PCDD, PCDF, AND DIOXIN-LIKE PCB IN FISH FROM SWISS LAKES

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Introduction

Dioxins and PCB are widespread, persistent and toxic environmental contaminants with high tendency to bioaccumulate in aquatic and terrestrial ecosystems. The hydrophobic substances have strong affinity to sediments and a high potential to accumulate in organisms. Humans are exposed to these contaminants mainly by the intake of food containing fat of animal origin such as dairy products, meat, and fish. Fish belongs to the food category exhibiting the highest WHO-TEQ concentrations[1].

Sixteen fish samples from 10 Swiss lakes were analysed for their content of polychlorinated dibenzo-*p*-dioxins (PCDD), polychlorinated dibenzofurans (PCDF) and polychlorinated biphenyls (PCB). All 17 2,3,7,8-substituted PCDD/F, the 6 PCB indicator congeners IUPAC no. 28, 52, 101, 138, 153, and 180, and the dioxin-like mono- and non-ortho-substituted PCB congeners 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189 were determined in filet of three species of food fish (bass, roach, and whitefisch) which are widespread in Swiss lakes. Total WHO-TEQ and total indicator PCB congener levels were calculated on lipid and wet weight basis. As PCB analyses are often based only on total indicator PCB levels, the correlation between total indicator PCB, total non-and mono-ortho substituted PCB (WHO-TEQ) as well as total PCDD/F (WHO-TEQ) was studied.

Materials and Methods

The fish samples were collected by the respective fishery authorities of the lakes. Each sample consisted of 5 to 34 individuals with equal numbers of males and females. In the laboratory, the skin was removed from the filets, and the skin was scraped off to collect the bulk of the subcutaneous fat. The filets were cut into small pieces and mixed manually. An aliquot of about 100 to 150 g of the mixture was suspended in about 300 mL of ultra pure water and homogenised thoroughly using a commercial household mixer. The homogenate was transferred into a 2 L separation funnel and the lipids were extracted as describe in the literature [2]. After gravimetrical determination of the lipid content, an aliquot of 1.5 to 4 g fat was spiked with the internal standard (the 17 2,3,7,8-substituted $^{13}C_{12}$-labeled PCDD/F, the $^{13}C_{12}$-labeled PCB indicator congeners 28, 52, 101, 138, 153, and 180, and the $^{13}C_{12}$-labeled mono- and non-ortho substituted PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189). The extract was passed through a multilayer silica gel column (60 g potassium silicate, 5 g 10% water deactivated silica and 60 g of 40% sulphuric acid silica from top to bottom) with 500 mL *n*-hexane, and the eluted was directed to an AX-21 column (300 mg of 8% carbon AX-21 on celite 545). The PCDD/F as well as the mono- and non-ortho-substituted PCB were eluted in reverse flow mode with 40 mL Toluene. After volume reduction to about 0.5 mL and addition of 15 mL *n*-hexane, the extract was further purified by chromatography trough silica gel (basic, neutral, acidic) followed by basic alumina using an automated sample cleanup system (Fluid Management Systems Inc., Waltham, MA, USA).The mono-ortho substituted PCB including the indicator PCB 28 were eluted from the alumina column with 80 mL 4% dichloromethane in *n*-hexane. PCDD/F and non-ortho substituted PCB 77, 81,

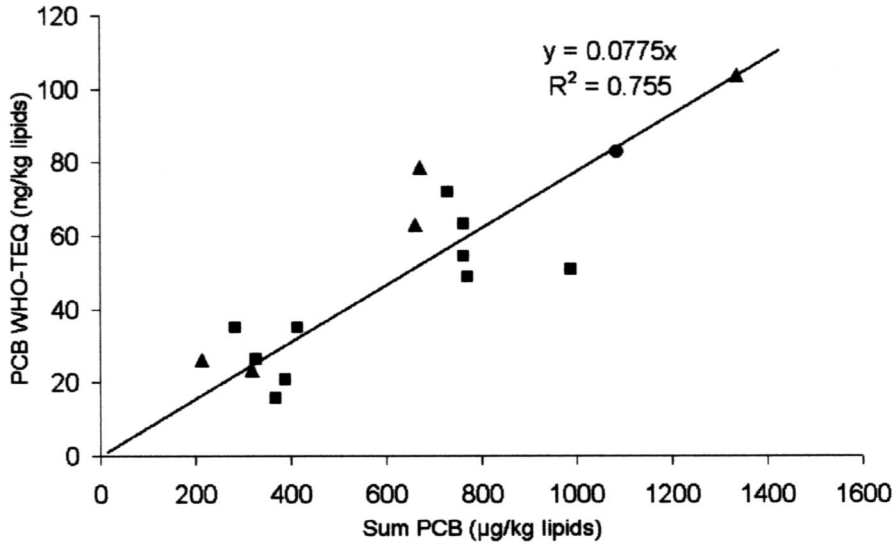

Figure 1. WHO-TEQ contribution of PCB vs. total indicator PCB in all fish samples (■: whitefish, ▲: bass, ●: roach; see Table 1).

