Geologia Croatica
Journal of the Croatian Geological Survey
and the Croatian Geological Society

2024 | 77/2 | 127–144 | 11 Figs. | 5 Tabs. | 2 Supplements | www.geologia-croatica.hr

Tracing Hydrological Processes: Insights from Hydrochemical and Isotopic Investigations in the Northern Part of Croatian Dinaric Karst

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doi: 10.4154/gc.2024.06

Article history:
Manuscript recieved: January 13, 2024
Revised manuscript accepted: April 18, 2024
Available online: June 21, 2024

Abstract

This study presents the findings derived from a three-year monitoring programme focusing on the hydrochemical composition and stable isotope signatures ($\delta^{18}O$, $\delta^{2}H$) within the vulnerable karst groundwater system in Croatia's northern Dinaric karst region. Covering an area of 1980 km^2 across Kapela Mountain and its foothills, this groundwater system falls within the Kupa River basin and encompasses the catchment areas of the main springs across two spring levels of the Dobra, Mrežnica, and Slunjčica Rivers (namely the Vitunj, Zagorska Mrežnica, Dretulja, Veliko Vrelo, Gojak, Tounjčica, Mrežnica, and Slunjčica springs). Given the complex hydrogeological framework, prior studies have not extensively addressed the hydrochemical characteristics of this region, thereby necessitating a comprehensive investigation to elucidate system dynamics. This paper outlines the first investigation employing stable isotopic analyses within the karst groundwater system of Kapela Mt.

The main results and conclusions of the research include: (i) the aquifers across Kapela Mt. drain mainly limestones, (ii) water–rock interaction and carbonate weathering are significant contributors to water geochemistry, (iii) there is a slight human impact on the Gojak and Tounjčica spring waters, (iv) the mean residence time of water in the observed aquifer is up to 1.5 years, (v) the new LMWL was calculated for Kapela Mt. based on a three-year dataset (June 2018 – May 2021), (vi) in the north Dinaric karst, the predominant origin of precipitation is from the Mediterranean air mass, (vii) Velebit Mt. has a strong influence on the precipitation isotopic composition of the study area.

Keywords: karst hydrogeology, environmental tracer, excess air, mean recharge altitude, local meteoric water line, Kupa River catchment

1. INTRODUCTION

Karst aquifers are challenging to exploit, manage, and protect due to the extreme variability of hydraulic properties (PALMER, 2010). The pathways and residence time of groundwater within the subsurface often depend upon not only the geometry of a complex underground network of conduits and fissures, but also the prevailing hydrological conditions (FORD & WILLAMS, 2007; VASIĆ et al., 2020; MILANOVIĆ et al., 2023; TORRESAN et al., 2020; TERZIĆ et al., 2012; TORKAR & BRENČIČ, 2015; ŽIVANOVIĆ et al., 2022). The Dinaric karst system represents a geologically heterogeneous, south European orogenic belt, developed in highly vulnerable carbonate aquifers, which are the main drinking water resource for the region. The system stretches from the Carso area in Italy in the north and crosses over several countries from Slovenia to Albania (STEVANOVIĆ et al., 2016). The north Dinaric karst in Croatia remains uniquely unaffected by its neighbouring countries, boasting very high groundwater quality (BIONDIĆ 2013; PAVLIĆ & PARLOV, 2019). Hence, it has been declared as part of the first-degree strategic reserve of drinking water by the Croatian Water Management Strategy (Water Management Strategy 2008). These strategic reserves include the Gacka River catchment in the south, aquifers across Kapela Mt., and the mountainous section of the Kupa River's immediate catchment to the north. The catchments of the Gacka River (MANDIĆ et al., 2008; LUKAČ REBERSKI et al., 2009, 2013; STROJ et al., 2023) and Kupa River (BIONDIĆ et al., 2021; PAVLIĆ & PARLOV, 2019; FRANČIŠKOVIĆ-BILINSKI et al., 2013), have been hydrogeological explored. However, there is limited knowledge regarding the hydrogeological and groundwater characteristics of the aquifer spanning Kapela Mt. and the Ogulin-Plaški Valley, with only local studies conducted (BOČIĆ et al., 2015; BONACCI & ANDRIĆ, 2010; BULJAN et al., 2019; GLADOVIĆ et al., 2023; TERZIĆ et al., 2012). This research endeavour is poised to address this gap in knowledge. The local hydrogeological studies, specifically focusing on hydrochemical and stable isotopic analyses were carried out in the neighbouring area of the Plitvice Lakes catchment (BABINKA, 2007; BIONDIĆ et al., 2006, 2010; ČANJEVAC et al., 2023; HUNJAK et al., 2013; MEAŠKI et al., 2016), Krbavica (STROJ et al., 2020) and Velebit Mt. (STROJ & PAAR, 2019).

Long-term hydrochemical monitoring provides valuable insights into the mechanisms governing water-rock interactions, dissolution processes, groundwater flow pathways, and anthropogenic impacts in karst aquifers (GIBBS, 1970;

MEYBECK 1987; AKTER & AHMED, 2019; MARKOVIĆ et al., 2022). Moreover, stable isotopes, such as oxygen-18 ($\delta^{18}O$) and deuterium (δ^2H), serve as natural tracers, offering clues about the origin (VREČA et al., 2007; HUNJAK, 2013; MEZGA et al., 2014), mean residence time (KRALIK, 2015), mean recharge altitudes (MOHAMMED et al., 2014; FIKET et al., 2021), mixing patterns (TERZIĆ et al., 2014), and the groundwater dynamic (MANCE et al., 2022) within the karst system. We conducted a comprehensive analysis using a three-year dataset, examining hydrochemical and physical parameters alongside the $\delta^{18}O$ and δ^2H stable isotope content of the groundwater. The investigation spanned eight distinct locations (Vitunj, Zagorska Mrežnica, Dretulja, Veliko Vrelo, Gojak, Tounjčica, Mrežnica, and Slunjčica springs) within two spring zones situated in the area of Kapela Mt. We integrated insights from the neighbouring catchments to interpret our research findings. This integration enriches the depth and scope of the analysis. The research holds significant value as it marks the inaugural regional study of its kind within the northern part of the Dinaric karst in Croatia.

2. SETTINGS

2.1. Study area

The study area belongs to the Black Sea basin and is located in the northern part of the Croatian Dinaric karst, spanning an approximate area of 1980 km^2. It encompasses the catchments of the main springs of the Dobra, Mrežnica, and Slunjčica Rivers catchments (Fig 1). The northern boundary of the investigated area is demarcated by the interface between the immediate catchments of the Kupa and Dobra Rivers. The western boundary coincides with the watershed between the Adriatic and Danube River basins, while the southern boundary extends from the Plitvice Lakes to Slunj. The eastern boundary is defined by the springs of the Dobra, Mrežnica, and Slunjčica Rivers. Catchment boundaries for the Zagorska Mrežnica, Dretulja, Veliko Vrelo, and Slunjčica springs were defined during the establishment of sanitary protection zones. However, it should be noted that these boundaries are zonal and depend upon the hydrological conditions prevailing within the respective watershed (TERZIĆ et al., 2012; BIONDIĆ, 2013; BULJAN et al., 2019).

The area falls within the continental climatic belt, characterized by mountain climate elements. Kapela Mt., with a peak of 1534 m a.s.l., acts as a barrier to moisture-laden air masses from the west, causing significant precipitation. This area lacks dry periods. Annual precipitation levels vary between 1750 and 2500 mm, conditioned by both vertical and horizontal relief divisions, generally increasing from SE to NW. The snow cover duration averages 50 days per annum over the period from 1949 to 2022, as per Croatian Meteorological and Hydrological Service (DHMZ) records. Average annual air temperatures oscillate between 3 to 6°C. The Ogulin-Plaški Valley, located at an altitude of 300 to 400 m a.s.l., experiences dry and hot summers contrasting with wet and cold winters. Average annual precipitation varies from 1250 to 1750 mm, and air temperature between 10 to 11°C. DHMZ records from 1949 to 2022 indicate an average yearly duration of snow cover lasting 39 days.

The northern part of the Dinaric karst in Croatia is predominantly composed of karstified carbonate rocks, which were deposited from the Triassic to Lower Cenozoic periods. Non-karstic rocks occupy small and scattered areas, often surrounded by karst terrain (BAHUN 1968; BULJAN et al. 2019). The typical orientation in a NW-SE direction can be attributed to thrust-related deformation between the Palaeogene and the Eocene or Miocene epochs (TARI, 2002; SCHMID et al., 2008; KORBAR, 2009). However, the region's evolution is still an essential subject of investigation (DRAGIČEVIĆ & VELIĆ, 2002; VLAHOVIĆ et al., 2005; VELIĆ, 2007; KORBAR, 2009;).

A comprehensive Basic geological map, at the 1:100,000 scale, was created for the entire research area, covered by six sheets, each accompanied by interpretations. The sheets include: Delnice (SAVIĆ & DOZET, 1983), Crikvenica (ŠUŠNJAR et al., 1970), Črnomelj (BUKOVAC et al., 1983), Ogulin (VELIĆ & SOKAČ, 1982), Otočac (VELIĆ et al., 1974) and Slunj (KOROLIJA et al., 1980). According to the structural-geological position and lithology, the rocks within the area were divided into the following distinct hydrogeological groups (Fig. 1):

Quaternary deposits – encompass heterogeneous depostits, mostly mixtures of rock fragments and fine-grained material. The soil covers the carbonate base across the entire area, but their hydrogeological significance is only notable within morphological depressions such as karst poljes: Ogulin, Plaški, Lička Jesenica.

High permeability carbonates – represented predominantly by limestones. These formations were deposited between the Jurassic and Eocene periods.

Permeable carbonate rocks – represented predominantly by dolomitic limestone to thinner beds or interbeds of dolomite, deposited during the Jurassic and Cretaceous periods.

Low permeability carbonates – characterized by lower karstification intensity, mainly composed of dolomite, dolomitized limestone, or dolomite/limestone exchange, with dissolution cavities often filled with secondary materials including silt, sand and rock fragments. Deposition occurred from the Upper Triassic to Lower Cretaceous periods.

The hydrogeological relationships in the study area result from compressional tectonics (TARI, 2002) and are intrinsically complex. The mountainous terrain of Kapela Mt. serves as the first recharge area formed by substantially fractured Mesozoic limestones and dolomites exhibiting high secondary porosity. Due to numerous karstic forms, the area is characterized by rare, ephemeral surface watercourses limited to karst poljes. Highly karstified rocks enable the substantial accumulation of groundwater. The monitored springs Vitunj, Zagorska Mrežnica, Dretulja, and Veliko Vrelo emerge at the foot of the mountain, where permeable carbonate rocks meet with less permeable dolomites. The hydrogeological barrier is represented by several karst poljes with short watercourses. Geomorphologically, the hydrogeological barrier is represented by the Una-Korana karst plateau, the largest plateau in Dinaric karst (BOČIĆ et al, 2003, 2015; 2010). Among these, the largest are Ogulin, Plaški, and Ličko-jeseničko polje, and smaller Begovac and Saborsko poljes.

