PCDD, PCDF and Coplanar PCB Levels in Blood from the Human Population of the Slovak Republic

Anton Kočan, Donald G. Patterson, Jr.*, Ján Petrík, Wayman E. Turner*, Jana Chovancová, Beata Drobná

GC/MS Laboratory, Department of Xenobiotics in the Environment, Institute of Preventive and Clinical Medicine, Limbová 14, SK-833 01 Bratislava, Slovak Republic

*Toxicology Branch, Division of Environmental Health Laboratory Sciences, National Center for Environmental Health, Centers for Disease Control and Prevention, 1600 Clifton Road, Atlanta, Georgia 30333, U.S.A.

1. Introduction

Levels of polychlorinated biphenyls (PCBs) and some persistent organochlorine pesticides (HCB, pp'-DDT, pp'-DDE) in blood, adipose tissue and milk samples taken from the general human population living in selected model areas of the Slovak Republic were reported in our recent papers[1-4]. The data shows that the levels are substantially higher in comparison with other countries as a consequence of extensive past use of these chemicals within Slovakia. It should be noted that the use of the organochlorine pesticides was banned in Slovakia in the 70's and 80's. The production of Slovak PCB formulations called DELOR® was stopped in 1984 after about 20 000 t were produced.

Up to the present there is no information on PCDD/PCDF and coplanar PCB (planPCB) levels both in the Slovak human general population and occupationally exposed workers. In this short paper the levels of PCDDs, PCDFs, and coplanar PCBs found in blood serum samples collected from the Slovak general human population are presented. These pollutants were also determined in blood samples taken from a limited number of workers employed for a long time at a municipal waste incinerator or a PCB production plant.

2. Experimental

In 1993 thirty persons from the general Slovak population (three men and three women from each district) living in five selected model districts (Bratislava, Michalovce, Myjava, Nitra, and Veľký Krtíš)[3] donated their blood for PCDD/PCDF/planPCB determinations. Blood samples were taken from 2 men working for about 10 years in PCB production and samples from 4 men employed as stokers and maintainers for 7-15 years at a municipal solid waste incinerator equipped with insufficient stack gas cleaning (mean I-TEQ concentration was 7.7 ng/m^3 in stack gases and 30 pg/m^3 in working environment)[5,6].

The blood from volunteers fasting overnight was collected by venipuncture (no anticoagulant was used). Clotted blood was centrifuged. A 50-ml portion of serum was used for PCDD, PCDF, and coplanar PCB analysis and 2 ml for lipid determination by an enzymatic method[7]. Individual questionnaires were completed to obtain information on age, body height and weight, dietary habits, previous and current occupation, smoking habits, and domicile. Selected questionnaire data summarized for the sampling locations are given in Table 1.

Lipids and lipophilic compounds present in a weighed 50-g serum samples spiked with an internal standard containing ^{13}C-labeled 2,3,7,8-substituted PCDDs/Fs were captured on an activated 10-g C_{18}-cartridge and then extracted with n-hexane. The hexane extract was processed through a two-part

five-column semi-automated enrichment procedure[8]. In Part I, the extract passed through a series of silica-based adsorbents* and then through activated carbon. Compounds with a planar structure selectively retained on the carbon column were recovered by reverse elution with toluene. In Part II, the samples were cleaned through a column filled with cesium silicate and sulfuric acid-impregnated silica gel and fractionated on an activated alumina column. PCDDs, PCDFs and coplanar PCBs (#126 and 169) were recovered with dichloromethane:hexane (1:1) in the last fraction.

Table 1. Some data on subjects donating blood for PCDD/PCDF and coplanar PCB determination

*Location**		BA		MI		MY		NI		VK		MWI	Chemko
Sex		M	F	M	F	M	F	M	F	M	F	M	M
No. of Donors		3	3	3	3	3	3	3	3	3	3	4	2
Age	Mean	39.3	31.3	36.7	34.0	33.3	37.7	34.0	32.7	41.3	38.7	41.3	42.0
	Range	27-53	23-42	28-47	24-52	21-43	27-49	23-47	20-47	33-51	27-48	40-43	41-43
No. of	Smokers	2	1	1	2	2	0	1	1	1	0	2	0
	Ex-smokers	1	1	1	1	0	1	1	1	0	1	2	1
	Nonsmokers	0	1	1	0	1	2	1	1	2	2	0	1
Diet	Mixed	3	3	3	3	3	3	3	3	3	3	4	2
	Vegetarian	0	0	0	0	0	0	0	0	0	0	0	0
Domicile	Urban	3	2	1	3	0	0	1	1	3	3	4	1
	Rural	0	1	2	0	3	3	2	2	0	0	0	1

