

# Environmental Levels (Air and Soil) of Other Organohalogenes and Dioxins

## ENVIRONMENTAL CONTAMINATION FOLLOWING PCB MANUFACTURE IN EASTERN SLOVAKIA

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### Introduction

A recent pilot study aimed at five selected Slovakia's districts has shown that PCB levels in the Slovak human population are substantially higher than those in many other countries [1-8]. Several times higher PCB content in comparison with other districts was found in human adipose tissue, blood and milk samples collected in Michalovce district, i.e. in the district in which PCBs were manufactured (at Chemko chemical factory in Strazske) from 1959 to 1984 in a total amount of about 21,500 tonnes [9]. Especially in the first half the manufacture, considerable amounts of PCBs released into the environment (mainly into watercourses and soil) due to poor technological measures. In addition, former ignorance about the environmental persistency of PCBs and their harmful effects on living organisms caused that almost no attention was paid to PCB releases at that date.

In this short paper, PCB levels found in ambient air, soil, surface water, sediment and wildlife (fish and game) samples collected in 1997/98 (i.e. 14 years after the manufacture had been stopped) at the broader neighbourhood of a former PCB production plant in eastern Slovakia are reported [10]. Stropkov district which is about 60 km (upwind and upstream) far from the contaminated Michalovce District was selected as a comparative background area.

### Material and Methods

#### *Sample collection*

Ambient air: Six 24-hr ambient air samples were collected according to the TO-4 USEPA method on precleaned glass fibre filters (GFFs) and polyurethane foam (PUF) plugs by high-volume samplers in September 1997 at the distance of 1 to 30 km from a former PCB production plant. Six ambient air samples were taken at the comparative area, as well.

Soil: Thirty-one samples were taken from an upper soil layer (20 cm) at disposal sites of the manufacturer, agricultural fields in Michalovce and Stropkov districts, and at asphalt-sand preparation plants which used PCBs in heat-exchangers. Each sample was created by averaging 5 to 10 soil plugs taken by a steel tube of 2-cm diameter being hammered into soil at a 10-m span following the pattern of dice five.

Surface water and sediment: Thirty-three 5-L water samples were taken from the effluent canal of the PCB manufacturer, the river Laborec (the canal is emptying into it) and Zemplinska Sirava (a large artificially created lake supplied with water from Laborec). Where possible sediment samples (30) were taken at the same sites using an Ekman bottom corer.

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## Wildlife:

Sixty-nine fish caught in the polluted area (the Laborec and Zemplínska Širava) area) and 48 fish caught in the comparative area (Ondava River and Domasa Lake) were pooled taking into consideration genera and catching sites to get 20/11 samples related to Michalovce/Stropkov waters.

Meat or adipose tissue from 9 game animals killed in Michalovce district, 9 in Sobrance district (samples came from the Vihorlat Hills that extend over both districts) and 16 in Stropkov district was used for analysis.

## Analysis

GFFs and PUF plugs from ambient air sampling were Soxhlet extracted with 5 % diethyl ether in n-hexane. Soil or sediment samples (50 g) after low-temperature drying and sieving were Soxhlet extracted with n-hexane. Water samples after paper filtering were repeatedly extracted with n-hexane using a separation funnel. Meat samples were ground and lipids extracted with diethyl ether.

Extracts were concentrated using a rotary evaporator and cleaned on an H<sub>2</sub>SO<sub>4</sub>/silica column as published elsewhere [1]. Eluates from ambient, water sediment and fish samples were analyzed by HRGC/LRMS using an isotope dilution method modified for PCBs [11]. Surface water and game samples were analyzed by HRGC with electron capture detection using external calibration. In all the cases 60-m DB-5 capillary columns were used for CG separation. Other GC and MS conditions are published elsewhere [12].

