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MONITORING OF pH VALUE AND CONCENTRATION OF COPPERIN RIVERSDOWNSTREAM FROM BOR MINE IN PERIOD 2015-2021

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Abstract

This paper presents the results of the monitoring of pH value and concentrations of the dissolved and particulate forms of copper in the period from 2015 to 2021 in wastewaters that form Bor River, and in the water ofBor River, Krivelj River, Bela River, and Timok River which are under the influence of mining and metallurgical activities in Bor. Copper was mainly present in dissolved form in acidic river water, whereas in neutral and alkaline river water, copper was present relatively equally in both dissolved and particulate form. According to the pH values and copper concentrations, the water quality of Bor River and Bela River did not improve during the studied period. On the other hand, the water quality of Krivelj River significantly improved, possibly due to the changes caused by the construction of the new flotation tailing pond "VelikiKrivelj Zero Field". The quality of Bor River, Bela River, and TimokRiver was largely controlled by the temporal influxes of highly acidic and copper-rich wastewater from metallurgical facilities in Bor.

***Keywords**: Bor mine, copper, acid mine drainage, river water.*

1. INTRODUCTION

Copper mining and metallurgical activities in Bor, Serbia, have caused significant environmental pollution of river water.Several projects were conducted to evaluate the quality of river water downstream from Bor mining and metallurgical facilities, and the results are published in scientific journals or as technical reports as separate studies [1-8].Although the water quality wasmonitored by the Serbian Government at one point at Bela River and one point at Timok River from 1990 to 2014 [3,7], systematic monitoring of river water quality downstream from Bor mining and metallurgical facilities have not been conducted recently.

Processing of copper sulfide ores in Bor generates acidic copper-rich wastewaters.Therefore, the pH values and copper concentrations are the two most important parametersfor the quality assessment of the river waters. This paper presents the results of the monitoring of the pH values and concentrations of the dissolved and particulate forms of copper in the period from 2015 to 2021 in wastewaters that affectBor River and in the water ofBor River, Krivelj River, Bela River, and Timok River.

2. EXPERIMENTAL

Rivers that are the focus of this study are located in eastern Serbia (Figure 1). Bor River is formed by mixing of overburden drainage waters, municipal wastewater from Bor City, and metallurgical wastewater. Bela River is formed by the merging of Bor River and Krivelj River.Bela River flows into the Timok River, and Timok River flows into the Danube River.

Unfiltered and filtered water samples were collected in 50 mL polypropylene bottles. Filtration was carried out using cellulose acetate filters with pore size 0.2μmor 0.45μm to investigate the

distribution of dissolved and particulate forms of copper. Samples were acidified with nitric acid after the sampling so that the final concentration of nitric acid in samples was 5 %. The pH valueswere measured in the field using IM-23P pH meter, and copper concentrationswere measured using ICP-MS in several laboratories depending on the sampling season: Actlabs in Canada (for samples collected in August 2015), Akita University in Japan (September2016, February 2017, August 2017, and September 2019), and Mining and Metallurgy Institute Bor in Serbia (February 2020, August 2020, and September 2021).

