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The influence of Geological Field Structure on Water Quality in the Selected Source of the Ljubija Area, B&H

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Abstract: Underground waters have very important role as sources for settlements' water supply. Pollution of underground waters from one side depends on the environment's burden with pollutants substances of anthropogenic origin, and from the other side, on physical-geographic conditions, of which geologic factors have the greatest role. Geological field structure, besides, affects determining of conditions on underground water's forming, as well as its chemical composition. In this work, the influence of geological structure was presented on the quality of underground waters in the area of Ljubija, the specific large deposits of iron ore. During researches for this paper's needs, analyses were carried out of the general physical-chemical parameters of underground waters' quality.

Key words: *underground waters, geological structure, physical-chemical parameters, iron ore deposits, Ljubija.*

Introduction

Underground waters divide on upper or shallow waters, waters above water-impermeable layers and artesian waters. Upper waters are waters in layer closest to the surface, in the aeration zone. At deeper plunge, waters gather themselves above water impermeable layers. At filtration through the ground layer, decreases the content which gives the color and content of microorganisms decreases as well, while the content of solutions increases. These waters are used for water supplying of rural areas (draw wells). For this paper's need, water was analyzed, from a source used by local population of Ljubija for water supplying.

Figure 1. Geographical position of the Ljubija

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Geological structure significantly affects maintaining of falling waters on surface and its absorption into the ground. Geological factors have a great role in movement of underground waters, their position, and movement speed, depth of hydrologic isolator and character of hydrologic collector.

For the Ljubija area, in geological terms, iron ore deposits are characteristic, found in composition of wide Paleozoic terrains of the Sana and Una Rivers. The mine place of Ljubija, is situated in the basin of the eponymous river, in the northwest of Bosnia and Herzegovina, about 12 km southeast from Prijedor. In mathematical-astronomical view, the following coordinates 44°55' N and 16°37' E determine it (Figure 1).

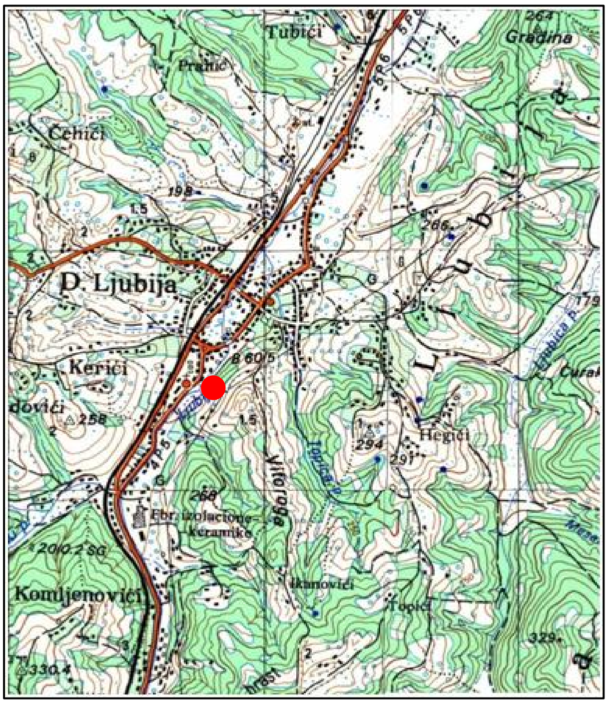

Figure 2. Topographic map of the Ljubija with locality of sampling water (1:25 000)

Material and methods

During the work, basic geological map sheet Prijedor, 1:100 000 (Figure 3), and with it interpreter of geological map as well as data on newer examinations of geological structure and their mineral, i.e. chemical composition, were used. Samples were caught using centrifugal or manual pump, conserved according to regulations for certain parameters, transported to laboratory and preserved on a temperature up to +4 ⁰C. Figure 2 presents the place of water sampling. A time from the moment of catching the sample to the beginning of sample processing was no longer than 24 h. In each examination cycle, on the very spot measures were done on basic physical-chemical parameters: water temperature, pH and conductivity. Underground waters' quality control for analyzed chemical and physical-chemical parameters was done according to the Regulation on health safety of drinking water, Official paper of B&H 40/10, and then were used standard determination methods.

Geological characteristics of the Ljubija areas

Territory of the researched area in geotectonic view belongs to Central Dinarides of Bosnia and Herzegovina, and within this unit, paleographically to allochthonous Paleozoic-Triassic Una-Sana formations (Čičić & Bašagić, 2001). The Una-Sana Paleozoic area is situated between structural units of Dinaric carbonate platform from the south and Ophiolite unit from the north side.

