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PHYSICAL-CHEMICAL CHARACTERISTICS OF GROUND WATERS IN THE AREA BETWEEN THE VILLAGES INJEVO AND KALUGERICA, RADOVIŠ

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A b s t r a c t: This paper presents the results obtained from the latest research of the physical-chemical parameters of ground water made in the area between the villages Injevo and Kalugerica. Investigation shows that the temperature of the tested waters is in the range of 8–140^{0}C, the measured pH values for analyzed waters are in the range of 6.2 – 8.0. TDS values measured in the tested waters range from a minimum value of 326 mg/l to a maximum value of 2252 mg/l. Their specified hardness is in the range from 18 to 138^{0}dH. The scope of certain concentrations of alkalinity ranges from 68 mg/l to a maximum 540 mg/l. Chlorides are determined in a concentration range of minimum 17.4 mg/l up to a maximum of 241 mg/l. The concentrations of sulphates in the examined waters range from minimum 14.6 mg/l to a maximum 535 mg/l. The results of measurements of dissolved phosphorus concentrations range from minimum 0.011 mg/l to an extremely high value of 4.62 mg/l. The scope of certain concentrations of nitrate anions ranges from the minimum value of 4.6 mg/l in Gorno Injevo – B7, to the maximum value of 477 mg/l, and for nitrites the maximum concentration is 0.12 mg/l. The detected maximum concentration of ammonium ions is 0.0579 mg. The determination of the chemical composition of ground water is of particular importance for water supply to these settlements.

Key words: cations; anions; pH; temperature; water hardness

INTRODUCTION

Ground water is one of the most suitable resources of fresh water with approximately balanced concentration of salts and it occurs in the Earth's crust in rock fractures (Brown et al., 1974). In many parts of the Earth using ground water as drinking water is disabled because of its contamination with industrial and municipal waste as one of the leading causes of pollution of both surface water and ground water. Ground water quality has been getting worse in recent decades, so it is of great interest to determine ground water quality and, if quality deterioration is found, to put efforts to determine the reasons for it and eliminate them.

Research was made in the area between the villages Injevo and Kalugerica that are situated 7 and 12 km from Radoviš (Fig. 1).

Fig. 1. Geological setting of the terrain

The geological structure (Fig. 2) in the vicinity of the area between Injevo and Kalugerica contains Precambrian rocks represented by different

types of gneisses, micashists, marbles; the Rifei Cambrian is represented by schist and phyllites. Old Paleozoic rocks are represented by schist carbonate series, marble, cipollinos, schists, phyllites and metasandstones, coarse porphyritic metarhyolites and aplitic granites; chalk rocks are represented by limestones. Tertiary rocks are represented by clays, sandstones, flysch, pyroclastic rocks, and andesites.

