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*Stručni članak*

# HYDROGEOCHEMICAL CHARACTERISTICS OF THE Sv. IVAN SPRING IN ISTRIA, CROATIA

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**Key-words:** Hydrogeochemistry, Karst, Groundwater, Istria, Croatia

In addition to geological, hydrological and hydrogeological investigations and groundwater tracing, detailed surveying of the groundwater quality is becoming particularly important for environmental impact monitoring on karst aquifers. Groundwater quality data contain two types of information, i.e. the natural chemistry of water and its modifications caused by anthropogenic impacts. The method of results presentation as well as the importance of water quality surveying, particularly with respect to the indicators showing its natural chemistry, are shown here exemplified by the Sv. Ivan spring in Istria, Croatia. Natural chemistry of the groundwater is a consequence of hydrogeochemical facies, and it is used here for interpretation of spring generating conditions and the origin of groundwater. Results obtained so far confirm that the extent of recharge area of the spring change in dependence of the hydrological conditions. Hydrogeochemical characteristics of the spring are presented graphically in the form of correlation diagrams showing major groundwater parameters, saturation conditions and trends of particular parameters as a function of time.

**Ključne riječi:** Hdrogeokemija, Krš, Podzemna voda, Istra, Hrvatska

Za promatranje utjecaja okoliša na krške vodonosnike, uz geološka, hidrološka i hidrogeološka istraživanja, te trasiranja podzemnih voda postaje posebice važno proučavanje i detaljno snimanje kakvoće podzemnih voda. Podaci o kakvoći podzemne vode u sebi sadrže dvije vrste informacija od kojih se jedna odnosi na njezin prirodni kemijski sastav, a druga na njezinu promjenu uslijed antropogenog utjecaja. Način prikazivanja rezultata i značaj snimanja kakvoće vode, i to posebice onih pokazatelja koji izražavaju njezin prirodni kemijski sastav prikazan je na primjeru izvora Sv. Ivan u Istri. Prirodni kemijski sastav podzemne vode posljedica je hidrogeokemijskog facijesa, pa su tako na osnovi njega interpretirani uvjeti pojavljivanja izvora i porijeklo vode, a polučeni rezultati ukazali su i da se površina priljevnog područja izvora mijenja ovisno o hidrološkim uvjetima. Hidrogeokemijska obilježja izvora prikazana su grafički, i to u vidu korelacije osnovnih parametara u podzemnoj vodi, uvjeta zasićenosti, te kretanja određenih parametara u funkciji vremena.

## Introduction

Sv. Ivan spring is located at the bottom of Mirna River valley, near the small town of Buzet, 49 m above the sea-level (Fig. 1). Tapped reinforced concrete building above the spring has cylindrical shape with 22 m in radius. It is founded in marls some 4 to 5 m below the surface.

The catchment area of the spring has been defined on the basis of the conclusive tracing data (Table 1), hydrogeological properties of rocks, geological and structural relations in the field, and by hydrological analysis, i.e. by the spring discharge analysis as a function of the recharge area surface and the rates of precipitation and evaporation (Bonacci & Magdalenić, 1993). In this way determined recharge area is approximated to 70 km$^2$. Generally, it turns out that the south-western parts of Mt. Ćićarija are drained by Sv. Ivan spring (Fig. 2). A more recent exploration connected with increasing groundwater exploitation and pollution mostly due to industrial and transport development showed different characteristics of this area. Namely, the drainage towards the spring predominates, but during a high groundwater level, part of the waters run out at the surface, while the rest flows under the ground to some other springs. Hence, the defined recharge area has a zoned character (Urumović et al. 1999, Vlahović, 1999). Consequently, the recharge area could considerably exceed the surface determined by sinkhole tracing points (Vazdar & Urumović, 1995). Hence, above mentioned circumstances asked for a study and monitoring of groundwater chemistry at Sv. Ivan spring, not only parameters that illustrate its modification caused by the anthropogenic impact, but also those related to its natural chemical composition.

## Occurrence and regime of the spring

Hydrogeological relations between recharge area and spring occurrence are strongly controled by local geology and morphology as well as by hydrological conditions. The latter has a strong impact on intensity of groundwater circulation and the occurrence of some specific karst phenomena due to underground saturation (Hlevnjak et al. 1995). Therefore, beside the main spring, there are tens of relatively small lakes with occasional water run off, all together composing a spring zone, particularly during a high water table period.

Part of the Mirna River valley where the spring is located is composed of Paleogene nummulitic limestones and flysch sediments both covered by Quaternary clay deposits. Water appears at the top of a crushed and karstified overturned anticline, running out through fissures and joints occupying its crest zone (Fig. 3).

Spring discharge is relatively uniform (Fig. 4). During dry seasons it drops down to the level of pumping rate ranging from 150 to 220 l/s. Maximal discharge occasionally exceeds 2000 l/s (Bonacci & Magdalenić, 1993). Minimal and maximal discharge rate is around 10, while ratio $Q_{max}/Q_{min}$ depends more on pumping rate in dry period than on maximal discharge due to a possibility of water level to decline below the surface. General properties of spring regime are relatively high minimal discharge value and relative uniformity of maximal discharges when compared with average hydrological conditions common for karst springs. This is enabled through established boundary conditions as well as through a high permeability of karst aquifer. Periodical karst spring Tombazin, located at the boundary of the Mirna valley at a contact of flysch and limestone, has a key role for maximal discharge regulation on Sv. Ivan spring which in fact represent an overflow of ground waters from karst aquifer during extremely high ground water levels (Hlevnjak et al. 1995).

