# MONITORING OF THE DRINA RIVER QUALITY IN THE CITY OF GORAŽDE*

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*Original scientific paper*

## Abstract

Surface water quality is a variable value that depends on the impact of many factors. The Drina River Quality Testing was one of the main motives for writing this paper. In order to get as complete and accurate insight into the water quality as possible, the monitoring lasted for two months (April-May). Sampling was carried out in five locations on the territory of the municipality of Gorazde over the given time intervals, at the hydrological station, 500 and 1000 meters downstream and 500 and 1000 meters upstream of it. The monitoring was carried out to determine the content of heavy metals: Pb, Cd, Fe, Zn, Cu, Ni, and selected alkali and alkaline earth metals: K, Na, Mg, and Ca. In order to complement the analysis, basic physical and chemical parameters of the water quality were also monitored: temperature, conductivity, redox potential, pH value and dry residue. The experiment was carried out in the Chemistry Laboratory at the Faculty of Agriculture and Food Sciences in Sarajevo.
Despite numerous attempts to disturb the Drina River's recognizable quality, the measured parameters did not show significant chemical contamination. The measured parameters should be broaden in the future in order to include organic pollutants too.

Keywords: *chemical contamination, monitoring, evaluation, water quality.*

## INTRODUCTION

Water is of crucial importance for the survival of all living beings. The fact that water occupies about 75% of the Earth's total surface is not something to be taken for granted. As such, water has an unquestionable influence on the living world.
Human existence depends on the use of a large amount of healthy water (microbiologically, physically and chemically), which unfortunately is becoming increasingly scarce today because not enough attention is paid to this extremely valuable resource. Today, due to human civilization practices, water contains many toxic

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products. More than 800 different impurities in water have been identified, and the number is still growing. All toxicants present in water have a direct or indirect effect on humans since they are at the top of the food pyramid (Mačkić et al. 2010). In order to raise awareness of the preservation of this resource, an ambitious water management concept is being introduced, addressing the importance of water quality preservation systems, including monitoring. Monitoring, together with evaluation, are the elements of water quality control, which aims to prevent or suppress the spread of infectious diseases caused by water. There is no ideally pure water in nature, because it dissolves numerous compounds from the place of origin to the place of capture or the way of use. Dissolution of various compounds leads to mineralization or contamination (depending on the type of dissolved particles). The state border between Bosnia and Herzegovina and Serbia spreads across the middle and lower water channel of the Drina River, and spans through four countries: Bosnia and Herzegovina, Serbia and Montenegro. It is a part of the Danube Basin, which empties into the Black Sea, and is the biggest tributary of the Sava River. A million or so people live in its watershed, and their activities (mining, industry, agriculture, and developments in rural and urban populations) significantly impact the aquatic ecology (Ivanovic *et al.*, 2011). River water sources could be influenced by natural factors and human activities (Who *et al.*, 2016). Increased urbanization and population growth have increased the strain on water environments and ecosystems. In order to accommodate the population increase, industrial activities have been encouraged, which may result in the release of pollutants and wastewater into the environment (Chen *et al.*, 2018; Estrada-Rivera *et al.*, 2022). The quality of river water may decline as a result of pollutants from emissions or wastewater. Seasonal and geographic climate differences result in seasonal and spatiotemporal variations in the quality of river water (Cruz *et al.*, 2019; Mena-Rivera *et al.*, 2017). The city of Goražde is situated on the banks of the Drina River in southeastern Bosnia. The city lies at the foot of the eastern slope of the Jahorina mountain at a height of 345 m (1,132 ft) above sea level. The settlement is situated on the alluvial terrace in a broad valley, formed by the erosion of the Drina River. With around 30 000 inhabitants it is one of the biggest settlements on the Drina River bank ("Goražde - Wikipedia" n.d.).

The purpose of this paper is to monitor and evaluate the content of selected metals and physicochemical parameters of water quality, and to compare the results with the current legal regulations and to define measures for improvement if the chemical contamination is found.

## MATERIALS AND METHODS

### Samples and sampling

The first step of the experiment was the river water sampling. The entire sampling process lasted for seven weeks (labeled as $W_1$, $W_2$, $W_3$, $W_4$, $W_5$, $W_6$ and $W_7$) and took place according to the pre-defined procedures (every Sunday around 12:00 p.m., always from the same locations). Sampling was carried out in the municipality of Goražde in five locations within 2 km of the river course.