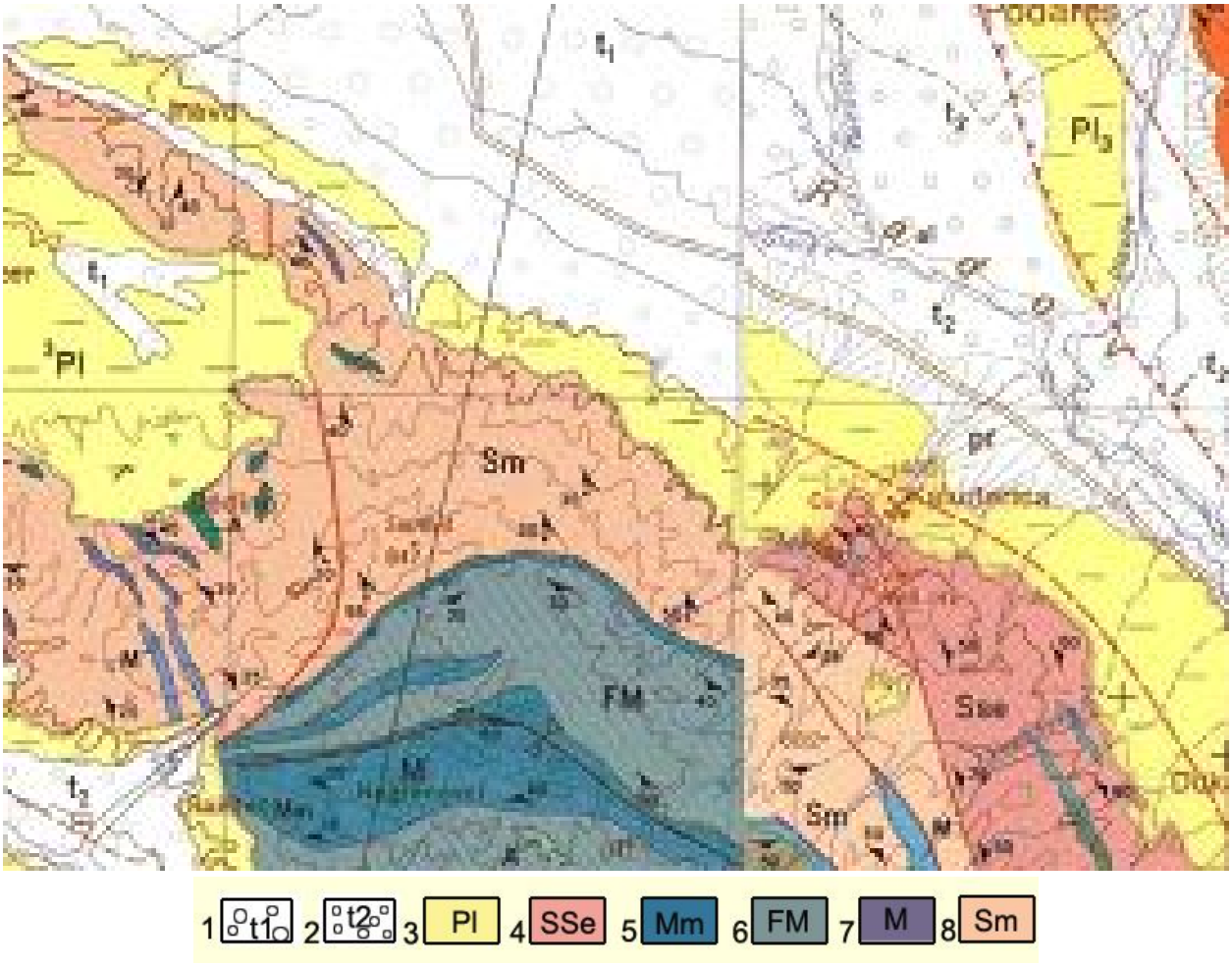

Fig. 2. Geological structure of the wider surroundings of the tested area
1) Lower river terrace, 2) Middle river terrace, 3) Sandy series, 4) Quartz-sericitic schists, 5) Cipollinos, 6) Schist-carbonate series, 7) Marbles, 8) Micashists

METHODS AND MATERIALS

For the purpose of determining the quality of ground water taken from the tested terrain single specimens were taken at previously determined points during the months of March–April 2012; the total number of taken samples for analysis is 22. Ground water samples were taken from nineteen dug wells and one spring.

All samples were taken in bottles made of chemically inert material, whose composition does not affect the composition of the water for analysis, with a volume of 2 liters, previously flushed with nitric acid (1:1), tap water and deionized water. Before taking samples, bottles are flushed three times each with 1/3 of the water that should be sampled and analyzed. Water samples were transported to the laboratory in the shortest period of time, but no longer than 12 hours after sampling.

In order to preserve the original composition of the tested specimens as reliably as possible and to preserve the correlation between individual components, the samples are preserved by adding concentrated nitric acid, c(HNO_3) = 15.8 mol/l to pH 2 (2 ml on 2 liters sample) for the determination of cationic composition.

The instrument on which analyses are performed is Libery model 110 from the firm Varian glass-concentric sprayer.

Physical-chemical analyses – The following parameters were assessed in 22 water samples: temperature, pH, total dissolved salts (TDS) from the filtered samples, total hardness, alkalinity, cationic composition (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}), and anionic compositionи: HCO_3^{-}, Cl^{-}, SO_4^{2-}, PO_4^{3-}, NO_3^{-}, NO_2^{-}.

Temperature, pH and electrical conductivity are determined when taking the samples with field digital pH meter calibrated with buffer solutions in three points, buffer with pH 4.2, 7 and 10. To determine the anion ground water quality standard EPA methods were used (gravimetric – TDS, volumetric – Cl^{-}, spectrophotometric- NO_3^{-}, NO_2^{-}, NH_4^{+} and turbidimetric- SO_4^{2-} with spectrophotometer 6715 UV/VIS, Jenway).

Later, the values of the tested parameters are compared with the drinking water quality standards and standards for water classes.

Conservation of samples is done with HNO_3, p.a., Fluka, and H_2SO_4, p.a., Fluka. For instrumental calibration and quantitative determination of each of the target elements multi-element standard solutions were used (Multi-element standard solution V and IV, single-element standard solutions for P, Ca, Mg, Fluka; NO_3^{-}, NO_2^{-}, NH_4^{+}, SO_4^{2-}).

RESULTS AND DISCUSSION

The knowledge of the physical-chemical characteristics of ground water in the area between the villages Injevo and Kalugerica is of particular importance, because these springs and wells are used by the residents as drinking water and for irrigation.

Locations where the trials were taken are presented in Fig. 3.

The physical-chemical parameters are determined (Table 1) and the results are presented in graphic form. The results obtained indicate a wide range of values for the tested parameters for assessing the quality of the tested ground water.