In most part of the spring catchment area characterised by a high plateau morphology, the spring Pivka occurs as well, active only during heavy rainy periods when water precipitation surpass the quantity that can be taken by underground flow. In all other circumstances groundwater circulates through limestones underneath the flysch cover and usually appears on the Sv. Ivan spring. As a rule, during a high water level when the

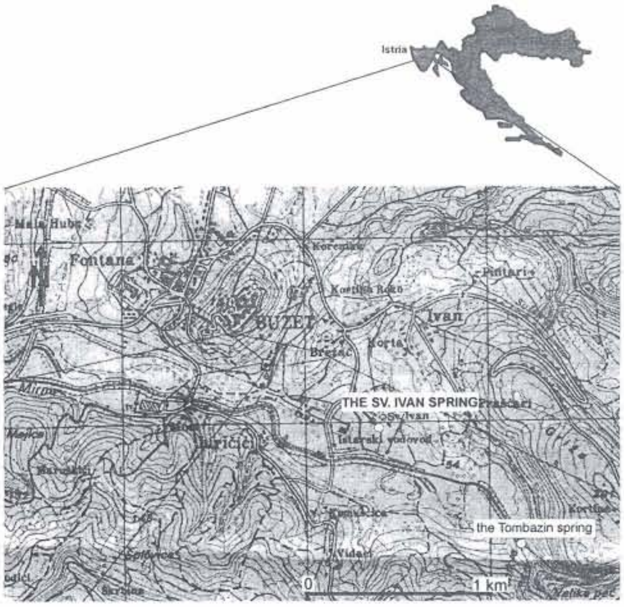

Fig. 1. Location map of the Sv. Ivan spring

groundwater level rises up above the limestone-flysch contact, several minor springs located along the Mirna valley become active as well. These springs, as well as all others located along the Mirna channel, probably represent a wide, very heterogeneous spring zone fed by the same karstic aquifer which has enormous economic importance because it stores considerable storage of groundwater during dry periods.

## Hydrogeochemical characteristics of the spring

Hydrogeochemical characteristics of the Sv. Ivan spring were monitored by the chemical analyses performed in the Institute for Public Health of Istrian County – Pula, also in the Croatian Institute for Public Health – Zagreb and in the Istrian Watersupply System – Buzet. The characteristics were monitored from the beginning of 1986 until the end of 1997. The reliable data were unequally distributed, which resulted in differences in number of measurements for various cations.

In the following text, the hydrogeochemical characteristics of the spring will be illustrated by means of correlation of the basic groundwater parameters, together with seasonal changes of some parameters during the year. In correlation charts, the concentration of dissolved matter in the water is shown in *mmolekv/l*, while

Table 1. Underground connections in the area surrounding Sv. Ivan spring

| LOCATION DATE, TRACER | | CONFIRMED CONNECTION WITH SPRINGS | ELEVATION OF SINK-HOLE (mn.m.) | ALTITUDE DIFFERENCE (m) | DISTANCE (km) | APPARENT VELOCITY OF GROUND WATER (cm/s) |
|---|---|---|---|---|---|---|
| Sink-hole Račice<br>6.V.1987.,20 kg of Na-fluoresceine | | Opatija<br>Sv. Ivan | 470 | 470 | 22,5 | 1,10 |
| Sink-hole Jezerina<br>13. V. 1986., 20 kg of rhodamine | | Rižana<br>Sv. Ivan<br>Mlini<br>Opatija | 510 | 360<br>461<br>410 | 15,4<br>18,8<br>24,7 | 0,97<br>2,00<br>1,86 |
| Sink-hole Male Loče | 10. IV. 1985.<br>3200 kg of potassium chloride (KCl) | Mlini<br>Sv. Ivan<br>Opatija | 500 | 400<br>451<br>500 | 17,4<br>18,7<br>27 | tracer were detected, but on the limit of detection |
| | 13. V. 1986.<br>20 kg of Na-fluoresceine | Rižana<br>Osapska reka | | 350 | 17<br>19,5 | |
| Sink-hole Prapoče | 5. XII. 1979.,<br>400 Ci of tritium | Sv. Ivan | 554 | 505 | 7,9 | 4,50 |
| | 30. V. 1984.,<br>400 Ci of tritium | Sv. Ivan | | 505 | 7,9 | 2,40 |
| Sink-holes near Dane | 6. V. 1987.,<br>15 kg of rhodamine | Opatija | 590 | 590 | 26 | 2,70 |
| | 27. VI. 1989., tritium | Opatija<br>Sv. Ivan | 440 | 440<br>395 | 26<br>9,5 | 1,70<br>0,30 |
| Sink-hole near Lanišće<br>12. VI. 1992., 400 Ci of tritium | | Sv. Ivan<br>Opatija | 500 | 451<br>500 | 10,5<br>16,5 | 1,13<br>1,70 |
| Sink-hole in Rečina valley | 1939. ?,<br>10 kg of barm | Sv. Ivan | 64 | 15 | 1,5 | |
| | 14. VI. 1989.,<br>1 Ci of tritium | Sv. Ivan | | 15 | 1,5 | 11,00 |

