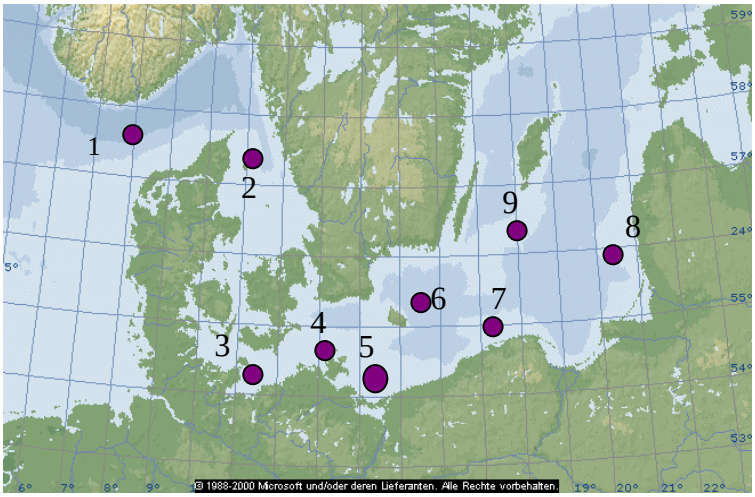
Contaminant levels in herring in relation to fishing ground

Baltic Sea herring samples were collected during a research cruise with the research ship Walther Herwig III in September 1999 using a pelagic net. North Sea herring was collected during other research trips. Size of the herring was selected according to size classes of interest for the German processing industry. Details on samples are given in Table 1 and 2. Sampling locations of the Baltic Sea herring are compiled in Figure 2.

Tab. 1: Data on Baltic Sea herring from September 1999

| Sample | Fishing area | Average length [cm] | Average weight [g] | Fat [%] | Size class |
|---|---|---|---|---|---|
| 1 | Skagerrak | 24.2 | 122.6 | 14.9 | 3 |
| 2 | Kattegat | 23.6 | 102.0 | 11.4 | 3 |
| 3 | Coast of Mecklenburg | 21.5 | 70.2 | 10.5 | 4 |
| 4 | Rügen area | 25.2 | 131.5 | 10.5 | 2 |
| 5 | South of Bornholm | 20.8 | 67.0 | 10.0 | 4 |
| 6 | East of Bornholm | 23.8 | 97.0 | 10.6 | 3 |
| 7 | Coast of Poland | 19.6 | 54.0 | 9.1 | 4 |
| 8 | Coast of Latvia | 23.2 | 79.5 | 5.5 | 4 |
| 9 | South of Gotland | 22.0 | 68.5 | 5.8 | 4 |

Fig. 2: Sampling locations




Tab. 2: Data on North Sea and Atlantic herring

| Year | Fishing aera | Average length [cm] | Average weight [g] | Fat [%] | Size class | WHO-PCDD/F-TEQ [ng/kg w.w] | WHO-PCB-TEQ [ng/kg w.w] |
|---|---|---|---|---|---|---|---|
| Feb. 1996 | Dogger Bank | 25 | 120 | 3.4 | 3 | 0.640 | n.d. |
| Sept. 2001 | Bressay Ground | n.d. | 140 | 18.4 | 2 | 0.623 | 0.991 |
| Okt. 2002 | West British Isles | 28 | 187 | 12.0 | 2 | 0.199 | 0.327 |
| Okt. 2002 | Fladenground | 29 | 248 | 21.0 | 1- 2 | 0.842 | 1.227 |

n.d.: not determined

**Dioxins**

Relatively low dioxin contents of 0.716 ng WHO-PCCD/F-TEQ/kg w.w. and 0.865 ng/kg w.w. were found in herring fillets from the Skagerrak (1) and the Kattegat (2), respectively. The concentrations agreed with those found in North Sea herring of comparable size (Table 2). The increased dioxin level measured in larger North Sea herring from the Fladenground, caught in Oktober 2002, has probably to be ascribed to the age accumulation effect of herring (Roots et al., 2003 ). North Sea herring with a size of 25 cm and 120 g is approximately 2-3 years old and a size of 29 cm and 250 g corresponds to an age of 5-7 years, respectively [8)]. Concentrations in herring caught at the coast of Mecklenburg (3) and in the area of Rügen (4) increased but they kept clear under the EU-limit. The more the fishing grounds moved to the eastern Baltic area, the higher dioxin levels were found. In some cases the EU- limit was exceeded east of Bornholm (Figure 3). The highest level of 6.972 ng WHO-PCCD/F-TEQ/kg w.w were found in herring fillets off the coast of Latvia.

