

# PCDD/Fs, PCBs AND FURTHER CONTAMINANTS IN FRESH WATER FISH FROM WATERBODIES IN BADEN-WÜRTTEMBERG, GERMANY

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## Introduction

From 2008 to 2010 monitoring programmes were performed, in order to compare the levels of contamination of various fish collected from fresh waterbodies in Baden-Württemberg according to legal maximum and action levels<sup>1,2,3</sup>. Therefore, 46 fresh water fish samples and 20 eels were analysed for polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs), polychlorinated biphenyls (PCBs), heavy metals (e.g. mercury) as well as organochlorine and organobromine pesticides and contaminants, nitro-musk compounds, pyrethroids and perfluorinated compounds (PFC). The collection of samples comprised edible fish species only, like European eel, bream, brown trout, rudd, whitefish, perch, grayling, pike, zander and roach originating from 14 different fresh waterbodies in Baden-Württemberg. 34 of these samples were collected at the Rhine River. This abstract focuses predominantly on the results of PCDD/Fs and PCBs.

## Materials and methods

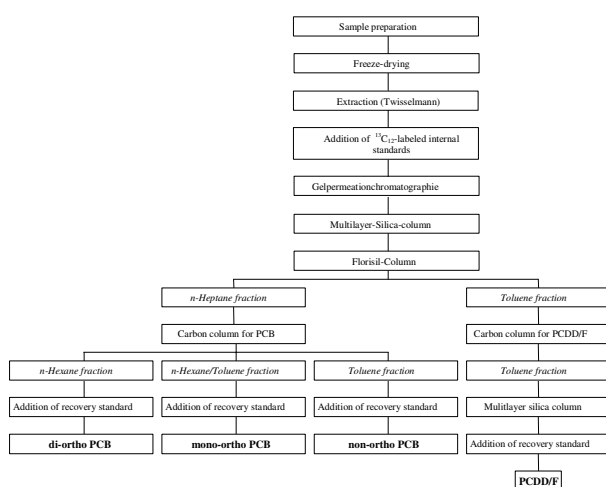
### Sampling and sample preparation

The selection of waterbodies, sampling sites, fish species, size and age of the sampled fish was carried out in close collaboration with experts of fishery departments in Baden-Württemberg, taking into account e.g. fishing quota and relevance of consumption. According to Commission Regulation (EC) 1883/2006<sup>4</sup> the 46 fish samples were analysed as pooled samples of at least 1 kg of fillet of fish (without skin, head, fishbone and offal). All eel samples were analysed individually (no pooled samples). The pooled samples were quite inhomogeneous, composed of 1 to 56 individuals of fish (length 6 - 66 cm, weight 10 - 1940 g, fish age 2 - 8 years). The average fat content of the 46 fish samples (except eel) was 1.7 %, ranging from 0.1 - 6.5 %. The fat content of the 20 eel samples ranged from 3.2 % to 35.0 % (average 17.1 %).

### Analysis

The samples were analysed for PCDD/Fs, PCBs<sup>5,6,7,8,9</sup>, heavy metals, organochlorine and organobromine pesticides and contaminants, nitro-musk compounds, pyrethroids and PFOS using validated methods.

For PCDD/Fs and PCBs the following extraction and clean-up steps and GC/MS measurement were applied:



### GC/MS measurement:

#### - PCDD/F

- PTV injector: Injection of 5 µl (solvent split)
- GC separation: 95%-Dimethyl-5%-diphenyl-polysiloxane
- HRMS: Resolution 10'000

