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Physico–Chemical Properties and Some Heavy Metal Contents in Public Water Sources in Tuzla and its surrounding, Bosnian and Herzegovina

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Authors' contributions

This work was carried out in collaboration between all authors. Authors AC and AŠ designed the study and wrote the protocol while author AŠ wrote the first draft of the manuscript. Authors AC, AŠ, AK, ZH and IŠ managed the analyses of the study. Authors AC and AŠ managed the literature searches. All authors read and approved the final manuscript.

Original Research Article

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ABSTRACT

This paper presents the results of physico-chemical parameters and heavy metals (Cu, Zn, Pb and Cd) contents in water sources of public supply of Tuzla and the surrounding area, as alternative sources of water supply. The study area was divided into six (6) sampling sites and their respective position was detected using GPS device (MAGELLAN EXPLORIST 210). The heavy metals were determined using Atomic Absorption Spectrophotometry (AAS), While, the physico-chemical parameters (pH, electrical conductivity (EC), carbonate, total hardness, nitrate (NO₃ -N), nitrite (NO₂ -N), ammonia (NH₃ -N), KMnO₄ and chlorides were determined using standard methods. The heavy metal contents: Cu (1-6 µg/L) and Zn (1-2 µg/L). Pb was only detected Simin Han well water at 2 µg/L. Cd was below detection limits in all samples. The levels of Zn, Cu, Cd and Pb in Tuzla and its surrounding alternative drinking sources are within the permissible limits according to the Regulations on the safety of drinking water of Bosnia and

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Herzegovina and WHO. The physico –chemical properties of the water samples from the study area are within the recommended level of exposure, except for ammonia in the well of Miladije 2 and pH of Miladije 1. Concentrations of the investigated parameters in samples of drinking water alternative sources of public supply of Tuzla and its surrounding area within the allowed limits according to World.

Keywords: Heavy metals; drinking water; atomic absorption spectrophotometry; WHO; sources of public supply.

1. INTRODUCTION

As the most valuable natural raw material, water is essential for the survival of all living organisms. In addition water is required for industrial and technological development for the progress of mankind. Water is part of this daily life and it has no boundaries. Although the amount of water on Earth is significant, water available for human consumption is largely limited. About 70% of the surface of this planet is covered by water, of which 97.5% is salt water. The remaining 2.5% is fresh water and is suitable for human consumption, of which only 1% refers to water that can be used for drinking. 1% represents the total available quantity of water available to the whole of humanity to meet their needs [1]. The need for fresh water continues to rise due to the exponential growth of the population.

Heavy metals are one of the most important toxic pollutants that severely restrict the use of water in households and for industrial purposes [2]. The content of heavy metals in natural waters is generally low due to the low representation in the lithosphere and pedosphere (except Fe). The main sources of heavy metals in the water are atmospheric precipitation, geochemical sources, industrial discharges, sediments and soil drainage. Iron and manganese are common metallic elements that are found on the Earth's crust [3], that water releases through the soil and rock, dissolving minerals containing iron and manganese [4]. Heavy metals can be found in a variety of emission sources such as car exhaust. Exhaust gases are the main sources of lead as a pollutant [5], due to the use of leaded gasoline. Urbanization [6,7], the development of industry and agriculture (use of fertilizers and pesticides in agriculture) [4] have a negative impact on the environment such as water pollution.

Heavy metals are classified into two categories according to their nutritional role: *essential* (Co, Mo, Cu, Zn, Fe, Mn) and *non-essential* (Pb, Hg, Cd, As, Sb, Sr and Cr). The presence of non-essential metal is undesirable and the absence of essential elements in the human diet over a long period of time may leads to unusual metabolic process thereby precipitating many diseases. Heavy metals at higher contents exert toxic effects and if involved in the food chain, can pose a great threat to the health of animals and humans [8].

Population of Tuzla and its surrounding is supplied by drinking water from a central water supply system of Tuzla. The emergence of intermittent problems with the lack of water (summer restrictions) and quality of water (accidental pollution) from the central water supply system in the city territory, emphasizes the importance of public water sources as alternative sources of water supply. Water quality is a decisive factor in the possibility of its use, it is therefore necessary to determine the water quality and to evaluate the quality of the change in the future for each source. Quality control of water from the wells of public supply is not satisfactory, because the basic physico-chemical parameters are controlled, number of

tested samples is insufficient and analyzes are carried out periodically. The tested samples are not analyzed for heavy metals whose presence in water, in content higher than allowed is not desirable because they cause different diseases.