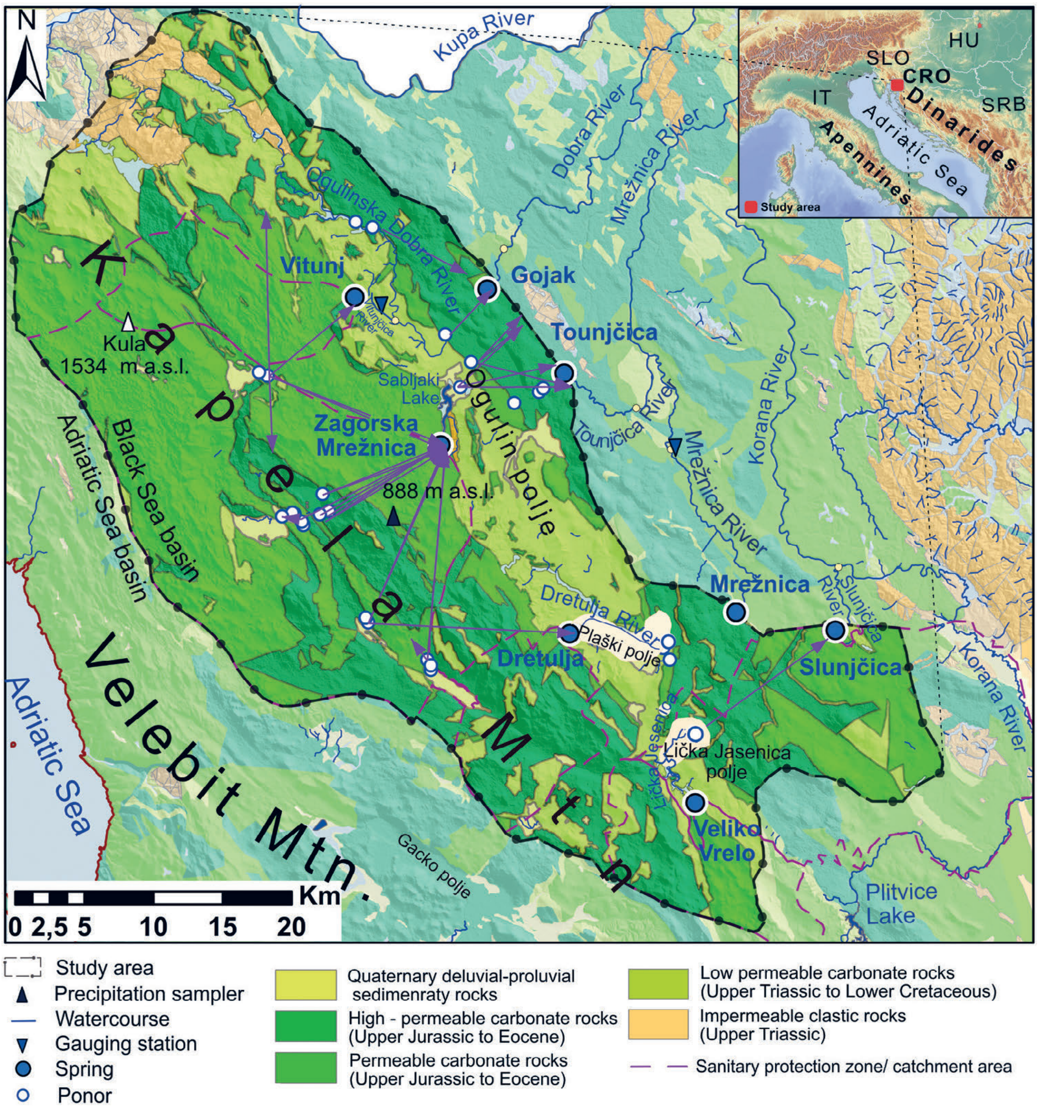

Figure 1. Hydrogeological map of the north Dinaric karst region in Croatia.

Watercourses of the Zagorska Mrežnica, Dretulja, and Lička Jesenica Rivers flow across the karst plateau, where they sink into the highly permeable limestones. They resurface at an elevation around 100 m lower than the plateau, eventually forming the Kupa River tributaries: Dobra, Mrežnica, and Slunjčica Rivers.

Eight springs have been strategically selected for monitoring, considering their spatial distribution and contribution to the hydrological network of the three Kupa River tributaries. The first spring zone encompasses four springs located at the foot of Kapela Mt. namely the Vitunj, Zagorska Mrežnica, Dretulja, and Veliko Vrelo springs. The second spring zone is represented by the Gojak, Tounjčica, Mrežnica, and Slunjčica springs, serving as the main outlets of the sinking rivers, which are formed by the springs in the first spring zone. The second spring area marks the transition between deep (classical) and shallow karst (fluviokarst) (BAHUN, 1968; KOVAČEVIĆ, 2005). Although this border is primarily descriptive and based solely on structural units, 1the entirety of the area east of the Kapela Mt. differs greatly from the rest of the Croatian Dinaric karst in terms of karstification depth.

The Vitunj spring forms the Vitunjčica River, a main tributary of the sinking Ogulinska Dobra River, which resurfaces at the Gojak spring, initiating the Dobra River's watercourse. The Zagorska Mrežnica spring is the main spring in the Ogulin polje, which feeds the catchment area of the Tounjčica River, or the west tributary of the Mrežnica River. The Dretulja spring forms the eponymous sinking river, which emerges through the Mrežnica spring, serving as the starting point of the Mrežnica River. The Veliko Vrelo spring forms the Lička Jesenica sinking river, proven to be connected with the Slunjčica spring (Engineering Project Institute, 1948).

The discharge regime of springs and rivers in the study area shows a distinctly karstic nature, characterized by notable differences in minimum and maximum discharges and fast responses (within a day) to precipitation in the hinterland (BULJAN et al., 2019). An illustration of substantial fluctuations in discharge under low and high hydrological conditions is shown in Figure 2. The supplementary material presents all monitored springs during varying water levels. The available literature data shows that the ratio of the lowest, medium, and maximum discharges in Veliko Vrelo spring is 1:6.75:100 (TERZIĆ et al., 2012), in Vitunjčica River 1:14:143

Figure 2. The Mrežnica spring during high (A) and low water conditions (B). The spring is located within the military training area "Eugen Kvaternik" and is inaccessible to the general population.

(PAVLIĆ & PARLOV, 2020), and the ratio of minimum and maximum discharge of the Zagorska Mrežnica spring is 1:222 (BIONDIĆ, 2013); 1:6:64 Slunjčica (DHMZ).

3. MONITORING, SAMPLING, AND DATA ANALYSIS

Hydrochemical and isotopic investigations have been conducted within the study area, focusing on eight springs: the Vitunj, Zagorska Mrežnica, Dretulja, Veliko Vrelo, Gojak, Tounjčica, Mrežnica, and Slunjčica springs. Table 1 provides details regarding the geographic position, sample numbers for chemical and isotopic analyses, and *in situ* measurements at selected sampling locations (Fig 1). Monthly observations of chemical and physicochemical parameters were undertaken over a span of 33 monitoring campaigns between September 2018 and May 2021. Stable isotopes were observed in spring waters during 40 campaigns, from February 2018 to May 2021. Additionally, isotopic precipitation analyses were performed in 36 campaigns, at monthly intervals from June 2018 to May 2021. The precipitation sampler was located at Kapela Mt.

The physico-chemical parameters (water temperature, pH, specific electrolytic conductivity (SEC), and oxygen concentration) were measured *in situ* using a WTW (Multi 3630 IDS SET G) multi-parameter probe. The HCO_3^- ion concentration or alkalinity was measured in the field through volumetric titration using 1.6N H_2SO_4 to pH 4.5, employing a HACH digital titrator.

The groundwater and precipitation samples were analysed in the hydrochemical laboratory of the Department of Hydrogeology and Engineering Geology of the Croatian Geological Survey. The concentrations of the major anions (Cl^-, NO_3^-, and SO_4^{2-}) and cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) were measured using ion chromatography (Thermo Scientific Dionex ICS-6000 HPIC System). The ion analyses balance was checked by the relative deviation from the charge balance ($\Delta meq = 100 \times (\Sigma meq+ - \Sigma meq-)/(\Sigma meq+ + \Sigma meq-) < \pm 5\%$) (MANDEL & SHIFTAN, 1981; DOMENICO & SCHWARTZ, 1990). Stable isotopes of oxygen and hydrogen were analyzed with a Picarro L2130-i Isotope and Gas Concentration Analyzer (Picarro, Santa Clara, CA, USA), using the Secondary Water Isotopes Standard Kit (Picarro) for calibration of the results. The results are presented in delta notation (‰), normalised to the international measurement standard VSMOW (Vienna Standard Mean Ocean Water) (CRAIG, 1961a).

Precipitation was collected using oil-free Palmex® rain collectors (Palmex d.o.o., Zagreb, Croatia) that effectively prevent evaporative isotopic enrichment (MICHELSEN et al., 2018). The sampler was positioned at the observation station of Croatian Roads (HAC) (45°05'3422 N, 15°12'42'' E) on Kapela Mt, at 888 m a.s.l. The direct distance by air between the sampler and the Adriatic coast is about 25 km. Out of 36 samples collected, three were excluded from further interpretation due to technical difficulties. Specifically, during the months of August 2018, May 2020, and January 2021, the precipitation collector funnel encountered blockages, causing

Table 1. Sampling location, altitude, type, and number of samples per analysis.

Location	Lat. (deg N)	Long. (deg w)	Altitude (m a.s.l.)	No. of samples for analysis of δ^2H and $\delta^{18}O$ isotopes	No. of samples for chemical analysis	*In situ* measurements of physical parameters
Vitunj spring	45.291221	15.140482	345	39	32	32
Zagorska Mrežnica spring	45.195624	15.221742	326	40	33	32
Dretulja spring	45.074659	15.342673	359	40	32	33
Veliko Vrelo spring	44.966213	15.460677	484	38	33	33
Gojak spring	45.297340	15.262693	197	40	33	33
Tounjčica spring	45.248871	15.322711	225	40	33	33
Mrežnica spring	45.090260	15.495816	320	29	29	28
Slunjčica spring	45.078297	15.588019	258	40	33	33
Kapela Mt. (precipitation)	45.092973	15.211796	888	36(33*)	-	-
			Total	339	258	257

* number of samples taken in the interpretation

inadequate data. The recorded values deviated by more than 200% from the obtained maximal/minimum value, necessitating exclusion from the analyses.

