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## Extended Abstracts

**Editors:**  
Andrzej Zuber  
Jarosław Kania  
Ewa Kmiecik



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title: **Integrated hydrochemical assessment of the carbonate aquifer of the Ivanščica Mountain**

author(s): **Tamara Marković**

Croatian Geological Survey, Croatia, tmarkovic@hgi-cgs.hr

**Ozren Larva**

Croatian Geological Survey, Croatia, olarva@hgi-cgs.hr

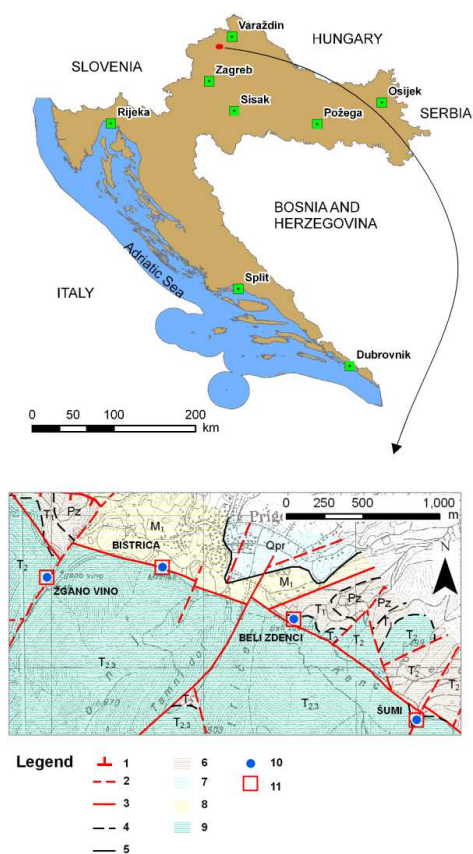
**Vinko Mraz**

Croatian Geological Survey, Croatia, vmraz@hgi-cgs.hr

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## INTRODUCTION

Groundwater is the dominant source of drinking water in Croatia. The main carbonate aquifers are situated in karstic part of Croatia. Also, some smaller but very valuable carbonate aquifers are situated in Panonian part of Croatia. Environmental isotopes such as  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$  and  $^3\text{H}$  and chemical data represent powerful tool to determine the origin of water, water dynamics, the storage properties of karstic catchments (Maloszewski et al., 2002; Einsiedl, 2005; Katz et al., 2001). The stable isotopes ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) and tritium are particularly suitable for tracing the origin of water in the hydrological cycle because they are constituents of water molecules (Maloszewski et al., 2002). The chemical data and environmental isotopes in combination with conventional hydrogeological methods provide additional information on investigated area. The Mt. Ivanšćica, mainly built of Triassic dolomites and limestones, is situated in the north-west part of Croatia and represent the main drinking water resource for the Ivanec town and surrounding settlements. The catchment area of about 6 km<sup>2</sup> is drained by four springs: Žgano Vино, Bistrica, Beli Zdenci and Šumi (Fig. 1).



**Figure 1.** Location and hydrogeological map. 1 — reverse fault; 2 — supposed fault; 3 — fault; 4 — supposed geological boundary; 5 — geological boundary; 6 — Paleozoic (Carbon - Perm), lower and middle Triassic sediments, Pz, T<sub>1</sub>, T<sub>2</sub>, — dominantly impermeable rocks; 7 — Quaternary proluvial sediments, Q<sub>pr</sub> — permeable rocks; 8 — lower Miocene sediments, M<sub>1</sub> — dominantly impermeable rocks; 9 — middle and upper Triassic sediments, T<sub>2</sub>, T<sub>2,3</sub> — permeable rocks; 10 — spring; 11 — intake.

During the hydrogeological investigations for determination of the sanitary protection zones of springs, environmental isotopes and chemical data were used as additional tool for better characterization of groundwater renewability, circulation and geochemical evolution.

### HYDROGEOLOGICAL SETTING

The study area (Mt. Ivanščica) is located in the north-west part of Croatia (Fig. 1). Ivanščica is the highest mountain in this area with the highest peak 1061 m a.s.l. The mean annual precipitation is about 1200 mm/a, and the mean air temperature is 10.4°C.

