XIV International Mineral Processing and Recycling Conference
Belgrade, Serbia, 12-14 May 2021

CONTAMINATION OF RIVERS WATERCOURSES IN BOR DISTRICT WITH As AND Cd IONS

Radmila Marković[1#], Ljubiša Obradović[1], Vojka Gardić[1], Renata Kovačević[1], Zoran Stevanović[1], Adriana Isvoran[2], Vladan Marinković[1]

[1] Mining and Metallurgy Institute Bor, Bor, Serbia,

[2] West University of Timisoara, Department of Biology-Chemistry and Advanced Environmental Research Laboratories, Timisoara, Romania

ABSTRACT – Four sampling campaigns are realized in the period from 10.09.2019 to 10.09.2020 aim to determine the As and Cd ions concentration in the rivers watercourses in Bor District. Sampling points are selected according to the influence on the water quality of Bor River, Krivelj River, Timok River and Danube River. Metallurgical wastewater has the dominant influence on the Cd ions concentration in the selected surface water. As ions distribution in the rivers watercourses is depend of the As ions concentration in the both type of wastewater, acid mine drainage and metallurgical wastewater.

Keywords: Wastewater, Amd, Arsenic, Cadmium.

INTRODUCTION

The common challenge of all human society is to reduce the pollution and environmental damages produced by different processes.

Based on the fact that the copper is an essential metal for many industries, there is an increasing necessity for production of this metal but copper ore mining and metallurgy activities conduct to environmental damages and health effects. Even if they are stopped, the accumulated waste continuously pollutes the environment.

Based on the historical data, in the immediate vicinity of Bor City, about 750 million tons of open pit overburden and 350 million tons of flotation tailings are delayed. Those delayed waste contains dangerous metals such as copper, nickel, arsenic, zinc, cadmium, iron, etc [1]. In the area of disposal the mining waste, the acid mine water (AMD) is generated as a consequence of the chemical reaction the sulfide rich minerals, with water and O_2. Sulphide oxidation process generated the sulphuric acid and decreasing the pH in solution. Generally, the pH drops to values below 4, which causes dissolving of the metal ions [2].

Copper and iron ions are dominant in the AMD from the area of active or closed copper mines. The concentration of the other heavy metal ions (As, Mn, Cd, Zn, Pb, Ni, etc.) is much lower than the concentration of copper or iron ions [3,4].

During the metallurgical treatment of copper ore, harmful and dangerous materials also are generated and discharged into the local watercourses [2].

All of the wastewater from the Bor mine area is released out to natural environment

Corresponding author: radmila.markovic@irmbor.co.rs

and through the Bor River and Timok River tributaries flowing in Danube River.

The aim of this work is to determine the As and Cd ions concentration in the rivers watercourses in Bor District. Starting point sample is the Bor River with the AMD tributaries. Fifteen sampling points are defined for monitoring the heavy metals contamination in a period from 10.09.2019 do 10.09.2020.

EXPERIMENTAL

Materials and methods

Wastewater generated in Bor copper mine area pollutes the Bor and Krivelj rivers. Bela River arises after confluence of Bor and Krivelj rivers downstream from the village of Slatina. After inflows of Ravna River in Bela River, a Bela River inflow in Timok River and Timok River flows in Danube River.

Bor and Krivelj rivers are polluted by the wastewater originating from the active copper mining activities or by the wastewater generated from delayed mine overburden and flotation tailings. Krivelj River is polluted with the wastewater originating from the active mines (Bor pit, Veliki Krivelj, Cerovo, tailing dam in operation), as well as with the wastewater from the waste dump and flotation tailings which are not in operation during the long period (field 2 of the large flotation tailings Veliki Krivelj). Bor River is polluted by the Bor municipal wastewater, by the metallurgical wastewater from copper ore processing plant (metallurgical plant), by the wastewater from the mine tailings dump of the old Bor mine and by the part of Bor flotation tailing (RTH tailing), as well as, from the old flotation tailings in Bor.

