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TRANSFORMERS AS A POTENTIAL FOR SOIL CONTAMINATION

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The aim of this paper is to investigate the presence of PCBs and heavy metals in the surrounding soil and also in the soil of the receiving pit located below the PCB contaminated transformer. Concentrations of PCBs in our samples are ranged from 0,308 to 0,872 mg/kg of absolutely dry soil.

Key words: heavy metals, Polychlorinated biphenyls (PCBs), contamination, oil pit, transformer

INTRODUCTION

PCBs are mixtures of synthetic organic compounds, nonflammable, highly electrically resistant, with good insulation properties and very stable at high temperatures and pressures. Therefore, they were at first used as dielectric fluids and insulators in transformers and capacitors. In addition to their use for the prevention of fire and explosion, they were used in hydraulic fluids, wax casting, production of carbonless copy paper, compressors, heat transfer systems, plasticizers, paints, adhesives, pesticides, etc. However, beside the good qualities they have, PCBs are highly toxic and carcinogenic substances that get into the human body usually through the skin or digestive tract. They are accumulated in the animal and human fatty tissues without any possibility of degradation. Because of the numerous data on their toxicity, production of PCBs has been banned.

According to the latest regulations (which are constantly innovated), the use and sale of PCB oils and devices using PCBs has been banned worldwide, excluding the devices already in use on June 30, 1986, which can be used until they reach their expiration date. Therefore, PCB compounds can now be found in all environmental compartments: sediment, soil, air, water, even in breast milk and fatty deposits of polar bears and whales, etc.

There are numerous studies researching the impact of PCBs on human health, but they have many deficiencies and uncertainties, so it cannot be concluded indisputably to what extent PCB disrupts the normal body functioning. Since it is impossible to get results otherwise, many animal tests have been conducted and credible information received about the harmful effects of PCBs. The studies on workers exposed to PCBs [1, 2] indicate the potential impact on liver and biliary tract cancers, as well as on respiratory tract irritation, blood changes, liver and gastrointestinal tract, depression and fatigue. PCBs are exceptionally dangerous for transformer maintenance and repair workers because their PCB concentration is much higher compared to other areas, such as the air in buildings that have electrical devices containing PCB or the air in the external environment, including the air in hazardous and toxic waste landfills.

PCBs AND HEAVY METALS IN TRANSFORMER OIL PITS

Today PCBs usually reach the environment as a result of transformer oil leakage caused by transformer failures, poor handling of damaged electrical equipment, spilling during oil changes and improper waste disposal. Transformer oils are found to contain some metals such as copper, iron, lead, aluminum, silver, tin and zinc. It is assumed that transformer oil contains the metals because of their presence in the materials of the transformer components. Copper can be found in transformer windings [3], lead in soldered joints and connectors, iron in the transformer core and tank, aluminum in coils and ceramic insulators and tin, zinc and silver in some peripheral components.

Oil pits are used to collect oil leakage from the devices. They are located below the transformers. Each power transformer or device that individually contains more than 1 000 kg of oil must have an oil collecting pit for quick oil removal or collection. An oil collecting pit consists of a sink funnel (tank), a grate, an oil tank, an outlet and the like. Its construction is governed by a specific Regulation, which states that an oil pit is not required to have the bottom, and that oil can be allowed to sink into ground: “if an electric power plant is located outdoors, in a separate facility (building) used exclusively for such a purpose, and in a separate pit outside the facility (building), it is permissible for oil to spill under and around the transformer and plunge directly into the ground” [4]. This causes soil contamination and environmental pollution with PCBs and heavy metals.

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In Serbia, a few researchers [5-7] have dealt with the presence of PCBs in the soil. The study on soil pollution in Novi Sad gardens in 2003, analyzes 20 soil samples, taken from the gardens in the city of Novi Sad [8]. The average total content of surveyed PCB congeners is 5,13 μg/kg and it ranges from 0,32 to 14,57 μg/kg. In 2004, the continued research examines 30 soil samples from Novi Sad gardens [9]. The PCB congeners are detected in trace amounts in the tested samples. The 2005 research examines the presence of PCBs both in the suburban and urban gardens [10]. The PCB content is found higher in the urban gardens than in the suburban ones. The PCB quantification limit value of 0,02 μg/kg, calculated as the total of 7 congeners and defined by the Soil Regulation [11], is not exceeded by any of tested soil samples from the city gardens, although these compounds have been frequently found in the soil.

