

Heavy Metal Pollution of Water Sources "Šićki Brod" and "Studenac" Due to the Exploitation of Coal

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Abstract – The article aims to determine the levels of water pollution by concrete measurements of heavy metals in the water sources "Šićki Brod" and "Studenac". Sampling of water from both sources as well as analysis of the content of the heavy metal elements in the water was carried out. All analyzed elements are classified into the group of heavy metals, which take second place (after pesticides) in terms of harmful effects if found in the environment. Heavy metals are ecologically very important because they are non-degradable and do not disappear, but move through the ecosystem and have a normal biogeochemical cycle. Considering the mining works that were carried out in the area near to source, the impact of mining works on the pollution of water sources was put into comparison.

Keywords – heavy metals, water sources, surface mining, pollution, ecology, mining.

1. Introduction

Water is the driver of life and makes up about 71% of the Earth's surface. By definition, water is a colorless, tasteless and odorless liquid.

DOI: 10.18421/SAR71-02

<https://doi.org/10.18421/SAR71-02>

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Received: 06 February 2024.

Revised: 11 March 2024.

Accepted: 18 March 2024.

Published: 27 March 2024.

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However, such water does not exist in nature. Already in the atmosphere where water droplets form rain or snow, water dissolves various particles and gases from the atmosphere and changes its natural properties. Already at that stage, the water is as pure as the atmosphere itself. When water in the form of rain or snow reaches the surface of the land, it picks up with its solubility many substances that are on the surface [19].

On a global scale, today humanity is faced with the appearance of an apparent disappearance of water due to heavy pollution. It can be concluded that the daily consumption of water amounts to only 10% of the total amount of water in rivers and lakes. Although humanity is well supplied with water, today about 25% of the world's population lacks water, and approximately 60% of the world's land does not have enough fresh water. Of the total amount of water on the planet Earth, 97.5% is salt water. It is estimated that only 1% of fresh water or 0.007% of the total amount of water on planet Earth can be used for human needs [13], [14].

Increased water consumption has led to an increase in the amount of waste water, the discharge of which into rivers and lakes leads to intense pollution. Due to the continuous pollution of surface water, in the future it is expected that the amount of hygienically correct underground water, which is most often used for drinking, will decrease [5], [15]. Bosnia and Herzegovina (BH) is one of the rare countries in Europe and the world, which has significant reserves of clean drinking water. But in recent years, a tendency towards a constant decrease in the quality of both surface and underground water has been observed. If these facts are taken into account, it becomes clear that water is a first-rate development factor for BH and one of the key natural resources.

The formation of the composition of natural waters occurs as a result of the interaction of water with the environment-minerals, soil and atmosphere.

The following processes take place: dissolution of compounds, chemical interaction of substances with water and aqueous solutions, biochemical reactions and colloid-chemical interactions [6], [14]. Environmental pollution with heavy metals can cause direct consequences for human health. The main polluters of natural waters with heavy metals are: manure, municipal waste water, use of municipal sludge in agriculture, flood waters rich in metals, plant protection products, mining processes and other anthropogenic sources [11].

Mining has important impact in economic development of country and on the environment. Active and abandoned mines may have negative impact on ecological systems [1], [6]. With exploration of mineral ore, it is possible to damage the ecological environment around the mine [3], [7]. Waste realized by mining processes is potential sources of contamination since they can consist toxic metals. The water resources are weakest point with big probability of contamination by the mining operations [12], [15]. Surface water and groundwater can be contaminated because of sinking of ground, erosion, sedimentation, mine drainage, and rainfall. Drainage at mines is the biggest threats to water resources, with impacts on rivers, and lakes. Pollutants released during mining operations contaminate water sources that lead to health impacts on humans, animals, and flora [4], [5], and [18]. All those factors are well known worldwide, causing big change in approach to solving the imposed problem from policy makers as well as researchers [8], [9], [14].

Some of elements such as Cd, Pb, Mn, and Zn are heavy metals that can be occurred in water with characteristics of their long-term existence, toxic and non-degradable. Some mining operations make consequences for the waters even long after the mines are close [2], [6], and [15]. These sites need to be controlled and managed for decades after they've been shut down [7], [17]. Environmental damages caused even after closed mine is hard to treat because they realized for a very long time [10].

