



Preliminary Analysis of Heavy Metals Content in the River Bosna Upstream and Downstream from the Industrial Plants in Zenica and Pollution Assessment

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Abstract: This paper presents the results of an analysis of monthly average contents of ten heavy metals in the flow of the river Bosna.. The amount of toxic heavy metals, Pb,As,Cd,Hg and in addition, potentially harmful metals such as Cr, Ni, Zn, Cu, Mn, Fe was determined in order to assess the influence of industry in Zenica on the quality of the river Bosna. Samples were collected during the period of three months: November of 2010, January and February of 2011, during the normal water level of river Bosna. The sampling sites were chosen upstream and downstream from the industrial plants in Zenica with the aim of determining the influence of industrial complexes, mainly ArcelorMittal Zenica, on the quality of the water in river Bosna. The rating of the level of pollution in the river Bosna is based on the comparison of concentrations of heavy metals from the results of the analysis with the highest allowable concentrations of heavy metals by individual classes of water, MRL. The results showed that the industrial waste in Zenica has no significant influence on increase of heavy metals' concentrations in river Bosna above the maximum allowable concentration for waters of I and II classes. The results showed increased mercury content in the river Bosna, not only in the downstream flow from the industrial complex in Zenica but also from the above of mentioned plants.

INTRODUCTION

Serious pollutants of natural waters include heavy metals. Special attention for the protection of the environment should be given to heavy metals which are toxic to living organisms. The following toxic heavy metals are present in natural waters: cadmium, lead, arsenic and mercury. Arsenic is a metalloid that is classified as a toxic heavy metal due to its extreme toxicity. However, the content of heavy metals in natural waters is generally low except iron, due to their low representation in the lithosphere and pedosphere, thus, they are called micronutrients. Water pollution by heavy metals occurs due to intensive industrial development,

ecosystems because of their high toxicity and tendency to accumulate. If heavy metals get into the water, accumulate in aquatic organisms, bacteria, hydrophytes, invertebrates and fish, through the food chains, they can get to land plants, animals and humans. The content of heavy metals in river bottom sediments is often used as an indicator of their anthropogenic pollution (Frankowski et al. 2008). If contaminated water is used for irrigation of agricultural land, heavy metals can also accumulate in soil and crop plants through which they can be further involved in a cycle, or in to the food chain, and cause different environmental consequences.

The use of cultivated plants from such soil for human and animal nutrition can threaten the health of people and animals. Some kinds of toxic sediments kill benthic organisms, reducing the food available to larger animals such as fish (Begum et al. 2009). The presence of heavy metals in contaminated water bodies may pose a threat to the existing ecosystem of an area as a whole (Nongbri et al. 2012).

Due to the increasing pollution of heavy metals and their toxic effects, many countries in the world have adopted strict regulations regarding allowable values for concentrations of heavy metals in the water used for drinking, fish cultivation and irrigation of agricultural land in order to protect human health. One of the biggest anthropogenic sources of environmental pollution with heavy metals is the metal industry. We should not forget mining, transport, urban waste, etc. (Bikić and Omerović, 2012). Inadequately treated industrial waste water discharged into rivers is a potential danger of pollution of rivers with heavy metals. The atmosphere is an important mean of transporting heavy metals. Soil is often polluted with heavy metals emissions whose origin could be hundreds of miles away. Metals are usually present in the atmosphere in the form of aerosol particles. Aerosols remain in the atmosphere usually for 10 to 30 days from where they deposit into water and soil. They are rapidly diluted and precipitated as insoluble carbonates, sulfates and sulfides at the bottom of the water system. When the adsorption capacity of sediments is exhausted, the concentration of metal ions in water increases (Goletić, 2005). Metals may exist in water as reversibly bound to inorganic anions or to organic compounds as metal complexes, or they may be present as organometallic compounds containing carbon-to-metal bonds (Stanley, 2003).

EXPERIMENTAL

The main objective of the research was to analyze the content of toxic heavy metals, Pb, As, Cd, Hg, and harmful and potentially harmful heavy metals Cr, Ni, Zn, Cu, Mn, Fe in the river Bosna.

Water samples were collected with appropriate access and possible places for sampling water from the river Bosna from following locations:

- Kamberovića Polje, under the bridge near the hotel Dubrovnik,
- Fifty meters under the main wastewater discharges from an industrial zone where ArcelorMittal Zenica is located,
- Fifty meters above the main wastewater discharges from an industrial zone where ArcelorMittal Zenica is located,
- Banlozi, under the railway bridge, about 2.5 km from the location of the last discharge of industrial zone of ArcelorMittal Zenica.

Samples from these locations were collected two meters from the shore and in the depth of half a meter. Water sampling was carried out at 4 locations, during the three months, four times a month. Samples were collected in November of 2010, January and February of 2011,

during the periods with normal water levels of the river Bosna. After sampling, the samples were properly stored in the chemical laboratory of the Faculty of Metallurgy and Materials. Water samples were filtered through filter paper "black tape". Then super pure HNO_3 was added to the samples in order to achieve a concentration of 0.2% HNO_3 (Somenath, 2003; PerkinElmer, 1996). For the preparation of calibration curves, standard metals from PerkinElmer producer were used.

Analysis of the samples of examined heavy metals was carried out in the chemical laboratory of the Faculty of Metallurgy and Materials on the device: "Atomic Absorption Spectrophotometer, Perkin Elmer, AAnalyst 800". Analysis of the majority of metals, Pb, As, Cd, Cr, Ni, Cu, Mn, Zn and Fe in part was done by graphite furnace technique. Zinc and iron were analyzed with graphite furnace technique and flame techniques. Mercury was analyzed by Flow Injection Mercury/Hydride technique.

