

CEROVO RIVER – ANNUAL MONITORING OF IMPACT OF THE CEROVO OPEN-PIT MINE

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Abstract

Cerovo River has been exposed to pollution associated with the operation of the Cerovo open-pit mine for decades and the long-term effects of mining have not been systematically quantified. In this study, annual monitoring was carried out from October 2023 to September 2024 at two strategic points: upstream (reference location, CR-1) and downstream in the zone of direct influence of the mine (CR-2). Key indicators of surface water quality, which have the greatest impact on the ecological classification of surface water, were analyzed: pH, concentration of SO_4^{2-} , Cu, Mn, and Fe. At the beginning of monitoring period, location CR-2 showed significant deviations in all tested parameters and was classified in class V - poor ecological status. After the implementation of remediation measures - redirection of acid mine drainage in February 2024, a statistically significant decrease in the concentrations of most pollutants was observed, improving the ecological status of the downstream location, whereby the ecological status was equal to the reference location, CR-1.

Keywords: Cerovo River, annual monitoring, acid mine drainage, Cerovo open-pit, Bor city

1. INTRODUCTION

Since the opening of the Cerovo Cementacija 1 open-pit mine in 1991, more than 25 million tons of tailings have been accumulated until the mine was temporary closed in 2002 [1]. This amount of tailings represents a significant reservoir of sulfide minerals, which have the potential to generate long-term acid mine drainage (AMD). The AMD process is initiated by the oxidation of sulfides, resulting in the formation of sulfuric acid, which accelerates the leaching of heavy metals and the release of soluble sulfates. Consequently, this chemical contamination poses a long-term risk to the water quality of the Cerovo River. Cerovo River is a small watercourse in Eastern Serbia, flowing into the Valja Mare and continuing as the Krivelj River, thereby posing a high risk of spreading contamination throughout the entire watershed of the region.

A significant number of studies have investigated the chemical composition and the impact of acid mine drainage originating from the Cerovo open-pit mine [1–6]. However, comprehensive research analyzing the broader ecological consequences of this mine on the surrounding ecosystem has thus far been limited. Filimon et al (2021) reported on the effects of the mine on soils and plant species, while Đordjević et al (2024) examined the impacts on the Cerovo River [1–6]. In their subsequent study Đordjević indicated that the Cerovo River, based on 28-day monitoring downstream of the mine, was classified as Class V of water quality. This classification was attributed to persistently elevated concentrations of sulfates, copper and cadmium, with additional observations of increased pH values (over a 24-day period) and iron concentrations (throughout

28 days). These findings unequivocally confirmed the presence and intensity of chemical contamination in the watercourse.

The aim of this study was to determine the ecological status of the Cerovo River under the influence of the Cerovo open-pit mine and to evaluate the effects of remediation measures implemented during 2024. For this purpose, one-year monitoring was carried out at two strategic sites: upstream of the mine (reference location) and downstream in the zone of direct mining impact. Special attention was devoted to the ecological classification of surface waters based on key parameters: pH, sulfates (SO_4^{2-}), copper (Cu), manganese (Mn) and iron (Fe). This approach enabled a comparative assessment of upstream and downstream conditions, the evaluation of seasonal and quarterly variations, as well as the quantification of changes following the diversion of acid mine drainage flows carried out in February 2024.

2. EXPERIMENTAL

Annual monitoring of the Cerovo River quality was carried out during the period October 2023–September 2024. Sampling was conducted at two points: CR-1 – a reference location upstream of the Cerovo open-pit mine (44.181790 N, 22.021121 E), and CR-2 – a downstream location within the zone of direct mining impact (44.164412 N, 22.036635 E). Sampling was performed quarterly: Q1 (October–December 2023), Q2 (January–March 2024), Q3 (April–June 2024) and Q4 (July–September 2024). At location CR-1, samples were collected weekly throughout the study period, while at location CR-2 sampling was performed daily in the interval from October 9th to November 6th, 2023, followed by weekly sampling until the end of the monitoring period.

Water samples were filtered through “white tape” filter paper (Lab Logistics Group GmbH) to remove suspended particles and subsequently acidified with concentrated nitric acid (Zorka Šabac, Serbia). Determination of Cu, Mn and Fe was conducted by inductively coupled plasma mass spectrometry (ICP-MS) NexION 1000 (Perkin Elmer, USA). All metal concentrations in this study are reported as total dissolved metal concentrations, although in natural river water these metals are predominantly present as dissolved ionic species, such as Cu^{2+} , $\text{Fe}^{2+}/\text{Fe}^{3+}$, and $\text{Mn}^{2+}/\text{Mn}^{4+}$, depending on local redox conditions. Quality control and data analysis were performed with the Syngistix software package.

