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Original article

Heavy Metals and Their Toxic Effect in the Water of the River Bregava, Bosnia and Herzegovina

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Abstract
Water is one of the basic, necessary conditions for the survival and development of living organisms on Earth. Any deviation of water quality from prescribed physical, chemical and biological characteristics of drinking water can be considered as pollution and contamination. Heavy metals as parameters of water quality should indicate the degree of contamination of watercourses with polluting substances as a consequence of anthropogenic influence, their dependence on climatic conditions, as well as their toxicity from an ecological point of view. In this paper, the concentrations of heavy metals in the water of the Bregava River were analyzed at eight localities in four seasons, when the water level of the river is different, and the anthropogenic influence on their concentration was analyzed. The concentration of toxic elements in the environment is determined by the amount that entered the environment, but also by the processes that influence their further fate. The experimental values for the heavy metals Cr, Pb, and Mn do not deviate from the MAC (Maximum Allowable Concentration) for surface water, based on which it is estimated that the analyzed heavy metals have no toxicological impact on the aquatic ecosystem of the Bregava River or on humans.

Keywords: ***Heavy metals, pollution, toxicity, concentration, climatic conditions.***

1. Introduction

Water represents one of the most important raw materials without which life on planet Earth would not be possible. Pollution endangers the biological balance of aquatic and terrestrial ecosystems, and depending on the amount and type of pollution, they can also call into question their survival.

Bregava is a river, a left tributary of the Neretva. Its catchment area lies between the Neretva in the west and Trebišnjica in the southeast and has an area of 722.4 km2. Bregava originates from the permanent springs of Bitunja and Hrgud and the periodic springs of Mali and Veliki Suhović. The town of Stolac was built on the bed of the river Bregava, which creates numerous waterfalls, waterfalls and ada with its diverging course. Downstream from Stoca Bregava receives the tributary Radimlje. The river turns to the west and receives the tributary Strk, then splits into two main branches: one goes to Čapljina, and the other larger one goes to the town of Klepci, where it flows into the Neretva. Bregava flows into the river at 7m above sea level. The length of the stream is 31 km, with an average drop of 3.7 m/km. The biological importance of the water of the Bregava River is manifested by the large number of living organisms that live from the river, whether they are in it or in its immediate vicinity. The living world of the Bregava River is diverse and represents one of its most important characteristics.

Ecotoxic metals are metals that are "poisonous" to the living world in their dissolved phase. It is more accurate to use the term "trace metals" or "trace metals" because their natural concentrations are very low (< 1µg/L), and it is said that they are found in nature only in traces [1]. When their concentrations increase (most often anthropogenically) and become dangerous for the living world of the aquatic environment, the term "ecotoxic metals" is the most appropriate. Metals in water are always naturally present, and their concentration is regulated by natural processes. The concentration of metals in the aquatic environment strongly depends on the area in which it is located, i.e. the composition of rocks and soil. Therefore, for each characteristic area, the natural level of metal traces is determined individually and is valid for the given conditions. The range of natural concentrations of trace metals ("background level") ranges from several micrograms to less than 1 nanogram per liter [1]. Water pollution with ecotoxic metals due to human activities (transport, agriculture, industry, municipal wastewater...) becomes a serious environmental problem, because metals are not biodegradable and once introduced into the environment they become a permanent part of it. Thus, the concentrations of ecotoxic metals are a very important parameter in the assessment of the quality of natural waters, and the limit values for the concentration of ecotoxic metals are listed in table 1. In order to be able to determine the anthropogenic impact on a river water system, we need to know its natural composition from source to mouth. Following the literature, we have witnessed that for the last thirty years, published concentrations of trace metals in natural waters have been decreasing. Unfortunately, the reason for this is not that the waters are becoming cleaner, but with the development of instruments and analytics, we are able to measure ever lower concentrations of trace metals [2]. Heavy metal toxicity can reduce energy levels and damage the functioning of the brain, lungs, kidneys, liver, blood composition and other important organs [3]. Long-term exposure can lead to gradual progression of physical, muscular and neurological degenerative processes that mimic diseases such as multiple sclerosis, Parkinson's disease, Alzheimer's disease and muscular dystrophy [4]. Repeated and long-term exposure to some metals and their compounds can even cause cancer [5]. Even if they do not have any biological function, the toxic effects of these metals remain in some other forms that are harmful to the human body and its proper functioning. Limit values of heavy metal concentrations in surface waters are regulated by the "Decision on the categorization of surface waters, the official Gazette of the Federation of Bosnia and Herzegovina 01/14" [6].