The aim of this paper was to determine the physico-chemical parameters and heavy metals (Cu, Zn, Pb and Cd) contents of public water sources in Tuzla and the surrounding area, as alternative sources of water supply.

2. MATERIALS AND METHODS

The map below represents Tuzla town and its surrounding areas viz: 1.Modrac; 2.Bistarac; 3.Miladije 1; 4.Miladije 2; 5.Par Selo and 6.Simin Han Fig. 1. Exact position and altitude was recorded for all sites using the Garmin GPS device (MAGELLAN EXPLORIST 210) and location of measurement points is indicated in Fig. 1.

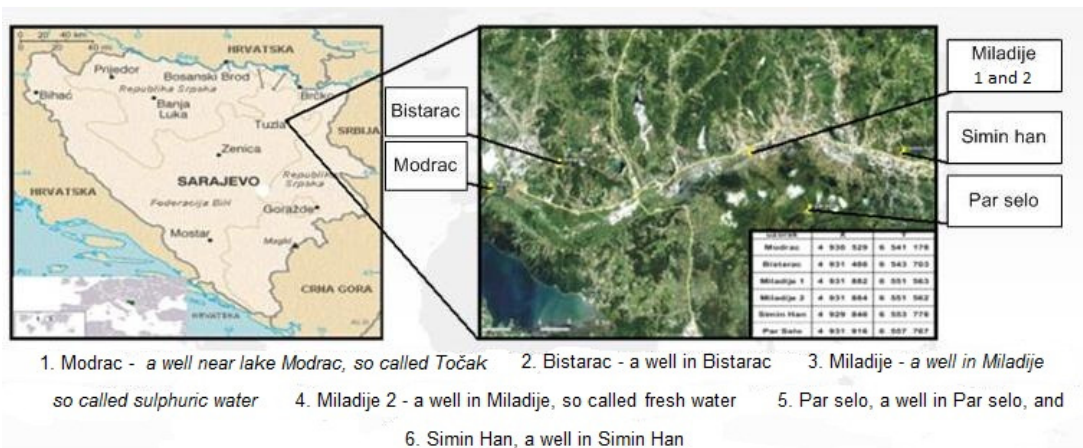


Fig. 1. Regional map of Bosnia and Herzegovina showing six sampling sites in Tuzla and its environs

The altitude of the site is different and ranges from 149.55 m (Modrac) to 270.51 m (Par selo). All the studied locations (except Modrac), in geological terms, belong to Tuzla basin. Sampling and analyses were carried out during the summer (July 21, 2009). Sampling was carried out using dry clean plastic containers (PVC bottles) 1.5 L in volume. Before sampling, bottles were washed three times minimum, using water for sampling, then filled to the brim and closed with plastic caps. Necessary labeling of samples and measuring temperature was done and then using a mini cooler of Italian manufacturer "Bravo 25" the samples were transported to the laboratory in a period of 1.5 h, where the analysis was carried out immediately. Analyses implied determination of organoleptic characteristics, determining the physico-chemical water quality parameters and the determination of heavy metals using AAS. Before analysis, all the instruments were calibrated according to the manufacturer's instructions. Accurate determination of *pH* was performed potentiometrically by a *pH*-meter WTW InoLab 730. Electrical conductivity was determined by the conductometer instrument WTW LF 318. Determination of nitrate contents (NO₃-N) was performed spectrophotometrically using a HACH DR/2000 spectrophotometer, using a reduction method with cadmium using NitraVer 5 pads. Quantitative determination of ammonia (NH₃-N) was done by the Nessler method. Analyses were performed on a HACH

DR/2000 spectrophotometer, with a maximum absorbance of 425 nm. The content of heavy metals (Pb, Cu, Zn and Cd) was determined by the atomic absorption "Perkin Elmer" ANALYST 200 spectrophotometer (AAS method). Statistical analysis was performed in the statistical package SPSS 17.0. Data was presented in tables as mean values.

