Persistent Organic Pollutants in the Slovak Republic

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Sources

A. PCBs

a) Production

PCBs called Delor (Delotherm, Hydelor) were produced in the Chemko chemical plant in Strazske (Michalovce District) from 1959 till January 1984 (Figure 1). The production started in 1959 with Delor 106 (corresponds to the composition of Aroclor 1260) that was prepared for a Czechoslovak paint factory (Barvy a laky, Uherske Hradiste) as a surrogate for imported Aroclor and Clophen. In 1967, the production of Delor 103 (~ Aroclor 1242) for capacitors and in 1968 Delor 105 (~ Aroclor 1254) launched. Delor 103 was used as a dielectric fluid in power capacitors produced in a Czech electrotechnical factory (ZEZ Zamberk) and Delor 105 in transformers produced also in the Czech Republic. Because at that time there was Czechoslovakia those products have been used on the territory of Slovakia, as well. In addition in 1969 the production of PCB formulations called Hydelor and Delotherm started. They were specially designed for hydraulic equipment and heat exchangers respectively. When the PCB production in Chemko Strazske was terminated in January 1984 officially 21 482 tonnes of PCBs were produced [Kocan et al. 1998].

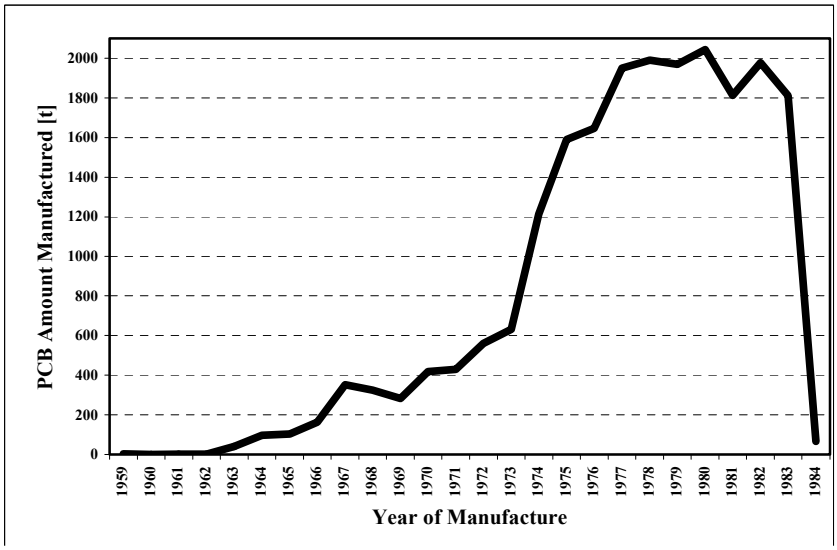

Figure 1 *Amounts of PCB formulations manufactured by Chemko Strazske in 1959-1984.*

9 869 tonnes, i.e. 46 percent, was exported mainly to former East Germany. The rest, i.e. 11 613 t was used inside former Czechoslovakia chiefly as heat exchanger fluids, capacitor and transformer dielectric fluids, and paint additives.

The production was based on the direct catalytic ($FeCl_3$) chlorination of pure biphenyl that was also manufactured in Chemko by the high temperature pyrolysis of benzene. When the expectable stage of chlorination was achieved reaction mixture was neutralized with sodium hydroxide and vacuum distilled. Lower chlorinated compounds were distilled off out of the mixture using steam-jet air pumps. Those compounds condensed in vacuum pump water and finally reached one of Chemko effluent canals. Distillation residues containing highly chlorinated biphenyls and terphenyls, and inorganic soils were filled into drums and stored. Be-

cause the residues were heated up to high temperature (sometimes about 500 °C) because of neutralization reactions one can expect a high content of PCDFs and other dioxin-like compounds.

There was an attempt to manufacture polychlorinated terphenyls in Chemko. About 35 t were produced of which about 30 t were used at glue production for furniture industry. Production devices as well as those for the PCB production corroded to a large extent resulting in leakage of a reaction mixture.

It has been estimated that in addition to the amount produced about 1 600 t of PCB waste were generated during the production. A part of the Chemko PCB waste entered the environment mainly via the factory effluent canal causing the contamination of the Laborec River and Zemplinska Sirava Lake. Another part could lie at a Chemko landfill site in a form of contaminated soil mixed with miscellaneous production waste.

Figure 2 *A specimen of waste from PCB production stored in the premises of a former Slovak producer*

The rest that is at least 1 000 tonnes is stored in storebuildings situated on the territory of the factory including drums (more than 1 000) that were collected in 1992 in a forest area above the Chemko factory.

This waste is composed of:

- Solid, resin-like or paste-like distillation residues containing besides organochlorines also inorganic salts, protective clothing, rags and other solid waste materials coming from the production processes; This waste is stored in 200-L and 60-L drums or in metal containers padded with polyethylene (Figure 2).
- Used transformer, capacitor and heat exchanger fluids, disabled power capacitors (currently about 350 pieces containing more than 5 t PCBs) and contaminated production equipment.

It should be noticed that during the production a part of the distillation residues was mixed with heavy oil and used as fuel in a factory heating plant. About 115 t of unsold and used PCBs stored at Chemko were burned in the 1970/80s in Slovakia's cement kilns.

b) Use

PCB formulations are still used in Slovakia in closed systems. According to questionnaires sent in 1997 to PCB users the PCBs are used only in power capacitors which are located at transformer and switchgear units. The summarized output of that pilot inventory is sketched in Figure 3 [Kocan et al. 1998, Kocan 2000, 2001].

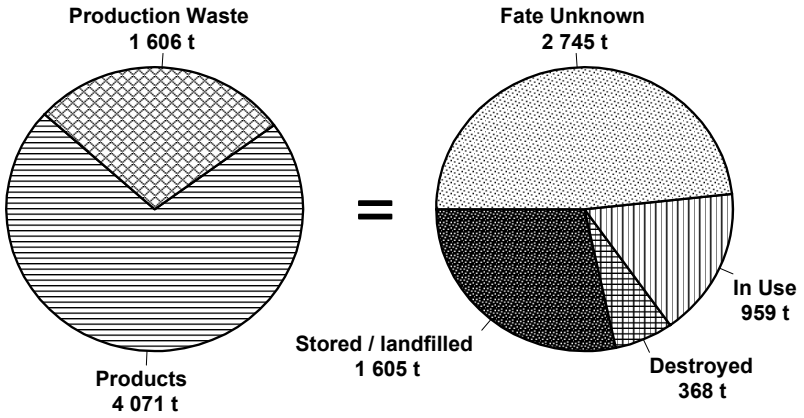

Figure 3 *Inventory estimation of PCBs used in Slovakia (a November 1997 situation)*

In 2001 another inventory aimed at PCBs still used in running equipment has launched in Slovakia. Devices, e.g. capacitors or transformers recognized to contain PCBs will be labeled and registered in order to be easily identified when POP disposal will start.

There is little information on the present use of PCBs in heat exchanging systems which were an important source of environmental contamination with PCBs in the past.

Except Chemko Strazske, almost no former users (many entertainments however were closed down) have admitted having waste PCBs. Lots of heat exchangers around Slovakia used PCB fluids (e.g. facilities preparing asphalted gravel for road construction). Because of leakage totally hundreds of tonnes of PCBs released to soil under the exchangers. Several years ago some companies managing those facilities collected used PCBs and ensured their disposal abroad by incineration. Contaminated soil however has not been removed.

We suppose that in spite of the respective law some institution keep secret waste PCBs to avoid or at least delay costly disposal. Besides Chemko having more than 1 000 t of PCB waste several tens/hundreds tonnes at former intensive users of PCBs in heat exchangers can be expected. Up to 1 000 t of PCBs could be encased in power capacitors that are still in use or disabled and stored at their users.

According to the Directive 473/2000 Z.z. of the Slovak Government waste oil containing more than 10 ppm PCBs/PCTs shall not be combusted (except cement kilns where exists 50 ppm limit).

B. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans

There are two municipal solid waste incinerators (MWI) in Slovakia (in Bratislava and Kosice) burning together about 200 000 tonnes of garbage per year. Currently, they are equipped only with electrostatic precipitators allowing to find, on average, about 8 ng I-TEQ in 1 m^3 of stack emissions. The complete reconstruction of the Bratislava waste incinerator involving stack gas cleaning installations reducing I-TEQ concentration below 0.1 ng/m^3 started in 2000 with planned completion in 2002. For a long time fly ash from the MWI electrostatic precipitators was dumped together with bottom ash [Kocan et al. 1991, 1993].

An important source of PCDD and PCDF generation is also industrial and medical waste incineration all over Slovakia usually presently equipped with insufficient flue gas treatment.

In Slovakia, only very few dioxin analysis of stack emissions from some municipal, industrial and hospital waste incinerators have been carried out in the early 90's. There is no information on dioxin emissions from coal and wood-burning installations and metallurgical plants.

Since January 1, 2007 (according to the Directive 473/2000 Z.z. of the Slovak Government) all waste incinerators and facilities co-burning fuel with waste shall meet 0.1 I-TEQ ng/m^3 (in the period of 2001-2006 only newly built and reconstructed waste incinerators).

Although natural gas is currently a major fuel in residential heating there is a number of houses in particular in the country burning low quality coal and wood and occasionally combustible garbage. Price-increase of natural gas and electric energy and generally the increase of living costs causes the reuse of fossil fuels especially in countryside houses leading to the increase of PCDD/PCDF emissions from those sources. Moreover, in rural areas the combustion of garden and household waste and dry grass in fields is commonly used practice.

Table 1 *I-TEQ (calculated from PCDDs/Fs) and PCB concentrations in stack emissions from some PCDD/PCDF stationary sources in Slovakia*

Combustion facility	No. of measurements	Concentration [ng/m^3]		
		Σ PCDDs/Fs	I-TEQ	Σ PCBs
MWI (in Kosice), 1991	1	2800	33	170
MWI (in Košice), 1994	2	434 – 490	7.0 – 8.1	300 - 958
MWI (in Bratislava)	5	170 - 385	3.4 - 11	60 - 208
HWI (in Kolarovo)	1	700	8.1	not analyzed
IWI (in Plastika Nitra)	1	3300	60.9	1000
IWI (in Duslo Sala)	2	23 - 26	0.35 – 0.41	161 - 575
IWI (in ChZ Novaky)	3	190 - 1200	2.0 - 28	90 - 620
IWI (in VUChT Bratislava)	2	0.5 – 8.0	0.003 – 0.14	1700 - 3200
IWI (in ZVL Povaz. Bystrica)	1	177	3.1	40
Heating plant (in Zilina)	1	28	0.48	not analyzed
Cement kiln (in Ladce)	2	5.5 – 10.0	0.099 – 0.2	181 - 423

MWI = municipal waste incinerator HWI = hospital waste incinerator IWI = industrial waste incinerator

Because PCB fluids in electrical and other devices still in use or withdrawn from use contain PCDFs these devices represent further source if improperly serviced or stored.

The use of chlorine agents in pulp and paper bleaching processes was replaced by non-chlorine technologies and therefore these productions do not pose a PCDD/PCDF pollution source.

Because chlorinated scavengers are already not used in automobile fuel sold in Slovakia the generation of PCDDs and PCDFs in car engines is expected to decline.

C. Hexachlorobenzene

Hexachlorobenzene (HCB) was manufactured in a Bratislava chemical plant in the 60's and 70's. It was used mainly as a pesticide until its use was banned in 1976. For example, in 1971 about 4.5 t of active ingredient was used in agriculture.

D. DDT

The insecticide p,p'-DDT was manufactured in a Bratislava chemical plant in the 60's and 70's. Its use for agriculture was banned in 1976, however, in spite of that fact it was used until the depletion of DDT stockpiles. For example, in 1970 about 140 t of active ingredient was used [Szokolay at al. 1970].

Currently there is almost no information on obsolete DDT stockpiles in Slovakia. One can expect that limited amounts of obsolete DDT could be still stored at cooperative farms and individuals. A certain amount is in the landfill site of the former producer outside Bratislava.

E. Other Chlorinated Pesticides (Aldrin, Chlordane, Dieldrin, Endrin, Heptachlor, Mirex, Toxaphene)

These organochlorine chemicals have neither been produced nor used (or perhaps only in small amounts, e.g. toxaphene) in Slovakia.

