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STUDENTS PAPER

SCOPE 2. OCCUPATIONAL HEALTH AND SAFETY AND FIRE SAFETY

MONITORING OF THE SURFACE WATER QUALITY IN COPPER MINING AND METALLURGY OPERATION AREAS IN BOR

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Abstract: *The influence of copper mining and metallurgy operations on the quality of surface water in Bor area watercourse has been taken into consideration in this paper. Monitoring of the water quality was performed on five rivers and one industrial wasterwater. The concentration of Cu, As, Ni, Cd, and Pb ions during four selected quarters in period November 2019 – June 2021 were determined on all samples. Water samples were analysed using atomic emission spectrometry with inductively coupled plasma or mass spectrometry with inductively coupled plasma depending on the ions concentration. The highest values of the concentration were recorded for the As ions in the metallurgical wastewater. Also, the concentration of Ni, Cd, Pb, and Cu ions had the highest values in samples from metallurgical wastewater.*
Keywords: mining, metallurgy, monitoring, surface water quality, heavy metal ions.

1. INTRODUCTION

The mining industry brings substantial economic growth and benefits to countries, generating revenues and creating jobs. Mining operations can have a huge local impact on the environment and population. They produce many types of air, water and soil pollutants that may ultimately affect human health. Furthermore, the disposal of an enormous volume of waste materials (from mining and metallurgy operations) poses a serious risk to the surrounding environment through air pollution with fine particles blown by the wind, land degradation by erosion and leaching of soluble inorganic potentially toxic chemical species (Cu, Ni, Pb, Zn, Cd, Cr, etc.) occurring in a variety of minerals present in those materials. Last but not the least, in the area of disposal of the mining waste, the acid mine drainage (AMD) is generated from sulphide-rich minerals.
Taking into account the complexity of the pollution produced by mining and metallurgy operations, adverse health effects of those leaving near, downstream or downwind of mines can be substantial. According to the EPA classification some of these pollutants are very harmful and belong to the group of substances that have been proven to be carcinogenic to humans [1].
The main goal of monitoring is to provide timely response and warning to possible negative processes and accident situations, gain a more complete insight into the state of the environment and determine

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the need to take protection measures depending on the degree of threat and type of pollution. Knowledge of water and soil quality from the point of view of the content of organic and inorganic pollutants is reflected in the possibility of risk assessment, location and remediation of polluted areas as well as urban planning in terms of identification and relocation of pollution sources.
Water monitoring involves testing the content of a number of inorganic elements and organic compounds by modern methods of instrumental chemical analysis. Some of the most hazardous elements that can be found in acid mine waters are arsenic, cadmium, lead, nickel, copper, etc.
Arsenic (As) and Cadmium (Cd) are widely distributed in the environment, come from natural and anthropogenic sources and have no biological role for human. Important anthropogenic sources of As and Cd include mining (usually wastewater), industry and waste management activities [2]. Arsenic induces the formation of reactive oxygen species and exposure deregulates several cellular processes at the molecular level [3]. Cadmium exposure is commonly associated with renal tubular dysfunction, osteomalacia, and osteoporosis as a result of calcium competition, endocrine disruption, glucose metabolism disorders, cerebral infarction, and heart failure [4,5]. Both elements can cause multiple cancers in humans [6]. Once inside the human body, cadmium and arsenic accumulate at high levels in several organs [7].
Lead (Pb) is the most toxic element present in the environment as a result of natural and anthropogenic sources. It is not necessary for human health, because it is not involved in biological processes. When absorbed, lead binds to erythrocytes and travels through the blood to various tissues (liver, kidneys, lungs, brain, spleen, muscles, heart) and further moves to bones and teeth, and affects every organ in the body by disrupting basic biochemical processes and has numerous effects on human health [8].
Nickel (Ni) is a metal broadly distributed in the environment. It is released from both natural sources and anthropogenic activity and is present in the air, water, soil and biological materials. Literature data illustrate that nickel at high doses and in certain forms is toxic to both humans and animals [9,10]. In case of consumption of water contaminated with nickel salts, the registered health effects were: gastrointestinal disturbances and altered hematological parameters.
Copper (Cu) has important roles in the metabolic processes of the human body being an essential element required for hemoglobin synthesis, absorption of iron, and cardiovascular integrity [11,12]. The toxicity of copper is relatively low compared with other heavy metals, but excess copper accumulation in subjects following high-dose chronic exposure and in sensitive populations results in hepatic cirrhosis with jaundice, hemolytic anemia, and degeneration of the basal ganglia, cardiotoxicity (hypotension, tachycardia, tachypnea) gastrointestinal disorders (ulcerations, mucosal acute hemolysis, and hemoglobinuria), nephropathy (azotemia, oliguria) and central-nervous-system manifestations (dizziness, convulsions, lethargy, headache, stupor, coma) [13]. In order to find measures and solutions for the reduction, rehabilitation and elimination of polluting substances, it is necessary to be aware of all consequences that more than a century of continuous mining and metallurgical activities have left in Bor area.
The main rivers in Bor mine area are Bor, Krivelj, Ravna, Bela River and Timok. There are also small river creeks and many AMD resulting from mining operations, along with industrial wastewater from metallurgical processes that flow in some of the mentioned rivers. As the consequence of mining and metallurgy activities, Bor and Krivelj rivers became very polluted mostly by heavy metals (Pb, Zn, Cd, Ni, Se, As, Fe). According to the Serbian legislation for surface water, contents for almost all of the analyzed elements in rivers from Bor city to the confluence of Bela River and Timok, are above the maximum allowed concentration (MAC).
This paper presents results of monitoring the water quality from rivers for five selected elements (Cu, As, Ni, Cd, and Pb) during four selected quarters in period from November 2019 to June 2021.

