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Northern Velebit (Croatia) karst hydrological system: results of a preliminary ^{2}H and ^{18}O stable isotope study

Dalibor Paar[1], Diana Mance[2]*, Andrej Stroj[3] and Mirja Pavić[3]

[1] University of Zagreb, Faculty of Science, Department of Physics, 10 000 Zagreb, Croatia
[2] University of Rijeka, Department of Physics, 51 000 Rijeka, Croatia; (*diana.mance@uniri.hr)
[3] Croatian Geological Survey, Zagreb, Croatia

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Abstract

Researching the hydrogeological properties of karst systems is very challenging due to their extreme heterogeneity. A grey-box approach in karst research combines the results from classical hydrogeological methods with direct observations within the karstic underground, i.e. in the caves. Isotope research has become a widely used method in the investigation of karst systems. The results presented are of a preliminary ^{2}H and ^{18}O stable isotope study of the Northern Velebit karst system (Croatia) employing the grey-box approach. Groundwater samples were collected during two summer expeditions in deep caves within the karst massif. Monthly precipitation samples were also collected (at three locations between approx. 900 m and 1600 m altitude), as well as water samples at some of the most significant springs, i.e. discharge outlets of the system. For a single expedition, the stable isotope composition is almost constant, i.e. the stable isotope measurements are within the measurement error across the complete cave profile. Similar characteristics across different caves during the same year were also noted. Samples of water from the springs were taken during base-flow conditions and they have similar isotopic contents to the cave water. The results obtained indicate that homogenization of the water already occurs within the subsurface epikarst zone above the sampling locations in the caves, but a future extended sampling campaign during variable hydrologic conditions is needed to confirm this. The final research goal is to establish a conceptual grey-box model for the functioning of this complex hydrogeological system.

Keywords: caves, hydrogeology, karst, Northern Velebit, stable isotopes

1. INTRODUCTION

Dissolution of soluble rocks such as limestone, dolostone and gypsum, forms a special type of hydrogeological system, which is often reflected at the surface by the distinctive landscape known as karst. Karst aquifers are characterized by extremely heterogeneous hydraulic properties manifested by rapid groundwater flows concentrated in conduits and disolutionally widened fractures, usually sparsely distributed, while the storage of groundwater is mainly related to surrounding fractured rock matrix and surficial epikarst (or subcutaneous) zone (GOLDSCHEIDER et al., 2007).

Because of its complexity, karst aquifer research necessitates an interdisciplinary approach (DREYBRODT, 1988; COVINGTON et al., 2011). In addition to conventional methods, the use of environmental stable isotope tracers supplemented by statistical analysis, contributes to a better understanding of karst hydrogeology (CRISS et al., 2007; PALMER, 2010; GRIMMEISEN et al., 2017). Stable isotopes of water (^{2}H and ^{18}O) are analysed for several reasons, e.g. to explore recharge processes and reservoir mixing (LONG & PUTNAM, 2004; MALOSZEWSKI et al., 2002), to explore vadose water mixing, residence times and storage in non-conduit parts of karst systems (PALMER, 2010; MOERMAN et al., 2014; DÓŠA et al., 2011), to estimate mean recharge area elevations (BARBIERI et al., 2005; CHARIDEH & RAHMAN, 2007), etc.

Detailed knowledge of the various processes within a karst hydrological system is crucial for the sustainable management of water resources, their allocation, and protection against pollution (MANCE et al., 2018 a, b). The black-box approach is often used in karst hydrogeological research. It is based on rainfall – spring discharge modelling and water quality relationships, which are usually insufficient to reveal all the complexity of the various processes that control groundwater flow through the karst underground. The grey-box approach to karst systems research, besides the input-output relations, employs additional data acquired directly from underground i.e. in caves. Therefore, grey-box models are often more realistic and should be able to determine in more detail the system's flow paths, linkages, stores, capacities, and throughput volumes than the black-box model (FORD & WILLIAMS, 2007).

The research area of interest, the area of Northern Velebit (Croatia), has been the subject of earlier hydrogeological investigations (PAVIČIĆ, 1997; STROJ, 2010), but a number of parameters required to model the system's behaviour are still unknown (MALOSZEWSKI, 2000). During the last few decades, many deep caves were discovered in the Northern Velebit karstic massif (BAKŠIĆ et al., 2013), providing an opportunity to gather some new and direct insights into its hydrogeology (STROJ & PAAR, 2019).

The aim of the present preliminary study was to gather new insights into water infiltration and vadose flow properties within the karst massif by determining the $\delta^{2}H$ and $\delta^{18}O$ of water in various compartments of the system. Precipitation samples were collected from three locations situated on Mt. Velebit hilltops, while groundwater samples were collected in the caves and at the main discharge outlets of the system. The results presented provide guidelines for establishing a new research project supplemented

by systematic and more frequent data collection. This could ultimately contribute to the development of a comprehensive conceptual hydrogeological model of the Northern Velebit system.

2. STUDY AREA

The study area is located in the Croatian part of the Dinaric karst, specifically in the northern part of a 145 km long Velebit coastal mountain range (Fig. 1), which is part of the external Dinaric mountains separating the Adriatic Sea coast from the large karst poljes of the Lika, and Gacka rivers that sink in its hinterland. The Northern Velebit area, designated a National Park, covers an area of approximately 109 km^2. It has a form of high karst plateau

Figure 1. Location of Mt. Velebit and the research area (National Park Northern Velebit) in the Croatian part of Dinaric Karst. NP – National Park

intersected by numerous karst depressions separated by peaks and ridges (the highest peaks are 1600 – 1700 m a.s.l.). The largest part of Northern Velebit is composed of Jurassic carbonate rocks, mainly limestones, and massive calcareous (limestone) breccias of Upper Paleogene to Lower Neogene age (MAMUŽIĆ et al., 1969; VELIĆ et al., 1974; VELIĆ & VELIĆ, 2009). Clastic rock formations of Triassic and Palaeozoic ages form a hydrogeological barrier in the middle-southern parts of the Velebit mountain range. The deeper position of these rocks in the northern part enables deep karstification and underground water flow from the hinterland towards the Adriatic Sea (Fig. 2).

The geological structure of the Velebit mountain range is the consequence of two principal periods of tectonic activity (BLAŠKOVIĆ, 1998; KORBAR, 2009). The first was the main phase of the Dinarides orogenesis (Eocene – Miocene) with compressive movements oriented NE – SW. As a result of the regional tangential stress, deep nappe structures, folds and regional faults of Dinaric strike (NW – SE) have been formed. The second, so-called neotectonic phase, started probably during the late Miocene or early Pliocene, when the main stress changed to NS, resulting in further uplifts and transpressive deformations of older structures. The later phase played a crucial role for the present mountain morphology.

