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Chemical Characterisation of the Spring Waters used for Health Care, Guber, Srebrenica, Bosnia and Herzegovina

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Abstract: The Guber spring waters in Srebrenica (Bosnia and Herzegovina) were used for centuries, and continue to be used for health-care purposes. The experts noted 48 mineral springs of different discharges and chemical composition. In this study, the physico-chemical properties, content of heavy metals and anions were determined in four selected spring waters (Mali Guber, Očna voda, Sinus voda and Ljepotica). Very low pH and very high concentrations of iron and sulphate are found in all springs. The highest concentrations of iron (2069 µg/mL) and sulphate (2486 µg/mL) and the lowest pH (1.67) were measured at spring Očna voda. The concentration of other metals and anions varied between different springs. Correlations between physico-chemical parameters and concentration of metals and anions in the water samples were also evaluated. Results for the spring water Sinus voda were evaluated for the first time.

INTRODUCTION

Water is essential for life on earth and its quality is of great importance to human health. It is an important source of trace elements for the proper functioning of the human organism (Ristić, Popović, Pocajt, *et al.*, 2011). Mineral water always contains various minerals and trace elements and can be defined as water containing minerals, which are natural compounds formed through geological processes, or other dissolved substances that alter its taste or give it therapeutic properties (Rezaee, Hassanzadeh-Khayyat, Mehri, *et al.*, 2012; Albertini, Dacha, Teodori, *et al.*, 2007). The World Health Organization (WHO) has been concerned with health aspects of the management of water resources for many years and publishes various documents (WHO, 1997; WHO, 1996) concerning the safety of water environment and its importance for health. In the European Community (EC), natural mineral water is strictly defined in the EC Directive 80/777 that it must be groundwater and clearly distinguishable from ordinary drinking water by its nature (Lau and Luk, 2002). Mineral water include groundwater, due to the general mineralization, ion composition, gas content, the presence of therapeutic active ingredients (mineral and organic), radioactive elements, alkalinity or acidity and elevated temperatures, have beneficial physiological effects on the human organism (Dragišić, 1997). The healing mineral water of Srebrenica is known from the time of the ancient Romans who called its spring *Domavia*, and the whole area in this beautiful corner of Eastern Bosnia - *Argentaria*. During the reign of the Turks the fame of the healing water from the Javor Mountain spring has spread, and it is interesting that today's name of Srebrenica spa dates from these times. Turkish soldiers came to Srebrenica to be treated for leprosy hence the name Guber (Operta and Hyseni, 2013).

The Srebrenica area is characterised by numerous Pb-Zn sulphide ore bodies and several iron-sulphate mineral water springs. Srebrenica is also well known for its long mining history (Dangić and Dangić, 2007). Recent sediment analysis of these water springs (Dangić and Dangić, 2001), showed that they are very rich in arsenic, lead and iron. These waters are rare and have effective physico-chemical components and are significant due to the high content of iron, arsenic and trace elements; they are similar to the well-known mineral resources Levico in South Tyrol (Italy) (Hasić, Lončarević, Marić, *et al.*, 1976). Due to its chemical composition spa Guber is

unique in Europe. Inside the spa Guber there are 48 springs, most notably: Veliki/Crni Guber (Big/Black Guber), Mali Guber (Small Guber), Kožna voda (Skin water), Očna voda (Eye water), Sinus voda (Sinus water) and Ljepotica (Beauty - water for face).The most important and known healing water is Crni Guber. It is potable in its natural state and experts verify it as curable for many diseases. This spring contains bivalent iron, copper, cobalt, nickel, manganese and a lot of other elements. It cures hypocrome anomalies, essential hypocrome anomalies, weak appetite, general weakness of the organism, weight loss, fatigue, exhaustion, asteny, neurovegetative defects, chronically skin diseases, rheumatism, multiple-sclerosis and many others health problems. Every-day consumption of the healing water from Crni Guber has to be under medical control (Pašagić, 2008). Few other mineral water springs appear near the Crni Guber spring. This spring is the most analyzed in many studies during previous years. Because of that, our research was based on the analysis of other important and often used springs. Among them, the spring Ljepotica has some similarities with the Crni Guber spring in the water composition and spring sediment formation.