The mountain is built of Carbon-Perm, Triassic, Cretaceous, Miocene and Quaternary sediments (Šimunić et al., 1979; Šimunić et al., 1983; Šimunić, 1992). The oldest Carbon-Perm sediments are clastic deposits which are generally impermeable. Lower Triassic silts, shales and sandstones, as well as middle Triassic volcano-sedimentary complex, are also dominantly impermeable rocks. Carbonate rocks of middle and upper Triassic age are dolomite and limestone which are the main aquifer. Cretaceous clastic carbonate sediments, as well as clastic and volcanic rocks of Miocene age, are also impermeable rocks. The permeable rocks of Quaternary age are proluvial sediments mainly found on slopes.

The catchment area of about 6 km<sup>2</sup> is drained by four springs: Žgano Vino (Fig. 2b), Bistrica (Fig. 2a), Beli Zdenci and Šumi, which are situated on the NW side of the mountain. The springs were formed on the fault zone which is the contact between permeable carbonate sediments and impermeable sediments. The water from the springs is tapped for the water supply system of Ivanec town and surrounding settlements. The highest mean yield has Bistrica — 60 l/s, Žgano Vino and Šumi follow with 20 l/s, and the lowest mean yield has Beli Zdenci — 4 l/s.

a)



b)



**Figure 2.** Photos of a) Bistrica and b) Žgano Vino.

### METHODS

Groundwater was sampled from all springs in July and September 2008 and in February 2009. Prior to taking water samples from individual springs, the following parameters were measured “in situ” by probes of WTW company: EC, TDS, T, pH, turbidity and oxygen content in waters. At the Hydrochemical Laboratory of the Department of Hydrogeology and Engineering Geology — Croatian Geological Survey, the concentrations of the basic anions and cations were measured. The content of chlorides, sulphates and nitrates were measured by ion chromatograph of the LabAlliance company, whereas the concentrations of orthophosphates and ammonium were measured by the spectrophotometer DL/2010 of the HACH company. The concentrations of

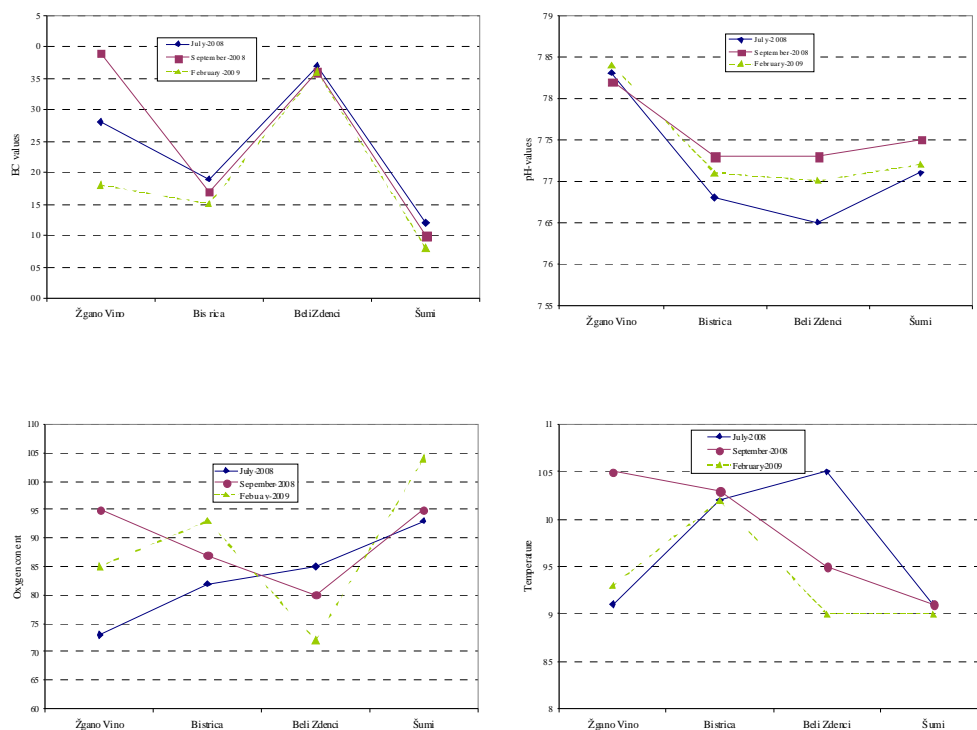
calcium, manganese, sodium and potassium were measured by the atomic adsorber of the Perkin Elmer company. The content of  $\text{HCO}_3^-$  was determined by titration. The results for ions were processed using the Netpath software. Data quality was further assessed using the charge balance between the sum of cations and anions (expressed in meq/l), which was always  $\pm 5\%$ .