The sampling points that are selected for the As and Cd ions concentration monitoring (presented in Figure 1) are:

- W1 Robule accumulation (AMD),
- W2 Robule accumulation 1 (AMD),
- W3 AMD from flotation tailing dam RTH (AMD),
- W4 Metallurgical wastewater,
- W5 Bor River divided into fourteen profiles,
- W6 Krivelj River,
- W7 Bela River after the confluence of Bor and Krivelj rivers,
- W8 Ravna River,
- W9 Bela River after flows of Ravna River,
- W10 Bela River before of confluence with Timok River,
- W11 Timok River before of confluence with Bela River,
- W12 Timok River after confluence with Bela River (near the village Rajac),
- W13 Timok River (near the village Mokranje),
- W14 Timok River (near the village Bukovce),
- W15 Danube River (near the village Radujevac).

Sampling is realized fourth times (quarterly) during the period from 10.09.2019 to 10.09.2020, by a hand tools, according to the sampling methods: SRPS EN ISO 5667-1; SRPS EN ISO 5667-3; SRPS ISO 5667-4; SRPS ISO 5667-6. Measurement of the samples pH values was conducted in the field.

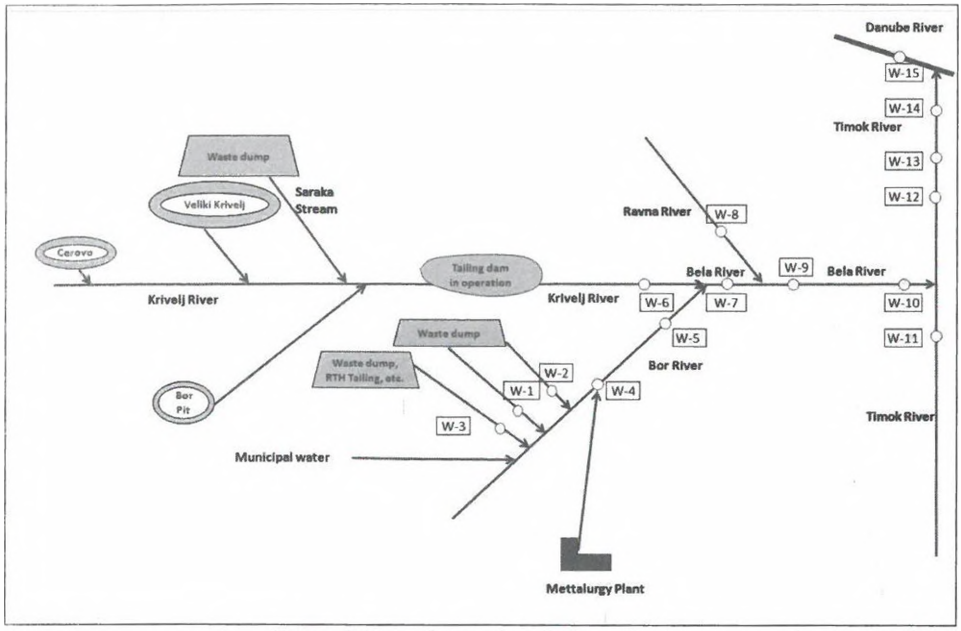

Figure 1 Sampling points in Bor District

The concentration of As and Cd ions in the water samples was determined in the laboratories of Mining and Metallurgy Institute Bor using atomic emission spectrometer with inductively coupled plasma (ICPAES), model Spectro Ciros Vision. The method of calibration curve was used. All reagents used for the chemical analyses were of high purity grade. The certified reference material (CRM) and blank samples were used for quality control of chemical analysis.

