

Levels of polychlorinated biphenyls in the soil and cotton wiping samples from the Zadar area (Croatia)

Violeta Čalić¹, Mladen Picer¹, Tatjana Kovac¹, Vedranka Hodak Kobasic¹

¹Institute Rudjer Boskovic

Introduction

Damage to electrical power plants increases the possibility of the environmental proliferation of PCBs, which are stable organic pollutants.^{1, 2} The city of Zadar is situated on karstic, porous soil. Spilled PCBs can spread through this medium towards the coastline. Due to the possible inflow of the spilled pollutants into the water ecosystems, the pollution levels at several locations in the city of Zadar have been investigated as part of the project APOPSBAL (The Assessment of Selected POPs (PCBs, PCDDs/F and OCPs) in the Atmosphere and Water Ecosystems from the Waste Materials Generated by Warfare in the Area of the Former Yugoslavia), which is co-financed by the European Commission. In order to determine testing sites where high concentrations of PCBs were suspected, we consulted with the local authorities and responsible persons in the local industrial plants and facilities.

Methodology

Area of investigation

The first soil sampling of the area within a 3 km radius of the Zadar electrical transformer station (E.T.S.) was performed in 2003. We also visited the TIZ textile mill in Zadar in order to perform an analysis of the PCBs in the soil surrounding the transformer equipment. Besides TIZ, during 2003 soil sampling was performed around the Adria fish factory, in Donat Park and at the Zadar weather station. The PCB value from Zavižan Peak on Mt. Velebit served as the reference value. A second soil sampling was organized at the end of February 2004. Sampling around the TIZ textile mill was repeated. Samples were also taken from the site of the ruins of the former BAGAT factory, at the building materials waste dump near the port of Gaženice and the scrap metal dump.

Analysis of PCBs

Air-dried soil samples were extracted after being sifted through 2 mm sieves using an ASE extractor with a mixture of acetone and n-hexane solvents (1:1 v/v). Surfaces of 100 cm² on concrete bases were wiped with n-hexane cotton wipes to obtain samples. Sample extraction was performed using an ultrasonic bath with a mixture of acetone and n-hexane solvents (1:1 v/v).

The analytical method used for the analysis of the extracts included filtration through a column of Na₂SO₄ anh, cleaning on an alumina column and the separation of the PCBs from organochlorine insecticides on a miniature silica gel column. Elutes were analyzed by an Agilent Technologies 6890N network GC system equipped with an electron capture detector (GC-ECD). Detailed descriptions of the methods used are presented in numerous published papers.^{1, 2, 3}

Results and Discussion

Results of the soil analyses in the Zadar area are presented in Table 1.

The levels of PCBs in the soil from the investigated localities in Zadar (Donat Park, the Adria factory and the Zadar weather station) do not deviate significantly from the level at Zavižan Peak on Mt. Velebit, which was used as an unpolluted reference value. However, in soil samples from the BAGAT factory and the scrap metal dump, the observed concentrations of total PCBs were elevated (ranging from 3 to 6 mg/kg).

Table 1. Levels of PCBs in the soil samples collected in 2003 and 2004 in the area of the city of Zadar (values in

mg/kgdry weight of sample)

Sampling position	Sampling date	Total PCBs as the sum of Aroclors 1248 and 1254	Sum of the 7 key PCB congeners *
Fish factory Adria	13.05.2003	0.01	0.004
Park Donat	13.05.2003	0.01	0.005
The weather station Zadar	13.05.2003	0.03	0.006
Zavižan-Mt.Velebit	13.05.2003	0.02	0.008
Textile mill TIZ 1	22.07.2003	454	118
Textile mill TIZ 2	29.02.2004	3.08	0.781
Textile mill TIZ 3	29.02.2004	976	244
Textile mill TIZ 4	29.02.2004	13	4.90
Factory BAGAT-NRP II	29.02.2004	4.86	2.06
Factory BAGAT-TS III	29.02.2004	0.89	0.07
Port Gaženice waste deposit 1	29.02.2004	0.07	0.01
Port Gaženice waste deposit 2	29.02.2004	0.09	0.02
Port Gaženice waste deposit 3	29.02.2004	0.07	0.004
Metal waste deposit 1	29.02.2004	3.06	0.18
Metal waste deposit 2	29.02.2004	7.49	1.53
Metal waste deposit 3	29.02.2004	6.12	1.05

*IUPACNo. PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153 and PCB 180

The results of the analyses of samples collected around the TIZ factory are disturbing. Concentrations of the sum of the 7 key PCBs (IUPAC No. PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153 and PCB 180) in two soil samples are markedly high: the TIZ 1 soil sample has 118 mg/kg and the TIZ 3 has 243 mg/kg of the 7 key PCBs.