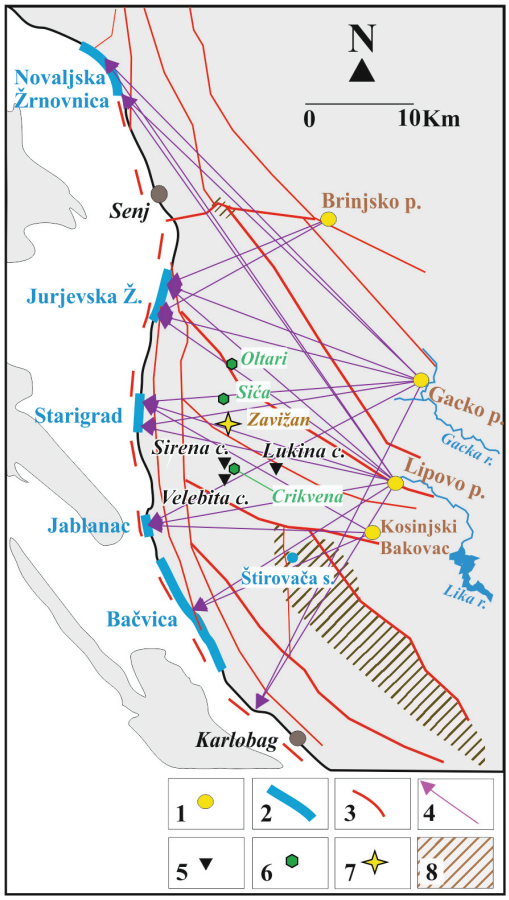

Figure 2. A simplified sketch of the Northern Velebit karst system. (1) traced sinkholes in the massif's hinterland, (2) main coastal discharge zones, (3) regional faults, (4) underground water flow connections determined by tracing tests, (5) sampled caves, (6) precipitation sampling locations, (7) meteorological station, (8) hydrogeological barrier formed by clastic rock formations, the rest of the area is built of various carbonate rocks (adapted with permission from STROJ, 2010).

Geological observations in caves revealed complex geological structures expressed by widespread occurrences of compact carbonate breccias down to depths of approx. 1000 m below surface, e.g. in the Lukina jama – Trojama and Velebita cave system (STROJ & VELIĆ, 2015). The breccias in the caves often irregularly intersect a normal succession of Jurassic limestones which points to their tectonic origin. This is commensurate with the assumption that the origin of the breccias observed at the surface is related to strong tectonic movements during the Upper Paleogene and Lower Neogene (BAHUN, 1974). Pronounced resistance to the mechanical erosion of massive carbonate breccia together with its solubility dominates the surface relief forming processes. This enhances the development of distinctive karst corrosion landscapes where the entrances of the most important caves are located. Such landscapes, together with occurrences of extremely deep caves, are instrumental in the National Park designation. Discovery and research of deep caves also revealed a very deep vadose zone of more than 1000 m inside the carbonate massif, as well as some characteristics of epiphreatic zone dynamics at the bottom of the vadose zone (BAKŠIĆ et al., 2013; STROJ & PAAR, 2019).

Sinkholes of the Lika and Gacka rivers are located on the eastern foothills of the Northern Velebit massif (Fig. 2). In the past, the rivers sank completely into the karst massif and reappeared at numerous coastal springs and vruljas (submarine

Table 1. Basic information about sampling locations.

Sampling location	Coordinates (latitude; longitude)*	Altitude (m a.s.l.)	Sample Type
Hilltops			
Sića	44.83970;14.96629	940	precipitation
Oltari	44.87348;14.98443	1300	precipitation
Crikvena	44.75878;14.98957	1641	precipitation
Caves			
Velebita Cave System**	44.75755;14.98633	1550	groundwater
Sirena Pit**	44.76797;14.98763	1500	groundwater
Lukina Jama**	44.76693;15.02638	1450	groundwater
Springs			
Jurjevska Žrnovnica (JZ)	44.90161;14.91036	0	springwater
Starigrad Senj (SS)	44.79790;14.88182	0	springwater
Bačvica (BC)	44.64268;14.94525	0	springwater
Štirovača (ST)	44.69803;15.04988	1100	springwater

*degree; WGS84 system
**entrance

springs) along the coast on the western side of the massif (Fig. 2) (PAVIČIĆ, 1997; STROJ, 2010). The distance from the sinkholes to the Adriatic Sea is approx. 20 km. Today, the water from the two rivers is used for electricity production and is routed via a tunnel to the power plant on the coast. Only occasional water surpluses sink into sinkholes occurring on average only a few days per year. Taking into account the present conditions, the precipitation in the massif area is assumed to be the main water input for the system.

3. SAMPLING AND DATA

Precipitation samples were collected on a monthly basis from May 2012 to September 2013 on Velebit at three locations - Oltari, Sića, and Crikvena (Fig. 2). Geographical coordinates and altitudes of the precipitation sampling sites are provided in Table 1. Precipitation sampling was performed usingsamples with anti-evaporation system (GRÖNING et al., 2012). A total of 35 monthly precipitation samples were analysed for their stable isotope content (Table 2). Some of the samples are missing due to

Table 2. Basic information about precipitation samples.

Sampling location	Sampling period	$\delta^{2}H$ (‰)	$\delta^{2}H$ st.dev. (‰)	$\delta^{18}O$ (‰)	$\delta^{18}O$ st.dev. (‰)	d-excess (‰)	d-excess st.dev. (‰)	amount (mm)
Sića	May 2012	-66.62	1.00	-9.90	0.00	12.58	1.00	123.2
	Jun 2012	-27.21	0.27	-4.79	0.02	11.11	0.28	42.2
	Jul 2012	-30.14	1.00	-4.62	0.00	6.82	1.00	29.6
	Sep 2012	-69.85	0.03	-10.52	0.00	14.31	0.04	292
	Oct 2012	-62.74	0.18	-9.57	0.02	13.82	0.19	250.4
	Dec 2012	-57.12	0.35	-9.33	0.01	17.52	0.36	220.5
	Jan 2013	-69.50	0.10	-10.30	0.01	12.90	0.10	212.3
	Apr 2013	-62.12	0.64	-9.48	0.02	13.72	0.64	219.9
	May 2013	-60.88	0.49	-9.80	0.02	17.52	0.49	219.1
	Jun 2013	-58.04	0.51	-8.87	0.02	12.92	0.51	21.1
	Jul 2013	-39.46	0.01	-6.16	0.02	9.82	0.06	36.5
	Aug 2013	-36.77	0.43	-6.49	0.04	15.15	0.44	59.2
	Sep 2013	-48.25	0.10	-8.00	0.01	15.75	0.10	197.2
Oltari	May 2012	-67.96	0.57	-9.84	0.01	10.76	0.57	132.6
	Jun 2012	-22.19	0.02	-3.92	0.01	9.17	0.02	32.4
	Jul 2012	-33.65	0.13	-5.17	0.00	7.71	0.13	32.8
	Sep 2012	-63.54	0.21	-9.53	0.00	12.70	0.21	241.1
	Oct 2012	-71.59	0.85	-10.73	0.01	14.25	0.85	220.5
	Dec 2012	-60.14	0.43	-9.56	0.00	16.34	0.43	220.5
	Jan 2013	-60.15	0.20	-9.39	0.00	14.97	0.20	208.5
	Apr 2013	-59.93	0.58	-9.04	0.02	12.39	0.58	219.2
	May 2013	-61.03	0.41	-9.50	0.04	14.97	0.43	220.4
	Jun 2013	-51.64	0.18	-7.76	0.01	10.44	0.18	27.8
	Jul 2013	-37.56	0.44	-6.00	0.03	10.44	0.45	37.1
	Aug 2013	-36.89	0.21	-6.50	0.03	15.11	0.22	53.6
	Sept 2013	-48.39	0.00	-7.95	0.00	15.21	0.01	195.3
Crikvena	May 2012	-67.12	0.16	-10.02	0.02	13.04	0.17	132
	Jun 2012	-32.32	0.22	-5.60	0.00	12.48	0.22	51.7
	Jul 2012	-40.91	0.86	-6.29	0.01	9.41	0.86	29.6
	Sep 2012	-41.34	0.13	-6.88	0.02	13.70	0.14	74.7
	Oct 2012	-70.81	0.40	-10.75	0.00	15.19	0.40	204.1
	May 2013	-61.16	0.08	-9.50	0.03	14.84	0.12	218.4
	Jun 2013	-	-	-8.42	0.10	-	-	3.2
	Jul 2013	-	-	-5.64	0.01	-	-	3.1
	Sep 2013	-58.41	0.08	-9.43	0.00	17.03	0.08	197.2