In 2006, in Novi Sad, the PCB content is tested in the park soils (n=4), in the soils of industrial plants (n=4) and near the roads (n=5). The study includes seven representative congeners of this group. None of the tested samples exceeds the quantification limit value defined by the Soil Regulation [12, 13]. The average content of the total PCBs in the soil samples taken near the roads is 1,89 μg/kg absolutely dry soil (d.w.), while the average content in the soil near the industrial zones is 0,71 μg/kg d.w. None of PCB congeners is detected in the soil of the Danube Park. The soil of the park in the Futoška Street contains 0,07 μg/kg d.w., while the highest concentration of PCB congeners with the value of 11,31 μg/kg d.w. is found in the soil of the park near the railway station. None of the test samples exceeds the limit value of 0,02 μg/kg d.w., defined by the Soil Regulation [11, 12].

The impact of the destruction of industrial facilities during the bombing of Serbia in 1999 is monitored within the APOPSBAL project. High concentrations of PCBs (305710 ng/g) are detected in the soil of the Pančevo refinery.

The content of PCBs in other soil samples at the site ranges from 7,0 to 650,4 ng/g. Two samples are found with high PCB content, one in the Pančevo refinery (122,65 ng/g) and the other in the Novi Sad refinery (581,44 ng/g) [13]. These soil samples have PCB content higher than the soil limit value defined by the Soil Regulation [11].

Because of the known risks arising from the presence of PCBs and heavy metals in the soil, it is necessary to determine the pollution, i.e. concentration of pollutants in the soil, efficiently and accurately. The application of multivariate statistical methods provides data that allow better understanding and interpretation of complex environmental data.

MATERIALS AND METHODS

This paper examines the presence of PCBs and heavy metals in the soil of the oil pit directly under the PCB-contaminated transformer (Figure 1) and in the surrounding soil near to the oil pit. The soil samples are taken at a distance of 1 m from the source of pollution to a depth of 30 cm with a drilling probe. A total of 10 soil samples are taken, one from the oil pit and nine from the surrounding soil.

Figure 1 Contaminated transformer

The soil is tested for the presence of the following PCB congeners: Bal 28, Bal 52, Bal 101, Bal 118, Bal 138, Bal 153 and Bal 180, and heavy metals: Cd, Cr, Co, Cu, Ni, Pb, Mn and Zn.

PCB Analysis. The results of PCB contents in soil are presented as the total of the seven congeners. The Soxhlet extraction (United States Environmental Protection Agency- USEPA 3540S) is used for the soil extraction, then the extracts are purified on a silica-gel column (USEPA 3630C). The analysis of the extracts is performed by gas chromatography with tandem mass spectrometry, using the device 1300 Thermo Scientific Trace ISQ with automatic injector AI 1310. The 30 m long column HP-5-MS, with a diameter of 0,25 mm and a 25 μm thick film of stationary phase is used for analyte separation. The method of selected ion monitoring (SIM) is used for detection of congeners. The working conditions of the mass spectrometer are set as follows: transfer line temperature 270 °C, the method of ionization in the electron beam energy 70 eV, injector temperature 240 °C. Carrier gas flow rate is 1,4 ml/min. The temperature mode of the column is the following: initial temperature of 70 °C is held for 2 minutes, then it is increased 25 °C/min to 150 °C, then increased 3 °C/min to 200 °C and 8 °C/min to 280 °C, where the temperature is retained for 10 min. The volume of inserted sample size is 2 ml.

The standard mix PCB 3 (Dr. Ehrenstorfer cat. No. 20030300) is used for quantification.