Environmental Pollution

Ambient Air

A. PCBs

Within the PHARE Project EU/93/AIR/22 "Local Studies of Air Quality in the Cities of Bratislava and Kosice. National Needs Assessment of Air Pollution" PCB concentrations were measured in 24-hr ambient air samples collected around Slovakia in 1996/97 (8-times at 20 sampling sites involving urban, industrial, agricultural, and background areas). Summarized results are shown in Figure 4. The highest geometric mean PCB concentration was found near a chemical plant in which PCBs were used in heat exchangers (Bratislava 3) – the highest individual value found there was 1 751 pg/m^3 [Petrik 1998].

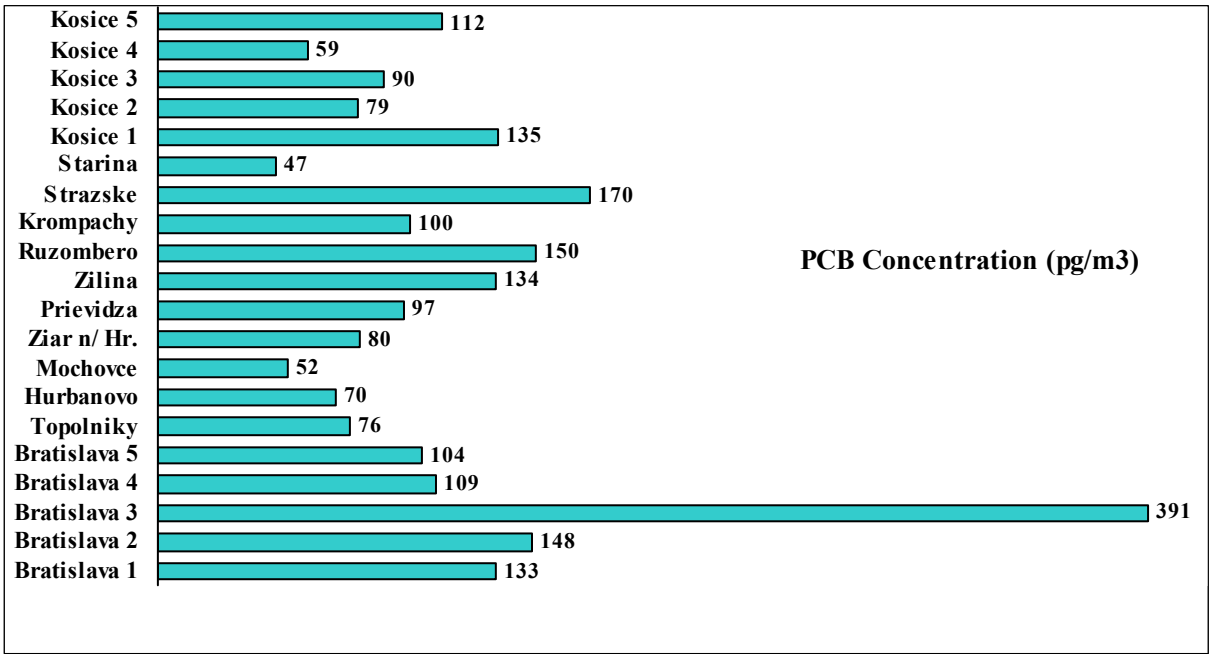

Figure 4 *PCB concentrations (sum of 28,52, 101, 138, 15, and 180 congeners) in ambient air in 20 Slovakia's site (geometric mean values from 8 measurements - twice in each season).*

Within a pilot project "The Burden of the Environment in an Area Contaminated with PCBs" solved in 1997/99 PCBs, HCB, and pp'-DDT were analyzed in environmental samples including ambient air collected in the District of Michalovce (polluted area) and Stropkov (control area) – see maps in Figure 5 and 11.

Six 24-hr high-volume ambient air samples were collected in September 1997 at the distance of 1 to 30 km from the Chemko factory (Michalovce District). Six ambient air samples were taken in the control area (Stropkov District), as well. All the samples were collected in residential areas. PCB concentrations (the sum of all congeners) determined in ambient air are presented in Figure 6. Several times higher values were found close to the Chemko factory and its landfill and storage sites in Strazske (sampling sites Vola, Strazske). Somewhat increased levels were observed in towns (Michalovce, Stropkov) what might be influenced by more intense traffic in the towns causing the higher air occurrence of PCB containing dust particles. PCB concentrations at the remoter sites of the Michalovce District were similar to

those in the control area. As expected, the air samples contained lower chlorinated congeners rather than higher chlorinated ones [Kocan et al. 2000, 2001]

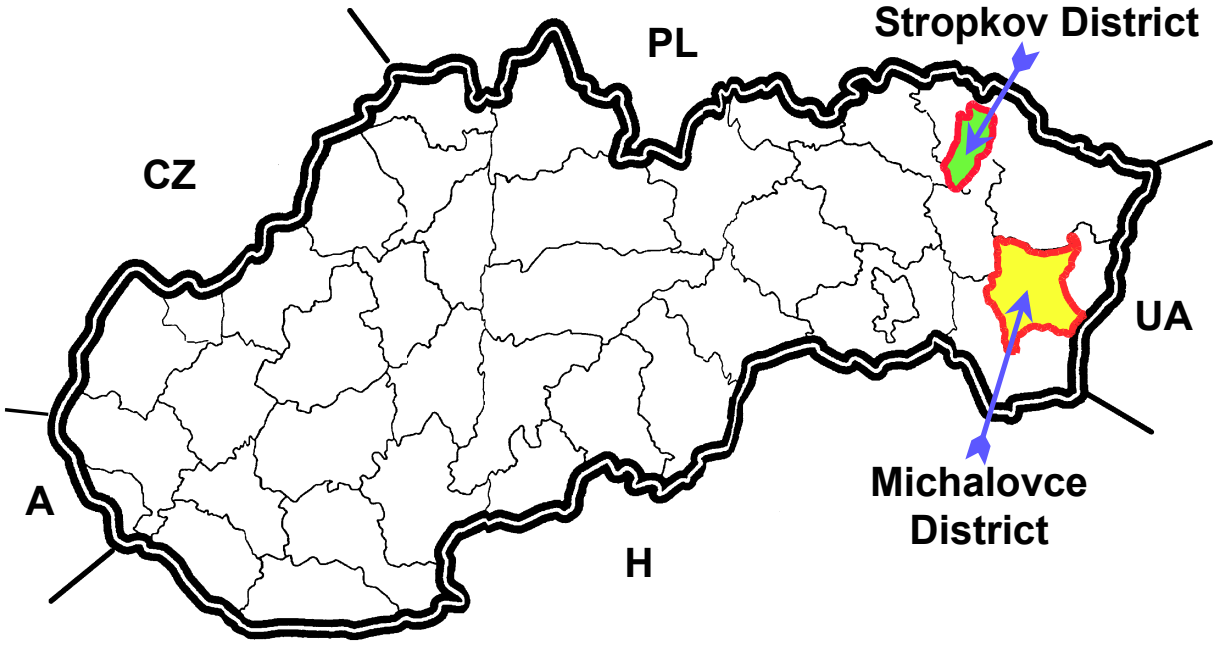

Figure 5 *The position of a polluted area (Michalovce District) and control area (Stropkov District) with background PCB pollution within the Slovak Republic.*

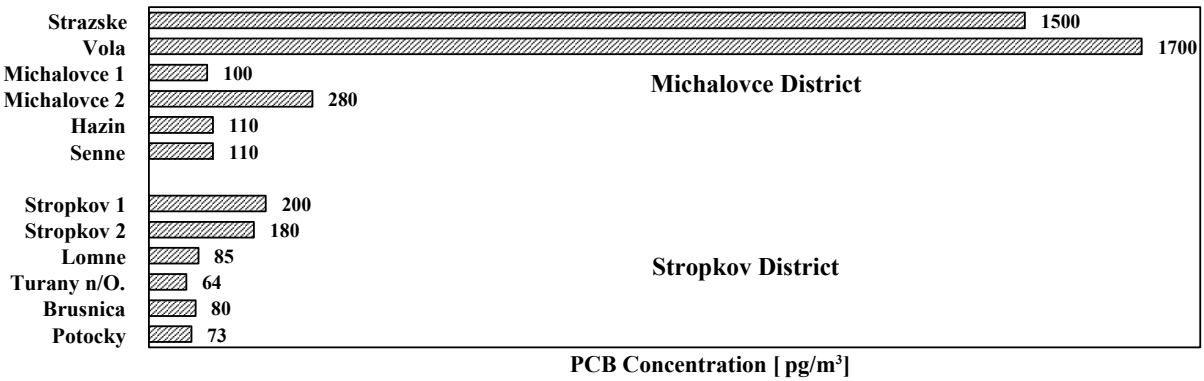

Figure 6 *PCB concentrations (the sum of all congeners) determined in ambient air samples collected in the residential areas of the districts of Michalovce and Stropkov.*

B. Polychlorinated dibenzo-p-dioxins and dibenzofurans

The only analyses of PCDDs and PCDFs have been carried out within the PHARE Project EU/93/AIR/22 (see PCBs chapter above). Concentrations in I-TEQ are shown in Figure 7 [Stenhouse et al. 1998, Kocan and Stenhouse 1999].

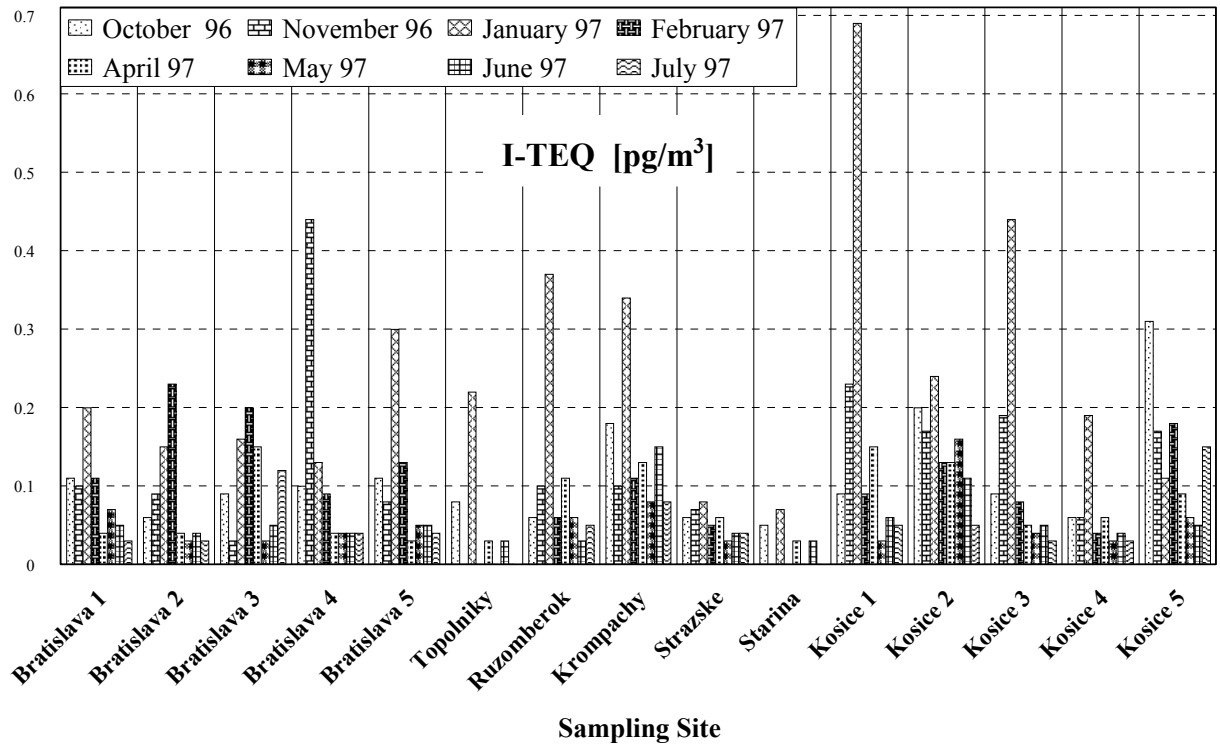

Figure 7 *Geometric mean PCDD/PCDF concentrations (expressed as I-TEQ) found in the ambient air in Slovakia collected 8 times at 20 sites*

C. Hexachlorobenzene

HCB concentrations (geometric mean) in ambient air samples collected 8-times (twice in each season) at 20 sites within the PHARE Project (see PCBs chapter above) are presented in Figure 8. There was no substantial difference between rural and urban sites with the exception of an industrial site (Bratislava 3) situated close to a former HCB producer (213 pg/m^3) [Petrik 1998].

