PCDD/PCDF LEVELS IN FRESHWATER FISH FROM SOUTHERN GERMANY

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Introduction

Consumption of fish is one of the main routes of daily intake of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF)[1,2]. Despite the fact that freshwater fish contributes only about 10 % to the total fish consumption in the federal republic of Germany[3], these foodstuffs may be relevant to PCDD/PCDF intake of people with special nutrition habits. Most of the consumed freshwater fish is produced in fish farms and it is generally assumed that in this case contamination of fish is caused mainly by PCDD/PCDF contents in feedingstuffs used in the farms. On the other hand wild freshwater fish, as a part of the aquatic food chain, is exposed to environmental PCDD/PCDF levels and bioaccumulation and biomagnification may lead to high contamination levels. For this reason wild fish is suitable for bioindication purposes and can be useful for identification of PCDD/PCDF sources. PCDD/PCDF contamination of wild freshwater fish should also be considered in relation to human exposure, because it is regularly consumed by anglers and offered in restaurants. Here we present PCDD/PCDF levels in the edible portion of freshwater fish from rivers and lakes in Bavaria in Southern Germany. Results are compared to contamination levels of freshwater fish raised in fish farms.

Methods and Materials

Wild freshwater fish was caught at background sites in Bavarian rivers and lakes or at sites close to outlets of municipal purification plants between 1992 and 1995. Skinless fillets of either single or composites of several individuals were homogenised and freeze-dried. Fat separation and determination of fat content was performed by extraction with n-hexane/acetone (2+1). After addition a mixture of 15 ^{13}C-labelled internal standards a clean-up with three chromatographic steps (mixed acid-base-silica, charcoal, florisil) was carried out. Determination of PCDD/PCDF was performed by HRGC/HRMS on a AutoSpec Ultima mass spectrometer at a resolution of 10,000 in the selected ion mode. Isomeric specific separation of PCDD/PCDF was carried out on DB5-ms and SP2331 capillary columns. For calculation of TEQ values TEFs according to WHO were used.

Results and Discussion

Table 1 shows a summary of sample data and TEQ results on fat basis and on basis of wet tissue. Average TEQ values on fat basis ranged between 6.6 pg/g and 73.5 pg/g. Fish species with low fat content (hike) showed relatively high contamination levels on fat basis whereas fish species with high fat content (eel) revealed significantly lower PCDD/PCDF levels in fat. On wet tissue basis these differences in PCDD/PCDF levels caused by different fat contents were more or less equalised and all

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TEQ mean values lay in a relatively narrow range between 0.5 and 2.2 pg/g wet tissue. For comparison purposes and for calculation of PCDD/PCDF intake results on wet tissue basis are more useful that results on fat basis. Highest median TEQ results on wet tissue basis were obtained in barbel followed by common bream and eel. The determined PCDD/PCDF levels in wild freshwater fish from Bavaria were in good correspondence with contamination levels in fish from other regions in Germany [4].

Table 1. PCDD/PCDF levels in wild freshwater fish

fish species	n	weight[a] [g] mean median (range)	fat [%] mean median (range)	WHO-TEQ [pg/g] mean median (range) fat basis	WHO-TEQ [pg/g] mean median (range) wet tissue basis
rainbow trout *(Onchor. mykiss)*,	19	427	4.2	15.2	0.52
trout *(Salmo trutta)*,		347	3.1	14.1	0.38
powan *(Coregonus lavaretus)*,		(224-1057)	(0.8-8.1)	(3.8-56.2)	(0.24-1.53)
grayling *(Thymallus thymallus)*					
pike *(Esox lucius)*	10	1481	0.6	73.5	0.5
		1370	0.6	68.6	0.31
		(447-3622)	(0.2-1.1)	(37.1-132)	(0.11-1.45)
chub *(Leuciscus cephalus)*	19	855	3.3	25.8	0.82
		713	3.1	21.8	0.66
		(218-1713)	(1.5-7.9)	(8.6-103)	(0.13-3.82)
common bream *(Abramis brama)*	17	984	3.9	39.2	1.63
		945	3.0	30.0	1.02
		(462-1530)	(0.5-15.1)	(18.2-97.6)	(0.49-11.7)
barbel *(Barbus barbus)*	19	1153	4.8	49.4	2.22
		1172	4.8	35.1	1.33
		(516-1844)	(1.2-8.7)	(15.2-180)	(0.65-11.2)
carp *(Cyprinus carpio)*	11	2250	6.8	26.0	1.55
		1626	4.6	17.5	0.36
		(932-6098)	(0.5-21.4)	(3.9-110)	(0.09-6.25)
roach *(Rutilus rutilus)*,	6	737	3.5	38.7	1.24
nase *(Chondr. nasus)*,		893	2.1	33.6	0.69
chrub *(Aspius aspius*),		(99-1246)	(0.8-10.8)	(17.5-64.9)	(0.17-3.73)
tench *(Tinca tinca)*					
eel *(Anguilla anguilla)*	10	409	24.8	6.6	1.58
		378	25.2	5.3	1.25
		(144-703)	(18.4-29.8)	(2.7-14.9)	(0.77-3.6)

a) fish without guts

Considering the frequency histogram of all TEQ results on wet tissue basis (figure 1) it was obvious that mean values were influenced by a small number of samples with elevated contamination levels. Most samples (87 %) showed low WHO-TEQ values below 2 pg/g.