Daily discharge data were acquired from the Croatian Meteorological and Hydrological Service (DHMZ) and the Croatian Electric Power Company (HEP).

To delineate the hydrochemical facies of springs, monthly water samples were subjected to major anion and cation analyses. The results were used to construct a Piper diagram (PIPER, 1944) that graphically represents the major ion ratios. The interactions among the chemical and physicochemical parameters were further analyzed using Pearson's correlation coefficient (r). This statistical measure is widely employed to explore relationships between the various parameters within hydrochemical samples. The dimensionless number in question falls between the range of +1 to –1, where +1 signifies a perfect positive correlation, 0 indicates no linear relationship, and –1 denotes a perfect negative correlation between the parameters. More precisely, parameters with a correlation coefficient $r > 0.7$ are considered to have a strong correlation, while values between 0.5 and 0.7 indicate a moderate correlation (FREEDMAN et al. 2007). The molar ratio Mg^{2+}/Ca^{2+} was utilized to derive information regarding the source, evolution, and geochemical processes influencing water chemistry in aquifers (APPELO & POSTMA, 2005).

Analyses of oxygen ($\delta^{18}O$) and hydrogen ($\delta^{2}H$) stable isotopes in spring water and precipitation samples were used to define spring water origin by comparing it with local precipitation characteristics. The local meteoric water line (LMWL) was calculated using the ordinary least square

Table 2. Main statistical descriptors of *in situ* measured parameters and major ion concentrations at the eight locations in catchment areas of Dobra, Mrežnica, and Slunjčica Rivers.

Site	statistic	T	pH	SEC (µS/cm)	O_2 (mg/l)	Na^+ (mg/l)	Mg^{2+} (mg/l)	K^+ (mg/l)	Ca^{2+} (mg/l)	Cl^- (mg/l)	NO_3^- (mg/l)	SO_4^{2-} (mg/l)	HCO_3^- (mg/l)
Vitunj	MAX	9.4	8.36	407	12.3	1.76	29.64	0.94	64.64	2.14	8.36	8.05	285.4
	MIN	7.6	7.0	272	10.9	0.0	4.5	0.0	42.4	0.7	1.4	1.6	165.9
	MEDIAN	7.8	7.9	319	11.6	0.6	7.0	0.3	55.5	1.3	5.2	5.4	203.7
	AVERAGE	7.9	7.9	326	11.3	0.6	9.2	0.3	55.4	1.3	4.9	4.9	208.4
	SD	0.4	0.2	33	2.0	0.3	5.7	0.2	5.4	0.3	1.7	1.9	27.2
Zagorska Mrežnica	MAX	10.9	8.3	437	14.6	5.0	23.6	1.0	82.8	4.1	7.9	11.1	295.2
	MIN	7.6	7.4	336	7.7	0.6	5.2	0.0	41.0	1.8	0.5	1.9	184.2
	MEDIAN	9.1	7.6	409	10.6	1.8	8.4	0.4	71.3	2.8	4.5	6.0	252.5
	AVERAGE	9.2	7.7	405	10.5	1.9	9.6	0.4	70.2	2.8	4.4	5.8	250.8
	SD	0.8	0.2	22	2.4	0.7	4.1	0.2	8.7	0.7	1.5	2.2	24.0
Dretulja	MAX	10.2	8.1	488	14.3	1.8	16.7	2.0	93.9	2.6	7.4	11.6	339.2
	MIN	8.2	0.0	423	9.0	0.0	7.2	0.0	61.8	0.5	1.3	2.3	219.6
	MEDIAN	8.7	7.4	462	10.4	0.6	10.7	0.3	83.5	1.1	4.4	6.4	292.8
	AVERAGE	8.9	7.2	461	10.2	0.6	11.1	0.4	82.6	1.3	4.4	6.4	292.1
	SD	0.7	1.3	11	2.0	0.3	2.3	0.4	6.1	0.5	1.5	2.3	22.2
Veliko Vrelo	MAX	8.7	8.1	506	14.3	1.7	22.9	0.8	84.8	2.3	8.5	8.3	347.7
	MIN	7.0	7.4	278	10.0	0.3	8.5	0.1	48.1	0.7	2.5	2.3	253.8
	MEDIAN	7.8	7.5	439	11.4	0.6	14.1	0.3	73.0	1.3	5.2	5.7	285.5
	AVERAGE	7.7	7.5	439	11.4	0.7	14.8	0.3	73.1	1.3	5.2	5.4	284.1
	SD	0.3	0.1	33	0.7	0.3	3.5	0.2	6.4	0.4	1.3	1.7	19.9
Gojak	MAX	16.9	8.4	432	12.8	5.2	24.0	2.8	75.7	10.6	10.4	10.3	273.3
	MIN	7.7	7.5	344	9.5	1.7	8.0	0.2	40.5	2.1	3.3	3.0	178.1
	MEDIAN	10.0	7.9	391	11.2	3.4	13.1	0.8	60.7	5.1	6.3	6.6	235.5
	AVERAGE	11.1	7.9	392	10.6	3.5	13.1	0.9	60.7	5.1	6.5	6.5	233.8
	SD	2.5	0.2	22	2.8	0.9	3.4	0.5	6.4	1.7	1.7	2.1	18.0
Tunjčica	MAX	16.1	8.2	659	12.1	34.9	15.0	2.4	88.3	67.1	17.6	10.9	305.0
	MIN	6.9	7.5	355	1.9	0.8	4.5	0.2	53.0	1.8	2.7	2.5	180.6
	MEDIAN	9.5	7.8	393	9.5	1.8	7.5	0.6	70.1	2.8	5.9	6.2	240.3
	AVERAGE	9.8	7.8	407	8.4	4.0	7.8	0.7	71.1	6.5	7.2	6.2	239.8
	SD	1.6	0.2	55	3.3	6.1	2.2	0.4	7.6	11.5	3.9	2.3	26.3
Mrežnica	MAX	13.7	8.1	470	12.6	1.2	18.0	1.8	86.0	2.8	7.7	9.2	324.5
	MIN	6.4	6.8	387	9.6	0.1	6.3	0.1	45.8	1.1	0.5	2.6	169.6
	MEDIAN	9.7	7.7	446	10.4	0.8	12.4	0.7	76.7	1.7	4.3	6.0	278.2
	AVERAGE	9.9	7.7	443	10.3	0.7	12.5	0.8	74.8	1.8	4.4	5.9	278.8
	SD	1.7	0.2	17.5	2.1	0.3	2.6	0.5	8.2	0.5	1.5	1.7	27.8
Slunjčica	MAX	10.9	8.0	460	14.2	2.2	15.7	1.4	94.9	3.1	7.8	10.5	345.3
	MIN	8.7	0.0	390	9.2	0.4	4.4	0.1	53.8	0.7	1.6	2.4	213.5
	MEDIAN	9.5	7.5	443	10.8	1.0	9.7	0.4	78.4	1.8	4.7	6.3	273.3
	AVERAGE	9.7	7.3	438	10.8	1.1	9.9	0.4	78.8	1.8	4.5	6.3	278.2
	SD	0.6	1.3	17	0.8	0.4	2.9	0.3	7.1	0.5	1.4	2.1	21.3

regression (OLSR), excluding improperly collected samples. Spring water isotope values were plotted and compared with the LMWL, and the groundwater lines (GWL) were calculated for the monitored springs (CLARK & FRITZ, 1997).

The d-excess was calculated for each sample following the equation: d-excess = $\delta^2H - 8\delta^{18}O$ (DANSGAARD, 1964). The d-excess can be used as an indicator of the origin of precipitation and conditions during the vapour formation (CLARK et al., 2015).

Isotopic analyses also enabled a rough estimation of spring water mean residence time (MRT) in the aquifer by using a simple equation based on observed annual oscillation amplitudes in rainwater and spring water samples. The MRT in the karst aquifers were a rough estimation using an exponential model by the following equation:

$$T=\omega^{-1}[(A/B)^{-2}-1]^{0.5} \quad (1)$$

where T is the mean residence time, A is the amplitude of precipitation $\delta^{18}O$, B is the amplitude of the spring water and the ω is the angular frequency. The theoretical background of the applied equation is elaborated upon in the works by MAŁOSZEWSKI et al. (1983), McGUIRE & McDONNELL (2006), and RODGERS et al. (2005). The calculation examines the sinusoidal oscillation of the stable isotope content in precipitation and the subsequent reduction of this oscillation in observed springs due to the mixing and retention of water in the karst aquifers.

4. RESULTS

The descriptive statistics of the physico-chemical and chemical parameters of the sampled waters are summarised in Table 2 and shown in Figure 3.

The pH ranges between 6.8 and 8.2, which indicates the slightly alkaline water, typical for karst aqifers. The most dispersed and highest values were observed in the Gojak spring