2. MATERIALS AND METHODS

Surface water samples (rivers water and industrial wastewater) were sampled by hand tools according to the standard sampling methods. Containers (cans of 1 l) for water sampling were rinsed three times in the river or water that was being sampled, prior to taking a sample, in order to prevent contamination of the sample with previous water that was sampled. Water sample was then poured in the plastic bottle of 50 ml without prior washing because there was present 2.5 ml HNO_3 conc (63%). Exactly 50 ml of the sample was poured in syringe and after that the bottle was sealed and labelled. Before using the syringe, it was rinsed three times with water sample and contents were discharged. The samples were properly stored and transported in the laboratory in Mining and Metallurgy Institute Bor for chemical analysis.

Methods prescribed by relevant international and European standards were used to measure pollutant concentrations. The procedure described the analysis of the following heavy metals ions: As, Cd, Cu, Ni, and Pb.Water samples were analyzed using atomic emission spectrometry with inductively coupled plasma (ICP-AES) and mass spectrometry with inductively coupled plasma (ICP-MS).

Quality control of chemical analysis was performed in the laboratory by running certified reference material (CRM). Analysis of replicate test portions will provide an indication of the repeatability and precisions of measurement.

3. EXPERIMENTAL PART

The impact of copper mining and metallurgy activities on water quality is analyzed by monitoring of surface water close to active and abandoned mines and metallurgical plants. Monitoring includes area from the copper mine in Bor, all the way to the confluence of the Bela River and Timok River. This area was chosen because the mine location has a negative impact on the surface water system, Bor, Krivelj, and Bela Rivers that belong to the watershed of the Timok, which is tributary of the Danube. All mentioned rivers flow near to the largest mining and metallurgy complex in the Republic of Serbia where mining activities continuously exist for more than 115 years.

The influence of copper mining and metallurgy operations on the quality of regional surface water has been taken into consideration in this paper. Accordingly, sampling was done from local defined profile of the Bor River (W5), as well as from locations upstream and downstream of the Bor River (marked W4, W6, W7, W8, W11 and W12). Coordinates of the locations of surface water sampling are measured by GPS device (Global Positioning System) and presented in Table 1. Sampling was performed during four campaigns, in the period from November 2019 to June2021.