Basically, ores appear as border stratuses of metasomatic bodies of iron carbonates inside carbonate limestones and dolomites as well as siderite intercalations inside carbonic phyllite and meta-sandstones. Primary mineralization is composed of siderite-ankerite-barite with three texture types: dark massive siderite, and zebra-kind siderite and in sense of change dark and light siderites with sulfides intercalations in caverns. When forming this area in geological terms is in question, (Palinkaš et al., 2016), consider that the most influential processes in forming of chemical fluid components were metasomatize of siderites and ankerites. In forming of fluid ore dominant were $NaCl$-$CaCl_2$-H_2O, with very changeable contribution of salinity and temperature between 100 and 310º C. Hydrothermal fluids are mixture of high temperatured and high salinated Perm evaporation of seawater, which is diluted by low temperatured and low salinated sea or meteor water. High fluid temperature and salinity variability contributed to water boiling in the ground hydrothermal reservoirs. Sulfur isotopes proved Permian seawater as the main sulfate source for barite formation. Thermal reduction of marine sulfates provides HS- for sulfide deposits, which were laid down, with exception of co-genetic pair galenite-sphalerite, formed on 245º C. Temperature of forming is determined with oxygen isotopes on co-genetic mineral pair of calcite-siderite-quartz in diapason between 164º C to 224º C. For determining the age, it is linked to two emphasized tectonic-thermal events, those are Variscan (332.8 ± 3.1 Ma and 342.9 ± 3.3 Ma), and later thermal post-Variscan event on about 265.6 ± 6.2 to 274.2 ± 3.1 Ma, which are defined as age of maximum hydrothermal activity of middle perm. The age and thermal characteristics correspond to neighbor Paleozoic deposits in Trgovska and Petrova gora (Peter's Mountain), for which they are linked in space and time (Palinkaš et al., 2016).

Geologically, Paleozoic rocks in the Ljubija area are rimed with Mesozoic creations. Carbon clastites, sandstones and aleurolites dominate, as well as Permian-Triassic sandstones, evaporites and breccia limestones, then Triassic creations (hornstones, sandstones, marls, spilites, and tuffs) (Figure 3). Mostly it is about light permeable and impermeable rocks so they have function of hydro geological isolators, what conditioned also establishing of surface flows' thick net in this area. The oldest Paleozoic rocks in these fields belong to lower and central Carbon, and their thickness is estimated about 600 m to 1000 m.

