HEAVY METAL CONCENTRATIONS IN SURFACE WATER AND SEDIMENT FROM DRINA RIVER, BIH

Aida Bilajac, Sabina Žero, Amar Karadža
University of Sarajevo, Faculty of Science
Sarajevo, B&H

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ABSTRACT
In this paper, an analysis of the surface water and sediment of the Drina River was carried out. Samples were taken from different six locations along the course of the Drina River in Bosnia and Herzegovina. Selected heavy metals were determined in the sediment after acid digestion using atomic absorption spectrometry - flame technique. The same method was used to determine Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in surface water samples. The obtained results indicate that the Drina River in the investigated part of the course meets most of the prescribed metal limit values. The results obtained for the river Drina were compared with the results obtained in the studies of the rivers Bosna, Trstionica, and Spreča in Bosnia and Herzegovina.

1. INTRODUCTION

The rapid process of urbanization and industrial activities has led to the pollution of rivers around the world [1,2,3]. Pollution of river water with heavy metals as a result of natural and anthropogenic processes represents a danger for ecosystems and humans due to their possibility of accumulation and toxicity [4]. The accumulation of heavy metals in water and sediment often has harmful effects on biota and inhabitants when the pollutant concentration exceeds the limit values [5].
Heavy metals are ecologically very important. They circulate through the ecosystem, i.e. they move through the ecosystem and have their own biochemical cycle. The circulation of heavy metals through the ecosystem depends on a number of factors, such as climatic conditions, proximity to pollution sources, as well as the activities of biological systems. Some of heavy metals such as Fe, Mn, Zn, and Cu belong to the group of essential elements for plants. In small amounts, they are necessary for numerous functions of a living organism. However, heavy metals in higher concentrations can cause toxic effects on living organisms, and when they reach the food chain; they can endanger the health of people, animals, and plants [6]. Metals such as Pb and Ni exhibit toxicological properties on the environment, which can lead to severe consequences in the ecosystem. Today, heavy metals are increasingly released into the environment through anthropogenic activities [7,8,9,10].
As Bosnia and Herzegovina (BiH) is rich in natural resources, especially rivers, and in the last few years there is not a large number of studies on the water and sediment of the Drina River in the literature, so the main aim of this study was to analyze the surface water and sediment of Drina River, so that the results can serve as a starting point for further research in the field of environment protection, especially rivers in Bosnia and Herzegovina. In this study, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn are determined in different river water and sediment samples of the Drina River by atomic absorption spectrometry, and flame technique (FAAS).

2. MATERIAL AND METHODS

2.1. Sampling area

Drina River belongs to the Sava River Basin. The considered part of the Drina River includes the area from the settlement of Hubjeri downstream from Goražde to the settlement of Vitkovići in a length of 14.5 km in Bosnia and Herzegovina. It is a relatively narrow valley in which the town of Goražde and its industrial zone Vitkovići are located.

2.2. Sample collection, preparation, and analysis

In this study, river water samples (n=6) and river sediment samples (n=6) were taken during May 2021. River water and sediment samples were taken side by side except for location 6. A sampling of river water was carried out in acid-clean polypropylene bottles. Prior to sampling, each sampling bottle was washed several times with river water. During the sampling the opening of the bottle facing the direction of the river flow; water sampling was done 20 cm below the river level during stable weather conditions. Sediment samples were also sampled in a similar manner to river water samples. Containers for sediment sampling were pre-washed, and at the sampling site rinsed with river water several times, then the surface part (from 0 cm to 5 cm depth) of the sediment was taken for the heavy metal analysis. General sampling data are given in Table 1.

Table 1. General sampling data for the river water and sediment of Drina River

River water and sediment samples							
Location	1	2	3	4	5	6 river water	6 sediment
Air temperature	24 °C	24 °C	24 °C	24 °C	23 °C	23 °C	23 °C
River water temperature	12 °C	12 °C	12 °C	12 °C	12 °C	12 °C	12 °C
GPS coordinates	N43.676765 E19.015765	N43.666504 E18.973296	N43.597469 E18.851106	N43.629139 E18.968890	N43.666070 E18.976347	N43.664808 E18.972116	N43.656008 E18.968466

To ensure the reliability of the results, appropriate quality procedures were taken. Recovery values for metals in spiked samples ranged from 89 % for Cr to 110 % for Zn. Double distilled water was used throughout the complete experimental work and the reagents were of analytical grade purchased by Merck (Darmstadt, Germany).