RESULTS AND DISCUSSION

Results of the analysis of heavy metals on defined locations given in Table 1 are calculated as the mean of the concentrations of heavy metals measured in different months.

Relative standard deviation (RSD) was calculated for all data, amounted to a maximum value of 3%. Rating of the level of pollution in the river Bosna is based on the comparison of concentrations of heavy metals from the results of the analysis with the highest allowable concentrations of heavy metals by individual water classes MRL (Uredba o opasnim i štetnim materijama u vodama, 2007; Uredba o klasifikaciji voda i voda obalnog mora Jugoslavije u granicama SR BiH 1990).

Table 1. Metal concentrations in Bosna river (μgL^{-1})

Location	Element	Mean concentrations by month, μgL^{-1}			MRL, μgL^{-1}
		Nov.	Jan.	Feb.	
A	Cr	1,19	1,57	2,42	1-6
B		1,06	1,88	1,92	
C		5,03	3,42	3,07	
D		1,20	2,27	1,88	
A	Ni	1,87	1,04	0,85	15-30
B		1,36	0,90	1,20	
C		0,69	0,30	0,60	
D		0,91	0,88	1,16	
A	Mn	51,73	43,18	44,63	50
B		38,63	53,93	62,65	
C		1,38	1,46	3,38	
D		30,87	40,61	61,90	
A	As	2,50	1,02	0,95	50
B		1,72	1,22	1,07	
C		0,18	0,20	0,00	

D		1,51	1,19	1,47	
A	Cd	0,04	0,65	0,01	0,5
B		0,10	0,54	0,02	
C		0,02	0,02	0,01	
D		0,11	0,04	0,01	
A	Pb	0,74	1,55	0,00	2
B		0,89	1,50	0,00	
C		0,20	0,20	0,00	
D		0,10	0,65	0,00	
A	Hg	0,48	0,67	0,57	0,02
B		0,19	0,35	1,40	
C		0,00	0,51	0,51	
D		0,16	0,75	1,04	
A	Fe	159,00	133,00	78,12	100
B		153,00	124,5	83,61	
C		144,50	91,50	98,10	
D		170,00	107,00	72,50	
A	Cu	1,33	10,87	1,29	2-10
B		0,85	1,08	1,65	
C		0,88	0,29	1,09	
D		1,33	0,96	0,46	
A	Zn	7,50	6,91	2,08	50-80
B		27,00	41,93	34,13	
C		13,5	11,11	0,61	
D		15,00	9,75	1,12	

Comparison of the heavy metal concentrations obtained from the performed analysis with MRL results show that the concentrations of certain heavy metals in certain locations and in certain months were higher than MRL of water I and II class. Specified overruns of concentrations are shown in Table 1 in the bold.

As Table 1 shows, the maximum allowable concentration for water I and II class exceeded in the case of following elements: Mn, Cd, Hg, Cu and Fe. With the exception of mercury, listed overruns of other elements are sporadic and are not as dangerous as it is the case with iron.

Mercury concentrations in all tested locations of the river Bosna exceeded the maximum permissible concentration for water I and II class. The results showed that downstream of the industrial complex in Zenica, specifically downstream of the plant ArcelorMittal Zenica, concentrations of heavy metals were not significantly altered in comparison to concentrations of these heavy metals in upstream from the industrial zone. As conclusion, the most of the measured values are within an allowable limits for water of I and II class.

CONCLUSION

Based on the results, we may draw two general conclusions:

1. Industry in Zenica has no significant influence on increasing concentrations of heavy metals in the Bosna river above the maximum allowable concentration for water of I and II class,
2. Mercury concentrations in all tested locations of the river Bosna exceeded the maximum permissible concentration for water I and II class.

Confirmation of the first conclusion comes out of comparison of the results of analysis of heavy metals in locations A, B, C and D.

Mercury concentrations were increased not only in the downstream flow of the industrial complex in Zenica but also at the upstream location of mentioned plants. Increased levels of mercury are caused by industrial plants upstream from Zenica. As the mercury and its compounds are very dangerous to a human health, the issue of mercury in the river Bosnia should be given a special attention.

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Summary/Sažetak

U ovom radu su dati rezultati analiza sadržaja deset teških metala u dijelu toka rijeke Bosne. Analiziran je sadržaj toksičnih teških metala, Pb, As, Cd i Hg, zatim štetnih i potencijalno štetnih teških metala Cr, Ni, Zn, Cu, Mn, Fe u cilju utvrđivanja uticaja industrije u Zenici na kvalitet rijeke Bosne. Uzorci su prikupljeni tokom tri mjeseca, u novembru 2010. godine, te u januaru i februaru 2011. godine, pri normalnom vodostaju rijeke Bosne za navedeno doba godine. Za uzorkovanje su izabrane lokacije ispod i iznad industrijskog kompleksa grada Zenice s ciljem utvrđivanja uticaja industrijskog kompleksa, prvenstveno kompanije ArcelorMittal Zenica na kvalitet rijeke Bosne. Ocjena stepena zagađenja rijeke Bosne ispitivanim teškim metalima je vršena na osnovu poređenja koncentracija navedenih teških metala iz rezultata dobivenih analiza s najvećim dozvoljenim koncentracijama teških metala po pojedinim klasama voda, MRL. Rezultati pokazuju da industrija u Zenici ne utiče značajno na povećanje koncentracije ispitivanih teških metala u rijeci Bosni iznad maksimalno dopuštenih koncentracija za vode I i II klase. Rezultati pokazuju povećan sadržaj žive u rijeci Bosni i to ne samo na toku nizvodno od industrijskog kompleksa u Zenici nego i iznad navedenih postrojenja.