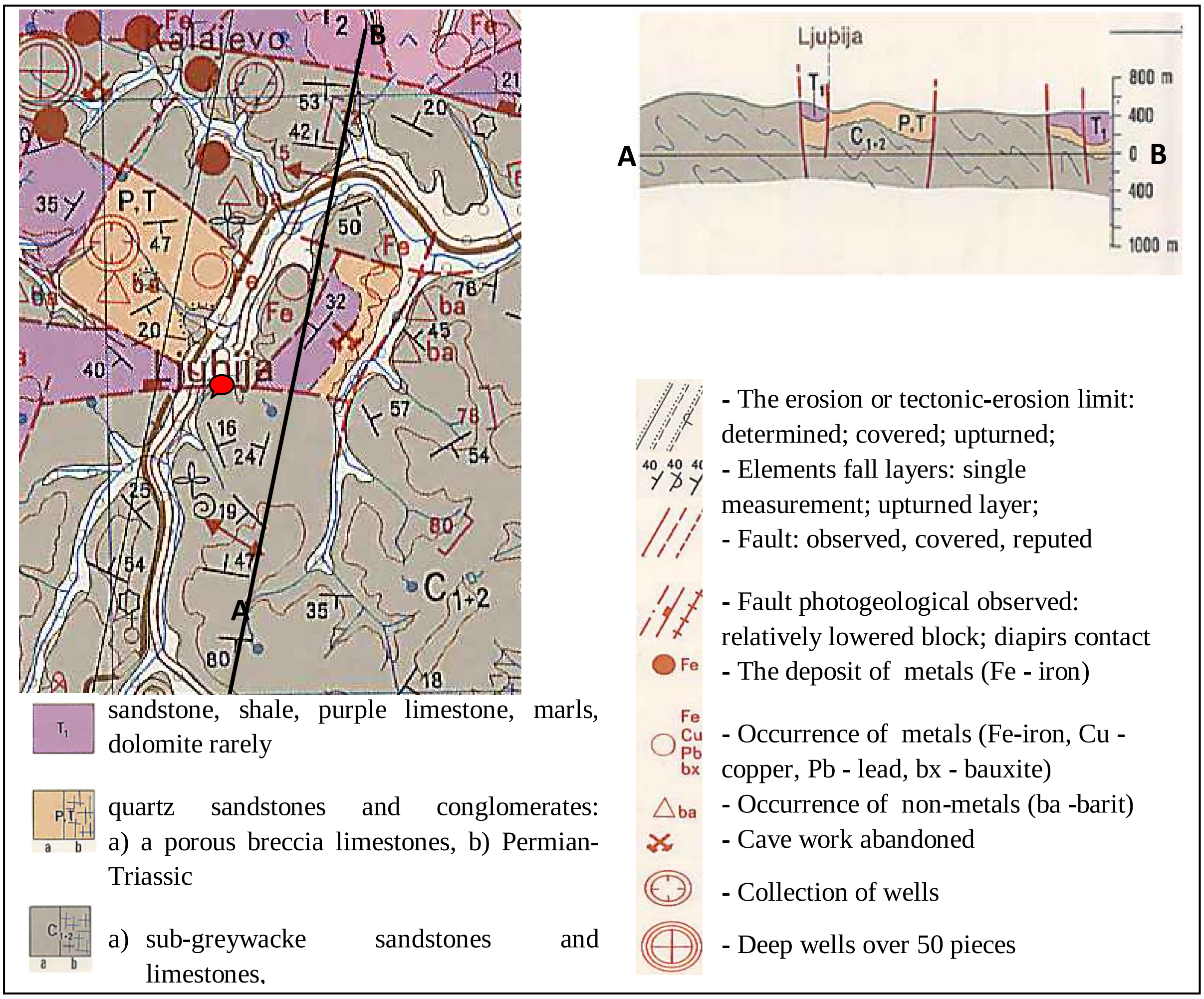

Figure 3. The geological map of the Ljubija areas (1:100 000)

Lower and Upper Carbon ($C_{1,2}$), are presented with clastic and carbonate products. Clastic deposits are made of sandstones sub-greywacke type and greywacke type, metasandstones, sericite-chlorite-quartz shales, clay and clayish shales in lateral and vertical changes. Carbonate sediments are subordinated, represented by lenses, rarely by layers or masses, grey-blue to blue color. Limestones have organogenic origin and they consist of many macrofossils. In carbonate products complex there are polymetallic ores, mostly iron ones. Besides the iron, in mines of Ljubija are registered reserves of zinc, barite and fluorite. Iron ore appears in the form of intercalations of siderites and ankerites in changing body types in limestones. Significant are also deposits of galenite, tethraedrite, chalcopyrite and sphalerite, while the wires of barite and fluorite go permeate side through dolomites.

Deposits of Upper Permian and Permian - Triassic (P, T), make rim parts of Paleozoic complex and core switched Paleozoic synclines. In composition of these deposits, there are clastic creations: conglomerates, sandstones and clayish slates, then poriferous tuffed-breccia limestones, marl slated limestones and gypsum lens.

Lower Triassic products (T_1), are spread in their own classical facial development of verfenic layers, mostly in border areas of Paleozoic complex. In the composition of Lower Triassic layers usually clastic rocks participate: sandstones, marls and shales, then carbonate ones: limestones and rarely dolomites. Clastic rocks are usually yellowish (reddish-brown) and grey-green color, while limestones are grey and grey-bluish. Metamorphic processes of lower degree affect all these rocks, so they in fact represent semi-metamorphic rocks (Korjenić, 2015).

Hydro geologically, allochthone Paleozoic-Triassic formation with rocks dominantly silicate and clastic composition, are usually slight permeable and impermeable rocks, and in first place they have hydro geological barrier function. From that reason, this area is very rich with surface waters, and infiltration of atmospheric waters is very slow. Appearances of underground waters' assert are mostly linked to fault zones along which are enabled circulation of underground waters, what is characteristic also for chosen locality in Ljubija (Figure 3). Chemism of rock masses, through which underground waters circulate, predestinates their chemical composition. Structural porosity type, as well as the size of this parameter predestinates the possibility of forming underground waters' accumulations that are more significant. Those accumulations in the researched terrain can be formed only within Mesozoic, dominantly Triassic limestones. In other parts of the terrain, forming of smaller accumulations can be possible in close-surface decomposed part of terrain, especially referred to Carbon age rocks.

Results and Discussion

Chemical composition of underground waters, besides, depends on contact surface, speed of underground water and geological field structure. In case that contact surface with surrounding rocks is larger, larger will be dissolving substances of organic and inorganic origin, with which it comes in touch. When the speed of underground water is in question, the water that quickly flows through the ground does not take part longer in its dissolving, while slow waters have greater mineralization. Besides, waters that go through or stop between magmatic or metamorphic rocks are slightly mineralized, while those from sediment ones are more mineralized due to different speed of dissolve of these rocks.