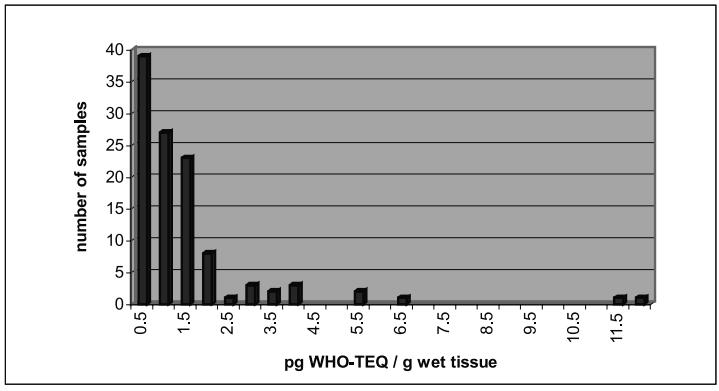

Figure 1. frequency histogram of TEQ results in freshwater fish

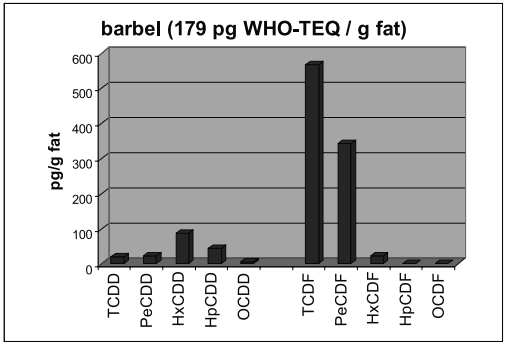

Figure 2. PCDD/PCDF homologue profile found in barbel

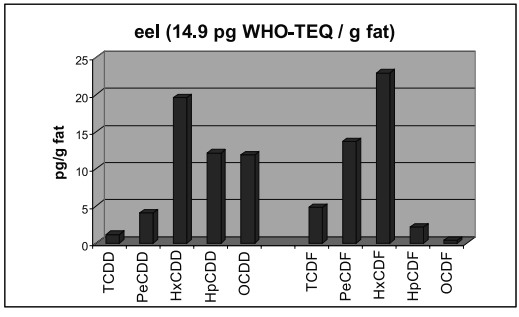

Figure 3: PCDD/PCDF homologue profile found in eel

Highest WHO-TEQ values of individual samples on wet tissue basis were found in a common bream (11.7 pg/g), in two barbel (11.2 and 5.4 pg/g) and in two carp (6.3 and 5.2 pg/g). These samples originated from different waters in Bavaria (rivers and lakes) and contamination levels could not be attributed to a common PCDD/PCDF source. The determined PCDD/PCDF values in freshwater fish were not connected with the origins of the samples and no general conclusion about contamination levels of certain waters or sampling sites could be drawn on the basis of the reported data.

A characteristic PCDD/PCDF homologue profile found in all fish species except from eel is presented in figure 2. Generally, 2,3,7,8-TCDF was the predominant congener followed by 2,3,4,7,8-PeCDF. In addition to 2,3,7,8-substituted congeners a number of non-2,3,7,8-substituted congeners, mainly TCDF and PeCDF were detected.

The PCDD/PCDF homologue profile found in eel samples differs significantly from the typical fish profile and shows higher relative amounts of PCDD compared to PCDF and another pattern of PCDF congeners (figure 3). Remarkably, no significant differences in PCDD/PCDF homologue profiles and congener patterns between low and high contaminated samples were detected and therefore no proof was obtained that specific PCDD/PCDF sources have been responsible for increased contamination.

Mean and median PCDD/PCDF levels in wild rainbow trout and related fish species in this study were 0.52 and 0.38 pg WHO-TEQ/g wet tissue, respectively. In another study rainbow trout raised in fish farms in Bavaria were analysed for PCDD/PCDF contents[5]. Samples had similar weights and fat contents as the wild rainbow trout in the present study and the determined average PCDD/PCDF level was 0.28 pg I-TEQ/g wet tissue, corresponding to 0.32 pg WHO-TEQ/g wet tissue (due to the higher WHO-TEF for 1,2,3,7,8-PeCDD, WHO-TEQ values in fish are about 110 to 115 % of the calculated I-TEQ values). Hence, there was no fundamental difference in contamination levels between wild and farmed rainbow trout in Bavaria. Slightly higher PCDD/PCDD contents were observed in other fish species like barbel, common bream and eel.

Acknowledgments

The technical assistance of M. Brimmers, V. Gebser, B. Picman, A. Richt, F. Stindl and R. Zeif is gratefully acknowledged.

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