3. RESULTS AND DISCUSSION

Water samples from the wells, which can be characterized as public fountains, were subjected to physical and chemical analysis and the analysis of heavy metals content. Results of physico-chemical analysis are shown in Table 1.

pH-value of water is an important parameter for determining the quality of drinking water. Drinking water reacts neutral to slightly alkaline. The buffer system which maintains the pH-value in the range from 4.2 to 8.3 is comprised of free carbonic acid and hydrogen carbonate ions. With increasing pH-value content of free carbonic acid decreases and the hydrogen content increases. At pH 8.3 to 8.4 only hydrogen carbonates are present in the water. pH of the water from the study areas ranged from 6.44 (Miladije 2) to 8.34 (Miladije 1), with a mean value of 7.46 ± 0.85 . Higher pH value at the location (Miladije1) is a consequence of the presence of hydrogen carbonates, because hardness value was greater than the total hardness only at this site. pH value of 6.44 may indicates the presence of some salts of Ca and Mg, such as chlorides, sulfates, nitrates, in the water in addition to hydrogen carbonates and carbonic acid.

Temperature determines the solubility of oxygen in water. Temperature of water samples ranged from 12°C (Miladije 2) to 24°C (Miladije1), with a mean value of 17.17°C. The temperature of water from the site Miladije 1 is higher compared to other sites and may be the result of increase in the speed of biochemical reactions.

Electrical conductivity gives the total concentration of the electrolytes. Increased values of electrical conductivity at sites Modrac 757 $\mu\text{S}/\text{cm}$ and Simin Han 747 $\mu\text{S}/\text{cm}$ indicate a higher content of mineral salts in the water (increased hardness 280 mgCaO /L and evaporation residues of 373 and 378 mg/L). The values of electrical conductivity ranged from 139 $\mu\text{S}/\text{cm}$ (Miladije2) to 757 $\mu\text{S}/\text{cm}$ (Modrac), with a mean value of 412.50 $\mu\text{S}/\text{cm}$.

Organic matter content is determined on the basis of used KMnO_4 . The results show it is possible to conclude that the value of consumption of KMnO_4 in mg/L ranged from 2 mg/L (Bistarac and Miladije 2) to 3.7 mg/L (Modrac), with a mean value of 2.63, indicating that the highest content of organic matter is at the Modrac site. The consumption of KMnO_4 up to 8 mg/L is tolerated according to the regulations [9].

Ammonia content in tested water samples was within the recommended exposure levels, and ranged from 0.03 mg/L (Par Selo) to 0.07 mg/L (Simin Han) with an average value of 0.25 mg/L except at the source (Miladije 1) with a maximum concentration of 1.24 mg/L. Increased ammonia content on this site is the result of the geological structure of the soil. Nitrate concentration in the range of 1.15 to 6 mg/L and the nitrite in the range of 0.004 to 0.006 mg/L and not more than MDK [9]. The European Union (EU) and the World Health Organization (WHO) allow nitrate concentration of 50 mg/L in chlorinating water and provided that member states must ensure compliance with the condition that:

$$\{[\text{nitrate}] / 50 + [\text{nitrite}] / 3\} \leq 1$$

Table 1. Physico-chemical characteristics of alternative public water sources of Tuzla and its environ

Sample	pH	Temp. [°C]	EC [μS/cm]	Evaporation residue [mg/L]	Total hardness [mgCaO/L]	NH ₃ -N [mg/L]	KMnO ₄ [mg/L]	NO ₃ -N [mg/L]	Chlorides [mg/L]
Modrac	7.92	17	757	378	280	0.04	3.79	6.10	18
Bistarac	7.77	15	221	110	80	0.06	1.9	4.90	14
Miladije 1	8.34	24	304	152	57	1.24	2.21	1.10	14
Miladije 2	6.44	12	139	65	58	0.04	1.90	1.20	12
Par Selo	6.80	15	307	153	117	0.03	2.84	3.60	15
Simin han	7.47	20	747	373	280	0.07	3.16	1.40	21
Mean value	7.46	17.17	412.50	205.17	145	0.048	2.63	3.05	15.67
B&H MAV*	6.50-9.50	-	2500	-	-	0,5	5	50	250
EU MAV**	6.50-9.50	-	2500	-	-	0.50	5	50	250

*B&H-the maximum allowed by the Regulations Bosnia and Herzegovina [9],

**EU -the maximum allowed concentrations under Council Directive 98/83/EC [10]

where the square brackets indicate the concentration in mg/L of nitrate (NO_3^-) and nitrite (NO_2^-) and the value of 0.10 mg/L of nitrite meets the conditions for water treatment plants [10,11,12]. Increased nitrate content indicate organic pollution, usually accompanied by the presence of bacterial flora.