In the very center of the town of Goražde, there is a hydrological station that measures basic parameters (water and air temperature, flow and water level of the river) on a daily basis. Below the hydrological station, on the left bank of the Drina River, is the mouth of the Podhranski stream. As the stream seemed to be contaminated, the sampling was targeted at this location and the locations around it. The water samples were taken facing the opposite direction of the river flow.
The locations from which the samples were collected (Figure 1) are numbered so that the location numbered 1 (the location from which the first sample was taken) was the lowest and is located 1000 meters below the hydrological station. Location number 2 was 500 meters below the hydrological station and location 3 was right next to the hydrological station. Location 3 is also close to the Hranjen stream, which is close to the source of contamination and industrial discharge pipe. Locations 4 and 5 were 500 and 1000 meters upstream from location 3. Locations of sampling are labeled as: $L_1$, $L_2$, $L_3$, $L_4$ and $L_5$.

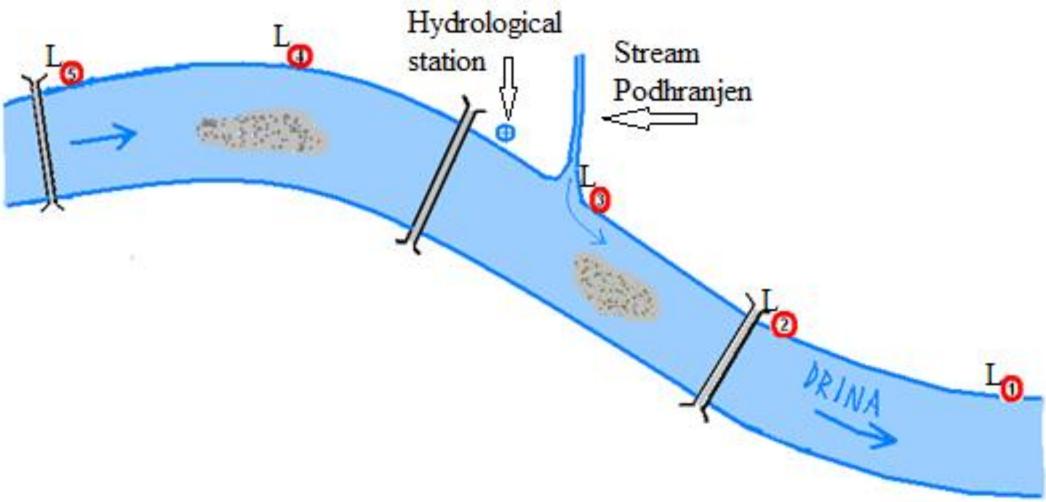


Figure 1. Drina River sampling locations

## Methods of analysis

*Dry residue*
15 250-ml laboratory glasses were oven-heated for one hour at 105 °C. After cooling in desiccator, the glasses were weighed using an analytical balance. The volume of 100 ml water samples were then added into the each of the marked glasses. The oven-drying method was performed at a temperature of around 105 °C until the constant mass was reached. The obtained results were expressed as mg/L (ppm).

*pH value*
The pH value was measured using a laboratory pH meter (Mettler Toledo MP 230) with a combined ionselective electrode. Prior to the measurement, the device was standardized with buffer solutions (4.00 and 7 .00 of pH).

*Electrical conductivity*
Electrical conductivity was measured using a conductometer (Mettler Toledo MC 126). The instrument was standardized with solutions of a known electrical conductivity.

*Oxidation reduction (redox) potential (ORP)*
The redox potential was measured in a similar way as electrical conductivity. The difference was in the instrument (HANNA ORP) and the standards which were used.