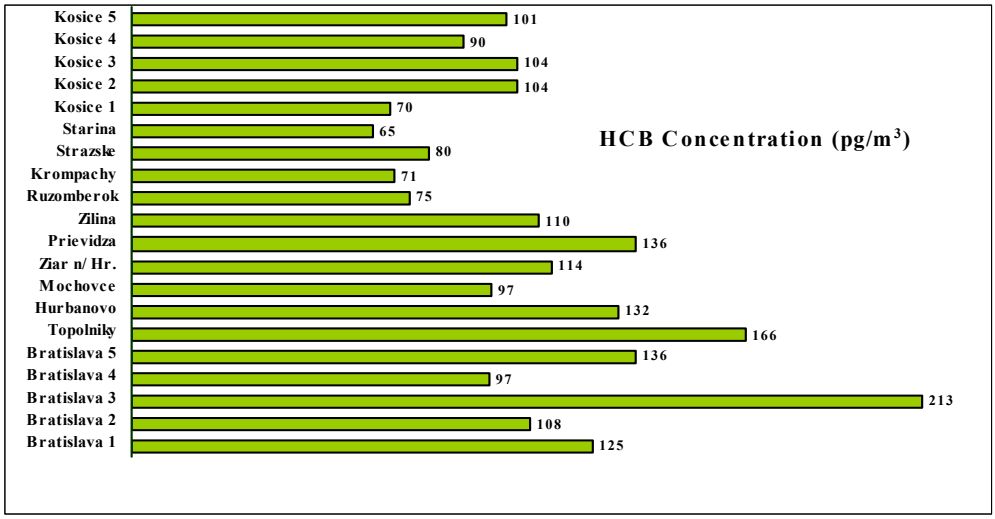

Figure 8 *HCB concentrations in ambient air in 20 Slovakia's site (geometric mean values from 8 measurements - twice in each season)*

HCB levels found in the ambient air in the District of Michalovce and Stropkov (for details see PCBs chapter above) are given in Figure 9 [Kocan et al. 1999].

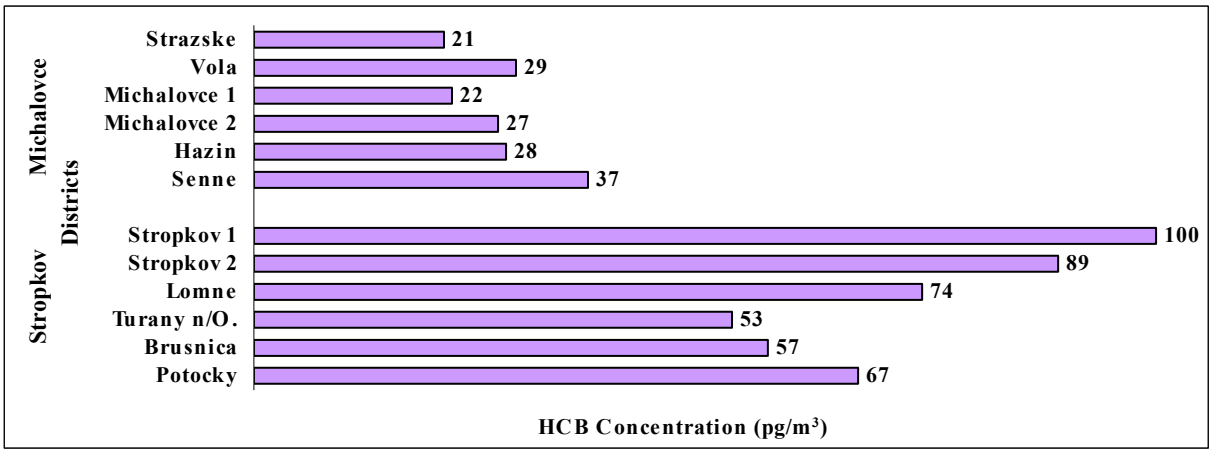

Figure 9 *HCB concentrations determined in ambient air samples collected in residential areas of the districts of Michalovce and Stropkov*

D. DDT

The concentrations of p,p'-DDT in ambient air samples collected 8-times (twice in each season) at 20 sites within the PHARE Project (see PCBs chapter above) were lower than the HCB ones. Average concentration was found to be 19 pg/m^3 (max value was 200 pg/m^3). pp'-DDE/pp'-DDT ratio varied from 2.3 to 5.3 [Petrik 1998].

The levels of p,p'-DDT+ p,p'-DDE found in the ambient air in the District of Michalovce and Stropkov (for details see PCBs chapter above) are given in Figure 10 [Kocan et al. 1999].

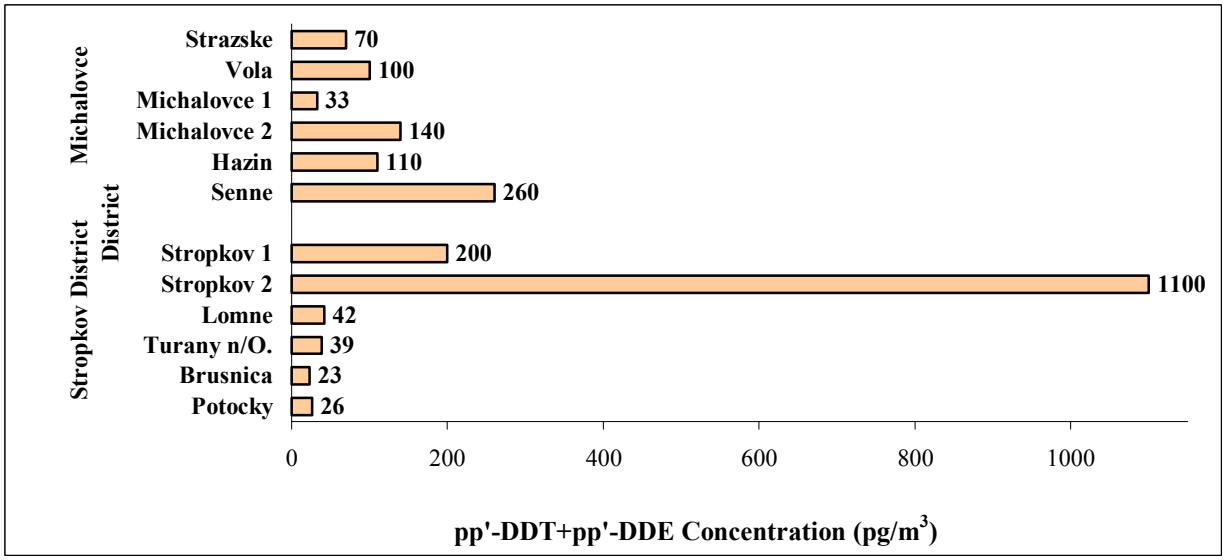

Figure 10 *p,p'-DDT+p,p'-DDE concentrations determined in ambient air samples collected in residential areas of the districts of Michalovce and Stropkov*

E. Other Chlorinated Pesticides (Aldrin, Chlordane, Dieldrin, Endrin, Heptachlor, Mirex, Toxaphene)

There is no available data on the levels of these organochlorines in the ambient air in Slovakia.

Water and sediment

A. PCBs

Within the framework of the national monitoring program for water quality more than 3 000 surface water samples taken from Slovak rivers and lakes were analyzed for PCBs in 1989-1997. Average total PCB levels has reached 5 to 30 ng/L while maximums peaked at more than 1 000 ng/L [Kocan et al. 1999].

Surface water and sediment samples were taken from an open effluent canal of the former Slovak PCB manufacturer, the Laborec River (the canal is emptying into it), Zemplinska Sirava Lake (a large water reservoir serving for flood-control, irrigation and recreational purposes supplied from the Laborec and several Vihorlat mountain streams), Ondava River and Domasa Lake (the latter two are situated in the control area of the Stropkov District). Where possible, sediment samples were collected at the same sites. A map in Figure 11 illustrates the position of the waterbodies.

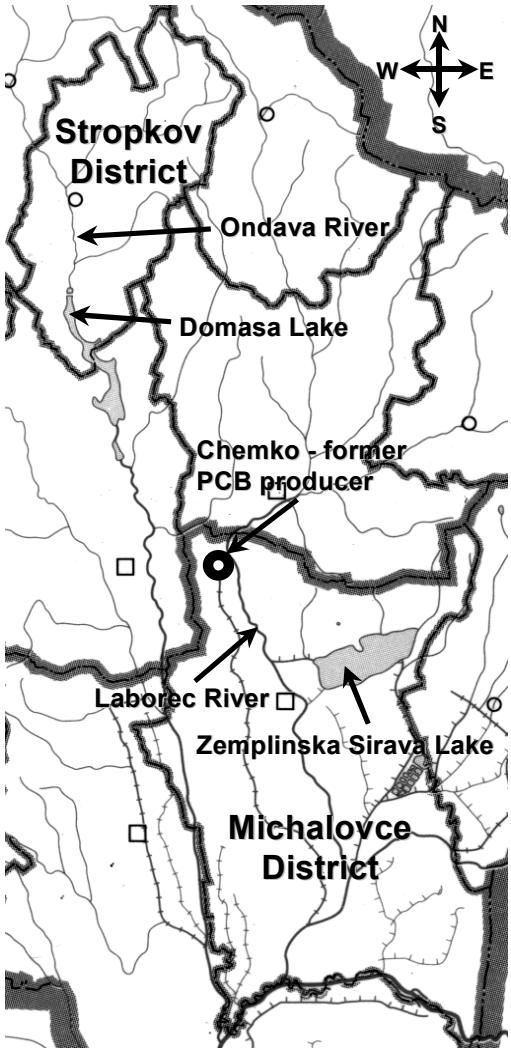

Figure 11 *More detailed map of the polluted and control areas with rivers and lakes; the population of the Michalovce district is 108 000 and the Stropkov one 20 500*

Figure 12 shows PCB concentrations determined in the sediment samples. As expected, the highest levels were found in a muddy part of an effluent canal flowing from the Chemko factory (one of the samples contained even 5 000 μg/g, dry weight). As the effluent canal between the factory and its merging with a municipal sewage canal contained sandy sediment (the bed of the canal is concreted over) having low adsorbing effects for PCBs, a lower value (48 μg/g) was found. No doubt that the polluted effluent canal emptying into the Laborec River has caused its contamination (3.9 μg/g). The Zemplinska Sirava Lake (33.5 km^2 in surface area) that is partly filled from the Laborec contained several hundred times higher PCB levels if compared with a similar lake in the control area (1.7 to 3.1 μg/g vs 0.007 to 0.01 μg/g). Based on those findings, one can estimate that at least tonnes of PCBs are still adsorbed in the sediments of the effluent canal, Zemplinska Sirava and Laborec. As can be seen in Figure 13, the sediment has caused the contamination of surface water although in this case the difference between the polluted and control area is not so substantial [Kocan et al. 1999, 2001, Petrik et al. 2001b].