The ratios of stable isotopes of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  in sampled water were measured at the Joanneum Research Forschungsgesellschaft mbH Institute of Water Resources Management (WRM) Hydrogeology and Geophysics in Graz, Austria and tritium was measured at Hydrosys, Budapest, Hungary.

## RESULTS AND CONCLUSIONS

According to major cations and anions of the spring waters, they belong to the CaMg- $\text{HCO}_3$  hydrochemical type. This is the primary water type which is principally derived from dissolution of carbonate minerals (calcite and dolomite) that compose the aquifer.

The spring water EC values vary from 408 to 439  $\mu\text{S}/\text{cm}$  (Fig. 3).

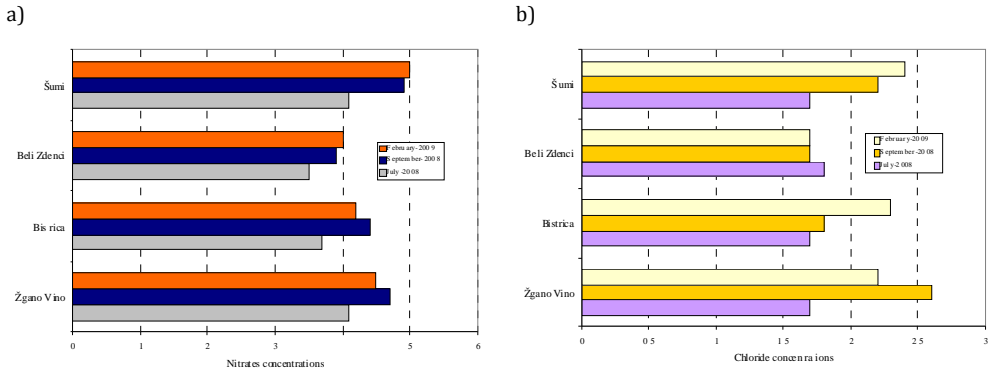


**Figure 3.** Distribution of EC, pH, oxygen and temperature in spring waters.

The highest values were measured in the spring water of Žgano Vино and Beli Zdenci and the lowest in the other two springs. It was observed that the EC values were uniform in all springs throughout the monitored period. The water temperatures at the springs were in accordance with the annual air temperature of the springs recharge area. In the karst areas, it prevails quick and turbulent groundwater flows, and the water temperature of the spring can be considerably influenced by seasonal changes in air temperature (Goldscheider, Drew, 2007). In the investi-

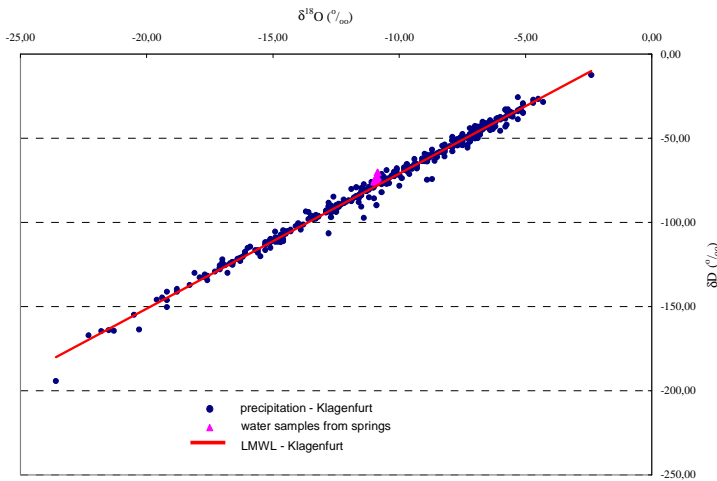
gated area the water temperatures are uniform as EC values throughout the monitored period. Uniform distributions of EC and T indicate a low degree of underground krastification.

Spring waters are characterized by very low concentrations of nitrate, sulfate and chloride. Concentrations of nitrates vary from 3.5 to 5 mg/l (Fig. 4). Sulfate concentrations are between 4 to 7.5 mg/l and chloride concentrations vary from 1.7 to 2.6 mg/l. Sampled spring waters have not been affected by anthropogenic influence in catchment areas. Concentrations of ammonium and phosphate were below detection limit of the instruments. The spring waters are not micro-biological polluted.