*Metals content determination*
In order to test the content of heavy, alkali and alkaline earth metals, it was necessary to conserve or acidify each batch of the samples. Preservation of the samples was carried out in special containers to which two to three drops of concentrated nitric acid (63% $HNO_3$) were added. After adding the acid, the samples were archived in chronological order (by dates and the markings of sampling locations) in a refrigerator.
Different metals, due to their different physicochemical properties, required different test methods. Lead, cadmium, iron, zinc, magnesium, calcium, copper and nickel were tested using the atomic absorption spectrophotometry with flame atomization (FAAS), while potassium and sodium were measured by flame photometry (FP). The first step in the analysis was the preparation of working standards in order of increasing concentration. An unknown concentration of the sample can be determined by way of a calibration curve created by entering the values of increasing concentrations of standards and absorbance. After standardization, the analysis of elements in a series of prepared samples was performed.

## RESULTS AND DISCUSSION

The next chapter shows, in tables and figures, and discusses the measurement results.

Determination of basic quality parameters

Table 1. Results of the basic quality parameters

| **Residue mg/kg** | $W_1$ | $W_2$ | $W_3$ | $W_4$ | $W_5$ | $W_6$ | $W_7$ |
|---|---|---|---|---|---|---|---|
| $L_1$ | 244.33 | 154.00 | 108.66 | 156.66 | 197.00 | 127.33 | 176.66 |
| $L_2$ | 274.00 | 201.00 | 138.33 | 148.66 | **228.00** | 149.33 | 203.66 |
| $L_3$ | **319.00** | **277.00** | 239.66 | 220.00 | 155.33 | **236.66** | **241.00** |
| $L_4$ | 299.00 | 107.00 | 177.00 | **298.33** | 170.00 | 184.66 | 202.66 |
| $L_5$ | 254.00 | 104.00 | **240.00** | 318.66 | 141.66 | 163.66 | 107.33 |
| Average | 278.06 | 168.66 | 180.73 | 228.46 | 178.39 | 172.32 | 186.26 |

| **pH value** | $W_1$ | $W_2$ | $W_3$ | $W_4$ | $W_5$ | $W_6$ | $W_7$ |
|---|---|---|---|---|---|---|---|
| $L_1$ | 6.87 | 7.33 | 6.69 | 7.13 | 7.40 | 7.21 | 7.11 |
| $L_2$ | 7.69 | 7.75 | 8.11 | 7.58 | 7.55 | 7.61 | 7.52 |
| $L_3$ | 7.75 | 7.67 | 8.08 | 7.71 | 7.64 | 7.65 | 7.62 |
| $L_4$ | **7.94** | **7.95** | 8.18 | **7.83** | 7.78 | 7.74 | **7.78** |
| $L_5$ | 7.91 | 7.91 | **8.22** | 7.79 | **7.80** | **7.78** | 7.71 |
| Average | 7.63 | 7.72 | 7.85 | 7.60 | 7.63 | 7.59 | 7.54 |

| **EC (µS/cm)** | $W_1$ | $W_2$ | $W_3$ | $W_4$ | $W_5$ | $W_6$ | $W_7$ |
|---|---|---|---|---|---|---|---|
| $L_1$ | 267.5 | 267.3 | 376.7 | 389.3 | 361.3 | 253.3 | 284.3 |
| $L_2$ | 266.3 | 284.3 | 409.3 | 380.7 | 393.0 | 398.0 | 310.7 |
| $L_3$ | **401.0** | **375.7** | **448.3** | **467.3** | **495.3** | **509.7** | **364.0** |
| $L_4$ | 305.0 | 253.0 | 354.7 | 334.0 | 344.3 | 346.0 | 269.0 |
| $L_5$ | 280.7 | 252.7 | 349.3 | 335.7 | 340.7 | 342.7 | 269.0 |
| **Average** | 304.1 | 286.6 | 387.66 | 381.4 | 386.92 | 369.94 | 299.4 |

| **ORP (mV)** | $W_1$ | $W_2$ | $W_3$ | $W_4$ | $W_5$ | $W_6$ | $W_7$ |
|---|---|---|---|---|---|---|---|
| $L_1$ | **197.7** | 46.3 | **167.7** | 77.7 | 73.0 | **53.7** | **43.0** |
| $L_2$ | 153.0 | 46.0 | 137.3 | 82.7 | 70.0 | 52.0 | 39.0 |
| $L_3$ | 183.0 | 77.7 | 111.3 | 82.3 | 77.0 | 51.3 | 31.0 |
| $L_4$ | 122.3 | 87.7 | 120.0 | **87.7** | **79.0** | 53.0 | 35.0 |
| $L_5$ | 74.66 | **92.3** | 143.7 | 86.3 | 78.0 | 53.7 | 38.0 |
| **Average** | 146.1 | 70.0 | 136.0 | 83.3 | 75.4 | 52.7 | 37.2 |