The used reagents are the following: Methanol, High-performance liquid chromatography – HPLC purity (Sigma-Aldrich, SZBB343SV) Acetone, HPLC purity (J.T. Baker, 1030900016); Hexane, HPLC purity (Sigma-Aldrich, SZBA246S); Silica gel (Sigma-Aldrich, Grade 923, 214477); Diethyl ether, HPLC purity (J.T. Baker, 0817704002).

Metal Analysis. For sample preparation automated system for microwave-assisted digestion (Berghof MSW 3+) were used. Homogenised samples were transferred to the reaction vessels and nitric acid and hydrogen peroxide were added.

Digested samples were quantitatively transferred into volumetric flask and diluted to 25 cm3 with ultra-

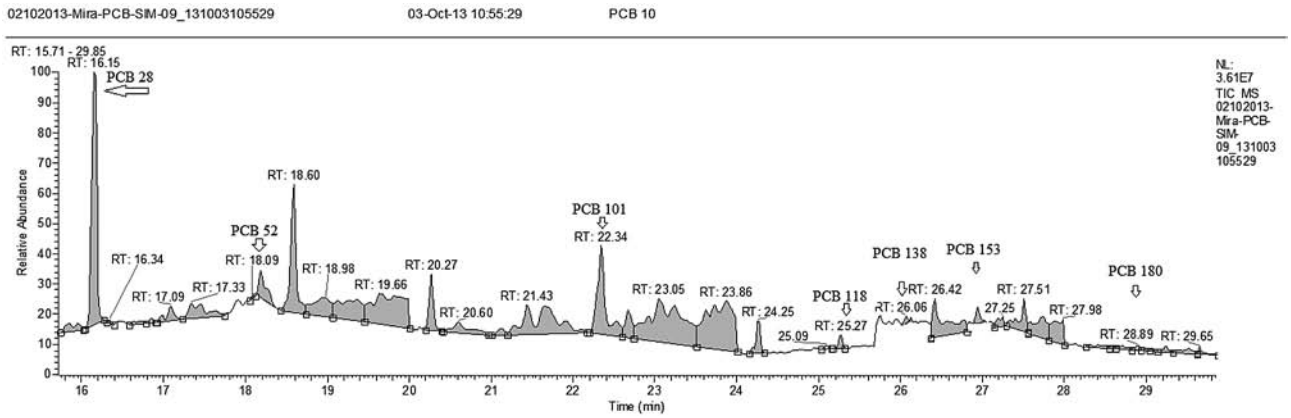

Figure 2 The chromatogram of the sample No. 10

pure water. A blank digest was carried out in the same way as the samples.

Analysis of metal content was performed using inductive coupled plasma with optical emission spectroscopy (ICP-OES) system - Thermo iCAP 6500 Duo (method EPA 6010C). Plasma of argon gas produces excited atoms and ions which are emitting electromagnetic radiation with wavelengths that are characteristic for analyzing elements. In one sample can be determined simultaneously several elements in one run.

Chemicals used in this analysis were of extra purity grade for trace element analysis (J. T. Baker, USA, INSTRA). Used chemicals were: HNO_3, H_2O_2, standard solutions of Cd, Cr, Co, Cu, Ni, Pb and Zn (1 000 mg/dm^3). For all dilutions and dissolutions was used ultra-pure water from EasyPure system. Working solutions were prepared daily by diluting standard solutions with 0,1 mol/dm^3 nitric acid.

All vessels and cells were washed with nitric acid (1:1), deionized and ultra-pure water.

RESULTS AND DISCUSSION

The testing results of ten soil samples are shown in Table 1.

The PCB values range is from 0,308 to 0,872 mg/kg of absolutely d.w. The sample No. 10, with the PCB content of 0,787 mg/kg, is the sample taken from the oil pit.

Figure 2 shows the chromatogram of the sample No. 10. It can be observed that other compounds of this group are also present, and Trichlorobiphenyl (PCB 28) is the most common.