2. Materials and Methods

As stated above, the importance of the existence of quality drinking water for the entire living world is immeasurable. From this difference, it is necessary to have a good knowledge of the influencing factors on the pollution of drinking water sources. In addition to the cause of pollution, it is necessary to collect information on the type and amount of heavy metals in water as the biggest factor of negative impact on human health as well as on plant and animal life.

2.1. Harmful Substances in the Hydrosphere

An essential parameter in process of defining of the quality of natural waters is the content of trace metals. The basic division of metals in the water is into toxic and non-toxic. Some metals, such as Hg, Cd and Pb, are already toxic, while some, such as Zn and Cu, at their natural concentrations, are essential, that is, very important factors in the physiological functioning of living organisms, and regulate many biochemical processes. However, the same metals, if present in increased concentrations, can have different toxicological effects on living beings [3], [14], and [18].

Natural concentrations of trace metals strongly depend on the area in which they are found, i.e. the composition of rocks and soil [2], [12]. An important fact about trace metals is that they are not (bio)degradable, but only change from one form to another, i.e. from living matter to non-living matter and vice versa [4].

2.2. Water Pollution

The term "polluted water" means water that has changed its original composition. Pollutants enter natural waters from various sources, of which industrial and municipal wastewater, washing of agricultural land and waste disposal sites have the greatest impact. Although there are numerous possibilities for the classification of chemical pollutants, they can be divided into: inorganic (nitrates, phosphates), organic (petroleum and its derivatives, pesticides, detergents), heavy metals (cadmium, mercury, lead, etc.) and radioactive [6], [7]. Water quality is assessed according to three groups of indicators: physical, biological and chemical. The most common pollution in water is chemical pollution, pesticides, coal and oil phenols, heavy metals (lead, copper, chromium, cadmium, mercury and zinc) [2], [15].

2.3. Origin and Ecological Properties of Heavy Metals

Metals, depending on their toxicity, can be affiliated to one of the groups. The first includes metals that are toxic regardless of their concentration, (lead, cadmium, mercury). The second (arsenic, bismuth, antimony, etc.) are toxic just if their concentration is higher. The third group (copper, zinc, cobalt, selenium and iron), are toxic only above a precisely determined concentration [8], [1], and [16].

Anthropogenic sources of heavy metals are manure, municipal waste water, use of municipal sludge in agriculture, flood waters rich in metals, plant protection agents, etc.

Some industrial and mining operations are responsible for negative impact on environmental [8]. They are one of the basic anthropogenic activities that could result in contamination with PTEs [14], [20].

Heavy metals can be accumulated in mineral resources, and after releasing pollutants into the environment, as a result of rainfall, snow, etc. [16], [17]. The chain of heavy metal contamination originating from anthropogenic sources almost always flows in the biogeochemical cycle: atmosphere - soil - water - plants - animals - man [6], [12]. They quickly break down in water and settle as hard-to-dissolve carbonates, sulfates or sulfides. The concentration of metal ions in the water increases with decreases of possibility of adsorption. Particular toxicity is exhibited by compounds of mercury, lead, chromium and selenium [7], [21]. In order to improve the degree of protection of regional surface and underground waters, it is necessary to have a good knowledge of the sources of pollution as well as the complete properties of pollutants [12], [19].

3. Experimental Part

In order to analyze the quality of the source of water in the immediate vicinity of the closed mine, it is necessary to apply a proven and acceptable methodology that refers to the methods of collecting samples, testing them, and analyzing the obtained results, and finally comparing the obtained values with the values prescribed by the world organization of the European Union and by national rulebook.

3.1. Study Area

The water source of the "Šićki Brod" is located in the western part of the city of Tuzla, and was found during the construction of the main road Tuzla – Orašje (Figure 1). The approach to the spring is from the main road, and from the lake, which was created after the coal mining at the Šićki Brod surface mine, which gave the spring its name. Due to the proximity of mining operations, it is particularly important to determine the content of heavy metals in relation to the "Studenac" location, which is somewhat further away from this water source.



Figure 1. The water sources "Šićki Brod" and "Studenac"

The water source "Studenac" is located in the western part of the city of Tuzla. The water source was found after the end of World War II (Figure 1). The source is located in the immediate vicinity of individual residential buildings. The local community did not arrange this source according to adequate regulations.

