

## POLYCYCLIC AROMATIC HYDROCARBONS IN URBAN AND RURAL SOILS OF VOJVODINA

**Snežana Kravić, Zorica Stojanović, Ana Đurović, Zvonimir Suturović, Tanja Brezo-Borjan**

*University of Novi Sad, Faculty of Technology Novi Sad, Bulevar cara Lazara 1, 21000 Novi Sad, Serbia  
e-mail: sne@uns.ac.rs*

### **Abstract**

Contents of 16 polycyclic aromatic hydrocarbons (PAHs) were determined in soil samples from urban and rural areas in Vojvodina Province, Serbia. Surface soil samples were collected from 15 different locations. The samples were Soxhlet extracted, cleaned-up and analyzed using gas chromatography-mass spectrometry in the selected ion monitoring mode. The total PAHs concentrations were in the range of 0.398-1.115 mg/kg for soils from urban areas, and 0.434-0.729 mg/kg for rural soils. Comparison with the relevant maximum allowed contents proposed by the Serbian legislative indicated that the concentration of PAHs in investigated soil samples is below the levels that would require the implementation of relevant soil remediation measures.

### **Introduction**

Polycyclic aromatic hydrocarbons (PAHs) are a group of stable organic compounds consisting of two or more fused aromatic rings. PAHs originate from natural processes such as forest fires, volcanic eruptions, and diagenesis, and also from anthropogenic sources such as vehicle emissions, coal and fossil fuel power generation, petroleum refining, industrial processing, chemical manufacturing, oil spills, and coal tars [1]. Although hundreds of PAHs exist in the environment, only 16 have been selected by the US Environmental Protection Agency (US EPA) as priority pollutants due to their potential mutagenic, carcinogenic, and teratogenic effects on human health [2,3].

Due to widespread sources, PAHs are present in all environmental matrices, including soil, water and air. Soil is the most important sink for PAHs in the environment [4,5]. Due to their persistence and hydrophobicity, PAHs accumulate in the soil. It has been estimated that approximately 90% of total residues remain in the soil [6]. These harmful pollutants accumulated in soil can be carried into surface and ground water through precipitation, emitted into atmosphere by vaporization, and transported into crops from polluted soil and air via root and leaf adsorption [7], consequently resulting in direct or indirect exposure to humans. Considering the harmful effects of PAHs, it is important to monitor their concentration in the environment, especially in soil which is the most potent reservoir of PAHs.

The principal objective of the present study was to determine the concentration levels of PAHs in soil from urban and rural areas in Vojvodina Province.

### **Experimental**

#### *Soil sampling, extraction and purification*

Surface soil samples were collected from 15 different sites in Vojvodina Province (Serbia) located in urban (8 sites) and rural (7 sites) areas. Samples were air-dried at room temperature, sieved to 100-mesh size particles and stored in amber glass containers at  $-4^{\circ}\text{C}$  until analysis. A 10 g soil sample was Soxhlet extracted for 24 h with 200 ml methylene chloride. The extracts were concentrated to 0.5 ml by rotary vacuum evaporation and then 2

ml cyclohexane was added. The extracts were cleaned up using silica gel column chromatography (250 mm × 10 mm ID). The glass chromatography column was packed with glass wool, 10 g silica gel (100/200 mesh) and 2 cm anhydrous sodium sulfate. The column was rinsed with pentane (40 mL) before use. After adding the sample extract, the column was sequentially eluted with 25 ml of pentane and 25 ml of methylene chloride/pentane (2/3, v/v). The second eluate was vacuum-evaporated to near dryness and re-dissolved with acetonitrile (1 ml).

#### Gas chromatography-mass spectrometry

PAHs were analyzed using a gas chromatograph with mass selective detector (GC-MS, Hewlett-Packard 5890A-5971A) equipped with an ULTRA 1 column (25 m × 0.20 mm i.d., 0.33 µm film thickness), using helium as the carrier gas. The following temperature program was used: the initial temperature of 80°C was held for 5 min, increased at rate of 5°C/min to 250°C and held for 10 min, and then increased at the rate of 20°C/min to 280°C and held at this temperature for 15 min. The injection port was set at 290 °C. A 1 µl aliquot of sample extract was injected in split mode (split ratio 1: 20). The mass spectrometer was operated in the electron impact ionization mode and data were acquired using the selective ion monitoring (SIM) mode. Identification of PAHs was based on the selected ions and the relative retention time between samples and the standard solution containing individual PAHs. Quantification was done using the internal standard method. Five deuterium-labeled PAHs were used as internal standards: naphthalene-*d8*, acenaphthene-*d10*, phenanthrene-*d10*, chrysene-*d12*, and perylene-*d12*. The SIM program used to determine PAHs in soil is indicated in Table 1. All reported concentration values of PAHs are expressed on a dry weight basis of soil determined by drying the soil for 24 h at 100°C.