Table 1: Values of parameters for the evaluation of the ecological state of water bodies (ecotoxic metals) of surface waters and their impact on human health [7]

Heavy metals	MAC (Maximum Allowable Concentration)	Limit values of surface water	Target organ	Clinical effects
Arsenic (As)	50 µg/L	0,1 mg/L	Lungs and nervous system, skin	Perforation of the nasal septum, cancer of the respiratory system, neuropathy, dermaomas, colic, cancer
Lead (Pb)	10 µg/L	0,5 mg/L	Nervous system, hematopoietic system, kidneys	Encephalopathy, peripheral neuropathy, central nervous system, anemia
Lame (Cr)	50 µg/L	0,5-2,0 mg/L	Pulmonary	Ulcer, perforation of the nasal septum, cancer of the respiratory system
Nickel (Ni)	20 µg/L	0,5 mg/L	Pulmonary skin	Cancer dermatitis
Copper (Cu)	2 mg/L	0,5 -1,0 mg/L	Kidneys, nervous system	Wilson's disease
Iron (Fe)	200 µg/L	200 µg/L	Cardiovascular and immune system, skin	Alzheimer's disease, anemia
Manganese (Mn)	50 µg/L	2 mg/L	Nervous system	Central and peripheral neuropathy
Mercury (Hg)	1µg/L	0,001 mg/L	Nervous system, kidneys	Proteinuria

2. Material and Methods

Developing an adequate sampling plan is the most critical step when organizing water monitoring studies, including in this research, where accessibility to sampling locations is also very important (**Table 2**). By going out into the field, localities for sampling were also selected. Accordingly, 8 locations were selected where in situ measurements were performed, followed by water sampling for laboratory analysis and determination of the concentration of selected heavy metals.

Table 2: Coordinates of localities where samples were taken for analysis

Locality	Geographic latitude	Longitude
1	43°07'21.28"	18°04'27.43"
2	43°07'93.39"	18°01'51.86"
3	43°08'75.61"	17°96'05.34"
4	43°07'92.79"	18°01'52.31"
5	43°09'17.09"	17°96'44.61"
6	43°08'31.55"	17°95'64.31"
7	43°08'00.05"	17°94'48.44"
8	43°08'40.28"	17°94'05.47"

Sampling was carried out in accordance with valid regulations and sampling methods [8] and good professional practice. Given that the results of the examination depend on the method of sampling [9,10], the water was taken according to hygienic requirements.

The localities where the sampling was carried out are marked with numbers from 1 to 8 on the situational map taken from Google Earth (**Figure 1**) with a brief description as follows:

Locality 1 - sample of surface water at the source of the river;
Locality 2 - sample of surface water below the hydropower plant;
Locality 3 - surface water sample in front of the restaurant;
Locality 4 - sample of surface water behind the restaurant;
Locality 5 - sample of surface water after pouring in precipitation and part of sewage water;
Locality 6 - sample of surface water below the inflow of the complete city sewage system;
Locality 7 - surface water sample in front of the slaughterhouse;
Locality 8 - surface water sample behind the slaughterhouse;

After delivery to the laboratory, the samples were analyzed for heavy metals. Determination of Cr, Fe, Mn, Pb content in water was performed on an optical emission spectrophotometer, which works on the principle of inductively coupled plasma - type ICP - OES OPTIMA 2100 DV, manufactured by Perkin-Elmer USA with the use of standard solutions for the tested elements of the same company. Sampling of surface water from selected localities and analysis of heavy metals was carried out during four seasons and the results will be presented through four seasons.

