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MONITORING THE HEAVY METALS CONCENTRATION IN THE RIVERS IN THE BOR AREA

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Abstract

The chemical quality of surface water in the Bor Area was monitored during the period of two years. The concentration of heavy metal ions: Cu, As, Ni, Cd, and Pb was defined through the eight sampling campaigns. The obtained values confirmed that the concentration of each element was higher than the maximal allowable for the appropriate water class.

Keywords: heavy metal, monitoring, mining, metallurgy.

1. INTRODUCTION

The mining industry includes the surface and underground exploitation of ore deposits and facilities for mineral processing, and the metallurgical industry (metallurgical facilities) deals with the further processing of useful components obtained from the ore. Generation of acid mine water (AMD) originating from surface mines, tailing ponds, and flotation tailing dumps lead to the pollution of surface and underground water. Remediation of the areas polluted by the mine and metallurgical wastewater can take a very long time and require the large financial resources [1]. Waste rock usually contains residues from the mining operation which are currently considered as the economically unprofitable. This material may be chemically inert and leachate should not have a detrimental effect on the surface water, except for a moderate increase in the electrical conductivity and increased content of suspended particles. However, if the waste rock contains minerals (e.g., disulfides or efflorescent minerals) that can increase the acidity or increase the concentration of pollutants due to the weathering in leachate, then it can have a harmful effect and pollute the surrounding watercourses [2]. Mining waste is almost always connected to the groundwater. Water from the waste dam is connected to the surface water in various ways, such as overflow and seepage into the surrounding watercourses or indirect seepage into the groundwater that could surface downstream of the dam [3]. On the other hand, the surface and underground watercourses are endangered by the acid mine drainage (AMD) and industrial wastewater from metallurgical facilities. Therefore, the monitoring of water quality is very important due to the possible toxic effects of heavy metals and other pollutants on the environment [4, 5].

The largest copper mine in the Western Balkans is situated in the Bor Area. Copper mines with surface and underground exploitation, facilities for mineral processing, and metallurgical plants are located in this area. The ore deposits consist mainly of sulfide copper minerals associated with pyrite, which are the main generators of acidic mine water [6].

The main rivers in the Bor Area are the Bor River, Krivelj River, Ravna River, Bela River, and Timok. There are also small creeks and many AMDs [7] resulting from mining operations, along with the industrial wastewater from metallurgical processes that flow in some of the mentioned rivers.

This paper presents the results of systematic monitoring the surface water quality for five elements (Cu, As, Ni, Cd, and Pb) in water samples taken from six rivers (Bor River, Krivelj River, Ravna River, Bela River, and Timok River) and three types of wastewater (from overburden, flotation tailings and metallurgical plants) during the eight sampling campaigns in the period September 2019 to September 2021, in the Bor Area.

2. STUDY AREA

This area was chosen because the mine location harms the surface water system which consists of three rivers: the Bor River, Krivelj River, and Bela River. The Bor River is formed from the Bor City municipal wastewater, AMD from overburden (W1) and AMD from flotation tailing pond (W2). The quality of the Krivelj River (W5) was monitored at the place where there is a significant influence of all wastewater (mine, drainage, flotation). At the chosen sampling location of the Bor River (W4), the influence of AMD from flotation tailing pond (W2) and the overburden (W1) as well as the influence of metallurgical wastewater (W3) were monitored. The Bela River (W6) was formed after merging the Bor, Krivelj, and Ravna River and flowing into Timok (W8) that is out of influence the mining and metallurgy activities from the study area. The next sampling location of Timok, which is a tributary of Danube, is after the confluence with the Bela River, and this point is marked as W9. The Ravna River (W7) was sampled at a location where the impact of the quartz sand facility can be monitored. Coordinates of locations the water sampling, measured by a GPS device (Global Positioning System) are: W1 - AMD from overburden (N: 04880494, E: 07591486), W2 - AMD from flotation tailing dump (N: 04880366, E: 07591043), W3 - Industrial wastewater (N: 04880342, E: 07591076), W4 - Bor River (N: 04877524, E: 07594505), W5 - Krivelj River (N: 04876932, E:07597572), W6 - Bela River (N: 04876866, E:07597572), W7 - Ravna River (N: 04876953, E: 07597650), W8 - Timok River (out of influence the mining and metallurgy activities from study area) (N: 04867539, E: 07605955) and W9 - Timok River after confluence with the Bela River (N: 04884420, E: 07625930).

2.1 Sampling Procedure

Water samples (AMD, industrial wastewater, water from rivers) were sampled by the hand tools according to the standard sampling methods, and interpretations were typed in the control lists for water samples. Details of the lists included all the information necessary to assist in data interpretation and repeatability of sampling. A plastic bottle of 1L was rinsed several times in the river or water that will be sampled before filling with sample. The unfiltered water sample is poured into a plastic bottle of 100 ml without prior washing because there is present 5 ml concentric HNO_3 (63%). In the syringe, exactly 100 ml of sample is poured. After filling, the bottle is sealed and labeled, properly stored, and transported to the Mining and Metallurgy Institute Bor for chemical analysis.

