THE LONG-TERM IMPACT OF HEAVY METALS FROM THE BOSNA RIVER ON HUMAN HEALTH

Aida Šapčanin
University of Sarajevo, Faculty of Pharmacy
Sarajevo, B&H

Farzet Bikić
University of Zenica, Faculty of Metallurgy and Technology
Zenica, B&H

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ABSTRACT
Heavy metals can enter into rivers through industrial and consumer waste, activities of acidic rain to soils, etc. Long-term exposure can result in damaging: mental and nervous function, blood composition, lungs, kidneys, liver, and other vital organs. Estimating a health risk based on the contents of heavy metals found in river Bosna was the aim of this study. The hazard coefficient (HQ), non-carcinogenic hazard index (HI), and carcinogenic risk (RI) have been calculated. Overall, HQ and HI did not show direct risk to human health from heavy metals in the investigated area; however, these levels should be monitored in a long-term perspective.

1. INTRODUCTION

1.1. Health risk assessment

The scientific aspects of risk assessment refer to the preparation of the protocols on which an assessment will be based. The application of risk assessment is carried out through risk management, i.e. by adopting specific measures to reduce risk, by adopting regulations, and by making decisions on risk acceptability. The risk assessment itself ensures the transition between scientific knowledge and social needs. It is based on the probability of an undesirable event and the intensity of the consequences of such an event [1]. Because of the above, HQ and HI are usually calculated, as well as non-carcinogenic and cancerogenic risk [2]. As with the water quality standard approach, a quantitative health risk assessment is a parameter-based approach that involves studying each component in the water separately. It is based on: the presence of harmful substances and microorganisms in the water; acceptable and infective doses; estimations of the exposure of the water users. Using these data, the health risk can be calculated and compared with the risk that is could be acceptable. Modeling techniques based on quantitative risk assessment allow quite accurate estimations of exposure and risk, provided the necessary input data are available. In the case of a chemical risk assessment, hazard identification consists of finding the components in the water that are hazardous and are present in sufficiently high concentrations to adversely affect health [2,3,4]. Furthermore, an investigation is being carried out into the harmful effects of chemicals on humans and on the environment. In the past, numerous new chemicals were released into the environment without estimating their consequences to humans and nature. Today, it is necessary to examine the toxicity of newly synthetized chemicals before commercial production. Additionally, international organizations have been created to identify and investigate potentially toxic chemicals, in order to minimize their harmful effects.

1.2. Heavy metals impact human health

Heavy metals in water, cause a certain effect, which may be beneficial or toxic depending on their concentration variation in the aquatic system. Heavy metals such as lead (Pb), arsenic (As), copper (Cu), antimony (Sn), mercury (Hg), and cadmium (Cd) reach the environment from anthropogenic and natural sources. Therefore, they can be found in soil, water, air, food chain, vegetable, and animal foods [4,5]. The biggest polluters of the environment are lead, zinc (Zn), iron (Fe), cadmium (Cd), molybdenum (Mo), As, cobalt (Co), manganese (Mn), and Hg, and their main sources are industrial production, metal processing, roads, vehicles, pigments and batteries [5,6,7]. Burning of fossil fuels leads to pollution of the atmosphere with particles of heavy metals and by their deposition, they pollute water, soil, plants, and fish [2,3,4,5]. Once absorbed by the body, heavy metals continue to accumulate in vital organs like the brain, liver, bones, and kidneys, for years or decades causing serious health consequences [4,6]. Some metals like Cu, Co, and Zn are essential for normal body growth and functions of living organisms and are referred to as essential elements. Other elements are referred to as non-essential, high concentrations of these metals like Cd, Cr, and Pb are considered highly toxic to human and aquatic life [6,7]. Cr(III) is much less toxic than Cr(VI). The respiratory tract is also the major target organ for Cr(III) toxicity, similar to Cr(VI). Cr(III) is an essential element in humans. The body can detoxify some amount of Cr(VI) to Cr(III). The respiratory tract is the major target organ for Cr(VI) toxicity, for acute (short-term) and chronic (long-term) inhalation exposures [4,5,8,9]. Like Cr, Co is also one of the required metals needed for normal body functions as a metal component of vitamin B12. However, high intake of Co via consumption of contaminated food and water can cause abnormal thyroid artery, polycythaemia, over-production of red blood cells, and right coronary artery problems [10,11]. All of these are reasons for the necessity of assessing the impact of heavy metals on human health.