Table 1. Coordinates and marks of sampling locations

Water sample mark	**Sampling location**	**GPS**
W4	Industrial wastewater	N 04880342, E 07591076
W5	Bor River (local defined profile)	N 04877524, E 07594505
W6	Krivelj River	N 04876932, E 07597572
W7	Bela River (after confluence of Bor River and Krivelj River)	N 04876866, E 07597572
W8	Ravna River	N 04876953, E 07597650
W11	Timok before confluence with Bela River	N 04867539, E 07605955
W12	Timok River after confluence with Bela River	N 04884420, E 07625930

4. RESULTS AND DISCUSSION

The present paper is one of the broadest investigations of the multi-element content in wastewater generated from copper mining and metallurgy activities. It may thus represent a reference point for observed concentrations in future studies conducted in Eastern Serbia or other areas of mining waste discharge. The water samples originated from different rivers and industrial wastewater stream are extremely enriched with toxic elements such as arsenic and cadmium. The results show that the concentration of almost all heavy metal ions from collected water samples during the period November 2019 - June 2021 are above the MAC value according to Serbian legislation for surface water.

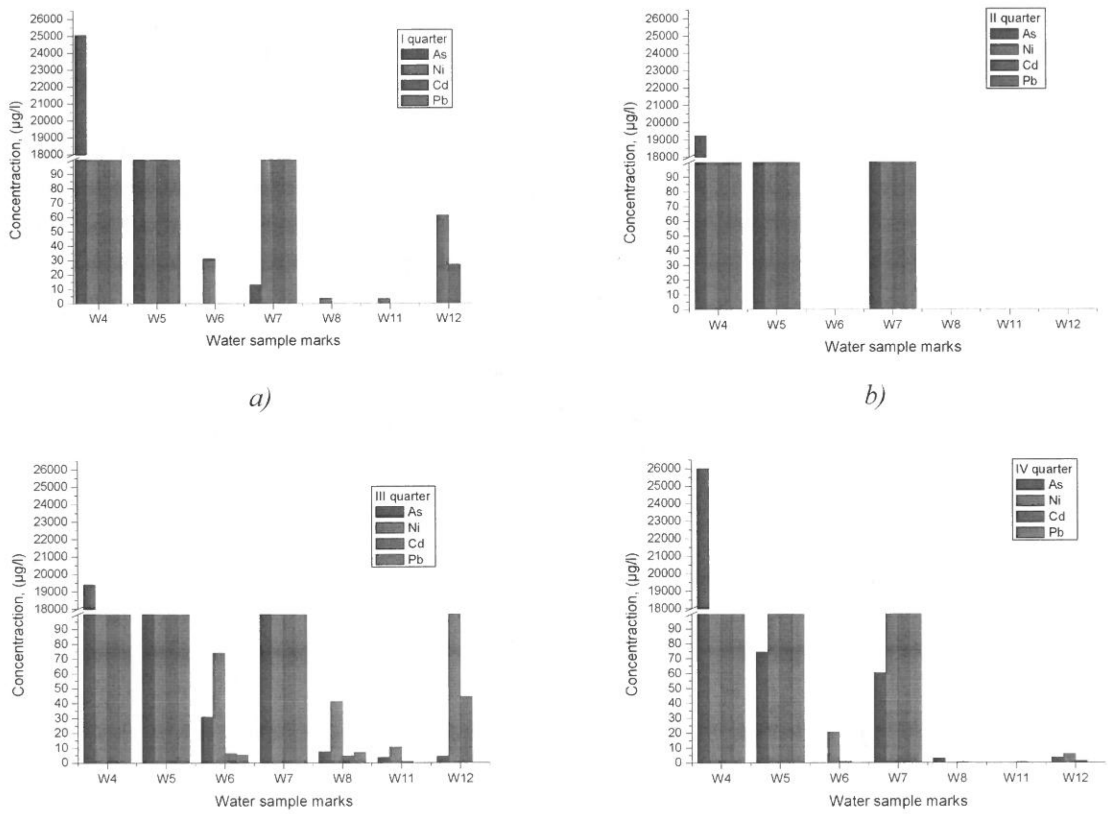
Table 2. Category of water and MAC values according to the Serbian legislation