2.2 Characterization of Samples

Methods, prescribed by the relevant international and European standards, were used to measure themetal ion concentrations (Cu, As, Ni, Cd, and Pb), pH, and electrical conductivity. Water samples were analyzed by the inductively following analytical techniques: Optical emission spectroscopy with inductively coupled plasma analytical technique (ICP-OES) was used for Cu ions concentration determination, and mass spectrometry with inductively coupled plasma analytical technique (ICP-MS) by the external calibration method was used for As, Ni, Cd, and Pb ions concentration determination.

3. RESULTS AND DISCUSSION

According to the Serbian Regulation on the categorization of watercourses, the observed rivers are categorized as III and IV categories [8, 9]. The maximum allowable concentration (MAC value) of:

- Cu ions (mg/l) for the III category rivers is 0.5, while for the IV category rivers, it is 1;
- As ions (μg/l) for the III category rivers is 50, while for the IV category rivers, it is 100;
- Ni ions (μg/l) for the III and IV category rivers are 34;
- Cd ions (μg/l) for the III category rivers are 0.6, while for the IV category rivers, it is 0.9;
- Pb ions (μg/l) for the III and IV category rivers are 14.

3.1 Cu, As, Ni, Cd and Pb ions concentration

Table 1 shows the mean values of the Cu ions (mg/l) concentration with standard deviation for the eight campaigns by the sampling locations. The highest content of Cu ions (mg/l) is at the measuring point W3 - metallurgical wastewater. The concentration of Cu above the legally prescribed MAC value was recorded at the sampling locations W1, W2, W3, W4, and W6.

Table 1. *The mean value of Cu concentrations (mg/l) with standard deviation in the realized sampling campaigns and sampling locations*

Sampling locations	W1	W2	W3	W4	W5	W6	W7	W8	W9
Cu (mg/l), Av.±St.dev.	48.815 ±11.917	5.850 ±2.136	217.583 ±57.750	60.219 ±38.563	0.177 ±0.205	40.900 ±29.36	0.115 ±0.156	0.044 ±0.035	0.123 ±0.122

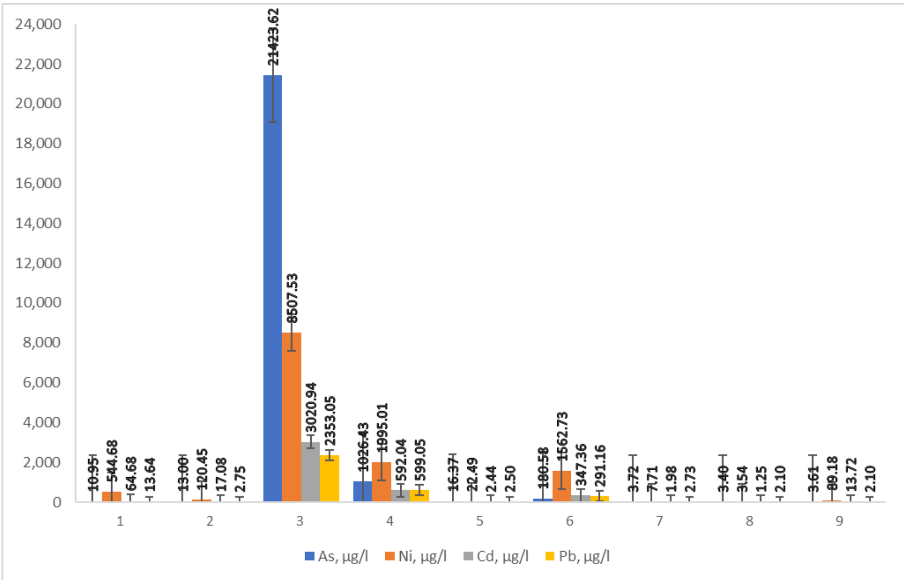

Figure 1. *The mean value of As, Ni, Cd, and Pb concentrations (µg/l) with standard deviation in the realized sampling campaigns and sampling locations*

Figure 1 shows the mean concentration values of As, Ni, Cd, and Pb ions with standard deviation for the eight campaigns by the sampling locations. The concentration of As ions (µg/l) above the legally prescribed MAC value was recorded at the sampling locations W3, W4, and W6. The concentration of Ni ions (µg/l) above the legally prescribed MAC value was recorded at the sampling locations W1, W2, W3, W4, W6, and W9. The concentration of Cd ions (µg/l) above the legally prescribed MAC value was recorded at all sampling locations. The concentration of Pb ions (µg/l) above the legally prescribed MAC value was recorded at the sampling locations W3, W4, and W6.

4. CONCLUSION

The main polluters of the Bor River are the industrial, i.e. metallurgical wastewater (W3). Based on the results for a concentration of Cu, As, Ni, Cd, and Pb ions in the Bor River, it is obvious that each element has a higher concentration than the MAC value. The concentration of Cu, As, and Pb ions in the Krivelj River (W5) and Ravna River (W7) is in all cases lower than the MAC value. Concentrations of Cd and Ni ions were increased during some sampling campaigns in the Krivelj River (W5) and Ravna River (W7). Concentrations of Cu, As, Ni, Cd, and Pb ions in the Bela River (W6), which is formed by the confluence of the Borska, Krivelj, and Ravna Rivers, were higher than the MAC values in each sampling campaign. The concentration of each observed element ion of samples from the Timok River (W8) was lower than the MAC value. The present paper is one of the broadest investigations of the multi-element content in wastewater, generated from copper mining and metallurgy activities in surface water. It may represent a reference point for future studies conducted in Eastern Serbia or other copper mining areas.

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