2. MATERIAL AND METHODS

a) The research area

The Bosna River is 273 km long, 1-3 m deep (up to 10 m deep in the springs), and 35-170 m wide. It narrows the most between Maglaj and Doboj. Its banks are 1.5 to 6 m high and are partially overgrown with forest and bushes. It creates waterfalls and rapids in several places. Its average drop is 1.48 m/km, and the average water flow is about 100 m^3/s. The highest water level is in the period March-May and November, and the lowest is in August and September. Surprisingly, it is also one of the few large Balkan rivers without hydroelectric power plants or large dams. The Bosna River Valley is the most populated area of Bosnia and Herzegovina and is home to almost a million inhabitants as well as the industrial center of the country. The settlements along river Bosnia are of the road type, in some places quite sparse. In the Bosna valley are the cities of Sarajevo, Visoko, Kakanj, Zenica, Zavidovići, Žepče, Maglaj, Doboj, Modriča, and Bosanski Šamac.

b) Sample collection

To evaluate the health risk posed by heavy metals (Cd, Pb, Cr, Ni, Cu, Zn, Co, and As) five representative water samples were collected from selected locations of river Bosna (Fig.1.) four times during 2022 in the different season (winter, spring, summer, and autumn) and analysed by using a graphite furnace atomic absorption spectrometry [10,11,12]. Samples were taken from selected locations of Sarajevo (43°49'04.8"N 18°16'08.4"E), Visoko

(43°59'27.2"N 18°10'58.5"E), Kakanj (44°08'10.2"N 18°04'50.5"E), Zenica (44°12'45.6"N 17°54'58.8"E), Maglaj (44°32'36.7"N 18°05'59.6"E) and Doboj (44°43'15.0"N 18°05'36.0"E). Samples were collected at a depth of 0-1 m, and stored in 500 mL PTE bottles with the addition of 2 mL 1% HNO_3 (for stabilization of heavy metals) prior to analysis.

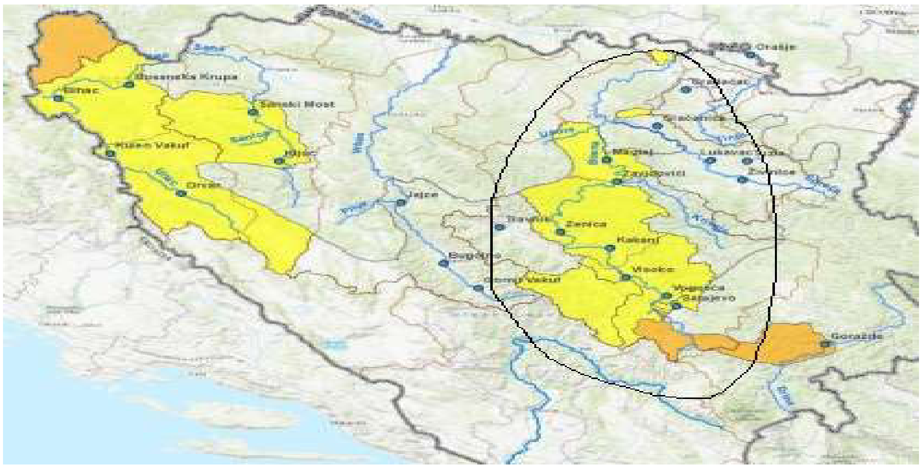

Figure 1. The Bosna river valley

c) Potential health risk assessment and correlation analysis
Furthermore, the potential health risk assessment was calculated for a lifetime of exposure (ingestion, inhalation, and dermal) based on USEPA model [2,3,4,5,13,14], also cumulative carcinogenic and non-carcinogenic risks were determined. The value of the total hazard index (HI) is calculated for minimal content of heavy metals for children and adults [10,15,16]. Correlation between determined heavy metals was calculated [15].