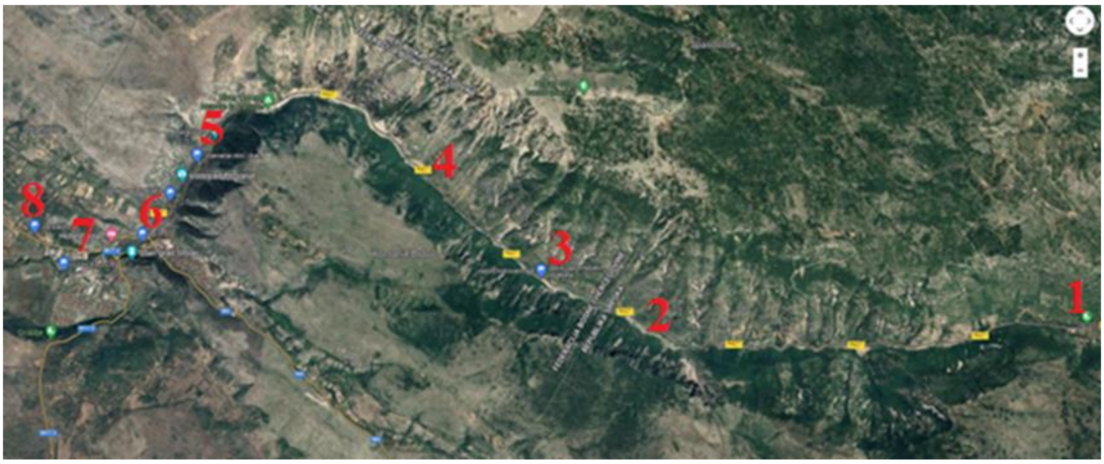

Figure 1: Situational map of the researched area

3. Results and Discussion

In the rest of the text, the basic toxicological properties of heavy metals (chromium, lead, iron and manganese) that were detected in the analyzed water samples of the Bregava River, starting from the source of the river and in four different seasons, when the water level of the river is different, are described. Also, a graphic representation of how far the obtained experimental values deviate from the MAC for surface water is given, based on which it is estimated whether the analyzed heavy metal will have a toxicological impact on humans. Chromium is carcinogenic, mutagenic and teratogenic [11,12]. Toxicity due to exposure to chromium in different media (air, water and sediment) is generally associated with the content of Cr (VI), which is known for its negative impact on health and the environment and for its extreme toxicity (it is 1000 times more toxic than trivalent chromium) [13].

The mechanism of toxicity depends on the pH value. Inside the cell, Cr (VI) is reduced to Cr (III) which further forms complexes with intracellular macromolecules, including genetic material and is ultimately responsible for the toxic and mutagenic capacity of chromium.

Health effects associated with exposure to hexavalent chromium include diarrhea, stomach and intestinal bleeding, cramps, and liver and kidney damage. Hexavalent chromium is a strong oxidant. When dissolved, chromic acid is formed, which corrodes the organs. It can cause convulsions and paralysis. The lethal dose is approximately 1-2 g. Most countries apply a legal limit of 50 ppb chromium in drinking water.

