

## Pollution of river sediments in Bosnia and Herzegovina and Kosovo with polychlorinated biphenyls

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### Introduction

Commercial PCB mixtures have been used in many industrial applications, especially in capacitors, transformers, and other electrical equipment. After they are released into the environment. PCBs tend to adsorb to organic soils and sediments. Throughout the passed war, areas of Bosnia and Herzegovina and Kosovo were endangered with the formation of dangerous wastes<sup>1</sup>. There are strong indications that various organic pollutants have entered the environment. Within the framework of the international project APOPSBAL, partially financed from the European Commission, the investigation of the pollution of river sediments with the PCBs has been carried out in areas of Bosnia and Herzegovina and Kosovo. Co-workers from Geological survey Sarajevo and Faculty of science Pristina have suggested the sampling locations with indications for the spilling of these very dangerous and stable organic pollutants into the environment<sup>2</sup>.

### Methodology

#### *Sampling locations*

Sediment samples were collected using a grab sampler. Sampling in Bosnia and Herzegovina was performed during two different periods, in 2003 and 2004, and in Kosovo in 2003. The sampling areas are shown in Figure 1.

During the first sampling campaign in Bosnia and Herzegovina, from September to December 2003, 27 sediment samples were collected around the cities of Bihac, Tesanj, Tuzla, Zenica, Sarajevo and Mostar. Second campaign was carried out in June 2004, after the first results of the PCB analysis. 33 samples were taken then.

Only one small sampling campaign was performed in Kosovo during 2003. Seven sediments from rivers Sitnica and Ibar were taken for the PCB analysis and one sample of the mud from the waste water in the TEPP Kosovo B.



**Figure 1.** Maps showing sampling areas in Bosnia and Herzegovina and Kosovo

*Analysis of PCBs*

Analyses of the PCBs in sediments collected in 2003 were performed at the Rudjer Boskovic Institute, Zagreb (IRB) and in those collected in 2004 at the Environmental Protection Institute, Maribor (EPI). Air-dried sediment samples were extracted after being sifted through 0.063 mm sieves using an ASE 200 extractor with a mixture of solvents acetone and n-hexane (1:1 v/v). The analytical method used for the analysis of the extracts included filtration through a column of Na<sub>2</sub>SO<sub>4</sub> 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 <sup>3,4</sup>.

**Results and discussion**

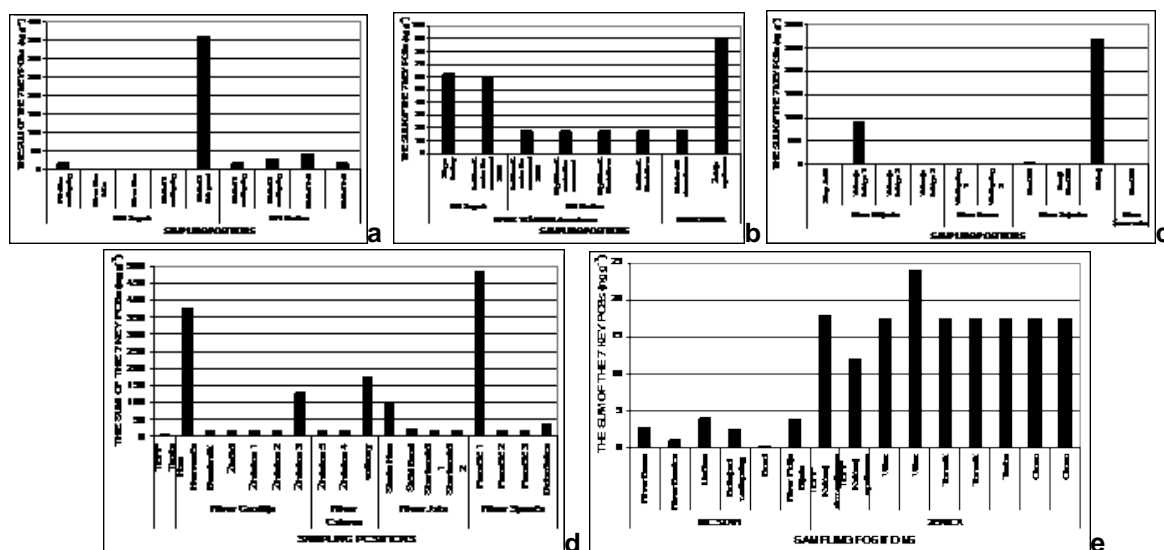
The observed levels of the sum of the 7 key PCBs (IUPAC No: PCB28, PCB52, PCB101, PCB118, PCB138, PCB153, PCB180) ranged widely, from less than 0.35 (below sensitivity of the method) to 2691 ng g<sup>-1</sup> d.w. (ppb). In Table 1 are presented minimal and maximal levels, as well as the geometrical means for levels of the sum of the 7 key PCBs obtained during the investigation of river sediment samples collected in Bosnia and Herzegovina in 2003 and 2004.