RESULTS AND DISCUSSION

In this paper will be discussed results for pH values as so as the values for As and Cd ions concentration. Measured pH values for the all sampling points are presented in Figure 2. pH value for the sampling point W5 (Bor River) is the average pH value obtained based on the data for each profile. From the Figure 2 it can be seen that pH has the lowest values for the sampling point W4 (metallurgical wastewater). Also, the pH values for the sampling points: W1 Robule accumulation, W2 Robule accumulation 1, W3 AMD from flotation tailing dam RTH, W4 Metallurgical wastewater, W5 Bor River divided into fourteen profiles, W7 Bela River after the confluence of Bor and Krivelj rivers, W9 Bela River after flows of Ravna River are lower than the allowable pH values regarding to Serbian legislation (range from 6.5 to 8.5) [5,6,7]. pH values for water samples W10 Bela River before of confluence with Timok River are lower than MAC values during the two quarters. pH values for other sampling points are in accordance with legislation.

In Figure 3 are presented the results of the As ions concentration in the water samples from the selected points.

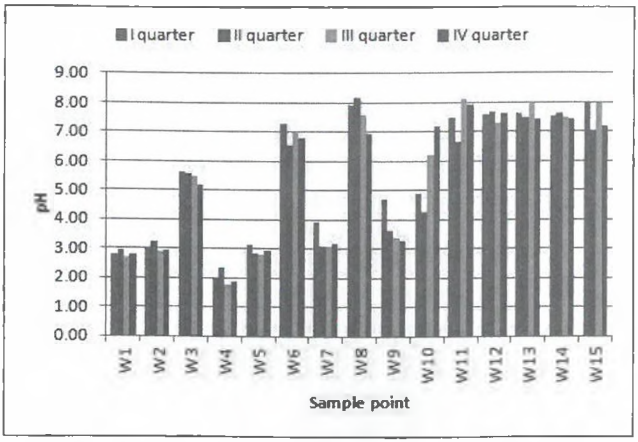

Figure 2 pH values for different sampling quarters

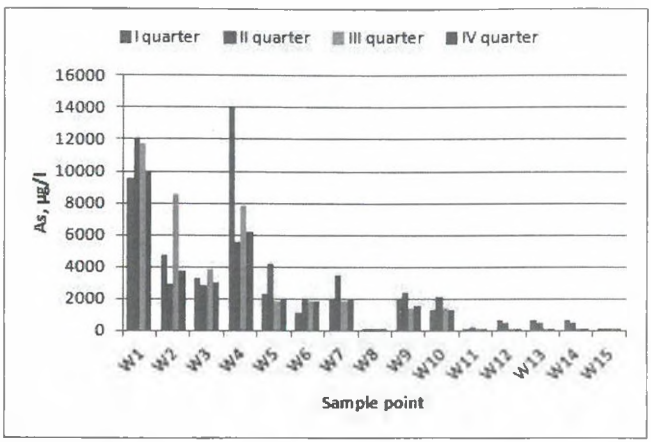

Figure 3 As ions concentration for different sampling quarters

The maximal value of As ions concentration is recorder for the sampling point W4 Metallurgical wastewater but this value is registered only in one sampling campaign. Samples marked as: W1 Robule accumulation, W2 Robule accumulation 1 and W3 AMD from flotation tailing dam RTH also have the high values of As ions concentration and the maximal value is about 120 times higher than the maximal allowed concentration (MAC) according to the Serbian legislation for the IV class waters (MAC = 100 µg/l). Only for a sampling point W11 Timok River before of confluence with Bela River, the concentration of As ions is below the MAC value in a two quarters, according to the river classification (Timok River: III surface water class). For all other sampling points the values for As ions concentration are the much higher than the MAC values.

Maximal value of Cd ions concentration is registered in the sample W4 Metallurgical wastewater and this value is about 6,000 times higher than MAC value. Based on the data presented in Figure 4, increased Cd ions concentration in Bor River and Bela River is consequence of the Cd ions content in metallurgical wastewater. In the water sample from location W11 Timok River before of confluence with Bela River not registered the

Cd ions and in the samples from location W15 Danube River (near the village Radujevac) concentration of Cd ions was lower than MAC value for II surface water class.