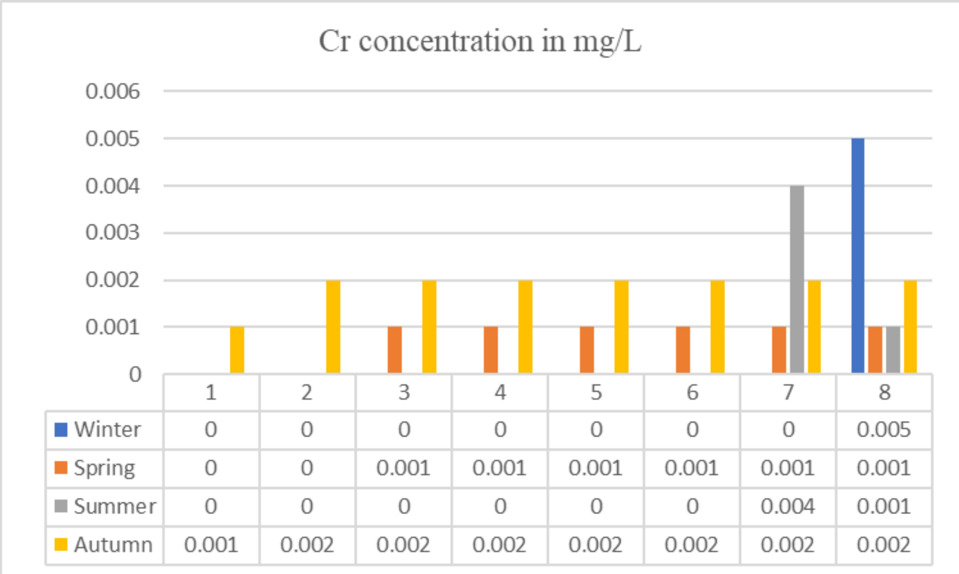

Figure 2: Chromium concentration in analyzed water samples at selected localities in four different seasons

Figure 2 shows that the total concentrations of chromium in the water of the Bregava River, in all localities and all seasons, are far below the MAC value for this metal in surface waters (below 0.5 mg/L). Experimental values for the concentration of this metal tell us that chromium, according to Limit values for the concentration of heavy metals in surface waters [7], does not have any negative toxicological effect on the water system of the Bregava River, the living world in the river itself, and therefore not on humans.

When it comes to the ecotoxic metal lead, it is toxic to all organisms. Generally speaking, organolead compounds are more toxic than inorganic lead components, and young, immature organisms are more sensitive to the effects of lead. After entering the body, lead is absorbed into red blood cells and successfully transported through the body, reaching all parts of the body. Lead is then stored as bound to metallothionein and in crystalline form in bone tissue (approximately 90% of absorbed lead). Even small doses of this metal cause neurotoxicity, probably as a result of competition with Ca2+ in nerve functions [14].

It is a systematic poison, which means that once it is absorbed into the circulatory system, it is transmitted throughout the body, seriously damaging human health.

It is most often introduced into the body through the consumption of contaminated food and water, and through the air. It is primarily accumulated in bone tissue, after which it is gradually released into the bloodstream.

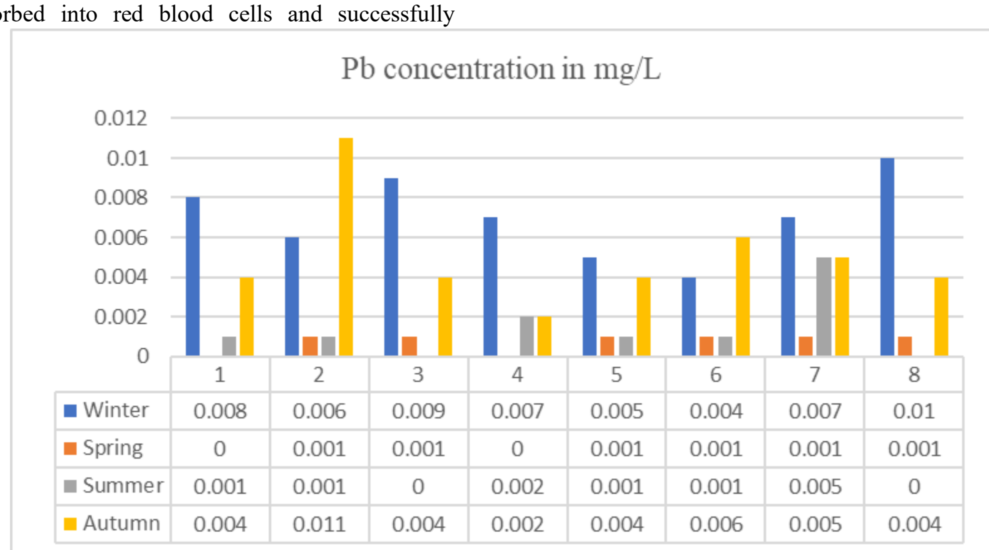

Figure 3: Lead concentration in analyzed water samples at selected localities in four different seasons

