Dioxins, dioxin-like PCBS and organochlorine pesticides in farmed salmon of various origin

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Introduction

With a market share of 8.4 % in 2001 (approx. 100,000 t) farmed salmon is one of the most important fish species on the German market. The world wide production of salmon in 2001 was approximately 1.2 Mio t. Norway has produced around 450,000 t of Atlantic salmon of which 60,000 t has been exported to Germany. Other important suppliers of salmon to the German market are Scotland, Denmark, Chile and Ireland. The annual amount from Ireland is relatively small, being approximately 2,000 t. Most salmon is raised under conventional farming conditions. During the last years also high priced organically grown salmon is available on the German market, mainly produced in Ireland. With 800 t per year the market share of organically farmed salmon is less than 1 %.

Within the context of a study to develop methods for the detection of organically produced products taking salmon as example it was checked if the contaminant levels and/or the contaminant patterns are suitable to differentiate between organically and conventionally farmed salmon. Conventionally farmed salmon, referred as to farmed salmon, was collected from different European farms; organically farmed salmon, referred as to organic salmon, came from Ireland as well as wild Atlantic salmon, which was included into the study. In the present study dioxins, dioxin-like PCBs , marker PCBs and a range of organochlorine pesticides (toxaphene, chlordane, DDT, HCB etc.) in the muscle meat of salmon were investigated.

Methods and Material

Samples

Salmon samples of superior quality (*Salmo salar)* from six locations were received as gutted fresh fish on ice. At least five individuals from each farm were analysed. Length and weight were measured, the fish was filleted by hand, deskinned and a part of the fatty belly flap was removed as being commercial practice for high quality salmon products in Germany. The meat was homogenised and deep frozen until analysis. Average size, fat content and origin of samples are compiled in Table 1.

Table 1: Average size, fat content and origin of salmon

Sample		**Origin**	**Length [cm]**	**Weight [g]**	**Fat %**
Farmed salmon I	**FL1**	South Ireland	73	3642	15.5
Farmed salmon II	**FL2**	Bergen/Norway	74	3641	10.8
Farmed salmon III	**FL3**	Northern Norway	76	4473	15.6
Farmed salmon IV	**FL4**	Northern Ireland	72	3727	10.4
Wild salmon 2	**WL2**	Ireland	69	3186	10.5
Organic salmon 2	**OL2**	West Ireland	72	4430	12.5
Organic salmon 1	**OL1**	West Ireland	70	3712	16.9

Analytical methods

Dioxin residues were analysed according to the method described in detail by Karl [1)]. Briefly after fat extraction, removal of fat by GPC and further clean up with different adsorbents the PCDD/Fs were determined and quantified by GC/HRMS. The determination of dioxin-like and marker PCBs was also done by GC/HRMS after addition of ^{13}C-labelled internal standard and fat extraction with ASE 200. Further chromatographic clean up included separation of fat on a Florisil and GPC column, respectively, followed by fractionation of PCBs into di- and mono-ortho PCBs and non-ortho PCBs on Carbopack B-columns.

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, 126,169), 8 mono-ortho PCB congeners (105, 114, 118, 123, 156, 157, 167, 189) and 6 di-ortho PCBs (28, 52, 101, 138, 153, 180; marker PCBs). 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.

Pesticide concentrations were determined after fat extraction, removal of fat by GPC and column fractionation on silica gel by capillary GC and ion trap mass spectrometric detection as described in detail by Karl [2)].

Results and Discussion

Dioxins

The median dioxin contents and the 90th and 10th percentiles in relation to the origin are given in Figure 1. Highest dioxin concentrations were found in organic salmon, sampled in September 2002 (OL1). Salmon from the same farm collected one year later (OL2) was significantly less contaminated, probably as a result of changes in the feed composition. Lowest concentrations of dioxins were measured in wild Atlantic salmon. In general, levels in farmed salmon were in the same range as in organic salmon. All mean concentrations, ranging between 0.2 and 0.48 ng WHO-PCDD/F-TEQ/kg wet weight (w.w.), were far below the EU-limit of 4 ng/kg w.w..