The spring Ljepoticais the most favorable among users, because only washing with it makes prettier someone complexion and skin of the face and by sinking and rinsing help to cure all kinds of skin diseases (Dangić and Dangić, 2001). One of the most-visited healing spring is called Očna voda. It has low abundance but it is highly mineralized. Washing helps to cure mucous membrane of eyes particularly conjunctivitis and it considerably improves sight (Hasić,*et al.*, 1976). Mali Guber contains twice more iron than Crni Guber, higher quantities of calcium and manganese but it has lower abundance. Because of high mineralization it is possible to use this water for specific diseases. In the vicinity of Mali Guber is the spring Kožna voda that is used for the treatment of psoriasis, dermatitis and warts. Sinus voda heals and cures inflammation and painful sinus. This treatment is performed by sniffing. With the constant use of Sinus water it is possible to neutralize pain in sinus (Pašagić, 2008). The composition and properties of all springs and the river water (after all inputs) resemble of an acid mine drainage (Lenoble, Omanovic, Garnier, *et al.*, 2013).

There are many parameters that determine the quality of water. This study include 20 parameters such as: temperature, pH, conductivity, total solid after evaporation at 105°C, chemical oxygen demand (COD), chlorides, phosphates, sulphates and heavy metals (Ag, Au, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb and Zn).

EXPERIMENTAL

Study area

Srebrenica is located in the mountainous area of north-eastern Bosnia and Herzegovina. The urban part of Srebrenica is situated in the valley of the Krljevica River at 448 m above sea level and is surrounded by the hills of the Sušica Mountain. The town is about 160 km away from Sarajevo, and 120 km from Tuzla. Near Srebrenica, at 560 m above sea level is Guber, Srebrenica's most renowned spa resort. The path to the Guber resort is beautified with gorgeous coniferous and deciduous forests.

The climate is temperate continental sub-mountainous under the influence of no wind and fog (Bećirović, 2004).

Sampling

The ISO standard method was used for sampling (ISO, 1992). Water samples were collected in polyethylene bottles. All glass and plastic ware used for sampling and analysis were washed with 10% HNO_3 and rinsed with Milli-Q water. Sampling was carried out in April 2012 at four mineral springs (Mali Guber, Očna voda, Ljepotica and Sinus voda). The sampling locations are presented in Figure 1.

Figure 1. Sampling sites at Guber, Srebrenica
Source: https://www.openstreetmap.org/copyright.

Instruments and Reagents

Four spring water samples in triplicates were analysed by 20 parameters: temperature, pH, conductivity, COD, total solids after evaporation at 105°C, metal concentrations (Ag, Au, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb and Zn) as well as anion mass concentration (chlorides, sulphates, phosphates).

Atomic absorption spectrometer (AA240FS, Varian, Australia) was used for the determination of metals except for Fe. UV/Vis spectrophotometer (Carry 50, Varian, Australia) was used for phosphates analysis. Conductivity meter (HANNA Instruments, Model HI 8733, Sigma, Singapore) and pH meter (CG841, Schott, Germany) were used for conductivity and pH measurements.

Content of sulphate was determined by gravimetric method (precipitation with barium chloride). The content of total solid after evaporation at 105°C was determined by gravimetric method. Iron and chloride content was determined by volumetric method, dichromometric and mercurimetric titration, respectively.

All used reagents were analytical grade. Milli-Q water was used throughout the complete experimental work. All samples were analysed in triplicate. Comparison of the triplicate results shows significant agreement, confirming the quality of analytical data.

The detection limits (LOD) were calculated on the basis of three times the standard deviation of the blank signal. The obtained values of LOD for the investigated metals are: Mn (0.002 µg/mL), Zn (0.001 µg/mL), Cu (0.003 µg/mL), Cr (0.006 µg/mL), Pb (0.01 g/mL), Cd (0.002 µg/mL), Ni (0.01 µg/mL), Co (0.005 µg/mL), Sb (0.02 µg/mL), Au (0.002 µg/mL)and Ag (0.01 µg/mL).