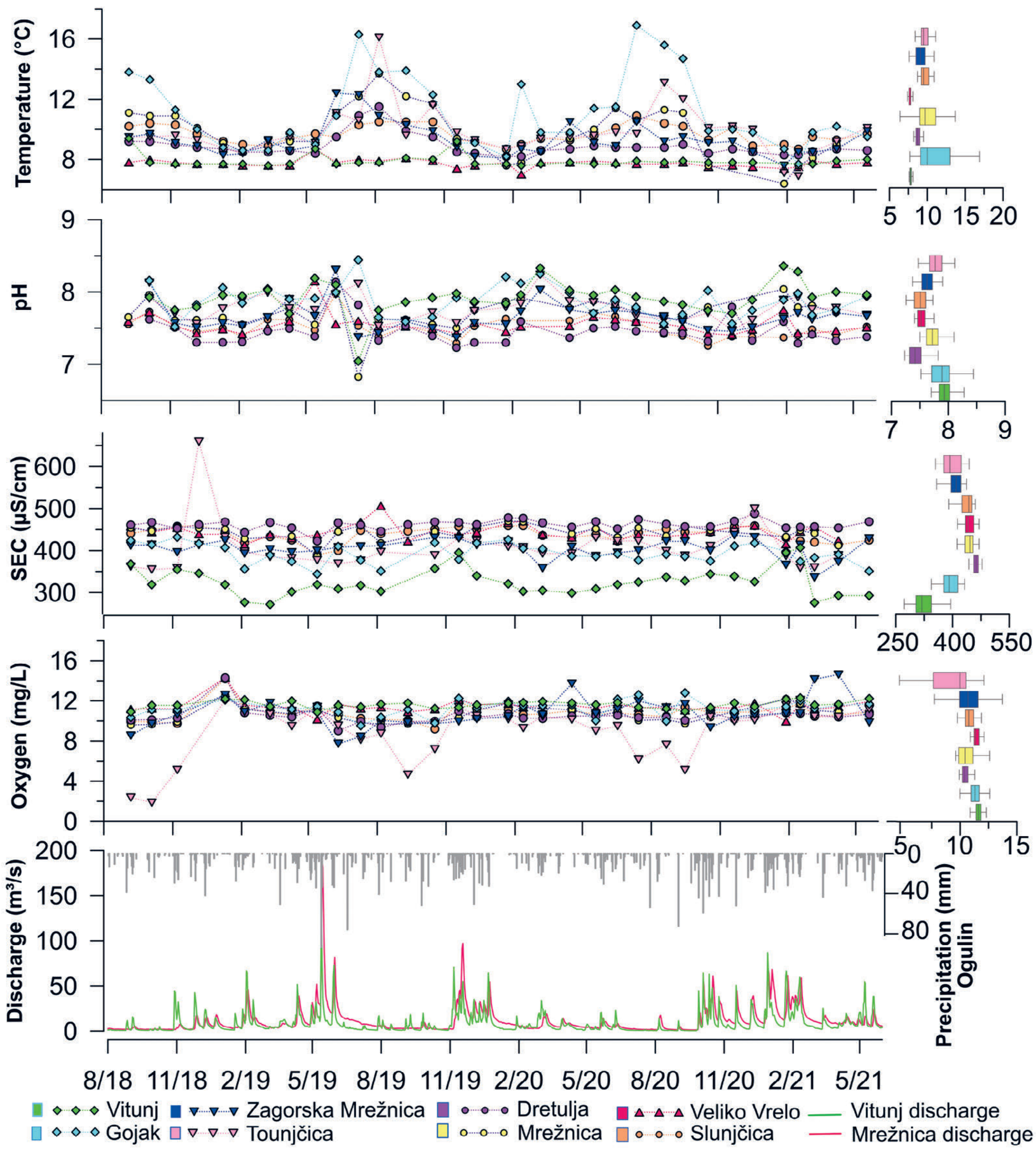

Figure 3. Dissolved oxygen, precipitation, pH, water temperature, and SEC compared with daily discharge and precipitation data, which represent hydrological conditions.

water. In general, the Dretulja spring water has the lowest, while the Vitunj spring water has the highest pH values.

The water temperature of the monitored springs ranges from 6.4 to 16.9°C, with pronounced temperature homogenization of the springs at the foot of the Kapela Mt. The most consistent water temperature was recorded in the Veliko Vrelo (Δ 1.7°C) and Vitunj (Δ 1.8°C) springs, while the water temperature in the Dretulja spring oscillates around 2.4°C, and in Zagorska Mrežnica spring around 2.8°C. The temperature oscillations in the spring water at the second spring level are more pronounced. Within the area of shallow karst, the temperature of the Slunjčica spring amounts to only 2.2°C. However, the springs to the north, such as Mrežnica, Tounjčica, and Gojak exhibit much larger temperature oscillations of Δ 7.3°C, Δ 9.2°C, and Δ 9.2°C, respectively.

The SEC in spring waters ranges between 272 and 506 µS/cm, with an anomaly noted in December 2019 in the Tounjčica spring, when the SEC measured 659 µS/cm. The observed anomaly is further explained in the discussion. In general, there is a trend of increasing SEC values in springs from the north to the south of the study area. The Vitunj spring water has the highest degree of oscillation, with the lowest overall values (median of 319 µS/cm). The median SEC value in Zagorska Mrežnica spring water was 409 µS/cm. However, at the foot of the Kapela Mt. slightly higher SEC values were detected in Dretulja (median of 462 µS/cm) spring waters than in the Veliko Vrelo spring (median of 439 µS/cm). This pattern is mirrored in the second spring zone, in Mrežnica (median of 446 µS/cm) and Slunjčica (median of 443 µS/cm) springs. The Tounjčica spring water (median of 393 µS/cm) has similar SEC values to the Gojak spring waters (median of 391 µS/cm), but with a higher degree of oscillation.

The oxygen concentration in the monitored spring waters ranges between 7.73 to 14.63 mg/l, except for Tounjčica spring water, where extremely low values up to 1.88 mg/l were observed. The median values of oxygen concentration showed the following order: Vitunj (11.6 mg/l) > Gojak (11.2 mg/l) > Veliko Vrelo (11.4 mg/l) > Slunjčica (10.8 mg/l) > Zagorska Mrežnica (10.6 mg/l) > Dretulja (10.4 mg/l) > Mrežnica (10.4 mg/l) > Tounjčica (9.5 mg/l).

The results of the chemical analysis indicated Ca^{2+} as a dominant cation in monitored spring waters, followed by Mg^{2+}, Na^{+}, and K^{+}. The average contribution of Ca^{2+} to the cation budget is 84 – 87% in all spring water, except Gojak spring water, which is 78%. The dominant anion in monitored spring waters is HCO_3^- followed by Cl^-, NO_3^-, and SO_4^{2-}. The average contribution of HCO_3^- is 96% to the anion budget in the Mrežnica, Veliko Vrelo, and Slunjčica springs, 95% in the Vitunj and Zagorska Mrežnica springs, and 93% in the Dretulja and Tounjčica springs. Spring water mineralization was calculated from a chemical analysis of major anions and cations. The mineralization during the monitoring period was in the range of 236 – 370 mg/L for the Vitunj spring, 267 – 430 mg/L for the Mrežnica spring, 273 – 378 mg/L for the Gojak spring, 273 – 495 mg/L for the Tounjčica spring, 281 – 395 mg/L for the Zagorska Mrežnica spring, 306 – 450 mg/L for the Dretlja spring, 317 – 455 mg/L for the Slunjčica spring, and 342 – 453 mg/L for the Veliko Vrelo spring.

The minimum, maximum, and median isotopic composition of $\delta^{18}O$ and $\delta^{2}H$ in monitored springs and precipitation collected on Kapela Mt. are reported in Table 3. In spring waters, the measured $\delta^{18}O$ values ranged from –10.65 to –8.01‰, and the $\delta^{2}H$ values ranged from –70.46 to –50.48‰. The results align with the previous study in Lika and Gorski Kotar regions (BRKIĆ et al., 2020; STROJ et al., 2020; PAAR et al., 2019; HUNJAK, 2013). The amplitude in precipitation is expectedly much higher; the measured $\delta^{18}O$ values ranged from –12.33 to –4.99‰, and the $\delta^{2}H$ varied from –88.00 to –25.55‰.

The higher amplitude of $\delta^{18}O$ was observed in the spring water of Vitunj spring (2.39‰), followed by the Gojak (2.08‰), Tounjčica (2.06‰), Zagorska Mrežnica (1.84‰), Slunjčica (1.80‰), Mrežnica (1.55‰), Veliko Vrelo (1.41‰) and Dretulja (1.30‰) springs. The amplitude of the observed isotope

Table 3. Minimum, maximum, median, and amplitude values of the $\delta^{18}O$, $\delta^{2}H$ and d-excess isotope compositions for Vitunj, Zagorska Mrežnica, Dretulja, Veliko Vrelo, Gojak, Tounjčica, Mrežnica and Slunjčica springs, and Kapela Mt. precipitation.

Location	Values	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	d-excess
Vitunj	Maximum	-10.65	-70.46	15.86
	Minimum	-8.26	-51.83	13.06
	Median	-9.12	-59.52	14.62
	Amplitude	2.39	18.63	2.80
Zagorska Mrežnica	Maximum	-10.28	-67.75	15.29
	Minimum	-8.43	-53.39	13.11
	Median	-9.50	-61.92	14.48
	Amplitude	1.84	14.36	2.18
Dretulja	Maximum	-10.60	-70.49	15.46
	Minimum	-9.30	-60.26	13.46
	Median	-10.20	-67.08	14.48
	Amplitude	1.30	10.22	2.00
Veliko Vrelo	Maximum	-10.48	-69.10	15.49
	Minimum	-9.07	-57.57	11.96
	Median	-10.10	-66.09	14.69
	Amplitude	1.41	11.53	3.53
Gojak	Maximum	-10.10	-67.40	14.69
	Minimum	-8.01	-50.48	12.84
	Median	-9.26	-60.23	12.84
	Amplitude	2.08	16.92	1.85
Tounjčica	Maximum	-10.51	-70.27	15.06
	Minimum	-8.46	-53.65	12.47
	Median	-9.49	-62.25	13.76
	Amplitude	2.06	16.62	1.85
Mrežnica	Maximum	-10.44	-68.75	15.39
	Minimum	-8.89	-57.23	12.80
	Median	-9.95	-65.69	14.08
	Amplitude	1.55	11.52	2.58
Slunjčica	Maximum	-10.58	-70.38	14.86
	Minimum	-8.78	-55.73	13.16
	Median	-9.94	-65.57	14.15
	Amplitude	1.80	14.64	1.70
Kapela Mt. Precipitation	Maximum	-12.33	-88.00	18.56
	Minimum	-4.99	-25.55	8.75
	Median	-7.87	-47.52	15.00
	Amplitude	7.34	62.45	9.81

indicates the residence time of water in the aquifer, characterizing the lowest amplitude with the highest homogenization, i.e., the longest retention (CLARK & FRITZ, 1997).

5. DISCUSSION

5.1. Major ion chemistry

The chemical composition analysis of spring waters was plotted on a Piper diagram (Fig. 4) to define their hydrochemical facies. All water samples from the monitored springs exhibited the Ca–Mg–HCO_3 hydrogeochemical facies, indicating the dissolution and weathering of carbonates (limestone and dolomite), with no discernible interaction between groundwater and non-carbonate rocks such as evaporites. The spring waters from Tounjčica, Veliko Vrelo, Slunjčica, and Dretulja displayed a more uniform and clearly defined Ca–HCO_3 facies, while the samples from Zagorska Mrežnica, Vitunj, Gojak, and Mrežnica showed mixed facies ranging from Ca–HCO_3 to Ca–Mg–HCO_3.

The pH indicates alkaline waters, which are vital for the dissolution of carbonate rocks within the watershed. The molar Mg^{2+}/Ca^{2+} ratio (Fig. 5) was used to determine the predominant dissolution of carbonate minerals. In all spring waters, the Mg^{2+}/Ca^{2+} ratio indicated the predominant presence of limestone rocks in the study area (Fig. 5a). Specifically, the calcite dissolution results in water characterized by a Mg^{2+}/Ca^{2+} ratio below 0.1. However, the simultaneous dissolution of calcite and dolomite results in a Mg^{2+}/Ca^{2+} ratio of about 0.33. If the Mg^{2+}/Ca^{2+} ratio is equal to 1, this indicates that the pure dolomite dissolution is in equilibrium with the water (MAYO & LOUCKS, 1995; SZRAMEK et al., 2011).

The ratio was higher during recession periods and lower during high water conditions in all monitored spring waters (Fig. 5b). Regardless of hydrological conditions, in the groundwaters of the Dretulja, Slunjčica, Tounjčica, and mainly Zagorska Mrežnica springs, the Mg^{2+}/Ca^{2+} ratio consistently indicates the dissolution of limestone rocks. In contrast, during recession periods in the Vitunj, Gojak, Mrežnica, and Veliko Vrelo spring waters, the increase in the Mg^{2+}/Ca^{2+} ratio was significantly more pronounced. This could be attributed to a higher proportion of dolomite in their respective catchment areas or to the extended water residence time within small aquifer fractures (STROJ et al., 2020).