Figure 3 shows that the total concentrations of lead in the water of the Bregava River, in all localities and all seasons, are far below the MAC value for this metal in surface waters (below 0.5 mg/L). Experimental values for the concentration of this metal tell us that lead in the water of the Bregava River, according to Limit values for the concentration of heavy metals in surface waters [7], does not have any negative toxicological effect on the water system and the living world in the river itself, and therefore not on humans. Iron is an essential element widely distributed on earth. It plays an important role as a constituent of cytochromes and catalase, as well as proteins responsible for oxygen transport (hemoglobin and myoglobin). However, despite its vital importance for most living organisms, iron is potentially harmful at high concentrations. The effect of iron on aquatic organisms and their habitats is mostly indirect.

Iron hydroxide and Fe-humus precipitates, on biological and other surfaces, indirectly affect the organisms present, disrupting normal metabolism and osmoregulation, as well as changing the structure and quality of the benthic habitat and food source. In oxic conditions and a pH value close to neutral, Fe(II) easily undergoes oxidation and builds colloidal hydrated iron oxides, which can further form complexes with natural organic substances.

The iron cycle means the reduction of trivalent iron by organic ligands (a process that is photocatalyzed in surface waters) and the oxidation of divalent iron. Iron is often the limiting factor for aquatic organisms in surface layers. When there are no chelating ligands, water-insoluble iron(III) hydroxides are deposited. This is not thought to be dangerous to aquatic life, as little is known about the dangers of iron from water.

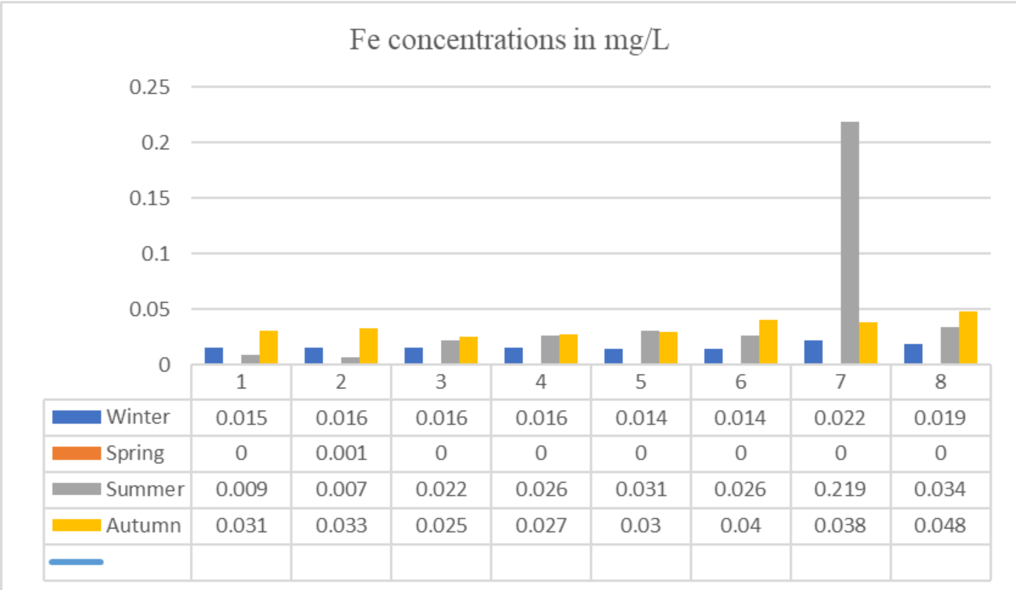

Figure 4. Iron concentration in analyzed water samples at selected localities in four different seasons

In Figure 4, it can be seen that the experimental values for the concentration of iron in the water of the Bregava River show that only in the summer period, and at locality number 7, we have an increased concentration of iron, i.e. a concentration above the MAC value, according to the Limit values for the concentration of heavy metals in surface waters [7]. The reason for the increased concentration is the result of the anthropogenic effect, since all city sewage, waste from septic tanks, stables, catering facilities come to the place of sampling number 7. Long-term exposure to this concentration can have a negative effect on the water system of the Bregava River, aquatic flora and fauna, and therefore on humans, because humans get most of the heavy metal load from the aquatic ecosystem through food (fish from the river).