Table 2. Concentration of some heavy metals ($\mu\text{g/L}$) of alternative public water sources of Tuzla and its environ

Sample	Zn [$\mu\text{g/L}$]	Cu [$\mu\text{g/L}$]	Pb [$\mu\text{g/L}$]	Cd [$\mu\text{g/L}$]
Modrac	2	6	BDL*	BDL*
Bistarac	1	2	BDL*	BDL*
Miladije 1	BDL*	1	BDL*	BDL*
Miladije 2	BDL*	BDL*	BDL*	BDL*
Par Selo	BDL*	1	BDL*	BDL*
Simin han	1	4	2	BDL*
Mean value	1.33	2.8	-	-
MAV WHO**	-	2000	10	3
MAV B&H***	-	2000	10	5

*BDL-below the detection limit

**MAV WHO -the maximum allowed value under Guidelines for drinking water quality (electronic resource), World Health Organization [12]

***MAV B&H-the maximum allowed by the Regulations Bosnia and Herzegovina [9],

Heavy metal content in the tested water samples Table 2 is far below the MAV. The results are consistent with the literature data, where the contents of heavy metals in natural spring waters range from a few micrograms to a few nanograms.

The content of copper in drinking water samples ranged from 1-6 $\mu\text{g/L}$. The lowest copper content was at the sources Miladije 1 and Par Selo and the highest on Modrac source. Content value of copper in the samples do not exceed the recommended limits of WHO (World Health Organization) for drinking water of 2 mg/L [12]. According to this data, it can be concluded that copper is mainly of mineral origin and there are no significant sources of copper pollution in the immediate area. Contamination of drinking water with high level of copper may lead to chronic anemia [13].

The values for the concentration of zinc are in the range of 1-2 $\mu\text{g/L}$, the smallest at the sources Bistarac and Simin Han (1 $\mu\text{g/L}$) and the highest on Modrac (2 $\mu\text{g/L}$) Table 2. In three of the six samples (50%), zinc concentration was below the detection limit. Zinc is one of the important trace elements that play a vital role in the physiological and metabolic process of many organisms. Nevertheless, higher concentrations of zinc can be toxic to the organism [11]. Lead concentration that was detected at the source Simin Han (2 $\mu\text{g/L}$) is likely due to anthropogenic activities (car exhaust) because the source is located near the busiest roads. In 80% of cases lead was below the detection limit. Lead enters the human body in many ways. It can be inhaled in dust from lead paints, or waste gases from leaded gasoline. It is found in trace amounts in various foods, notably in fish, which are heavily subjected to industrial pollution. Some old homes may have lead water pipes, which can then contaminate drinking water. Most of the lead we take is removed from our bodies in urine; however, as exposure to lead is cumulative over time, there is still risk of buildup, particularly in children. Studies on lead are numerous because of its hazardous effects. Cadmium is highly toxic and responsible for several cases of poisoning through food. Small quantities of cadmium cause adverse changes in the arteries of human kidney. It replaces zinc

biochemically and causes high blood pressures. Cadmium was below the detection limit in 100% of samples and all of this at the time of the hydrological minimum (summer time) when the metal content is fairly constant.

4. CONCLUSION

Values of tested physico-chemical parameters are within recommended exposure levels, except the value of ammonia at the source Miladije 2 (1.24 mg/L) and pH on source Miladije 1 (6,44). The content of heavy metals (Cu, Zn, Pb and Cd) were far below the MAV values according to current regulations of Bosnian and Herzegovina, EU (Directive 98-83- quality of water intended for human consumption) and the WHO recommended values. The heavy metal content is within the limits that are specified for natural water from a few micrograms to a few nanograms and suggest that metals are mainly of mineral origin.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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