In the soil samples taken from the dump at the port of Gaženice, the level of total PCBs found is up to 1 mg/kg. It is important to remark that this area is large. Hundreds of truckloads of various building wastes have been unloaded and it is possible that some of the waste is polluted with PCBs. For this reason, results from the analysis of only 3 soil samples cannot cover the whole area of the waste dump. A more systematic analysis of the PCB pollution in this area is required. In order to determine whether leaking PCBs are penetrating into the sea sediment, tracking around the port Gaženice should be performed.

In Figure 1, levels of the total PCBs found in soil samples from the investigated Zadar area are presented (E.T.S. stands for the 110/35 kV Zadar electrical transformer station which was repeatedly damaged during the war; TIZ stands for the damaged textile mill; BGT is the factory BAGAT; GAŽ is the building waste dump near the port of Gaženice; WST is the scrap metal dump). Columns represent the geometrical means of the PCB concentrations expressed as the sum of Aroclors 1254 and 1248 (mg/kg dry weight of sample). The level of PCBs at the Zadar E.T.S., a known contaminated location^{4, 5} is presented for purposes of comparison. To facilitate comparison, contamination levels are expressed in logarithmic scale.

In order to determine how a significant level of total PCBs (the 454 mg/kg) was found in the soil sample from the TIZ factory collected in 2003, a detailed investigation of the PCB pollution of this site is being considered. Repeated collections of soil samples in 2004 and analysis have confirmed the presence of PCB contamination around the transformer station. A detailed presentation of the sampling sites in the TIZ factory is illustrated in Figure 2. In Figure 3, the levels of the total PCBs in the soil samples collected inside the TIZ factory complex are presented. Again, to facilitate comparison, contamination levels are expressed in logarithmic scale. There were markedly high levels of PCBs in the samples taken around the transformer stations, samples TIZ 1 and TIZ 3.

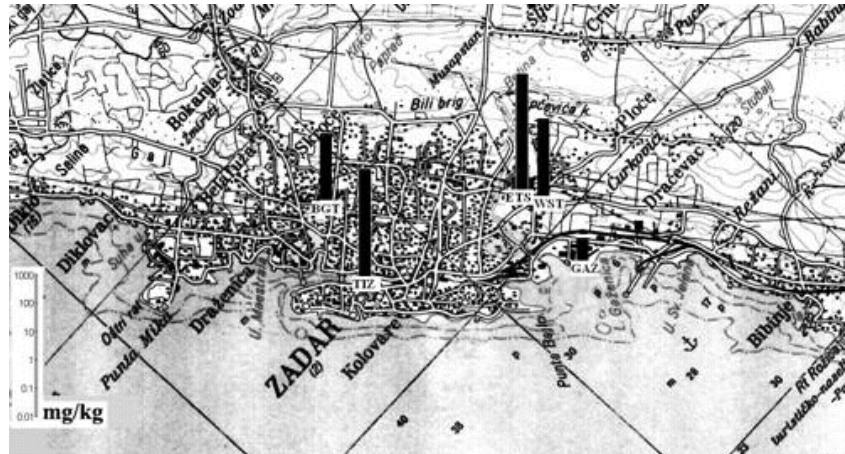


Figure 1. Comparison of levels of the PCBs in the soil collected in various places around the city of Zadar (The columns are the geometric mean values of the total PCBs expressed as the sum of the Aroclors 1254 and 1248)

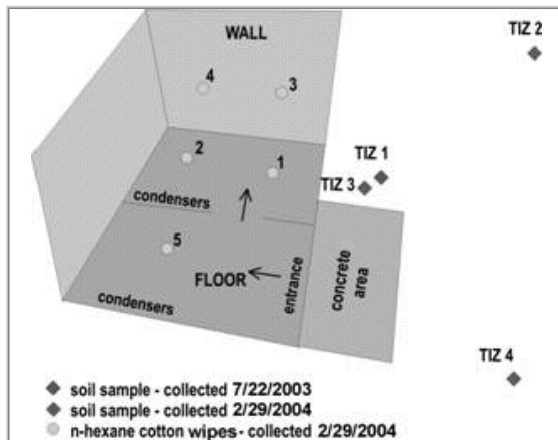


Figure 2. Detailed diagram of sampling sites of the soil and n-hexane wipes around the electrical transformer station at the TIZ factory

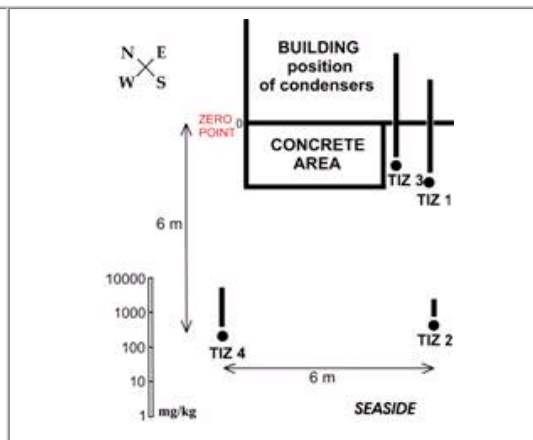


Figure 3. Comparison of levels of PCBs expressed as the sum of the Aroclors 1254 and 1248 in soil samples collected in the TIZ E.T.S. in 2003 and 2004

