Planar PCBs in selected freshwater fish from Czech Republic

Pavel Gregor and Jana Hajšlová

Institute of Chemical Technology, Department of Food Chemistry and Analysis,
Technická 3, 166 28 Prague 6, Czech Republic

Introduction

Relatively high levels of "indicator" PCBs were found (1) in various fish species collected at some of sampling sites involved in monitoring program funded by the Czech Ministry for the Environment. Since more detailed information on the occurrence of particular congeners in aquatic environment was needed, analytical procedure employing GC system currently used for routine analysis of major PCBs was implemented for determination of *non-ortho* substitute PCBs (No.77, 126 and 169) and other congeners (No. 105, 114, 118, 156, 157, 167 and 189) showing similar toxic properties as 2,3,7,8 -TCDD. To assess health risk due to consumption of contaminated freshwater fish, samples of species used as "biomonitors" in respective locality were analysed for the content of these compounds.

Material and Methods

Following samples of pooled fish (fillets, skin removed) collected in autumn 1997 were analysed : (i) barbel (20 pieces, weight in range 800-1000 g) caught in Elbe river, locality Hřensko - close to the German border, (ii) yellow eel (24 pieces, 30-44 g) from the same sampling site, (iii) roach (18 pieces, 510-640 g) caught in Skalice river, locality downstream from Rožmital and (iv) roach (17 pieces, 530-650 g) caught in Skalice river upstream from Rožmital.

The procedure used for fillets analysis consisted of these steps: homogenised sample (approx. 300-500g) was mixed with anhydrous sodium sulphate to obtain a free-flowing powder. Analytes were extracted with three portions of hexane:acetone mixture (2:1, v/v) using sonication (the lipid content was determined gravimetrically). 1-2 gr of lipids are redissolved in hexane (20 ml) and mineralized with the equal volume of 98% conc. sulphuric acid. The upper layer was taken out and bottom acid one was extracted two times with hexane. Combined hexane extract was carefully evaporated to approx. 1 ml and then transferred on the top of disposable silica gel column (2g, silica activated 5 hours at 170°C and partially deactivated to 3% water content). PCBs were eluted with 15 ml of hexane, the volume of this fraction was reduced to 1 ml and injected into HPLC-PYE system (Cosmosil PYE column, 2-/1-pyrenyl/ethyl silica, 250×4.6 mm, 5 µm particles, operated at 0°C with hexane as eluent, 0.5 $ml.min^{-1}$). Fractions of *multi-* (0-6 ml), *mono-* (6-10 ml) and *non- ortho* (10-20 ml) PCB were collected and then the solvent was changed to isooctane (200 µl for *non-ortho* fraction, 1000 µl for other two). Identification / quantitation of analytes was carried out by two dimensional HRGC-ECD, the columns (used in parallel) were DB-5 and DB-17 (both 60m × 0.25mm, film 0.10 µm).

Results and Discussion

The levels of *non-ortho* and *mono-ortho* PCBs found in the examined fish samples are summarized together with calculated values of toxic equivalents (TEQ) in Table 1. Toxic equivalency factors (TEFs) recently recommended by WHO (2) were used for calculation of PCB toxic equivalents (TEQ). Due to the coelution with congener 118, PCB 123 was not quantitated, similarly it was not possible to determine PCB 81 which was coeluted on both columns with traces of p,p′- DDE (tailing from previous fraction); it should be noted that levels of these PCBs compared to other "toxic" species are typically negligible.

Elbe river, locality Hřensko, was selected for fish sampling because of contaminated sediments occurrence of which was documented in our preliminary monitoring study. Barbel was chosen as a biomonitor of site-pollution since it represents relatively non-migratory species feeding on bottom macrobentos. The choice of yellow eel was based on its proved suitability for monitoring purpose (3). Although the fat content in tissues of barbel was distinctly lower than that in eel, still significantly higher TEQ (expressed on fresh weight basis) were calculated for pooled samples of this fish species. Unfortunately, due to the variability of TEF values utilized to express TEQ, the direct comparability of presented values with data shown in other studies is rather limited (in many recent papers TEF according to Ahlborg (4) are used). In any case, the concentrations of *non-ortho* and *mono-ortho* substituted PCBs determined in barbel from Elbe river even exceeded values reported by de Boer et al. (5) for some freshwater fish (pike-perch, perch) collected in seriously polluted Rhine, Meuse and their side-rivers. Hence, considering results obtained for barbel, Elbe may be assigned among the strongest PCB-contaminated waters in Europe. However, for the assessment of the extent of contamination on the basis of PCBs content found in this fish, the influence of biomagnification has to be considered in particular case. Moreover, unbiased comparison of available data is possible only for identical fish species of equal age (lenght, weight) category. Young fish should be preferably sampled within monitoring programs (3). This was the case of eels analysed in presented study. While relatively old (approx. 6-8 years) and, consequently, considerably contaminated barbels were sampled, analysed eels were very young and therefore the levels of PCBs in their tissues were relatively low. Noticably higher relative contribution of the "most toxic" PCB 126 to the total concentration of TEQ was observed for in this species, see Table 2. On the other hand, compared to barbel, the contribution of other *non-ortho* substituted PCB 77 was lower almost by one order of magnitude. This phenomenon may be due to relatively strong metabolic degradation capacity for this PCB in eel.