Table 3. Basic information about groundwater samples collected in caves.

Sampling location	Altitude (m a.s.l.)	Cave depth (m)	Sampling date	δ^2H (‰)	δ^2H st.dev. (‰)	δ^{18}O (‰)	δ^{18}O st.dev. (‰)	d-excess (‰)	d-excess st.dev. (‰)
VCS	1462	-95	31-Jul-12	-63.05	0.73	-9.3	0.01	11.35	0.73
VCS	977	-580	31-Jul-12	-61.49	0.72	-9.66	0.00	15.79	0.72
VCS	977	-580	31-Jul-12	-60.66	0.28	-9.6	0.00	16.14	0.28
VCS	772	-785	1-Aug-12	-60.92	0.03	-9.47	0.01	14.84	0.04
VCS	707	-850	1-Aug-12	-62.17	0.11	-9.57	0.01	14.39	0.11
VCS	687	-870	1-Aug-12	-62.17	0.09	-9.59	0.01	14.55	0.09
VCS	582	-975	1-Aug-12	-62.39	0.02	-9.72	0.01	15.37	0.04
VCS	531	-1026	2-Aug-12	-62.98	0.49	-9.78	0.00	15.26	0.49
VCS	777	-780	2-Aug-12	-60.69	0.85	-9.47	0.00	15.07	0.85
VCS	597	-960	2-Aug-12	-61.47	0.96	-9.7	0.01	16.13	0.96
VCS	531	-1026	2-Aug-12	-62.17	0.68	-9.72	0.00	15.59	0.68
VCS	531	-1026	2-Aug-12	-62.24	0.65	-9.56	0.01	14.24	0.65
VCS	531	-1026	2-Aug-12	-61.84	0.83	-9.69	0.00	15.68	0.83
VCS	1457	-100	3-Aug-12	-62.13	0.42	-9.39	0.02	12.99	0.42
VCS	707	-850	4-Aug-12	-62.02	0.8	-9.6	0.01	14.78	0.8
VCS	531	-1026	4-Aug-12	-61.34	0.11	-9.68	0.00	16.1	0.11
VCS	977	-580	1-Aug-13	-66.29	0.11	-10.23	0.01	15.55	0.12
VCS	977	-580	1-Aug-13	-65.86	0.2	-10.19	0.02	15.66	0.2
Lukina jama	475	-1000	2-Aug- 13	-68.11	0.14	-10.44	0.03	15.41	0.16
Sirena Pit	1453	-45	5-Aug-13	-70.19	0.15	-10.85	0.04	16.61	0.18

VCS – Velebita Cave System

sampling locations inaccessible during severe winter weather conditions. Also, some samples had to be discarded due to an overflow of collectors (November 2012), while others were not suitable for the analysis due to insufficient volume (August 2012, summer 2013).

Water samples in the Velebita cave system (VCS, entrance approx. 1550 m a.s.l., Fig. 2) were collected during Summer 2012 and Summer 2013 spelaeological expeditions. A total of 20 groundwater samples were collected in the caves. Samples were collected during dry summer days as summer storms increase the probability of sudden, increased water flows through cave passages, which is dangerous for cavers. The VCS sampling in 2012 started at a depth of approx. 100 metres, and continued to 1026 metres depth (Table 3). In 2013, two samples were collected in the VCS at a depth of approx. 600 m, and one sample was collected in the Lukina jama cave (entrance at approx. 1450 m a.s.l., Fig. 2) at a depth of 1000 m. The 2013 expedition also included the Sirena Pit (entrance approx. 1500 m a.s.l., Fig. 2) where one sample was collected at 45 m depth. Basic information about groundwater sampling in the caves is provided in Tables 1 & 3.

The main coastal springs along the western foothills of the massif: Bačvica (BC), Jurjevska Žrnovnica (JZ) and Starigrad Senj (SS), were sampled in the summer of 2012 (Fig. 2). Additionally, two samples were collected from Štirovača spring (ST), located in the central part of the Velebit massif at 1100 m a.s.l. (Fig. 2). A total of 9 spring water samples were collected (Table 4).

All collected samples (precipitation, groundwater collected in caves and spring water) were stored in 50 ml, double capped, polyethylene bottles until analysis.

The Meteorological and Hydrological Service provided meteorological data for the Zavižan meteorological station (1600 m a.s.l.), the only permanent meteorological station on Northern Velebit.

4. MEASUREMENT AND ANALYSIS

Stable isotope measurements were performed using the water equilibration technique (HORITA & KENDALL, 2004) on a Delta plusXP (Thermo Finnigan) isotope ratio mass spectrometer. An HDO eq48/24 (IsoCal) equilibration unit and a Dual Inlet

Table 4. Basic information about spring water samples.

Sampling location	Sampling date	δ^2H (‰)	δ^2H st.dev. (‰)	δ^{18}O (‰)	δ^{18}O st.dev. (‰)	d-excess (‰)	d-excess st.dev. (‰)
JZ S1	31-Jul-12	-54.59	0.55	-8.08	0.02	10.05	0.55
JZ S2	31-Jul-12	-54.17	0.59	-8.12	0.01	10.79	0.59
SS	31-Jul-12	-47.29	0.13	-7.17	0.01	10.07	0.13
BC S1	31-Jul-12	-52.35	0.01	-8.11	0.01	12.53	0.02
BC S2	31-Jul-12	-52.11	0.82	-8.10	0.01	12.69	0.82
BC SV	06-Aug-12	-51.9	0.34	-8.18	0.01	13.54	0.34
SS	06-Aug-12	-48.19	0.44	-7.34	0.01	10.53	0.44
ST S1	07-Aug-12	-58.18	0.17	-9.18	0.01	15.26	0.17
ST S2	07-Aug-12	-57.64	0.58	-9.16	0.01	15.64	0.58

JZ S1 – Jurjevska Žrnovnica Sample 1; JZ S2 – Jurjevska Žrnovnica Sample 2; SS – Starigrad Senj; BC S1 – Bačvica Sample 1; BC S2 – Bačvica Sample 2; BC SV – Bačvica Spring Vrulja; ST S1 – Štirovača Sample 1; ST S1 – Štirovača Sample 2

system (Thermo Finnigan) were peripheral units. $\delta^{2}H$ and $\delta^{18}O$ values are expressed relative to the Vienna Standard Mean Ocean Water (VSMOW) standard. The measurement precision was better than 0.1 ‰ in case of $\delta^{18}O$, and better than 1 ‰ for $\delta^{2}H$. Accordingly, the measurement error for d-excess is calculated to be 1.04 ‰ (CRISS et al., 2007). Normalization and analyses of measurements were performed by the US Geological Survey Laboratory Information Management System.