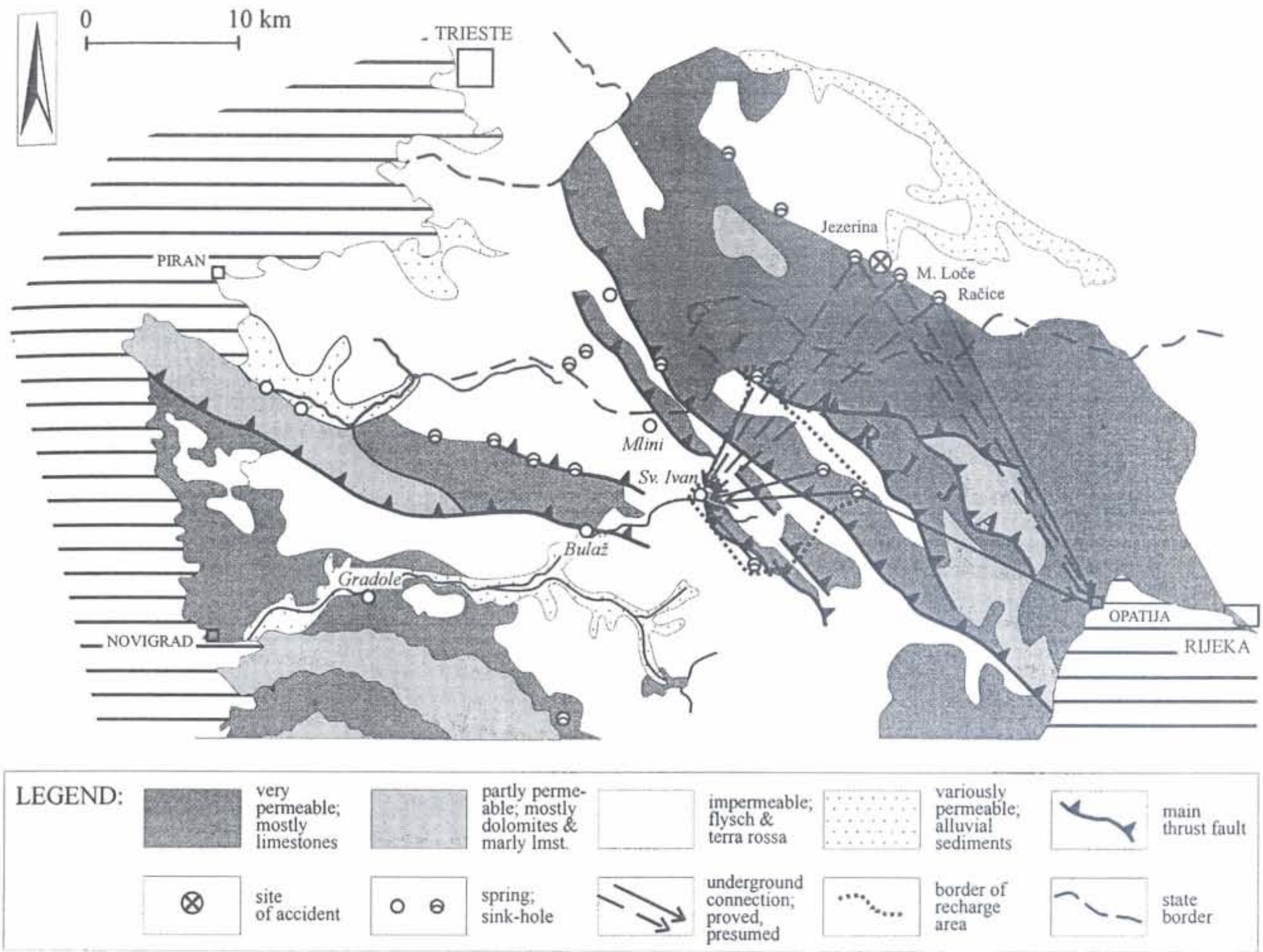

Fig. 2. Hydrogeological sketch map of the area surrounding the Sv. Ivan spring (the northern part of Istria) with catchment area

the correlation coefficient *(r)* is calculated after Spearman. The values of $0.75 \leq r < 0.99$ present a clear dependence, respectfully the clear correlation, those in the range $0.5 \leq r < 0.75$ mean the mild dependence, and $r < 0.5$ presents the indicated correlation (Lecher, 1982). The calcite saturation index *($SI_{calcite}$)* and the dolomite saturation index *($SI_{dolomite}$)* as well as the partial pressure of $CO_2$ *($\log pCO_2$)* are calculated by utilisation of the NETPATH geochemical model (Plummer et al. 1994). Thereby, for the $SI=0$, there is a thermodynamic equilibrium between the mineral and the solution; the $SI<0$ reflects the subsaturation with the specific mineral, and $SI>0$ the supersaturation. The $SI<0.3$ reflects the slightly saturated water and the *SI* in the range of 0.3−0.7 the strongly saturated one (Appelo & Postma, 1994).

*General hydrogeochemical characteristics of the spring*

The rain season is characterised by the turbidity of the spring water with concentration of suspended particles exceeding the maximally allowed value, and can even reach the 2000 mg$SiO_2$/l. The hydrogen-ion activity *(pH)* is between 7.0 and 8.3. The residue on evaporation lies in the broad range of 145 to 465 mg/l, as well as is the content of suspended matter (2.3−139 mg/l). The chemical oxygen demand is also quite variable −0.4 to 6,23 mg $O_2$/l while the biochemical oxygen demand lies within the marginal values of 0.12 and 9,1 mg/l, respectfully. The water contains 6.86−17.08 mg/l of dissolved oxygen and 8.0−16.0 mg/l of $CO_2$. The silicon was measured in the 0.1−15 mg $SiO_2$/l range. Since the chemistry of waters in karst aquifers is mostly influenced by the partial pressure of $CO_2$ in the soil and in the unsaturated zone as well as by the dissolution of carbonate minerals (calcite, dolomite), the dominant anions in the Sv. Ivan spring waters are bicarbonates. They were measured in concentrations of 189 to 336 mg/l, where the dominant cation is calcium that was found in the range of 54 to 90 mg/l, while the magnesium content varies from the 3.4 to 25.7 mg/l. The bicarbonate content of water solution is a part of the carbonate hardness. In the range of 6.5 to 8.5 pH this is the dominating indicator of hardness. The determined hardness values are in the 8.4−1.36 °dH. The concentration of chloride is found to be from 7 to 50 mg/l, and sulphate in the 0.3−30 mg/l range. The range of electrical conductivity is quite wide −208 to 784 μS/cm.