Concerning analyzed physical-chemical water parameters from the chosen locality in Ljubija, one can concludes that the water pH value is 6.88, what points to mild acid reaction and greater concentration of cation H^+. Electrical conduction numerously expresses ability of some water system to conduct electrical power. This ability depends on ion presence, their total concentration and on temperature on which measures are conducted. Electro-conductivity of underground waters is conditioned by presence of dissolved mineral matter in it. The size of conductivity depends on quantity of dissolved mineral matter, means; it is in proportion to total water mineralization. Gained electro conductivity values show that it is about little mineralized waters that, concerning geological field structure, are located mostly in metamorphic rocks (shale). Total hardness of water represents total concentration of ion in calcium and potassium, expressed as calcium carbonate. Determined total water alkalinity of examined water is 160 mg/L $CaCO_3$ or 16° dH which indicates that is hard water. This data confirms that ions of calcium and magnesium are presented in overage, due to geological field structure alone. Lithologicaliy, fig. 3, this area is plentiful with limestone rocks, what affected high degree of water hardness. Geological composition in great measure affects chemical composition of underground water, what is shown by participation of chloride, sulfates, as well as iron, which had leading role in formation of rock deposits in this area, like siderite, galenite, chlorite and others.

Participation of nitrogen matter in underground water, first of all, nitrates and nitrites as well as ammoniac are important from health aspect. Low values of nitrates and nitrites concentration in examined sample, tell us that the soil and underground waters are not affected by human activities, agriculture, industry or other wastewaters from households. Presence of ammoniac in drinking water points on organic contamination, and it is also indicator of inappropriate water disinfection and negatively affects smell and taste of water.

Value of concentration of ammonium ion, < 0.04 mg/L, tells about it didn't come to chemical contamination of underground water. Chlorides in water are found in a shape of sodium, calcium and magnesium salts. If presented in water as NaCl, high concentration of chlorides provoke salty water taste, while if presented as $CaCl_2$ and $MgCl_2$ high concentrations do not cause salty taste. Chlorides by selves are not toxic for people. Concentration of chloride ions10,0 mg/L, doesn't cross allowed maximum limit, according to Regulations, what means that examined sample doesn't have salty taste, that is presence of natrium ion reduced on minimum. Presence of iron ions in examined sample, <30 μg/L, will not trigger organoleptic problems, such are bittersweet and bitter taste. Sulfates are ones of the least toxic anions. Revising papers and studies which refer to experimental determination of sulfate dose that cause health issues at adults, gastrointestinal problems, it is recommended that sulfate content in maximum contamination level is 250 mg/L.

Table 1. The results of physical and chemical parameters of water quality

Parameter of testing	Measurement unit	The result of testing	Reference value
Smell	---	---	**
Taste	---	---	**
Color	Co-Pt scale	0	**
pH value	---	6,88	≥6,5 i ≤9,5
Electrical conductivity at 20°C	μS/cm	380	2500
Turbidity	NTU	0,50	**
Total alkalinity	mg/L	160	---
Chloride	mg/L	10,0	250
Sulfates	mg/L	33	250
Residual chlorine	mg/L	---	0,5
Ammonium	mg/L	< 0,04	0,5
Nitrites	mg/L	< 0,007	0,5
Nitrates	mg/L	1,6	50
Phosphates	mg/L	---	5,0
Iron	μg/L	<30	200

By the Regulations on health safety of drinking water in table 1 was given MAC (maximum allowed concentrations) which refer to following parameters: electro conductivity and pH, as well as for physical-chemical parameters. Measured value of all parameters is in the frame of allowed reference value, regulated by the Regulations on health safety of drinking water (Official paper B&H 40/10).

Conclusion

Geological-tectonical factors, among others, represent natural framework, that is, they form basic media, which has underground waters. Very often, faults are also roads for underground waters, what is the case in the Ljubija selected locality. Ore deposits in this area appear as border stratuses of metasomatic bodies of iron carbonates inside carbonate limestones and dolomites as well as siderite intercalations inside carbonic phyllite and meta-sandstones. Lithologically, carbon clastites, sandstones and aleurolites dominate, as well as Permian-Triassic sandstones, evaporites and breccia limestones, then Triassic creations (hornstones, sandstones, marls, spilites, and tuffs).

Solubility of minerals belongs to the most important factors in forming of underground waters' chemical composition. Thus, in underground water one can find soluble chlorides and sulfates which determine the chemical type of water, while group of minerals such are carbonates, sulfides and silicates are slightly soluble in water but with presence of O_2, CO_2 and organic matter, their solubility can be increased.

The results of the laboratory examination on physical-chemical parameters show that the geological structure of the area had a significant effect on the chemical composition of groundwater. Also, sampled water from examined locality satisfies regulated conditions according to the Regulation on water classification intended for human need. Sampling and examining of underground water quality in the Ljubija area was carried out during summer time. Total of 15 analyzed parameters, all meet the criteria regulated by the Regulations on health safety of drinking water.

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