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SEASONAL AND HISTORICAL CHANGES IN COPPER AND IRON IN RIVER WATER OF THE BOR MINING AREA

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Abstract

This study investigates seasonal variations in copper (Cu) and iron (Fe) concentrations in river waters of the Bor mining area, Serbia, and compares current conditions with historical data. Water samples were collected during four hydrological periods to evaluate temporal changes and the effectiveness of recent environmental protection measures. The highest Cu and Fe concentrations were observed during the autumn low-flow period, while the lowest values occurred during the snowmelt season. Compared with historical records, Cu and Fe concentrations decreased by approximately 740- and 2650-fold, respectively. The results indicate a substantial improvement in river water quality.

***Keywords**: copper, iron, Bor mining area, water pollution*

1. INTRODUCTION

The Bor mining area in Eastern Serbia is one of the largest and longest-operating copper mining districts in Europe. More than a century of intensive mining and metallurgical activities has profoundly affected the surrounding river systems through the discharge of acid mine drainage and untreated metallurgical wastewater. Previous studies identified copper (Cu) and iron (Fe) as the principal indicators of mining-related contamination, with elevated concentrations detected in rivers downstream of mining facilities and evidence that mining-derived pollution extended as far as the Danube River, approximately 100 km downstream [1,2].

In recent years, environmental protection measures have been strengthened, and mine wastewater neutralization was introduced in 2022 prior to wastewater discharge into the river system. Although this measure is expected to reduce contaminant inputs, the transport, dilution, and distribution of dissolved metals remain strongly controlled by seasonal hydrological conditions, highlighting the need for continuous environmental monitoring. This study aimed to investigate the seasonal variability of Cu and Fe in river water of the Bor mining area and to compare river water quality before wastewater neutralization (2015) and after its implementation (2025, 2026). This comparison

provides a basis for evaluating the effectiveness of wastewater neutralization in reducing mining-related contamination and improving surface water quality.

2. EXPERIMENTAL

Twelve sampling locations (W1–W12) were selected within the study area (Figure 1). The monitoring network was designed to include both background rivers and streams directly affected by mining activities, enabling spatial comparison of water quality. Surface water samples were collected during four monitoring campaigns representing the summer (June–July 2025), autumn (October–November 2025), winter (January-February 2026), and Spring (April-May 2026) seasons. A total of 43 samples were collected, as sampling was not possible at locations W4 and W5 during summer, at W7 and W8 during autumn, and at W12 during spring. The sampling network included background streams (W1–W3), the Timok River (W4–W5), and rivers affected by mining activities (W6–W12).

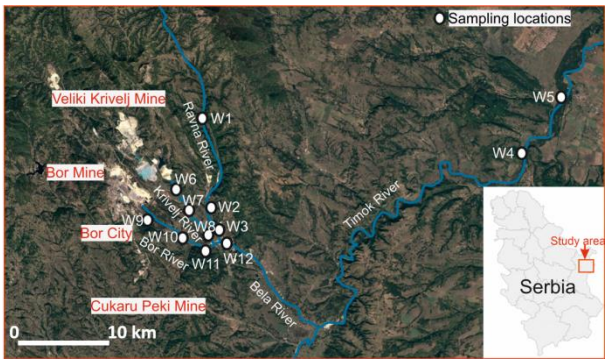


Figure 1. *Study area showing rivers, sampling locations, mines, and Bor City*

During the field survey, water samples were collected, preserved, and transported to the laboratory. Copper (Cu) and iron (Fe) concentrations were determined at the SRPS ISO/IEC 17025-accredited laboratory of the Mining and Metallurgy Institute Bor [3]. Acidified water samples were analyzed by ICP-MS (PerkinElmer NexION 1000) for Cu and Fe. Quality assurance included procedural blanks and certified reference materials, with analytical accuracy ±5%.

3. RESULTS AND DISCUSSION

3.1. Copper and iron concentrations in river water

The visual appearance of the sampled rivers reflected the influence of mining activities. Water from the Ravna River (W1–W3) and the Timok River (W4–W5), representing background conditions, remained clear and odorless during all sampling campaigns. The Krivelj River (W6–W8) was generally transparent, although orange precipitates were observed at the upstream site (W6), indicating iron precipitation. In contrast, the Bor River (W9–W11) showed persistent brownish-grey coloration, while the Bela River (W12) was consistently grey. These characteristics did not show noticeable seasonal variation.

Copper concentrations differed markedly between background and mining-affected rivers (Figure 2). Background streams generally contained low Cu concentrations, whereas substantially higher concentrations were recorded downstream of mining activities. The

highest Cu concentration (393 µg/L) was measured during the autumn low-flow period, indicating that reduced river discharge promotes the accumulation of dissolved copper.

