XVI International Mineral Processing and Recycling Conference
28-30 May 2025, Belgrade, Serbia

DOI: 10.5937/IMPRC25435D Original research article

IMPROVEMENT OF BOR RIVER WATER QUALITY THROUGH TREATMENT AND RECIRCULATION OF MINING AND METALLURGICAL WASTEWATER

Stefan Đorđievski[1#], 0000-0003-1737-8766,
Dragana Adamović[1], 0000-0003-3683-4122,
Miloš Đukić[1], 0000-0002-3307-4669,
Ana Petrović[1], 0000-0002-9815-6884,
Jelena Petrović[1], 0000-0002-3749-5110,
Zoran Štirbanović[2], 0000-0001-7571-2844,
[1]Mining and Metallurgy Institute Bor, Bor, Serbia
[2]University in Belgrade, Technical Faculty in Bor, Bor, Serbia

ABSTRACT – The Bor, Krivelj, and Bela Rivers, impacted by mining and metallurgy, have historically exhibited acidic conditions and high dissolved metal concentrations. This study evaluates the effects of wastewater treatment and smelter reconstruction in 2022 on water quality. The pH of the Bor River increased from 2.37 to neutral in mid-2022, leading to a sharp decrease in dissolved Cu and As concentrations. However, resuspension of contaminated sediment increased particulate form of Cu in water. The results showed significant water quality improvement due to environmental investments.

Keywords: Mining, Metallurgy, Wastewater, River, Monitoring.

INTRODUCTION

The Bor and Krivelj Rivers have been receiving wastewater from the mining and metallurgical facilities operating in the Municipality of Bor in Eastern Serbia. These two rivers merge to form the Bela River, a tributary of the Timok River, which ultimately flows into the transboundary Danube River, affecting Bulgaria and Romania as well.

The oldest recorded information about the quality of Bor River dates back to 1931, when its acidity downstream from the mine and near the village of Slatina was 171 and 105 mg$CaCO_3$/L, respectively [1]. The pH value measured close to these locations in 1935 were 4.5 and 5.7, respectively, indicating the acidic signature as well [2]. More recent measurements from 2011 and 2015 also indicated acidic pH values in the water of Bor River before merging with Krivelj River (4.8 and 4.2, respectively) [3,4]. Besides acidic pH value, high concentrations of sulfates, Cu, As, Mn, and other elements were measured in these rivers, indicating the influence of copper mining and smelting [3,4].

In 2022, the reconstruction of copper smelter in Bor included building wastewater treatment plant that would stop the release of acidic metallurgical wastewater into the

corresponding author: stefan.djordjievski@irmbor.co.rs

Bor River [5]. Additional investments in environmental protection were made, aiming to achieve measurable improvements in the state of the environment [6].

Preliminary research has confirmed that the water quality of Bor, Krivelj, and Bela Rivers has improved [7,8], however, additional research is needed to understand the changes resulted from the innovations in treatment of wastewater from mining and metallurgy operations. This paper aims to give contribution in evaluating the effects of the new wastewater treatment plant and other recent investments in environmental protection on the quality of water in Bor, Krivelj, and Bela Rivers impacted by copper mining and smelting in Eastern Serbia.

EXPERIMENTAL

Water samples from the Bor, Krivelj, and Bela Rivers were collected monthly from January 2022 to February 2025. The sampling locations for the Bor River (44.029342, 22.208157) and Krivelj River (44.030524, 22.207850) were about 50 m upstream of their confluence, while the sampling location for the Bela River (44.030729, 22.210704) was about 200 m downstream of the confluence. The pH and electrical conductivity (EC) were measured in the field. Samples were filtered in the laboratory to remove particulate matter, and the filtrate was analyzed for dissolved sulfates, Cu, As, and Mn.

To investigate the partitioning of Cu, As, and Mn between particulate and dissolved forms, both filtered and unfiltered water samples from the Bor, Krivelj, and Bela Rivers were collected on December 18, 2023, and the pH was measured in the field. The concentrations of these elements in particulate form were calculated by subtracting their concentrations in the filtrate from those in the unfiltered samples.

