

PCBs in Samples from the Environment of the Southern Moravia Region, Czech Republic

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Abstract The determination of polychlorinated biphenyls (PCBs) in water, sediment and fish samples from the Czech Republic was carried out using high resolution gas chromatography with electron capture detection. PCBs concentrations in water and sediment samples were rather low and corresponded with the findings from some prior studies. On the other hand, investigated samples of fish tissue were highly contaminated (on average 1.3–266 ng/g fat for individual PCBs), thus, a continuing contamination of fish species with PCBs was proved.

Keywords Polychlorinated biphenyls · Water · Sediment · Fish

Polychlorinated biphenyls (PCBs) are a group of chlorinated hydrocarbons widely used for industry in many different applications. However, their physical and chemical stability, and also their lipophilic character make them serious environmental pollutants, which are highly persistent and tend to accumulate in soils, tissues and aquatic biota. The main sources of PCBs in ecosystems after the ban of their industrial production are soils, in which over 90% of these substances are deposited (Korinek 1999).

PCBs were produced on the territory of Slovakia of the former Czechoslovakia and were also massively used in the whole country in the first half of the 1980s. Therefore, whole territory of the Czech Republic is still under the impact of this increased load and that this fact is naturally present also in the PCBs occurrence in the components of the hydrosphere. The load of the hydrosphere in the CR is manifested by a number of findings with the increased concentrations (Holoubek et al. 1990).

The purpose of this study was to evaluate concentrations of selected important PCB congeners in water and sediment samples and fish adipose tissues (*Barbus barbus*) from different areas of the Moravia region and to compare found concentrations with some previous corresponding studies and/or monitoring programs.

Materials and Methods

Water, sediment, soil and fish samples used in the investigations were taken from localities with a suspected secondary pollution, due to reclaimed and illegal waste sites for industrial waste containing Delor 106 (a commercial product based on PCBs). Water samples (1 L each) were taken from both watercourses and stagnant waters (reservoirs, river branches etc.). Both polluted sampling areas and those assumed to be relatively clean were chosen. All water samples were stored in dark glass bottles at 4°C until extraction. Sediment and soil samples (1 kg each) were taken from fourteen sampling sites. Top 10 cm were taken into PE bags using a grab sampler.

Fish samples were taken from the Korycany reservoir (46°6'42.05", 17°12'10.86"). One species was collected for analyses: barbel (*Barbus barbus*, fam. Cyprinidae) (2 × 32

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samples of muscle tissue). The tissue of this species has higher content of fat (on average 5%).

Sulphuric acid and organic solvents for trace analysis were purchased from Merck (Darmstadt, Germany). Anhydrous sodium sulphate (Onex, Czech Republic) was activated in an oven at 650°C for 5 h, Florisil (60–100 mesh, Aldrich, Germany) was heated at 550°C for at least 16 h, and then allowed to cool down at room temperature in a desiccator. Standards and certified reference material containing PCBs were purchased from St. Dr. Ehrenstorfer, Germany. In addition, two technical mixtures of PCBs (Aroclor 1242 and 1260, 1 µg/ml, isooctane) were used as well. All solutions were conserved in dark at 4°C.

All samples were analysed for 7 indicator (No. 28, 52, 101, 118, 138, 153 and 180) and 7 minor (No. 8, 18, 47, 49, 187, 189 and 209) PCB congeners.

Water samples with a volume of 1 L were extracted three times with *n*-hexan (30, 20, 20 ml). The extracts were cleaned by SPE using Florisil columns. The solvent was removed in a rotary vacuum evaporator and the residue was dissolved in 1 ml of isooctane.

Sediment and soil samples were dried in an oven at 85°C for 12 h, homogenized and weighed for the analysis (approx. 30 g). The samples were then extracted with dichlormethane using pressurised solvent extraction (PSE; 100°C, 14 MPa, static cycles 2 × 5 min). Florisil columns were further used to clean-up extracts.

Homogenized fish tissues (100–200 g) were mixed with anhydrous sodium sulphate and extracted by agitation three times (3 × 30 min). The mixture of *n*-hexane/diethylether (94:6) was used at laboratory temperature. Clean-up of extracts was done using Florisil columns.

GC conditions: HP 6890N gas chromatograph, series II (Agilent, USA), equipped with two electron capture detectors (µECD, ⁶³Ni, temp. 300°C) and two different columns connected parallelly to a common inlet. HT-8 fused silica capillary column (50 m × 0.22 mm × 0.25 µm) was used for quantification and a confirmation column of different polarity (DB-17MS, 60 m × 0.25 mm × 0.25 µm) was used to verify chemical identity. PTV injector: 90°C for 6 s, increased to 350°C at 750°C/min, held for 5 min and then to 220°C at 10°C/min. Injected amount: 2 µL. Carrier gas: hydrogen – linear speed 27 cm/s. The column temperature was programmed at 80°C, increased to 180°C at 20°C/min, then to 250°C at 10°C/min, ramped to 270°C at 2°C/min and held for 28 min.