The correlation analysis of physico-chemical and chemical parameters, conducted on 258 samples, is presented in Table 4. A strong positive correlation was observed between the dominant Ca^{2+} cation and the dominant HCO_3^- anion, indicating a robust linear relationship. Furthermore, the SEC showed a strong positive correlation with both Ca^{2+} and HCO_3^- ions, while its correlation with Mg^{2+}, Cl^-, Na^+, and K^+ was weak to moderate. This is attributed to an interaction between the groundwater and mainly limestone. No correlation was present with the NO_3^- ion. Conversely, the NO_3^- ion displayed a strong positive correlation with SO_4^{2-} ions and moderate correlation with Cl^- and Na^+ ions, indicating the anthropogenic source of those ions. Moreover, Na^+ ions had a strong positive correlation with Cl^-, and weak correlation with K^+, NO_3^-, and SO_4^{2-}. The temperature values positively correlated with K^+ and SO_4^{2-} ions. pH did not display any conspicuous correlations with any of the studied parameters.

Despite the high quality of the spring waters in the study area, with all parameter values falling significantly below their Maximum Allowable Concentrations (MAC), there is a

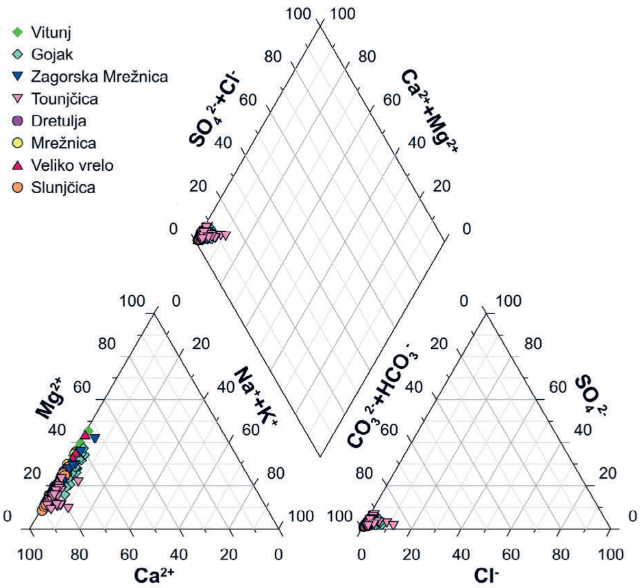

Figure 4. The Piper diagram of hydrochemical facies within the study area.

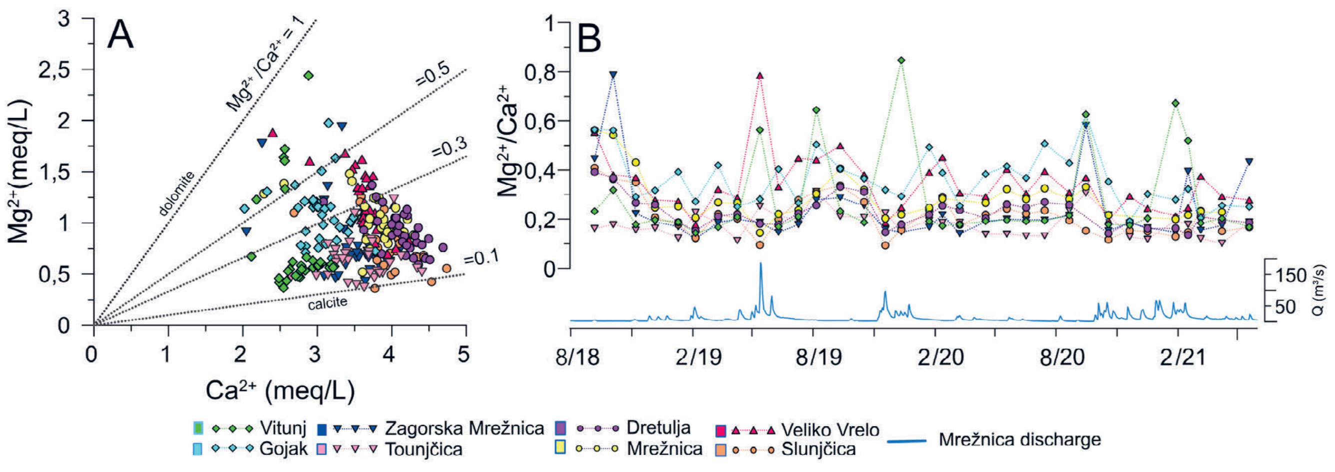

Figure 5. The Mg^{2+}/Ca^{2+} ratio in monitored springs.

Table 4. Pearson correlation analysis of physico-chemical and chemical parameters in the eight karst spring waters in the north Dinaric region of Croatia.

Variables	T	pH	EC	O_2 (mg/l)	Na^+ (mg/l)	Mg^{2+} (mg/l)	K^+ (mg/l)	Ca^{2+} (mg/l)	Cl^- (mg/l)	NO_3^- (mg/l)	SO_4^{2-} (mg/l)	HCO_3^- (mg/l)
T	1											
pH	0.033	1										
EC	0.094	−0.245	1									
O_2 (mg/l)	−0.265	0.016	−0.042	1								
Na^+ (mg/l)	0.243*	0.061	0.234*	−0.061	1							
Mg^{2+} (mg/l)	0.193	0.009	0.279*	0.086	−0.040	1						
K^+ (mg/l)	0.330*	0.078	0.197*	−0.164	0.473*	0.053	1					
Ca^{2+} (mg/l)	−0.085	−0.282	0.687	0.012	−0.029	−0.147	0.061	1				
Cl^- (mg/l)	0.184	0.049	0.261*	−0.052	0.975	−0.050	0.458*	−0.013	1			
NO_3^- (mg/l)	0.166	0.091	−0.053	−0.432	0.313*	−0.053	0.145	−0.296	0.346*	1		
SO_4^{2-} (mg/l)	0.342*	−0.024	0.192	−0.364	0.158	0.286*	0.174	−0.171	0.166	0.688	1	
HCO_3^-(mg/l)	−0.050	−0.208	0.737	0.088	−0.080	0.262	−0.027	0.643	−0.050	−0.251	−0.005	1

*week correlation

noticeable anthropogenic impact. The natural sources of sulfates are the dissolution of gypsum and anhydrite, as well as the oxidation of sulfide minerals (FERNANDO et al., 2018; LUKAČ REBERSKI et al., 2009). However, the strong correlation with nitrate (r=0.69) and weak correlation with Cl^- (r=0.17) and K^+(r=0.17) and its spatial distribution and seasonal variation indicate human impact, such as inputs from wastewater, agriculture, or fertilizer usage. In general, it can be observed that the concentration of nitrates and sulphates is diluted in all springs during periods of higher water levels, e.g. in February and May as well as November 2019 and October 2020. (Fig. 6). The slightly higher sulfate, nitrate, and chloride concentrations are determined in the Gojak and Tounjčica spring waters, located downstream from the Ogulin urban area

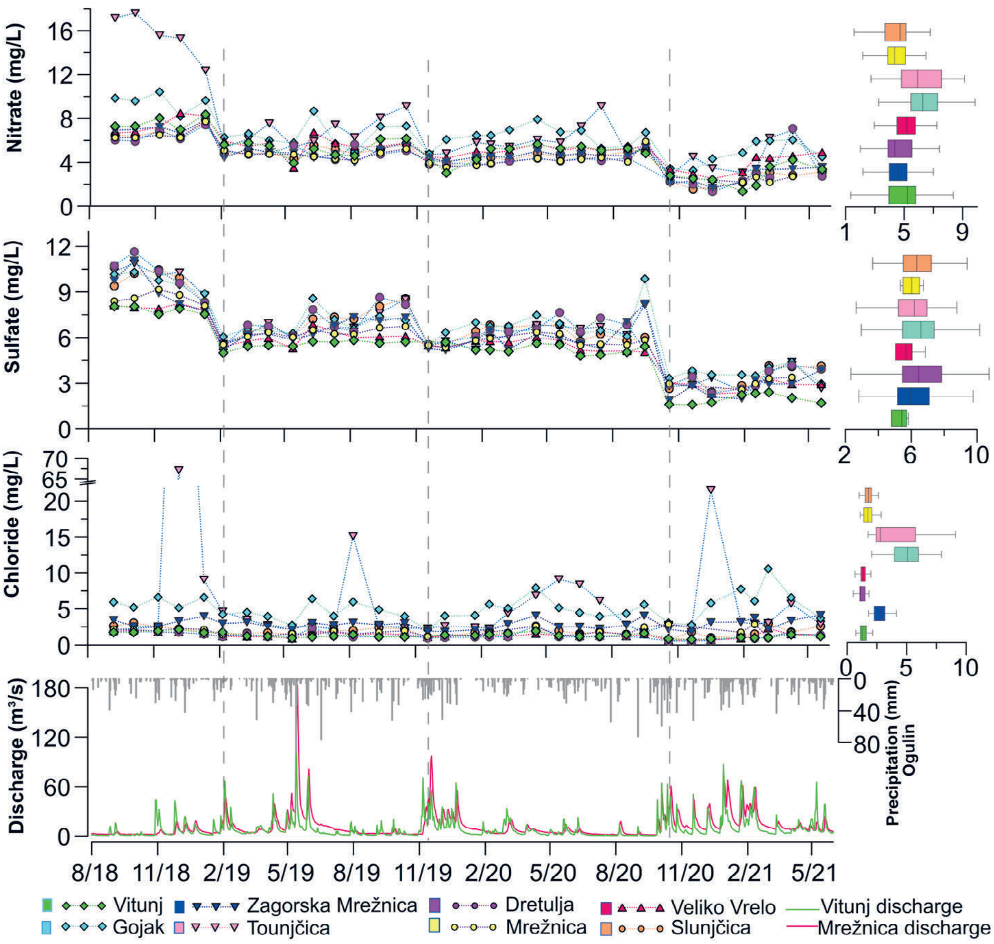

Figure 6. Time series of sulfates, nitrates and chlorides in Vitunj, Zagorska Mrežnica, Dretulja, Veliko Vrelo, Gojak, Tounjčica, Mrežnica and Slunjčica spring waters.

and Ogulin polje, where agriculture activities are prevalent. In both springs, a slight increase in the chloride content was observed during recession periods. Furthermore, three monitoring campaigns determined extremely high concentrations of Na^+ and Cl^-, as well as elevated SEC values in the Tounjčica spring water. While these occurrences in December of 2018 and 2019 could be attributed to road salting practices, it is not the case for August 2018. The data suggests that the cabbage pickling plants, located between the Sabljaki Lake dam and the southern part of the Ogulin City urban area, are within the Tounjčica catchment area, and anecdotal evidence suggests overflow from salty water tanks may end up in the underground under certain conditions. In addition, in the springs of Tounjčica, unusual movements of dissolved oxygen can be observed, which drops to very low values during the recession periods. Hydrogeological relationships do not explain this phenomenon; it is more likely due to the impact of wastewater, particularly water from a wastewater treatment plant situated within the catchment area.