Before the sieving and homogenization process, the sediment samples were air-dried for two weeks. Each homogenized sample was transferred to a sieve, and sieved for 5 min, at about 150±3 vibrations/min. The sediment fraction with a diameter of 0.063 mm was used for the analysis of heavy metals in the sediment.

In order to determine the metal content in the sediment of the Drina River, the following procedure was applied: 1.5 g ± 0.10 mg of the sediment sample was weighed. All samples were prepared in triplicate to ensure analytical quality control of the results. A blank sample was also prepared, and the blank sample was treated in the same way as the samples were treated. The samples were transferred to glass beakers and 15 mL aqua regia (HNO_3+3HCl) and 5 mL of hydrogen peroxide (30 % H_2O_2) were added. After digestion at temperatures below 100 °C, the samples were filtered on a blue strip filter paper, then the samples were quantitatively transferred into a measuring vessel of 50 mL. Measuring vessels were filled with double distilled water up to the mark and transferred to polypropylene bottles until further analysis.

The content of Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in different river water and sediment samples of the Drina River was determined by atomic absorption spectrometry, flame technique (FAAS), using an AA240FS atomic absorption spectrometer (Varian, Australia).

3. RESULTS AND DISCUSSION

The concentration of eight heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn) in river water and sediment samples of Drina River was determined, and the results are presented in Figures 1 and 2. The results were compared with the values given in Rulebooks (1, 2, and 3) given in Table 2. Moreover, the obtained results have been compared to the results obtained in the studies of the rivers Bosna [11], Trstionica [12]and Spreča [13]in Bosnia and Herzegovina. The studies are carried out by Kevilj-Olovčić et al. (2018), Delibašić et al. (2020) and the Center for Ecology and Energy in Tuzla (2016), respectively.

Table 2. Limit values for metals in surface water and sediment

Legal framework	Cr	Cu	Mn	Fe	Ni	Cd	Pb	Zn
	(mg/L)							
Rulebook 1*	0.5	0.3	1.0	1.0	0.5	/	0.2	1.0
Rulebook 2**	0.5	0.3	1.0	2.0	0.5	0.01	0.2	1.0
	Cr	Cu	Mn	Fe	Ni	Cd	Pb	Zn
	(μg/g)							
Rulebook 3***	50	50	/	/	30	0.5	50	100

**Rulebook on limit values of dangerous harmful substances of water that after purification from the public sewage system is discharged into a natural receiver [14];*
***Rulebook on limit values of hazardous harmful substances for technological wastewater before its discharge into the public sewage system or into another receiver [15];*
****Rulebook on the determination of permitted amounts of harmful and hazardous substances in the soil and methods of their testing [16].*

Manganese in the water samples (52.6 μg/L) of Drina River was determined only in the sample from location 2, while the concentration in the other samples was not detected by using FAAS. Moreover, Mn content in sediment samples of Drina River was the highest (773 μg/g) also in the sample from location 2, and the lowest (242 μg/g) in the sample from location 3. If we compare the obtained results with the results for the river water of Trstionica and Bosna, we observe the following: the concentration of Mn determined in the river water of Trstionica (0.024 mg/L) is higher compared to results for River Drina (except for sample from location 2). Mn concentration in Bosna River (0.007 mg/L to 0.128 mg/L) is slightly higher compared to the Mn concentration values in Drina River. Manganese concentration in Spreča River sediment samples ranged from 724.6 μg/g to 941.7 μg/g. By comparing the results of this study with the results for the River Spreča it can be seen that the Mn concentration values in Spreča River sediment samples are higher compared to the Mn concentrations in the Drina River samples.

The highest **copper** content in the river water (148 μg/L) and sediment (493 μg/g) samples of the Drina River was determined at location 2, and the lowest Cu concentration was found in the river water sample (3.1 μg/L) from the location 5. The lowest Cu content (14.10 μg/g) in sediment samples was determined in the sample from location 3. Compared to the river water of River Trstionica, where the concentration of Cu ranged from 0.06 mg/L to 0.61 mg/L, lower results were obtained for River Drina, except for the sample from location 2. The results for River Bosna are higher compared to the results of this study, Cu concentration in the Bosna River ranged from 0.074 mg/L to 0.112 mg/L. Copper concentration in Spreča River sediment samples ranged from 58.4 μg/g to 69.3 μg/g. In comparison with the results of this study, the results for Spreča River are higher, except for the sample from location 2. The concentration of Cu in Drina River sediment samples does not exceed the limit values, except for the sample from location 2.