Statistical calculations were conducted in Statistica 13.0 (Statsoft Inc., Tulsa, OK, USA). The descriptive statistics for data that are normally distributed are presented with arithmetic mean and standard deviation, while data that do not follow a normal distribution are presented with the median and minimum and maximum values. To test whether a sample distribution matches the characteristics of a normal distribution we used the Kolmogorov-Smirnov test. A measure of the linear correlation between two variables is expressed with the Pearson correlation coefficient (R). The relationship between two variables was determined by linear regression analysis. Testing the differences between the continuous variables was accomplished by t-test (for normally distributed data) or Mann-Whitney test (for data that do not follow a normal distribution), and regarding the categorical variables by χ^{2}-test. The level of statistical significance was chosen at $p < 0.05$.

5. RESULTS AND DISCUSSION

5.1. Meteorological conditions in the hydrological years 2012 and 2013

Daily air temperatures of the hydrological year 2012 (Oct 2011 – Sep 2012) and the hydrological year 2013 (Oct 2012 – Sep 2013) do not differ significantly (Mann-Whitney test, $p = 0.43$). The average monthly air temperatures for the period showed typical seasonal behaviour with the highest temperatures in summer and the lowest temperatures in the winter months (Fig. 3A).

Monthly precipitation during the hydrological year 2013 (median 218.6 mm; minimum 45.1 mm; maximum 462.9 mm) was significantly higher compared to the hydrological year 2012 (median 86.2; minimum 0.8 mm; maximum 278.3 mm) (Mann-Whitney test, $p = 0.04$). As shown in Fig. 3A, this is particularly evident during the period Jan – Mar 2012 (very low precipitation) and Jan – Mar 2013 (rainy period).

During the hydrological year 2013 snow was present for longer in comparison to the previous hydrological year (χ^{2}-test, $p = 0.003$, Fig. 3B). In the hydrological year 2013 the snow cover was continuously present for 164 days (melting in May 2013), while during the hydrological year 2012 the snow cover was present for 100 consecutive days (melting in March 2012; with fresh snow in April and May 2012). Also, the snow layers were thicker in the winter season 2012–2013 in comparison to the same season in 2011–2012 (Mann-Whitney test, $p = 0.001$). The thickest snow layer of 2011–2012 was 120 cm (Feb 2012), while in the winter season 2012-2013 the maximum snow thickness was 322 cm (March 2013, Fig. 3B).

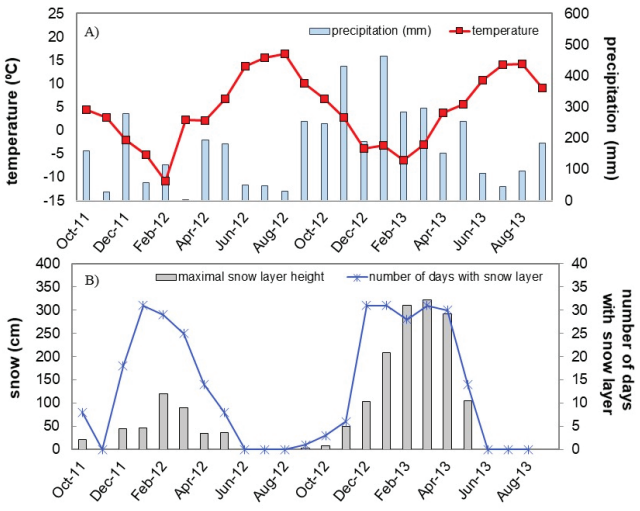

Figure 3. Meteorological conditions at the Zavižan station over the study period. Time series of A) average monthly air temperatures and monthly precipitation amounts; B) number of days with the presence of a snow layer and maximum snow layer thicknesses.

5.2. Precipitation

Due to the small number of precipitation samples, we weren't able to set up a Local Meteoric Water Line (LMWL) that would be relevant for a longer period. Nevertheless, there is a statistically significant correlation between $\delta^{2}H$ and $\delta^{18}O$ precipitation values ($R = 0.99$; $p < 0.001$). A corresponding precipitation regression line: $\delta^{2}H = 7.15 \cdot \delta^{18}O + 6.14$ ‰ ($R^{2} = 0.98$) plots close to the Global Meteoric Water Line (GMWL) that expresses the worldwide average (CRAIG, 1961) (Fig. 4).

Given the strong correlation between $\delta^{2}H$ and $\delta^{18}O$ precipitation values, only $\delta^{18}O$ values are mentioned below. The time series of precipitation $\delta^{18}O$ shows higher values in the summer months than during the rest of the year (Fig. 5A). This is typical for low latitudes where 'the amount effect' accounts for δ variations: low isotopic signals in months with significant precipitation, and more positive isotopic signals in months with scarce rainfall (DANSGAARD, 1964).

The average d-excess value of precipitation samples is (13.16 ± 2.72) ‰. Fig. 5B shows that precipitation d-excess values are lower during summer than during the rest of the year. This is comparable to previously reported results from the bordering region with similar climatic conditions (MANCE et al., 2014). Therefore, we can conclude that the sources of the precipitation are comparable, i.e. that the dominant summer precipitation in the area of Northern Velebit originates in the Atlantic Ocean, while in winter there is the predominance of Mediterranean-originated precipitation.

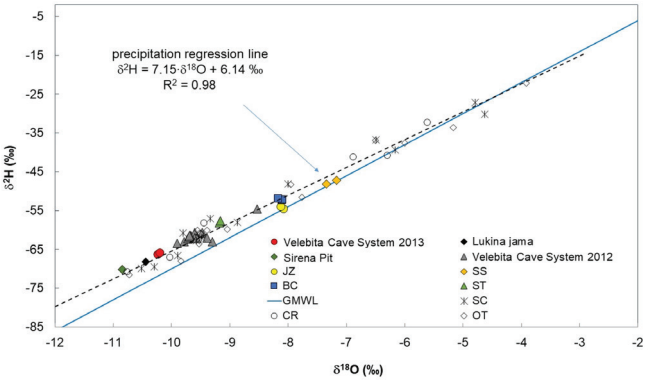

Figure 4. $\delta^{2}H$ – $\delta^{18}O$ diagram of monthly precipitation samples (OT – Oltari, SC – Sića, CR – Crikvena), groundwater samples collected in caves during expeditions 2012 & 2013 (Sirena Pit, Lukina jama, VCS – Velebita cave system), and groundwater samples collected at springs (JZ – Jurjevska Žrnovnica, SS – Starigrad Senj, BC – Bačvica, ST – Štirovača). GMWL – Global Meteoric Water Line.