*Ion relations*

The performed correlation analysis of the basic cation and anion concentration in the groundwater gave the following results:

1. The bicarbonate and calcium ions show the clear dependence on each other (r=0.95) where the increase in concentration of one is followed by the

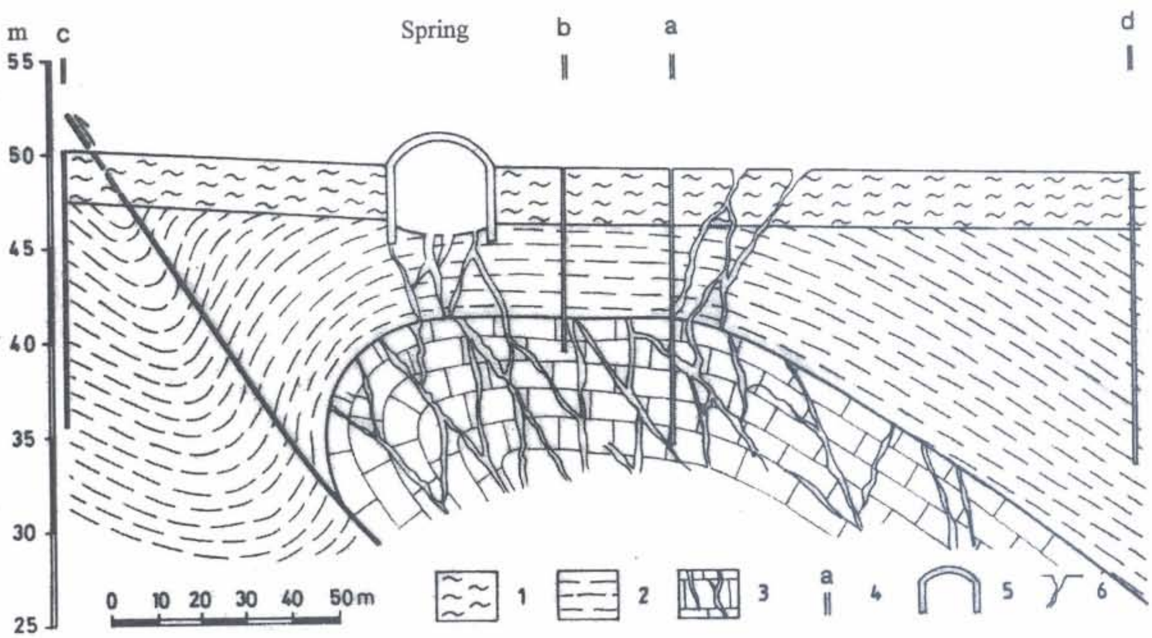

Fig. 3. Detailed hydrogeological cross – section of the Sv. Ivan spring.
*Legend:* 1 – Quaternary clays; 2 – flysch deposits; 3 – karstified limestones; 4 – bore holes; 5 – capture of spring; 6 – periodic springs (after Hlevnjak et al. 1995)

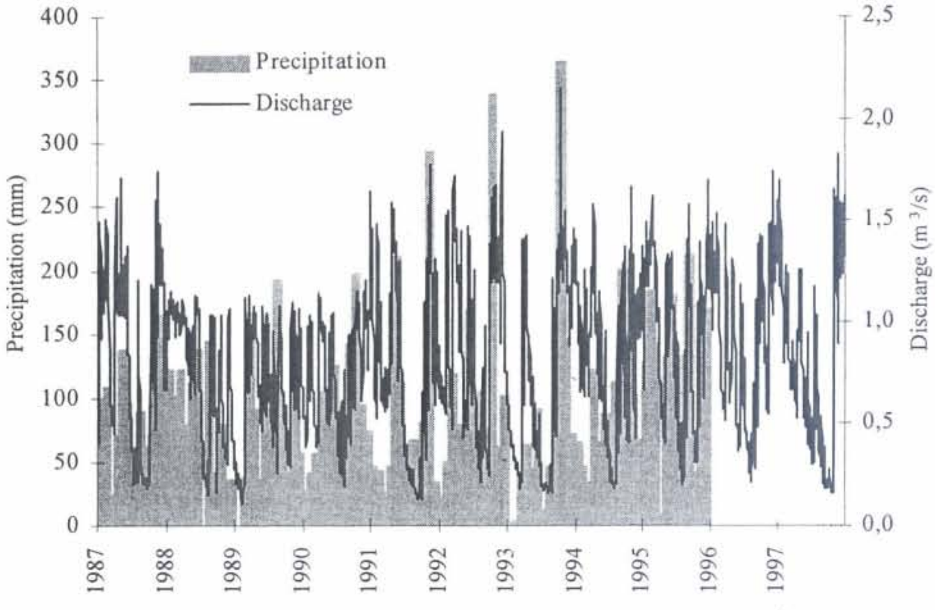

Fig. 4. Hydrograph of the Sv. Ivan spring in correlation with precipitation (the nearest station of the spring – station Abrami)

increase in concentration of another (Fig. 5). That's why the conclusion is drawn that $Ca^{2+}$ originates from the dissolution of carbonate minerals, mostly of calcite in limestones and to a lesser extent of the calcite in the carbonate fraction on the flysch. A mild correlation between the bicarbonate and $Mg^{2+}$ (r=0.74) points out that weathering the dolomites and the classic flysch deposits also contribute to basic ion water composition of the spring, but relatively unimportant. Bicarbonate with the $Na^{+}+K^{+}$ didn't show any correlation.