Quantitative assessment was carried out using the method of external standard (absolute calibration) within the linear range of the detector. The certified reference material (CRM) [fish tissue extract and harbour sediment with PCBs] used for the determination of PCB recoveries was purchased from St. Dr. Ehrenstorfer, Germany. Analyte recoveries were 88%–95% in water samples, 82%–92% in sediments and soils and 86%–96% in fish. The method detection limit (MDL) for PCBs ranged from 0.6 to 0.7 ng/L in water samples, from 0.05 to 0.06 µg/kg in sediments and 1 µg/kg of fat in fish.

Results and Discussion

The concentrations of PCBs in both water and sediment samples are presented in Table 1 and Fig. 1. In water samples these compounds, particularly PCB 28 and 153,

Table 1 Concentrations of selected PCB congeners in water samples and in soils and sediments

PCB congener	Water samples (ng/L)			Soils and sediments (ng/g dry wt)		
	Mean	Median	Range	Mean	Median	Range
PCB 8	2.72	2.30	1.30–4.80	0.61	0.15	0.05–2.78
PCB 18	6.82	4.30	2.40–18.70	0.76	0.32	<0.05–3.05
PCB 28	14.22	8.35	0.90–56.40	1.03	0.70	0.05–3.42
PCB 47	4.28	2.50	<0.60–17.10	0.40	0.21	0.06–1.12
PCB 49	3.86	1.95	<0.60–18.30	0.44	0.23	<0.05–1.27
PCB 52	4.82	3.15	0.80–21.20	0.46	0.20	0.07–1.32
PCB 101	3.10	1.48	0.60–15.83	1.97	1.06	0.59–5.56
PCB 118	1.65	0.85	<0.60–5.80	0.92	0.59	0.06–2.92
PCB 138	3.62	1.40	0.60–29.33	2.88	2.20	0.37–7.17
PCB 153	6.21	2.20	0.90–52.93	3.54	2.31	0.60–9.76
PCB 180	4.92	1.20	<0.60–34.57	3.55	2.66	0.41–10.88
PCB 187	0.70	0.70	<0.60–0.80	2.47	1.67	0.32–6.50
PCB 189	ND	ND	ND	0.14	0.14	<0.05–0.23
PCB 209	ND	ND	ND	0.14	0.10	0.09–0.23

ND under MDL

were detected in increased concentrations. On the basis of values determined for single congeners it was possible to identify a respective commercial mixture containing PCBs. Total PCB concentrations observed in water samples ranged from 5.2 to 190.8 ng/L. The highest PCB water concentrations were observed in the water sample from a field drain ditch (the locality of Lisci near the town of Novy Jicin, Central Moravia) and in the Smradavka reservoir (near the town of Uherske Hradiste, Southern Moravia), which showed a strong pollution of these sites. The limit concentration of indicator PCB congeners for surface water (Czech Government Regulation No. 82/1999 Coll.) –10 ng/L (now recommend 12 ng/L) was exceeded in 11 of 19 samples.

In sediments, only moderate concentrations were found for low chlorinated congeners No. 28 and 52. On the contrary, higher levels were determined for highly chlorinated PCBs such as PCB 138, 153, 180 and one minor PCB 187. In the case the probable source of pollution was Delor 106 (equivalent to Aroclor 1260) used in the manufacture of dyes. It is apparent that the range of values is rather broad.

In general, the sum of the indicator PCBs in 3 of 10 sediment samples exceeded the background value of 20 ppb (according to the Regulation No. 3/1996 of the Czech Ministry of Environment) and after including contribution of minor PCB congeners four samples exceeded the limit. The highest concentration reaching 50 ng/g dry wt. was found in the sediment from the Smradavka reservoir (Southern Moravia), the notorious locality with an occurrence of illegal waste sites of dyes containing PCBs.

The levels of monitored PCB congeners in fish are summarised in Table 2 and Fig. 1. It can be seen that the levels of differently chlorinated congeners varied significantly and there were considerable ranges of the concentrations of the same PCB congeners (from tens up to hundreds of ng per g of fat). The levels of PCB congeners

Table 2 Concentrations of selected PCB congeners in muscle tissue of barbel (ng/g fat)

PCB congener	Mean	Median	Range
PCB 8	1.30	1.22	1.04–1.70
PCB 18	1.49	1.29	1.04–2.79
PCB 28	32.89	23.07	5.22–247.44
PCB 47	1.92	1.63	1.07–3.27
PCB 49	2.60	1.51	1.01–9.17
PCB 52	37.94	18.67	2.19–708.17
PCB 101	44.74	28.25	1.03–257.57
PCB 138	140.39	75.96	1.33–922.67
PCB 153	266.52	128.29	3.39–1677.52
PCB 180	167.34	69.97	1.18–1164.78
PCB 187	3.68	1.81	1.01–19.19
PCB 189	ND	ND	ND
PCB 209	ND	ND	ND