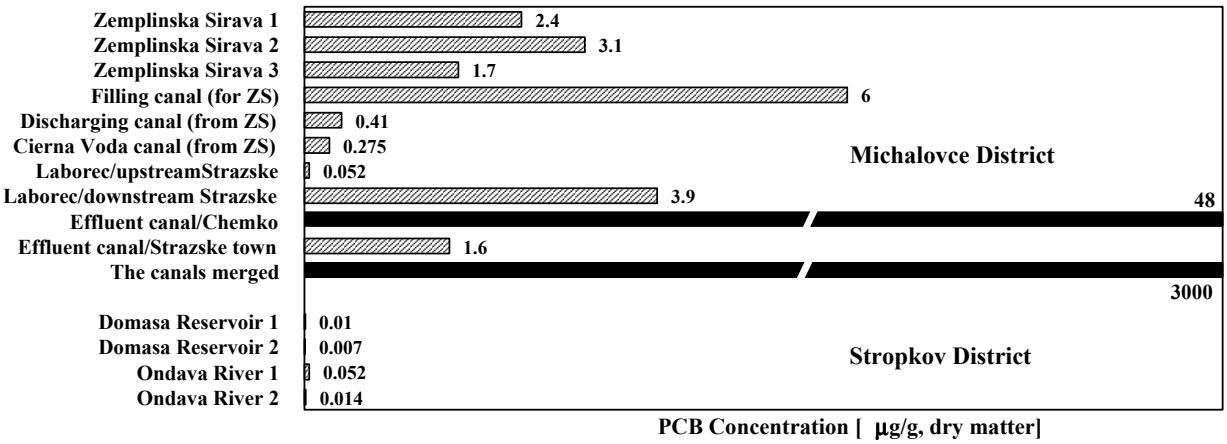

Figure 12 *PCB levels (the sum of all congeners) in bottom sediment samples taken from some watercourses in the districts of Michalovce and Stropkov*

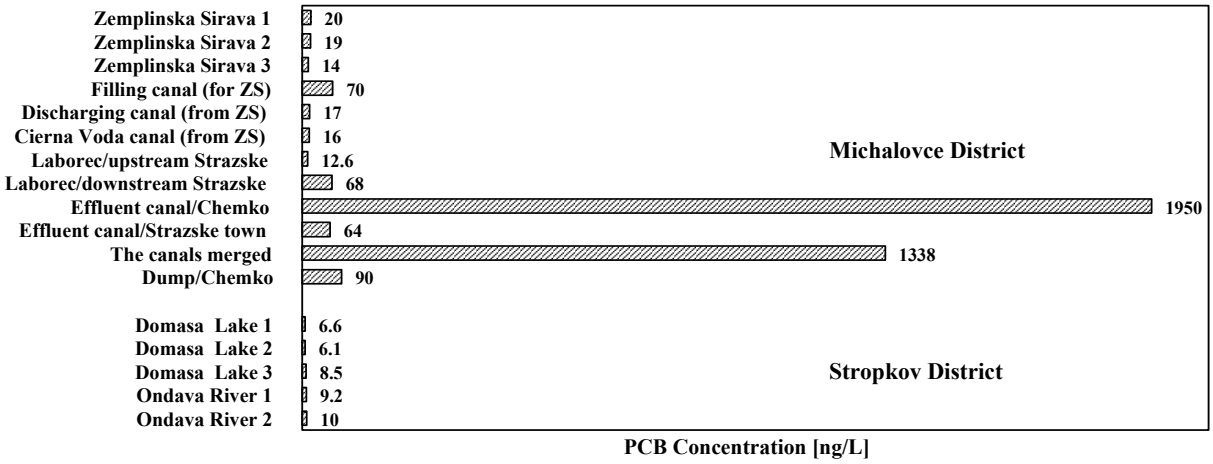

Figure 13 *PCB levels (the sum of all congeners) in surface water samples (solid particles were filtered off) taken from some watercourses in the districts of Michalovce and Stropkov*

B. Polychlorinated dibenzo-p-dioxins and dibenzofurans

No data are available on PCDD and PCDF levels in water sediment and surface water in Slovakia.

C. Hexachlorobenzene

HCB concentrations in sediment samples taken from lakes and rivers in the Michalovce District and Stropkov District were low – maximal values reached 2 ng/g (dry weight). However, HCB levels found in sediment from a sewage treatment plant canal (Strazske town) ranged from 24 to 120 ng/g (dry weight) [Kocan et al. 1999].

D. DDT

DDT + DDE concentrations in surface water and bottom sediment samples taken from lakes and rivers in the Michalovce District and Stropkov District are presented in Figure 14 and 15.

Unlike the PCB levels (see Fig. 12 and 13) the districts did not differ in the DDT+DDE concentrations (except the effluent canal of the Strazske town sewage treatment plant) [Kocan et al. 1999].

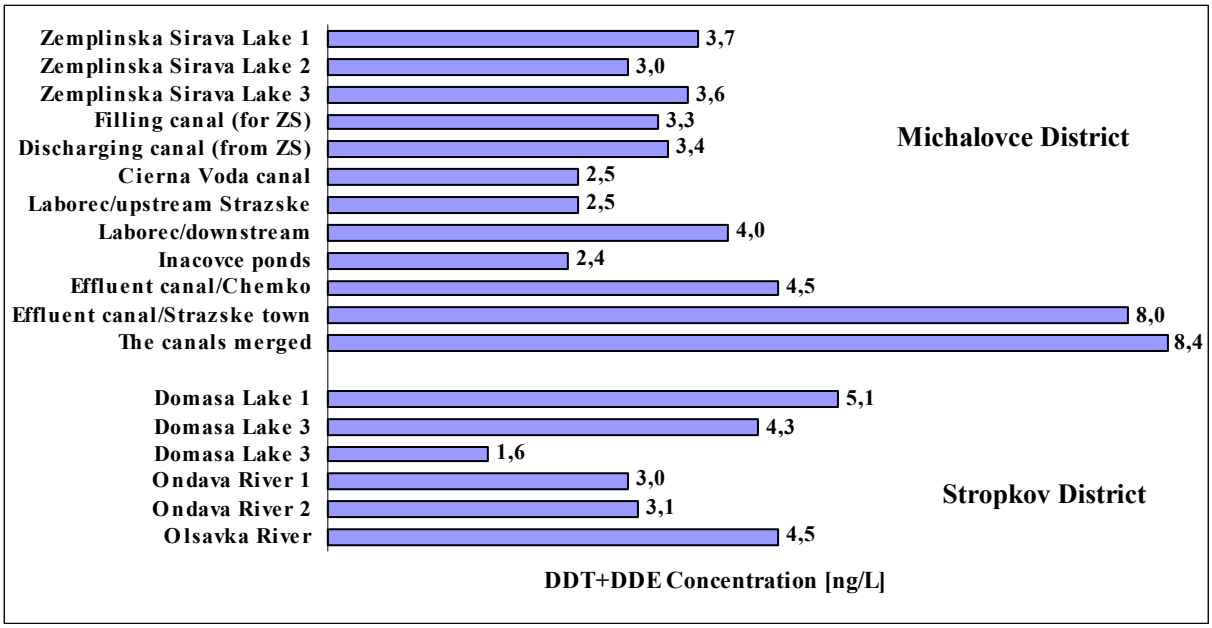

Figure 14 *The concentrations of p,p'-DDT+p,p'-DDE in surface water samples taken from some watercourses in the districts of Michalovce and Stropkov*

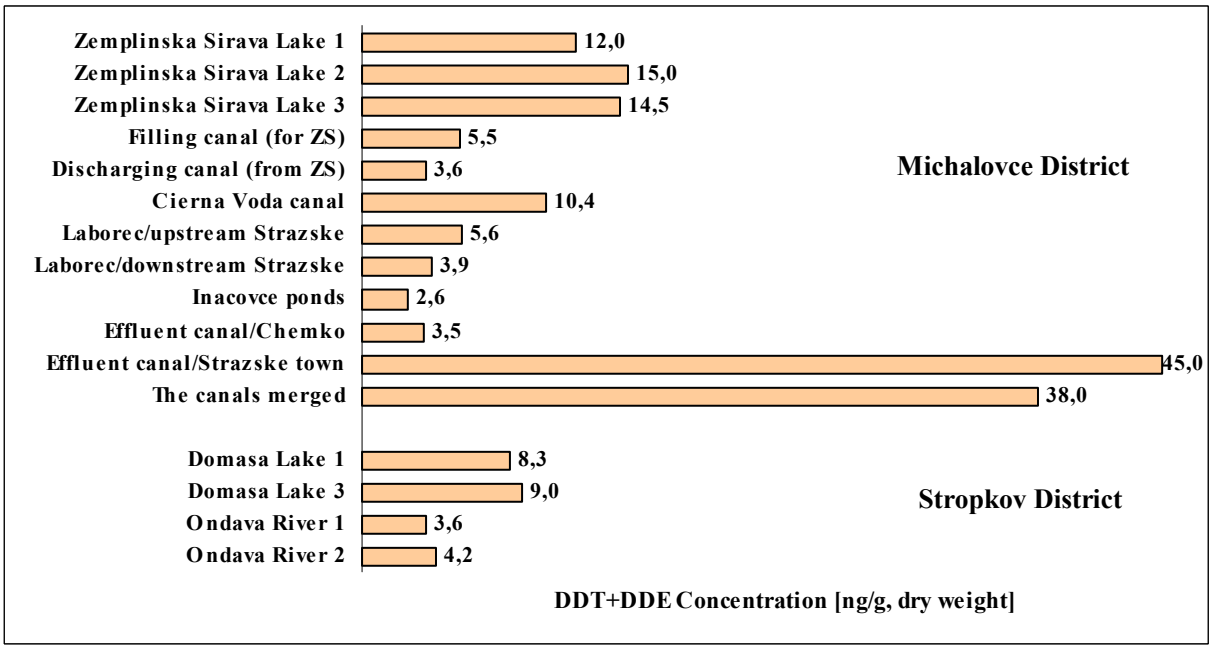

Figure 15 *The levels of p,p'-DDT+p,p'-DDE in bottom sediment samples taken from some watercourses in the districts of Michalovce and Stropkov*

E. Other Chlorinated Pesticides (Aldrin, Chlordane, Dieldrin, Endrin, Heptachlor, Mirex, Toxaphene)

No data are available on these organochlorines in water sediment and surface water in Slovakia.

Soil

A. PCBs

Thirty-one samples were taken from an upper soil layer (20 cm) near the disposal sites of the PCB manufacturer (Chemko), agricultural fields in the districts of Michalovce and Stropkov, and at several plants around Slovakia preparing gravel coated with asphalt formerly using PCBs in their heat-exchangers. Each sample was created by averaging 5 to 10 soil subsamples taken at a 10-m span following the pattern of dice five.

Soil samples taken close to the waste disposal sites of Chemko and the plants preparing asphalted gravel contained PCB levels as illustrated in Figure 16. As can be seen in Figure 17, PCB levels in the soil samples taken from the agricultural fields near some towns and villages were considerably lower (on average 0.008 μg/g) than those taken from the neighbourhood of disposal sites and plants mixing asphalt and gravel (compare with Figure 16). Those plants situated often close to quarries, i.e. in mountains on rocky ground, have been preparing gravel coated with asphalt to be used for road construction. It is known that because of the untightness in heat-exchanging systems filled with PCBs hundreds of tonnes of PCBs leaked from those systems. PCB concentrations peaked at 53 000 μg/g in a soil sample taken under one of the heat-exchangers. However, high PCB levels were also observed in agricultural (35 and 38 μg/g) or forest soil (3.9 and 7.5 μg/g) taken near those plants. As soil from the vicinity of a major Chemko landfill site, which could be contaminated by air transported particles only, contained increased PCB levels (0.4 to 5.8 μg/g), it is likely that this dump may contain large quantities of PCBs. Similarly PCB waste might be present at the municipal dump of Michalovce (district town) since increased PCB concentrations were found in a sample collected close to the dump (0.17 μg/g) [Kocan et al. 1999, 2001].

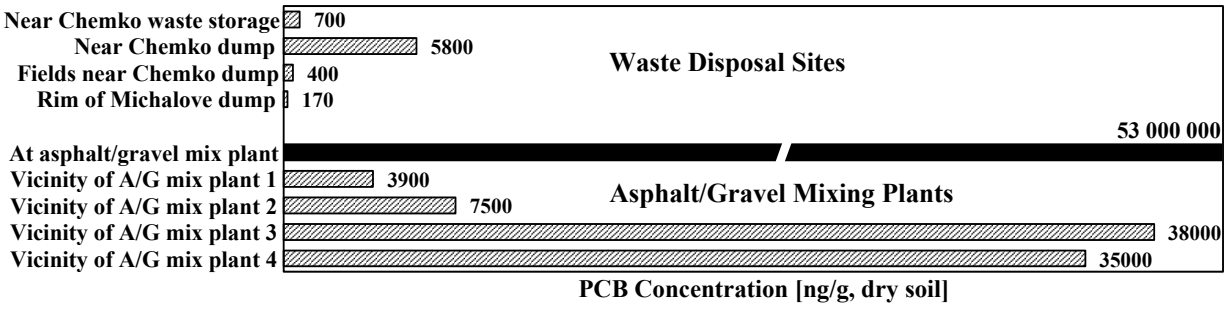

Figure 16 *PCB levels (the sum of all congeners) in soil samples collected in the vicinity of asphalt/gravel mixing plants and the waste disposal sites of the Chemko chemical factory.*

Hundreds of soil samples around Slovakia were analyzed for PCBs in the 90's. Average levels ranged between 0.1 to 970 ng/g [Kocan et al. 1998].