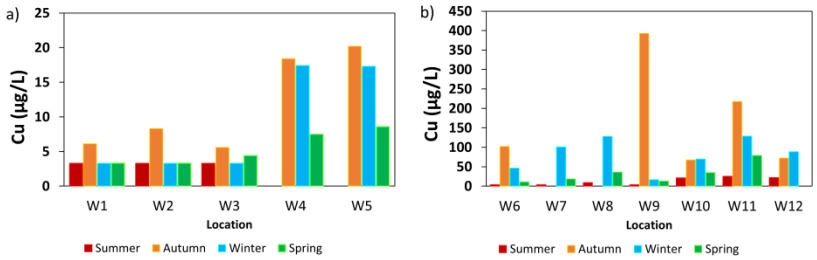


Figure 2. *Seasonal variation of copper concentrations in a) unpolluted river water, and b) polluted river water*

Iron concentrations exhibited lower spatial variability than copper (Figure 3). Most sampling sites contained less than 172 µg/L Fe; however, the highest concentration (417 µg/L) was recorded at location W6 during autumn. This peak coincided with the occurrence of orange ferric precipitates, confirming the influence of historical mining contamination.

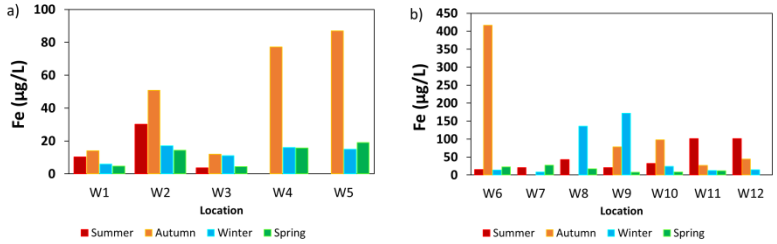


Figure 3. *Seasonal variation of iron concentrations in a) unpolluted river water, and b) polluted river water*

3.2. Seasonal variation of copper and iron in river water

Previous investigations and the present analytical results confirmed that copper and iron are among the main contaminants in the surface waters of the study area [4,5]. At sites unaffected by mining activities, both copper and iron exhibited clear seasonal variability, with the highest concentrations during the dry autumn period and the lowest in winter, reflecting the influence of river discharge on dilution. In mining-affected rivers, the same seasonal pattern was observed, although concentrations were considerably higher due to additional anthropogenic inputs. The largest seasonal fluctuations in iron were observed at location W6, where ferric precipitates indicate the influence of historical mining pollution. These findings demonstrate that seasonal contaminant dynamics are controlled by both natural hydrological processes and ongoing mining impacts, consistent with observations from other mining-affected catchments worldwide [6].

3.3. Effect of wastewater neutralization

Before the implementation of mine wastewater neutralization in 2022, untreated mining and metallurgical effluents were discharged directly into the Bor River, causing severe surface water contamination and acidic conditions [7]. To evaluate the effectiveness of the implemented measures, river water quality prior to wastewater neutralization (2015) was compared with recent results (2025, 2026) using a reduction analysis across seven monitoring locations (Table 1). The results showed a significant decrease in copper and iron

concentrations throughout the study area. Iron exhibited the greatest reduction, reaching a 100% decrease at one monitoring location (W12). At location W10, iron concentrations decreased by approximately 2,650-fold and copper by about 740-fold compared with 2015. These results demonstrate that wastewater neutralization has substantially reduced mining-related contamination and significantly improved the quality of surface waters in the Bor mining area.

Table 1. *Percentage reduction of copper and iron concentrations between 2015 and 2025–2026.*

	W10	W11	W7	W8	W12	W4	W5
Fe, Reduction (%)	99.96	99.97	99.98	99.90	100.00	97.58	64.42
Cu, Reduction (%)	99.87	99.51	99.73	99.57	99.77	90.81	86.40

4. CONCLUSION

The present study reassessed the impact of long-term mining activities on surface water quality in the Bor mining area by focusing on seasonal variations and temporal changes in copper and iron concentrations. Both elements showed clear seasonal variability, with the highest concentrations occurring during the autumn low-flow period, indicating the combined influence of hydrological conditions and mining-related contamination. Copper concentrations were consistently higher downstream of mining operations, while elevated iron concentrations were associated with historical mining pollution.

A comparison of the 2015 and 2025–2026 datasets showed a significant reduction in copper and iron concentrations following the implementation of mine wastewater neutralization. Iron concentrations decreased by up to 2,650-fold and copper by approximately 740-fold, confirming the effectiveness of the implemented environmental protection measures. These findings indicate a substantial improvement in surface water quality and highlight the importance of continuous monitoring for evaluating the long-term effectiveness of remediation measures in mining-affected river systems.

ACKNOWLEDGEMENTS

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