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THE IMPACT OF THE VELIKI KRIVELJ OPEN PIT AND MINE WASTES ON THE WATER OF THE KRIVELJ RIVER IN OCTOBER 2023

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Abstract

In October 2023, significant impacts on the Krivelj River's water quality were observed, with parameter values higher downstream of the Veliki Krivelj open pit compared to upstream. The river's ecological status was poor, and concentrations exceeded the background levels for eastern Serbia. However, water quality at the downstream site has improved since 2015. Acid mine drainage was the cause of pollution.

***Keywords**: Acid mine drainage, ecological status, daily monitoring*

1. INTRODUCTION

The Veliki Krivelj open pit (VKOP) was established in 1982 and is located about 5 km north of Bor in the Krivelj River valley. Initially, overburden was deposited around the VKOP, and since 1998, it has also been deposited in the closed Bor open pit area. Flotation tailings from processed porphyry copper ore were deposited in three tailing ponds downstream of VKOP: Field 1, Field 2, and Field 0. Acid mine drainage (AMD) from these tailings has polluted the Krivelj River.

The Krivelj River flows through Veliki Krivelj village, around the southwestern side of the VKOP, and via tunnels and collectors beneath the flotation tailing ponds. In 2015, the water of Krivelj River before junction with the Bor river was acidic (pH = 4.49) and contained high levels of sulfates (2060 mg/L SO_4^{2-}), copper (30500 µg/L Cu), and cadmium (6.4 µg/L Cd) [1]. By 2021, the pH value had become neutral, and copper concentrations fell below 200 µg/L [2].

This paper, based on daily monitoring of pH, electrical conductivity (EC), suspended matter (SM), sulfate (SO_4^{2-}), copper (Cu), and cadmium (Cd) from October 9 to November 5, 2023, aims to: 1) assess ecological status using regulatory limits [3], 2) evaluate the impact on water quality, 3) analyze trends of these parameters over time, and 4) identify the cause of pollution.

2. EXPERIMENTAL

Water samples were collected daily from the Krivelj River at locations upstream and down-stream of the VKOP from October 9 to November 5, 2023. The upstream location, marked as KR1 was in the center of Veliki Krivelj Village (44.129269, 22.095138), while the downstream location, marked as KR2, was before the junction with Bor River (44.030233, 22.207980).

Samples were collected using a telescopic sampler and stored in plastic bottles. In-field measurements of pH and EC were conducted using a Thermo Scientific PC450 Meter. SM was measured with a HACH DR/890 portable colorimeter. SO_4^{2-} was determined using a WTW Turb 550 IR turbidimeter. Cu and Cd were analyzed in filtered water samples using an inductively coupled plasma mass spectrometer (ICP-MS) model NexION 1000 (PerkinElmer, USA).

3. RESULTS AND DISCUSSION

Minimum (min), maximum (max), average (avg), and median (med) of the measured parameter values in water samples from the sites KR1 and KR2 are presented in Table 1. The ecological status of the Krivelj River was assessed by comparing the measured parameter values with Serbian regulatory limits for five surface water classes (Table 1) [3]. Surface water is classified as excellent (Class I), good (Class II), moderate (Class III), weak (Class IV), or poor (Class V). The changes in the parameter values during the monitoring period is presented in Figure 1.

Table 1. *Statistical summary of parameter values measured in the water of Krivelj River before and after the open pit Veliki Krivelj, and regulatory limits for surface water classes [4]*

Parameter	Location	Unit	Statistical values				Limits for surface water classes				
			min	max	avg	med	I	II	III	IV	V
pH	KR1	-	6.35	7.78	7.18	7.19	6.5-8.5	6.5-8.5	6.5-8.5	6.5-8.5	<6.5>8.5
	KR2	-	6.89	7.80	7.44	7.47					
EC	KR1	µS/cm	617.7	818.7	727.4	731.3	<1000	1000	1500	3000	>3000
	KR2	µS/cm	1191	2010	1621	1631					
SM	KR1	mg/L	<1	21	-	3	25	25	-	-	-
	KR2	mg/L	21	149	57	53					
SO_4^{2-}	KR1	mg/L	267	326	304	308	50	100	200	300	>300
	KR2	mg/L	1105	1945	1498	1517					
Cu	KR1	µg/L	16	128	80	84	112	112	500	1000	>1000
	KR2	µg/L	69	942	254	206					
Cd	KR1	µg/L	<0.14	0.24	-	0.17	0.45	0.6	0.9	1.5	>1.5
	KR2	µg/L	0.7	3.0	1.8	1.8					

Water at KR1 was classified as Class IV for 10 days and Class V for 18 days due to sulfate levels exceeding regulatory limits. KR2 consistently fell into Class V because sulfate and cadmium levels exceeded regulatory limits, indicating poor ecological status.

Đorđievski, 2018 [5] and Adamović et al, 2021 [6] established threshold values between background and anomalous concentrations in river water from eastern Serbia. The measured concentrations from the present study at both tested sites (KR1 and KR2) exceeded the threshold values for cadmium (0.1 µg/L Cd according to both authors) and sulfates (200 and 180 mg/L, respectively) during the entire monitoring period. This

implies that the concentrations of Cd and SO_4^{2-} in the Krivelj River were above the background concentrations in eastern Serbia.