A multielement standard solution containing Cu, Mn and Fe (AccuStandard, USA) was used for calibration, along with individual Re and Rh standards (AccuStandard, USA) as internal standards. Quality assurance was ensured using certified standard reference material WP Trace Metals VHGLABS, USA). The limits of quantification for Cu, Mn and Fe, were determined during the validation process: 1.07, 0.071 and 1.69 $\mu\text{g/L}$, respectively [7]. The pH measurements were determined in the field using a Thermo Scientific PC450 multiparameter instrument and the sulfate concentration was measured with a WTW Turb 550 IR turbidimeter using barium chloride as precipitant.

3. RESULTS AND DISCUSSION

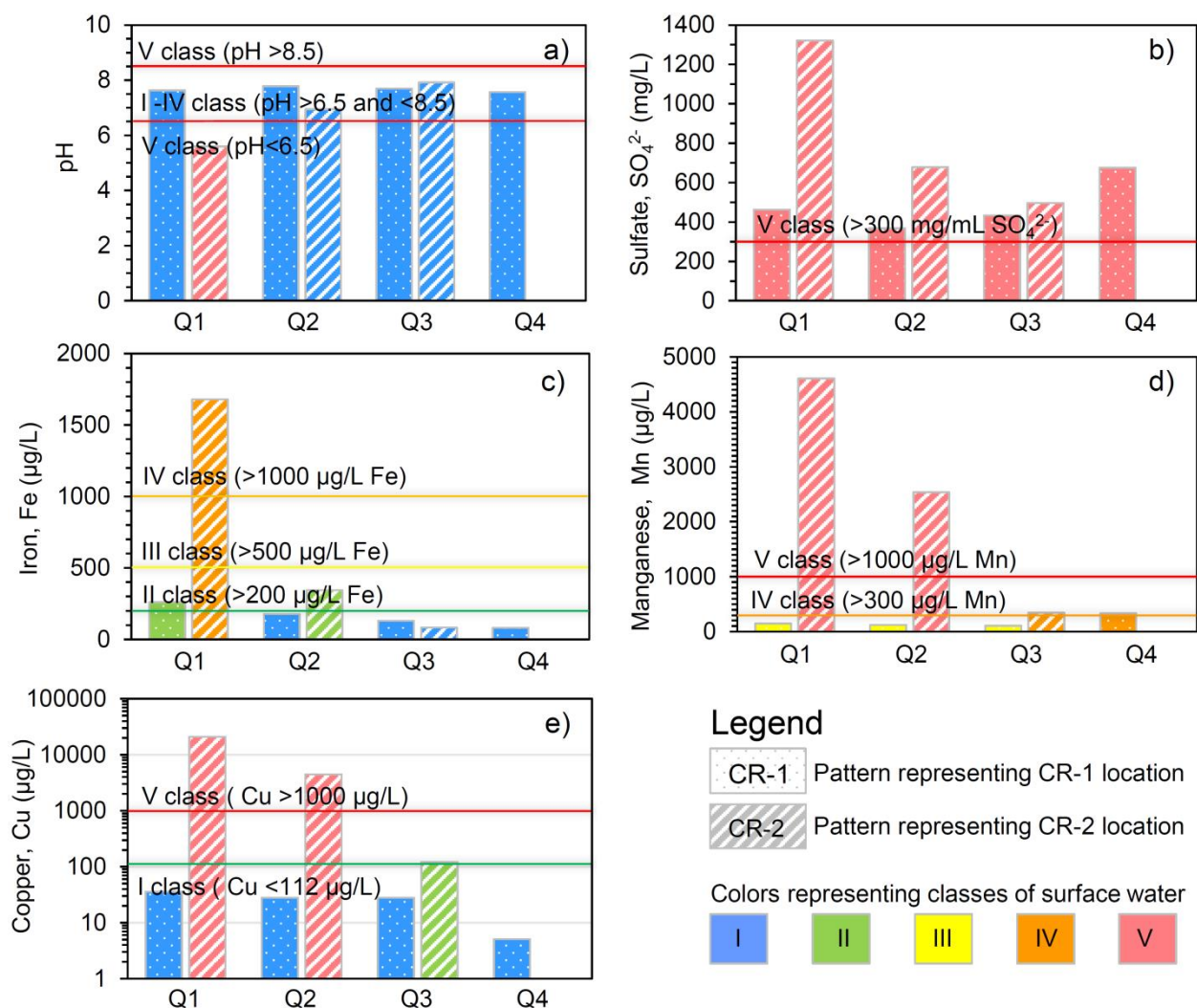
The ecological status of the Cerovo River at sites CR-1 and CR-2 was assessed by comparing the measured values with the reference threshold values for pollutants in surface waters and sediments, as defined by national regulations („Službeni glasnik RS“ br. 50/2012). Classification was carried out according to five categories (I–V), where Class I corresponds to excellent status, II to good, III to moderate, IV to poor and V bad ecological status [8].

