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PCBs and Dioxins in Sediments and Surface Waters of the Michalovce Region

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Abstract. 21 sediments (Zemplínska Šírava – water reservoir, Laborec River, Veľká Domaša – water reservoir, Ondava River, Váh River, Nitra River) and 11 samples of surface water (Zemplínska Šírava - reservoir, Morské oko Lake, Vinianske Lake, Laborec River) were analyzed for polychlorinated dibenzodioxins and dibenzofurans (PCDDs/Fs) and polychlorinated biphenyls (PCBs) including mono-ortho-substituted and planar congeners.

The content of PCDDs/Fs in sediments was determined by the US EPA 1613 method using high-resolution mass spectrometry (HRGC/HRMS). In total, 17 "dioxin" congeners and 12 mono-ortho-substituted and planar toxicologically important PCB congeners were analyzed in the samples collected.

Analysis of PCBs in sediments was done by low-resolution mass spectrometry (modified US EPA 1668) and in surface water samples by the method of gas chromatography with electron capture detection.

Samples were collected from December 2002 to May 2003. The obtained results point to carrying over contamination with PCBs in the Michalovce region.

Key words: sediment, surface water, PCBs, dioxin, PCDD/Fs

Introduction

The environmental fate and behavior of individual PCB congeners are influenced by physical-chemical properties, mainly by volatility, water solubility and lipophilicity. Less chlorinated congeners have higher vapor pressure and are more water-soluble than higher chlorinated ones. The congeners with higher number of chlorines are more lipophilic. These differences influence composition of individual congeners in different environmental matrices. PCBs present in surface water are adsorbed on particulates, accumulate in sediments and subsequently concentrate in tissues of water organisms. Due to their possible mobilization from sediments, accumulation in the food chain, and finally in the human body they represent a potential risk for human health (Salizzato et al., 1998). Major sources of environmental contamination with PCBs in the Slovak Republic are PCB production in eastern Slovakia during the period of 1959-1984 and PCB use. In total, 21,482 tones of PCB formulations were produced there. It has been declared that 11,613 t were used inside former Czechoslovakia chiefly as heat exchanger fluids, capacitor and transformer dielectric fluids, and paint additives. It is estimated that about 1,600 tones of PCB wastes were generated during the production. PCBs are positively detected in all environmental compartments of Slovakia such as air, surface water, sediments, soil, foodstuffs and human biological tissues as well (Kočan et al., 1998).

Sediments from the area of former PCB production in Slovakia show high values even 14 years after its ceasing – up to 4.1 $mg.kg^{-1}$ (avg. 0.3 $mg.kg^{-1}$) (Kočan et al., 1999, Petrík et al., 2001). Sediment PCB levels from water bodies from the other areas of Slovakia range between 0.01-2.8 $mg.kg^{-1}$. Samples with high content of PCBs come mainly from the areas of high industrial activities. The measu-rements conducted in 1983-2001 document that 24 % of surface water samples (SHMÚ, 2003) contained more than 10 ng PCBs/L - recommended maximum concentration.

Material and methods

The sediment samples for this study were collected using UWITEC sampler and/or manually with a scoop. The water samples were collected according to STN ISO 5667-4,6. Collection of sediments was performed from October to December 2002 and water samples in May 2003. All samples were processed immediately after delivery to the laboratory.

Determination of PCDD/F/dioxin-like PCBs in sediments (HRGC/HRMS)

The sediment was dried at max. 50 °C, grinded and sieved. The fraction below 2 MM I.D. was used for next processing. Approximately 5 grams of homogenized sample was extracted in Soxhlet apparatus after spiking with a known amount $^{13}C_{12}$ labeled extract standards. The toluene extract was after concentration cleaned-up by a modified silica column. The final eluate was fractionated using basic alumina and subsequently by an activated carbon column. After evaporation to dryness the

sample was reconstituted with known volume of the syringe standard and analyzed by HRGC/HRMS in MID (Multi Ion Detection) mode. Individual PCDD/Fs and dioxin-like PCBs were identified by comparing GC retention time and ion-abundance ratio of two exact m/z 's with the corresponding retention time of an authentic standard and the theoretical or acquired ion-abundance ratio of two exact m/z's. Quantitation was done by isotope dilution mass spectrometry technique using calibration standards containing $^{13}C_{12}$ labeled and unlabelled congeners according to USEPA 1613 and USEPA 1668 methods.