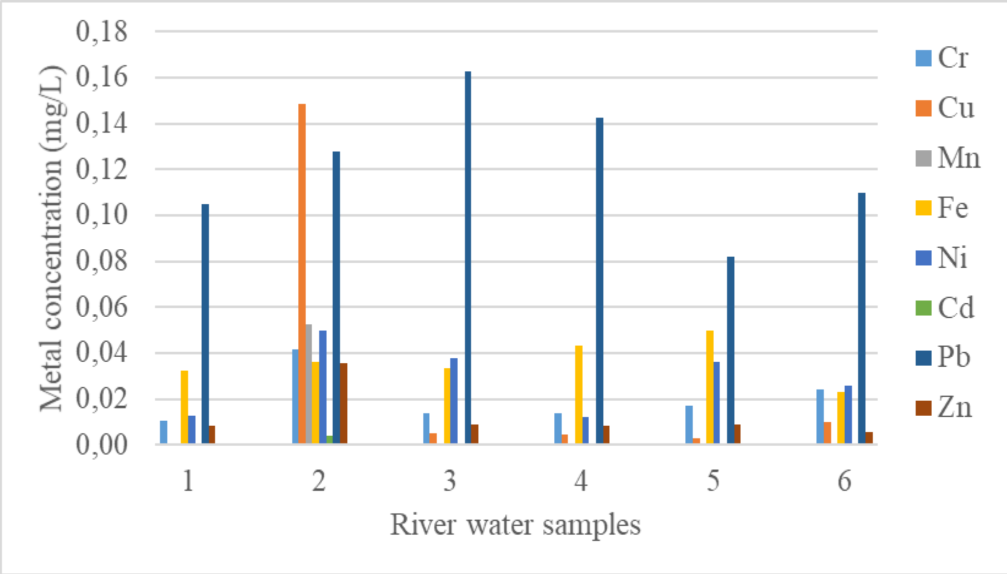

Figure 1. Heavy metal concentrations in surface water samples from Drina River, BiH

The highest **chromium** content in river water (41.5 µg/L) and sediment (290 µg/g) samples of Drina River was found at location 2, and the lowest in river water (13.8 µg/L) from location 3, while in the sediment, the lowest content (17.3 µg/g) was determined in the sample from location 1. By comparing the results of this study with the results for the River Trstionica (in all samples it was below the detection limit except for the sample taken from the location Brežani-0.006 mg/L) and Bosna (0.05 mg/L) it can be noted that the concentration of Cr is higher in Drina River in relation to the Trstionica and Bosna rivers. The obtained values were compared with the Cr results for the Spreča River sediment samples (400.5 µg/g to 890.2 µg/g). The Cr content values in the Spreča River sediment samples are significantly higher than the results obtained in this study. The limit value according to Regulation 3 for Cr is 50.00 µg/g, and the value obtained at location 2 is almost 6 times higher.

The highest **iron** content in river water (43.4 µg/L) and sediment (1649 µg/g) samples of Drina River was found in the sample from location 4. The lowest Fe concentration in river water (23.3 µg/L) was found at location 6, while the lowest Fe content in the Drina River sediment sample (1584 µg/g) was from location 1. The concentration of Fe in the water samples of the River Trstionica ranged from 0.04 mg/L to 0.21 mg/L, which are higher values for Fe compared to the results of this study. The results for Bosna River (0.13 mg/L-0.92 mg/L) are higher in comparison to the results obtained in this study.

The highest concentration of **nickel** and **cadmium** in water samples (Ni: 49.7 µg/L; Cd: 3.8 µg/L) of the Drina River was in the sample from location 2, and the lowest Ni concentration in the sample from location 4 (11.9 µg/L), while Cd was not detected by FAAS in water samples from the locations of 1, 3, 5 and 6. The contents of Ni (49.6 µg/g) and Cd (1.60 µg/g) in the sediment samples of the Drina River were the highest in the sample from location 6. The lowest content of Ni and Cd (Ni: 28.10 µg/g; Cd: 0.60 µg/g) in the sediment samples is found at location 3. Ni concentrations found in Drina River were higher compared to the values (below the limit of detection) obtained for the Trstionica River. The concentration of Cd in the water samples of Drina River does not exceed the limit values given in Rulebook 2. The concentration of Ni in the sediment samples of Spreča River ranged from 94.6 µg/g to 322,5 µg/g. The Ni concentration values in Spreča river sediment samples are significantly higher compared to the Ni content in the Drina River sediment samples. The Ni content in the sediment samples of

Drina River exceeds the limit value given by Rulebook 3, except for the sample from location 3. The limit value for Cd was exceeded in all sediment samples of Drina River.

