Levels of Selected Non-, Mono- and Di-ortho substituted Polychlorinated Biphenyls in Some Fish Species from Swiss and French Environment

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Abstract

Samples of some selected fish species from Swiss and French fresh water were analyzed for contamination with non-ortho (77, 126, 169), mono-ortho (105, 118, 156) and di-ortho (52, 101, 128, 138, 153, 170 and 180) chlorine substituted PCB congeners. The levels of Toxic Equivalents (TEQs) for the coplanar and mono-ortho substituted PCB were calculated using the Toxic Equivalency Factors (TEFs) proposed by WHO-ECEH for dioxin-like PCBs.This report provides the new data on the levels of individual PCB congeners and their contribution to the TEQs in fish fresh water species.

Introduction

AHH active PCB congeners are found in environmental samples at level orders of magnitude greater then PCDD/Fs, thus presence can not be neglected when establishing the risk associated with dioxin-like contaminants [1]. The relatively recent addition of the dioxin-like PCBs to the assessment of risk associated with 2,3,7,8 chlorine substituted dioxins and furans caused an increasing of interest for the individual congeners determination in the biotic and abiotic samples [2,3] . Often, the analysis of PCBs to the coplanar and mono- ortho substituted congeners is limited [4-6].

The aim of this study was to evaluate the levels of selected non- (77,126, 169), mono- (105, 118, 156) and di-ortho substituted (52, 101, 128, 138, 153, 170 and 180) congeners of PCB in random samples of some fish species, coming from Swiss and French fresh water environment. The chlorobiphenyls studied were selected according to their substitution patterns and the choice was based on their abundance, persistence and toxicity[7].

Experimental Methods

Fish samples were grinded, freeze dried during 24 h and homogenized before the analysis. The fat content in examined fish species, was determined according to de Boer method [8]. The analysis of selected PCBs congeners was performed with a modified method of Tanabe at al. [9]. The lipids were hydrolyzed by saponification with KOH/ 1M EtOH (200 ml) at 60^0 C for 2 h under reflux. The reaction mixture was cooled and diluted with bidististilled water (100 ml) and extracted with hexane (3 x 50 ml) in a separation funnel. The combined hexane layers were dried with anhydrous Na_2SO_4 and concentrated to ca. 3 ml in a rotary evaporator. To eliminate the remaining lipids, H_2SO_4 conc. (4 ml) was used. The cleaned-up and concentrated sample was transferred to a WAKO activated charcoal column (ID 0.6 cm). The mono- and di-ortho substituted congeners (fraction I) were eluted with a mixture of CH_2Cl_2 : hexane [3:7] (120 ml). The column was turned round and the planar PCBs (fraction II) were recovered from activated charcoal in reversed elution with toluene (30 ml). Both fractions containing PCBs were concentrated and purified with H_2SO_4 conc. (2 ml). C_7 - DCBE as internal standard was added before GC analysis. Three or two µl of the cleaned-up and concentrated extracts were injected on capillary columns (RT_x-35 - 60 m, ID 0.25 mm, 0.25 µm and PTE-5 - 60 m, ID 0.25 mm, 0.25 µm), respectively of Varian 3300 and Hewlett-Packard 5890 Series II gas chromatographs. The presence of planar PCB in selected samples was confirmed by GC-MS analysis on Hewlett-Packard 5890A gas chromatograph.

Results and Discussion

The analytical procedure used in the present study has been tested with fish samples spiked with different levels of 13 individual congeners. The recovery was determined to be over 75 % for planar (77, 126, 169) and mono- ortho substituted (118, 105, 156) CBs. The recovery levels were between 82 % and 101 % for chlorobiphenyls di- ortho substituted. The precision of analytical procedure was less than 10 % for all examined congeners, except 77 and 101 CBs [10].

For this preliminary study randomly selected samples of fish from Swiss lake and river and from French river water were chosen. The characteristics and concentration of the sum of 13 specified non- (77, 126, 169), mono- (105, 118, 156) and di- ortho substituted congeners (52, 101, 128, 138, 153, 170 and 180) in examined fish samples are shown in Table 1. The Figure 1 shows that all fish species exhibited similar di- ortho congener profiles. The concentration range (expressed as the content of Σ 13 individual congeners) varied from 1.14 µg/g fat in the trout 1 to 10.60 µg/g fat in bream fish. The content of PCBs in fish from Saône river was three to ten times higher then in the other species. The concentration of selected congeners in all samples corresponds to the results presented by Malisch[11] for fish coming from upper Rhine.

The profiles of planar and mono- ortho substituted PCB congeners, presented in Table 2 are similar. The levels of planar congeners (ng/g wet weight) ranged from 0.055 - 0.330; 0.024 - 0.105 and 0.007 - 0.013 for PCB 77, 126 and 169 respectively. These values correspond to the those determined by Atuma et al.[12] in different Baltic fish species. The concentrations of mono- ortho substituted (between 0.45 ng/g wet weight for PCB 156 to 27.99 ng/g wet weight for PCB 118) were by one to three order of magnitude higher then from the planar PCB.