Table 1 clearly shows that sampling location 3 leads in the content of dry residue in relation to other sampling locations due to the vicinity of the extended discharge pipe and this is the case in almost all of the sampling series. The lowest values in all of the sampling series were found in the samples from location 1 and location 2. The results for dry residue correspond to the ones reported recently (Rajković *et al.*, 2012). Going upstream towards the location 5, the pH value increases. Going downstream from location 3 lower pH value was recorded, probably as a result of the presence of acidic substances in the wastewater. It is important to mention that all the measured pH values were within the permitted limits defined by the applicable legislation. The case study of the Sutla River in Croatia (Dragun *et al*., 2011) showed comparable pH ranges. Sample 3 had the highest value of EC. Wastewater, which enriches the mentioned location with its present ions, contributed to this increased value. As a result of ion dilution in the water, a rapid drop in values is noticeable from location 3 downstream. Samples 4 and 5 have the lowest values because they were collected upstream of the critical zone and do not have the potential for contamination like the samples from other locations. According to the Regulation on dangerous and harmful substances in water ("Pravilnik o opasnim materijama u vodama" 2007), the conductivity value must not exceed 500 µS/cm. In the present case, the sixth series of sampling, namely in the sample 3, slightly exceeded the upper limit, which is in line with the expectations. Leščešen *et al*. (2016) presented almost the same results for electrical conductivity of the Drina River samples. By observing Table 1., it is clearly seen that the total redox potential per sampling series was highest in the first sampling series, which may be a consequence of the low water level and temperature of the river, and the lowest in the sixth and seventh series when the water level was increased. In general, the redox potential results were irregularly distributed within the different sampled locations, making their interpretation difficult. It can be seen that the highest value was found in sample number 1 in a larger number of series, and the lowest in sample number 3, but in each case the obtained values were positive (oxidative medium). All positive and similar values of ORP were found by Ting and Rizaludin Mahmud (2020) and Mehmedinović *et al.* (2021).

The greatest attention during the entire process of preparing the paper was paid on the monitoring of heavy and selected metals, i.e. their quantitative analysis. In this section, the analysis of alkali and alkaline earth metals (Ca, Mg, K and Na) are presented and discussed. The measured metal content was compared with the limits defined in the applicable regulations, the Regulation on dangerous and harmful substances in water ("Official Gazette of the Federation of Bosnia and Herzegovina", number 286/07). In order to obtain more complete information, the mean, minimum and maximum values and their maximum allowable limits are presented in Table 2 below.

Table 2. Maximal, minimal values and maximum allowable limits

| | Ca | Mg | K | Na |
|---|---|---|---|---|
| Maximum (mg/kg) | 49.06 | 18.56 | 5.40 | 86.00 |
| Minimum (mg/kg) | 18.50 | 3.18 | 3.72 | 14.40 |
| Maximum allowable limit (mg/kg) | 200 | 30 | 12 | 150 |