**Table 1.** Levels 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 sediment samples from Bosnia and Herzegovina collected 2003 and 2004

| SAMPLING AREA | SAMPLING LOCATIONS   | Number of samples | The sum of the 7 key PCBs (ng g <sup>-1</sup> ) |               |                  |
|---------------|--|-------------------|---|---------------|------------------|
|               |  |                   | Minimum value                                   | Maximum value | Geom. Mean value |
| BIHAC         | Klokot 1 and 2, Privilica, river Una                         | 9                 | < 0.35  | 361           | 9.5              |
| TESANJ        | Rivers: Tesanjka, Usora                                      | 8                 | 17.50   | 90            | 29.3             |
| TUZLA         | Rivers: Gostilja, Oskova, Jala, Spreca; Tuzla town           | 18                | 6.05  | 483           | 34.7             |
| SARAJEVO      | Rivers: Miljacka, Zuvovnica, Zujevina, Bosna                 | 10                | < 0.35  | 2691          | 27.9             |
| MOSTAR        | Rivers: Buna, Bunica, Polje Bijela; Borci, Livcina, Bosnjaci | 6                 | < 0.35  | 4             | 1.9              |
| ZENICA        | Rivers: Lasva, Grovnica, Biostica, Krivaja; Bosna            | 9                 | 12.06   | 24            | 17.4             |

For a better review of the real situation PCB levels from the 6 different areas in Bosnia and Herzegovina are presented in Figure 2. In a few locations in Bosnia and Herzegovina exceptionally high levels of the 7 key PCBs are determined: river Miljacka 929 ppb and river Zujevina 2691 ppb in the Sarajevo area; the fish pond Klokot 2 near Bihac 361 ppb; in rivers of the Tuzla area: Gostilja (Han Nevrenca) 377 ppb and Spreca (Puracic) 483 ppb. Some other samples also showed the significant PCB content: rivers Oskova (estuary) 176 ppb, Jala (Simin Han) 100 ppb and Gostilja (Zivinice) 129 ppb near Tuzla; 60 and 62 ppb river Tešanjka and 90 ppb in the sample from river Usora in the Tešanj area. High concentrations were found in the samples close to the industrialized areas. The most probable origin of these contaminations is vicinity to the spots where the oil leaking from the damaged capacitors was observed, vicinity of coal mines, places of waste water spilling over, and also damaged military relays.

The other sediment samples do not show significant PCB levels.

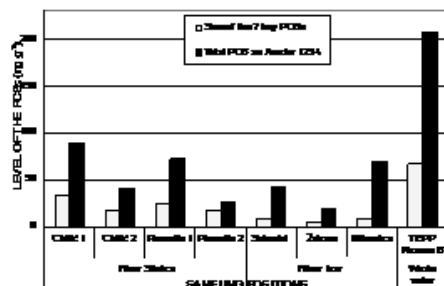


**Figure 2.** Levels of the sum of the 7 key PCBs in the river sediment samples from: a) the Bihac area; b) the Tesanj area; c) the Sarajevo area; d) the Tuzla area and e) the Mostar and Zenica areas

All these rivers belong to Black sea divide area. Sediments collected in 2004 are conditioned by different hydrologic and hydrogeological circumstances, which were completely various related to those conditions in 2003. We must stress that the reasons of higher concentrations of the PCBs in these sediments are not definitive and exact. It is possible that different levels of the PCBs are stipulated by hydrodynamic conditions of movements of waters, regime of precipitation of sediments, their size and characteristics of grains, age and the speed of creating, the distance from source of pollution and in which conditions of aquatic water systems does happen the precipitation, migration and transportation of PCBs.

It would be necessary to carry out adequate investigations, to determine geological and hydrogeological characteristics of a cover and a bedrock, filtration properties of cover and bedrock, hydrogeological functions, hydraulic mechanism of movement of ground and surface waters, depth to groundwater, thickness of water horizon, drainage area, residence time of waters, velocities of ground and surface waters, to perform boring of drill-holes and taking samples of sediments through the depth of terrain and in this way to contour the dissemination of PCBs as vertically and also horizontally in the space.

Research of the PCB pollution in areas of Kosovo has not been extensive as in Bosnia and Herzegovina. Only 8 samples were analysed. Results of the PCB analysis in these sediment samples are presented on Figure 3. Obtained range of total PCBs as the sum of the 7 key PCBs is from 5 to 67 ppb. The total PCB levels are also presented as Aroclor 1254 equivalents. Samples taken in river Sitnica, Obilic 1 (89 ppb) and Plemetin 1 (72 ppb), and sediment from river Ibar in the Mitrovica town (70 ppb) have increased levels of total PCBs, while the sample from TEPP has the significant level of total PCBs, 208 ppb.



**Figure 3.** Levels of total of PCBs as Aroclor 1254 equivalents and the sum of the 7 key PCBs in the river sediment samples collected in Kosovo in 2003

## Conclusion

This study has provided data on the levels of selected PCBs in the river sediments of Bosnia and Herzegovina and Kosovo.

From the obtained results of the PCB analysis we can conclude the followings:

- Great differences are noticed in the sum of the 7 key PCBs in sediments from Bosnia and Herzegovina, from less than 0.35 to 2691 ppb
- High levels of the PCBs were found in sediment samples collected in the rivers: Zujevina (2691 ppb), Miljacka (929 ppb), Spreca (483 ppb) and Gostilja (377 ppb); also in fishpond Klokot 2 (361 ppb)
- Significant levels of PCBs (60-180 ppb) were also found in a few other samples in Bosnia and Herzegovina
- Sediments in the Mostar area do not have increased levels of the sum of the 7 key PCBs (less than 5 ppb)
- In 3 sediment samples from rivers Ibar and Sitnica in Kosovo increased levels of total PCBs is found. The sample from TEPP Kosovo B has significant level of total PCBs (208 ppb).

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## References

1. Picer M. and Hodak Kobasić V. (2004) *Croatian Water Management* XIV, No. 144: 22-27. (in Croatian)
  2. Picer N., Miošić N., Hodak-Kobasić V., Kovač T., Čalić, V. and Hrvatović H. (2004) *Organohalogen compounds* 66: 1313-1320.
  3. Picer M. and Picer N. (2003) *Periodicum Biologorum* 105 (3): 345-354.
  4. Picer M. (2000) *Croatica Chemica Acta* 73: 123-186.
- Picer, M. and Picer, N. (1993) *Water, Air and Soil Pollut.* 68: 435-447.