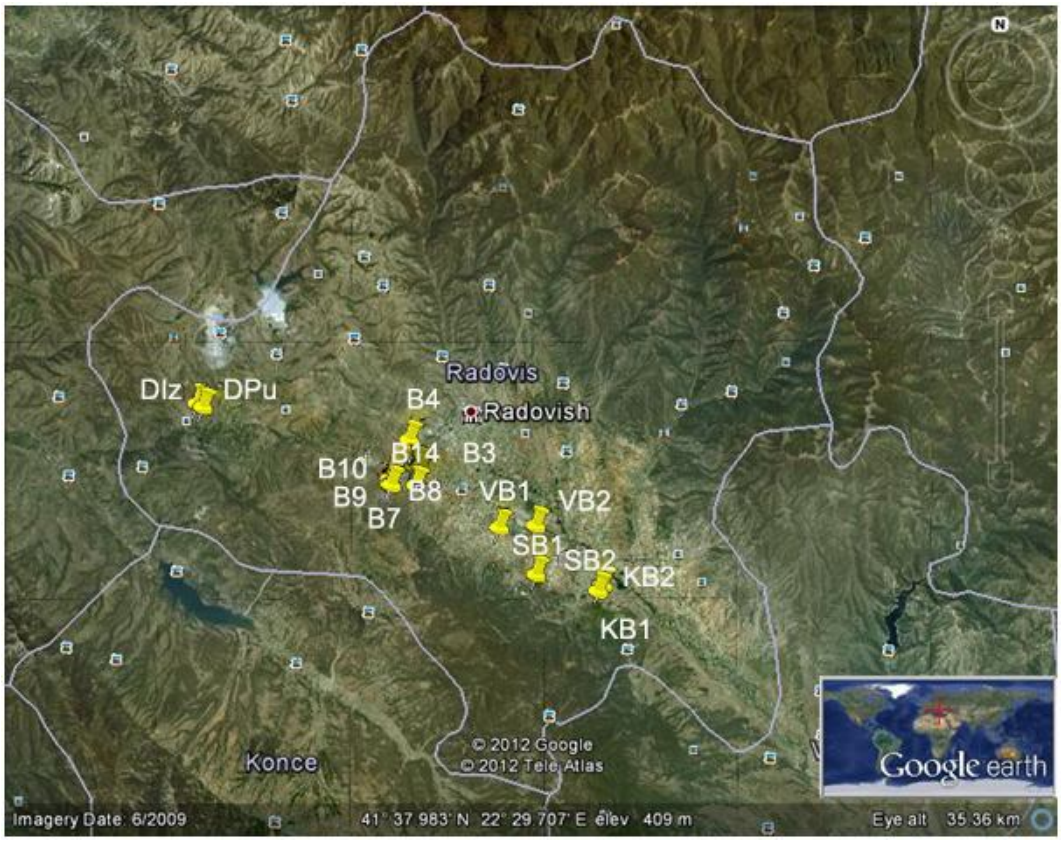

Fig. 3. Location of the samples taken

Table 1

Physical-chemical parameters of water samples

	Ca	Mg	Na	K	HCO_3^-	SO_4^{2-}	Cl^-	NO_3–	PO_4^{3-}	NO_2–	NH_4^+	TDS	pH	T
D. Injevo B1	271	116	38	2.05	72	81	117.0	204	0.160	0.009	<0.0025	884	7.5	10
D. Injevo B2	165	141	129	1.09	255	78	116.5	213	0.094	0.004	<0.0025	1041	7.0	11
D. Injevo B3	286	104	73	1.26	213	78	103.9	180	0.011	0.0012	<0.0025	1030	7.2	8
D. Injevo B4	102	56	36	2.63	160	8	38.7	45	0.598	<0.001	<0.0025	452	7.2	8
D. Injevo B5	160	146	136	2.36	540	8	37.8	40	0.350	0.006	<0.0025	1095	6.2	9
D. Injevo B6	171	102	70	2.46	198	73	86.5	135	0.269	0.004	<0.0025	841	6.9	10
D. Injevo B11	229	143	60	1.54	232	60	74.3	122	0.622	<0.001	<0.0025	916	7.5	11
D. Injevo B12	235	132	45	0.78	160	43	54.3	172	0.257	<0.001	<0.0025	836	7.5	11
D. Injevo B13	125	155	21	6.43	152	82	99.1	33	0.094	0.003	<0.0025	674	7.5	10
G. Injevo B7	103	42	16	1.53	144	4	22.6	5	0.016	0.012	<0.0025	326	7.5	10
G. Injevo B8	160	83	56	1.30	186	82	72.2	89	0.016	0.009	<0.0025	736	7.3	9
G. Injevo B9	733	250	103	4.17	259	194	241.3	477	0.557	0.011	<0.0025	2252	7.6	11
G. Injevo B10	221	100	33	1.26	91	165	97.8	81	0.011	<0.001	<0.0025	771	7.1	11
G. Injevo B14	109	61	52	3.31	129	33	34.3	143	0.193	<0.001	0.0080	576	7.3	9
G Voislavci GVB1	91	104	61	2.82	274	84	40.4	12	0.744	0.007	<0.0025	641	7.8	11
G Voislavci GVB2	40	240	59	157.23	376	206	110.4	212	4.618	0.008	<0.0025	1405	7.6	12
Surdulci SB1	241	188	35	6.76	298	94	56.1	124	0.051	0.009	<0.005	1045	7.7	12
Surdulci SB2	256	161	35	21.87	342	112	52.2	62	0.520	0.014	<0.005	1042	7.5	11
Kalugerica KB1	73	87	52	44.26	164	123	47.8	75	0.624	0.043	0.019	672	7.5	11
Kalugerica KB2	74	72	25	9.54	216	21	23.5	12	0.131	0.049	0.021	468	7.8	10
Damjan Izvor DIz	219	73	26	4.96	**68**	524	17.4	37	0.016	0.122	0.058	974	8.0	10
Damjan Pumpa DPu	66	64	95	9.17	**281**	114	31.3	6	0.100	<0.001	0.053	649	7.2	14
Min	40	42	16	1	68	4	17	4.615	0.011	<0.001	<0,0025	326	6.2	8
Median	163	104	52	3	205	81	55	85.038	0.177	0	<0,0025	839	7.5	11
Max	733	250	136	157	540	524	241	476.722	4.6	0	0	2252	8.0	14
MDK drinking water (MDC)	200	50	200	12		250	250	50	6.7	0.03	0.1	2000	6.5–8.5	

Temperature

The impact of the temperature on the composition of ground water depends on the depth on which the ground water is located.

The temperature of the tested waters in March–April 2012 is in the range of 8-14^{0}C, with a median of 10.5^{0}C (Fig. 4). The maximum value is measured in the water pumped from Damjan. The higher value in Damjan pump may be due to climate conditions, because these waters were taken from Damjan in mid-April, in contrast to the remaining 20 investigated waters that were harvested at the end of March. Since there is no information about the depth of the drill, one possible reason for this higher temperature could be the lower depth in relation to others.

Ground water temperature is an important factor that controls chemical and biological reactions in water, solution of nutrients that these waters are in contact with, and the development of the type and quantity of plankton flora (Hutchinson 17 Heath, 1989).

