The 56th International October Conference on Mining and Metallurgy
22-25 October 2025, Bor Lake, Bor, Serbia
www.ioc.tfbor.bg.ac.rs

DOI: 10.5937/IOC25674P
Original scientific paper

ASSESMENT OF PAH AND PCB CONCENTRATIONS IN BOR RIVER BED SEDIMENTS AFFECTED BY MINING AND METALLURGY

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Abstract

The aim of this study was to investigate the presence of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in river bed sediment samples collected from the Bor River, an area strongly influenced by mining and metallurgical activities. The concentrations of PAHs and PCBs were determined using gas chromatography - mass spectrometry (GC-MS), which provides high sensitivity and reliability for the detection of such compounds. The results showed that the levels of PAHs and PCBs in the analyzed samples were below the limits of quantification. The results showed that, despite intensive mining and metallurgical activities in this area, there is no increase in the levels of these organic compounds in river sediments. The importance of this research lies in assessing the influence of mining and metallurgy on the environment and in evaluating the current ecological status of the Bor River.

Keywords*: PAHs, PCBs, River sediments, Bor River, GC-MS*

1. INTRODUCTION

In this study, the concentrations of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in river bed sediment samples from the Bor River were determined using Gas Chromatography – Mass Spectrometry (GC-MS). To date, a large number of studies have addressed how mining and metalurgy in the Bor region affect the contamination of water, air and soil with heavy metals and arsenic [1-3]. In the reviewed literature, no studies were found that address the pollution of river water and sediments with organic contaminants such as PAHs and PCBs. The Bor River, located in an area vulnerable to contamination, highlights the necessity of monitoring these organic compounds.

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds that are colorless, white or pale yellow in solid state. They can enter in environment by dispersing through air and water as a result of many human activities [4]. Sources of PAHs in environment are: natural sources – volcanic eruptions and biomass combustion, or anthropogenic sources – combustion of fossil fuels (oil, gas), traffic emissions, industrial processes (metallurgy, petroleum refining), and waste incineration [5]. When organic substances such as fossil fuels or biomass are exposed to high temperatures under oxygen-free or low-oxygen conditions, pyrogenic PAHs are formed [5].

Polychlorinated biphenyls (PCBs) are synthetic organic compounds that contain 1–10 atoms of chlorine covalently bound to a biphenyl molecule. PCBs are synthesized through the direct chlorination of biphenyl, using $FeCl_3$, as a catalyst. The reaction proceeds via a free radical mechanism, resulting in a mixture of biphenyls with different numbers of chlorine atoms [6]. PCBs can enter environment through industrial discharges, improper waste disposal and atmospheric deposition. PCBs can be absorbed via inhalation and, to a lesser extent, through dermal contact. PCBs are considered potent toxicants that have a negative impact on endocrine, reproductive and immune system [7,8].

Gas chromatography – mass spectrometry (GC–MS) is a powerful analytic technigue that combines the separation capabilities of gas chromatography (GC) with the detection and identification abilities of mass spectromety (MS). GC is used to separate complex mixture based on the volatility and interaction of analytes with the stationary phase of the column, while MS provides qualitative and quantitative data by ionizing the separated compounds and analyzing their mass – to – charge ratios [9]. Today, this technique is widely used for detection of trace organic pollutants such as PAHs and PCBs in environmental samples due to its high sensitivity, selectivity and accuracy [9].

The objective of this study is to evaluate the levels of PAHs and PCBs in sediment samples from the Bor River, as the scientific literature lacks data on such analyses, despite the existence of numerous studies reporting concentrations of metals and arsenic.

2. EXPERIMENTAL

The sampling sites are located downstream of the village of Slatina, before the confluence of the Bor River with Krivelj River. Sampling was carried out on April 16, 2024, with the folowing labels and coordinates: BS1 (44°01'43.5"N, 22°11'10.3"E); BS2 (44°01'43.9"N, 22°11'11.6"E); BS3 (44°01'43.2"N, 22°11'13.8"E). Untampered river sediment samples were air dried at room temperature for 24 hours. After drying, the samples were homogenized and 5 g of each sample was weighed out. In each sample 1 g of Na_2SO_4 was added to additionally dry the samples and improve extraction.

Samples were prepared for extraction using the following protocol. Speed extractor (E – 916) tube bottom was covered with a paper filter, followed by a metal filter, and then 2 g of diatomaceous earth. The tube was then filled halfway with quartz sand, then 5 g of previously prepared sample was added, followed by 100 µL of internal standard (mix of deuterated PAHs in concentration of 2 mg/mL), and topped off with more quartz sand and sealed with a paper filter. Blank sample was prepared in the same way, containing everything but the sample. Extraction was performed on the Speed extractor for 52 minutes, at 100 °C, 1 bar pressure. Extraction was performed twice, each with 30 mL acetone:hexane 1:1 mixture. The acetone from the extract was then evaporated to 2–3 mL volume using a Buchi rotavapour (R – 215) at 945 mbar, 60 °C, 80 rpm. To each acetone extract, 10 mL of hexane was added, and then evaporated again at 556 mbar, 60 °C water bath, 80 rpm, also to 2–3 mL volumes. These samples were purified using chromatographic columns, packed with glass wool at the bottom, 2 g of silica gel, and 2 g of Na_2SO_4. Columns were pre-eluted with 20 mL of hexane, and then the sample was added. Elution was performed using 2x10 mL hexane, followed by 2x20 mL dichloromethane. Dichloromethane from purified samples was evaporated at 945 mbar, 60 °C water bath temperature, 80 rpm, also to 2–3 mL final volume. Hexane was added to each sample in volume of 10 mL and again evaporated under the same conditions (556 mbar, 60 °C water bath, 80 rpm) to final volume of 1 mL. The prepared samples were transferred to 2 mL vials (1 mL of sample in each) and were analyzed on Agilent 7890 B (GC) and Agilent 5977A (MSD).