3.2. Methods and Instruments for Sampling and Testing

The rulebook for laboratory analysis of drinking water prescribes the method of taking samples and methods of bacteriological, virological, biological, parasitological, physical-chemical, chemical and radiological analysis and super-analysis of drinking water. Table 1 presents the maximum allowed concentrations of heavy metals.

Table 1. Maximum allowed concentrations of heavy metal

Heavy metal	Rulebook BH	EU Directive	WHO Guidelines
As	0,01	0,01	0,01
Cu	0,10	2,00	2,00
Cd	0,005	0,005	0,003
Al	0,2	0,2	0,2
V	0,005	0,005	0,005
Co	-	-	-
Cr	0,05	0,05	0,05
Fe	0,2	0,2	0,2
Mn	0,05	0,05	0,5
Ni	0,02	0,02	0,02
Pb	0,01	0,01	0,01
Zn	5,0	-	3
Se	0,01	0,01	0,01

3.3. Determination by Atomic Adsorption Spectrometry

The first atomic adsorption spectrometry (AAS) was assembled in the laboratory of A. Walsh (Figure 2).



Figure 2. AAS AANALIST 200

The sample is introduced into the flame of a temperature ranging from 2400 to 2700°C, excites the atoms of element, and by returning them to their basic state, light of a certain wavelength is emitted, which is measured on the detector and translated into an electronic signal. The signal is read using a detector that is an integral part of the device. The gases used by AAS are: acetylene, nitrogen-suboxide, compressed air, hydrogen and oxygen. Its software automatically calculates the calibration curve from the signal intensity of the calibration standards and the blank test with the correction of the measured signals to "background", and then from the thus obtained curve it recalculates the concentration of the tested element from its signal intensity.

3.4. Determination by Optical Emission Spectrometry

Determination of nickel, manganese and thallium by optical emission spectrometry on an instrument of inductively coupled plasma ICP-OES model Optima 2100 DV, company Perkin Elmer. The device is shown in Figure 3.



Figure 3. ICP-OES, model OPTIMA 2100 DV

The ISP-OES instrument was invented by Stanley Greenfield (1964) and has become an important analytical tool for the determination of about 75–90 elements from various matrices. Inductively coupled plasma (ICP) is a stream of highly ionized argon that passes through the magnetic field of a coil. Plasma develops temperatures of 8000–10000°K. The technique used by ICP to measure samples is optical emission spectrophotometry (OES). When we put the sample into the plasma, electrons are excited. When returning to the basic state, light of a certain wavelength is emitted, this is measured on the detector. The gases used by ICP are argon, nitrogen and compressed air.

4. Results

The analysis of the samples taken for the analysis of water from the sources "Šićki Brod" and "Studenac" was done in the Geo-ecology Laboratory of the Faculty of Mining, Geology and Civil Engineering in Tuzla, using the previously mentioned instruments. The analysis determined the concentrations of the following heavy metals in the water: aluminum, arsenic, copper, lead, cadmium, cobalt, manganese, nickel, chromium, iron, selenium, vanadium and zinc. Concentration of aluminum and iron in two water sources and maximum allowed concentrations is presented in Figure 4, and for vanadium and cadmium in Figure 5.

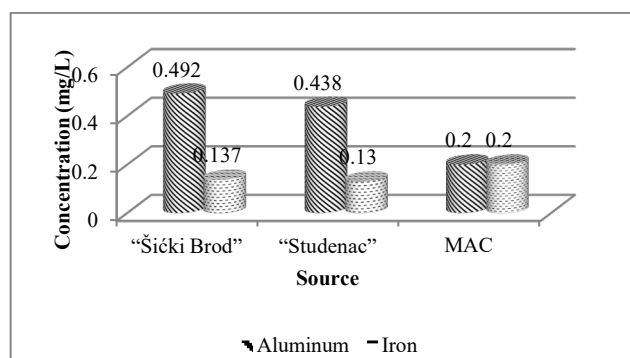


Figure 4. Concentration of aluminum and iron

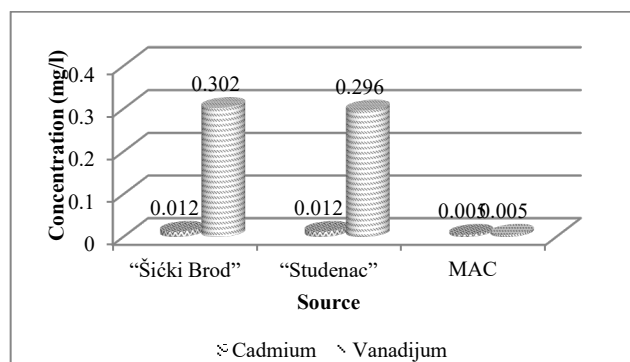


Figure 5. Concentration of vanadium and cadmium

Concentrations of tree heavy metals (arsenic, lead and selenium) and MAC for those are presented in Figure 6.