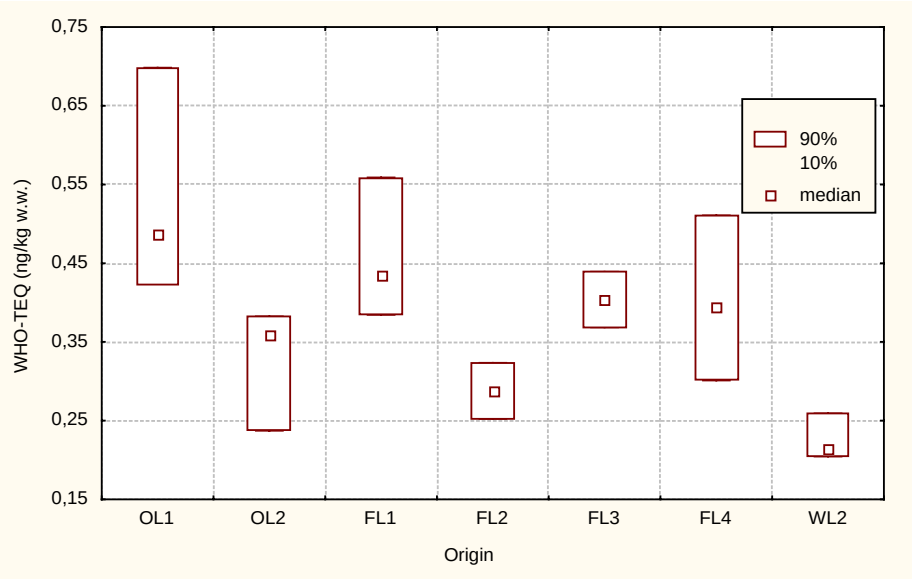

Figure 1: Dioxin content of salmon (ng WHO-PCDD/F/kg w.w.)

Differences in dioxin levels on fat basis between single fishes from the same farm were relatively low (RSD between 8 and 15 %) but concentrations on product weight could vary considerably due to large variations in individual fat content (e.g. range of fat content of OL 1: 15 – 20 %).

Dioxin-like PCBs

The concentrations of dioxin-like PCBs (given as WHO-PCB-TEQ) are compiled in Figure 2. Unlike the dioxin contamination, the dioxin-like PCB contents of conventional farmed salmon were higher than of organic salmon. Lowest concentrations were found in wild salmon. The results indicate that contamination levels of dioxin-like PCBs are not related with dioxin concentrations, although both exposures are mainly associated with the fish oil [3, 4]. The contents of dioxin-like PCBs in the muscle meat of farmed salmon (1.4 – 2.7 ng WHO-PCB-TEQ/kg w.w.) are higher than corresponding concentrations found in fatty marine fish species like mackerel and herring from the North Sea or Atlantic, being less than 1 ng /kg w.w. [5].