* BA = Bratislava, MI = Michalovce District, MY = Myjava area, NI = Nitra District, VK = Veľký Krtíš District, MWI = a municipal waste incinerator in Bratislava (about 100 000 t waste/year), Chemko = PCB production at the Chemko Co. in eastern Slovakia

Analyses were conducted on a VG-70SE mass spectrometer equipped with a VG 11/250J data system and a Hewlett-Packard 5890 gas chromatograph (GC). The spectrometer was operated at 10K resolution as defined by a 10% overlap using the peak match unit. Multiple group analyses consisted of two groups - in the first, m/z 292.98241 of PFK was used as the reference compound and, in the second, m/z 342.97922 of PFK. Injections were 2 µl of 5 µl of toluene containing 250 pg of $^{13}C_6$-1,2,3,4--TCDD. The GC and MS analyzers were operated under computer control to calibrate, acquire raw data, detect and integrate peaks, and print out chromatograms and ASCII output files that are transferred to rBase for DOS data storage on the Division of Environmental Health Laboratory Sciences (EHLS) network system. The analyses were conducted in a isomer-specific mode, with a 60-m, 0.25-mm i.d., 0.2-µm film thickness SP 2331 capillary column. The GC injector was at 240°C, and the interface at 250°C. The initial column temperature of 100°C was held for 2 min, then programmed to 220°C at 25°C/min and held for 2 min, and then programmed to 250°C at 15°C/min and held for 54.2 min. Seven channels were monitored for each analyte: 1 channel for $^{13}C_6$-1,2,3,4-TCDD, which was added to each sample to assess the instrument resolving power, 2 channels for the 2 lockmasses; and 4 channels to monitor the native 2378-substituted PCDD/PCDF and coplanar PCB analytes, and ^{13}C-labeled internal standards. Each analyte was quantified by the isotope-dilution technique using linear calibration curves established for each analyte[9].

3. Results and Discussion

The levels of PCDDs, PCDFs, and two of the most toxic coplanar PCB congeners (#126 and 169) expressed as TEQ's** determined in the blood serum samples are given in Table 2. The mean total lipids

* Potassium silicate and sulfuric acid-impregnated silica gel (column I), potassium silicate and silica gel (column II).

** If some congener was present at a concentration lower than its limit of quantification half of the LoQ was used for TEQ calculation.
International toxic equivalency factors (I-TEFs) according to NATO/CCMS were applied to PCDD/PCDF TEQ calculation and according to WHO/IPCS[10] (WHO-TEFs) to coplanar PCB TEQ calculation.

in the serum samples were 6.79 $g.L^{-1}$. Mean TEQ_{PCDD}, TEQ_{PCDF}, and $TEQ_{planPCB}$ values for each sampling location are presented in Figure 1. The values were similar in all the locations, including the MWI samples, whereas TEQ_{PCDF} and $TEQ_{planPCB}$ values were several times higher in the Chemko samples.

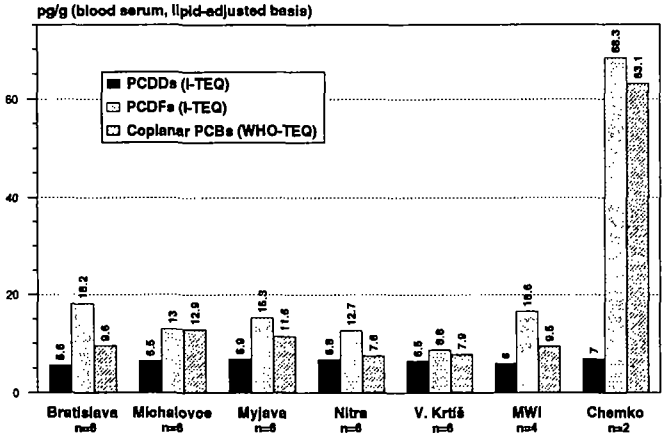

Figure 1.
PCDD, PCDF, and coplanar PCB levels (as toxic equivalents) found in blood serum (lipid-adjusted basis) of the general human population from five selected model districts of Slovakia and occupationally exposed workers from a municipal waste incinerator of Bratislava (MWI) and from former PCB production at the Chemko Co. (Chemko).

As shown in Figure 2 increased TEQ levels in the Chemko samples are caused mainly by higher concentrations of 2,3,4,7,8-PeCDF and 3,3',4,4',5-pentaCB (#126). 2,3,4,7,8-PeCDF has contributed 53% to the total mean TEQ found in the Slovak general population, 60% in the case of the MWI workers, and 80% in the case of the occupationally exposed workers in PCB production. There were no substantial differences between the PCDD, PCDF and planPCB levels in the general population samples from the sampling districts.