#### - PCB:

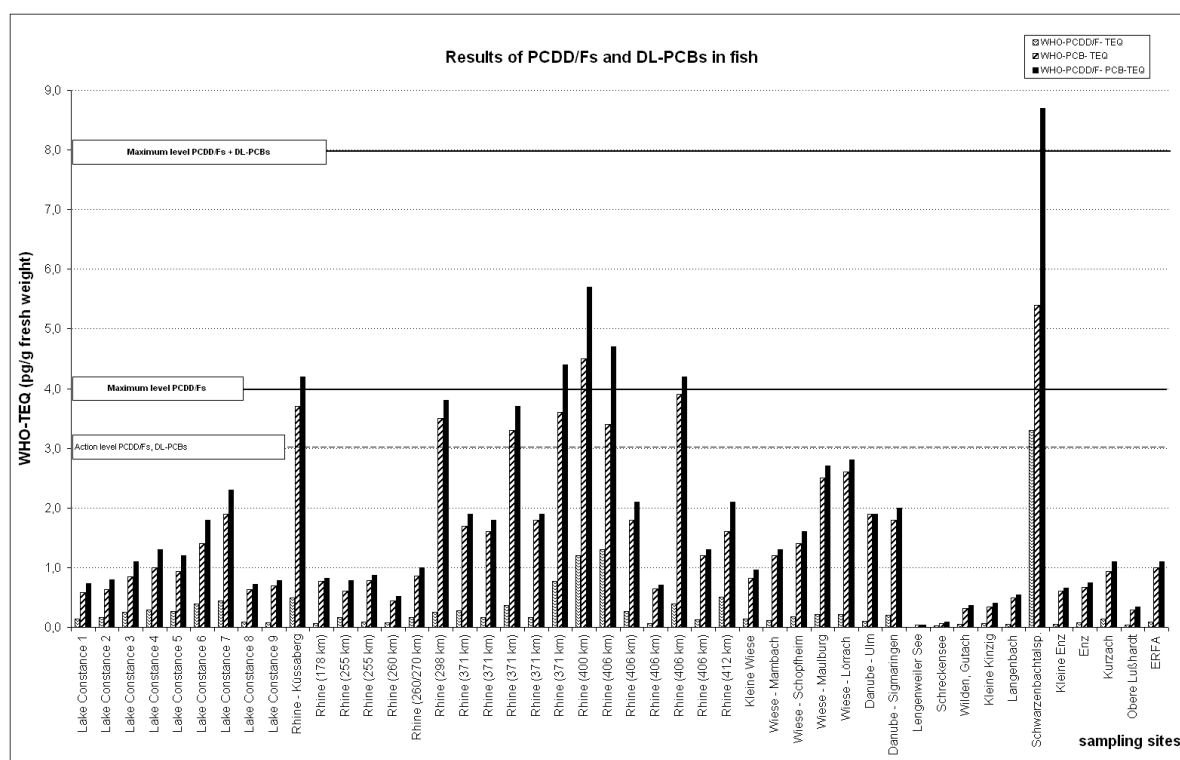
- SSL injector: Injection of 1 µl splitless
- GC separation: HT-8 PCB
- HRMS: Resolution 10'000

## Results and discussion

### PCDD/Fs and PCBs

#### 1. Results for fish samples (except eel)

All 46 analysed fish samples showed PCDD/F values below the maximum level for fish of 4 pg WHO-PCDD/F-TEQ/g fresh weight (see figure 1). The maximum level for the sum of PCDD/Fs and dioxin-like PCBs of 8 pg WHO-PCDD/F-PCB-TEQ/g fresh weight was exceeded by one sample consisting of two, more than 7 year old breams (length > 40 cm, weights > 700 g). Only this sample also exceeded the action level for PCDD/Fs (3 pg WHO-PCDD/F-TEQ/g fresh weight). As the metabolism of PCDD/Fs and PCBs in fish is low, organochlorine contaminants are accumulated in lipid tissue with increasing age of the fish. Eight samples showed levels above the action level for dioxin-like PCBs (3 pg WHO-PCB-TEQ/g fresh weight): the above mentioned bream sample and seven samples originating from the Rhine. The majority of these samples consisted either of fish species with relatively high fat contents (e.g. grayling, bream) or fish of advancing age (e.g. perch).