Geologia Croatica

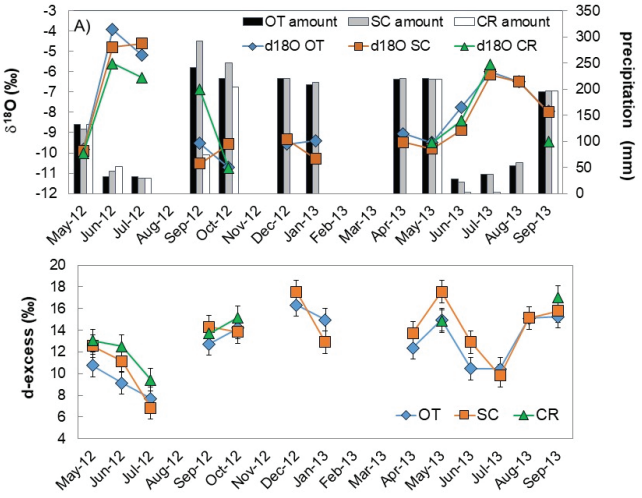

Figure 5. A) $\delta^{18}O$ series and the amount of monthly precipitation samples; B) d-excess series for the monthly precipitation samples. Error bars represent a measurement error of 1.04 ‰. OT – Oltari, SC – Sića, CR – Crikvena.

5.3. Groundwater

The isotope measurements for samples collected in 2012 across the VCS profile (depths >1000 m) show a very small variation of $\delta^{18}O$ values (Figure 6, Table 3). The average $\delta^{18}O$ value of these samples is (-9.59 ± 0.13) ‰. The values are within a narrow range (< 0.5 ‰) and without the presence of a uniform vertical gradient. Stable isotope composition of the samples collected in caves corresponds to the lower part of the precipitation cluster (Fig. 4), indicating that the groundwater flowing through the cave during low water conditions is dominantly fed by the September – May precipitation (Fig. 5).

The relatively constant isotopic composition of the samples suggests that groundwater homogenization already occurs within the epikarst zone. The epikarst zone comprises a relatively shallow, but most intensely fractured and karstified subsurface zone where precipitation quickly infiltrates and could be temporarily stored (MANGIN, 1974; WILLIAMS, 1983). Water stored in such epikarst storages during the wet season slowly drains into the underlying vadose zone during the dry summer season. Therefore, we can conclude that consistent water characteristics across the VCS profile suggest that the cave streams are dominantly fed from the epikarst storages. The substantial inflow of water with different characteristics from deeper storages, i.e. from fractures in rock walls along the cave profile, would probably be reflected by more pronounced variations in the stable isotope composition with cave depth. It should be mentioned once again that all samples were taken during low water conditions. If samples were collected during summer storms, when fast infiltration can bypass epikarst storages through fractures widened by dissolution, $\delta^{18}O$ would probably show different values, i.e. the isotopic composition would be more influenced by recent (summer) precipitation.

Cave samples collected during the 2013 expedition have lower $\delta^{18}O$ values than those from the 2012 expedition (Fig. 6, Table 3). These observed differences are tentatively explained by the characteristics of the rainfall period that preceded the second expedition. Namely, lower isotopic values could be associated with higher levels of snow and rainfall during the hydrological year 2013 in comparison with hydrological year 2012 (Fig. 3).

Unfortunately, sampling along the complete VCS profile was not performed in 2013, and only samples at approx. 600 m depth were available. It is interesting that the sample taken in the Lukina jama in the same year has a very similar isotopic value. This suggests similar recharge mechanisms for different caves in the area.

It is generally considered that the preserved seasonal amplitude of the spring water isotopic signal indicates a mean residence time of ≤ 1 year (TRČEK & ZOJER, 2009, LAUBER & GOLDSCHEIDER, 2014). If lower isotopic values of the sampled groundwater in 2013 (Fig. 6) are a consequence of the characteristics of the preceding wet season, this points to a relatively short mean residence time of groundwater in storages before draining to the cave conduits. Nevertheless, this should be confirmed by longer and more extensive sampling of the precipitation, and groundwater in the caves.

The sample collected at a depth of 45 m from the Sirena pit in 2013 was depleted in comparison to other samples collected

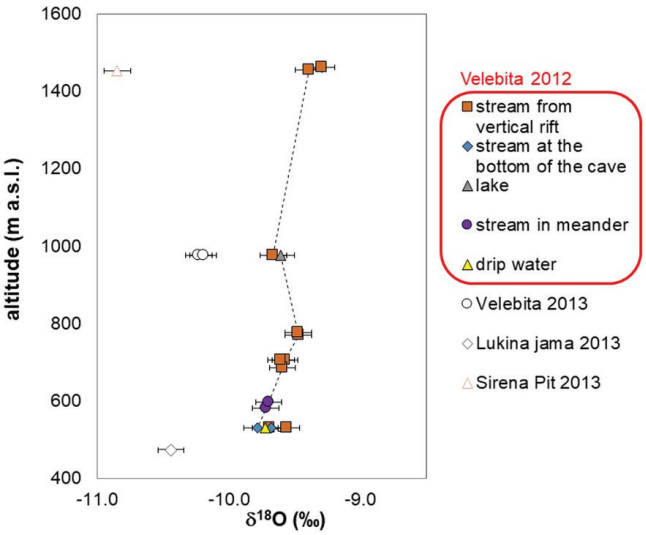

Figure 6. Groundwater $\delta^{18}O$ values at corresponding sampling altitudes. Error bars represent a measurement error of 0.1 ‰. Lower altitudes indicate greater cave depths. Isotopic signals connected with a dashed line originate from samples collected in the Velebita cave system in 2012.

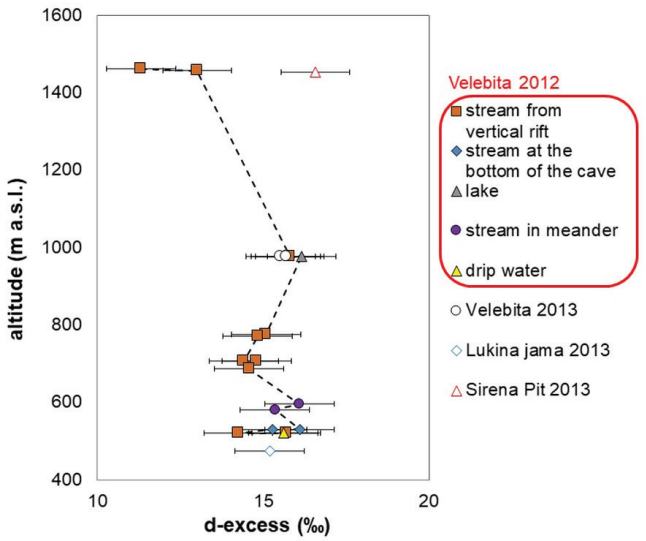

Figure 7. Groundwater d-excess values at corresponding sampling altitudes. Error bars represent measurement errors of 1.04 ‰. Lower altitudes indicate greater cave depths. Isotopic signals connected with dashed line originate from samples collected in the Velebita cave system in 2012.