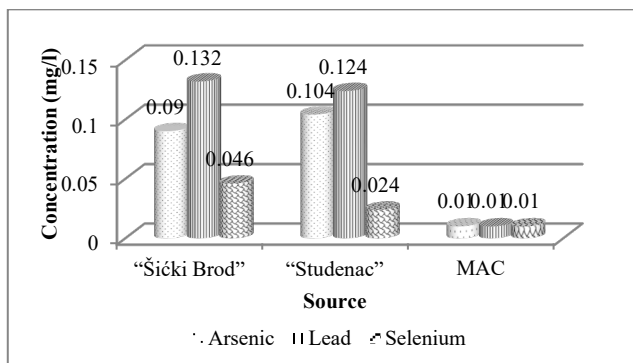


Figure 6. Concentration of arsenic, lead and selenium

Concentration of cobalt and nickel is presented in Figure 8, and copper and zinc in Figure 9.

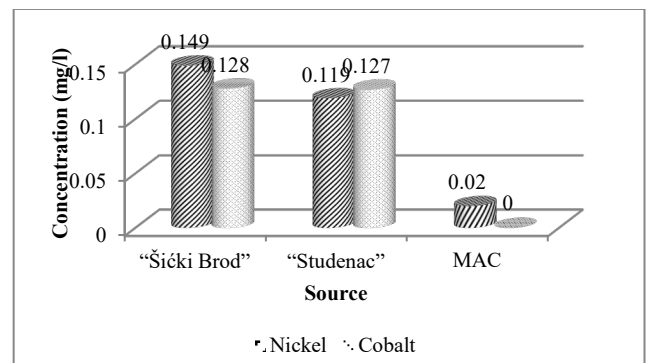


Figure 8. Concentration of cobalt and nickel

Figure 7 shown contributions of chromium and manganese in related water sources.

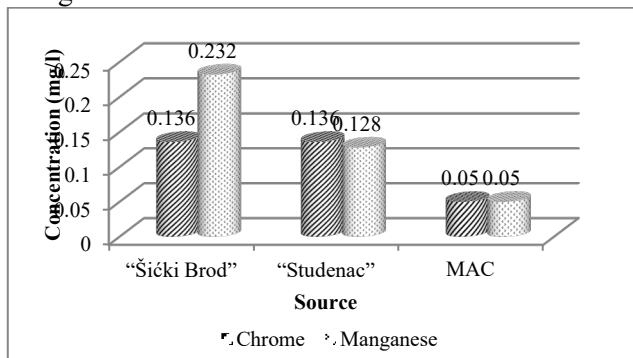


Figure 7. Concentration of chromium and manganese

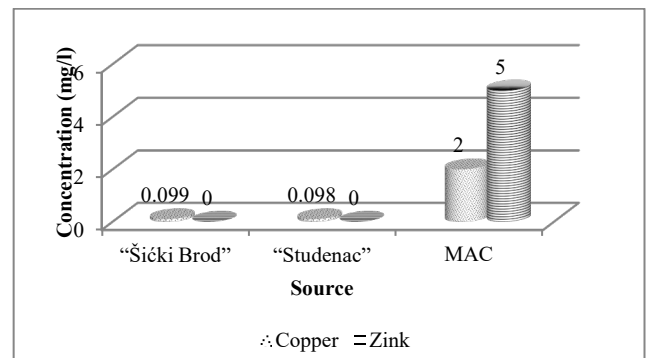


Figure 9. Concentration of copper and zinc

Figure 10 presents the distribution of the concentration of heavy metals in two sources of drinking water, as well as the distribution of their MAC.