2. The correlation between the basic cations and $Cl^{-}$ and $SO_4^{2-}$ in the water wasn't obtained. However, in cases when the $(Na^{+}+K^{+})/Cl^{-}$ ratio exceeds 0.55, and where the chloride concentration lowers the sodium and potassium content increases, both indicate that source of these cations must be the hydrolysis of the $Na^{-}$ and $K^{-}$ alumosilicates in flysch or soil (Hem, 1985).
3. The correlation between the basic anions in the water wasn't obtained.
4. The total hardness of water and $HCO_3^{-}$ exhibit a clear dependence (r=0.75), while between the $SO_4^{2-}$ and the total hardness there is only the indicated one, at all, as is also between the $Cl^{-}$ and the total hardness. All these show that predominant part of hardness is related to carbonate hardness, more exactly $HCO_3^{-}$ (Fig. 6). Moreover, the clear correlation was calcu-

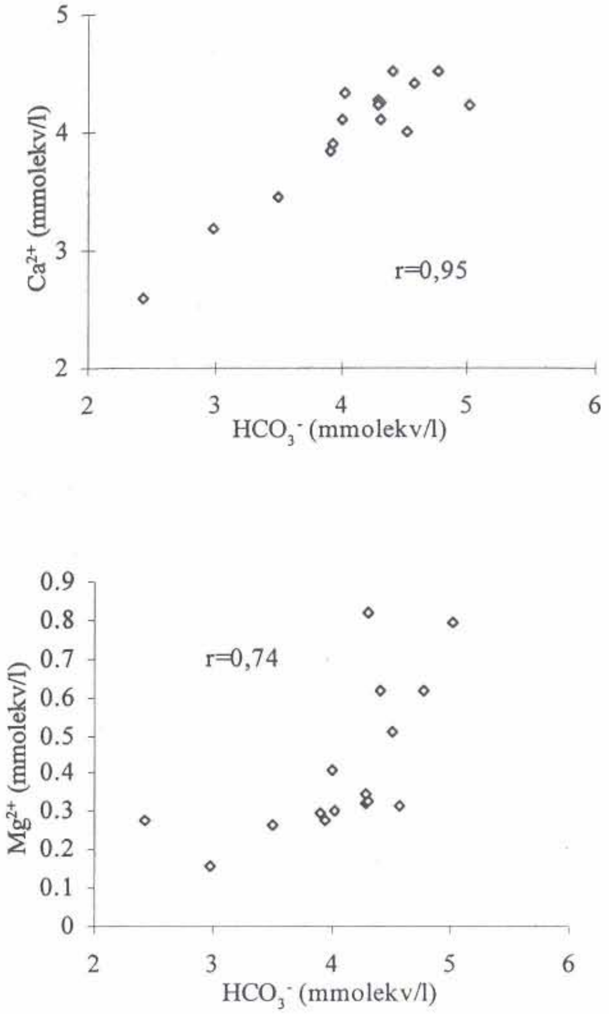

Fig. 5. Relation between bicarbonates and calcium and magnesium ion content

lated between the total hardness and the $Ca^{2+}$ (r=0.79), until correlation with the $Mg^{2+}$ is mild (r=0.65). It means that Ca – salts take the major part in water composition. $Na^+$ i $K^+$ in the water there are in relatively low concentrations and don't affect on the value of total hardness in the water.

5. There is a clear correlation between the electric conductivity and $HCO_3^-$ (r=0.94). The mild correlation was calculated between the electric conductivity and $Cl^-$ (r=0.66) and there is none between the conductivity and concentrations of $SO_4^{2-}$, what illustrates the predominantly carbonate composition of water (Fig. 7).
6. The clear correlation between the electric conductivity and $Ca^{2+}$ was obtained (r=0.88), and the mild correlation was calculated between the electric conductivity and $Mg^{2+}$ (r=0.63). The low content of $Na^+$ and $K^+$ didn't affected essentially neither on the value of electric conductivity (Fig. 8).
7. The correlation between the two main cations ($Ca^{2+}$ and $Mg^{2+}$) is only the indicated one. There are two groups of values (Fig. 9): the one of them pertain to content of $Mg^{2+}$ to 0.5 mmolekv/l and has no influence on the $Ca^{2+}$ concentration, and the another to content of $Mg^{2+}$ above 0.5 mmolekv/l which results in decrease of $Ca^{2+}$ content. Thereby, the clear correlation between this two major cations (r=0.93) has been obtained. The higher concentration of $Mg^{2+}$ was measured during the low and mean water on the spring, so can be conclusion that the spring drainage at that time from area where in limestones is major part of $Ca^{2+}$ in crystal structure of calcite changed with $Mg^{2+}$, relatively that drainage aquifer that in the its structure has as well as dolomitic limestones and dolomites.