Determination of other PCB congeners in sediments (HRGC/LRMS)

The samples were prepared as written above. Homogenized samples were extracted with n-hexane/diethyl ether mixture. The clean-up procedure was performed on an H_2SO_4/silica column. Quantification was carried out by high-resolution gas chromatography (HRGC) with low-resolution mass spectrometry (LRMS) in a single ion-monitoring (SIM) mode using USEPA 1668 method. More details are given in (Petrík et al., 2001, Kočan et al., 1994).

Determination of other than dioxin-like PCBs in surface water samples (HRGC/ECD)

Surface water samples spiked with clean-up standard were filtered. Combined extracts from the aqueous and solid portions were cleaned-up on a florisil-silica/H_2SO_4 column. The eluates were allowed to evaporate to dryness and subsequently were reconstituted with the syringe standard solution. HRGC/ECD conditions and method of quantitation are given in detail in (Kočan et al., 1999, Krupčík et al., 1992).

Results and discussion

The results of „dioxins" and PCBs in sediments and surface water samples from different sampling sites of Slovakia are presented. Just PCB analyses were performed in water samples.

It is obvious from the results of surface water samples (Table 1) that the contamination of waterways is not on very high level even though the values from Zemplínska Šírava and the river of Laborec are still slightly above the recommended limit (10 ng.L^{-1}) for surface water in the Slovak Republic (Regulation 491, 2002). We found out almost the same values as were determined in the previous study (Kočan et al., 1999).

As it can be seen from Table 1 the highest concentrations were determined in Zemplínska Šírava (sampling sites inflow and outflow canals). These samples were taken below the Chemko Co. effluent canal merges the Laborec River. Laborec is the main source, which the reservoir is filled from. Sampling sites ZŠ Paľkov and Kamenec located on the eastern side of the reservoir without direct influence of Laborec waters present a little bit lower level of PCB pollution. Similarly, rather low values were determined in the forest lakes Morské oko and Vinianské Lake. Both these ecosystems have no direct (through the river of Laborec and/or ZŠ) connection to contaminated industrial effluent canal of Chemko Co. Low PCBs were also found in Laborec above the former producer (Chemko Co.). Atmospheric deposition is the most probable contributor of PCBs to these waters.

Table 1 Concentration of PCBs in surface water samples.

	Kočan et al., 1999	This study
	ng.L^{-1}	
Zempl. Šírrava (Biela h.)	20	20.7
Zempl. Šírrava (Medvedia h.)	19	25.3
Zempl. Šírrava (Kusínn)	14	-
Zempl. Šírrava (Palkov)	-	15.3
Zempl. Šírrava (Kamenec)	-	14.4
Zempl. Šírrava (Hôrka)	-	24.6
Zempl. Šírrava (inflow canal)	55	43.3
Zempl. Šírrava (outflow canal)	17	29.3
Laborec (above Chemko co.)	13	7.0
Laborec (below Chemko Co.)	68	-
Čierna voda Channel	16	-
Senné fish ponds	10	-
WWT plant (outflow canal)	64	-
Effluent canal (Chemko Co.)	1950	-
Merged canal (WWT-plant+Chemko Co.)	1338	-
Domaša	7	-
Ondava	9	-
Olšavka	10	-
Morské oko (inflow)	-	4.0
Morské oko (outflow)	-	5.4
Vinianské Lake	-	8.1

Sediments analyzed within this study were sampled from different water bodies around Slovakia. By assumption the highest values of PCBs and „dioxins" were determined in sediments from the industrial – effluent canal from the factory of Chemko Co.). The increased values were observed also in sediments from the river of Laborec and Zemplínska Šírava as well. The other watercourses (Nitra and Váh) show PCB values on the background levels measured in the previous study (Kočan et al., 1999). Comparison of PCB data measured in Zemplínska Šírava sediments collected in 1997/98 (Kočan et al., 1999) and 2002 (this study) is shown in Fig. 1.

The results of PCDD/Fs show very low contamination in the Laborec and Ondava rivers and in Veľká Domaša reservoir. The moderate contamination was observed in Zemplínska Šírava. These data are comparable with published data (Schramm et al., 1997, Bruckmeier et al., 1997, Fattore et al., 1997, Rappe et al., 1997, Buckland et al., 1997) for background and/or not industrially contaminated areas.