Source: [14,15,16]

Heavy metal	Category of water and MAC values		
	II category (Danube River from the Hungarian border - to the Bulgarian border)	**III category (from the confluence Bela River and Timok River till to confluence of Timok and Danube River**	**IV category (from Bor city to the confluence Bela River and Timok River)**
Cu, mg/l	0,005 (T=10) to 0,112 (T=300)	0.5	1
As, µg/l	10	50	100
Ni, µg/l	34	34	34
Cd, µg/l	0.45	0.6	0.9
Pb, µg/l	14	14	14

T - water hardness (mg/l $CaCO_3$)

In the Figure 1 are presented the concentration of As, Ni, Cd, and Pb ions in water samples from: a) I quarter (November 2019), a) II quarter (June 2020), c) III quarter (November 2020) and d) IV quarter (June 2021), respectively.



c) *d)*

Figure 1. Concentration of As, Ni, Cd and Pb ions in the water samples

Ni, Pb and Cd ions concentration values are higher than MAC values, for samples from locations: W4, W5 and W7. Middle values for concentration of the target ions in Bor River (W5) before the influence of mining and metallurgy activities are as follows, µg/l: As: 5.4; Ni: < 7; Cd: 0.32; Pb:< 2.1; and Cu: 480. Comparing values for Bor River from the Figure 1 with ones before the influence of the mining and metallurgy operations, it is obvious that the concentration of all monitored metal ions became much higher after inflows of metallurgical wastewater. Arsenic ions concentration in the

industrial wastewater is extremely high (more than 19000 μg/l), in all tested samples. As the industrial wastewater inflows in the Bor River it is clear that increasing of As ions concentration is the consequence of its presence in W4 sample. Also, high concentration of Ni, Cd, and Pb ions are the consequence of their presence in W4 which inflows in the W5.
Bela River (W7) which arises by confluence of W5 and W6 is also with high concentration of target ions. Ravna River is out of the influence of mining and metallurgy activities, so the concentration of monitored metal ions are below MAC values.
Negative impact of mining and metallurgy activities on the water in Timok (W12) can be seen in I and III sampling periods. The same situation is registered for the concentration of the Cu ions (Table 3). Higher values than MAC are registered in the samples from the locations: W4, W5 and W7. The concentration of Cu ions in W4 has the direct impact on its concentrations in W5 and W7 samples.

Table 3. Cu ions concentration in the water samples

Water sample mark	Cu (mg/l)			
	I Quarter	II Quarter	III Quarter	IV Quarter
W4	291.40	209.16	171.63	155.27
W5	68.31	38.26	37.09	25.50
W6	<0.005	<0.005	0.58	0.14
W7	46.27	16.70	60.45	19.70
W8	0.04	<0.005	0.37	0.01
W11	<0.005	<0.005	0.10	0.02
W12	0.24	0.05	0.24	0.04

5. CONCLUSION

The recorded values for Ni, Pb and Cd ions concentration are higher than MAC values for the samples from locations: W4, W5 and W7 according to the surface watercourses category, excluding W4 which is wastewater originated from the copper metallurgical plants. Based on the results for target ions concentration in Bor River before the influence of mining and metallurgy activities (μg/l): As: 5.4; Ni: < 7; Cd: 0.32; Pb:< 2.1; and Cu: 480, it is clear that industrial wastewater has essential impact on the quality of the surface water.
Bor River (W5) and Krivelj River (W6) form Bela River (W7) which inflows in Timok River before the confluence with Bela River (W11) and after those confluence Timok River (W12) flows to Danube River. The contents of recorded metals exhibited a high degree of contamination, indicating that these surface water may pose a significant to extreme risk to nearby residents.

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