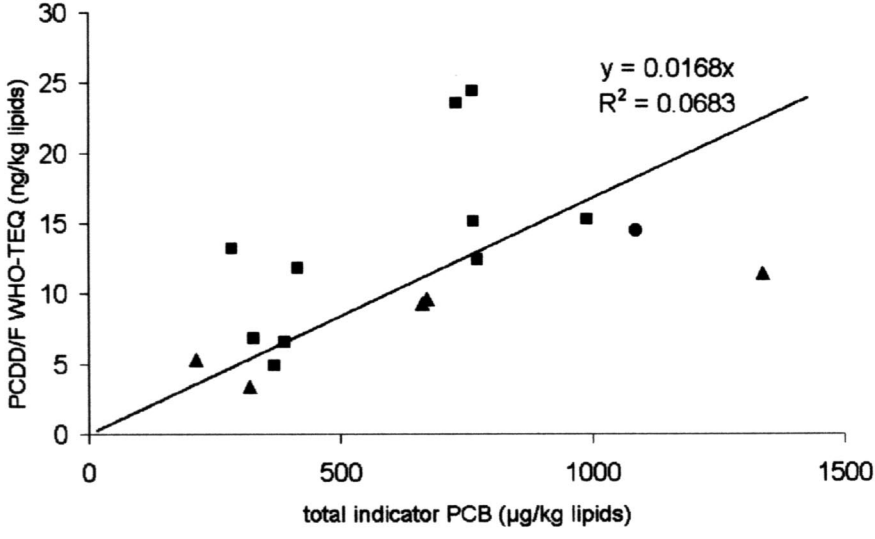

Figure 2. WHO-TEQ contribution of PCDD/F vs. total indicator PCB in all fish samples (■: whitefish, ▲: bass, ●: roach; see Table 1).

Table 1. PCB and PCDD/F levels (ng/kg lipid weight) in fish from Swiss lakes (B: bass, *Perca fluviatilis*; R: roach, *Rutilus rutilus*; W: whitefish, *Coregonus sp.*)

Lake	Species	total indicator PCB	PCB WHO-TEQ	PCDD/F WHO-TEQ	Total WHO-TEQ
Bielersee	W	988	51	15	66
	B	662	63	9.3	72
Bodensee	W	389	21	6.6	27
	B	320	24	3.4	27
Genferersee	W	328	27	6.8	33
	B	673	79	9.7	88
Greifensee	W	763	63	24	88
Neuenburgersee	W	415	35	12	47
	B	214	26	5.3	32
Sempachersee	W	367	16	4.9	21
Thunersee	W	284	35	13	48
Vierwaldstättersee	W	771	49	12	61
Zugersee	W	730	72	24	96
	R	1‘085	83	15	97
Zürichsee	W	764	54	15	70
	B	1‘336	104	11	115

126, and 169 were eluted with 80 mL of 50% dichloromethane in *n*-hexane. Similarly, the eluate from the carbon column containing the indicator PCB 52, 101, 138, 153, and 180 was further purified by multilayer silica and basic alumina chromatography as mentioned above. After addition of the recovery standard ($^{13}C_{12}$-1,2,7,8-TetraCDF), the 3 fractions were analysed by HRGC/MS. using a 60 m × 0.25 mm DB-Dioxin (film thickness 0.15 ìm) capillary column. The resolution of the mass spectrometer was 8’000.

Results and Discussion

The results of the investigation are summarised in Table 1. The profiles of the six indicator PCB 28, 52, 101, 138, 153, and 180 are typical for fish with maximum level for PCB 153 followed by PCB 138 and 101 (data not shown). The total indicator PCB concentrations were 2.5 - 57 ìg/kg wet weight and 210 - 1’300 ìg/kg lipid weight, respectively. The total WHO-TEQ of the non- and mono-ortho-substituted PCB (77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189) was 0.30 - 3.4 ng/kg wet weight and 16 - 104 ng/kg lipid weight, respectively. The congeners contributing most to the WHO-TEQ concentration are PCB 126 (60% ± 6.5) followed by PCB 118 (18% ± 6.5), PCB 156 (11% ± 2.6), and PCB 105 (4.8% ± 1.5). The high contribution of PCB 126 is mainly due to its high TEF of 0.1 whereas the contributions of PCB 105, 118, and 156 are due to their relatively high levels compared to PCB 126. The total WHO-TEQ concentration of the PCDD/F was 0.034 - 1.1 ng/kg wet weight and 3.4 - 24 ng/kg lipid weight, respectively. The total WHO-TEQ concentration including PCB and PCDD/F was 0.34 – 4.5 ng/kg wet weight and 21 – 115 ng/kg lipid weight. As shown in Figure 1, the correlation between the total indicator PCB and the WHO-TEQ contribution of the PCB allows an estimation of the WHO-TEQ contribution of the PCB based on the total indicator PCB (WHO-TEQ contribution of

the PCB corresponding to ca. 0.008 % of the total indicator PCB). On the other hand, the comparison of the total indicator PCB and the WHO-TEQ due to the PCDD/F shows a clearly poorer correlation (see Figure 2).

Acknowledgement

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References

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