Sulfates were determined in the filtrate by developing turbidity with barium chloride, which was measured using a WTW Turb 550 IR turbidimeter. The concentrations of Cu, As, and Mn were determined using an ICP-MS Perkin Elmer NexION 1000.

A sediment sample was collected from the Bor River riverbed at a location approximately 2 km upstream of its confluence with the Krivelj River (44.028667, 22.187167). The sample was dried at 40°C, sieved to pass a 2 mm sieve, and milled in a ring mill. The sample was digested using a microwave system (ETHOS UP) and analyzed with an ICP-MS Agilent 7700 according to the standard method EPA 6020A.

RESULTS AND DISCUSSION

The pH value of Bor River from January 2022 to April 2022 was very acidic, with values below 3, and minimum measured value 2.37 (Table 1 and Figure 1). In May and June 2022, the pH value slightly increased to 3.52 and 3.25, respectively. However, in July 2022, a drastic increase in pH value was observed, reaching the value of 7.24. From July 2022 until February 2025, which is the final month of the monitoring period, the pH value was constantly neutral, never going below 7.00, with the maximum value of 9.04.

The pH value of Krivelj River was acidic only in January and February 2022 (3.49 and 3.20, respectively), after which it increased and stayed neutral until the end of the monitoring period, with the maximum value of 8.28. The change of pH in Bela River followed the similar pattern of Bor River, reflecting the significant influence of its water.

EC in the Bor and Bela Rivers was relatively higher from January to April 2022, peaking at 8676 and 2870 µS/cm, respectively. In contrast, from May 2022 to February 2025, EC levels in the Bor, Krivelj, and Bela Rivers remained relatively stable, with moderate fluctuations around their median values of 1347, 1585, and 1350 µS/cm, respectively.

Sulfate concentrations in the Bor, Krivelj, and Bela Rivers varied throughout the study period, reaching maximum values of 2954, 1700, and 2500 mg/L, respectively.

Copper and arsenic concentrations in the Bor and Bela Rivers exhibited similar temporal trends, with high values recorded from January to June 2022, followed by a sharp decline and stable conditions. However, arsenic decreased more rapidly, reaching near-background levels by April 2022, whereas copper remained elevated until June. This difference in removal dynamics is closely linked to pH variations, as shown in Figure 1. Until April 2022, the pH in the Bor and Bela Rivers remained below 3, preventing significant metal precipitation. In May, the pH rose above 3, facilitating iron(III) hydroxide [$Fe(OH)_3$] particle formation. Since arsenic readily adsorbs onto $Fe(OH)_3$, its removal occurred rapidly. In contrast, copper does not sorb as efficiently onto $Fe(OH)_3$ and remained in solution until the pH reached near-neutral conditions in July 2022. From mid-2022 to February 2025, both metals remained at low, stable concentrations, indicating that pH stabilization played a crucial role in long-term water quality improvement.

Although the pH remained stable from July 2022 onward, Mn concentrations in all three rivers did not decrease as drastically as those of Cu and As. This is because Mn remains in dissolved form across a wide pH range, and the transition from acidic to neutral conditions did not significantly affect its concentration.

Table 1 Minimum, median, and maximum values of parameters measured monthly in water from Bor, Krivelj, and Bela Rivers from January 2022 to February 2025

Parameter	unit of measure	Statistical value	Measured concentrations in river water		
			Bor River	Krivelj River	Bela River
pH	-	minimum	2.37	3.20	2.25
		median	7.63	7.80	7.63
		maximum	9.04	8.28	8.92
Electrical Conductivity (EC)	µS/cm	minimum	453	505	528
		median	1347	1585	1350
		maximum	8676	2870	8902
Sulfate (SO_4^{2-})	mg/L	minimum	373	338	337
		median	699	1144	805
		maximum	2954	1700	2500
Copper (Cu)	µg/L	minimum	6.2	11.0	6.8
		median	41.2	88.3	46.6
		maximum	74328	25231	42483
Arsenic (As)	µg/L	minimum	<2.1	<2.1	<2.1
		median	2.8	<2.1	2.9
		maximum	7541	1069	4440
Manganese (Mn)	µg/L	minimum	370	358	445
		median	2764	4292	3310
		maximum	23826	9583	10634