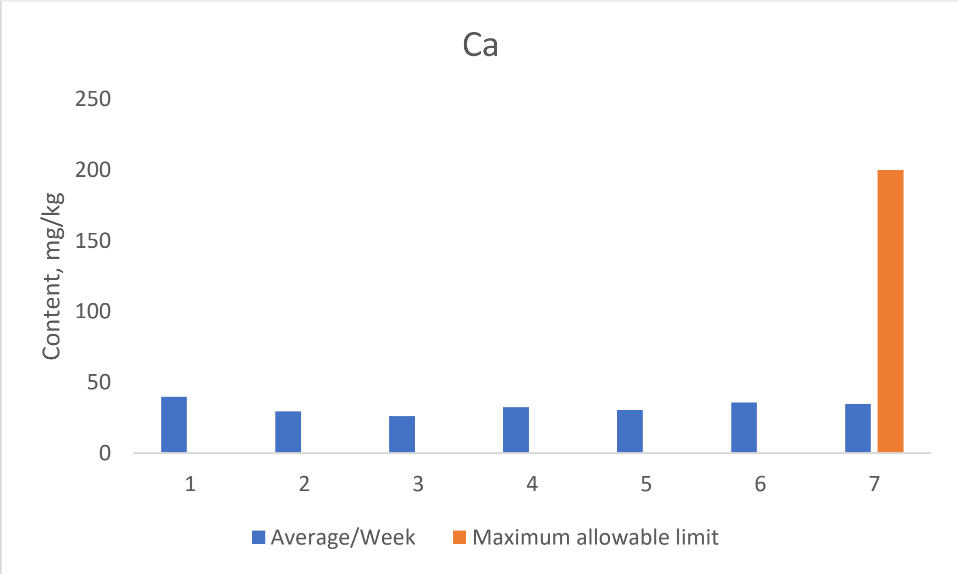

Figure 2. Results for calcium content compared with a maximum allowable limit

The analysis established that the examined calcium content was unevenly distributed within the sampling series, and for this reason, no single sampling series or sample can be singled out as the richest in that element. The Figure 2 shows that the element is present in all of the samples, with sample 1 of the second and sixth series having the highest results. Sample 3, which proved to have highest values in earlier tests carried out in this analysis, did not continue the same tendency for calcium, that is, the metal concentration in the sample was relatively stable and ranged from 30 to 40 mg/L. Despite the fact that the Drina River belongs to the type of surface waters that are abundant with this metal, this was not recorded in this case. It is clearly seen that the calcium content was far within the permissible limits.

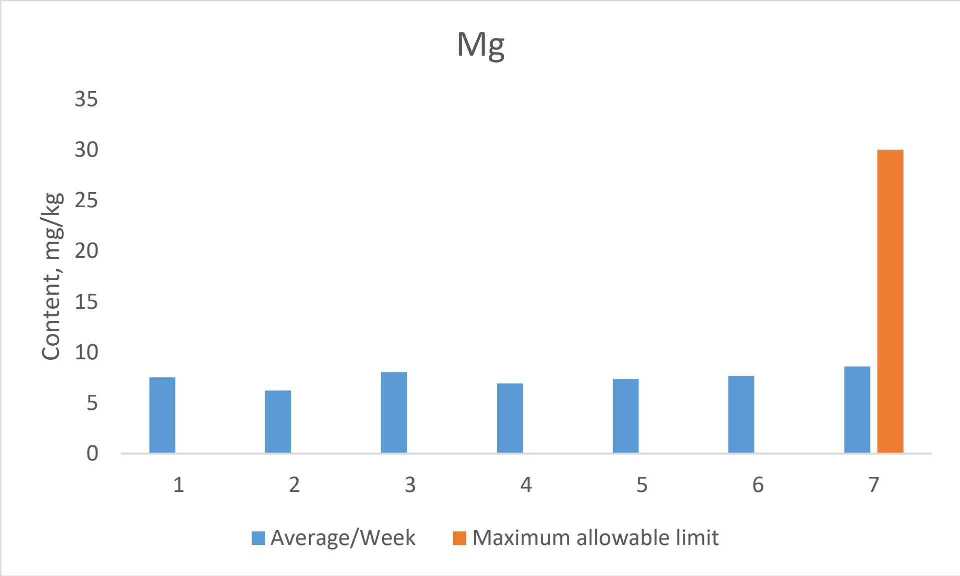


Figure 3. Results for magnesium content compared with a maximum allowable limit

The Figure 3 above clearly indicates that sample number 3 in all of the sampling series was the richest in magnesium content which was relatively equally distributed within different sampling locations. Samples 2 and 1 followed, while samples 4 and 5 were characterized by the lowest and almost equal content of the tested metal. Analyzing the overall picture, it becomes clear that the industry wastewater that reaches the watercourse of the river near location 3 (sample 3) is rich in chemical substances that contain this metal, enriching the river flow downstream from it. A regressive drop in the content of the element is noted downstream from location 3, with uniform content upstream from it. This means that location 3 is a point with the highest content, making it a "demarcation line" between the two concentration intervals. It is important to note that all the measured values of the metal content were within the maximum permissible limit defined by the applicable legal regulations.