**Dioxin-like PCBs**

The level of dioxin-like PCBs (given as WHO-DioxPCB-TEQ) found in herring from the Skagerrak correspond with 1.178 ng WHO-DioxPCB-TEQ /kg w.w. to those of herring from the North Sea. The concentrations of dioxin-like PCBs increased from the western to the eastern Baltic Sea. Highest concentrations of 5.6 ng WHO-DioxPCB-TEQ /kg w.w. were measured in herring fillets from samples caught east of Bornholm.

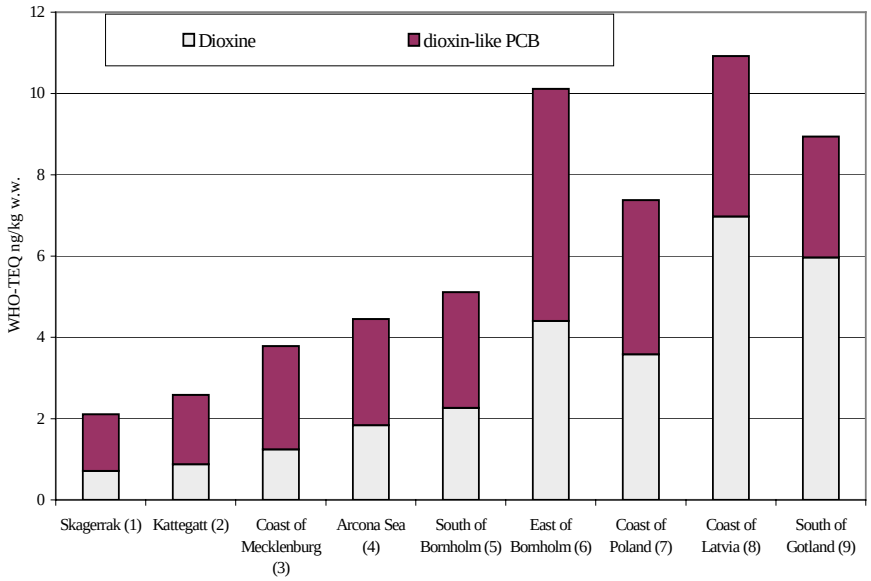



Fig. 3:. Dioxins and dioxin-like PCBs in Baltic Sea herring caught in September 1999

Comparing the relation of dioxins and dioxin-like PCBs a spatial dependence of the concentration levels were found. In samples from the western Baltic Sea the dioxin-like PCBs dominated the dioxin concentrations by a factor of approx. 1.6:1, whereas the relation changed in the

central/eastern part of the Baltic Sea to 0.5 :1 (dioxin-like PCBs: dioxins). The sum of DioxPCB and Dioxin WHO-TEQs ranged between 2 ng/kg wet weight to 11 ng/kg w.w.
The results are shown in Figure 3.

Time trend of dioxin levels in Baltic spring herring from the Greifswalder Bodden

The western Baltic Sea herring concentrates during spawning time in spring around the island of Rügen and in the Greifswalder Bodden, where it is caught by gill net and trap fishery. The Greifswalder Bodden is located close to the fishing ground No. 5 in Figure 2. Samples were collected from commercial landing ports in that area. Each sample consisted of 20 individuals.
The length of each herring was measured and a pooled fillet sample was prepared as described.
Unfortunately it was not possible to receive every year herring samples of the same size. In 2003 the average size of the herring samples was smaller than the years before.
Length, fat content and the corresponding dioxin concentrations on wet weight basis (WHO-PCDD/F-TEQ ng/kg w.w.) of the pooled fillets are compiled in Table 3. Measurement of dioxin-like PCBs started in 2003.