2.1. Non-carcinogenic Risk Assessment
Non-carcinogenic and carcinogenic effects of heavy metals were estimated by using equations, as follows:

$$ADDing = Cw\ X\ \frac{IngR\ X\ EF\ X\ ED}{BW\ X\ AT}\ X\ 10^{-6}$$

1)

$$ADDinh = Cw\ X\ \frac{InhR\ X\ EF\ X\ ED}{PEF\ X\ BW\ X\ AT}$$

(2)

$$ADDder = Cw\ X\ \frac{SA\ X\ AF\ X\ ABS\ X\ EF\ X\ ED}{BW\ X\ AT}\ X\ 10^{-6}$$

(3)

Where: ADDing - Average daily doses (mg/kg per day) via ingestion; ADDinh - Average daily doses (mg/kg per day) via inhalation; ADDder - Average daily doses (mg/kg per day) via dermal contact; *C*w is the concentration of selected heavy metals in the water sample; *IngR* is the ingestion rate; *InhR* is the inhalation rate*; ED* is the exposure duration; *EF* is the exposure frequency and *BW* is the body weight of children and adults given; *AT* is the average time for both adults and children; *SA* is the surface area of the skin exposed to heavy metals.

$$HQ = \frac{ADD}{RfD} \quad (4)$$

$$HI = \sum_{k=1}^{n} HQ_k = \sum_{k=1}^{n} \frac{ADD_k}{RfD_k} \quad (5)$$

Where: HQ – Hazard quotient; HI-hazard index; RfD – Chronic reference dose (mg/kg per day) of specific heavy metal. According to the USEPA [13] classification, at HI < 1, the non-carcinogenic risk of the exposed individuals occurs within the acceptable range. At HI > 1, the non-carcinogenic heavy metals are potentially harmful to human health. Values of RfD among the health risk assessment model parameters for each heavy metal are listed in [3,5, 13].

2.2. Carcinogenic Risk (RI) Assessment

Due to the lack of available values for the slope factors (SF), we only estimated the carcinogenic risk for exposure to metals whose concentrations were the highest measured in the tested samples.

$$Risk_{pathway} = \sum_{k=1}^{n} ADD_k\, CSF_k \quad (6)$$

Risk –unitless probability of an individual developing cancer over a lifetime;
ADD_k- Average daily intake (mg/ kg per day) for kth heavy metal
CSF_k – Cancer slope factor (mg/ kg day)$^{-1}$ for heavy metal

$$Risk_{total} = Risk_{ing} + Risk_{inh} + Risk_{der} \quad (7)$$

$Risk_{ing}$, $Risk_{inh}$, and $Risk_{der}$ are risks contributions through ingestion, inhalation, and dermal pathways. The assessment is based on the following: If RI < 10^{-6}, the carcinogenic risk to health can be considered as negligible; If the RI is in the range of 1×10^{-6} to 1×10^{-4}, then these values are within the acceptable risk for human health, and If RI > 10^{-4}, then there is a high risk for the development of cancer in humans.

3. RESULTS AND DISCUSSION

The obtained results of noncarcinogenic children's health risk, based on metal concentrations in river water and exposure by three different pathways (ingestion, inhalation, and dermal) are shown in Figure 2.

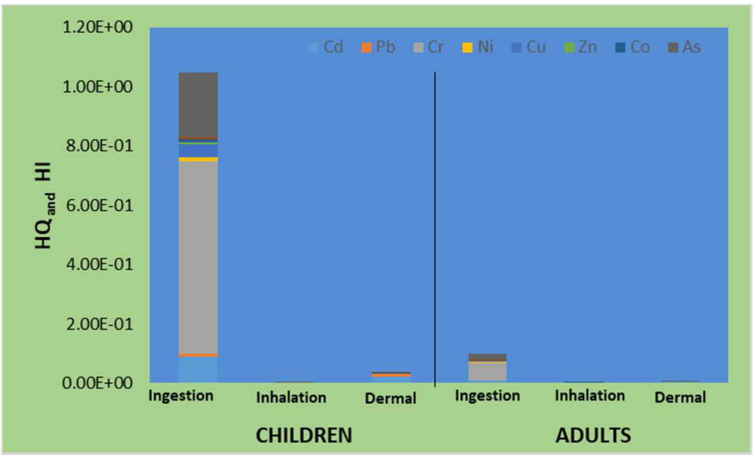

Figure 2. The hazard coefficient (HQ) and hazard index (HI)

The obtained results of carcinogenic children's health risk, based on metal concentrations in river water and exposure by three different pathways (ingestion, inhalation, and dermal) are shown in Figure 3.