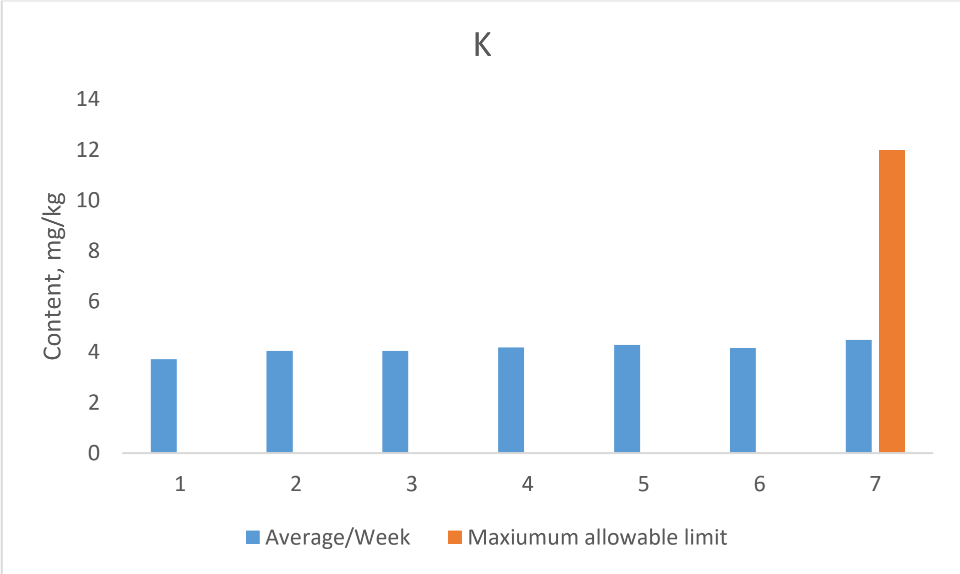


Figure 4. Results for potassium content compared with a maximum allowable limit

Observing the Figure 4, it can be seen that sample 3 leads in terms of potassium content compared to the other tested samples. The reason for this increase is the wastewater that reaches the river at this point. It is likely that the wastewater contains a chemical substance rich in potassium that enriches the water mass from the point of inflow and downstream from it. Going upstream from the point where the stream enters the river, the location 3, the content of the element decreases. Samples 4 and 5 contain smaller amounts of the tested element. It is worth noting that the content of the element in all of the tested samples was below the maximum allowed limit defined by the applicable legal regulation.

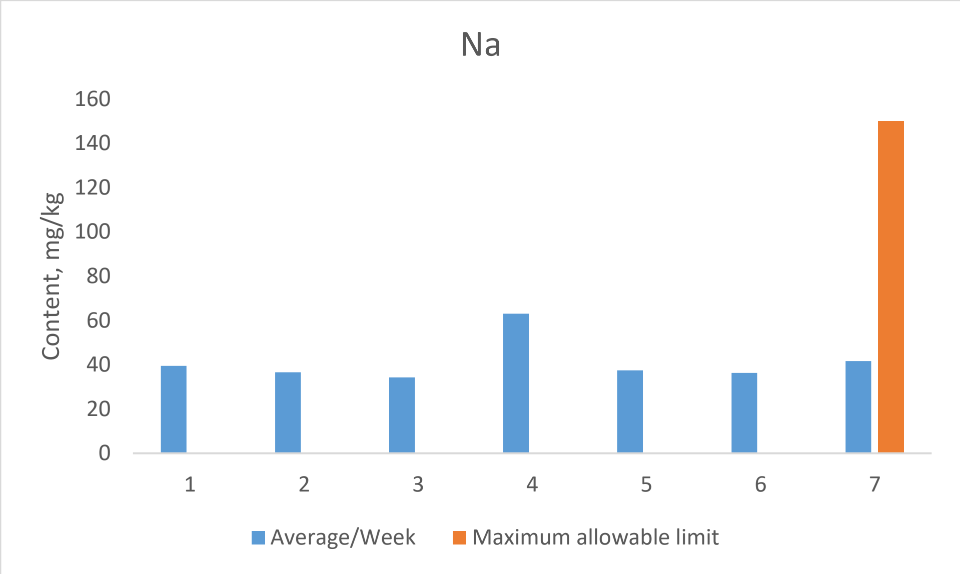


Figure 5. Results for sodium content compared with a maximum allowable limit

As the above figure shows, sample 3 was the richest in sodium content, while sample 5 was the poorest. The reason for this increase in sample number 3 is the same as in the previous cases. Going up or down towards the initial or final location, the metal content decreases, making this location again the line of demarcation between the two value intervals. The obtained values were below the margin of the maximum allowed content determined by the relevant regulation.