5.2. Stable isotopes

The isotopic composition of spring waters displays muted seasonal fluctuations in contrast to the isotope composition of precipitation collected at the Kapela Mt. (Fig. 7c). The changes in discharge exerted a stronger influence on the $\delta^{18}O$ and δ^2H content in spring waters than the seasonal variations. The noticeable enrichment in stable isotopes is observed in two water waves, in December of 2019 and November of 2020, indicating the sampling of spring water with a noteworthy component of freshly infiltrated precipitation. Conversely, a noticeable decrease in the isotope content was observed in April 2018, likely caused by the impact of melted snow cover on the Kapela Mt. Therefore, samples collected during the hydrograph peaks should be discarded if seasonal variations are considered, as well as in the mean residence time and mean recharge altitude calculations.

The precipitation isotope data were plotted in a binary $\delta^{18}O$– δ^2H diagram to create the LMWL of Kapela Mt (Fig. 7A) based on three-year series of $\delta^{18}O$ and δ^2H values, as follows:

$$\delta^2H = 7.81\ \delta^{18}O + 13.72$$

The obtained relationship coincides well with the regional Western Mediterranean Meteoric Water Line (WMMWL) established by CELLE-JEANTON et al. (2001), suggesting that the air mass has predominant Mediterranean sources. Calculated d-excess values (Fig. 7B) of monthly precipitation mixtures in almost all samples also indicate a predominant origin from the Mediterranean air mass, (d-excess value higher than 10‰ taken as a reference as suggested by MERLIVAT & JOUZEL (1979)). Considering the precipitation amount and frequency, only two monthly precipitation samples could be predominantly originating from the Atlantic, collected in July 2019 and February 2020 (Fig. 7B).

Monthly values of $\delta^{18}O$ and δ^2H isotopic composition in spring waters are plotted in Figure 8 and compared with the Kapela Mt. LMWL. The plotted δ values for all springs construct the Groundwater Lines (GWLs).

The GWLs of the monitored springs conform to the Kapela LMWL, veryfing the meteoric origin of groundwater (Fig. 8). Based on the GWLs, we observed two distinct isotopic fingerprints of precipitation influencing the Vitunj and

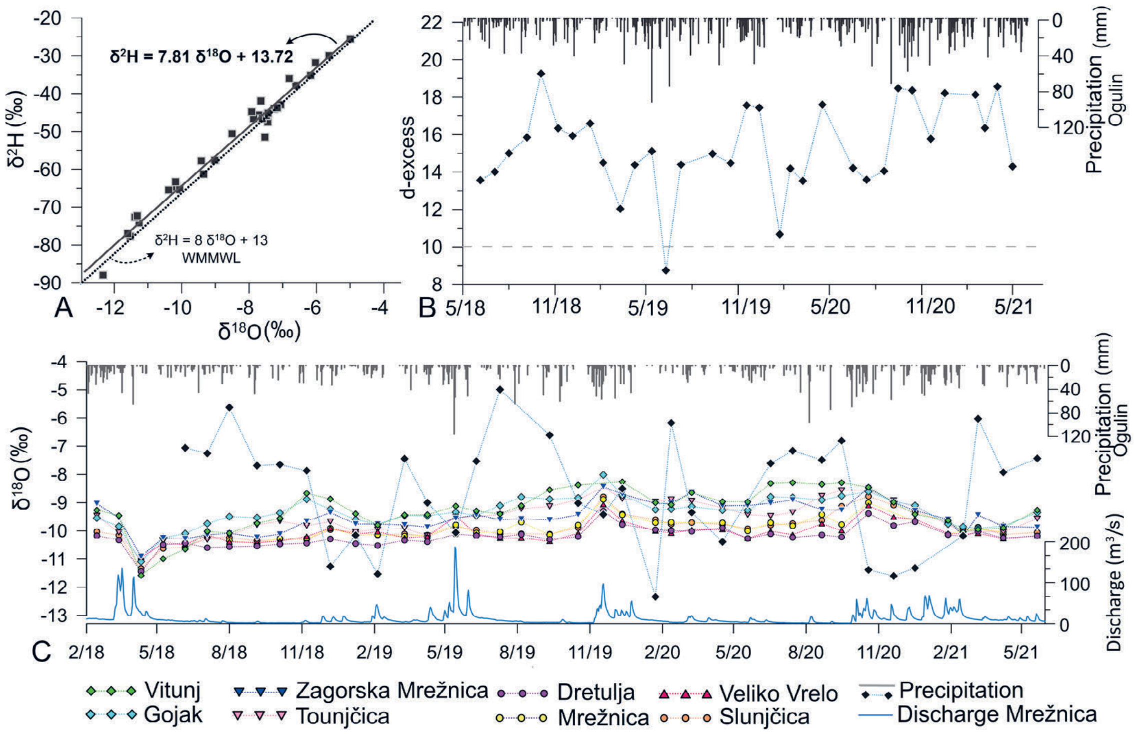

Figure 7. A. Local meteoric water line (LMWL) for the Kapela Mt vs. Western Mediterranean meteoric water line (WMMWL) (CELLE-JEANTON et al. 2001); **B.** d-excess of precipitation; **C.** Time series of the isotope composition of a $\delta^{18}O$ in monitored springs, compared with precipitation of the Ogulin station and discharge data for the Mrežnica River station.

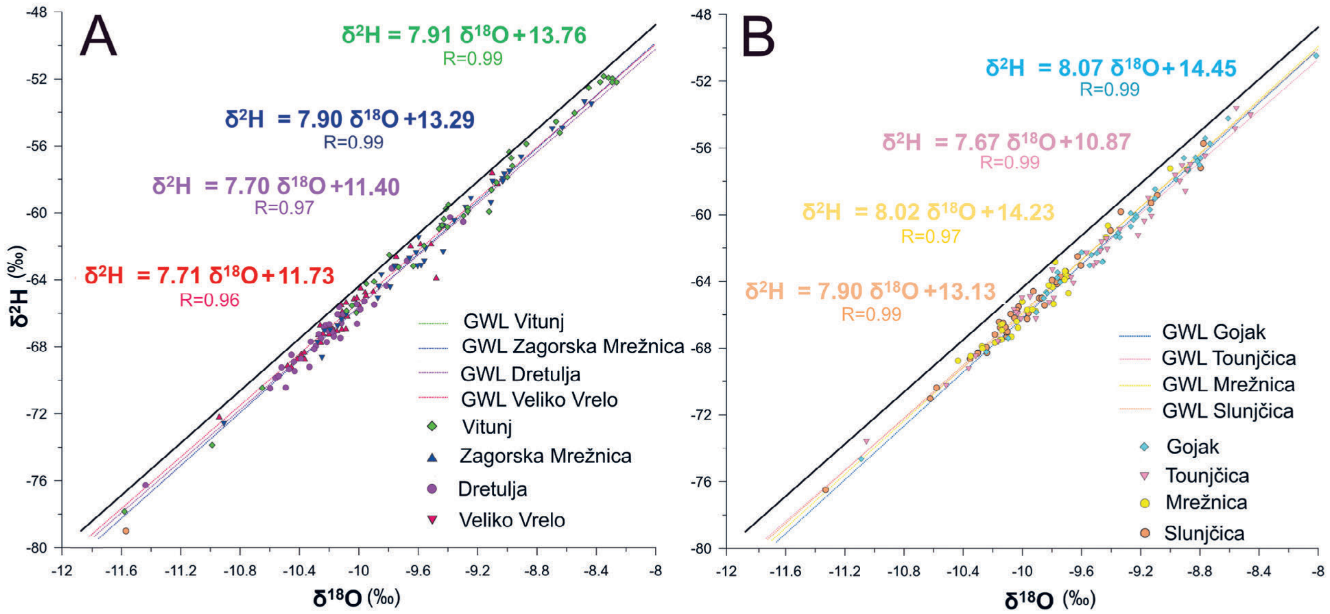

Figure 8. Correlation diagram of $\delta^{18}O$ and δ^2H values and Groundwater Lines for four springs in the first spring zone, situated at the foot of the Kapela Mt (A), and four springs in the second spring zone situated in the shallow karst zone (B).

Zagorska Mrežnica springs vs. the Veliko Vrelo and Dretulja springs. The Veliko Vrelo and Dretulja springs generally have more negative values of $\delta^{18}O$ and δ^2H than the Vitunj and Zagorska Mrežnica water springs. The GWLs of monitored springs across the Kapela Mt. coincide well with the Kapela Mt. LMWL showing the lack of precipitation evaporation before infiltration to the subsurface. During periods of elevated water levels, the Zagorska Mrežnica spring is fed from surface waters originating from flooded poljes in the hinterland (BULJAN et al., 2019). However, the impact of evaporation is insignificant due to the relatively short duration of flooding and the low temperature, which render the evaporation effect negligible (CLARK & FRITZ, 1997).

In the second spring zone, the content of stable isotopes in the spring waters follows the trend across Kapela Mt.; decreasing in heavy isotopes from north to south. In the north, the Gojak spring is generally enriched in heavy isotopes in relation to the upstream Vitunj spring, which was especially noticeable during the recession period of 2018, indicating a large proportion of water from other directions and the lower immediate hinterland. This corroborates the results of tracer testing linking the Gojak spring with sinkholes in the Ogulin Dobra watercourse (known only from unpublished reports, as the original reports are unavailable).

The slope of the Tounjčica GWL (Fig 8.) indicates a slight evaporation effect in the spring waters, probably caused by a more lengthy atmospheric influence on the spring water, which suggests that Sabljaki Lake belongs to its catchment area.

The Mrežnica and Gojak springs have interesting, similar GWLs, with the same slope and intercept. Still, the observed isotope values in Mrežnica spring waters have more negative values than those of the Gojak spring water.

In the southern part of the study area, the $\delta^{18}O$ average contents of spring waters exhibited the most negative values in Dretulja, followed by the Veliko Vrelo, Mrežnica, and Slunjčica springs. The impact of precipitation impoverishment is clearly visible in this area, since the Dretulja spring is 110 metres lower in elevation but located 11 kilometres north of the Veliko Vrelo spring.