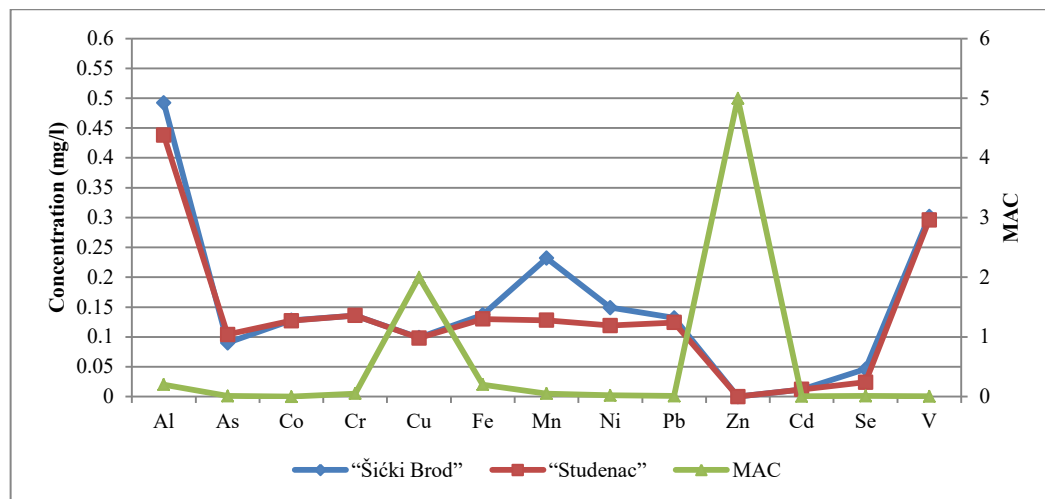


Figure 10. Concentration of heavy metal in water sources

5. Discussion

The presence of any metal in natural spring water through MAC has negative consequences for human health [20], [21]. According to all the obtained values of water analysis from the source for the determined metals, it is evident that out of 13 metals, only 3 metals (copper, zinc and iron) have concentrations

that are within the MAC limits and meet the values prescribed in accordance with the Rulebook on natural mineral and natural process waters from 2010.

All of these 13 metals, which were found by laboratory testing in the sources of "Šićki Brod" and "Studenac" with higher concentrations than allowed, can significantly endanger the health of citizens.

Based on the harmful effects of certain metals and the complications that their presence in water can cause to human health, it is necessary to inform citizens about these effects through various forms of education, but that the competent services of the Municipality actively inform and warn citizens about the incorrectness of that water and the prohibition of its consumption [13], [20].

6. Conclusion

Water conservation is important because the need for quality water in the world is rapidly increasing, threatening to become a limiting factor in the further development of our civilization.

Water pollution means any qualitative and quantitative change in the physical and biological properties and composition of water. The problem of environmental pollution with heavy metals is becoming more and more pronounced. Heavy metals are introduced into the organism of animals and humans through contaminated soil and growing plants, then contaminated water and air.

The introduction of regulations on the permitted concentrations of heavy metals in emissions into the atmosphere, the effective implementation of technical and technological measures for their reduction and the consistent implementation of monitoring ensure a reduced quantity of heavy. The presence of any metal in natural spring water through MAC has negative consequences for human health.

According to the obtained values of water analysis from the springs "Šićki Brod" and "Studenac", it can be observed that out of 13 analyzed metals, only 3 metals (copper, zinc and iron) have concentrations that are within the MDK limits and meet the values prescribed in accordance with the Rulebook. All analyzed metals with concentrations above the permitted levels can significantly endanger the health of citizens who consume this water every day.

The analysis of the collected data for two springs indicates the fact that the abandoned/closed surface coal mine does not have a significant effect on water quality because the parameters of the metal content in the spring in the immediate vicinity of the mine are similar as in the spring that is far from the former mining operations. The existence of heavy metals can be linked to other influencing factors, such as the composition of the soil itself and other industrial and agricultural activities in the immediate environment, as well as the impact of pollution from the thermal power plant located in the immediate vicinity of these two sources.

It is to be expected that the obtained research results will be a good starting point for all institutions in the chain of responsibility when making decisions for the improvement of environmental protection, with special reference to the way mining activities are carried out and the application of laws and good practices in the process of mine closure, which may have an impact on the protection of drinking water sources.

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