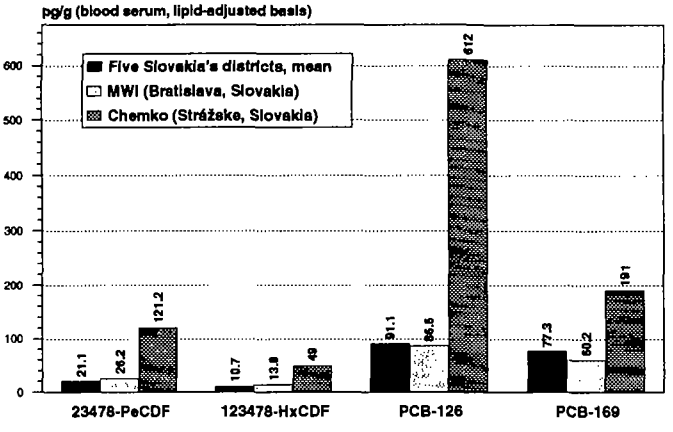

Fig.2. The levels of main contributors to total TEQ's in the Slovak general human population, MWI and Chemko workers.

In spite of long-term work at the old-type waste incinerator, PCDD/PCDF and coplanar PCB levels in the workers' blood were found to be within the range of the levels reported for the general population samples (Table 2, Figs. 1 and 2). This is in agreement with published data[11,12] although in some studies[13-15] a slight increase in the concentrations of higher chlorinated congeners was observed.

It is noteworthy that the ratio of $I\text{-}TEQ_{PCDD}$ to $I\text{-}TEQ_{PCDF}$ found in the Slovak general population is less than 1 (about 0.5), whereas according to published data from other countries this ratio is expressively higher - from about 1 for Germany and Spain to 2.7 for the U.S.A. (Figure 3)[16-20]. This is due to relatively high levels of 2,3,4,7,8-PeCDF (I-TEF=0.5) in the Slovak human samples in proportion to the *total TEQ's. On the other hand,* the levels of 1,2,3,7,8-PeCDD (a congener with the same I-TEF) were found to be very low. We assume that the increased 2,3,4,7,8-PCDF levels observed in the Slovak samples are due to increased exposure to PCBs. This assumption is supported by findings of a high

2,3,4,7,8-PeCDF content in the blood lipids of the Chemko workers occupationally exposed to PCBs. The ratio of the mean 2,3,4,7,8-PCDD level in the Chemko to the mean level in general population samples was 6 (121.2 : 21.1) which is also the ratio of total PCB levels found in the same samples[21].

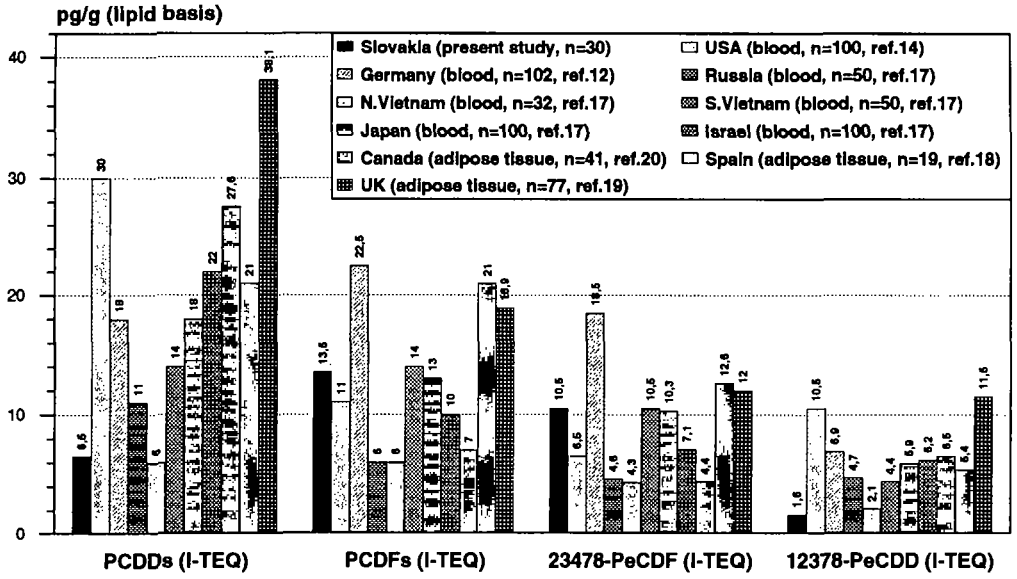

Fig.3. PCDDs, PCDFs, 2,3,4,7,8-PeCDF, and 1,2,3,7,8-PeCDD levels in blood and adipose tissue from general population samples