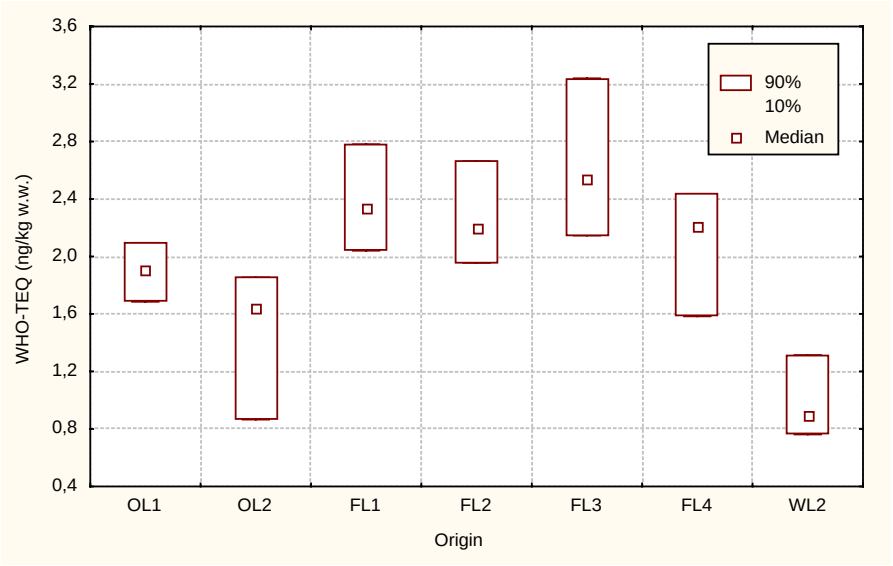

Figure 2: Dioxin-like PCBs in salmon from different origin (ng WHO-PCB-TEQ/ kg w.w.)

Total WHO-TEQ in salmon

The total WHO-TEQ in salmon is dominated by the dioxin-like PCBs. The contribution to the total toxicity equivalents is 4 - 7 times above that of dioxins. Similar results have been reported for Irish [6)] and Scottish farmed salmon [7)]. Differences between organic and conventionally farm raised salmon are no longer detectable. The mean WHO-PCDD/F + PCB-TEQ ranged between 1.8 and 3.1 ng/kg w.w. (Table 2). Wild Atlantic salmon was less contaminated than farmed salmon but significantly higher than wild Pacific salmon [8)].

Table 2: Mean WHO-TEQs of dioxins and dioxin-like PCBs in salmon

Sample	Dioxin Sum WHO-TEQ [ng/kg w.w.]	DioxPCB SumWHO-TEQ [ng/kg w.w.]	Dioxin and PCB SumWHO-TEQ [ng/kg w.w.]	Relation PCB:Dioxin Dioxin=1
OL 1	0.5236	1.897	2.421	3.6
OL 2	0.3268	1.464	1.791	4.5
FL 1	0.4528	2.398	2.851	5.3
FL 2	0.2855	2.250	2.536	7.9
FL 3	0.4007	2.684	3.085	6.7
FL 4	0.4040	2.077	2.481	5.1
WL 2	0.2267	0.980	1.207	4.3

Toxicity pattern of dioxins and dioxin-like PCB congeners

The dioxin toxicity patterns of organic and farmed salmon were comparable. The total toxicity was mainly determined by the two congeners 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF, with 2,3,4,8-TCDF as major compound. The ratio in wild salmon was significantly different, the toxicity being clearly dominated by the 2,3,4,7,8-PeCDF congener (Figure 3). The toxicity of dioxin-like PCBs was determined by the congener PCB 126, which contributes to more than 65 % of the total PCB toxicity. No differences in the PCB ratios were observed between wild, organic and farmed salmon.