RESULTS AND DISSCUSION

Srebrenica area is well known for its long mining history, as well as for its spring waters of specific composition (Dangić and Dangić, 2007). The healing springs from spa Guber in Srebrenica are the only springs of this kind in Bosnia and Herzegovina. Due to the great interest in the healing waters of the spa Guber in Srebrenica, and just a few available previously published papers which are mainly related to the spring Crni Guber (Lenoble, *et al.*, 2013; Blagojević, Lazić, Škundrić, *et al.*, 2008; Pašagić, Pašagić, Jatić, *et al.*, 2006; Miholić, 1954) the aim of this work was to determine the 20 selected parameters that characterise the spring waters and determine their invaluable quality. Ernst Ludwig, a Viennese chemist published the first chemical analysis of Srebrenica area mineral waters in 1890 in "Die Mineralquellen Bosniens — Die arsenhaltigen Eisenquellen von Srebrenica" ("Bosnian mineral sources — iron sources from Srebrenica containing arsenic") (Lenoble, *et al.*, 2013). The yield of springs is in most cases low (Q < 0.1 L/s – Očna voda) (Miholić, 1954).

Results of analysis of spring waters Mali Guber, Očna voda, Ljepotica and Sinus voda are shown in Table 1. The content of anions and metals is presented as the average values ± standard deviation of triplicate measurements.

Physico-chemical parameters and content of anions

All springs were of very acidic pH, and the lowest pH is determined at Očna voda (1.67), where also the highest sulphate content was found (2486 µg/mL). High sulphate concentration, originating from sulphide oxidation, results in low pH of these spring waters. That low pH leads to the dissolution of minerals, which then enriches the water with different elements and can lead to excessive concentrations (Lenoble *et al.*, 2013; Casiot, Lebrun, Morin, *et al.*, 2005). This is the common scenario in active or abandoned mines with acid mine drainage waters, which are considered to have such harmful effects on aquatic life that only adapted microorganisms can encountered (Bruneel, Duran, Casiot,*et al.*, 2006). High values of Pearson´s correlation coefficient obtained between pH and content of sulphate (r = 0.9646), pH and content of phosphate (r = 0.9915), conductivity and total solid after evaporation at 105°C (r = 0.9759) and conductivity and content of sulphate (r = 0.9832) confirms the strong chemical relationship between these parameters. There was no significant correlation between pH and chloride (r = 0.1086). The chloride content in all samples was significantly lower than the limit values prescribed by legislation (Službeni glasnik BiH, 26/10).

According to the Ordinance on natural mineral waters and natural spring waters (Službeni glasnik BiH, 26/10) limit value for COD is 5.00 µg/mL. Significantly higher values were obtained for all analysed springs. The lowest COD value was determined in Očna voda (111 µg/mL), while the highest value of 323 µg/mLwas found in Sinus voda. This can be probably explained by the presence of fulvic acid completely complexed by trace/major metals, humic acids are not expected at so low pH (Mounier, Zhao, Garnier, *et al.*, 2011).