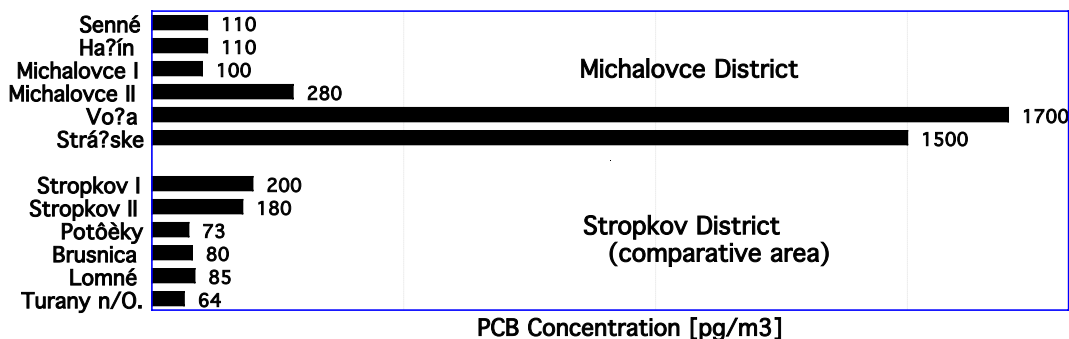


Fig. 1. PCB concentration in pg/m<sup>3</sup> in ambient air samples collected around Michalovce and Stropkov districts.

## Results and Discussion

PCB concentrations (the sum of all congeners) determined in ambient air are presented in Figure 1.

Several times higher values were found close to Chemko and its dumping and storage sites in Strážske (Voľa, Strážske). Somewhat increased levels were observed in towns (Michalovce, Stropkov) what might be influenced by traffic. PCB concentrations at the remoter sites of Michalovce

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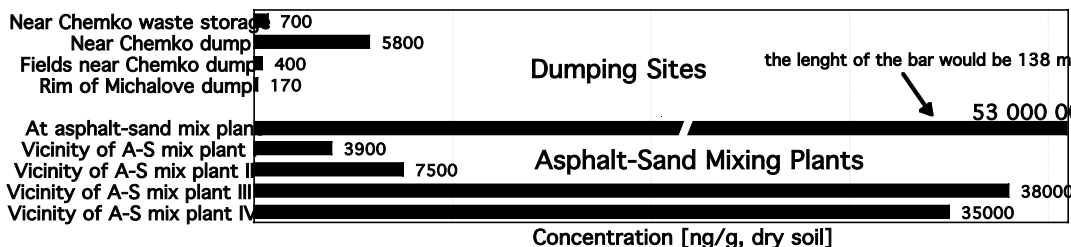


Fig. 2. PCB levels in soil samples collected in the vicinity of storage and dumping sites of Chemko chemical plant and asphalt-sand mixing plants.

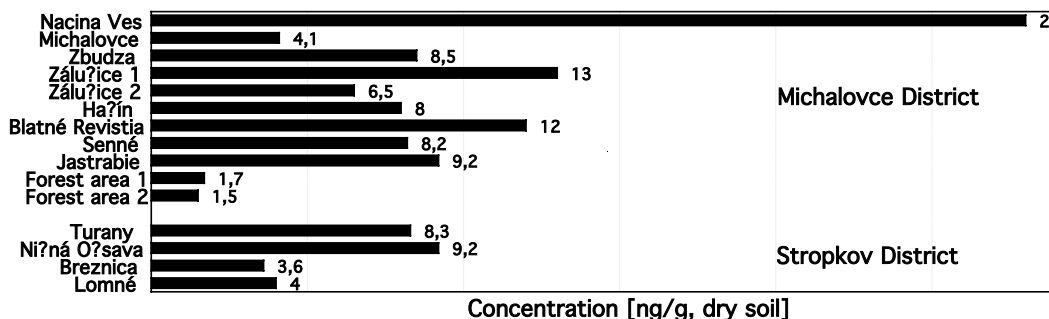


Fig. 3. PCB levels in soil samples collected at the fields of some municipalities in Michalovce and Stropkov districts.

district were similar to those in the comparative background area.

Soil samples taken close to the waste disposal sites of Chemko and asphalt-sand mixing plants have shown PCB levels as illustrated in Figure 2.

As can be seen in Figure 3, PCB levels in soil samples from the fields of some towns and villages of are considerably lower than those taken from the neighbourhood of dumps and plants mixing asphalt and sand (PCBs were used in heat exchangers).