3. RESULTS AND DISCUSSION

Table 1 presents the concentrations of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in three sediment samples collected from the Bor River (BS-1, BS-2, BS-3). The concentrations of all assessed PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene) and PCBs (PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153, and PCB 180) were below the limit of detection (LOD) of 0.0050 mg/kg for each individual compound. Since all measured values were below the detection limit, it can be concluded that these organic pollutants were either absent or present in concentrations below

0.0050 mg/kg. Given the environmental setting of the Bor River, this result is expected. The dominant pollution sources in the area are related to copper mining, flotation tailings, metallurgical processing, and smelting activities, which primarily release metals and arsenic, not organic compounds such as PAHs and PCBs.

Table 1. Concentration of PAHs and PCBs in river bed sediment samples from the Bor River

Parameter	Unit of measure	Sample label		
		BS-1	BS-2	BS-3
Polycyclic aromatic hydrocarbons (PAHs)				
Naphthalene	mg/kg	<0.0050	<0.0050	<0.0050
Acenaphthylene		<0.0050	<0.0050	<0.0050
Acenaphthene		<0.0050	<0.0050	<0.0050
Fluorene		<0.0050	<0.0050	<0.0050
Phenanthrene		<0.0050	<0.0050	<0.0050
Anthracene		<0.0050	<0.0050	<0.0050
Fluoranthene		<0.0050	<0.0050	<0.0050
Pyrene		<0.0050	<0.0050	<0.0050
Benzo(a)anthracene		<0.0050	<0.0050	<0.0050
Chrysene		<0.0050	<0.0050	<0.0050
Benzo(b,k)fluoranthene		<0.0050	<0.0050	<0.0050
Benzo(a)pyrene		<0.0050	<0.0050	<0.0050
Indeno (1,2,3,c,d)pyrene		<0.0050	<0.0050	<0.0050
Dibenzo(a,h)antrachene		<0.0050	<0.0050	<0.0050
Benzo(g,h,i)perylene		<0.0050	<0.0050	<0.0050
Total PAHs		<0.0750	<0.0750	<0.0750
Polychlorinated biphenyls (PCBs)				
PCB 28	mg/kg	<0.0050	<0.0050	<0.0050
PCB 52		<0.0050	<0.0050	<0.0050
PCB 101		<0.0050	<0.0050	<0.0050
PCB 118		<0.0050	<0.0050	<0.0050
PCB 138		<0.0050	<0.0050	<0.0050
PCB 153		<0.0050	<0.0050	<0.0050
PCB 180		<0.0050	<0.0050	<0.0050
Total PCBs		<0.0350	<0.0350	<0.0350

As discussed in the Introduction, PAHs are typically formed during combustion of organic matter from natural or anthropogenic sources [5], whereas PCBs are synthetic industrial chemicals produced through chlorination of biphenyl [6-8]. Since the Bor River catchment area lacks significant combustion-related or industrial PCB sources, their concentrations remain below the detection limits.

This is consistent with previous studies on environmental pollution in the Bor region. For instance, Petrović et al. [1] analyzed riparian soils affected by mining activities in Bor region and found extremely elevated copper concentrations, ranging from 188.71 mg/kg to 2,888.8 mg/kg. According to Đorđievski et al. [2], the copper concentration in riverbed sediments of the Bor River reached 14,100 mg/kg at a site situated close to the sampling location of the present study. For comparison, according to Serbian regulations, the maximum allowable concentration (MAC) for copper is 36 mg/kg, and the remediation value (RV) is 190 mg/kg [1]. These findings indicate severe soil contamination with copper, directly linked to mining and metallurgical emissions, while also explaining the absence of significant contamination from PAHs and PCBs in the studied sediments.

4. CONCLUSION

This study assessed the levels of PAHs and PCBs in sediment samples from the Bor River using GC-MS analysis. All individual compounds and total concentrations were below the detection limit of 0.0050 mg/kg, indicating that these organic pollutants are either absent or present at negligible levels. The results highlight that, despite intensive mining and metallurgical activities in the Bor region, the dominant environmental burden arises from metals and arsenic, not organic contaminants. Consequently, monitoring efforts in this area should primarily focus on metal(loid) pollution, while periodic screening for organic pollutants remains relevant to confirm potential changes in contamination sources over time.

ACKNOWLEDGEMENTS

This work was funded by the Ministry of Science, Technological Development, and Innovation of the Republic of Serbia under contract no. 451-03-136/2025-03/200052 (Mining and Metallurgy Institute Bor).

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