Table 1. Summary results of spring waters (Guber, Srebrenica) analysis

Parameters	Mali Guber (Small Guber)	Očna voda (Eye water)	Sinus voda (Sinus water)	Ljepotica (Beauty)	Limit value*
Temperature (°C)	12.0	7.0	13.5	11.5	-
pH	4.91	1.67	2.82	2.36	6.5-9.5
Conductivity (mS/cm)	0.7	7.9	2.70	2.00	up to 2.5
Total solid after evaporation at 105 °C (mg/L)	907	7153	3413	1279	-
COD (µg/mL)	139	111	323	315	5.00
SO_4^{2-} (µg/mL)	595±7	2486±38	1422±22	930±16	250.00
PO_4^{3-} (µg/mL)	0.05±0.03	0.08±0.00	0.06±0.01	0.07±0.01	-
Cl^- (µg/mL)	2.98±0.20	3.42±0.15	2.63±0.12	2.43±0.16	250.00
Fe (µg/mL)	148±2	2069±26	1011±2	313±2	0.20
Mn (µg/mL)	5.80±0.50	1.42±0.03	14.06±0.90	< LOD	0.50
Zn (µg/mL)	13.20±1.20	4.30±0.09	10.57±0.80	2.29±0.04	3.00
Cu (µg/mL)	2.81±0.01	22.39±0.06	0.24±0.01	0.90±0.03	1.00
Cr (µg/mL)	< LOD	0.05±0.01	0.07±0.008	< LOD	0.05
Pb (µg/mL)	0.26±0.02	0.95±0.02	1.42±0.10	0.57±0.01	0.01
Cd (µg/mL)	0.06±0.00	0.07±0.00	0.17±0.002	< LOD	0.003
Ni (µg/mL)	0.09±0.00	0.26±0.01	0.20±0.01	0.09±0.00	0.02
Co (µg/mL)	0.05±0.01	0.34±0.01	0.18±0.00	0.07±0.00	-
Sb (µg/mL)	0.02±0.00	0.41±0.00	0.23±0.01	0.16±0.00	0.005
Au (µg/mL)	< LOD	< LOD	< LOD	< LOD	-
Ag (µg/mL)	< LOD	< LOD	< LOD	0.11±0.00	-

*Limit value according to the Ordinance on natural mineral and natural spring waters (Službeni glasnik BiH, 26/10); < LOD– below detection limit

Content of heavy metals

Following heavy metals Mn, Zn, Cu, Cr, Pb, Cd, Ni, Co, Sb, Au and Ag were analysed by flame atomic absorption spectrometry (FAAS) in spring waters from spa Guber Srebrenica. The content of iron was very high and was determined by volumetric method. Iron content ranged from 148 mg/mL (Mali Guber) to 2069 mg/mL (Očna voda). The obtained results shows that the concentrations of iron in samples of Guber spring waters are far above the limit value. Such a high concentration of iron is one of the main features of healing springs. According to the amount of iron, Očna voda is ranked on third place of the European mineral springs (Hasić,*et al.*, 1976).

Srebrenica mineral waters which contain $FeSO_4$ and sulphuric acid are unstable in contact with atmospheric oxygen. The water quickly turns yellow and slurred, causing brown precipitate of $Fe(OH)_3$. Additionally, while it is consumed during the oxidation of $FeSO_4$ to $Fe_2(SO_4)_3$, the amount of free sulphuric acid increases during the precipitation of $Fe(OH)_3$ (Miholić, 1954). Since $Fe(OH)_3$ already starts to precipitate from a weak acid solution (pH = 3), it is a characteristic of all Guber spring waters that after a short-time exposure to air, they begin to precipitate iron (III) hydroxide and are, thus, necessary to be conserved (e.g. by vitamin C). Guber waters lose almost all of their medicinal qualities for health-care purposes after a longer period of time, with the exception of Očna voda which has a lower pH amounting to 1.67. The content of metals except iron was presented in Figure 2.

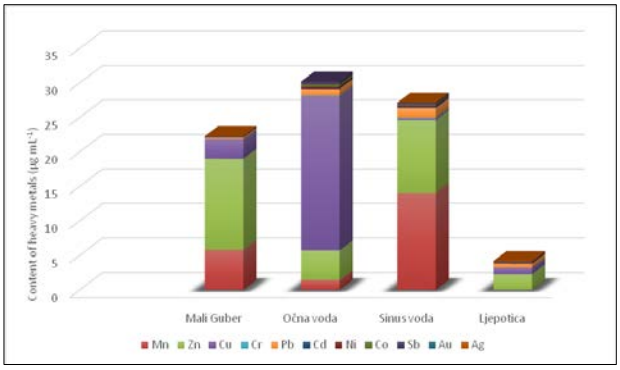

Figure 2. Content of heavy metals in the water springs Guber, Srebrenica

The concentration of heavy metals varied between different springs (Figure 2). By concentrations in different water springs, the elements were arranged as the following descending series:

Mali Guber: Fe>Zn>Mn>Cu>Pb>Ni>Cd>Co>Sb

Očna voda: Fe>Cu>Zn>Mn>Pb>Sb>Co>Ni>Cd>Cr

Sinus voda: Fe> Mn>Zn>Pb >Cu>Sb>Ni>Co>Cd

Ljepotica: Fe>Zn>Cu>Pb>Sb>Ag>Ni>Co

Enrichments of microelements are significant (Mn = 14.06 µg/mL and Pb = 1.42 µg/mL in Sinus voda, Zn = 13.20 µg/mLin Mali Guber, Cu = 22.39 µg/mL in Očna voda).

Concentrations of some heavy metals in the spring waters were compared with the limit values prescribed by the Ordinance on natural mineral and natural spring waters (Službeni glasnik BiH, 26/10). Obtained concentration for most of metals were above these limit values.

The resulting concentrations of most analysed parameters were the highest in the spring Očna voda.

Although Srebrenica has always been known for its mineral deposits of silver, the content of this metal in the concentration of 0.11 µg/mLwas only determined in the Ljepotica spring. The Ljepotica spring is particularly popular among women, because the washing water results in more beautiful and healthier complexion, and cleaner facial skin. Moreover, many users of this water healed and removed facial acne and blackheads (Pašagić, 2008). Scientific studies have shown that colloidal silver quickly "kills bacteria". Perhaps the presence of silver is one of the reasons for the effective purposes of Ljepotica on skin diseases.

The results were compared with the results given in the previous published paper (Lenoble, *et al.*, 2013). Generally, the obtained results in this study are in agreement with the previous published data. There are no available previously published papers relating to Sinus voda. First results for Sinus voda are presented in this paper.

CONCLUSION

The physico-chemical properties (temperature, pH, conductivity, chemical oxygen demand (COD) and total solid after evaporation at 105°C), the content of metals (Fe, Mn, Zn, Cu, Cr, Pb, Cd, Co, Sb, Au and Ag) and content of anions (Cl^-, SO_4^{2-}, PO_4^{3-}) were determined in four spring waters (Mali Guber, Očna voda, Sinus voda and Ljepotica) near Srebrenica town (Bosnia and Herzegovina). Correlations between physical-chemical analyzed parametres and concentration of metals and anions of the water samples were also evaluated.

Chemical analysis showed that spring waters contain very high concentrations of elements, particularly iron, and also of many other heavy metals and sulphate (causing low pH).

The highest concentrations of iron (2069 µg/mL) and sulphate (2486 µg/mL) and the lowest pH (1.67) were measured at spring water Očna voda. The concentration of other metals and anions varied between different springs. High sulphate concentration results in the low pH of these spring waters. A good correlation was found between pH-sulphate, pH-phosphate, conductivity-sulphate and conductivity-total solid after evaporation at 105°C.

Bearing in mind that people still use these spring waters for health-care purpose; that there is a plan for restarting the bottling of these mineral waters; that some plans for reactivation of the spa Guber Srebrenica are under consideration, further evaluation of chemical analysis is necessary.

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Summary/Sažetak

Izvorske vode Guber u Srebrenici (Bosna i Hercegovina) koristile su se stoljećima i koriste se u zdravstvene svrhe. Istraživači navode 48 mineralnih izvorarazličitih hemijskih sastava. U ovom radu određene su fizikalno-hemijske osobine, sadržaj teških metala i aniona u četiri odabrane izvorske vode (Mali Guber, Očna voda, Sinus voda i Ljepotica). Jako nizak pH i veoma visoka koncentracija željeza i sulfata nađena je u svim izvorima. Najviša koncentracija željeza (2069 µg/mL) i sulfata (2486 µg/mL) i najniži pH (1.67) izmjereni su za izvor Očna voda. Koncentracije ostalih metala i aniona varirale su između različitih izvora. Izračunate su korelacije između fizikalno-hemijskih parametara i koncentracija metala i aniona uzoraka vode. Rezultati za izvor Sinus voda predstavljeni su po prvi put u ovom radu.