Table 1. presents the results of the annual monitoring shown quarterly for both studied sites. The table provides mean values (average) and standard deviations (sd) for the analyzed parameters, for each quartal, at upstream (CR-1) and downstream (CR-2) sites of the Cerovo River.

Table 1. Quarterly average values of analyzed parameters (mean $\pm$ standard deviation) at upstream (CR-1) and downstream (CR-2) locations on Cerovo River

Parametar	Location	Q1	Q2	Q3	Q4
pH	CR-1	7.63 $\pm$ 0.29	7.78 $\pm$ 0.19	7.70 $\pm$ 0.41	7.57 $\pm$ 0.25
	CR-2	5.60 $\pm$ 0.85	6.95 $\pm$ 0.87	7.92 $\pm$ 0.18	/
SO ₄ ²⁻ , mg/L	CR-1	463.2 $\pm$ 81.3	367.7 $\pm$ 44.4	432.7 $\pm$ 81.6	675.2 $\pm$ 70.7
	CR-2	1321.4 $\pm$ 391.8	679.0 $\pm$ 258.4	496.8 $\pm$ 85.8	/
Cu, μ g/L	CR-1	35.8 $\pm$ 24.2	27.9 $\pm$ 14.2	27.8 $\pm$ 17.9	5.1 $\pm$ 1.3
	CR-2	21075.2 $\pm$ 15221.7	4489.6 $\pm$ 5337.3	122.3 $\pm$ 36.3	/
Mn, μ g/L	CR-1	150.3 $\pm$ 16.0	122.7 $\pm$ 13.5	105.6 $\pm$ 33.4	331.9 $\pm$ 120.0
	CR-2	4609.5 $\pm$ 644.9	2535.5 $\pm$ 1852.8	343.2 $\pm$ 67.7	/
Fe, μ g/L	CR-1	259.7 $\pm$ 155.7	176.0 $\pm$ 101.9	130.3 $\pm$ 55.2	80.2 $\pm$ 76.1
	CR-2	1680.1 $\pm$ 1392.4	343.8 $\pm$ 733.0	82.7 $\pm$ 48.6	/

The height of each bar on Figure 1 represents the measured value of the parameter, while the bar color indicates the ecological class of the surface water: blue for Class I, green for Class II, yellow for Class III, orange for Class IV and red for Class V. Threshold values between surface water quality classes are shown as horizontal lines. Vertical axes are shown in linear scale, except for copper where logarithmic scale was used due to large differences in concentrations.

Figure 1. Variation of a) pH, b) SO₄²⁻, c) Fe, d) Mn, and e) Cu across four quarters (Q1–Q4)

In Q1, at location CR-2, the Cerovo River was classified as Class V (poor ecological status) due to elevated concentrations of SO_4^{2-} , Cu, and Mn, as well as acidic pH values. Following the diversion of acid mine drainage flows in February 2024, a marked recovery of pH was observed during Q2 and Q3, and the water quality improved to Class I (good ecological status), indicating the cessation of active acid mine drainage inputs. Although SO_4^{2-} concentrations remained within Class V thresholds, they exhibited a substantial decrease, with Q3 levels approaching those measured at the upstream reference point (CR-1). Copper concentrations decreased by approximately fivefold in Q2 and by nearly 200-fold in Q3 compared to Q1, while Mn concentrations were reduced by about twofold in Q2 and became comparable to CR-1 values in Q3. A similar trend of Fe concentration equalization between upstream and downstream sites was also observed. During Q4, however, downstream monitoring could not be performed due to the drying of the river channel. Overall, the significant reductions in pollutant concentrations compared to Q1 indicate that the implemented wastewater management measures effectively mitigated the immediate impact of the open-pit mine on the Cerovo River ecosystem.

4. CONCLUSION

Annual monitoring of the Cerovo River clearly demonstrated the significant negative impact of the Cerovo open-pit mine on water quality, especially in terms of pH values and concentrations of sulfates and heavy metals. However, after the implementation of the remediation measure of wastewater diversion, a significant improvement in the ecological status of the downstream section was recorded, which in the final period reached the level of the reference site. This indicates the effectiveness of the applied remediation strategy.

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