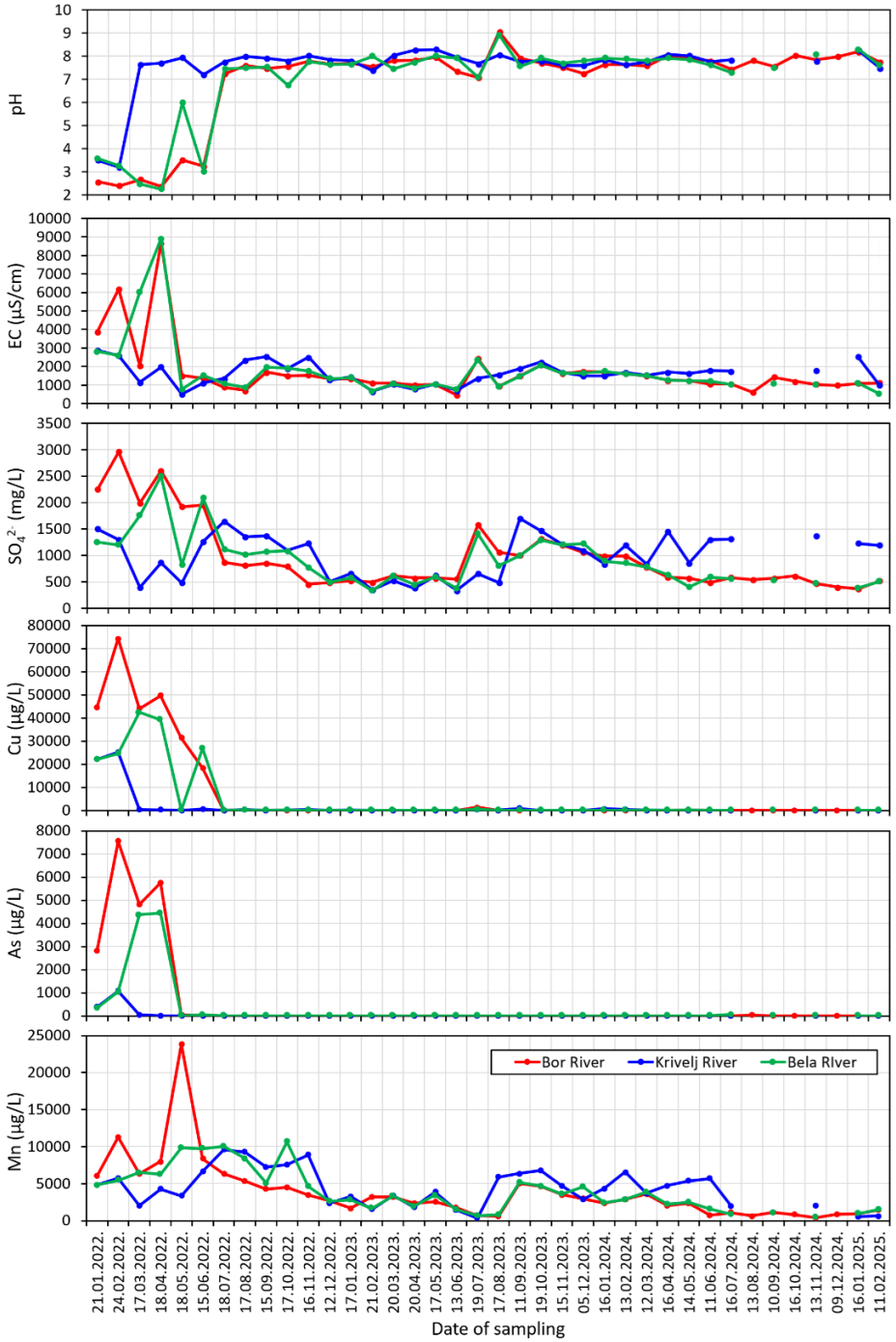

Figure 1 Diagrams showing the changes of pH and EC values, and the concentrations of SO_4^{2-}, Cu, As, and Mn in water of Bor, Krivelj, and Bela Rivers in the studied period