Table 1. SIM program used to determine PAHs

Group	PAHs	Time (min)	m/z	Dwell time (ms)
1	naphthalene, naphthalene - <i>d8</i>	12.00	136, 128	50
2	acenaphthylene	19.00	152	50
3	acenaphthene - <i>d10</i> , acenaphthene	21.50	164,154	50
4	fluorene	23.50	166	50
5	phenanthrene - <i>d10</i> , phenanthrene, anthracene	28.00	188,178	50
6	fluoranthene, pyrene	34.00	202	50
7	chrysene - <i>d12</i> , benzo[a]anthracene, chrysene	41.00	240, 228	50
8	benzo[b]fluoranthrene, benzo[k]fluoranthrene, benzo[a]pyrene, perylene- <i>d12</i>	50.00	252, 264	50
9	indeno[1,2,3-cd]pyrene, dibenzo[ah]anthracene, benzo[ghi]perylene	59.00	276, 278	50

#### Results and discussion

The levels of the individual and the sum of 16 US EPA priority PAHs ( $\Sigma 16\text{PAHs}$ ) and seven carcinogenic PAHs ( $\Sigma 7\text{cPAHs}=\text{BaA}+\text{Chr}+\text{BbF}+\text{BkF}+\text{BaP}+\text{IcdP}+\text{DahA}$ ) determined in the soil samples, expressed as mg/kg dry weight, are given in Table 2.

Table 2. Concentrations of PAHs in soils from urban and rural areas in Vojvodina (mg/kg dry weight)

Compound/Abbreviation	Urban areas				Rural areas			
	Min	Max	Mean	SD	Min	Max	Mean	SD
Naphthalene/Nap	nd	0.101	0.045	0.029	0.005	0.054	0.022	0.017
Acenaphthylene/Acl	nd	0.017	0.017	0.002	nd	0.012	0.012	0.001
Acenaphthene/Acn	nd				nd			
Fluorene/Flu	nd	0.086	0.039	0.031	nd	0.031	0.021	0.009
Phenanthrene/Phe	0.046	0.183	0.090	0.048	0.004	0.132	0.069	0.042
Anthracene/Ant	nd	0.057	0.026	0.017	nd	0.102	0.054	0.046
Fluoranthene/Flt	0.060	0.184	0.136	0.047	0.056	0.142	0.097	0.038
Pyrene/Pyr	0.055	0.168	0.118	0.039	0.048	0.122	0.079	0.029
Benz[a]anthracene/BaA	0.046	0.174	0.105	0.057	0.015	0.098	0.058	0.032
Chrysene/Chr	nd	0.090	0.061	0.034	nd	0.052	0.031	0.020
Benzo[b]fluoranthene/BbF	0.026	0.191	0.112	0.058	0.045	0.165	0.096	0.050
Benzo[k]fluoranthene/BkF	nd	0.082	0.032	0.027	nd	0.032	0.025	0.010
Benzo[a]pyrene/BaP	0.046	0.142	0.073	0.029	0.049	0.091	0.070	0.014
Indeno[1,2,3-cd]pyrene/IcdP	nd	0.028	0.020	0.012	nd	0.041	0.036	0.007
Dibenz[a,h]anthracene/DahA	nd	0.042	0.028	0.012	0.012	0.044	0.022	0.012
Benzo[g,h,i]perylene/BghiP	nd	0.084	0.048	0.030	0.025	0.073	0.054	0.016
$\Sigma_{16}$ PAHs	0.398	1.115	0.822	0.276	0.434	0.729	0.642	0.116
$\Sigma_{7c}$ PAHs	0.140	0.549	0.361	0.146	0.157	0.372	0.280	0.077

SD - standard deviation; nd - not detected (below the limit of detection)

PAHs were detected in all analyzed soil samples. The content of  $\Sigma_{16}$ PAHs was in the range of 0.398-1.115 mg/kg for urban soils, and 0.434-0.729 mg/kg for rural soils. The most abundant PAHs found in urban soils were fluoranthene, pyrene, benzo[b]fluoranthrene and benzo[a]anthracene with mean concentrations of 0.136, 0.118, 0.112 and 0.105 mg/kg, respectively. In rural soils, the most frequently detected PAHs were fluoranthene, benzo[b]fluoranthrene, pyrene and benzo[a]pyrene with mean concentrations of 0.097, 0.096, 0.079 and 0.070 mg/kg, respectively.

Seven of the 16 PAH compounds prioritized by the EPA were determined as possible carcinogenic compounds for humans by the International Agency for Research on Cancer (IARC) [8]. The total levels of these compounds ( $\Sigma_{7c}$ PAHs) varied between 0.140 and 0.549 mg/kg for urban soils and 0.157-0.372 mg/kg for rural soils. The contribution of the seven carcinogenic PAHs to the total PAHs was similar for urban and rural soils, and it was about 43%.