Sodium was the last surface water quality element to be monitored. All the obtained results were at a satisfactory level, which will be generally discussed in the next chapter. It is noted that the content of the measured metals (average values) was highest in the period of reduced river water level and vice versa. The reason for the increase in their concentration when the water level was low is due to the reduction of the amount of water to the same amount of metal in a given volume unit. Similar concentrations of calcium and magnesium, but lower content of sodium and potassium, were reported by (Grsic *et al*., 2018).

Determination of heavy metals content

The content of heavy metals (lead, cadmium, iron, zinc, nickel and copper) was too low to be determined by means of atomic absorption spectrophotometry. The detection limit for many of the heavy metals was above 1 mg/kg and the content of heavy metals in the present case were much lower.

## CONCLUSIONS

The results of the analysis of the basic indicators or physicochemical parameters: pH value, conductivity, turbidity, redox potential and dry residue of the Drina River (for the implementation of which appropriate test methods are specified by law) were within the permitted limits. Therefore, the water quality of the Drina River, according to the mentioned parameters, during the mentioned monitoring period (April/May), was at a satisfactory level.

The obtained values of the analysis of heavy and selected metals, in accordance with the Regulation on hazardous and harmful substances ("Official Gazette of the Federation of Bosnia and Herzegovina", number 286/07), indicate that the quality of the Drina River meets the criteria of the first category of surface waters as defined by this Regulation.

The results reported in this paper should be considered in the light of some limitations. Namely, the instrumentation used herein was not sensitive enough which is why we suggest sampling in the larger area of the Drina River and usage of more sensitive equipment in future research investigations (GFAAS, ICP-MS, ICP-OES).

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# MONITORING KVALITETE RIJEKE DRINE NA PODRUČJU GORAŽDA

## Sažetak

Kada se govori o kvalitetu kao jednoj cjelini, bitno je naglasiti da u njegovoj izgradnji učestvuje veći broj elemenata. Kvalitet površinskih voda je varijabilna vrijednost koja zavisi od uticaja mnogobrojnih faktora. Ispitivanje kvaliteta rijeke Drine je bio jedan od osnovnih motiva izrade ovog rada.

Da bi se dobila što potpunija i tačnija slika kvaliteta vode vršen je njen monitoring. Monitoring je trajao dva mjeseca (april-maj), kada je primjetan povećan vodostaj rijeke. Uzorkovanje je vršeno sa pet lokacija na teritioriji opštine Goražde u zadanim vremenskim intervalima i to kod hidrološke stanice, zatim 500 i 1000 metara nizvodno i uzvodno od nje. Praćenje je ustremljeno na elemente hemijske kontaminacije, odnosno

na kvantitativni sadržaj teških metala (olovo i kadmij) i odabranih elementa: željezo (Fe), cink (Zn), magnezij (Mg), kalcij (Ca), bakar (Cu), nikl (Ni), kalij (K) i natrij (Na). U cilju kompletnosti analize praćeni su i osnovni fizičko-hemijski parametri kvaliteta vode. Mjerena je temperatura, provodljivost, redoks potencijal, pH vrijednost i suhi ostatak. Ispitivanje je vršeno u hemijskoj laboratoriji Poljoprivredno-prehrambenog fakulteta u Sarajevu, a dobiveni rezultati su hronološkim redom pohranjivani radi evaluacije kvaliteta vode. Evaluacijom dobivenih rezultata, odnosno usporedbom sa važećom regulativom zaključuje se da je kvalitet rijeke Drine ispitivanog područja u vremenskom periodu mjesec april-maj bio na zavidnom nivou.
Uprkos mnogobrojnim pokušajima narušavanja prepoznatljivog kvaliteta, rijeka Drina se uspjela odbraniti od nemilih destruktivnih pokušaja.

Ključne riječi: *hemijska kontaminacija, monitoring, evaluacija, kvalitet vode.*