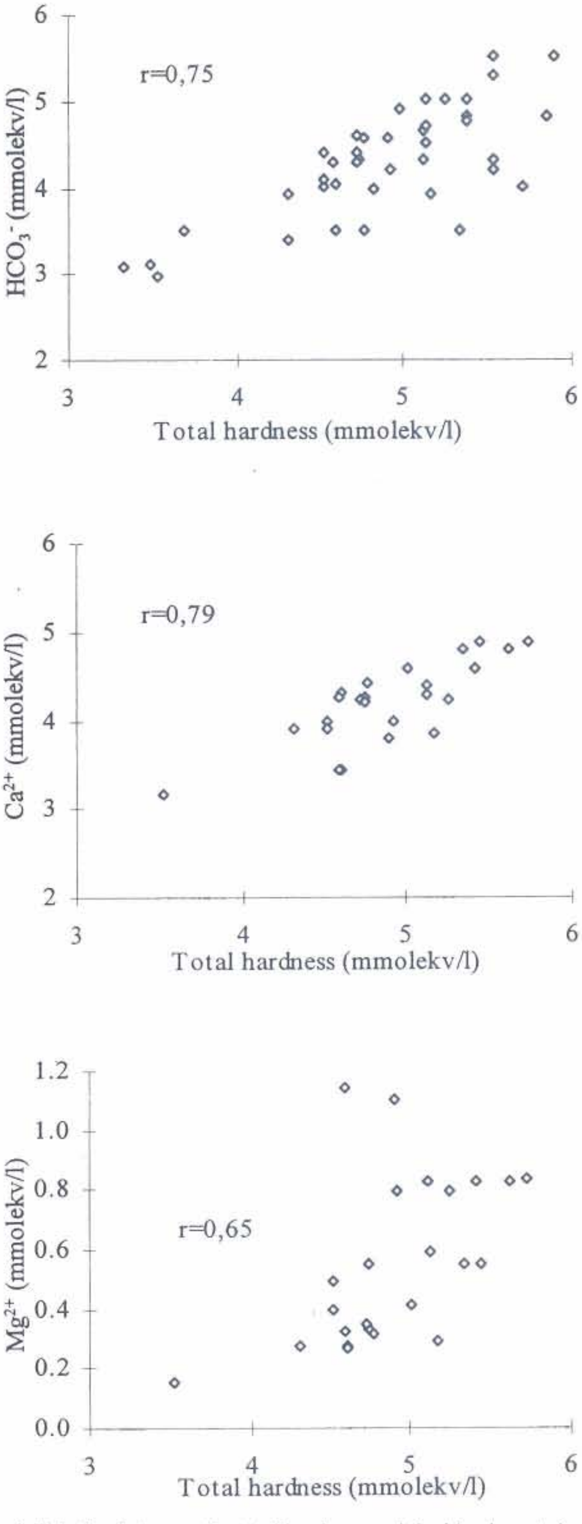

Fig. 6. Relation between the total hardness and the bicarbonate ions, and between the total hardness and the calcium and magnesium ion content

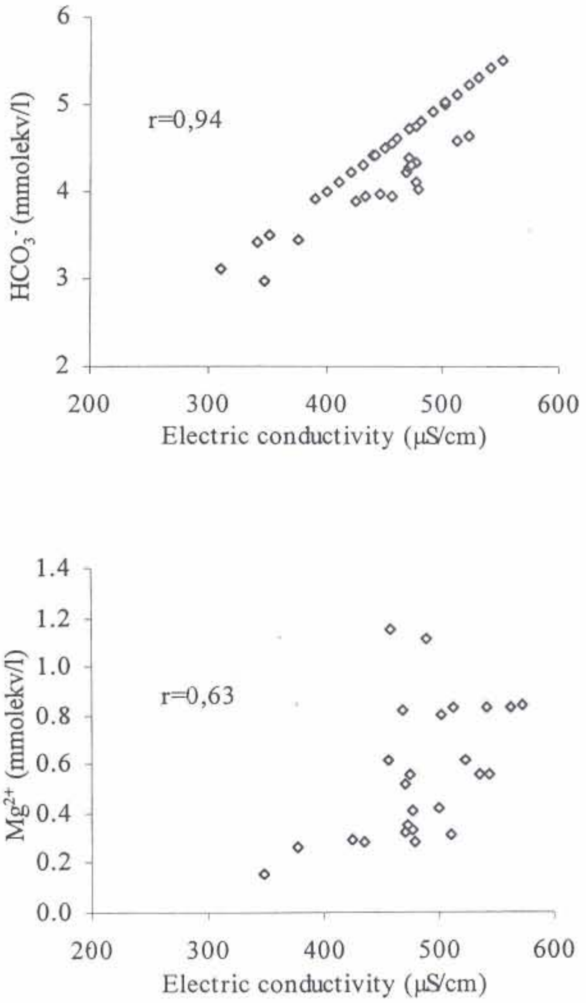

Fig. 7. Correlation charts of the electric conductivity vs. the bicarbonate and chloride ions

*Saturation states*

Based on the calculation by the means of geochemical model of the saturation states and variation of $CO_2$ partial pressure, the following results were obtained (Fig. 10):

1. During the year there is a variation of the partial pressure of $CO_2$ in the groundwater. Increase of $p_{CO_2}$ is observed during rainy season, when leaching of $CO_2$ in water is higher due to percolation of water through the soil and nonsaturation zone where $CO_2$ is formed by decay of organic matter and by root respiration.
2. The groundwater is undersaturated to saturated with respect to calcite. The saturation is reduced due to the infiltration of fresh rainfall during the rainy season, because increase of $CO_2$ in ground and this pointing out to the longer residence time.
3. The groundwater is undersaturated with respect to dolomite.