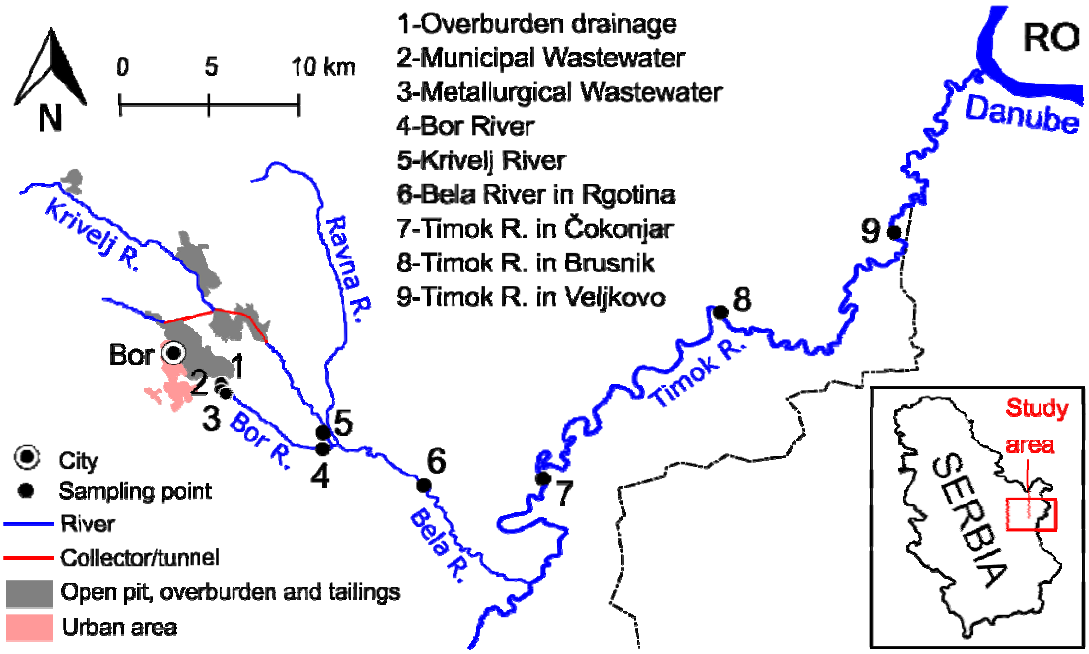

Figure 1Map of the study area with locations of the sampling points

3. RESULTS AND DISCUSSION

Metallurgical wastewater was the most acidic, with pH values ranging from 1.2 in August 2017 to 2.6in August 2015 (Figure 2). Overburden drainage had a moderately acidic signature, with pH values ranging from 4.4 in September 2021 to 6.0 in February 2020. Municipal wastewater was neutral to moderately alkaline during the studied period, with pH ranging from 6.8 in September 2021 to 8.6 in August 2015. The highest concentrationof copper was observed in metallurgical wastewater, reaching 275 mg/L in September 2020. Copper was always present in dissolved form in metallurgical wastewater during the studied period due to the very acidic pH value. In overburden drainage, copper was equally present, however relatively, in dissolved and particulate forms, while in municipal wastewater copper was dominantly present in particulate form, possibly due to the sorption of copper onto the suspended fecal material.

In Bor River, pH value was mostly acidic, and copper was present dominantly in dissolved form with relatively high concentration, except in August 2017 when the pH value was near-neutral, and copper was present in particulate form with 10 to 30 times lower concentration than usual. On the same sampling day in August 2017, the pH value of Bela River was acidic, and copper concentration reached 131 mg/L. The possible cause of these fluctuations is the temporal influx of a large quantity of highly acidic and copper-rich metallurgical wastewater.

The concentration of copper in the water of Krivelj River decreased gradually during the studied period from 31.5 mg/L in August 2015 to below 0.2 mg/L in February 2020 and onwards. The increase in pH value followed the decrease of copper concentration in Krivelj River.As the pH value increased, the form of copper in river water changed from dissolved to particulate. These results have shown that the water quality of Krivelj River improved over time.