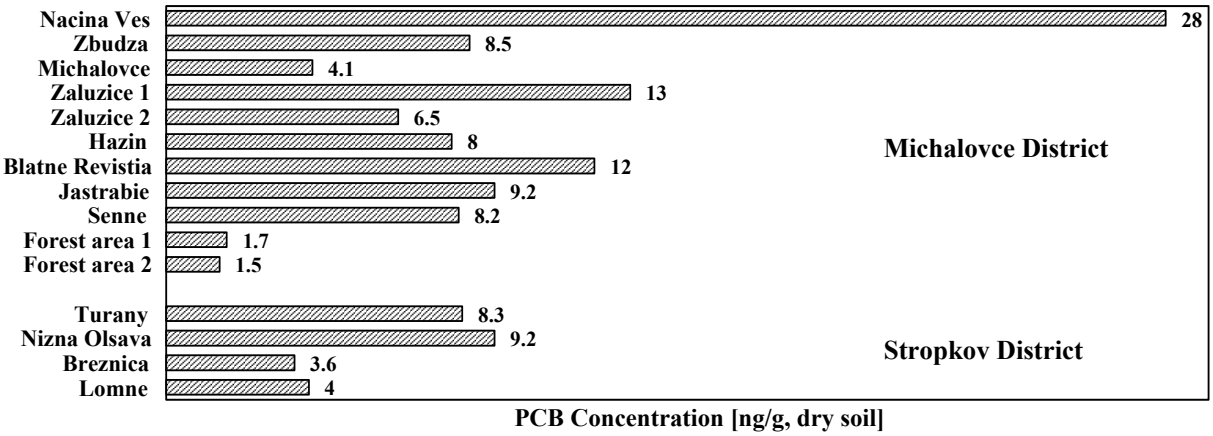

Figure 17 *PCB levels (the sum of all congeners) in soil samples collected at the agricultural fields of the districts of Michalovce and Stropkov*

B. Polychlorinated dibenzo-p-dioxins and dibenzofurans

No data are available on PCDD/PCDF levels in soil in Slovakia.

C. Hexachlorobenzene

HCB levels in soil samples taken at the same sites as the samples for PCB analysis (see above) ranged from not detectable values < 0.05 to 8.9 ng/g (dry weight) [Kocan et al. 1999].

D. DDT

The levels of p,p‘-DDT+p,p‘-DDE in soil samples taken at the same sites as the samples for PCB analysis (see above) ranged between 0.65 to 490 ng/g (dry weight). 1 080 ng/g were found in a soil sample taken close to a Chemko storehouse [Kocan et al. 1999].

E. Other Chlorinated Pesticides (Aldrin, Chlordane, Dieldrin, Endrin, Heptachlor, Mirex, Toxaphene)

No data are available on these organochlorines in soil in Slovakia.

Biota

A. PCBs

PCB content in Slovakia’s vegetation has been determined in the fodder of vegetable origin only. Thousands of samples have been analyzed mainly by veterinary institutions. Levels varied from not detected (low ppt) to 500 ng/g values.

About 1,000 meat samples form wild animals were analyzed in last ten years. Yearly averages varied from 24 to 203 ng/g fat (the sum of 6 indicator congeners). The maximal level reached 9 439 ng/g fat [Kocan et al. 1998].

Sixty-nine fishes caught in the polluted area (the Laborec River and Zemplinska Sirava Lake) and 48 fishes caught in the control area (the Ondava River and Domasa Lake) were pooled

taking into consideration genera and catching sites to get 20/11 samples related to the Michalovce/Stropkov waters. Meat samples from 9 game animals, such as deer, roe deer, wild boar, and duck, killed in the Michalovce District, 9 in the adjacent Sobrance District (the samples came from the Vihorlat Hills that extend over both districts) and 16 in the Stropkov District were used for analysis.

Likewise the sediment, fish from the Michalovce waters contained much higher PCB levels than those from the Stropkov ones (Figure 18). A maximal lipid adjusted values peaked even at more than 900 mg/kg. It was confirmed that predatory fishes are more exposed than fishes feeding on plankton or benthic food. The environmental pollution of the Michalovce District with PCBs is reflected in exposure of forest and field wildlife, as well (Figure 19) [Kocan et al. 1999, 2001].

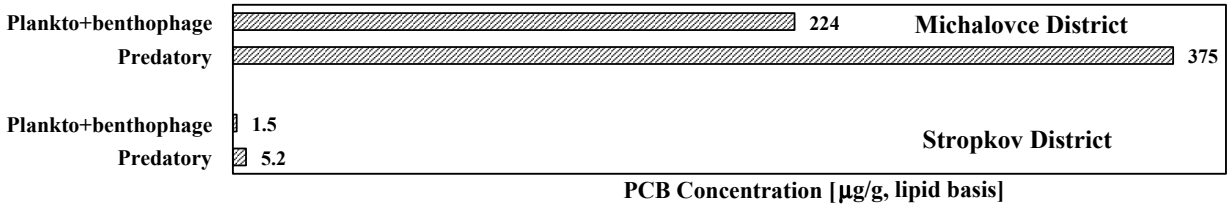

Figure 18 *PCB levels (the sum of all congeners, in ppm!) in lipids from fish caught in some water-courses in the districts of Michalovce and Stropkov.*

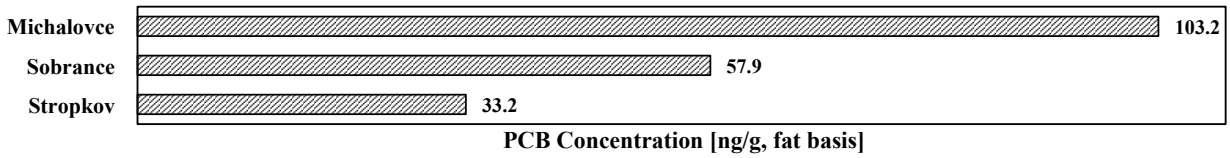

Figure 19 *PCB levels (the sum of 28, 52, 101, 118, 138, 153, 156, 170, and 180 congeners) in lipids from game animals shot in forests and fields in the districts of Michalovce, Sobrance and Stropkov.*

B. Polychlorinated dibenzo-p-dioxins and dibenzofurans

No data on PCDD/PCDF levels in biota samples coming from Slovakia have been published.

C. Hexachlorobenzene

HCB lipid levels found in the fish and game samples described above ranged from 17 to 172 ng/g (average 58 ng/g) and from 18 to 112 ng/g (average 51 ng/g) respectively in the Michalovce District and 37 to 156 ng/g (average 82 ng/g) and 12 to 44 ng/g (average 30 ng/g) respectively in the Stropkov District [Kocan et al. 1999].

D. DDT

The levels of p,p'-DDE and p,p'-DDT are presented in Figure 20 and 21 respectively. One can notice that predatory fish contained the distinctly higher levels of those pollutants [Kocan et al. 1999].

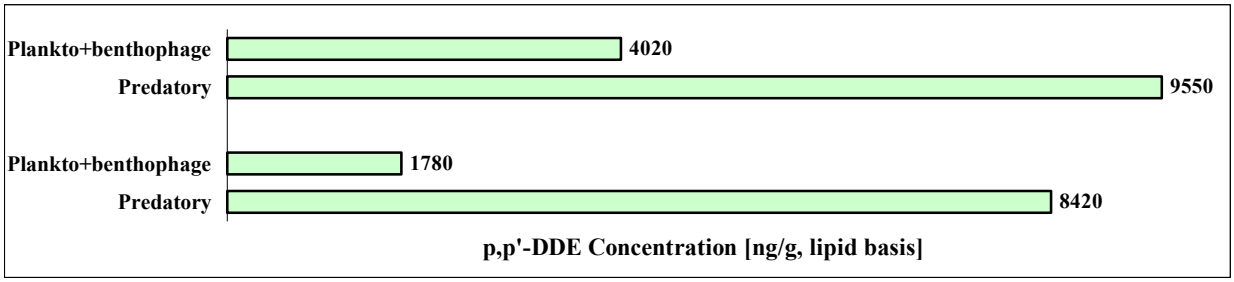

Figure 20 *p,p'-DDE levels in fish samples from the rivers and lakes of the Michalovce and Stropkov Districts*

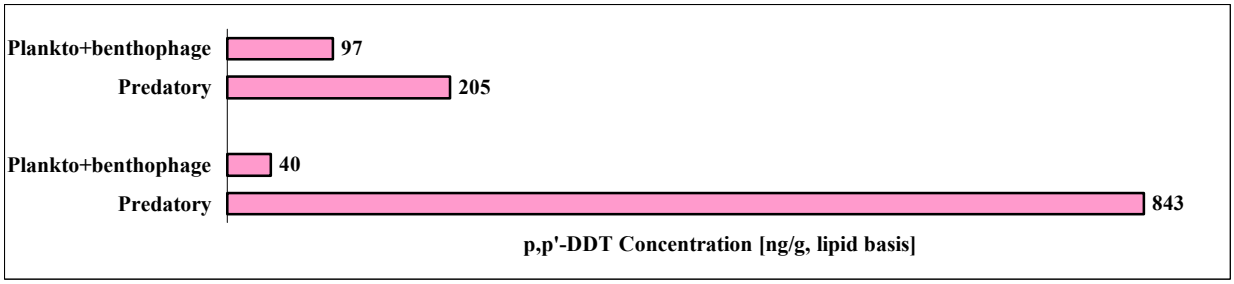

Figure 21 *p,p'-DDT levels in fish samples from the rivers and lakes of the Michalovce and Stropkov Districts*

E. Other Chlorinated Pesticides (Aldrin, Chlordane, Dieldrin, Endrin, Heptachlor, Mirex, Toxaphene)

No data on the levels of the organochlorines in biota samples coming from Slovakia have been published.

Food Contamination

A. PCBs

PCBs are analyzed within Slovakia by veterinary institutions within the framework of monitoring and inspection programs. At least 40 000 beef, milk, pork, mutton, chicken, egg, and fish samples have been analyzed during last ten years [Kocan et al. 1998].

Food samples (N=138) were collected around Slovakia in 1993-1995 and analyzed for PCBs, HCB, pp'-DDT and pp'-DDE. Results (ppb, lipid basis) are shown in Figure 22 [Kocan et al. 1995b]. Increased levels in eggs coming from small family farms are remarkable (see also Figures 23-26).