The concentrations of Cu, As, and Mn discussed here refer to their dissolved forms, as the measurements were conducted on filtered water samples. Although the dissolved concentrations of these elements significantly decreased from mid-2022 onward, the extent to which they persisted in particulate form remained unclear. To address this, concentrations of Cu, As, and Mn in particulate form were measured on December 18, 2023 (Table 2). At the time of sampling, the pH in the Bor, Krivelj, and Bela Rivers was approximately 8. The concentrations of copper in particulate form were 1444, 3725, and 1481 µg/L, respectively, indicating that approximately 98% of the total copper was present in particulate form. Although copper remained predominantly in particulate form after the pH stabilized at neutral values, its concentrations were about 50 times lower than the dissolved copper concentrations observed under acidic conditions. The concentration of arsenic in particulate form was negligible, similar to its dissolved form, while a significant portion of manganese remained in dissolved form.

The source of particulate copper remains unclear; however, one possible explanation is contamination from riverbed sediment. A sediment sample collected from the Bor River on April 16, 2024, approximately 2 km upstream from its confluence with the Krivelj River, contained 9770 mg/kg of copper. The resuspension of this sediment could contribute to elevated concentrations of particulate Cu in the water.

When the reconstruction of the smelter in Bor began in April 2022, metallurgical operations were discontinued, leading to the cessation of metallurgical wastewater generation. Since the newly built wastewater treatment facility within the metallurgical complex became operational in April 2023, the treated wastewater has been recirculated within the technological process. Stopping the direct discharge and implementing wastewater recirculation significantly improved the water quality of the Bor River by reducing free acid and dissolved metal and arsenic concentrations.

On the other hand, treated wastewater from the Čukaru Peki mine was discharged into the Bor River after treatment at the wastewater treatment facility. However, measurements confirmed that the pH of this treated wastewater remained consistently neutral or slightly alkaline, while parameters such as EC, SO_4^{2-}, Cu, As, and Mn were either lower or close to those in the Bor River before the discharge of this wastewater. This suggests that the treated wastewater from the Čukaru Peki mine did not negatively impact the water quality of Bor River.

Table 2 pH and the concentrations of particulate and dissolved forms of Cu, As, and Mn in water samples collected from Bor, Krivelj, and Bela Rivers on December 18, 2023

Parameter	Unit of measure	Form	Measured concentrations in river water		
			Bor River	Krivelj River	Bela River
pH	-	-	8.09	8.36	8.35
Copper (Cu)	µg/L	Particulate	1444	3725	1481
		Dissolved	28.7	69.6	27.3
Arsenic (As)	µg/L	Particulate	22.2	<2.1	8.6
		Dissolved	<2.1	<2.1	<2.1
Manganese (Mn)	µg/L	Particulate	2933	158	748
		Dissolved	407	5196	1685

CONCLUSION

This study confirms significant improvements in the water quality of the Bor, Krivelj, and Bela Rivers following the reconstruction of the Bor smelter and the implementation of a wastewater treatment and recirculation system. Prior to mid-2022, the Bor River exhibited extreme acidity and high dissolved metal concentrations, but a sharp pH increase in July 2022 led to sustained neutral conditions. As a result, arsenic levels rapidly declined after pH increased above 3, while copper remained in dissolved form until the pH reached neutrality. Manganese persisted in dissolved form due to its stability across a wide pH range. After mid-2022, copper was present in particulate form in river water, likely due to the resuspension of contaminated riverbed sediment. The release of treated wastewater from the Čukaru Peki mine did not negatively impact the water quality of Bor River. These findings highlight the effectiveness of recent environmental measures and emphasize the need for continued monitoring.

ACKNOWLEDGEMENT

This work was funded by the Ministry of Science, Technological Development, and Innovation of the Republic of Serbia under contracts no. 451-03-136/2025-03/200052 (Mining and Metallurgy Institute Bor) and 451-03-137/2025-03/200131 (Technical Faculty in Bor).

The data presented in this paper were obtained from test reports on surface water, wastewater, and sediment, which were issued by the Mining and Metallurgy Institute Bor for Serbia Zijin Mining d.o.o. Bor. The latter granted permission and provided support for their use in this study.

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