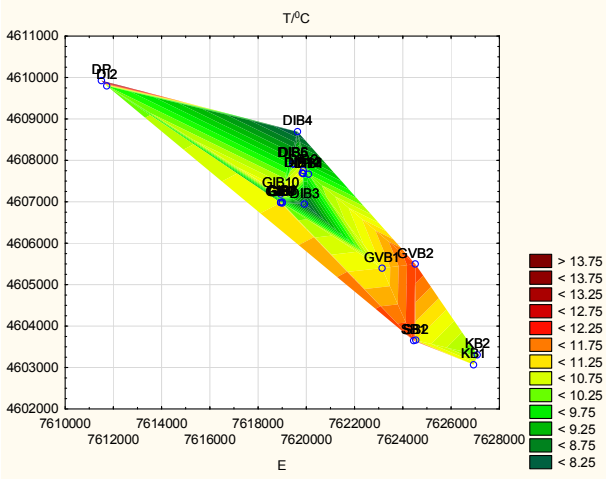

Fig. 4. Spatial distribution of temperature

pH

pH is an important environmental factor that provides information about many types of geochemical balances (Shyamala et al., 2008). pH affects not only the reaction with CO_2, but also the solubility of organic and inorganic substances in water (Wetzel et al., 1975). The normal range of values for surface and ground water is 6.5 – 8.5.

The measured pH values of the tested ground water are in the range of 6.2 (Dolno Injevo B5) – 8.0 (spring in Damjan) with median 7.5. In the 22 examined samples the measured values (Fig. 5) are within the allowed values according to the rulebook for drinking water (6.5 to 8.5); only the water with a minimum pH value of 6.2 (Dolno Injevo B5) exceeds the allowable value according to the rulebook for drinking water. It can be concluded that pH values outside the biological optimum were found only in three water samples: Gorno Voislavci CVB1 (7.8), Surdulci SB1 (7.7), and Kalugerica KB2 (7.8).

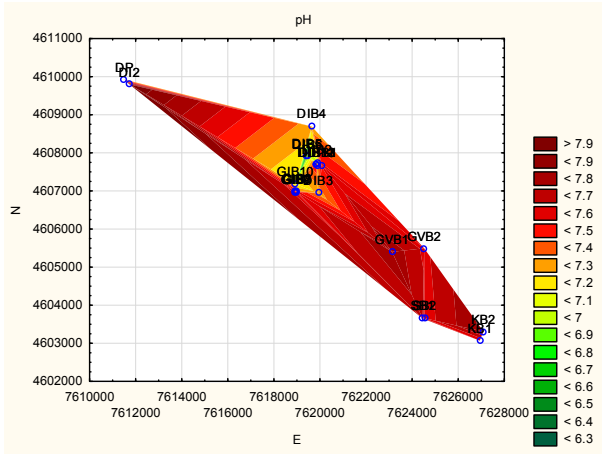

Fig. 5. Spatial distribution of pH

TDS

TDS values indicate the total content of salts in water-salinity and are in direct relation to the content of total dissolved ionic substances (Harilal et al., 2004). It serves to estimate the total dissolved salts in water (Purandara et al., 2003; Sandeep et al. 2011), which may affect the water taste and its usability for different purposes. TDS values measured in the examined waters range from a minimum value of 326 mg/l in Gorno Injevo B7 up to a maximum value of 2252 mg/l in Gorno Injevo B9 with median 839 mg/l. In all waters, except in Gorno Injevo B7, TDS values do not exceed the recommended MAC for drinking water, 2000 mg/l. (Fig. 6).

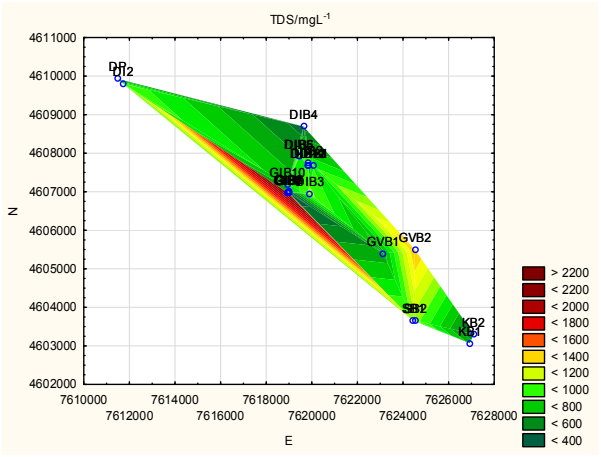

Fig. 6. Spatial distribution of TDS/mgl^{-1}

High TDS values indicate high concentrations of cations of calcium, magnesium, sodium, potassium and anions of hydrogen carbonates, chlorides, sulfates, nitrates and phosphates (10, 10–11). The increased concentrations of total dissolved ionic substances are a consequence of the terrain geology and suggest possible contaminations with municipal wastewater.

According to WHO, 500 mg/l are the allowed values for TDS (total dissolved salts). Waters containing more than 500 mg/l TDS are not suitable for drinking and can lead to certain diseases due to excess dissolved salts. (EPA, 2002; Ballester and Sunyer, 2000).

Water hardness

Hardness is an important parameter for reducing the toxic effects of some of the elements (Campbell et al., 2010). In the tested waters (Fig. 7), the designated hardness is in the range from 18

in Damjan pump up to 138^{0}dH Gorno Injevo B9 with median 400 dH. Most of the calculated values exceed MAC for hardness of drinking water determined by the MAC concentrations for Ca 200 mg/l and for Mg 50 mg/l (35^0 dH). The examined waters are very hard waters.