*Seasonal variation*

Since in the karst region the average water temperature equals the average temperature of air, the spring water temperature makes a significant indicator of the recharge area. The temperature of the Sv. Ivan spring water is relatively uniform in the annual cycle. This results from the good mixing of the waters in the aquifer and relative long residence time. The water temperature is the highest in August, and the lowest in January (Fig. 11).

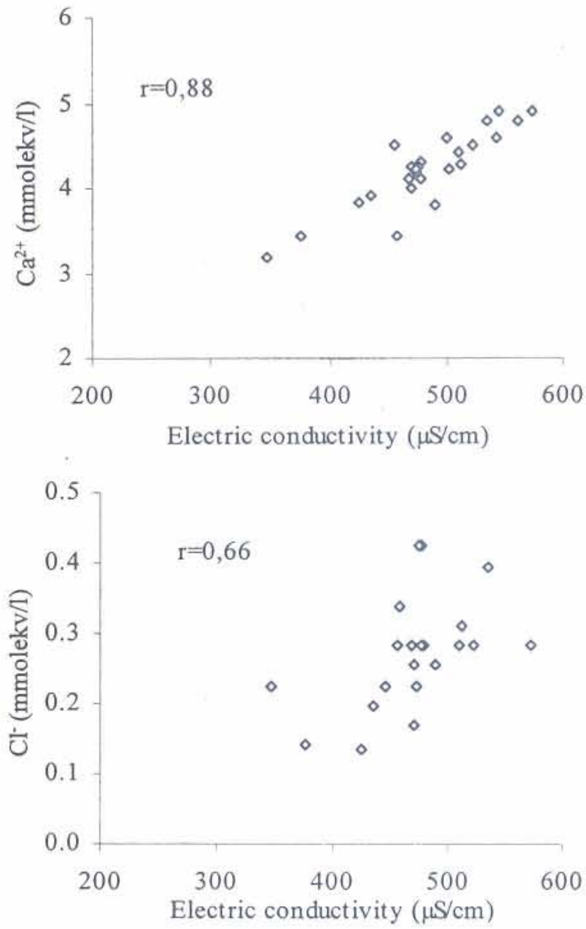

Fig. 8. Correlation charts of the electric conductivity vs. the calcium and magnesium ion content

The total hardness of, mostly carbonate, water often exhibits seasonal variations in concordance with the vegetation period and hydrologic conditions (Fig. 11). The lowest hardness appears in the dry summer months, and increased one in autumn and winter months. Namely, during the vegetation period there is a gradual accumulation of $CO_2$ in the soil, which causes the increase of $CO_2$ partial pressure. This results in the faster dissolution of carbonate minerals in the soil and in the upper part of the unsaturated zone, together with alteration and hydrolysis of alumosilicates in flysch sediments.

During the summer dry season there is no infiltration to the groundwater level. The first significant autumns rainfall starts leaching the dissolved matter from the soil and from the upper part of the unsaturated zone. The groundwater is thereby enriched in dissolved matter, especially in the $HCO_3^-$, $Ca^{2+}$ and $Mg^{2+}$, meaning that there is an increase in carbonate hardness paralleled by the increase in total hardness (Vlahović, 1999).

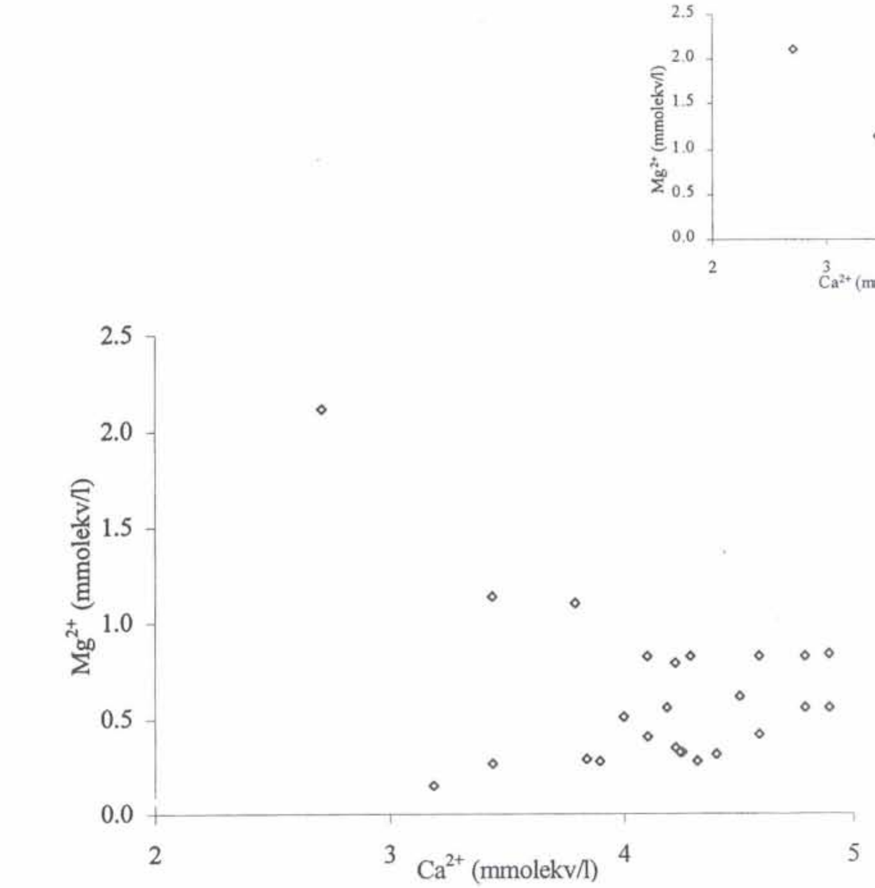

Fig. 9. Correlation between the two main cations ($Ca^{2+}$ and $Mg^{2+}$)