**Figure 4.** Distribution of a) nitrates, b) chloride.

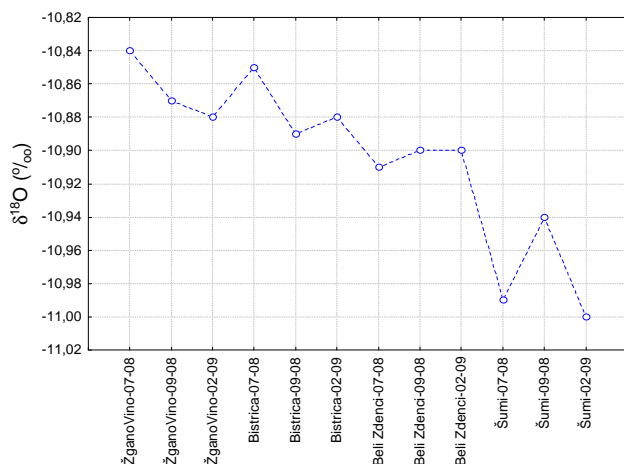
The measured hydrogen and oxygen ratios of sampled spring waters lie on or near the LMWL and clearly are derived from local precipitation that substantially homogenized in the underground (Fig. 5).



**Figure 5.** Stable isotope composition of water samples collected from springs relative to the meteoric water line for Klagenfurt.

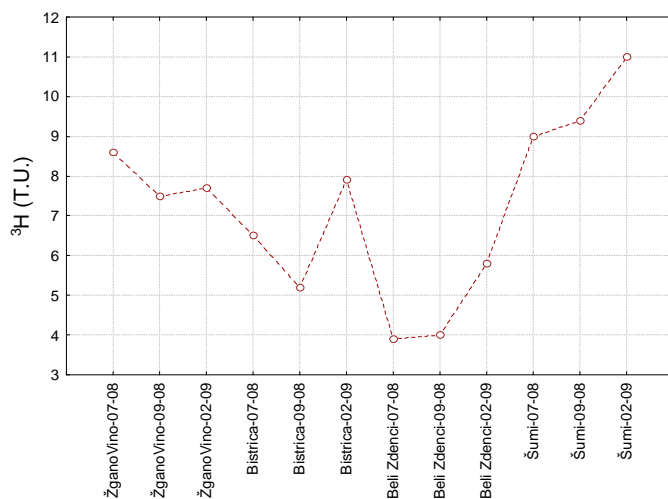
The most depleted ratios of  $\delta^{18}\text{O}$  were measured in the waters from spring Šumi (Fig. 6). In general, the spring which recharge is at the higher altitudes where temperatures are lower precipitation will be isotopically depleted (Gat, Gonfiantini, 1981; Clark, Fritz, 1997; Malo-

szewski et al., 2002; Einsiedl et al., 2009; Land, Huff, 2010). Large variations in ratios of  $\delta^{18}\text{O}$  were not observed in sampled spring waters (Fig. 6). Also, the discharges of the springs are uniform through the monitored time.



**Figure 6.** Distribution of  $\delta^{18}\text{O}$  in sampled spring waters.

The lowest tritium content was measured at spring waters of Beli Zdenci. It varies from 3.9 TU (in July) to 5.8 (in February) (Fig. 7). The measured  $^3\text{H}$  concentrations suggest a mixture between submodern and recent recharge at that spring (Clark, Fritz, 1997). Also, very low concentrations of  $^3\text{H}$  were measured at spring Bistrica (Fig. 7). The highest values were measured in spring waters of Šumi. They varied from 9 (in July) to 11 (in February) TU (Fig. 7). The variation of the spring discharge was from 21.3 l/s to 25 l/s. The tritium content and ratio of  $\delta^{18}\text{O}$  of the spring Šumi indicate groundwater renewability by precipitation from higher altitudes.



**Figure 7.** Distribution of tritium in sampled spring waters.

The measured hydrochemical and isotopical data of the investigated area showed that the underground system of the springs is a good mixer, consisting of a regularly distributed network

of fractures with absence of conductive channels. Also, the underground system has large storage volume. In the process of defining the protection zones for the springs, particularly during the definition of the II. zone of sanitary protection, these data helped.

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