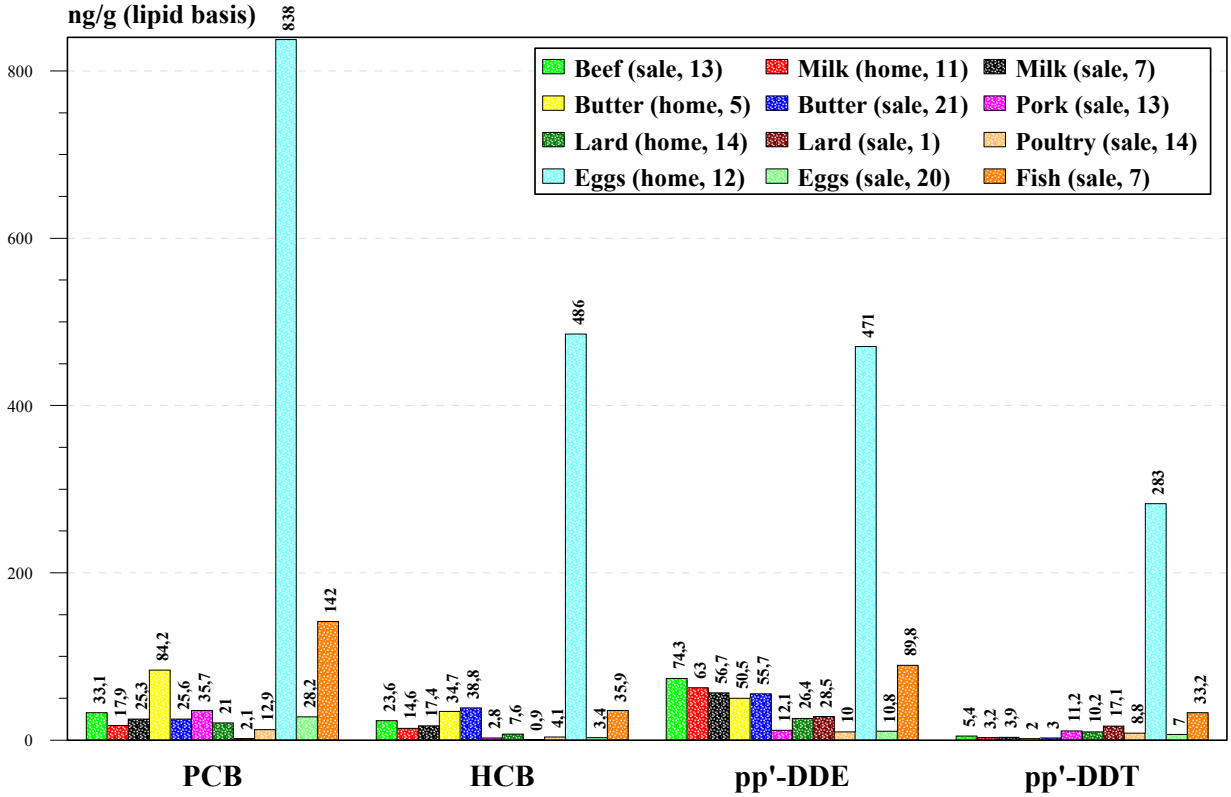

Figure 22 *Mean PCB, HCB, DDE and DDT levels in food collected in five selected Slovak districts (Myjava, Bratislava, Nitra, Michalovce and Velky Krtis)*

Six hundred fifty-nine food samples bought in shops and markets in the districts of Michalovce and Stropkov in 1997-98 were pooled to 54 samples from the Michalovce District and 49 pooled samples from the Stropkov one according to (e.g. everyday milk samples from a dairy collected within one month were pooled). Additionally, 108 food samples from the Michalovce District and 43 from the Stropkov district originating from animals kept on small family farms located at family houses in villages. These farm-raised samples were not pooled. All the food samples were of animal origin such as cow's milk, butter, beef, pork, salamis, frankfurters, chicken, lard and eggs.

As can be seen in Figure 23, PCB levels in the farm-raised (homemade) food samples especially chicken eggs were, on average, higher than those kept on big farms where animals are fed with feedstuff mixtures often imported from other parts of Slovakia and possibly less contaminated with PCBs and other organochlorines. Especially, chicken eggs from the small fam-

ily farms in the Michalovce District contained very high PCB levels. That can be caused [Kocan et al. 1999]:

a) Feed for animals raised at family houses contains a higher portion of plants such as grass, beet, potatoes, vegetable, etc. than feed used within large-scale breeding.

b) Animals in particular chicken and livestock kept on the small farms close to family houses used to have a run and thus they can reach potentially contaminated water, soil or waste much more easier than animals kept on closed stables typical of large-scale breeding.

c) Animals raised at family houses live longer than animals from large-scale breeding – it is known that the POP levels increase with age.

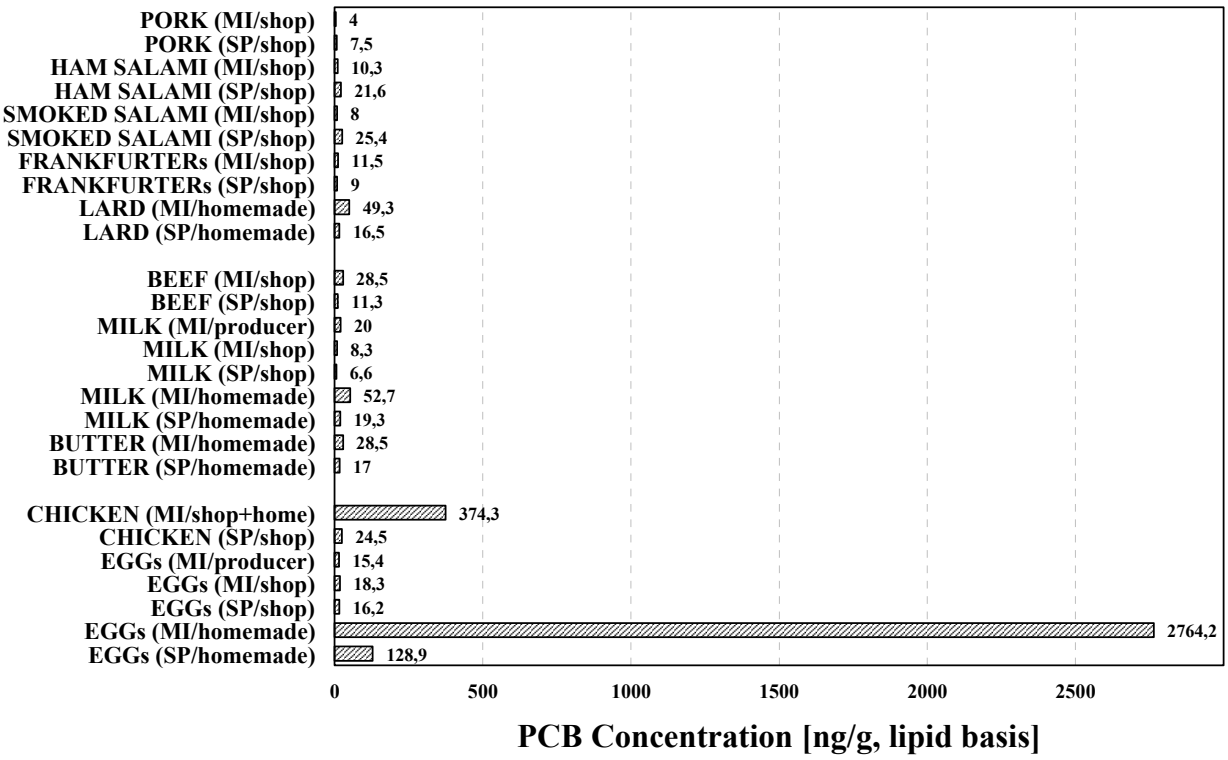

Figure 23 *PCB levels (the sum of 28, 52, 101, 118, 138, 153, 156, 170, and 180 congeners) in foods of animal origin collected in the districts of Michalovce (MI) and Stropkov (SP).*

B. Polychlorinated dibenzo-p-dioxins and dibenzofurans

No published data on food contamination with PCDDs/Fs is available in Slovakia. Currently about 60 Slovak food products collected in selected districts including homemade animal food are analyzed. As maximum levels for PCDDs/PCDFs in food are going to be set in Slovakia in April 2002 number of dioxin analysis in food should increase considerably.

C. Hexachlorobenzene

HCB levels in food samples collected in five selected districts (N=138) in 1993-1995 and in the Michalovce and Stropkov districts (N=810) in 1997-1998 (for more details, see PCBs chapter above) are presented in bar charts in Figure 22 and 24. Bovine samples contained slightly more HCB than beef and chicken samples except poultry kept on small family farms [Kocan et al. 1999].

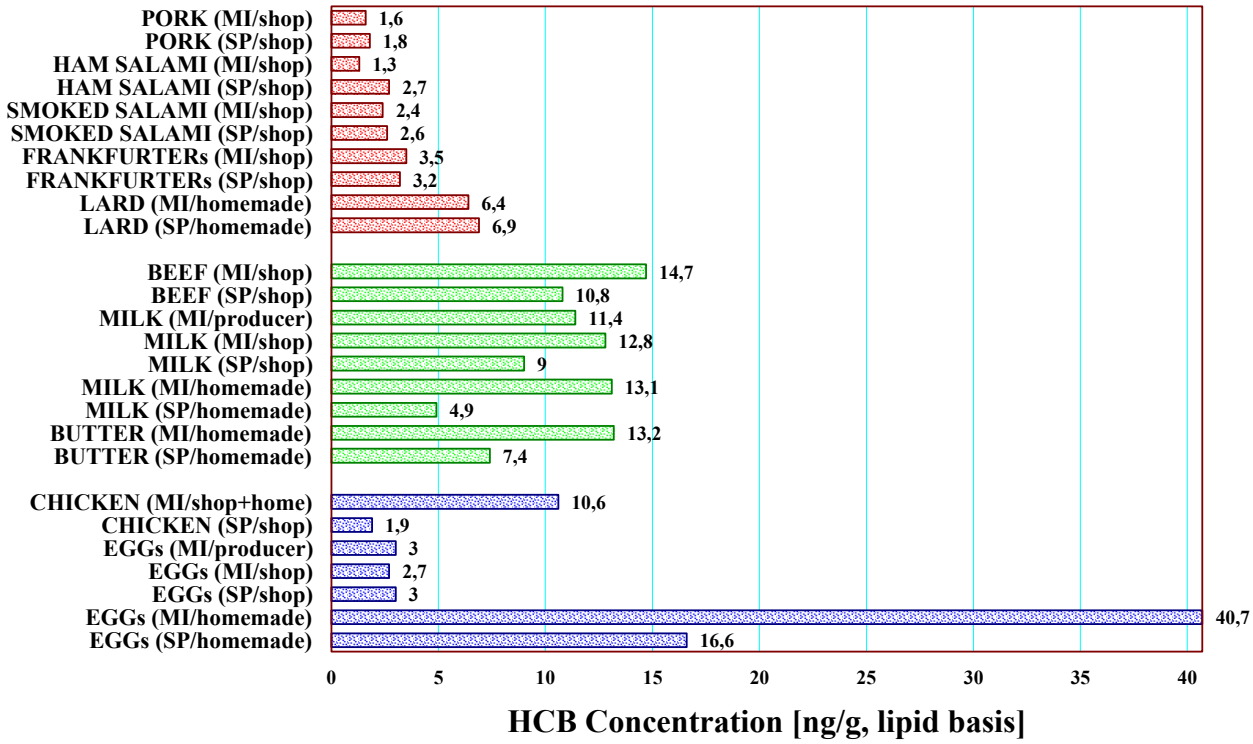

Figure 24 *HCB levels in foods of animal origin collected in the districts of Michalovce (MI) and Stropkov (SP)*

D. DDT

The levels of p,p'-DDT and p,p'-DDE in food samples collected five selected districts (N=138) in 1993-1995 are presented in Figure 22 and samples collected in the Michalovce District and Stropkov District (for more details, see PCBs chapter above) are presented in bar charts in Figure 25 and 26.