Table 1. Characteristics and levels of the sum of 13 specified PCB congeners in different fresh water fish species from Swiss and French environment

Fish type	Place of catch	Fat content [%]	Σ of selected PCB congeners*	
			ng/g wet weight	ng/g fat weight
Trout 1** *Salmo truta fario*	Maggia River (upper)	5.8	65.98	1 137
Trout 2 *Salmo truta fario*	Maggia River (bottom)	7.4	237.46	3 235
Artic char *Salvelinus alpinus*	Lake Geneva (Minor)	16.0	254.43	1 594
Burbot *Lota lota*	Lake Geneva (Morges)	4.7	101.97	2 179
Bream *Abramis brama*	Saône River	3.8	402.42	10 590

* - sum of congeners no. 77, 126, 169 ,105, 118, 156, 152, 101, 128, 138, 153, 170 and 180.
** - the separation of the PCB congeners groups was performed on Hypercarb HPLC column[10].

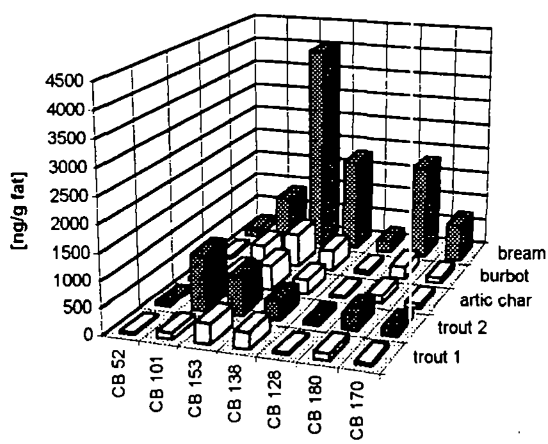

Figure 1. Content of some di- ortho substituted PCB congeners in selected fresh water fish species.

The sum of TEQs for coplanar and mono- ortho substituted PCB congeners, calculated using TEFs values proposed by WHO-ECEH[13)], is presented in Table 2. The contribution of each individual congeners to the total TEQ values in the fish samples is illustrated at Figure 2.

Table 2. Dioxin - like PCB concentrations [ng/g wet weight] and sum of TEQ in some selected fish species

Fish type	CB 77	CB 126	CB 169	CB 105	CB 118	CB 156	Σ TEQ [ng/g wet]	Σ TEQ [ng/g fat]
Trout 1	0.088	0.095	0.011	0.86	1.31	0.45	0.010	0.175
Trout 2	0.330	0.104	0.007	6. 43	23.10	5.89	0.017	0.226
Artic char	0.141	0.105	0.010	6.72	27.99	6.82	0.018	0.110
Burbot	0.055	0.024	0.003	2.79	11.59	2.05	0.005	0.104
Bream	0.151	0.099	0.013	3.86	21.81	14.53	0.020	0.523

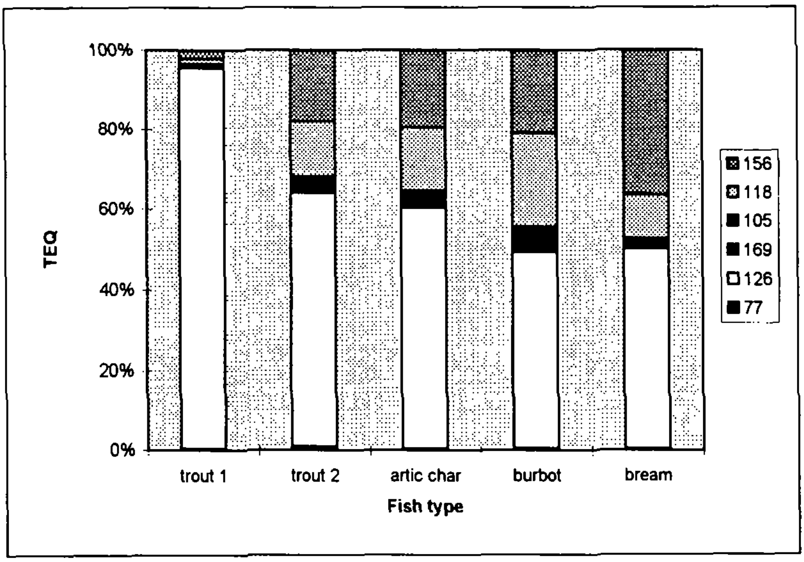

Figure 2. Contribution [%] of some planar and mono- ortho substituted PCB congeners in TEQ of selected fresh water fish species.

The percentage of CB 126 in ΣTEQ exceeded 50% for all samples under investigation and the next is CB 156 with about 18 - 36 % (except in trout 1). It shows that the planar and mono- ortho substituted CB congener patterns in examined fish were similar to these observed by other authors [12, 14]. It is worth to note, however, that the level of contribution to the total TEQ values varied slightly between the different fish species. Further work is needed to improve the data on the level and the contribution to the TEQ of the dioxin - like PCB congeners in different fresh water species.

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