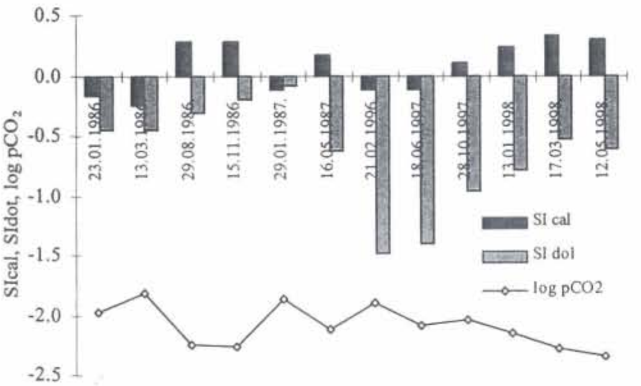

Fig. 10. Variability of log $CO_2$ and saturation with respect to calcite and dolomite in the samples of the Sv. Ivan spring water

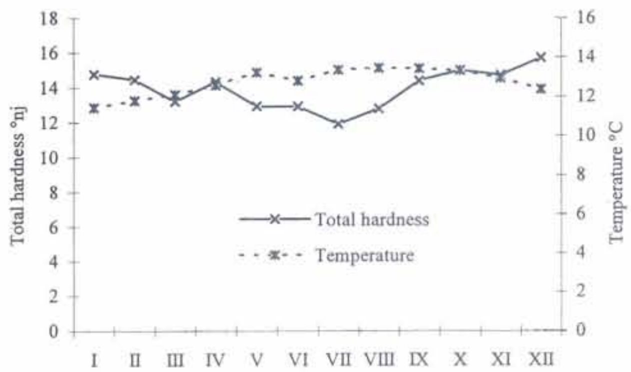

Fig. 11. Annual variation of the average water temperature and the total hardness of water

## Discussion and conclusions

The carried out analyses of hydrogeochemical characteristics of the spring compared together with basic geological, hydrological and hydrogeological characteristics, and groundwater tracing results, all point to the conclusion that earlier defined chatcment area is valid for the area of predominant drainage in direction of the spring only. A much broader recharge area exists connected to the spring in dependence of the hydrological conditions.

The origin of Sv. Ivan spring waters is connected with exclusively carbonate aquifer. Established relative uniformity of water temperature during year, when compared with other springs in Istria, indicates a relatively longer residence time of major water mass in aquifers and good homogenisation of water. These are characteristics of disperse type of flow and relatively increased role of seepage flow of groundwater. Therefore, the predominant quantity of water comes to the spring from the Mt. Ćićarija area during the dry seasons, mostly. During the rain season, the water cached in the immediate vicinity of spring prevails. Namely, after intensive precipitation, the water becomes undersaturated with respect to calcite. This represents the effect of short local flow paths along fracture and privileged flows in catchment area, and shorter residence time of waters in aquifers. Therefore, like to undersaturated could came as well as due to associating with water from different parts of aquifers, so and during high water level there is also the inflow from the Mt. Ćićarija area. In other words, there is a contemporaneous influence of the privileged currents and the seepage flow, but the privileged currents ratio in the spring capacity is much smaller (Vlahović, 2000).

Clear correlation between $HCO^{3-}$ , electric conductivity and total hardness with $Ca^{2+}$, and mild one with $Mg^{2+}$ purport that in water content beside $Ca^{2+}$ $Mg^{2+}$ is considerably present as well. This speaks for the fact that carbonate rocks forming the aquifer are at least in part composed of dolomite minerals. These rocks, mostly dolomitic limestones, dolomites and dolomite breccias are known outcropping only on Ćićarija area. Minor part of $Mg^{2+}$ could also originate from flysch sediments, which has Mg-alumosilicates in composition through the process of $Mg^{2+}$ leaching.

Additionally, the accidental spilling of oil in the Slovenia high karst region caused the long lasting and relatively widespread regional groundwater pollution (Vlahović, 1999, Urumović, et al. 1999), thereby the highest concentrations of mentioned pollutants appeared during low and mean water levels, while they were very low during a high levels. The latter could be explained by predominant drainage of aquifer that is not polluted (i.e. a narrow recharge area of spring), while the former indicates that the real spring drainage area exceeds that previously proposed catchement area and that it extends up to the highest region of the carbonate plateau, i.e. up to the Ćićarija massif. Thereby there is wide areas of mutual recharge area with other springs in Istria, but with various part of drain, therewith the portions of drain toward to several springs change in time depends of water level in underground and distribution of pluvial regime.

The conclusion can be pointed out that regional flow of groundwater is established as a consequence of geology, while the hydraulic conditions affecting the spring occurrence are controlled by the relation among the morphology and hydrogeological relations. In these circumstances the Sv. Ivan spring is mostly fed from the narrow recharge area in duration of the rainy seasons and the high water levels. This is so, because the groundwater flows in the high-water season have increased speed and are oriented to the more karstified upper zone of the aquifer, which results in increased capacity of springs. At the same time, this reduces the residence time of water in the aquifer. On the contrary, in the dry season, the recharge area is gradually enlarged to the parts of aquifer where the drainage is reduced by the relatively lower regional permeability of sediments. The water that springs out in the dry season belongs to the base flow, and is marked by relatively longer aquifer residence time.

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