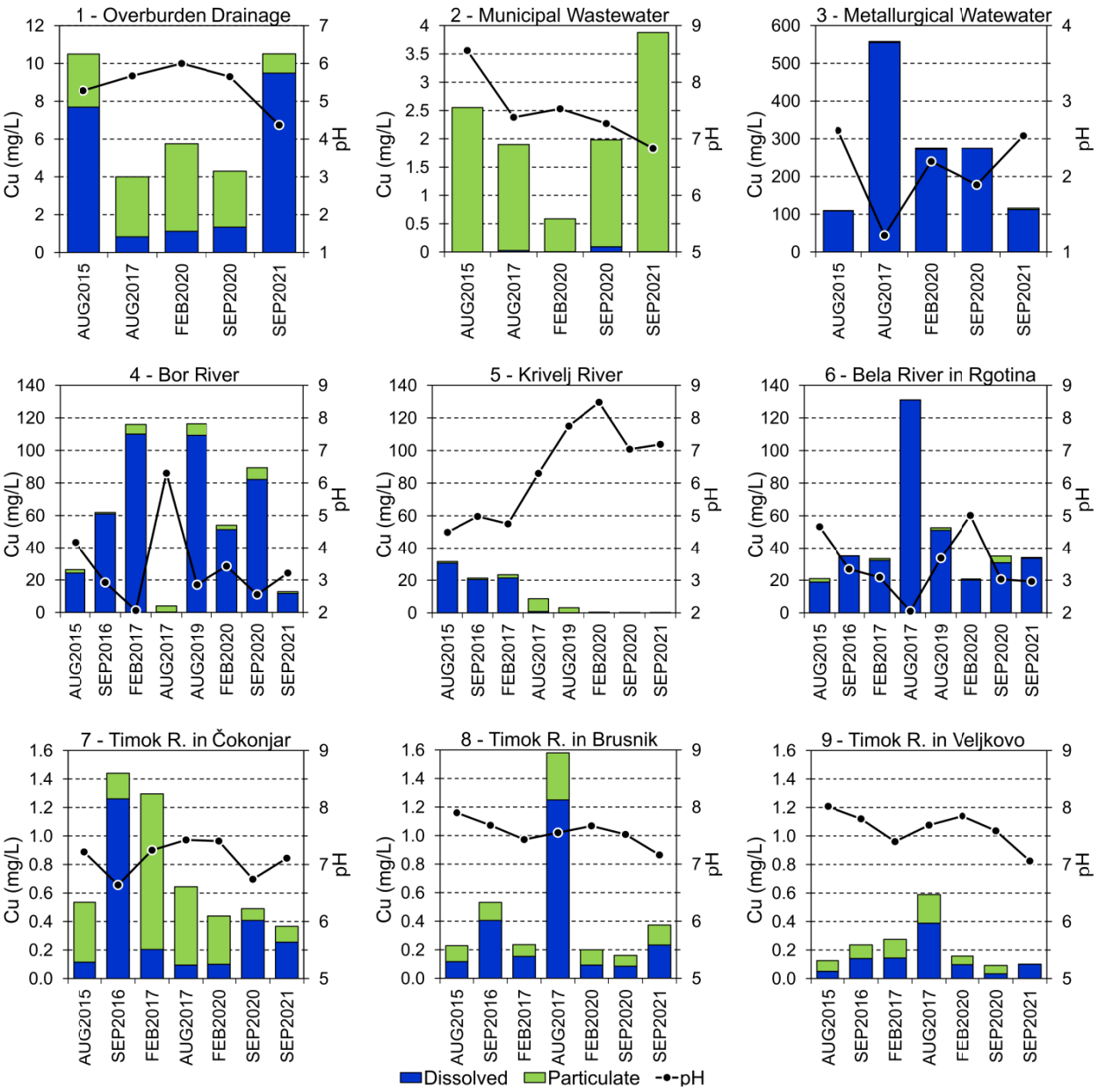

Figure 2Variations of pH and concentrations of dissolved and particulate forms of copper in wastewater and river water downstream from mining and metallurgical facilities in Bor in the period 2015-2021

Timok River, with its larger discharge, diluted the copper-rich and acidic water of Bela River.Therefore, after the confluence with Bela River, the copper concentration in Timok River was lower, and the pH value wasmore alkaline than those in the water of Bela River. As a result of near-neutral pH value, copper in Timok River was relatively equally present in dissolved and particulate forms. However, a higher percentage of the particulate form of copper was present in Timok River near Čokonjar Village because this point is close to the confluence with Bela River. Theprecipitation of particulate forms of copper on the river bed contributed to the decrease of total copper concentrations in the water of Timok River toward the Danube River.

The variations of pH values and copper concentrations during the summer and winterperiods did not show any significant trend, although it could be expected that the copper concentration inTimok River inthe winter season should be lower due to the dilution by a significantly higher

discharge of the unpolluted river water. A large fraction ofthe particulate form of copper was recorded in February2017 and February 2020, in the water of Timok River near Čokonjar, which could be caused by the resuspension of the particulate forms of copper that was precipitated in summer on the river bed.

4. CONCLUSION

In acidic river water, copper was present in dissolved form, whilein near-neutral and alkaline river water copper was relatively evenly present in dissolved and particulate form. Although the pH value of municipal wastewater was similar to the pH value of Timok River, copper was dominantly present in particulate form in thiswastewater, possibly due to the sorption of copper onto the suspended fecal material.Inthe water of Krivelj River,the concentration of copper decreased, and pH value became near-neutral, which is a significant improvement caused by the construction of the new flotation tailing pond "VelikiKrivelj Zero Field" in the watershed of Krivelj River. On the other hand, the concertation of copper and the pH value in the water of Bor River and Bela River did not improve during the studied period. The quality of BorRiver, and consequently the quality of Bela River and Timok River,was largely controlled by the temporal influxes of wastewater from metallurgical facilities in Bor.

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