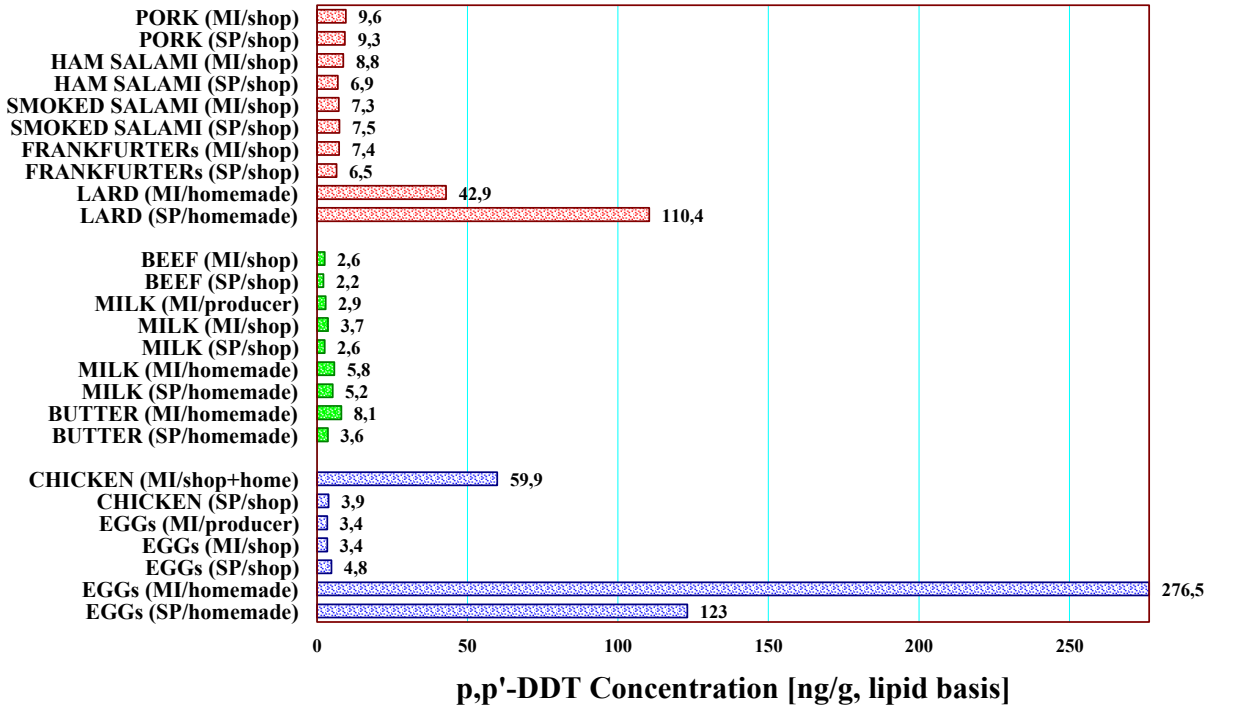

Figure 25 *p,p'-DDT levels in foods of animal origin collected in the districts of Michalovce (MI) and Stropkov (SP)*

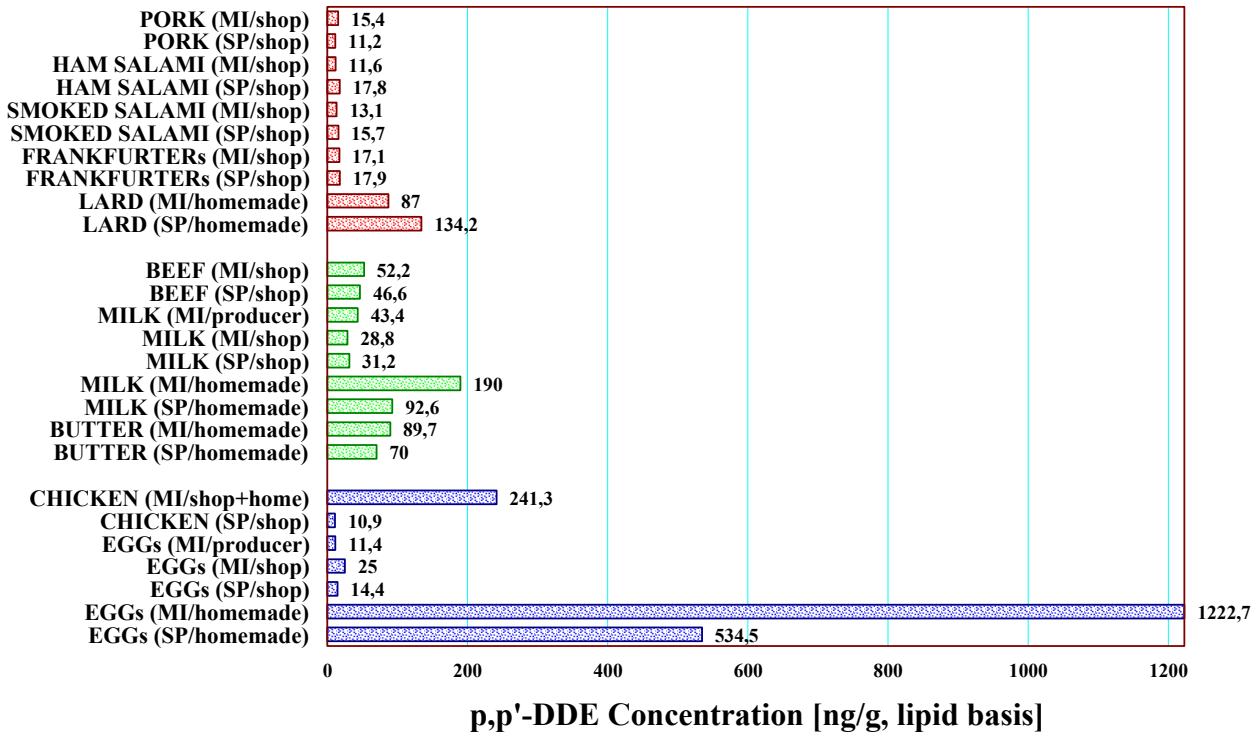

Figure 26 *p,p'-DDE levels in foods of animal origin collected in the districts of Michalovce (MI) and Stropkov (SP)*

E. Other Chlorinated Pesticides (Aldrin, Chlordane, Dieldrin, Endrin, Heptachlor, Mirex, Toxaphene)

There are no published data on food contamination with these organochlorines.

Human Exposure

A. PCBs

Within the period of 1989-1990, 152 samples of mother's milk collected in central Slovakia's region were analyzed for PCBs [Lengyelova et al. 1991]. The samples were taken 4-5 days after the delivery. The first set consisted of 64 samples from this region. Mean 1.46 μg/g (0.27-5.78 μg/g) were determined. 12.5% of samples exceed a value of 2.5 μg/g. Second set composed of 53 samples taken exclusively from the district of Velky Krtis gave an average value of 1.93 μg/g (0.7-4.6 μg/g). In this set also the second sampling was carried out between the 18th and 30th day of breastfeeding. The results indicated moderate decrease. In the set mentioned, the dependence of PCB content in milk on age of mothers was acknowledged: PCB = 0.06 × age. Third set was created by 35 samples of mother's milk no further precisely specified. The average value of PCB concentrations was 1.33 μg/g (0.31-3.4 μg/g).

Petrík et al. [1991] found PCB concentrations in a range of 0.4-10.4 μg/g (ppm, lipid basis) in adipose tissue autopsy samples from the general human population of the Slovak Republic. The highest levels in three monitored districts (Bratislava, Trencin, Martin) were measured in Bratislava. Later, autopsy samples from the district of Michalovce (only men) were also analyzed. Average PCB concentration attained 12.3 μg/g. Five samples of subcutaneous adipose tissue taken by biopsy from workers of a solid municipal waste incinerator contained PCBs in a range of 2.6-3.7 μg/g. These concentrations were slightly lower than the average PCB concentration found in the general population of Bratislava.

Biopsy adipose tissue (N=68), blood (N=111) and milk (N=67) samples intended for PCB and Cl-pest analysis were collected in the period 1993-94 from the general human population living in five selected districts. The adults of both sexes were chosen randomly. Mean PCB results are presented in Figure 27 [Kocan et al. 1994a, 1994b, 1995a, 1995b, Petrik et al. 2001a].

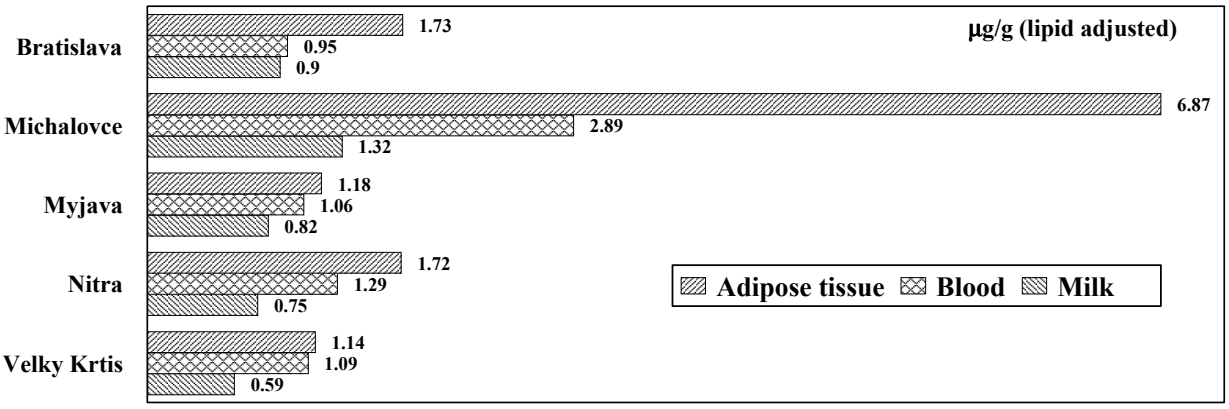

Figure 27 *PCB (the sum of 6 indicator and 8 monoortho- congeners) levels in human blood lipids taken from the human population living in selected Slovakia's districts (adipose tissue, blood and milk samples were collected from different donors)*

Within the 2nd round of the WHO-coordinated exposure study on the levels of PCBs, PCDDs and PCDFs in human milk running in 1993 ten mother's milk samples were collected in a potentially polluted area (Michalovce District) and ten samples in a control one (Nitra District). The samples collected in the same district were polled and analyzed for PCDDs, PCDFs, WHO-PCBs and indicator PCBs. The concentrations of six indicator PCBs in milk lipids from the Nitra District were comparable with European developed countries (see Figure 28). Indi-

cator PCB levels in the Michalovce district was considerably higher (1 015 ng/g, lipid basis). The Czech milk samples (Kladno vs Nitra and Uherske Hradiste vs Michalovce) contained almost the same PCB levels. The influence of common food, animal feed and goods during existence of former Czechoslovakia on similar exposure of the human population is obvious [WHO/ECEH 1996].

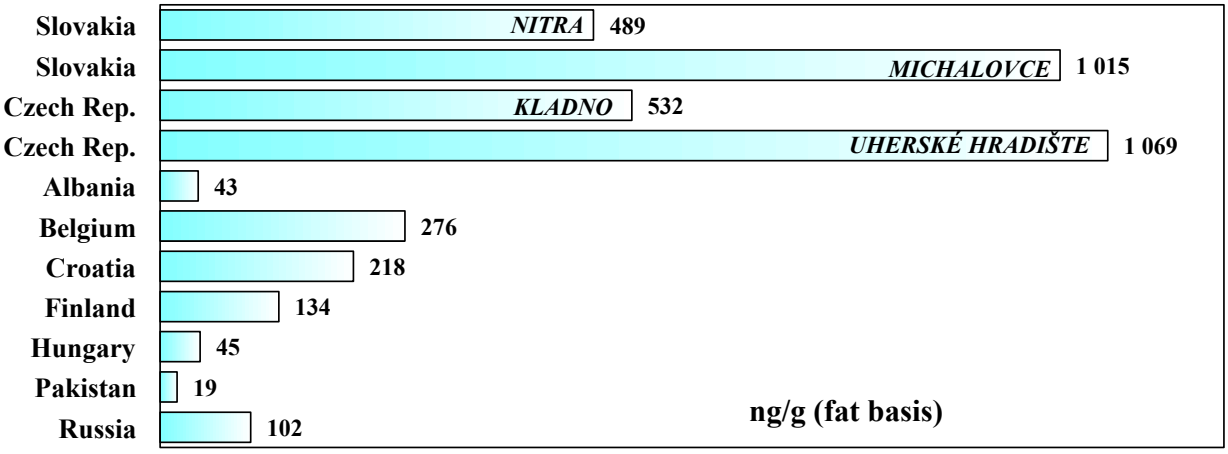

Figure 28 *Comparison of PCB (the sum of 6 indicator congeners) levels in human milk samples collected in a polluted area (Michalovce District) and control one (Nitra District) within the 2nd round of the WHO exposure study) with some other participating countries*

In October 1998 blood from 215 people (107 males and 108 females) and from 205 people (101 males and 104 females) long-term living in the Michalovce District (polluted area) and the Stropkov District (control area) respectively was taken. Among those 215 blood donors from the Michalovce District there were 11 fishermen eating fish caught in the Laborec River and Zemplinska Sirava Lake. In addition, blood was taken from 38 people (27 males and 11 females) working in former PCB production in Chemko Strazske situated in the Michalovce District. Summarized results are given in Figure 29.