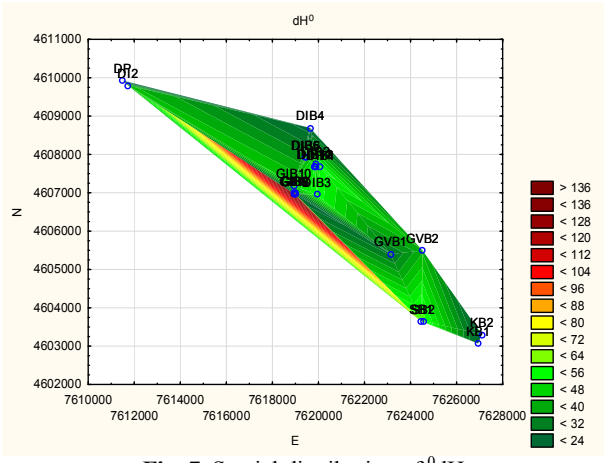

Fig. 7. Spatial distribution of ^{0}dH

The high values of total hardness of the tested waters is mainly due to dissolutions from magmatic and carbonate rocks (dolomite, calcite and limestone). MAC for Ca and Mg in drinking water are 200 and 50 mg/l respectively. In the waters from Dolno Injevo the concentrations of both elements exceed MAC values for drinking water. On average, the number of waters in which the measured magnesium concentrations are higher than 50 mg/l of the value for MAC for drinking water, compared with calcium (Figs. 8 and 9).

The maximum concentrations of Ca^{2+} and Mg^{2+} were measured in the water from Gorno Injevo B9.

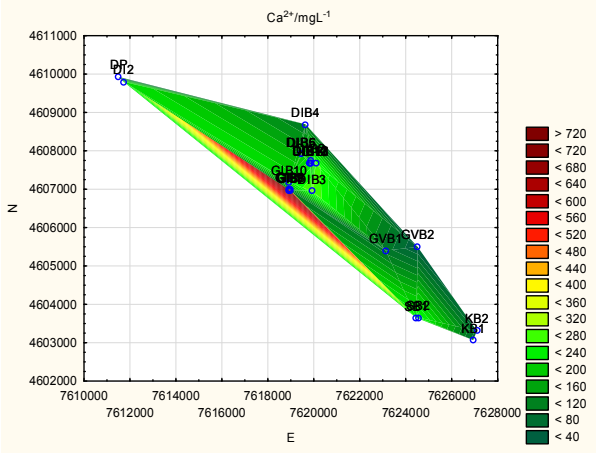

Fig. 8. Spatial distribution of Ca^{2+}/mgl^{-1}

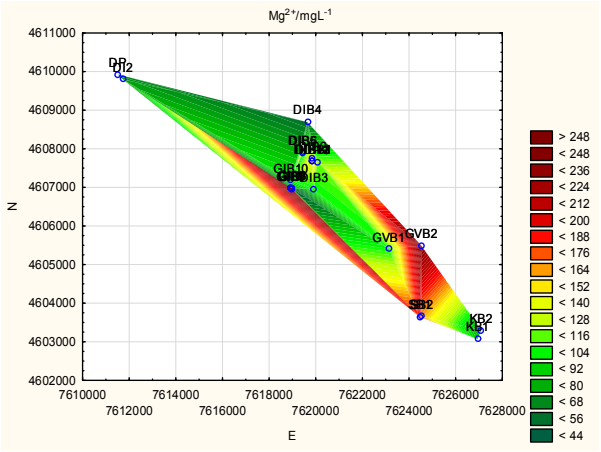

Fig. 9. Spatial distribution of Mg^{2+}/mgl^{-1}

Sodium, NA^+

The range of certain concentrations of sodium is from a minimum value of 16 mg/l in Gorno Injevo B7 up to a maximum of 136 mg/l in Dolno Injevo B5 with a median of 52 mg/l. In all tested waters (Fig. 10), the sodium content is lower than the MAC for drinking water, 200 mg/l.

Potassium

The range of certain concentrations of potassium is very wide (Fig. 11), the minimum value of 0.78 mg/l in Dolno Injevo B12 up to a maximum of 157 mg/l in Gorno Voislavci GVB2 with a median of 2.7 mg/l. In the tested waters, the content of potassium is higher than the MAC for drinking water, 12 mg/l, in three waters – Suldurci SB2, Kalugerica KB1, and an extremely high concentration of potassium found in Gorno Voislavci GVB2.

