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RESEARCH ON THE NATURAL FEATURES OF KARST WATER, ON THE EXAMPLE OF SOME WATER INTAKES

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Abstract: The existence of safe and abundant raw water sources is a priceless treasure for any country. Water resources are of particular importance for Montenegro, especially for the development of tourism and agriculture which represent the backbone of its economic development. With respect to water potential, Montenegro is at the top of Europe. However, it is not a sufficient factor, but the very way it is used and protected, as well as the improvement of its valorization. Economic development which is not based on the conservation and good governance of natural resources may have negative consequences for the overall development.

The aim of the paper is the study of natural properties of karst ground waters and their changes through interrelation of some ions, as indicators, on the example of five intakes in use. The paper presents the results of the research on the said waters and the values of indicators which point to their exceptional benefits for the water supply. However, the effects of the anthropogenic factor are evident, which are reflected in the range of the mole ratio of Ca /Mg ions ranging from 5.4 to 9.6, and the values (eqv.SO4/Cl) ranging from 0.3 to 2.0. Protection of the environment, especially preservation of the quality of water resources of Montenegro, imposes the urgency of implementation of the objectives of the Water Framework Directive.

Key words: water *characteristics, water intake,* water management

Introduction

In its natural condition, water is essential for the survival of all living beings, but as such it is not available nowadays in many parts of the world. Some analysts put the access to water on a level with basic human rights. Gleick for example, recommends that "50 liters of pure water per person daily should be considered a fundamental human right today" (Gleick, 1995). Water is not only a natural but also a socio-economic resource with characteristics which classify it parametrically as pure public, private, mixed and meritorious goods.

Fresh water is a vulnerable resource, which is essential for life sustention, development and the environment. Therefore, a large number of authors (Dimkic and Milovanovic, 2009) believe that water management, based on the principles of integrated management, is a prerequisite for its protection. According to Stevanovic (2011), management of groundwater resources in karsts areas is of essential importance. Compared to other porous environments, karsts aquifers are unpredictable, but much more vulnerable to the occurrence of pollution. Hydro geological characteristics of these environments cause a very rapid circulation of groundwater, and therefore the shortest retention of water in the underground, and low self-purifying ability. The water from more than 75 water intakes from the karst underground of Montenegro is used for the purposes of the municipal water supply system. Pollution is particularly noticeable at the time of significant intense short-term precipitation, which is most evident in the coastal region of Montenegro and its immediate hinterland.

The aim of the paper is the study of natural properties of groundwater in terms of the reflection of the unique characteristics of water sources on physical-chemical properties, on the example of the intakes for the water supply of Budva. The purpose of the paper is to encourage the implementation of the objectives of the Water Framework Directive (defining of water bodies, monitoring, and other elements), which are a prerequisite for the integrated water management in Montenegro.

Method of work

Within hydrogeological research, the properties of the following groundwater intakes used for the water supply of the Coastal region were monitored: Piratac-label 1; Rezevica Rijeka- label 2; Loznica- label 3; Podgorska vrela- label 4. The capacity of the mentioned water intakes is 257 l / s. During the summer period, this quantity is significantly increased by the water of the intake “Bolje sestre” through the regional water supply system. During field examination of the drainage basins of the intakes, among other things, 53 “instantaneous” water samples were taken for laboratory tests (APHA 1995, 2005). As indicators of anthropogenic influence, mole ratios of Ca/Mg and ekv.SO4/Cl were used.

According to many authors, (Patrick, 1976; Preka-Lipold et al., 1984, Langmuir, 1971, Thrailkill, 1976) that ratio, among other things, is an indicator of the impact of chemicals in plant production on the changes in natural properties of waters. Thus, according to Buljan (1962) the ratio of sulfate to chloride suggests the influence of fertilizer ingredients from land surfaces. Moreover, the ratio Ca / Mg <1, for example, points to the penetration of fertilizer ingredients into fresh water (Rahman and Rowell, 1979).

In the case of soil salinity, the consequence is the dominance of Ca2 + in fresh water, resulting in a higher mole ratio of Ca/Mg in water than 3.5 (Howard and Adams, 1965; Carter and Webster, 1979; Mostafa and Ulrich, 1976). According to Aljtovski (1973), the ratio in fresh water is 3.6, while smaller or larger ratio points to the influence of sea water, or other man-made factors, such as fertilizers. In fresh natural water this ratio is in the range from 2.1 to 3.4, while it is 3 in waters of distinctly karst terrains (Geochemical et Cosmochemical Acta, 1971).