Higher PCB content in some foods available in the polluted district of Michalovce (see Figure 23) has evidently caused increased exposure of the human population living in that district. Average PCB concentration of 4.2 ppm in human blood lipids taken from the human general population long-term living in the Michalovce District was 3.5-times higher than that in the Stropkov District (1.2 ppm). People eating foods coming from animals kept on small family farms at their houses contained significantly higher PCB levels in their blood serum lipids.

While average 8.6 ppm was found in the blood lipids of the former Chemko workers fishermen's blood lipids contained even 11.2 ppm on average (max value was 60 ppm).

PCB levels in men were somewhat higher both in the Michalovce and Stropkov District however these differences were not statistically significant.

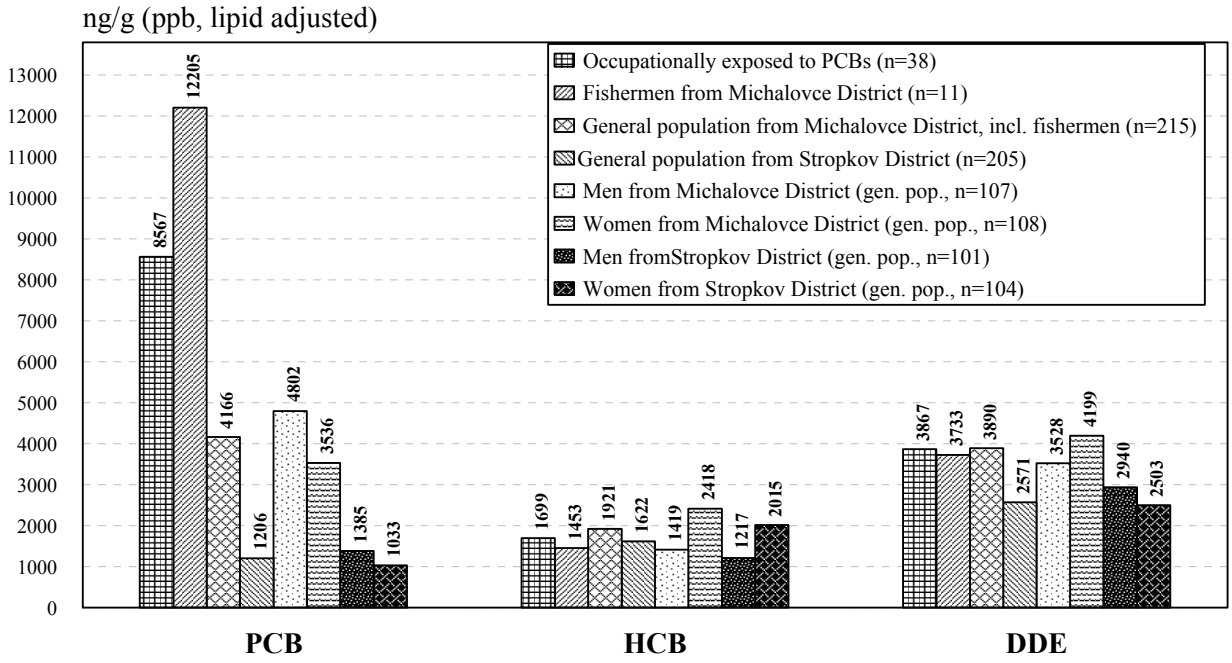

Figure 29 *Average PCB (the sum of 28, 52, 101, 138, 153, 118, 156, and 170 PCB congeners), HCB, pp'-DDE, and pp'-DDT levels in human blood lipids from workers working for a former Slovak PCB producer, fishermen consuming fish from PCB-polluted waters in Michalovce District and the general human population long-term living in Michalovce (polluted area) and Stropkov (control and background area) districts.*

B. Polychlorinated dibenzo-p-dioxins and dibenzofurans

Blood specimens intended for PCDD, PCDF and planar PCB analysis were taken 1992 from human adults living in five selected Slovak districts (3 males and 3 females from each district). These pollutants were also analyzed in blood taken from workers working long-term in a municipal waste incinerator of Bratislava, Chemko Strazske (former PCB producer) and a dioxin analytical laboratory. Results are shown in Figure 30.

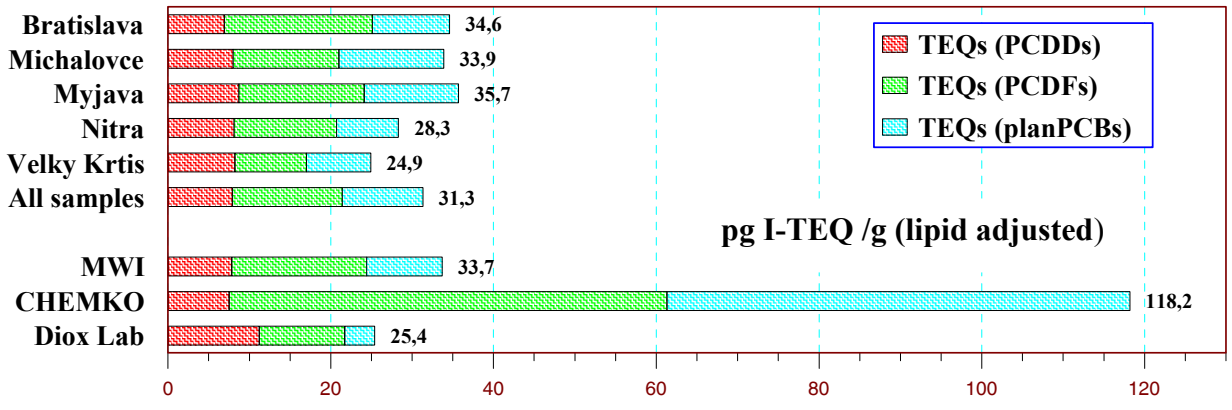

Figure 30 *Average PCDD, PCDF a planar PCB levels (as I-TEQ) in blood serum lipids taken from the human population living in selected Slovakia's districts, workers from a municipal waste incinerator, former PCB producer (Chemko) and dioxin analytical laboratory.*

C. Hexachlorobenzene

Biopsy adipose tissue (N=68), blood (N=111) and milk (N=67) samples intended for PCB and Cl-pest analysis were collected in the period 1993/94 from the general human population living in five selected districts. The adults of both sexes were chosen randomly. Mean HCB results are presented in Figure 31 [Kocan et al. 1994a, 1994b, 1995a, 1995b]. One can notice a remarkable difference in HCB content between adipose tissue/blood samples and milk samples probably caused by lower age of mothers and the donors of the adipose tissue and blood samples.

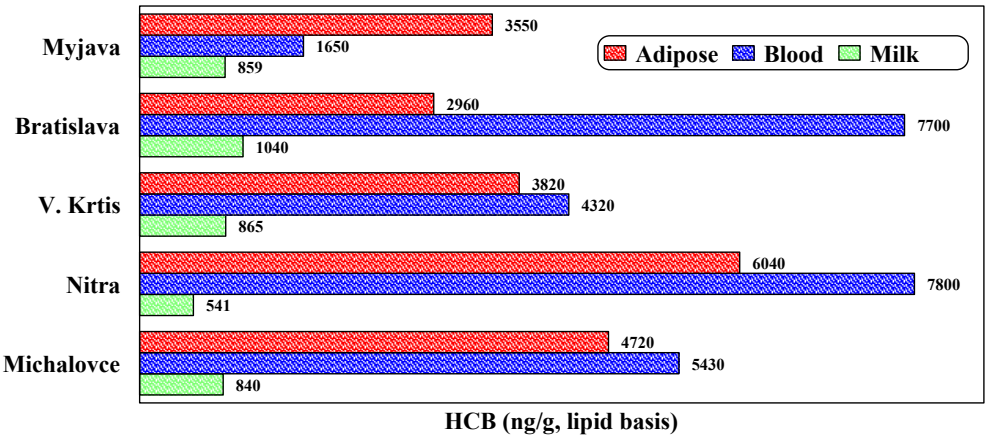

Figure 31 *HCB levels in human blood lipids taken from the human population living in selected Slovakia's districts (adipose tissue, blood and milk samples were collected from different donors)*

HCB levels in blood taken in 1998 from the general human population living in the Michalovce District and Stropkov District (for more details see PCBs chapter above) are shown in a bar chart in Figure 29.

D. DDT

Biopsy adipose tissue (N=68), blood (N=111) and milk (N=67) samples intended for PCB and Cl-pest analysis were collected in the period 1993/94 from the general human population living in five selected districts. The adults of both sexes were chosen randomly. Mean p,p'-DDT and p,p'-DDE results are presented in Figure 32 and 33 respectively. [Kocan et al. 1994a, 1994b, 1995a, 1995b]. One can notice a remarkable difference in HCB content between adipose tissue/blood samples

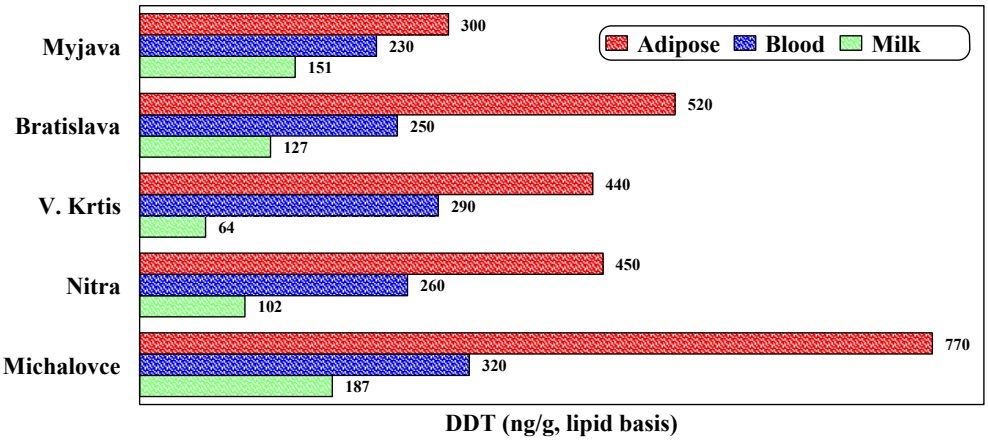

Figure 32 *pp'-DDT levels in human blood lipids taken from the human population living in selected Slovakia's districts (adipose tissue, blood and milk samples were collected from different donors)*

and milk samples. Lower DDT and DDE levels in mother's milk in comparison with adipose tissue and blood are also noticeable.

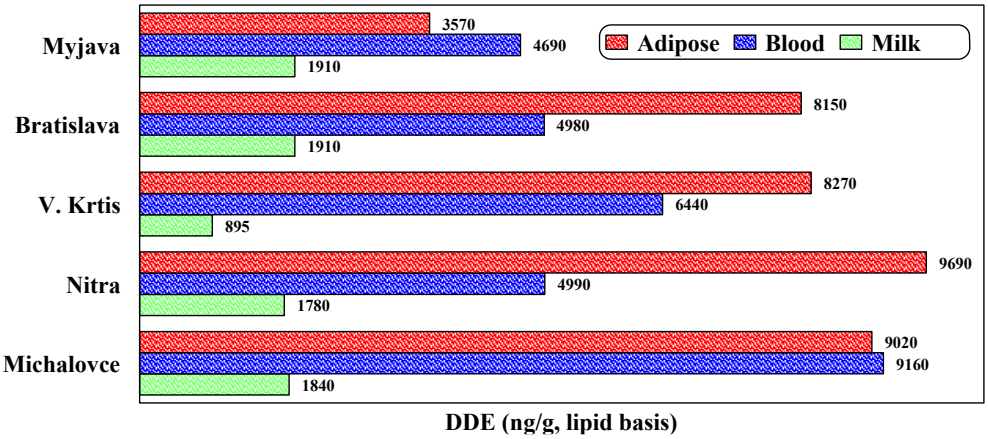

Figure 33 *pp'-DDE levels in human lipids taken from the human population living in selected Slovakia's districts (adipose tissue, blood and milk samples were collected from different donors)blood*

pp'-DDE levels in blood taken in 1998 from the general human population living in the Michalovce District and Stropkov District (for more details see PCBs chapter above) are shown in a bar chart in Figure 29.

E. Other Chlorinated Pesticides (Aldrin, Chlordane, Dieldrin, Endrin, Heptachlor, Mirex, Toxaphene)

No published data are available on the levels of these organochlorines in human samples.

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