**Figure 1:** Levels of PCDD/Fs and dioxin-like PCBs in fish samples sorted by water body and Rhine kilometers

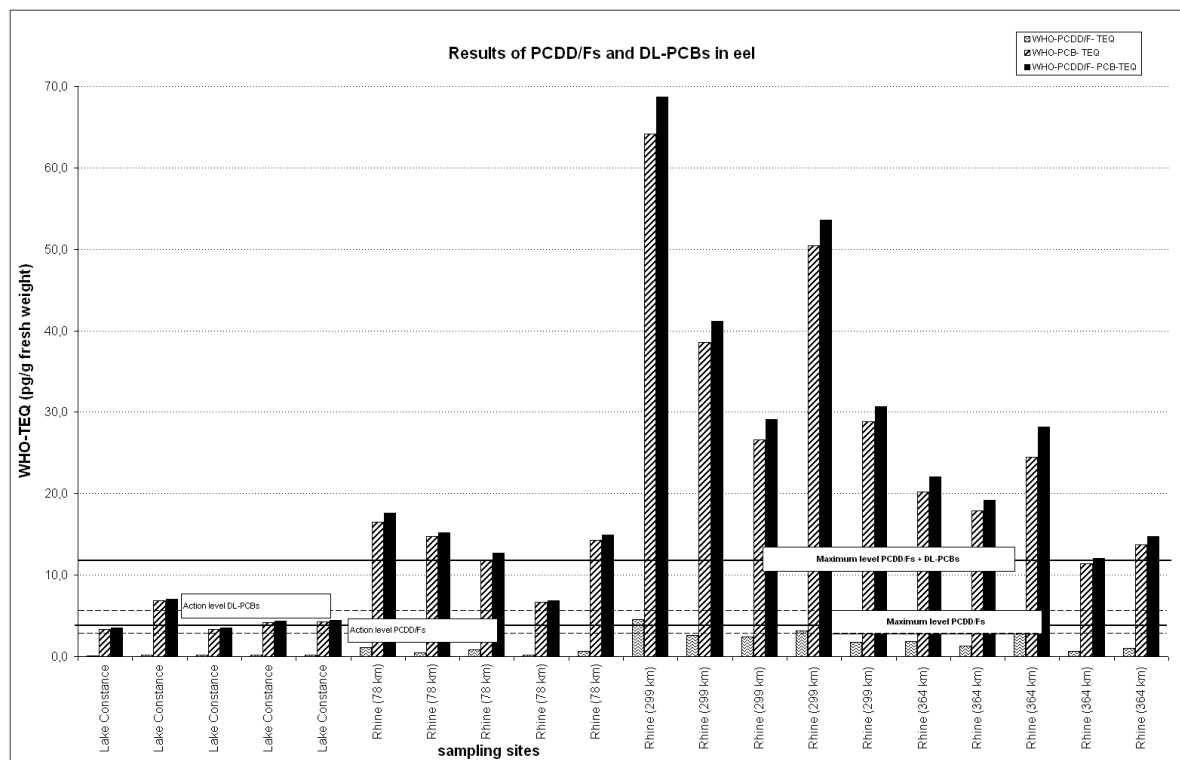
#### 2. Results for eel samples

The eel samples originated from Lake Constance (5 samples) and from the Rhine (15 samples).

Whereas all eel samples from Lake Constance contained levels for the sum of PCDD/Fs and dioxin-like PCBs considerably below the existing maximum level of 12 pg WHO-PCDD/F-PCB-TEQ/g fresh weight, the majority (14 of 15) of the eel samples, originating from the Rhine, showed values either within the range of, or above the maximum level for the sum of PCDD/Fs and dioxin-like PCBs due to high contribution of dioxin-like PCBs (see figure 2).

Only one eel sample exceeded the maximum level for PCDD/Fs of 4 pg WHO-PCDD/F-TEQ/g fresh weight, while two others contained PCDD/F levels above the action level (3 pg WHO-PCDD/F-TEQ/g fresh weight).

The amount of dioxin-like PCBs in all eel samples collected from the Rhine and one sample from Lake Constance were above the action level for dioxin-like PCBs in eel of 6 pg WHO-PCB-TEQ/g fresh weight.



**Figure 2:** Levels of PCDD/Fs and dioxin-like PCBs in eel samples sorted by water body and Rhine kilometers

The samples collected at the same sampling site contained levels of PCDD/Fs and dioxin-like PCBs in the same range. The highest levels were found in eel samples originating from the Rhine, sampling site 299 km. It has to be taken into account however, that the lipid range of the individual eel samples was quite high, having a great influence on the results. E.g. the lowest levels of PCDD/Fs and dioxin-like PCBs were found in eel samples from the Rhine with less than 10 % fat.

#### *Pesticides and other organic contaminants*

Organochlorine and organobromine pesticides and contaminants, nitro-musk compounds and pyrethroids were analysed in 46 fish samples (except eel). All samples showed levels considerably below the legal maximum residue levels. The highest DDT levels of 24 and 28 µg/kg fresh weight were observed in two samples collected at the Rhine, while two other samples, also originating from the Rhine, contained the highest levels of HCB.

#### *Heavy metals*

None of the samples contained detectable levels of cadmium while small amounts of lead were detected in some cases. Several samples showed levels of mercury in the range of the maximum level. The highest levels were determined in samples originating from the Rhine. The legal maximum levels were not exceeded in any sample.

#### *PFCs*

Perfluorinated (PFCs) compounds have not been regulated in the European Union until this stage. However, levels of contaminants should be minimised as far as possible in general. Detectable values of PFOS (perfluorooctanesulfonic acid) up to 124 µg/kg fresh weight were found in 22 of 46 samples. Other PFCs were

below the limit of detection (LOD) in all analysed samples. The highest PFOS levels were detected in fish samples originating from the Rhine. Samples from Lake Constance contained an average PFOS value of 15 µg/kg. The majority of samples from other waterbodies comprised PFOS levels below the limit of detection (4 µg/kg).

### Conclusions

The levels of PCDD/Fs, PCBs, pesticides, heavy metals and PFCs varied considerably in fish samples from waterbodies in Baden-Württemberg. This depended on the load situation of the water body at the sampling site and the mixture of the samples (e.g. fat content, age/size, fish species). The results provide a comprehensive estimate of the human intake of contaminants through consumption of fresh water fish, but however, owing to the type of sampling, can not be considered as representative for the load situation of the waterbodies. In general, fish species with high fat content are more likely to accumulate lipophilic contaminants. In this context it has to be mentioned that none of the pooled fish samples contained more than 10 % fat.

14 of 15 eel samples originating from the Rhine showed values in the range of or above the maximum level for the sum of PCDD/Fs and dioxin-like PCBs. Because of a decrease in eel population in the Rhine, a year-round protection for eel has been introduced in Baden-Württemberg. It is thus currently not allowed to catch and market eel.

Persistent, lipophilic contaminants and pesticides have been accumulating through the food chain in fatty tissue of animals. Therefore, the background contamination of fish is still quite high. As fresh water fish is one of the foodstuffs with comparatively high concentration of contaminants, consumption of fresh water fish may contribute considerably to an undesired body burden. However, this should be considered in light of the fact that fish is regarded as a nutritionally important foodstuff and thus is recommended to be consumed on a regular basis. For that reason recommendation of fresh water fish consumption should take into account species and origin of fish in particular.

### Acknowledgements

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