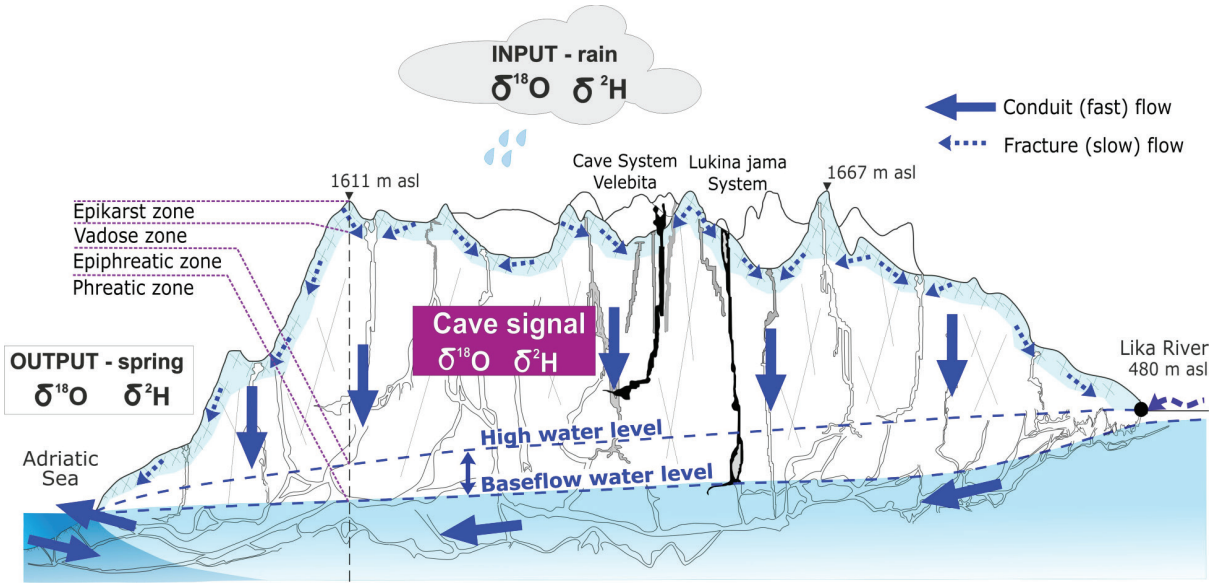

Figure 8. Conceptual model of Northern Velebit karst hydrological system. Sampled caves are shown in black, other known caves are in grey, and the remaining conduits are schematic.

that year (Fig. 6). We may attribute the depletion of the sample to the probable origin of the water sampled from the snowmelt, as for snow lower isotopic values are expected (MANCE, 2014). Also, perennial snow accumulation was reported by the cavers in a deep dolina where the cave entrance is located.

For d-excess values of the samples collected in caves, we may also see that most of the data plots within the range of the measurement error (Fig. 7). The average d-excess value of cave collected samples is (14.89 ± 1.26) ‰. Approximately constant d-excess values of cave water samples indicate the absence of significant evaporation before infiltration, i.e. fast infiltration of precipitation to the epikarst storage. Similar d-excess values of cave samples collected in 2013 and 2012 indicate similar geographic origins of the precipitation recharging the system. The average d-excess value of samples collected in caves corresponds to the d-excess of precipitation collected in the period Sep 2012 – May 2013 (14.61 ± 1.57) ‰ (t-test, p = 0.28). This is an additional indicator of predominant groundwater recharge by the winter precipitation. The extreme d-excess values have samples collected at the highest altitudes i.e. the lowest cave depths. This may be explained by some contribution of newly infiltrated precipitation in the sampled water.

Fig. 4 shows that the samples from springs plot above the samples collected in caves. Water from coastal springs was slightly brackish due to seawater intrusion into the karst aquifer, which was manifested by the elevated conductivity of the spring water. Specific conductivity measured during sampling at the BC, JZ and SS springs was 6.7-7.0 mS/cm, 7.9 mS/cm and 13.8-14.7 mS/cm, respectively. Specific conductivity of the spring water during high flow conditions (when seawater intrusion doesn't affect it) was approx. 0.3-0.4 mS/cm (STROJ, 2010). We estimated the seawater proportion in the spring water samples by applying two-component mixing analysis (PETERLLA & CELICO, 2013) based on the sample conductivities, unaffected groundwater conductivity and seawater conductivity (55 mS/cm, measured during sampling). The calculated proportion of seawater in the spring water was approx. 12 % at BC, 14 % at JZ and 25 % at SS springs. We further applied two-component mixing analysis for corrections of coastal springs' isotopic compositions. Corrections were based on the estimated proportion of seawater and presumed seawater isotopic composition of $\delta^{18}O \approx +1‰$ (GAT et al., 2003). After the correction, groundwater samples from the springs have similar values to water from the caves in the same year (Tables 3 & 4), confirming the coastal springs are predominantly fed by the recharge from the massif.

Stable isotope compositions of groundwater collected in both, caves and springs, coincide with the precipitation regression line (Fig. 4). This indicates the meteoric origin of the groundwater without significant influence of additional post-precipitation fractionation.

The only sampled inland spring, located in the central, but somewhat lower part of the massif (1100-1300 m a.s.l.) is the Štirovača (ST) spring (Fig. 2). Both ST samples have $\delta^{18}O$ values which are comparable to, but slightly less depleted than those collected in caves (Tables 3 & 4) suggesting it is fed from its immediate surroundings. This is consistent with the geological situation: the spring is located close to the geological boundary with the impermeable clastic rocks situated on the southern margin of the Northern Velebit.

The $\delta^{18}O$ values of samples collected in the caves and the ST spring are comparable to values for some of the Gacka river springs sampled during summer months of 2005 – 2011 (MANDIĆ et al., 2008; OZYURT et al., 2014). This indicates similar mechanisms of winter (wet) season recharge of water storages, which are slowly drained during the dry season. The ST d-excess values are comparable to d-excess values of samples from the caves (Tables 3 & 4). This is another indication of similar water feeding into the caves and the ST spring. Lower d-excess values of coastal springs are probably a consequence of mixing with seawater or/and a small contribution from recent summer precipitation.

5.4. Preliminary conceptual model of the Northern Velebit hydrogeological system

Taking groundwater samples directly from the deep caves within the massif permitted the use of the grey-box model instead of the black-box model that takes into account only system's input and output data. Fig. 8 shows a conceptual model of the Northern

Velebit hydrological system developed on the basis of the results presented here, including the results of previous spelaeological and hydrogeological research (PAAR et al., 2008; STROJ, 2010; BAKŠIĆ et al., 2013; STROJ & PAAR, 2019).