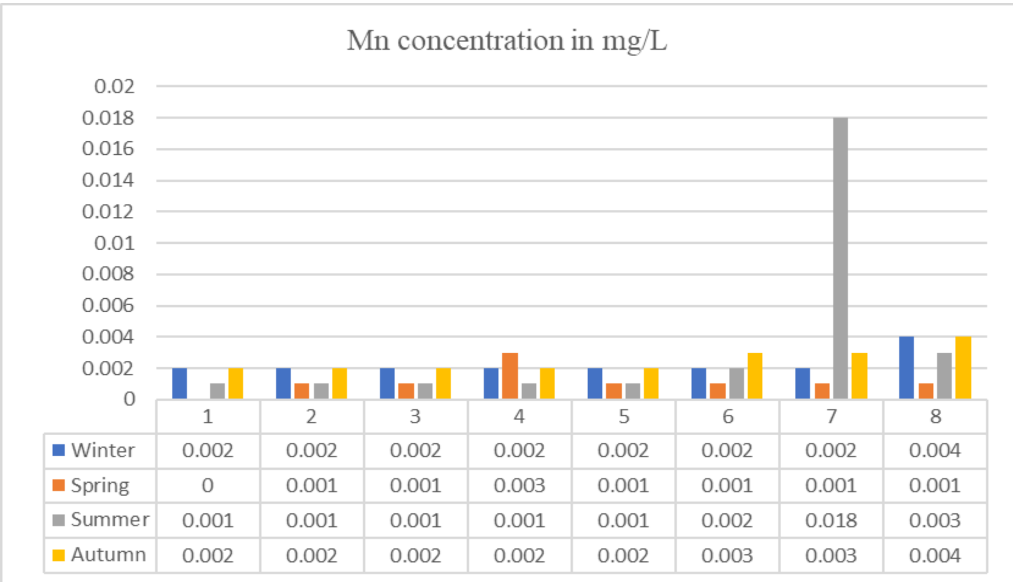

Figure 5. Manganese concentration in analyzed water samples at selected localities in four different seasons

Manganese has only recently become a subject of environmental concern [15]. Manganese is an essential element for all forms of life, and it accumulates in the body of fish primarily through nutrition. However, so far no one has pointed out any harmful effects in fish related to their exposure to manganese through nutrition. The acute toxicity of manganese in animals manifests itself primarily in the nervous system, that is, manganese acts as a neurotoxin, interfering with neurotransmission and affecting the level of enzymes in the brain.

Figure 5 shows that the concentrations of dissolved manganese in the water of the Bregava River, in all localities and all seasons, are far below the MAC value for this heavy metal in surface waters (below 2 mg/L) [7]. Experimental values for the concentration of this metal tell us that, according to the Limit values for the concentration of heavy metals in surface waters [7], it does not have any negative toxicological effect on the water system of the Bregava River, the living world in the river itself, and therefore not on humans.

Conclusion

The obtained results of the total concentrations of heavy metals confirm that the metal contents sampled in winter and spring are relatively lower compared to the values during the autumn and summer periods, which is a consequence of the climatic influence.

The analyzed heavy metals, Cr, Pb, Fe and Mn, if they are present in increased concentrations, can have different toxic effects on living beings within the aquatic ecosystem, and thus indirectly on humans, because humans at the top of the food chain receive most of the metal load from the aquatic ecosystem via of their food, especially where fish are present, so there is potential for considerable biomagnification.

The experimental values for the heavy metals Cr, Pb, and Mn do not deviate from the MAC for surface water, based on which it is estimated that the analyzed heavy metals have no toxicological impact on the aquatic ecosystem of the Bregava River or on humans.

Experimental values for the concentration of iron in the water of the river Bregava show that in the summer period, after the inflow of sewage water, we have an increased concentration of iron, i.e. a concentration above the MAC for surface water. Long-term exposure to this concentration can have a toxicological effect on the water system of the Bregava River and on human health.

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