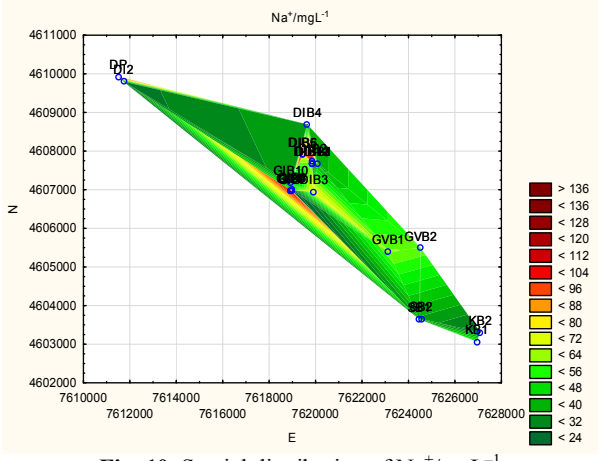

Fig. 10. Spatial distribution of Na^+/mgL^{-1}

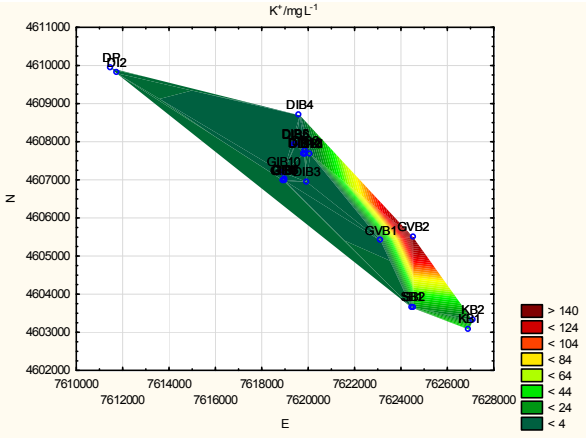

Fig. 11. Spatial distribution of K^+/mgL^{-1}

Anionic composition

The values of alkalinity concentrations expressed as hydrogen carbonate anions determined in waters indicate the nature of the salts present in the water. The reasons for waters' alkalinity, is the dissolution of minerals from the soil into the waters. Different ions have a stake in alkalinity, for example, hydrogen carbonates, hydroxides, phosphates, borates and organic acids. These factors are characteristics of the water springs and natural processes that occur (Sharma, 2004). The concentration of bicarbonate is mainly reflected through the specified values for alkalinity (Sandeep, et al. 2011). They act as buffers again stacidic effects (Dawodu et al., 2008).

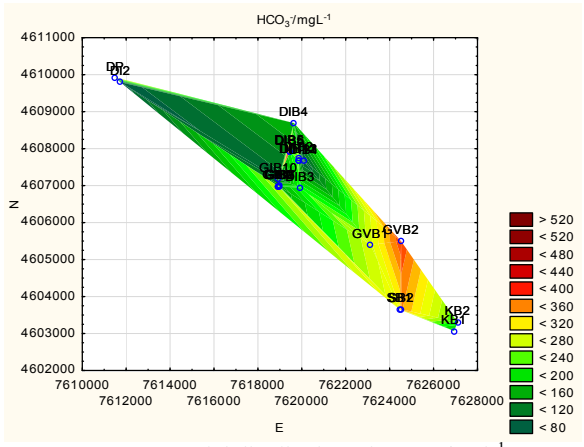

Fig. 12. Spatial distribution of HCO_3^-/mgl^{-1}

The range of certain concentrations of hydrogen carbonate determined as alkalinity is from minimum value of 68 mg/l in Damjan Izvor to a maximum of 540 mg/l in Dolno Injevo B5 with a median 205 mg/l (Fig. 12).

Chlorides, Cl^-

Chlorides are normally found as NaCl, $CaCl_2$ and $MgCl_2$ at a wide range of concentrations in natural waters. They can be ground water contaminants whose source is sewage water and municipal waste (Shaikh and Mandre, 2009).

Chlorides (Fig. 13) are determined in a concentration range from a minimum of 17,4 mg/l in Damjan izvor to a maximum of 241 mg/l in Gorno Injevo B9, with a median of 55 mg/l.

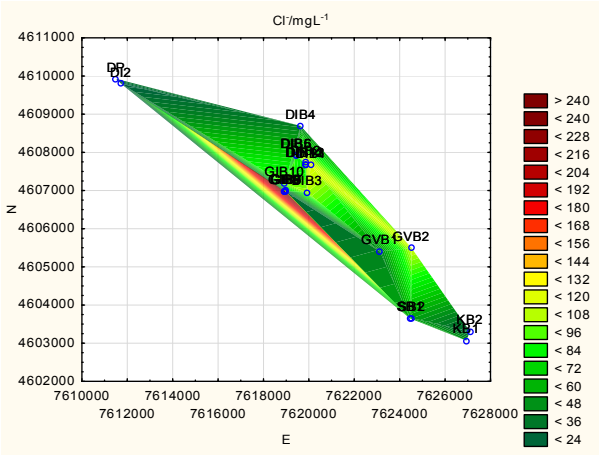

Fig. 13. Spatial distribution of Cl^-/mgL^{-1}

The maximum permitted concentration of chloride in drinking water according to drinking water security policy of Macedonia, is 250 mg/l. According to the content of the determined chlorides, only the water from Gorno Injevo B9 (241 mg/l), which is also the maximum value determined in this study, is very close to the value according to the Regulations for drinking water.

Sulphates, SO_4^{2-}

Sulphates can also be be an indicator of water contaminations with mining waste water for which there is an indication in our tests because the highest concentration of sulphate anions is measured in the water from the Damjan izvor that is relatively nearest to the mine Bučim.

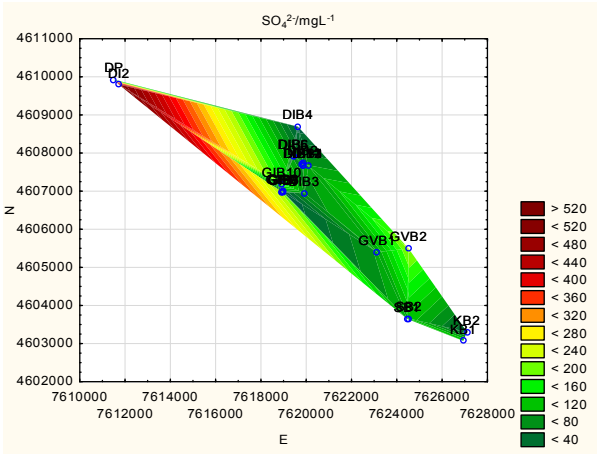

Fig. 14. Spatial distribution of SO_4^{2-}/mgl^{-1}

The concentration range for sulphates in the tested waters (Fig. 14) is from the minimum value of 4 mg/l in Gorno Injevo B7 to maximum 524 mg/l in Damjan spring and the median 91.7 mg/l. Higher concentrations of sulphate ions (>100 mg/l) were observed in two samples from Gorno Injevo B9 and B10, Gorno Voislavci, Surdulci B1 and two samples from Damjan. Only the concentration of sulphate anions determined in the water from Damian izvor exceeds the MAC for drinking water, so that water is unsuitable for drinking.