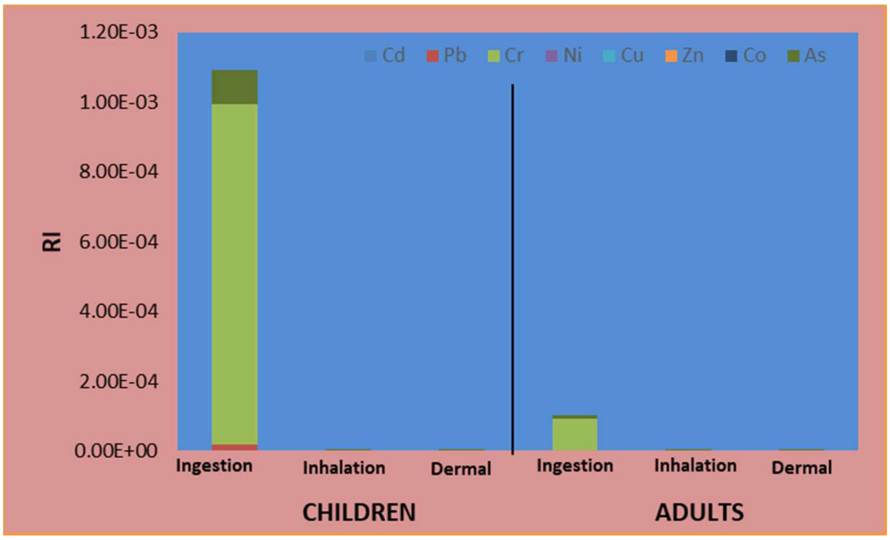

Figure 3. The carcinogenic risk estimation

Generally, results showed that ingestion and dermal are the main pathway of contamination by heavy metals from river water. Some foreign authors did not calculate HI, HQ, and RI for inhalation exposure hypothetically [15,16]. As same as to the HI values, the RI values for children were also higher compared to the values for adults. The RI value for adults was less than 10^{-6}, which indicates that the carcinogenic risk of Pb, Cr, and As in water could be neglected. However, the RI value for children indicates an acceptable risk to human health. These results suggest that children have a higher health risk than adults posed by heavy metals exposure. Similar conclusions were stated by other authors [5,6].
The correlation between investigated heavy metals was calculated and shown in Table 1.

Table 1. Pearson correlation coefficients of heavy metal concentrations in the river water

	Cd	Pb	Cr	Ni	Cu	Zn	Co	As
Cd	1							
Pb	0.13039	1						
Cr	0.07519	0.163246	1					
Ni	0.678469	-0.29651	0.594147	1				
Cu	-0.36986	-0.44097	-0.4469	-0.39615	1			
Zn	-0.33704	-0.84015	0.259798	0.318862	0.313788	1		
Co	0.643337	0.776055	0.307002	0.249959	-0.41714	-0.75662	1	
As	-0.03827	0.802859	0.59441	-0.08652	-0.24538	-0.41015	0.663672	1

Based on a statistical analysis of the contents of the eight heavy metals in the river water, in the study area, the correlation between the various heavy metals was analyzed, and the Pearson correlation coefficient was calculated. The results shown in Table 1 reveal that the correlations between the heavy metals were different, and higher correlation coefficients ($r > 0,7$) between certain elements suggest similar sources. These results could indicate that their concentration changes are very similar and that the sources and migration paths of these elements could be the same [15].

4. CONCLUSION

This study gives a short view of the inorganic pollution levels and health risks posed by heavy metals in river water, and the health risks assessment should be a priority considering the continuous increase in heavy metals and general environmental pollution globally in water, air, and soil. The risk assessment, especially in industrial and populated regions, such as the watercourse of the river Bosna, needs to be carried out periodically. This will enhance proper monitoring and ensure the safety of adults especially children who are more vulnerable to the toxicity of heavy metals. RI calculations suggest that children have a greater health risk than adults for exposure to potentially contaminated water.

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