The research data was analyzed with the statistical package “Excel”. The correlation analysis was performed in order to evaluate the interdependence of physical and chemical indicators of water quality. The degree of interdependence between ions in water is expressed through simple correlation coefficients and tested for the significance level of 5%.

The basic data on the physical and chemical characteristics of tested waters in these water sources are shown in Tables 1, 2 and 3 and Figures 1 and 2.

Results and discussion

In terms of elemental composition, the tested waters belong to the calcium bicarbonate type, with a slightly marked alkaline character and a relatively low content of dissolved salts, as well as a very low content of micro elements, which makes them very suitable for drinking.

The data presented in Table 1 show extreme and mean values of physical-chemical parameters of the waters from the intakes labeled from 1 to 4. These are waters of a suitable water temperature from 12.5 ° C to 13.2 ° C, enriched with dissolved oxygen (Xsr = 15.2mgO2 /l.). The water from these intakes is odorless and colourless, has the characteristic taste and a very low content of organic matter (Xsr = 2.3mgKMnO4 /l). The said waters occasionally become turbid to a greater or lesser degree, usually at the end of a dry period, after abundant rainfall, which is also a characteristic of the intakes of a significantly larger capacity, such as the “Mareza” water source (Corovic, A. et all.1999; Filipovic et al., 1993; Krivokapic, Filipovic, 1995.). During the period of low water levels, the hardness of water is very stable (Xsr = 10.8odH) in the water of the water intake – 2 of a higher capacity, while in others, it slightly varies, which is explained by the pressures in the sanitary protection zones.

Table 1: Extreme and mean values of physical-chemical parameters of the raw karst water of the water intakes labeled (1 to 4).

Test Parameters	max	Min	Xsr
Temperature 0C	13.2	12.5	12.9
Odour	without	without	without
Color (oCo – Pt. scale)	<5	<5	<5
Turbidity (NTU)	0.85	0.29	0.44
Ammonium – NH4 (mg/l)	<0.05	<0.05	<0.05
Nitrite N (mg/l)	<0.005	<0.005	<0.005
Nitrate N (mg/l)	1.43	1.33	1.39
Fluoride (mg/l)	0.040	0.025	0.036
Chloride (mg/l)	9.5	6.5	8.8
Consumption $KMnO_4$ (mg/l)	2.55	1.92	2.29
Total hardness ^{0}dH	11.9	10.2	10.8
Carbonate hardness ^{0}KdH	10.6	9.5	9.8
Oxygen O_2 (mg/l)	15.5	15.0	15.2
pH value	7.78	7.52	7.70
Conductivity (µS/cm)	302	253	265
The rest of the vapor (mg/l)	218	201	210
Iron (mg/l)	0.08	0.05	0.06
Copper (mg/l)	0.003	0.003	0.003
Manganese (mg/l)	0.006	0.003	0.005
Zinc (mg/l)	0.01	0.01	0.01
Lead (mg/l)	<0.005	<0.005	<0.005
Chromium (mg/l)	<0.003	<0.003	<0.003
Nickel (mg/l)	0.015	0.008	0.010
Cadmium (mg/l)	<0.001	<0.001	<0.001
Mercury (mg/l)	<0.0005	<0.0005	<0.0005
Alkalinity (M) $CaCO_3$ mg/dm^3	190.1	170.1	175.1
Sulfates (mg/l)	25.6	5.8	10.7
Bicarbonate (mg/l)	231.8	207.4	213.5
Aluminum (mg/l)	<0.02	<0.02	<0.02
Detergent anions (mg/l)	<0.05	<0.05	<0.05
Orthophosphate (mg/l)	<0.05	<0.05	<0.05
Sodium (mg/l)	4.59	4.23	4.50
Potassium (mg/l)	0.514	0.320	0.466
Calcium (mg/l)	84.0	62.8	78.7
Magnesium (mg/l)	7.05	4.62	5.23
The mole ratio of Na/K	22.4	15.1	17.0
The mole ratio of Ca/Mg	11.0	5.4	9.6

In order to highlight the pressures on the basin of the intakes (Piratac-1, Rezevica Rijeka-2; Loznica-3 and Podgorska vrela-4), Figure 1 presents the values of the hydrogen exponent and the mole ratio of the ions of alkali elements (Na / K), which are not factors of the total hardness, and earth alkaline ions (Ca / Mg), as its dominant factors.

