# **Environmental Levels P27**

## Determination of Polychlorinated Biphenyls in Soil Samples from Poland

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#### Introduction

Polychlorinated biphenyls are ubiquitous pollutants present in all compartments of the environment (atmosphere, soil, sediments, water etc.)<sup>1,2)</sup>. Due to the toxicity of certain congeners, high stability and resistance to degradation, the PCBs determination in environmental samples is of major concern<sup>3)</sup>. Since 1993, in Poland the waste oils containing PCBs are included on the list of hazardous substances<sup>4)</sup>, but to the present day the flux of these pollutants is not subject to any regulation. The presence of PCBs in about 50 % of analysed random samples of waste motor and transformer oils from different regions of Poland<sup>5)</sup>, have indicated that uncontrolled collection and improper oils regeneration may be a potential source of these xenobiotics in Polish environment.

The aim of this study is to report the level of selected PCBs congeners (28, 52, 101, 118, 138, 153 and 180) as well as the results of qualitative analysis of certain chlorinated pesticides (lindane, heptachlor, p,p' DDT and methoxychlor) performed in random soil samples from different sites in Poland.

#### **Material and Methods**

<u>Samples collection</u> Thirteen soil samples from different regions of Poland, randomly selected near the potential sources of PCBs emission into the environment (transformer stations, spill sites, waste dumps) were collected between August and November 1997. An additional soil sample from the area of Wielkopolski National Park was taken in November 1997. Sampling sites are presented in Figure 1.

<u>Samples preparation</u> Soil samples, each about 1 kg wet weight, were collected from areas  $\sim 15 \times 15$  cm, from the depth  $\sim 5$  cm and placed in aluminium bags. In the laboratory, all analysed soils were air-dried and passed through a 1.0 mm sieve.



Fig. 1. Sampling sites of soils in Poland

Aliquots of soil (10 - 20 g) were mixed with the same amount of anhydrous Na<sub>2</sub>SO<sub>4</sub>, transferred to a Soxhlet thimble and extracted with 300 ml of n-hexane : acetone mixture (50:50) for 5 h. After a change of solvents, the soil samples were extracted second time (5 h) with 300 ml of the same solvent mixture. The combined extracts were evaporated on a rotary evaporator and concentrated to ~ 2 ml in a stream of nitrogen gas. Then they were transferred in a centrifuge tube and cleaned-up with concentrated H<sub>2</sub>SO<sub>4</sub>.

The qualitative analysis of selected pesticides and identification and quantification of PCBs were performed by HRGC/ECD. A Shimadzu GC-14A gas chromatograph equipped with a <sup>63</sup>Ni electron capture detector and split injector was used. Analytical separation of the purified extracts was carried out on a 60 m Rtx -5 (0.25 mm i.d., film thickness 0.25 um) fused silica capillary column (5% diphenyl polysiloxane, 95% dimethyl polysiloxane). The detector temperature was 320° C with nitrogen as make-up gas at a flow rate 48.9 ml/ min. The temperature program of the column was 2 min. at 125°C, 7.5°C/min. until 190°C and 2° C/min. until 280° C, holding for 10 min. Each PCB was identified and confirmed using second column - Rtx - 1701 (60 m; 0.25 mm i.d., film thickness 0.25 µm), coated with more polar stationary phase (14 % cyanopropylphenyl- 86 % methyl polysiloxane). The detector temperature was 300° C with nitrogen as make-up gas at a flow rate 49.4 ml/ min. The temperature program of the column was 1 min. at 125°C; 7.5°C/min. until 190°C and 2° C/min. until 275° C, holding for 10 min. For both columns, helium as a carrier gas was used with a flow rate of 0.6 ml/min. The injector temperature was held at 250° C and the split flow rate was 28 ml/min. In GC analysis, PCB 30 was used as an internal standard. Three ul of each purified extract were injected on the GC column.

#### **Results and discussion**

Before PCBs analysis was performed, the linear range of the ECD detector was determined according to Wells *et al.*<sup>6)</sup>. The detector response was established for three congeners containing different number of chlorine atoms (28 tri, 101 penta and 153 hexa-substituted).

To validate the analytical procedure a certified industrial soil CRM 481 has been treated in the same way as the other soil samples and the recovery of selected congeners (28, 52, 101, 118, 138, 153 and 180) was established. The concentrations of concerned PCBs determined in environmental samples were corrected for recovery.

Taking into consideration, that the clean-up procedure with concentrated  $H_2SO_4$  is not powerful to remove certain chlorinated pesticides, the qualitative analysis of extracts additionally included the identification of lindane, heptachlor, p,p' DDT and metoxychlor.

Identification of the analysed compounds was performed by a comparison of relative retention times (RRT) of the peaks from standard solutions with the peaks from the chromatograms of purified soil extracts.

Soil N <sup>o</sup>	Lindane	Heptachlor	p,p' DDT	Metoxychlor	PCBs	Σ7 PCB [ng/g]
1	+	+	+	-	-	-
4	+	+	+	+	+	5
5	+	+	+	-	-	•
6	+	+	+	+	+	2
7	+	+	+	+	+	5
8	+	+	+	+	+	3
9	+	+	+	-	+	20
10	+	+	+	-	- 1	•
12		•	+		-	-
16	-	-	+	-	-	-
22	-	+	-	+		-
25	•	- <u>-</u>	+	+	+	81
29	-	· · ·	+		+	288
30	-	-	+	-	+	102

Table 1. Chlorinated pesticides and PCBs in random soil samples from Poland

Table 1 shows the occurrence of the investigated compounds in soil samples. The p,p' DDT was detected most often then PCBs and other analysed pesticides. This analyte was found in all samples except one ( $N^0$  22). It confirms the results of other authors<sup>7,8</sup>), that the environment in Poland is considerably contaminated by DDT and its metabolites. Heptachlor was detected in about 60 % of soils, when lindane and metoxychlor in < 50 % of samples were presented. It is worth to note, that some analysed soils were collected in the sites situated at the same time near the potential source of PCBs (transformer stations) and near the agricultural area (vegetable gardens). It explains the presence of all investigated pesticides in samples N<sup>0</sup> 4 and 6-8.

The PCBs in six from fourteen soils were identified, but the profile of none of the chromatograms containing picks of PCBs congeners do not correspond to the profiles of specific PCBs mixture. It results probably to the fact that in Poland the PCBs mixture from different countries were used. The content of selected congeners (28, 52, 101, 118, 153, 138 and 180) in soil samples was calculated using chromatographic peak highs provided by C-R6A Chromatopac Shimadzu integrator. The results of PCBs quantification in Table 1 and Figure 2 are presented.



Fig. 2. Content of selected PCBs in the random soil samples from Poland

The analysed samples  $N^0$  4 and 6-9 showed a concentration range of the sum of 7 PCBs from 2 to 20 ng/g dry weight (table 1). It corresponds well to PCBs content determined by Falandysz *et al.* in different soils from northern part of Poland<sup>9)</sup>. The greatest levels of concerned PCBs congeners, between 81-288 ng/g dry weight of the soil, in the samples N<sup>0</sup> 25, 29 and 30 were determined. These samples were collected near the transformer station (sample N<sup>0</sup> 9) or from the spill site of waste motor oils (samples N<sup>0</sup> 29 and 30). It confirms earlier suggestions<sup>5)</sup>, that the uncontrolled and improper circulation of waste motor and transformer oils may be one of PCBs sources in the environment in Poland.

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