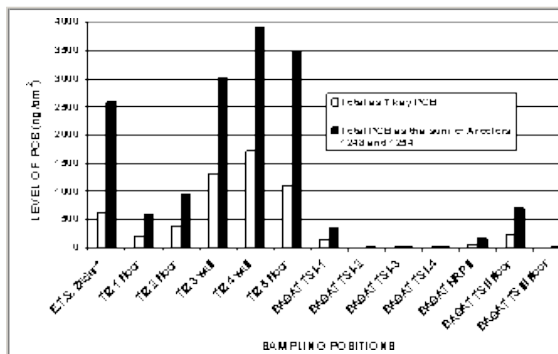


Figure 4. Levels of total PCBs as the sum of Aroclors 1248 and 1254 and the sum of the 7 key PCB congeners in samples of the n-hexane wipes collected from the floors and walls of the TIZ E.T.S. and the BAGAT E.T.S. in Zadar during 2004
(*geometrical mean values of the PCB concentration in the wipes collected at the Zadar E.T.S. in 2002 and 2003)

In order to obtain a more detailed and accurate assessment of the pollution inside the TIZ and BAGAT factory complexes in 2004, in addition to the soil samples, sampling of the concrete surfaces at the transformer stations of these factories was also performed using cotton n-hexane wipes. Figure 4 presents a comparison of the levels of the PCBs in the analyzed wipe samples. Concentrations of PCBs are expressed in nanograms on wiped surface (cm²). For purposes of comparison, the level of the PCBs in the wipe samples from the Zadar E.T.S. is also presented. High levels were observed in samples collected inside the TIZ E.T.S., probably due to leaking oil from the damaged

condensers. These results also explain the high concentrations of PCBs determined in the soil around the TIZ E.T.S. The specific wipe sampling positions at the TIZ E.T.S. are presented in Figure 2.

Conclusion

- The results of analyses of the PCBs in the soil of the Zadar area suggest contamination with PCBs at some locations.
- The levels of the PCBs in the soil surrounding the investigated TIZ are alarming (even around 1000 mg/kg) and a pollution problem with PCBs exists.
- Samples taken from the concrete surfaces in the TIZ E.T.S. using n-hexane cotton wipes confirm the pollution of this object.
- The levels of PCBs in the soil at certain localities in the city of Zadar (Donat Park, the Adria factory and the Zadar weather station) are not significantly different from the reference level at Zavižan Peak on Mt. Velebit. However, elevated concentrations of PCBs were found in soil samples from the ruins of the BAGAT factory and the scrap metal dump (ranging from 3 to 6 mg/kg of the total PCBs).
- In soil samples from the waste dump at the port of Gaženice, the level of the PCBs found is as high as 1 mg/kg. In this locality, hundreds of truckloads of various building wastes have been dumped and there is a possibility that the waste is polluted with PCBs. Therefore, a more systematic analysis of the contamination of this area with PCBs should be performed by tracking their potential penetration towards the sea sediment around the port of Gaženice.

Acknowledgements

The authors wish to express their gratitude for financial support from the Ministry of Science, Technology and Sports of the Republic Croatia and the European Commission. This project and presentation have been carried out as part of the contract ICA2- CT-2002-10007 (APOPSBAL project) between the European Commission and the Ruđer Bošković Institute, Zagreb, Croatia.

References

1. Picer M., Picer N. (2003) Hazards posed by petroleum oil and some chlorinated hydrocarbons to aquatic ecosystem in Croatian karst during the 1991–1995 war in Croatia, *Periodicum Biologorum* 105 (3): 345–354.
2. Picer M. (2000) DDTs and PCBs in the Adriatic sea, *Croatica Chemica Acta* 73: 123–186.
3. Picer M. and Ahel M. (1978) Separation of polychlorinated biphenyls from DDT and its analogues on a miniature silica gel column, *J. Chromatogr.* 150: 119–127.
4. Picer M., Picer N., Hodak Kobasić V. (2003) PCB levels in soil inside electrotransformer station 110/35 KV in Zadar, Hunt G. and Clement R.: *Environmental levels, Emerging POPs, Site Assessment, TRC Environmental, USA, Boston USA Dioxin 2003, Organohalogen compounds* 62: 472– 475.
5. Picer M., Picer N., Holoubek I., Klanova J., Hodak Kobasić V. (2004) Chlorinate hydrocarbons in the atmosphere and surface soil in the areas of the city Zadar and Mt. Velebit-Croatia, *Fresenius Environ. Bull.* 13(8):712–718.