Statistical analysis. After the performed statistical analysis of the research results, it is found that the standard deviation value shows concentration variations of some metals (S, Mn and Zn), as opposed to ΣPCB with the relative standard deviation of 29,84 %. The following values of relative standard deviation are determined: Cu (119,83 %) > Zn (49,55 %) > Pb (22,84 %) > Cd (21,48 %) > Ni (14,26 %) > Mn (10,4 %) > Cr (9,79 %) > Co (5,76 %). Significant variations of the metals show the different sources of soil contamination, such as: transformer oil, compound materials of the transformer itself and various anthropogenic factors.

No significant correlation (higher than 0,8) is observed between PCB and metals. However, there is a correlation matrix between PCBs and some metals: Cd, Co, Ni and Zn, which can be seen in Table 2.

The insignificant correlation between PCB and metals suggests that these metals have no significant effect on the persistence and concentration of PCB extracted from the soil, and that there is no important relationship between the PCB level in transformer oil and the metals in it resulting from the transformer operation, which confirms the results published in the research [14].

Table 1 **The content of PCBs and heavy metals in soil**

Samples	ΣPCB /mg/kg	Cd mg/kg	Cr /mg/kg	Co /mg/kg	Cu /mg/kg	Ni /mg/kg	Pb /mg/kg	Mn /mg/kg	Zn /mg/kg
1	0,70	0,09	41,76	5,52	13,43	24,02	15,46	319,95	86,51
2	0,45	0,09	38,43	5,22	25,77	22,72	15,33	333,10	89,10
3	0,31	0,08	40,82	4,97	14,55	21,65	13,40	324,10	75,94
4	0,52	0,07	48,74	5,70	22,78	30,64	14,82	419,75	126,40
5	0,87	0,10	41,03	5,49	16,51	27,33	20,86	313,95	245,65
6	0,56	0,09	38,64	5,12	19,47	23,47	14,06	340,45	217,25
7	0,54	0,09	34,45	4,81	16,35	19,54	15,01	317,15	152,85
8	0,44	0,09	36,11	5,09	22,83	19,83	14,24	317,85	75,67
9	0,53	0,11	43,05	5,56	159,20	26,30	22,29	365,40	94,06
10	0,79	0,15	39,77	5,62	70,16	24,47	10,04	297,70	81,88

Table 2 **Correlation matrix for PCB and metals from the soil next to the transformer pit**

	ΣPCB	Cd	Cr	Co	Cu	Ni	Pb	Mn	Zn
ΣPCB	1,00								
Cd	0,56	1,00							
Cr	0,10	-0,18	1,00						
Co	0,57	0,36	0,77	1,00					
Cu	0,05	0,51	0,23	0,41	1,00				
Ni	0,41	0,00	0,91	0,85	0,26	1,00			
Pb	0,17	-0,18	0,23	0,22	0,45	0,36	1,00		
Mn	-0,30	-0,50	0,76	0,39	0,20	0,67	0,26	1,00	
Zn	0,48	-0,14	-0,04	-0,04	-0,27	0,27	0,35	0,01	1,00

CONCLUSIONS

The Soil Regulation, published in the Official Gazette 88/2010, defines the limit value of 0,02 mg/kg and the value of 1 mg/kg of soil indicating significant contamination for the total content of PCB congeners (the total of PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153 and PCB 180). The PCB values range in our samples are from 0,308 to 0,872 mg/kg d.w. The results show that the PCB congeners migrate from the oil pit and that their concentration is close to the value indicating significant soil contamination. Previous studies by other authors have also found these compounds in soil used for different purposes (agricultural soil, park soil, soil near industrial zones, urban and suburban garden soil), with the concentrations usually at the level of mg/kg and none exceeding the defined value of the Soil Regulation.

The presence of the certain metals in the soil next to the transformer oil pit is also proven, but their concentrations do not exceed the limit values published in the Official Gazette 88/2010.

The results indicate that PCBs slowly migrate and spread through the environment; in order to implement the Stockholm Convention, it is necessary to carry out a detailed research of PCB presence in all oil pits, identify contamination with these compounds and take appropriate measures to prevent their environmental dispersion.

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