The ring distributions of the PAHs that were determined in soil samples are given in Figure 1. In urban soils, the rate of 4-ring PAHs ranged between 38 and 53%, with average rate of 46%, followed by 6-ring, 3-ring and 5-ring compounds with average rate of 18, 17 and 15%, respectively. Similar ring distributions of PAHs were obtained for rural soils. The contribution of 4-ring PAHs varied between 28 and 50% (mean value was 38%), followed by 6-ring, 3-ring and 5-ring compounds with average rate of 25, 17 and 16%, respectively. It is evident that high molecular weight (HMW) PAHs with 4 to 6 rings were dominated. The mean percentage concentration of HMW PAHs was 79%, which correlated to those found in the literature [1, 4].

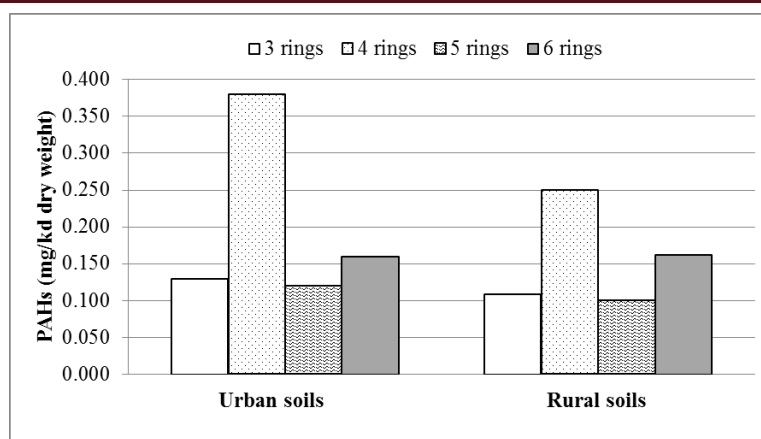


Figure 1. Ring distribution of PAHs in urban and rural soil from Vojvodina

Serbian law has no limitation for the maximum level of individual PAH compound, but the maximum allowed concentration (MAC) and remediation concentration (RM) for sum of 10 PAHs ( $\Sigma_{10}\text{PAHs} = \text{Ant} + \text{BaA} + \text{BkF} + \text{BaP} + \text{Chr} + \text{Phe} + \text{Flt} + \text{IcdP} + \text{Nap} + \text{BghiP}$ ) are defined. MACs are defined as the maximum values at which functional properties of the soil are still fully achieved and indicate level at which a sustainable soil quality is reached, while RM represent values at which basic functions of land are threatened or seriously disrupted, requiring remediation and other measures [4, 9]. According to the Serbian national limits for PAHs in soil [9] defined MAC and RM values for soil samples with organic matter less than 30% are 1 and 40 mg/kg, respectively. The concentration of  $\Sigma_{10}$  PAHs for all samples was below the Serbian MAC, indicating no significant contamination. According to the obtained results soil from urban and rural areas of Vojvodina could be classified as suitable as residential soils.

### Conclusion

Soil samples collected from urban and rural areas of Vojvodina were analyzed for pollution level of sixteen PAHs from the US EPA priority list. PAHs were detected in all samples with average concentrations of 0.822 mg/kg for urban soils, and 0.642 mg/kg for rural soils. The high molecular weight PAHs were predominant compounds in all samples. The concentration of  $\Sigma_{10}\text{PAHs}$  was lower than maximum allowable limit set by the Serbian legislation, indicating no significant contamination of soil.

### Acknowledgements

The present work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, under the Projects No. III 46009.

### References

- [1] C. Wang, S. Wu, S. Zhou, H. Wang, B. Li, H. Chen, Y. Yu, Y. Shi, *Sci. Total Environ.* 527–528 (2015) 375.
- [2] J.S. Cvetkovic, V.D. Mitic, V.P. Stankov Jovanovic, M.V. Dimitrijevic, G.M. Petrovic, S.D. Nikolic-Mandic, G.S. Stojanovic, *Anal. Methods* 8 (2016) 1711.
- [3] G. Karaca, *Arch. Environ. Contam. Toxicol.* 70 (2016) 406.
- [4] B. Škrbić, N. Đurišić-Mladenović, Đ. Tadić, J. Cvejanov, *Environ. Sci. Pollut. Res.* 24 (2017) 16148.
- [5] C.Q. Yin, X. Jiang, X.L. Yang, Y.R. Bian, F. Wang, *Chemosphere* 73 (2008) 389.
- [6] Y. Hu, J. Wen, D. Wang, X. Du, Y. Li, *Chem. Ecol.* 29 (2013) 476.

- [7] L. Wang, S. Zhang, L. Wang, W. Zhang, X. Shi, X. Lu, X. Li, X. Li, *Int. J. Environ. Res. Public Health* 15 (2018) 607.
- [8] International Agency for Research on Cancer, *IARC Monographs on the evaluation of carcinogenic risks to humans*, 92 (2010) Lyon, France.
- [9] *Official Gazette of the Republic of Serbia* 88/2010.