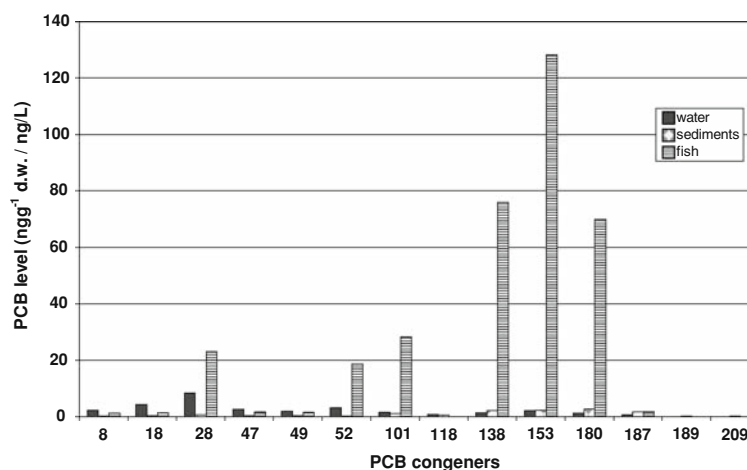
138, 153 and 180 were the highest in all fish samples. The amount of PCBs found in these fish demonstrably correlated with the higher content of fat as well.

Investigated minor PCB congeners were present in the samples at much lower levels than the indicator congeners except of PCB 189 and 209 that were under the MDL value in all samples. The occurrence of remaining minor congeners in the fish (PCB 8, 18, 47, 49 and 187) was very different and they were not detected in many samples at all. Shown in Fig. 2 is a typical chromatogram of fatty tissue extract of fish.

In most samples the PCB levels did not exceed hygienic limits (500 ng/g fat), however, a significant exceeding of this limit was found in 19 samples. The highest levels of individual PCBs can be seen in Table 2 from the range values.

The results obtained in this study demonstrate that the levels of organic pollutants in fish tissue taken from the

Fig. 1 Median levels of selected PCB congeners in investigated samples



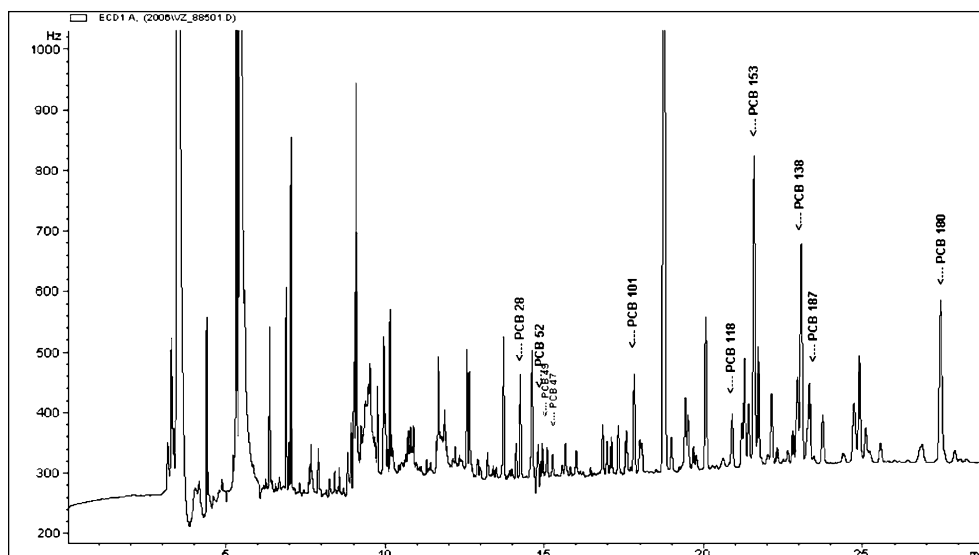


Fig. 2 Chromatogram of the fat extract from the fish muscle tissue

Korycany fresh-water reservoir were relatively high, however, they were comparable with the results published in earlier studies (Vavrova et al. 2003; Hajslova et al. 1997; Sapozhnikova et al. 2004).

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References

- Hajslova J, Schoula R, Kocourek V, Holadova K, Poustka J, Kohoutkova J, Svobodova Z (1997) Toxicological and Environmental Chemistry 59:279–291
- Holoubek I, Houskova L, Seda Z, Holoubkova I, Kott F, Korinek P, Bohacek Z, Caslavsky J (1990) Project TOCOEN. The fate of selected organic compounds in the environment. III. Water and Sediments 1988. Toxicol Environ Chem 29:29–35
- Korinek P (1999) The fate of selected chlorinated hydrocarbons in the system of water–sediment–soil. PhD thesis, MUNI, Czech Republic
- Sapozhnikova Y, Bawardi O, Schlenk D (2004) Pesticides and PCBs in sediments and fish from the Salton Sea, California, USA. Chemosphere 55:797–809
- Vavrova M, Sucman E, Pac J, Zlamalova-Gargosova H, Stoupalova M, Jiruskova J, Navratil S, Palikova M (2003) Assessing contamination levels in a reservoir on the basis of the determination of xenobiotics in fish. Fresenius Environ Bull 12:901–905