Figure 1 shows that the pH value was relatively neutral and stable during the entire monitoring period at both tested sites. EC at KR2 was about twice as high as EC at KR1, and showed a mild decreasing tendency, which suggests that the total dissolved substances gradually decreased over time. The concentrations of SM in water at KR2 were much higher than that at KR1, with the median value being about 18 times higher. Therefore, along with dissolved substances, the Krivelj River also received suspended matter from the mine and mine's wastes. SO_4^{2-} and Cd concentrations at KR2 were about 5 and 10 times higher than at KR1, respectively. Cu concentrations showed great variability and were relatively higher at KR2 than at KR1.

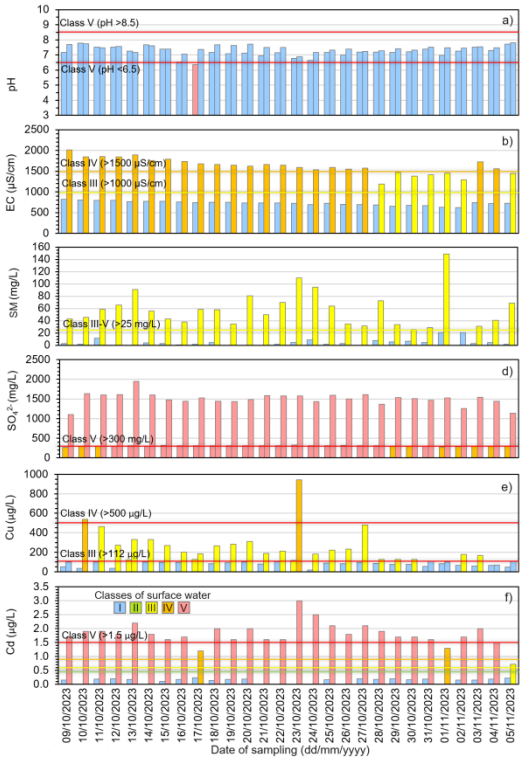

Figure 1. *Bar diagrams showing the change of a) pH value, b) electrical conductivity (EC), and concentrations of c) suspended matter (SM), d) sulfate (SO_4^{2-}), e) copper (Cu), and f) cadmium (Cd) in Krivelj River from October 9 to November 5, 2023 [4]. The first and the second bars in the pair of bars refer to upstream (KR1) and downstream (KR2) sampling sites, respectively*

The impact of VKOP and surrounding mine wastes was evident, with KR2 showing significantly higher parameter values than KR1. Comparisons of median concentrations for SO_4^{2-}, Cu, and Cd from this study with 2015 values show a decrease over time, particularly for copper, which fell from 30500 µg/L in 2015 to 206 µg/L in October 2023, representing a reduction of 148 times.

Pyrite is the most abundant sulfide mineral in the Veliki Krivelj open pit, while chalcopyrite is the most abundant copper mineral [7]. Oxidation of pyrite and other sulfide

minerals in mine wastes produces AMD which contains oxidation products such as SO_4^{2-}. The concentrations of SO_4^{2-} at KR2 (1105 – 1945 mg/L) were significantly higher than the concentrations of SO_4^{2-} at KR1 (267 – 326 mg/L). Therefore, the impact of sulfide ore exploitation at VKOP on the Krivelj River was evidenced by the high SO_4^{2-} concentrations in water at KR2, which was caused by the release of SO_4^{2-}-bearing AMD into the river water.

4. CONCLUSION

From October 9 to November 5, 2023, the Krivelj River downstream of the Veliki Krivelj open pit had a poor ecological status due to elevated sulfate and cadmium concentrations, exceeding regulatory limits and background levels in eastern Serbia. However, the measured concentrations in the present study were significantly lower than those measured in 2015, which suggests that the water quality has improved over time. No significant trend in parameter changes was observed over the 28 days, except for a slight decrease in electrical conductivity. The higher concentrations at KR2 compared to KR1 confirm the continued impact of VKOP, with the primary pollution source being the oxidation of pyrite and subsequent formation of AMD.

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REFERENCES

[1] S. Đorđievski, D. Ishiyama, Y. Ogawa, Z. Stevanović, Environ. Sci. Poll. Res. 25 (2018) 25005–25019.
[2] S. Đorđievski, D. Ishiyama, Y. Ogawa, Z. Stevanović, O. Osenyeng; D. Adamović, V. Trifunović, 52nd International October Conference on Mining and Metallurgy November 29-30 2021, Bor, Serbia, p. 137.
[3] Regulation on limit values of polluting substances in surface water and groundwater and sediment and deadlines for their achievement ("Official Gazette of RS", No. 50/2012). *Available on the following link*: https://pravno-informacioni-sistem.rs/SlGlasnikPortal/eli/rep/sgrs/vlada/uredba/2012/50/1/reg
[4] S. Đorđievski, S. Stanković, J. Petrović, (2023) Test report 4779/23, Mining and Metallurgy Institute Bor, *Available on the following link*: https://bor.rs/wp-content/uploads/2023/12/4779-23-GU-Bor-vode-Mesecni-izvestaj-za-oktobar-.pdf
[5] Đorđievski S. (2018) PhD Thesis, Akita University, Japan, *Available on the following link*: https://air.repo.nii.ac.jp/record/3301/files/kouhakukou1272.pdf
[6] Adamovic D., Ishiyama D., Đorđievski S., et al., Resour. Geol. 71 (2) (2021) 123–143.
[7] R. Jelenković, M. Banjesević, V. Cvetković, A. Pačevski, Field Guide, A field conference, Rtanj Balasevic Motel, Bor area, Serbia, September 4-7, 2007.