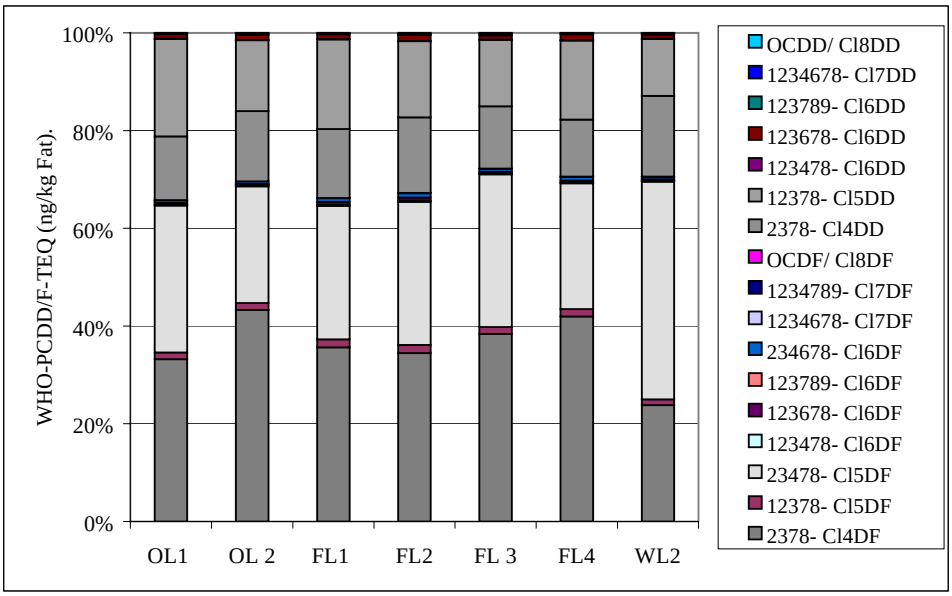

Figure 3: Toxicity ratio of PCDD/F congeners in salmon

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Marker PCBs

In Germany maximum allowable limits exist for PCB 28, 52, 101,138,153 and 180. Table 3 gives the limits and the values of the marker PCBs determined in the edible part of the salmon samples. All concentrations were far below the limits and differences between wild and farm raised salmon were not detected.

Table 3: Mean concentrations of Marker PCBs in salmon [µg/kg w.w.]

Sample	PCB 52	PCB 101	PCB 138	PCB 153	PCB 180
Limit	80	80	100	100	80
OL1	1.25	3.22	8.52	9.63	2.23
OL2	1.18	2.74	6.32	7.19	1.58
FL1	1.21	3.35	7.57	8.10	1.76
FL2	1.10	2.77	5.40	5.97	1.66
FL3	1.98	4.04	6.39	6.96	1.89
FL4	1.52	3.25	7.04	8.26	1.80
WL2	1.25	2.19	4.75	5.55	1.18

Organochlorine pesticides

Figure 4 shows the actual contaminant levels of ∑ DDT, ∑ chlordane, ∑ toxaphene , γ-HCH, HCB and dieldrin in salmon samples. All residue levels were far below the allowable German limits for pesticides in fish. Each concentration reached at the most 10 % of the limit, respectively. Different contaminant levels were observed between farmed salmon from Norway and Ireland but not between organic and conventional farm raised salmon from Ireland. Residue levels in Norwegian farmed salmon correspond well with low concentrations found in wild Atlantic salmon.

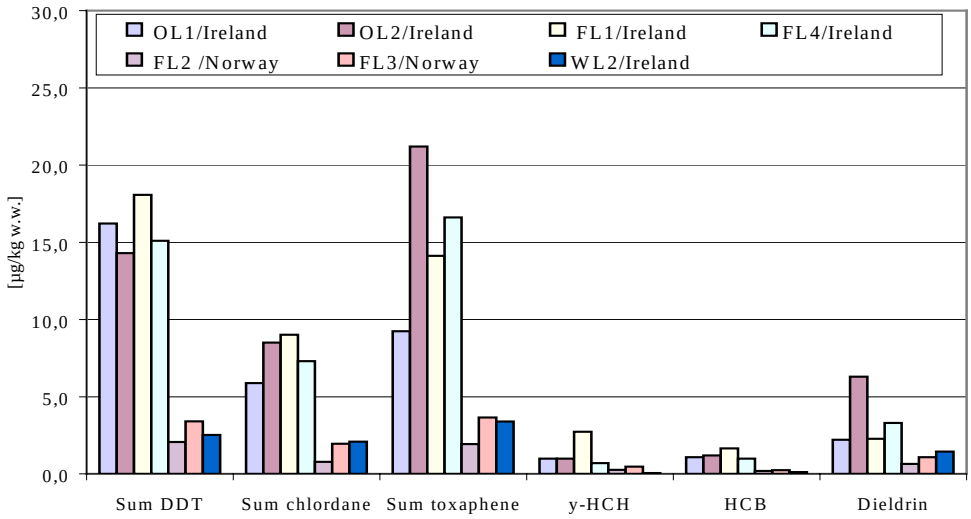

Fig. 4: Mean pesticide residues in salmon
Sum DDT = p,p´-DDT + o,p´-DDT + p,p´-DDE + o,p´-DDE + p,p´-DDD
Sum chlordane = oxy-+ cis-+ trans chlordane + cis-+ trans nonachlor
Sum toxaphene = Parlar 26 + Parlar 50 + Parlar 62

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