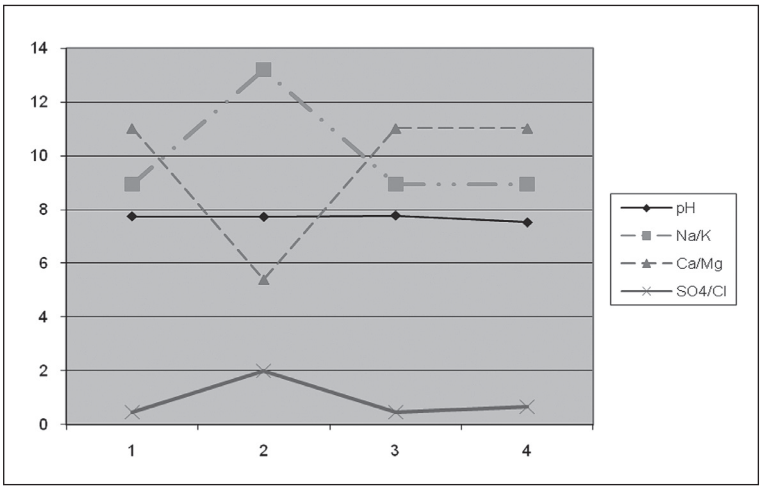

Figure 1: Average values of pH and the mole ratio of alkali and alkaline earth elements

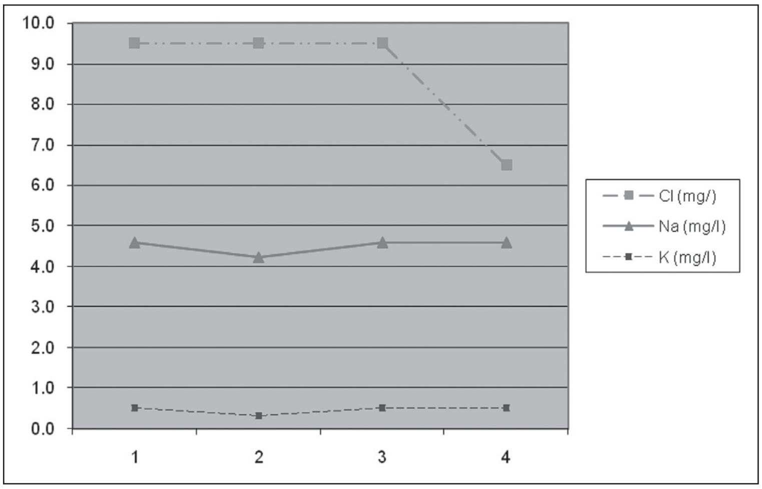

Figure 2: The behavior of the values of Na, K, and Cl in the water of the intakes

As we can see from the figure, depending on the water intake, changes in the value of the hydrogen exponent are insignificant, which is reflected in the extreme pH values from 7.52 to 7.78. In contrast, changes in the values of the mole ratios of Na/K and Ca/Mg ions by different sources are noticeable, indicating the obvious impacts of pollutants from the land surface of the basin.

Comparing the obtained values of the mole ratios Ca / Mg of the water of the water intake “Podgorska vrela”-4, for example, to a previously determined value of 3.7 (Filipovic, 1991), it can be argued that the level of protection of this water source has still not improved.

Figure 1 also indicates that the water quality of “Rezevica Rijeka” -2 differs from the water quality of other intakes, which is indicated by the determined contents of sodium and chloride (Figure 2). This phenomenon is explained by a significantly larger drainage basin area and the pressures in the basin. The obtained values or the mole ratio of SO_4/Cl ions (Figure 1) indicate an excessive use of fertilizers, that is, their ingredients are most common in the established pollution in the basin area. Disturbance of constant natural balance (buffering capacity) of water endangers its biological value, as well as the organic food production.

Exploring the water of the water intake “Bolje sestre” also indicates that the change of natural characteristics has occurred. This is reflected in the values of the basic indicators of quality, particularly in the obtained range of the mole ratio Ca/Mg ions and ekv.SO_4/Cl (Table 2).

As seen in the table, the ranges of extreme temperature values, pH values, and electrolytic conductivity are significant, while the ranges are lower for other parameters. The determined values of presented quality indicators are reflected in the very high range (from 2.1 to 18.8) for the mole ratio Ca / Mg, than it is in the case of the mole ratio ekv.SO_4/Cl from 0:33 to 1:20. The determined state points not only to the penetration of fertilizer ingredients, but to the ingredients of industrial origin.

In relation to this, it should be noted that the water source “Bolje Sestre“is situated at the far northwestern edge of Lake Skadar. The wider area of the basin where precipitation intensity ranges from 34-231mm for the period 1971–1990, is built of carbonate rocks represented by limestone, dolomitic limestone and dolomites of the Jurassic and Cretaceous age. These are very permeable rocks characterized by cavernous and fracture porosity. Through various geologic methods a large number of faults with different directions were determined, among which the most notable are the faults at the eastern edge of Malo blato (Devic et al. 2011).