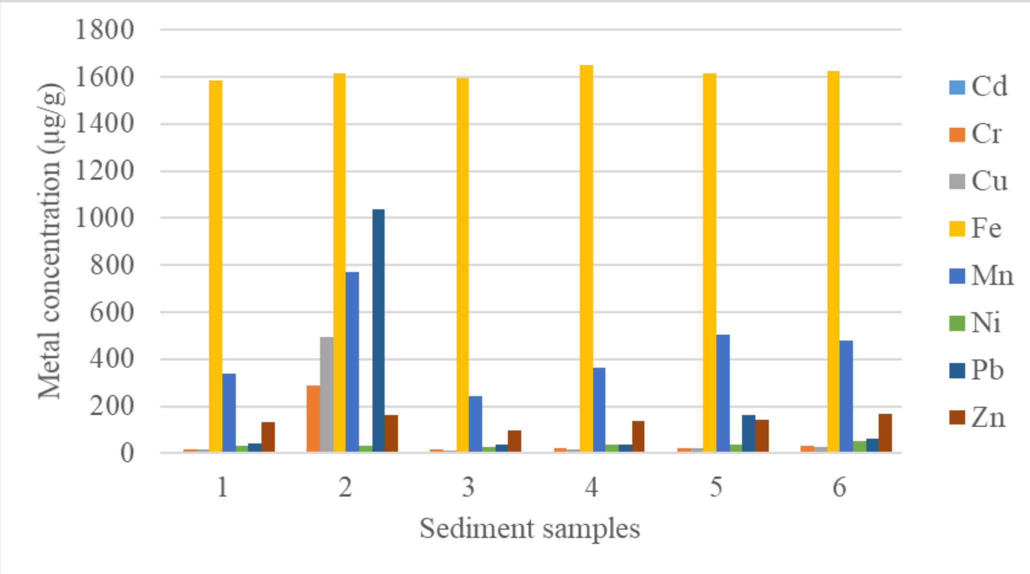

Figure 2. Heavy metal concentrations in sediment samples from Drina River, BiH

The highest concentration of **lead** in water samples (162.9 µg/L) of Drina River was in the sample from location 3, and the lowest concentration (82.2 µg/L) was in the sample from location 5. While the Pb content in the sediment samples (1037 µg/g) of Drina River was the highest in the sample from location 2, and the lowest (36.90 µg/g) in the sample from location 4. Pb concentrations in water samples of Drina River are significantly higher than Pb concentrations in water samples of the Trstionica River (0.04 mg/L-0.21 mg/L) and Bosna River (0.004 mg/L-0.009 mg/L). The Pb concentration in sediment samples of Spreča River (20.5-25.1 µg/g) is much lower compared to the values of Pb content in Drina River sediment. The Pb content exceeded the limit value in samples from locations 2, 5, and 6.

The highest **zinc** concentration in Drina River water samples (35.4 µg/L) was in the sample from location 2, and the lowest concentration (5.8 µg/L) was in the sample from location 6. Zn content in the Drina River sediment was the highest (166 µg/g) in the sample from location 6, and the lowest (98.20 µg/g) in the sample from location 3. Compared to the water samples of River Trstionica (0.004 mg/L-0.07 mg/L) and Bosna (0.0003 mg/L-0.035 mg/L), the obtained Zn values in River Drina are lower. The Zn concentration in Spreča River sediment samples ranged from 87.1 µg/g to 100.2 µg/g. By comparing the results for the Drina and Spreča rivers, it can be seen that Zn concentrations determined in the Spreča River samples are lower compared to the Zn content values for Drina River. The Zn content in all samples was higher than the limit value, except for the sample from location 3.

4. CONCLUSION

The concentrations of the examined heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) did not exceed the limit values in river water samples, while for Cd, Ni, Pb, and Zn they exceeded the limit value in almost all sediment samples (for Ni and Zn the sample from location 3 did not exceed the limit value, for Pb the sample from location 4 did not exceed the limit value). In the river sediment, Fe is the most abundant, along with Mn, which could be expected considering that they occur in nature in the form of various ores and minerals. The content of heavy metals in water samples compared to the content of heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) in the sediment of Drina River is quite low. It is necessary to carry out additional research with the aim of determining the heavy metal contamination of the river water and sediment of River Drina in Bosnia and Herzegovina.

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