As a large amount of PCBs entered the effluent canal of Chemko emptying into the Laborec one can expect the contamination of the large Zemplínska Sirava that is filled from the Laborec. As presented in Figure 4 a relatively low PCB level in sediment from the Chemko effluent canal (48 vs 3000 mg/kg in the same canal after merging with Strazské sewage one) is caused by a very low content of PCB adsorbing organic matter in sandy sediment present in the concrete canal (the bottom of the merged canal is already muddy). The contaminated effluent canal has polluted the Laborec and Zemplínska Sirava (compare with several hundred times lower findings in Stropkov district).

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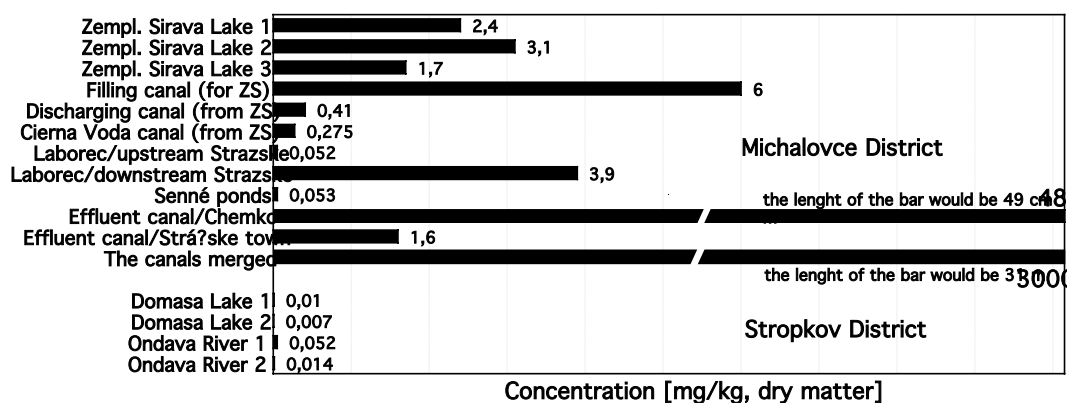


Fig. 4. PCB levels in sediment samples from some waters in Michalovce and Stropkov districts.

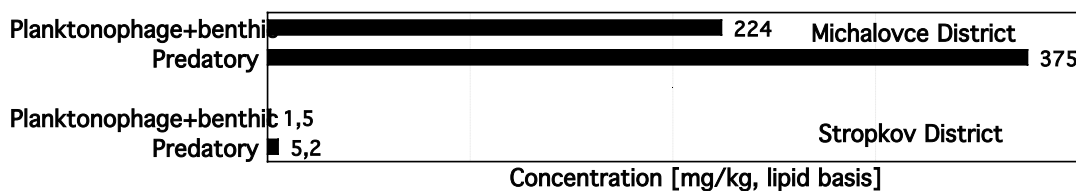


Fig. 5. PCB levels in benthic + planktonophage and predatory fish caught in Michalovce (Zemplinska Sirava Lake, Laborec River) and Stropkov (Domasa Lake, Ondava River) districts.



Fig. 6. PCB levels in game animals from the forests and fields of Michalovce, Sobrance (formerly a part of Michalovce district) and Stropkov districts.

Likewise the sediment, fish from Michalovce waters contained much higher PCB levels than those from Stropkov waters (Fig. 5). It was confirmed that predators are more exposed than fish feeding on plankton or benthic food. The environmental pollution of Michalovce district with PCBs is reflected in exposure of forest and field wildlife, as well (Fig. 6).

Environmental contamination starting through manufacturer's effluent canal has manifested itself in increased PCB levels observed in ambient air, soil, surface water and water sediment around Michalovce district and other sites where PCBs were applied. As a consequence of that, wildlife living in local forests and fields and especially fish caught in contaminated waters and contained PCBs often at very high levels. Results from an ongoing project are also showing that the food and

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human population of Michalovce district is much more contaminated with PCBs than the rest of Slovakia.

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