The dynamic of stable isotopes in spring waters in the south is similar, but seasonal fluctuations depend on hydrological conditions (Fig. 7). In the summer of 2018, during the recession period, the water of Dretulja spring had a noticeably lower stable isotopic content compared to the Veliko Vrelo spring. In contrast, differences were relatively minor during the moderate water levels. This observation suggests a greater influx of water into the Veliko Vrelo spring. The Mrežnica and Slunjčica springs were enriched in heavy isotopes compared to the upstream Veliko Vrelo and Dretulja springs.

Possible interpretations of the spatial distribution and general depletion of the stable isotope content from north to south can be interpreted as follows: (1) the precipitation continental effect (KERN et al., 2020; MEZGA et al., 2014), (2) the more significant influence of the Atlantic air mass, evident in the neighbouring area of Plitvice Lake (BABINKA, 2008), (3) the potential impact of lake water evaporation on precipitation composition (HUNJAK, 2015). Although the calculated gradients for the continental effect in the Adriatic-Pannonian region are much lower than those observed in this area (KERN et al., 2020); it is essential to consider the significant altitude effect caused by the rugged terrain. In the south, the Mediterranean air masses must cross the Velebit Mt., with a peak of 1754 m a.s.l, before reaching the Kapela Mt., or ~ 60 km to the catchment areas of Dretulja and Veliko Vrelo. Conversely, in the north, the Kapela Mt. is the first significant barrier for Mediterranean air masses, affecting the catchment areas of Vitunj and Zagorska Mrežnica, with an aerial distance to the Adriatic coast of ~20 km. In addition, the d-excess value depends on humidity, sea temperature, and wind speed during primary evaporation (or geographic location of forming air masses). The three-year data set reveals

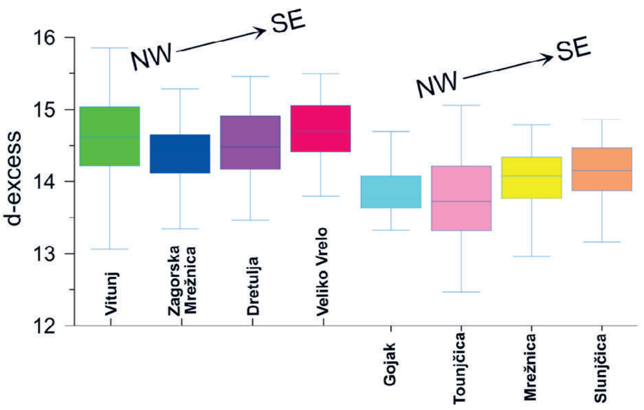

Figure 9. The box plots of the d-excess values observed in monitored spring waters.

average d-excess values ranging between 14.48 and 14.69 in aquifers within the Kapela Mt., or in the spring water of the first spring zone. Conversely, in the second spring zone, the d-excess values range from 13.72 to 14.15 (Fig. 9, Table 3). The calculated d-excess values are very similar in the observed groundwater and undoubtedly suggest the spring being fed predominantly from the Mediterranean air masses. Slightly lower values were expected in the second spring zone, as its immediate catchment area is located on the NE side of Kapela Mt. The mountain obstructs air masses with a lower d-excess coming from the north, which are emptied before crossing the mountain range. Similar d-excess values were calculated for the Plitvice Lakes area (HUNJAK, 2015), but with a different interpretation emphasizing the impact of lake water evaporation on precipitation composition.

A detailed interpretation of the origin of the precipitation origin is beyond the scope of this research. However, the authors lead towards understanding the intricate interplay between the influence of relief and continental effect on the isotopic signatures observed in the region (Fig. 10).

The stable isotopes and spring water temperature are widely recognized natural tracers for assessing groundwater's origin, retention time, and dynamics. Higher groundwater residence times result in greater homogenisation of the observed parameters (CLARK & FRITZ, 1997). To estimate groundwater mean residence times (MRT) and elevation of the recharge area, only $\delta^{18}O$ values are considered due to the strong correlation between $\delta^{18}O$ and $\delta^{2}H$ values (R >0.96) (Fig.8)

5.3. Estimation of the groundwater mean residence times

In determining MRTs, it is crucial to be careful due to established variations in spring GWLs caused by differences in the composition of stable isotopes in precipitation. However,

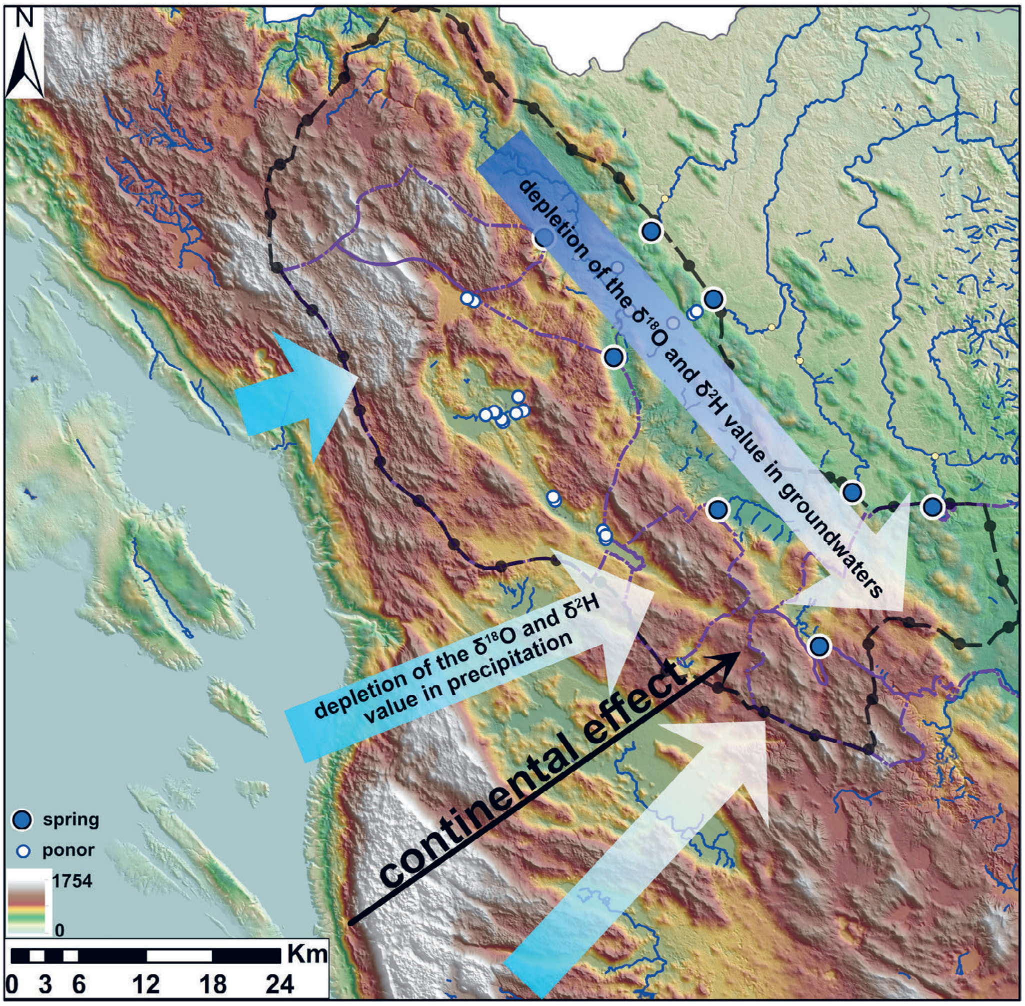

Figure 10. Interplay between relief and continental effect on depletion of the $\delta^{18}O$ and $\delta^{2}H$ composition across the north Dinaric karst region.

Table 5. Average recharge altitudes and mean residence times for the monitored springs.

Spring	Average recharge altitude (m a.s.l.)	Average temperature (3-year data set)	Mean residence times (month)	$\delta^{18}O$ Amplitude (‰)	Temperature amplitude (°C)
Vitunj	1080	7.9	16	0.81	1.8 (1.2*)
Zagorska Mrežnica	840	8.9	15	0.83	2.3
Dretulja	840	8.9	13	0.97	1.6
Veliko Vrelo	1120	7.7	12	1.19	1.7 (1.4*)
Gojak	400	11.1	10	1.25	9.2
Tounjčica	660	9.8	13	0.97	9.2
Mrežnica	440	9.9	11	1.12	7.3
Slunjčica	680	9.7	9	1.32	2.2

*the amplitude without two measurements in the highest hydrogram peaks

given that the precipitation sampler was situated in the middle of the study area, the MRTs could be calculated since the calculation does not consider absolute but relative values (Eq. 1).

The MRTs of groundwater were determined based on Equation 1 using the amplitudes of $\delta^{18}O$ isotopes in precipitation as input data and amplitudes of spring waters as output data, (without extreme values caused by a single event and assumed high proportion of freshly infiltrated water). The data in Table 5 represent the average MRT values of three calculations, one per monitored year.

The MRT for monitored springs is between 9 and 16 months (Table 5), indicating a system with significantly low storage capacity, similar to the nearby regions in the Dinaric karst: in Northern Velebit ≤ 1 year (PAAR et al., 2019); in Postojna, the established MRT in the systems was 7 months to 10 years (MANDIĆ, et al., 2013); in the catchment area of Plitvice lakes 1.3–2.9 year (MEAŠKI, 2011). The MRT for the water that drains Kapela Mt. (in the aquifers of Vitunj, Zagorska Mrežnica, Veliko Vrelo, and Dretulja springs) was ascertained over one year, and the established average retention of water in aquifers in shallow karst area is for less than one year. The temperature fluctuations are correlated with the obtained values in spring waters as a water retention indicator. The pronounced temperature fluctuation in the water of the Zagorska Mrežnica springs may be attributed to the recharge of spring with water from flooded poljes during high water conditions (Fig.3).

5.4. Estimation of the mean recharge altitude

The precipitation isotope content is linearly depleted with increasing altitude due to the water's physical characteristics, known as the altitude effect, meaning that spring waters fed from higher altitudes are more depleted in heavy isotopes (CLARK & FRITZ, 1997). In the study area, anomalies are detected by comparing the isotopic content in spring water (Fig.11B.). Based on the mean $\delta^{18}O$ value, the Tounjčica and Gojak catchment areas are situated at higher elevations compared to the upstream Zagorska Mrežnica and Vitunj springs within their respective catchment areas. The obtained data indicates the impact of evaporation from surface waters within the immediate catchment of springs and the intake from other directions in the Gojak spring.

Furthermore, geomorphology attributed to mean spring temperature data contradicts the isotope data's assertion that the Dretulja catchment area is at a higher elevation than the Veliko Vrelo watershed. (Fig. 11 A). These anomalies are in line with the interpreted continental effect (Fig. 10).