PO_4^{3-}

The results obtained from measurements of the concentrations of dissolved phosphorus (expressed in the form of phosphate) in 22 analyzed samples, range from minimum 0.011 mg/l (Dolno Injevo B3 and Gorno Injevo B10) to an extremely high value, 4.62 mg/l (Voislavci VB2), with a median of 0.177 mg/l (Fig. 15). All measured values for phosphates in the examined water do not exceed the MAC value. Higher values, which are unusual for the natural presence of phosphates in natural waters, indicate possible water contaminations with fertilizers and pesticides in the tested area.

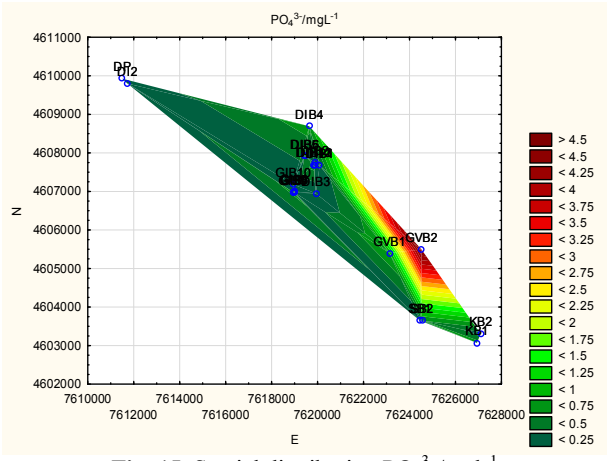

Fig. 15. Spatial distribution PO_4^{3-}/mgl^{-1}

Nitrates, NO_3^-

The concentration of nitrates in water indicates biological contamination of water. The range of certain concentrations of nitrate anions (Fig. 16) is from the minimum value of 4.6 mg/l in Gorno Injevo B7 to maximum 477 mg/l in Gorno Injevo-B9 with a median of 85 mg/l. In 13 investigated waters the values measured for nitrate anions exceed the limit value of 50 mg/l according to the Regulations for drinking water safety.

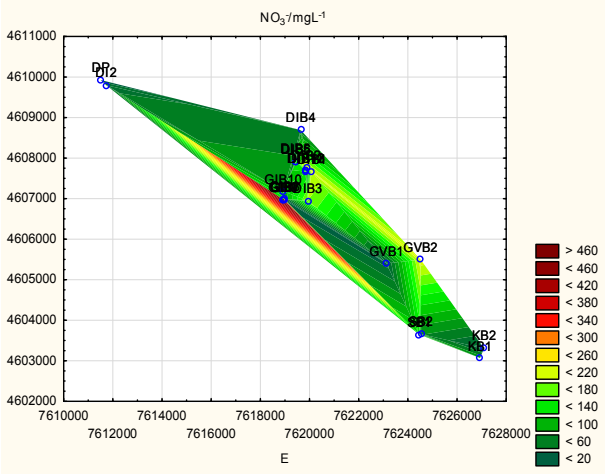

Fig. 16. Spatial distribution of NO_3^-/mgl^{-1}

The values obtained in the examined waters indicate greater load of ground waters with organic matter as a result of pollution from municipal waste water or waste water from farms and agricultural goods, or e pollution of the tested waters with fertilizers containing nitrate anions (Manassaram et al., 2006).

Nitrites, NO_2^-

Nitrite ions (Fig. 17) are detected in 12 of 22 examined water samples with a maximum concentration of 0.12 mg/l in Damjan Izvor. Nitrite anions are not detected in the waters of Dolno Injevo B4, B11 and B12, in the waters of Gorno Injevo B14 and B10 and in the water from a pump in Damjan. In all samples from Surdrulci, Kalugerica and Damjan Izvor these anions are present. The specified maximum concentration of nitrite ions in the water from Damjan spring and Kalugerica KB1 and KB2 are higher than the upper limit of maximum permissible concentrations for drinking water.

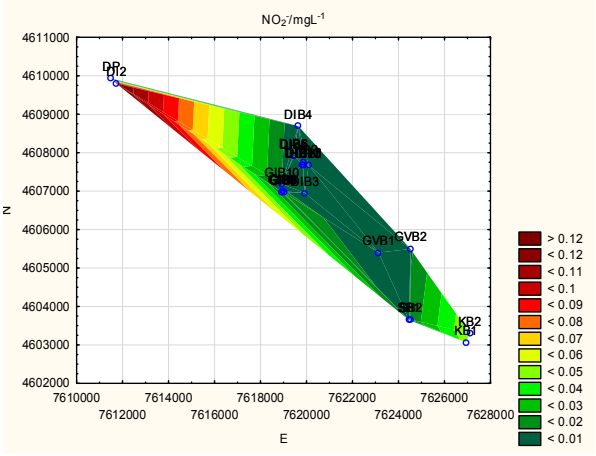

Fig. 17. Spatial distribution of NO_2^-/mgl^{-1}

NH_4^+

Ammonium ions are an indicator of the dynamics of the contaminated waters self-cleaning.