Tab. 3: Dioxin content in pooled samples of herring fillets from the Greifswalder Bodden and in sprat and flounder from various fishing grounds

| **Year** | **Sample** | **Average length [cm]** | **Fat [%]** | **Origin** | **Sampling date** | **WHO-PCDD/F-TEQ** [ng/ kg w.w.] | **WHO-PCB-TEQ** [ng/kg w.w ] |
|---|---|---|---|---|---|---|---|
| 1996 | Herring | 29.4 | 7.4 | Island Vilm | May | 2.426 | n.d |
| | Herring | 25.0 | 4.6 | Greifswalder Bodden | June | 2.102 | n.d |
| | Herring | 29.5 | 13.8 | Arcona Sea | Feb. | 2.623 | n.d. |
| | Herring | 28.0 | 8.0 | Greifswalder Bodden | May | 2.710 | n.d. |
| | Herring | 28.1 | 4.1 | Greifswalder Bodden | June | 1,855 | n.d. |
| 1999 | Herring | 28.0 | 6.5 | Greifswalder Bodden | March | 2.497 | n.d. |
| | Herring | 27.2 | 4.6 | Greifswalder Bodden | March | 2.239 | n.d. |
| 2003 | Herring | 26.0 | 5.2 | Greifswalder Bodden | March | 1.094 | 1.785 |
| | Herring | 25.5 | 4.2 | Greifswalder Bodden | April | 1.094 | 1,704 |
| | Herring | 26.0 | 3.8 | Greifswalder Bodden | May | 1.105 | 1.385 |
| | Herring | 25.0 | 2.8 | Greifswalder Bodden | May | 0.998 | 1.490 |
| 2002 | Sprat | 13.5 | 9.7 | Bornholm | Feb. | 2.407 | 4..974 |
| 2002 | Sprat | 13.0 | 18.4 | Kattegat | | 1.119 | 1..936 |
| 2003 | Flounder | 28.0 | 2.52 | Usedom | July | 0.198 | 0.302 |

Comparing the dioxin content in spring herring from commercial landings on wet weight basis the concentration seems to decrease from 1996 to 2003. Comparing the results based on fat content shows that the contamination level of Baltic Sea herring is significantly higher (28-43 ng WHO-PCDD/F-TEQ/ kg fat) than the concentration in North Sea herring (15 ng/kg fat) but a time trend is not clearly indicated. Relatively large variations were found between samples of same year and the differences between 1996 and 2003 can be presumably traced back to the different size and fat content of the samples. The monitoring will continue every two years, including dioxin-like PCBs . Results found in sprat correspond to that of herring. Fishes from the western part of the Baltic are less contaminated.

**References**

1.Kiviranta, H.; Vartiainen, T.; Parmanne, R.; Hallikainen, A.; Koistinen, J., 2003. PCDD/Fs and PCBs in Baltic herring during the 1990s. Chemosphere **50**, 1201-1216.
2. Shelepchikov, A.A.; Kluyev, N.A.; Shenderyuk, V.V.; Baholdina, L.P.; Brodsky, E.S., 2003: Contamination of Russian Baltic fish by PCDD/F. Organohalogen Compounds, Vol 60-65.
3. Roots, O.; Lahne, R.; Simm, M.; Schramm, K.-W., 2003: Dioxins in the Baltic herring and sprat in Estonian coastal waters. Organohalogen Compounds, Vol 60-65.
4. Isosaari, P.; Kiviranta, H.; Hallikainen, A.; Parmanne, R.; Vuorinen, P.J.; Vartiainen, T., 2003: Dioxin levels in fish caught from the Baltic Sea in 2001-2002. Organohalogen Compounds, Vol 60-65.
5. Bjerselius, R.; Aune, M.; Darnerud, P.O.; Andersson, A.; Tysklind, M.; Bergek, S.; Lundstedt Enkel, K.;Karlsson, L.; Appelberg, M.; Arrhenius, F.; Wickstöm, H.; Glynn, A., 2003: Study of dioxin levels in fatty fish from Sweden 2001-2001 Part II.. Organohalogen Compounds, Vol 60-65.
6. Karl, H.; Münkner, W., 2002: Quality and Processing Possibilities of Western Baltic Sea Spring Spawning Herring. J Aquatic Food Product Technology **11** (3/4), 31- 43.
7. Karl, H.; Ruoff, U.; Blüthgen, A., 2002: Levels of dioxins in fish and fishery products on the German market. Chemosphere **49**, 765-773.
8. Zimmermann, Ch., 2004: Personnel communication. Data bank of the Federal Research Centre for Fisheries, Institute for Sea Fishery, Hamburg, Germany.