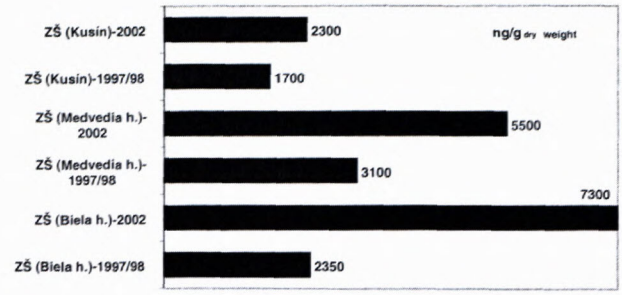

Figure 1 PCB content in sediments from Zemplínska Šírava.

None of the sediments had quantifiable levels of 2,3,7,8-TCDD. Except OCDD and 1,2,3,4,6,7,8-HpCDD none of other CDD congeners were determined almost in all sediments. The main contributors of the „dioxin" toxicity in the samples from the area of Chemko Co. are shifted from PCDD to PCDF as a consequence of PCB pollution. It can be seen from the Figure 2 that even in low contaminated sediment samples TEQs from PCBs comprise considerable contribution to the total TEQ values.

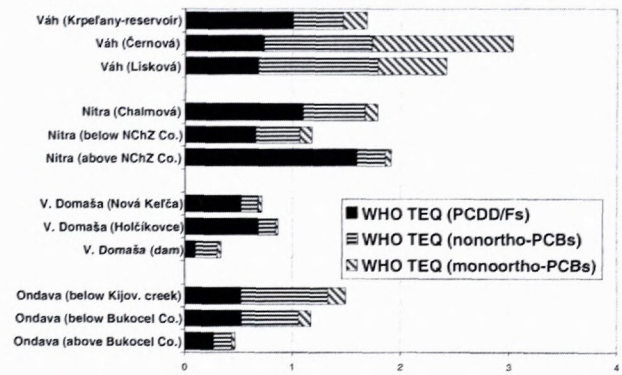

Figure 2 Contribution of PCDD/Fs and dioxin-like PCBs to the total TEQ values in selected sediments.

Conclusions

It is obvious from the comparison of water samples from Zemplínska Šírava and other Slovak water bodies collected in 1997/98 and 2003 that just samples taken in surroundings of the former PCB producer reach values above recommended value for surface waters. Although the PCB production was ceased almost 20 yrs. ago the industrial effluent canal from the factory (see *Table 1*) is the most probable source of contamination with PCBs in this area. PCBs accumulated in sediments are just slowly mobilized into water. This situation will last probably till the remediation starts.

PCDD/Fs levels in sediments represent the first data in Slovakia. The PCDD/F ratio reflects the source of possible contamination. TEQ values of the samples collected near the Chemko Co. effluent canal consist mainly of PCDFs. The other samples with low PCDD/F concentrations show approximately similar contribution of PCDDs and PCDFs.

Table 2 PCBs and „dioxin" concentrations in sediments.

	PCDD/Fs	0-ortho-PCBs	1-ortho PCBs	PCBs
	[WHO-TEQ, pg/$g_{D.W.}$]			[ng/$g_{D.W.}$]
Ondava (above Bukocel Co.)	0.27	0.17	0.032	19
Ondava (below Bukocel Co.)	0.53	0.53	0.11	27
Ondava (below Kijov. Creek)	0.52	0.81	0.16	40
Effluent canal (below Chemko Co.)	56	233	113	108611
Effluent canal (below WWT plant)	341	1963	1236	733210
Effluent canal (road Strážske-Michalovce)	586	1992	1039	566726
Laborec (Voľa)	0.23	11	6	1377
Laborec (Nacina Ves)	0.098	6.8	3.6	967
Laborec (Petrovce)	261	712	431	98445
Zemplínska Šírava (Biela hora)	20	53	20	7308
Zemplínska Šírava (Medvedia hora)	21	74	22	5511
Zemplínska Šírava (Kusín)	13	27	7.6	2277
V. Domaša (dam)	0.1	0.2	0.039	36
V. Domaša (Holčíkovce)	0.68	0.16	0.029	16
V. Domaša (Nová Kelča)	0.52	0.16	0.038	11
Nitra (above NChZ Co.)	1.6	0.26	0.05	22
Nitra (below NChZ Co.)	0.66	0.41	0.11	133
Nitra (Chalmová)	1.1	0.57	0.11	74
Váh (Lisková)	0.68	1.1	0.64	116
Váh (Černová)	0.73	1	1.3	204
Váh (Krpeľany reservoir)	1	0.46	0.23	45

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