4. Acknowledgment

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HUM (po)

Table 2. PCDD, PCDF, and coplanar PCB levels (expressed as toxic equivalents, lipid-adjusted basis) in blood serum samples taken from the human general population of five model areas of the Slovak Republic and persons working in a municipal waste incinerator of Bratislava and Chemko Strážske, a former producer of PCB formulations (NR = not reported)

Area	Sex	Age	BMI [kg.m^{-2}]	Content [pg.g^{-1}, lipid adjusted]				
				I-TEQ$_{PCDD}$	I-TEQ$_{PCDF}$	I-TEQ$_{PCDD/F}$	WHO-TEQ$_{plusPCB}$	Σ TEQ's
Bratislava	Male	27	34.3	6.2	14.3	20.5	8.8	29.3
	Male	38	28.3	6.4	50.6	57	16.1	73.1
	Male	53	23.3	3.9	10.4	14.3	4.7	19
	Female	23	21.6	6.6	9.3	15.9	8	23.9
	Female	39	27.7	5.5	13	18.5	10.3	28.8
	Female	42	22.7	7.1	11.4	18.5	9.4	27.9
Average		37.0	26.3	5.6	18.2	24.1	9.6	33.7
Michalovce	Male	28	25.4	4.6	11.8	16.4	6.8	23.2
	Male	35	26.0	5.8	14.9	20.7	13.3	34
	Male	47	25.9	7	13.8	20.8	20.8	41.6
	Female	24	27.3	4.7	9.1	13.8	9.1	22.9
	Female	26	29.4	6.3	8	14.3	5.6	19.9
	Female	52	27.5	10.3	20.6	30.9	21.6	52.5
Average		35.3	26.9	6.5	13	19.5	12.9	32.4
Myjava	Male	21	24.2	3.6	9.6	13.2	3.3	16.5
	Male	36	20.5	NR	NR	NR	7.1	NR
	Male	43	27.8	11	22.9	33.9	29.3	63.2
	Female	27	20.5	4.3	12	16.3	7.1	23.4
	Female	37	25.6	6.7	12.4	19.1	5.6	24.7
	Female	49	30.5	8.9	19.8	28.7	17	45.7
Average		35.5	24.9	6.9	15.3	22.2	11.6	34.7
Nitra	Male	23	30.5	7.3	16.4	23.7	8.8	32.5
	Male	32	23.9	5.1	8.3	13.4	2.9	16.3
	Male	47	22.0	7	15.2	22.2	6.5	28.7
	Female	20	22.8	3.7	5.9	9.6	3.4	13
	Female	31	24.5	9	17.3	26.3	14.6	40.9
	Female	47	30.3	8.5	12.8	21.3	9.3	30.6
Average		33.3	25.7	6.8	12.7	19.4	7.6	27
Veľký Krtíš	Male	33	24.3	13.9	8.5	22.4	4.4	26.8
	Male	40	30.2	3.6	6.2	9.8	5.4	15.2
	Male	51	27.8	7.5	11.7	19.2	11.3	30.5
	Female	27	21.3	5.1	9.2	14.3	9.2	23.5
	Female	41	24.6	4.7	8.5	13.2	7.1	20.3
	Female	48	33.7	4.4	8.8	13.2	10.2	23.4
Average		40.0	27.0	6.5	8.8	15.4	7.9	23.3
Average$_{Males}$		36.9	26.3	6.6	15.3	22	10	32.1
Average$_{Females}$		35.5	26.0	6.3	12	15.3	9.6	28
Average$_{Females}$		*36.2*	*26.1*	*6.5*	*13.5*	*20*	*9.9*	*30*
MWI (Bratislava)	Male	40	27.1	4.2	10	14.2	5.4	19.6
	Male	41	26.0	6.8	9.5	16.3	5.8	22.1
	Male	41	24.2	6.6	10.8	17.4	3.5	20.8
	Male	43	35.9	6.4	36.2	42.6	23.4	65
Average		41.3	28.3	6	16.6	22.6	9.5	31.9
Chemko Co. (Strážske)	Male	41	28.4	8	52.2	60.2	104.5	164.7
	Male	43	33.1	6	84.3	90.3	21.7	112
Average		42.0	30.8	7	68.3	75.3	63.1	138.4