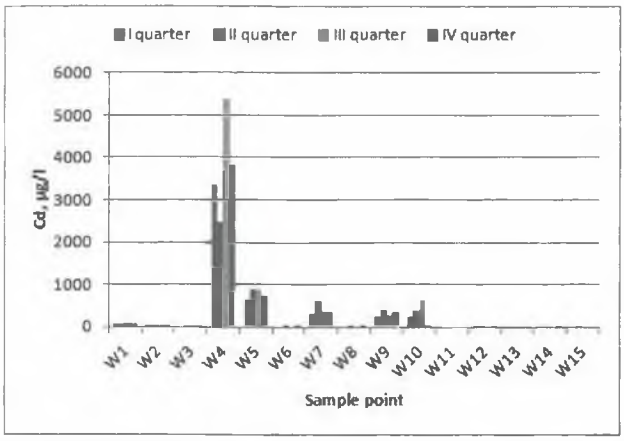

Figure 4 Cd ions concentration for different sampling quarters

CONCLUSION

Obtained results for As and Cd ions concentration in the rivers watercourses in Bor District are confirmed the negative impact of mining and metallurgy activities in the Bor copper mine area. As ions concentration is increased in the each water samples except in the sampling point W11 Timok River before of confluence with Bela River. Obtained results confirmed that presents of As ions in the rivers watercourses in Bor District is a consequence of the impact of two type of wastewater (AMD and metallurgical wastewater). Results for concentration of Cd ions in all samples are confirmed that the metallurgical wastewater has the main impact on the Cd ions concentration.

ACKNOWLEDGEMENTS

We acknowledge the financial support of the Project RoRS 337- ROmania Serbia NETwork for assessing and disseminating the impact of copper mining activities on water quality in the cross-border area (RoS-NET2), implemented under the Interreg-IPA Cross-border Cooperation Romania-Serbia Programme that is financed by the European Union under the Instrument for Pre-accession Assistance (IPA II) and co-financed by the partner states in the Programme.

This work was also financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, Grant No. 451-03-9/2021-14/ 200052.

REFERENCES

1. Project name: ROmania Serbia NETwork for assessing and disseminating the impact of copper mining activities on water quality in the cross-border area, Programme 2014 - 2020 Interreg IPA CBC Romania - Serbia, https://keep.eu/projects/22351/ROmania-Serbia-NETwork-for--EN/

2. Stevanović, Z., Obradović, Lj., Marković, R., Jonović, R., Avramović, Lj., Bugarin, M., Stevanović, J. (2013) Chapter 2: Mine Waste Water Management in the Bor Municipality in order to Protect the Bor River Water, Advances in Waste Water-Treatment Technologies and Recent Analytical Developments, Edited by Dr. Fernando Sebastian Garcia, Edited by Fernando Sebastian García Einschlag and Luciano Carlos, Published by InTech, First published January, 41-63.
3. Masuda, N., Marković, R., Bessho, M., Božić, D., Obradović, Lj., Marinković, V., Ishiyama, D., Stevanović, Z. (2017) A new approach to recover dissolved metals in AMD by two-step pH control on the neutralization method, 13th International Mine Water Association Congress – Mine Water & Circular Economy, 25-30 June 2017, Lappeenranta, Finland, proceedings, 1111-1118.
4. Marković, R., Bessho, M., Nobuyuki, M., Stevanović, Z., Božić, D., Apostolovski Trujic, T.Lj., Gardic, V. (2020) New Approach of Metals Removal from Acid Mine Drainage, Appl. Sci., 10, 5925.
5. Regulation on the categorization of watercourses ("Official Gazette of the SRS", no.3/1968) (In Serbian).
6. Regulation on Pollutant Limit Values into Surface and Groundwater and Sediment and Deadlines for their Achievement ("Official Gazette of the RS", no.50/2012) (In Serbian).
7. Regulation on Limit Values Priority and Priority Hazardous Substances that Pollute Surface Water and Deadlines for Achieving them, ("Official Gazette RS", no.24/2014) (In Serbian).