Comparing the determined range of values (2.1–18.8) of the mole ratio Ca / Mg, for the water of the water intake “Bolje sestre” with the range (1.6–22.8) for groundwater and surface water of the Skadar Lake basin (Djuraskovic and Tomic, 1997), it can be said that the waters of this basin are burdened with identical pressures.

Table 2: Extreme and mean values of some indicators of water quality

Label	Ext. and mean values	T °C	pH	EC_{25} µS/cm	°dH	mol Ca/Mg	Na^+ mg/dm³	K mg/dm³	ekv. SO_4/Cl	NO_3 mg/dm³	PO_4 mg/dm³
Water intake “Bolje sestre”	min	11.5	7.3	260	8.0	2.1	0.9	0.2	0.33	1.72	0.01
	max	14.8	8.1	310	9.7	18.8	3.2	1.5	1.20	2.44	0.08
	Xsr	13.2	7.6	281	8.9	7.2	2.0	0.6	0.76	2.01	0.04

In order to examine the interdependence of other physical-chemical indicators of the characteristics of the quality of natural, karst water of the said intakes, a correlation analysis was performed (Table 3).

Table 3: Values of the correlation coefficient (r) of some quality parameters of raw water

Correlation coefficient (r)	pH values	Na (mg/l)	Cl (mg/l)
pH value	–	–0.197	0.985
Na (mg/l)	–0.197	–	*–0.333*
K (mg/l)	–0.197	*1.000*	*–0.333*
Ca (mg/l)	–0.197	*1.000*	*–0.333*
Mg (mg/l)	0.197	*–1.000*	*0.333*
Cl (mg/l)	*0.985*	–0.333	–
Total hardness ^{0}Dh	*–0.957*	0.362	*–0.945*
Consumption of $KMnO_4^-$ (mg/l)	*–0.525*	*0.849*	*–0.587*
O_2 (mg/l)	*–0.529*	*–0.931*	*0.490*
Alkalinity (M)	0.197	*–1.000*	*0.333*
Conductivity (μS/cm)	0.197	*–1.000*	*0.333*
Nitrate – NO_3^- (mg/l)	–0.426	0.174	*–0.522*
Sulfate (mg/l)	0.197	*–1.000*	*0.333*
Fe (mg/l)	*–0.876*	*0.639*	*–0.938*

As seen in Table 3, the average pH values of water have a very negative effect on total hardness, then iron, dissolved oxygen and consumption of potassium permanganate, while the effect of pH on the ions of sodium, potassium and calcium is negligible.

The positive reaction of pH value is with: total alkalinity, electrolytic conductivity, magnesium and sulfates. A significant positive relationship (r = 0985) is between pH and chloride. A high dependence level (r = 1) in water is between sodium and calcium, as was found in karst water from other areas (Devic and Filipovic, 2005). A strong negative correlation between sodium and magnesium, and sodium and sulfate, can also be noticed, which clearly shows the inflow of fertilizer ingredients into the water of the intakes.

Conclusion

Reconnaissance of the subject water sources has proved that their protection is not at a high level. This is proved by the data of field and laboratory study of 53 "instantaneous" water samples from five water intakes for the water supply of Budva. The values of the used indicators show the extent of changes of the natural properties of water that have occurred. It is concluded that the present condition is a consequence of the inflow of pollution into the waters from the land surface of the basin areas. This is reflected in the increase of buffering capacity of water, expressed by a significant exchange of bicarbonate ions with carbonate ions, which is most affected by a higher content of alkali and alkaline earth elements, as well as chlorides, sulfates and phosphates in a lower degree. The phenomenon caused by fertilizer ingredients in plant production does not exclude the impact of other sources of pollution, which is still in accordance with hygienic regulations.

Inadequate management of water resources that Montenegro has can in the long run have negative effects on the overall development. A potential vulnerability of water source areas is only part of a much broader and deeper issue that need to be addressed systematically, respecting the EU recommendations and regulations. The demonstrated vulnerability of the water source areas points to the need for active intervention in water protection. Everybody must be involved in resolving this issue, starting from state institutions, through public and private companies, educational institutions up to the individual themselves. Protection of the environment, raising environmental awareness among the population and the regulation of the situation in the field of environmental management are essential priorities of the society that strives for development. Water is a valuable resource that Montenegro has available and it must be preserved and exploited through active protection measures in the function of economic and overall development.

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