Skalice was further river of concern as regards potentially increased incidence of PCBs in fish. 12 years ago, a serious breakdown pollution by Delor 103 (PCBs -containing technical mixture with 48%, w/w, chlorine) occurred at the locality Rozmital. Roach, which is the most abundant fish among locally available species, was sampled close to the site of PCBs leakage. Data shown in Table 1. indicate unequivocally continuing high PCBs input at sampling site downstream from Rozmital. 10-fold higher total TEQs were found in fish living here compared to that collected upstream.

Table 2 : PCBs congeners in pooled fish samples from Skalice river (A- upstream from Rozmital, B- downstream from Rozmital) and from Elbe river and relevant TEQ values

PCB	TEF $\times 10^{-3}$	roach A * (ng/kg)		TEQ (ng/kg) $\times 10^{-3}$		roach B** (ng/kg)		TEQ(ng/kg) $\times 10^{-3}$		eel *** (ng/kg)		TEQ(ng/kg) $\times 10^{-3}$		barbel† (ng/kg)		TEQ (ng/kg) $\times 10^{-3}$	
		T	L	T	L	T	L	T	L	T	L	T	L	T	L	T	L
Sum of 7 indicator PCB	-	23,290	2,329,000			97,890	5,758,000			118,370	607,000			545,470	24,794,000		
non-ortho																	
77	*0.1*	32	3,156	3.2	316	247	14,986	24.7	1499	3	16	0.3	2	188	8,410	18.8	841
126	*5*	2	196	10	979	36	2,150	177.3	10,748	16	80	77.8	399	55	2,445	272.5	12,223
169	*0.05*	0.4	42	0	2.1	2	121	0.1	6	2	11	0.1	1	5	235	0.3	12
mono-ortho																	
105	*0.005*	500	49,000	2.5	245	3,064	185,700	15.3	929	604	3,097	3	16	4,692	210,400	23.5	1,052
114	*0.005*	28	2,700	0.1	14	282	17,100	1.4	86	34	175	0.2	1	462	20,700	2.3	104
118	*0.005*	1,207	118,300	6	592	8,077	489,500	40.4	2448	2,707	13,882	13.5	69	25,685	1,151,800	128.4	5,759
156	*0.005*	404	39,600	2	198	2,183	132,300	10.9	662	815	4,180	4.1	21	11,759	527,300	58.8	2,637
157	*0.005*	152	14,900	0.8	75	426	25,800	2.1	129	147	753	0.7	4	1,824	81,800	9.1	409
167	*0.005*	667	65,400	3.3	327	3,258	197,400	16.3	987	1,236	6,340	6.2	32	8,195	367,500	41	1,836
189	*0.005*	25	2,400	0.1	12	383	23,200	1.9	116	87	444	0.4	2	1,142	51,200	5.7	256
Σ TEQ non-ortho				13.2	1297			202.2	12,253			78.2	401			291.6	13,076
Σ TEQ mono-ortho				14.9	1462			88.4	5,355			28.1	144			268.8	12,054
Total TEQ				28.1	2758			290.5	17,608			106.3	546			560.4	25,129

** lipid content 1.0%* *** lipid content 1.7%* **** lipid content 19.5%* *† lipid content 2.2%*
T... tissue basis *L... lipid basis*

To determine whether relative concentration of the Ah - active congeners were enriched relative to the major PCBs, TEQ was normalized to the sum of indicator PCBs (TEQ divided by sum of seven indicator PCBs). 3-fold higher values were found in roach from contaminated sampling site.

Table 2 : Relative contribution of individual "toxic" PCB to total TEQ value in pooled fish samples from Skalice river (A- upstream from Rozmital, B- downstream from Rozmital) and from Elbe river

PCB	roach A	roach B	eel	barbel
non-ortho				
77	11.46	8.51	0.37	3.35
126	35.50	61.04	73.08	48.64
169	0.08	0.03	0.18	0.05
mono-ortho				
105	8.88	5.28	2.93	4.19
114	0.51	0.49	0.18	0.41
118	21.46	13.90	12.64	22.92
156	7.18	3.76	3.85	10.49
157	2.72	0.73	0.73	1.63
167	11.86	5.61	5.86	7.31
189	0.44	0.66	0.37	1.02

Acknowledgments

The authors wish to thank for financial support provided by Ministry of the Environment. The part concerned with analytical methodology was initiated within project (contract No. Vav/340/2/97) supported by Grant Agency of Czech Republic.

References

1. Hajšlová J, Schoula R, Kocourek V, Gregor P, Kohoutková J, Holadová K, Poustka J, Svobodová Z, Vykusová B; *Bull. Environ. Contam. Toxicol.* **1997**, 59, 452
2. Leeuwen van F X; WHO Toxic Equivalency Factors (TEFs) for dioxin-like compounds for human and wildlife, 15-18 June 1997, Stockholm, Sweden
3. de Boer J and Brinkman U A Th; *Trends Anal. Chem.* **1993**, 13, 397
4. Ahlborg U G, Becking B C, Birnbaum L S et. al; *Chemosphere* **1994**, 28, 1049
5. de Boer J, Stronck C J N, Traag W A, Meer van der J; *Chemosphere* **1993**, 26, 1823