The proposed conceptual model includes provision of significant storage capacities within the epikarst zone, situated immediately below the surface, down to the depth of a few metres (or few tens of metres in case of massive and well lithified carbonate breccias). During the dry season, the flow in cave conduits is mostly fed by the water stored in the epikarst during the previous winter / wet season. Across the vadose zone, the flow is fast and predominantly concentrated in conduits, which is expressed by constant isotope characteristics. The preliminary findings presented earlier suggest that the mean residence time of water stored in the system is relatively short, possibly less than a year. This is indicated by the cave water stable isotope composition influenced by characteristics of the preceding winter / wet season. Coastal karst springs, that are the main discharge points of the system, are predominantly fed by the water of similar characteristics as that observed in the caves. The infrequent nature and short duration of concentrated inflows from sinkholes on the Lika and Gacka rivers under present conditions limits their significance. Therefore, it may be concluded that epikarst storages on the massif are probably the main source of spring water during the base flow conditions.

6. CONCLUSIONS

The paper presents the results of a preliminary stable isotope study of the waters of the Northern Velebit karst hydrological system. The aim of the study was the application of a grey-box modelling approach to karst hydrogeological research. The approach combined the results from classical hydrogeological methods with the findings from the sampling of the water in the caves.

The study used stable isotope analysis of water samples as a tool to investigate the functioning of the karst hydrogeological system.

The results of this study, together with the results from previous research enabled us to develop a preliminary conceptual recharge and storage model of the Northern Velebit karst system. The main features incorporated in the model are:

- groundwater storage is mainly related to the function of the epikarst zone;
- recharge of the epikarst occurs mainly during the wet / winter season;
- the mean residence time of epikarst storage is relatively short, probably within one year;
- the deeper vadose zone has a low storage capacity and water flows within are concentrated in conduits;
- system outflow via coastal springs and vruljas (submarine springs) in the base flow conditions is dominantly fed by epikarst storage of the massif.

Based on the obtained results, we conclude that the grey-box modelling approach is an improvement in the investigation of complex karst systems. In addition to classical hydrological methods, spelaeological investigations play an important role in this type of approach and give researchers the opportunity to study different hydrological processes *in situ*.

Although the number of analysed water samples is relatively low, limiting their interpretation, this study provides preliminary results, enabling the establishment of a recharge and storage model for the system that will serve as a basis for future research.

Establishing a future longer term monitoring programme for the Northern Velebit hydrogeological system would provide data required to further test and upgrade the presented model. This would provide a better and more detailed understanding of the functioning of the Northern Velebit karst system and enable efficient water management and nature conservation to be undertaken.

REFERENCES

BAHUN, S. (1974): Tectogenesis of the Velebit and the formation of the Jelar deposits.– Geološki vjesnik, 27, 35–51.

BAKŠIĆ, D., PAAR, D., STROJ, A. & LACKOVIĆ, D. (2013): Northern Velebit Deep Caves.– In: FILIPPI, M. & BOSAK, P. (eds.): Proceedings of the 16th International Congress of Speleology, Brno, Jul. 21–28, 2013. Czech Speleological Society and UIS, Brno, 2013, 24–29.

BARBIERI, M., BOSCHETTI, T., PETTITA, M. & TALLINI, M. (2005): Stable isotope (2H, 18O and 87Sr/86Sr) and hydrochemistry monitoring for groundwater hydrodynamics analysis in a karst aquifer (Gran Sasso, Central Italy).– Appl. Geochem., 20, 2063–2081. doi: 10.1016/j.apgeochem.2005.07.008

BLAŠKOVIĆ, I. (1998): The Two Stages of Structural Formation of the Coastal Belt of the External Dinarides.– Geol. Croat., 51/1, 75–89. doi: 10.4154/GC.1998.09

CHARIDEH, A & RAHMAN, A. (2007): Environmental isotopic and hydrochemical study of water in the karst aquifer and submarine springs of the Syrian coast.– Hydrogeol. J., 15/2, 351–364. doi: 10.1007/s10040-006-0072-x

COVINGTON, M.D., DOCTOR, D.H., KING, J.N. & WICKS, C.M. (2011): Research in karst: A model for future directions in hydrologic science? – AGU Hydrology Section Newsletter [Internet, cited 2019 Feb 14], 5 p. Available from: https://hydrology.agu.org/wp-content/uploads/sites/19/2014/10/AGUHydro-201107.pdf

CRAIG, H. (1961): Isotopic Variations in Meteoric Waters.– Science, 133/3465, 1702–1703. doi: 10.1126/science.133.3465.1702

CRISS, R., DAVISSON, L., SURBECK, H. & WINSTON, W. (2007): Isotopic methods.– In: GOLDSCHEIDER, N. & DREW, D. (eds.): Methods in Karst Hydrogeology. Taylor & Francis, London, 123–146.

DANSGAARD, W. (1964): Stable isotopes in precipitation.– Tellus, 16/4, 436–468. doi: 10.1111/j.2153-3490.1964.tb00181.x

DÓŠA, M., HOLKO, L. & KOSTKA, Z. (2011): Estimation of the mean transit times using isotopes and hydrograph recessions.– Bodenkultur., 62/1–4, 47–52.

DREYBRODT, W. (1988): Processes in Karst Systems.– Springer-Verlag, Berlin. doi: 10.1007/978-3-642-83352-6

FORD, D. & WILLIAMS, P. (2007): Karst hydrogeology and geomorphology.– Wiley Chichester. doi: 10.1002/9781118684986

GAT, J.R., KLEIN, B., KUSHNIR, Y., ROETHER, W., WERNLI H., YAM, R. & SHEMESH, A. (2003): Isotope composition of air moisture over the Mediterranean Sea: an index of the air–sea interaction pattern.– Tellus B, 55, 953–965. doi: 10.1034/j.1600-0889.2003.00081.x

GOLDSCHEIDER, N., DREW, D. & WORTHINGTON, S. (2007): Introduction.– In: GOLDSCHEIDER, N. & DREW, D. (eds.): Methods in karst hydrogeology. Taylor & Francis, London, 2–7 p. doi: 10.1201/9781482266023

GRIMMEISEN, F., LEHMANN, M.F., LIESCH, T., GOEPPERT, N., KLINGER, J., ZOPFI, J. & GOLDSCHEIDER, N. (2017): Isotopic constraints on water source mixing, network leakage and contamination in an urban groundwater system.– Sci. Total Environ., 583, 202–213. doi: 10.1016/j.scitotenv.2017.01.054

GRÖNING, M., LUTZ, H.O., ROLLER-LUTZ, Z., KRALIK, M., GOURCY, L. & PÖLTENSTEIN, L. (2012): A simple rain collector preventing water re-evaporation dedicated for $\delta^{18}O$ and $\delta^{2}H$ analysis of cumulative precipitation samples.– J. Hydrol., 448–449, 195–200. doi: 10.1016/j.jhydrol.2012.04.04

HORITA, J. & KENDALL, C. (2004): Stable Isotope Analysis of Water and Aqueous Solutions by Conventional Dual-Inlet Mass Spectrometry.– In: de GROOT, P.A. (ed.): Handbook of Stable Isotope Analytical Techniques. Elsevier, 1–37. doi: 10.1016/B978-044451114-0/50003-X

KORBAR, T. (2009): Orogenic evolution of the External Dinarides in the NE Adriatic region: a model constrained by tectonostratigraphy of Upper Cretaceous to Paleogene carbonates.– Earth Sci Reviews., 96/4, 296–312. doi: 10.1016/j.earscirev.2009.07.004