Ammonium ions are detected in only five tested samples (Fig. 18), in Gorno Injevo B14, in the waters from Kalugerica and Damjan, with a maximum concentration of 0.0579 mg/l in Damjan Izvor, although the value of ammonium ions in the water from the pump in Damjan also contains concentrations of ammonium ions very close to the maximum of 0.0528 mg/l.

The maximum concentration obtained of ammonium ion is lower than the MAC value for drinking water 0.1 mg/l.

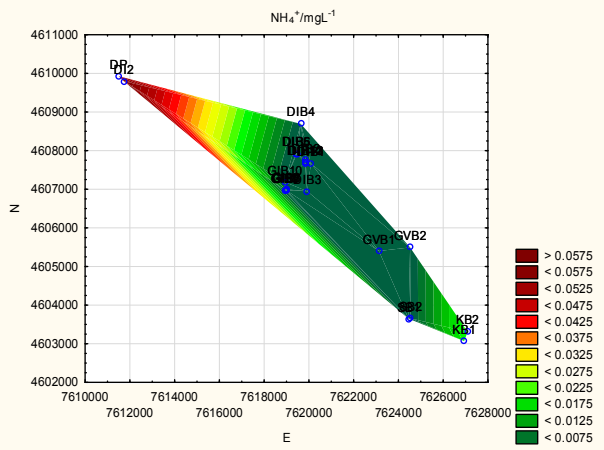

Fig. 18. Spatial distribution of NH_4^+/mgl^{-1}

CONCLUSION

Based on the presented results of the examinations a number of conclusions can be made.

– The temperature of the tested waters in March-April 2012 is in the range of 8 – 14 °C. The maximum value is measured in the water pumped from Damjan.

– The measured values of pH for the tested ground waters are in the range of 6.2 – 8.0 with a median of 7.5. The measured values are within the permissible values according to the Regulations for drinking water, only the water with a minimum pH of 6.2 exceeds the value according to the regulations for drinking water.

– TDS values measured in the examined waters range from a minimum value of 326 mg/l to a maximum value of 2252 mg/l. In all waters except in sample B7, TDS values do not exceed the recommended MAC for drinking water, 2000 mg/l.

– In the examined waters the determined hardness is in the range of 18 to 138^{0}dH. In most cases, the values obtained exceed MAC. These are very hard waters.

– The concentrations of hydrogen carbonate determined as alkalinity range from a minimum value of 68 mg/l to a maximum of 540 mg/l.

– Chlorides are determined in a concentration range from a minimum of 17.4 mg/l, up to a maximum of 241 mg/l and within the maximum permissible concentrations according to the Regulations for drinking water security policy of the Republic of Macedonia (250 mg/l).

– The range for sulphates in the examined waters is from 4 mg/l to 524 mg/l and are within the permissible limits. Only the concentration of sulphate anions determined in the water from Damjan spring exceeds the MAC for drinking water, so this water is unsuitable for drinking.

– The results obtained from measurements of the concentrations of dissolved phosphorus range from a minimum of 0.011 mg/l to an extremely high value, 4.62 mg/l. All measured values for phosphates in the examined waters do not exceed the MAC value.

– The concentration of nitrates in water ranges from a minimum value of 4.6 mg/l to a maximum of 477 mg/l. In 13 tested waters the values obtained for nitrate anions exceed the limit value of 50 mg/l according to the Regulations for drinking water safety.

– Nitrite ions are detected in 12 of 22 examined water samples with a maximum concentration of 0.12 mg/l. The specified maximum concentrations for nitrite ions in water samples KB1 and KB2 are higher than the upper limit of maximum permissible concentrations for drinking water.

– Ammonium ions are detected only in the five tested samples, with a maximum concentration of 0.0579 mg/l. The resulting maximum concentration of the ammonium ion is lower than the MAC value in drinking water of 0.1 mg/l.

– Studies suggest that due to the high values for TDS the examined 22 ground waters cannot be used directly as drinking water.

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Р е з и м е

ФИЗИЧКО-ХЕМИСКИ КАРАКТЕРИСТИКИ НА ПОДЗЕМНИТЕ ВОДИ НА ПОТЕГОТ ОД С. ИЊЕВО ДО С. КАЛУЃЕРИЦА, РАДОВИШ

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Клучни зборови: катјони; анјони; pH; температура; тврдост на водата

Во овој труд се прикажани резултатите од најновите испитувања на физичко-хемиските параметри на подземните води извршени на потегот од селото Калуѓерица до селото Ињево.

Испитувањата покажаа дека температурата на испитуваните води е во распон од 8 до 14°C, измерените вредности на pH на анализираните води се движат од 6,2 до 8,0. Измерените вредности за TDS во испитуваните води се движат од минималната вредност 326 mg/l до максималната вредност од 2252 mg/l. Определената тврдост се движи од 18 до 138°dH. Опсегот на определените концентрации на алкалноста се движи од минимални 68 mg/l до максимални 540 mg/l. Хлоридите се во концентрационен опсег од минимално 17,4 mg/l, до максимално 241 mg/l. Концентрациониот опсег на сулфатите во испитуваните води е од минималните 14,6 mg/l до максималните 535 mg/l. Добиените резултати од мерењата на концентрациите на растворениот фосфор се движат од минималните 0,011 mg/l до екстремно високата вредност, 4,62 mg/l. Опсегот на концентрациите на нитратните анјони се движи од минималните 4,6 mg/l во Горно Ињево Б7 до максимално 477 mg/l, а нитритите имаат максимална концентрација од 0,12 mg/l. Амониумските јони се детектирани во максимална концентрација од 0,0579 mg/l. Определувањето на хемискиот состав на подземните води е од посебно значење за водоснабдувањето на овие населени места.