Therefore, the spring's MRA is determined based on the mean spring water temperature as a reliable indicator and compared with isotope content. The spring water temperature reflects the annual air temperature of the spring catchment area. Vertical temperature gradients in continental Croatia, including the study area, amount to 0.5°C/100 m (ZANINOVIĆ et al., 2008). Therefore, based on water temperature, the MRA of the monitored springs spreads within 710 metres from the lowest positioned catchment area of Gojak to the highest

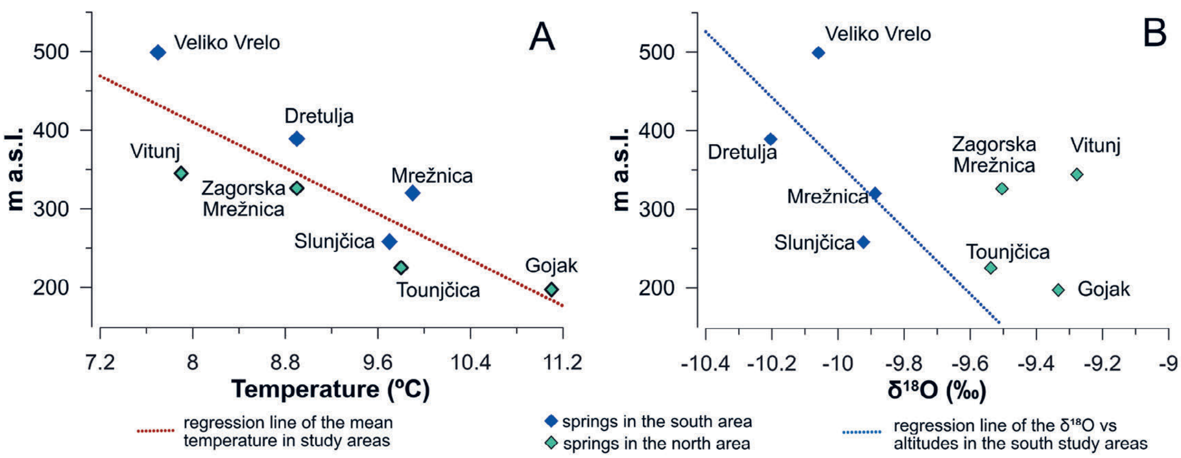

Figure 11. The mean spring water temperature vs. springs' elevation (A), the $\delta^{18}O$ value vs. springs' elevation (B).

situated at Veliko Vrelo. The lowest elevation of the Gojak catchment area corresponds to the previously mentioned northward connection. According to the morphological characteristics, the estimated mean recharge altitude of the Gojak catchment is approximately 400 m a.l.s. The springs MRA in shallow karst areas of Tounjčica, Mrežnica, and Slunjčica, extends to ~640–680 m a.s.l. In the Kapela Mt, the Zagorska Mrežnica and Dretulja springs feed from similar average altitudes ~840 m a.s.l, as well as the Vitunj and Veliko Vrelo springs ~1080–1120 m a.s.l.

6. CONCLUSION

Here, the hydrochemical and isotopic fingerprints have been used to gain insight into the highly karstified aquifers situated across Kapela Mt. These aquifers play a pivotal role in the provision of drinking water within the region. The study area comprises two spring zones: the first one is represented by four springs located at the foot of Kapela Mt., with the Vitunj spring to the north, and Zagorska Mrežnica, Dretulja, and Veliko Vrelo spings to the south. The second spring zone is represented by the Gojak, Tounjčica, Mrežnica, and Slunjčica springs.

The results of major ion analysis reveal a monolithological drainage basin. All eight springs exhibit calcium–hydrogen carbonate ($Ca–HCO_3$) to calcium-magnesium hydrogen carbonate ($Ca–Mg–HCO_3$) hydrochemical facies, indicating the dissolution and weathering of carbonates (limestone and dolomite), with the absence of evaporites and other non-carbonate rocks. From the Mg^{2+}/Ca^{2+} ratio and the Piper diagram, we observed a higher proportion of dolomite component in the Vitunj and Gojak springs which belong to the Dobra River catchment, and in the Veliko Vrelo and Mrežnica spring waters. Groundwater mineralization generally increases from the north to the south of the area, with the lowest mineralization observed in the Vitunj spring and the highest in the Dretunja and Veliko Vrelo springs. The concentrations of nitrates, sulfates, and chlorides are low, indicating the relatively unpolluted quality of the groundwater, but the human impact is still observed in the Gojak and Tounjčica springs located downstream from the urban area and Ogulin polje. Although the observed concentrations are not alarming, it is crucial to consider the aquifers' high vulnerability when planning the spatial development of the region.

The new LMWL calculated for Kapela Mt. based on a three-year dataset (June 2018 – May 2021) can be used as a background for investigating precipitation, groundwater, and surface water origin and their interrelationships. From the new LMWL we observed a predominant origin of precipitation from the Mediterranean air mass regardless of the season, in contrast to earlier studies which suggested a much more significant influence of Atlantic air masses on winter precipitation in the neighbouring areas.

The isotopic composition of spring waters indicates the meteoric origin of groundwater, rapid dynamics, and a mean residence time in the aquifer of up to 1.5 years. The seasonal fluctuations of isotopic composition are muted in spring waters due to water mixing in the subsurface. However, all calculated d-excess values in the monthly spring samples indicate a dominant reach from the Mediterranean air masses. Based on the spatial distribution of monitored springs, a significant continental (altitude) effect is detected on the isotopic composition of spring waters in the southern area, which are depleted of the heavier isotopes. The air masses from the Mediterranean have to cross Velebit Mt. and several smaller massifs to the Dretulja and Veliko Vrelo catchment areas. On that path, the heavier isotopes are broken down by the high mountain's obstruction of the air masses, resulting in depletion of the $\delta^{18}O$ and $\delta^{2}H$ in the groundwaters. Due to the significant enrichment of stable isotopes from south to north, the mean recharge altitude calculation based on stable isotopes is not applicable in the study area. The MRA was calculated based on the average spring water temperature as a reliable indicator, the MRA of the monitored springs ranges over 710 metres from the lowest positioned catchment area of Gojak to the highest situated at Veliko Vrelo.

ACKNOWLEDGEMENT

The authors express their gratitude to the Croatian Meteorological and Hydrological Service and the Croatian Electric Power Company for the provided data. This work was financially supported by Interreg Danube CAMARO-D project co-funded by the European Regional Development Fund, project B2Z30-76/19 funded by the Croatian Electric Power Company, and NONa project funded by the National Recovery and Resilience Plan 2021–2026 of the European Union – NextGenerationEU, and monitored by the Ministry of Science and Education of the Republic of Croatia. The field investigations and analysis were funded and supported by the Croatian Geological Survey, Department of Hydrogeology and Engineering Geology.

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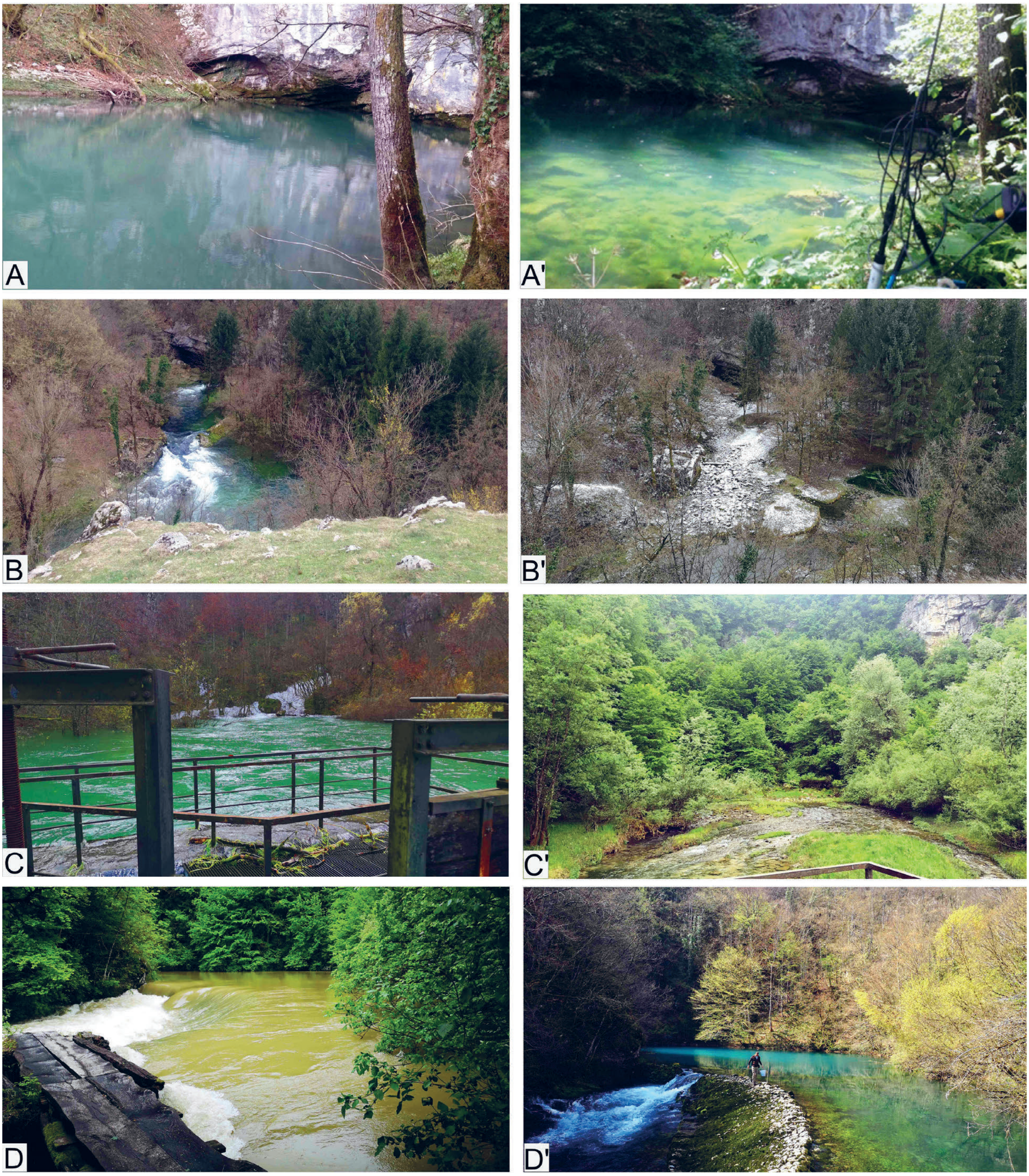
The Gojak spring during high (A) and low water conditions (A'); The Tounjčica spring during high (B) and low water conditions (B'); The Mrežnica spring during high (C) and low water conditions (C'); The Slunjčica spring during high (D) and low water conditions (D')



The Vitunj spring during high (A) and low water conditions (A'); The Zagorska Mrežnica spring during high (B) and low water conditions (B'); The Dretulja spring during high (C) and low water conditions (C'); The Veliko Vrelo spring during high (D) and low water conditions (D')