LAUBER, U. & GOLDSCHEIDER, N. (2014): Use of artificial and natural tracers to assess groundwater transit-time distribution and flow systems in a high-alpine karst system (Wetterstein Mountains, Germany).– Hydrogeol. J., 22, 1807–1824. doi: 10.1007/s10040-014-1173-6

LONG, A.J. & PUTNAM, L.D. (2004): Linear model describing three components of flow in karst aquifers using ^{18}O data.– J. Hydrol., 296, 254–270. doi: 10.1016/j.jhydrol.2004.03.023

MALOSZEWSKI, P., STICHLER, W., ZUBER, A. & RANK, D. (2002): Identifying the flow systems in a karstic-fissured-porous aquifer, the Schneealpe, Austria, by

modeling of environmental ^{18}O and ^{3}H isotopes.– J. Hydrol., 256, 48–59. doi: 10.1016/S0022-1694(01)00526-1

MALOSZEWSKI, P. (2000): Lumped-parameter models as a tool for determining the hydrological parameters of some groundwater systems based on isotope data.– In: DASSARGUES, A. (ed.): Tracers and Modelling in Hydrogeology, International Conference, Liège, 2000, IAHS Press, London, 271–276.

MAMUŽIĆ, P., MILAN, A., KOROLIJA, B., BOROVIĆ, I. & MAJCEN, Ž. (1969): Osnovna geološka karta SFRJ 1:100000, list Rab [*Basic Geological Map of SFRY 1:100000, Rab Sheet* – in Croatian].– Institute of Geology, Zagreb, Federal Geol. Inst., Belgrade.

MANCE, D., HUNJAK, T., LENAC, D., RUBINIĆ, J. & ROLLER-LUTZ, Z. (2014): Stable isotope analysis of the karst hydrological systems in the Bay of Kvarner (Croatia).– App. Radiat. Isotopes, 90, 23–34. doi:10.1016/j.apradiso.2014.03.001

MANCE, D. (2014): Karakterizacija krškog vodonosnika temeljena na prostornim i vremenskim promjenama stabilnih izotopa vodika i kisika [*Characterization of a karst aquifer based on the spatial and temporal variations of hydrogen and oxygen stable isotopes* – in Croatian, with an English Abstract].– Unpubl. PhD Thesis, Faculty of Science, University of Zagreb, 124 p. https://repozitorij.pmf.unizg.hr/islandora/object/pmf%3A1770

MANCE, D., MANCE, D. & VUKIĆ LUŠIĆ, D. (2018a): Environmental isotope ^{18}O in coastal karst spring waters as a possible predictor of marine microbial pollution.– Acta Adriat., 59/1, 3–15. doi: 10.32582/aa.59.1.1

MANCE, D., MANCE, D. & VUKIĆ LUŠIĆ, D. (2018b): Marine Pollution Differentiation with Stable Isotopes of Groundwater.– Pomorstvo, 32/1, 80–87. doi: 10.31217/p.32.1.10

MANDIĆ, M., BOJIĆ, D., ROLLER-LUTZ, Z., LUTZ, H.O. & KRAJCAR BRONIĆ, I. (2008): Note on the spring region of Gacka River (Croatia).– Isot. Environ. Healt. S. 44/2, 201–208. doi: 10.1080/10256010802066364

MANGIN, A. (1974): Contribution à l'étude hydrodynamique des aquifères karstiques.– Ann. Spéléol. 29(3), 283-332; (4), 495-601.

MOERMAN, J.W., COBB, K.M., PARTIN, J.W., MECKLER, A.N., CAROLIN, S.A., ADKINS, J.F., LEJAU, S., MALANG, J., CLARK, B. & TUEN, A.A. (2014): Transformation of ENSO-related rainwater to drip water $\delta^{18}O$ variability by vadose water mixing. Geophys.– Res. Lett., 41, 1–9. doi: 10.1002/2014GL061696

OZYURT, N.N., LUTZ, H.O., HUNJAK, T., MANCE, D. & ROLLER-LUTZ, Z. (2014): Characterization of the Gacka River basin karst aquifer (Croatia): Hydrochemistry, stable isotopes and tritium-based mean residence times.– Sci. Total Environ., 487, 245–254. doi: 10.1016/j.scitotenv.2014.04.018

PAAR, D., UJEVIĆ, M., BAKŠIĆ, D., LACKOVIĆ, D., ČOP, A. & RADOLIĆ, V. (2008): Physical and Chemical Research in Velebita Pit (Croatia).– Acta Carsol., 37/2–3, 273–278. doi: 10.3986/ac.v37i2-3.151

PALMER, A.N. (2010): Understanding the hydrology of karst.– Geol. Croat., 63/2, 143–148. doi: 10.4154/gc.2010.11

PAVIČIĆ, A. (1997): Hydrogeological evaluation of water retaining properties of the Kosinj reservoir (Lika, Croatia).– Geol. Croat., 50/2, 289–298.

PETERLLA, E. & CELICO, F. (2013): Mixing of water in a carbonate aquifer, southern Italy, analysed through stable isotope investigations.– Int. J. Speleol., 42/1, 25–33. doi: 10.5038/1827-806X.42.1.4

STROJ, A. (2010): Podzemni tokovi u zaleđu krških priobalnih izvora na području Velebitskog kanala [*Underground water flows in the hinterland of the Velebit channel coastal karst springs* – in Croatian, with an English Abstract].– PhD Thesis, Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, 259 p.

STROJ, A. & VELIĆ, I. (2015). Geološki profil Jamskog sustava Lukina Jama–Trojama na Sjevernom Velebitu [*Geologic cross-section along the Lukina jama –Trojama Cave system* – in Croatian].– Presentation at: 5th Croatian Geological Congress with international participation, Sep 23–25, 2015; Osijek, Croatia.

STROJ, A. & PAAR, D. (2019): Water and air dynamics within a deep vadose zone of a karst massif: Observations from the Lukina jama–Trojama cave system (−1,431 m) in Dinaric karst (Croatia).– Hydrol. Process., 33/4, 551–561. doi: 10.1002/hyp.13342

TRČEK, B. & ZOJER, H. (2009): Recharge of springs. In: KRESIĆ, N., STEVANOVIĆ, Z. (eds.): Groundwater hydrology of springs.– Elsevier, Amsterdam, 87–127.

VELIĆ, I., BAHUN, S., SOKAČ, B. & GALOVIĆ, I. (1974): Osnovna geološka karta SFRJ 1: 100 000, List Otočac L 33-115. [*Basic Geologic Map of SFRY 1:100000, Geology of Otočac sheet* – in Croatian].− Geološki zavod, Zagreb, Savezni geološki zavod, Beograd, 44 p.

VELIĆ, I. & VELIĆ, J. (2009): Od morskih plićaka do planine. Geološki vodič kroz Nacionalni park Sjeverni Velebit [*From Marine Shallows to the Mountain: Geological Guidebook through the Northern Velebit National Park* – In Croatian].– NP Sjeverni Velebit, Krasno (Croatia).

WILLIAMS, P.W. (1983): The role of the subcutaneous zone in karst hydrology.– J. Hydrol., 61/1–3, 45–67. doi: 10.1016/0022-1694(83)90234-2