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An estimation of groundwater type and origin of the complex karst catchment using hydrological and hydrogeochemical parameters: A case study of the Gacka river springs

Jasmina Lukač Reberski[1], Sanja Kapelj[2] and Josip Terzić[1]

[1] Department of Hydrogeology and Engineering Geology, Croatian Geological Survey, Sachsova 2, 10000 Zagreb, Hrvatska; (jlukac@hgi-cgs.hr)

[2] Geotechnical Faculty, Hallerova aleja 7, 42000 Varaždin, Hrvatska

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ABSTRACT

Karst aquifers are heterogeneous terrains, where it is hard to assess any hydraulic parameter. Therefore, a multidisciplinary approach is necessary for research on karst aquifers. The catchment area of the Gacka river springs is typical Dinaric karst terrain formed of karstified carbonates. Groundwater flow is mostly directed by preferential flow paths usually connected with main faults and fracture zones. In the presented case study, structural, geological, and tectonic characteristics were defined. A recession diagram was created, and the water balance was calculated. Tracer-test data were also used for analysis. All data were compared with the bulk hydrogeochemical and isotopic analyses of spring and surface waters. For this purpose, samples were obtained every month for one hydrological year at 17 sampling locations. Processing of all these data allowed a tenable definition of the Gacka spring catchment area.

Keywords: hydrogeology, karst, hydrogeochemistry, isotopic research, river Gacka, Croatia

1. INTRODUCTION

Many difficulties encountered during investigation of the karst area demand a multidisciplinary approach for its characterization. The significant heterogeneous characteristics of the karst aquifers, in addition to ignorance about the real geometry of the underground cavities, necessitate the application of different hydrogeological methods so that indirect conclusions can be made. Hydrogeochemical investigations play an important role in this approach, which enables the inspection, verification, and supplementation of results from all other investigations. Analyses of hydrological and hydrogeochemical data were carried out in order to characterize the Gacka river springs catchment area and groundwater origin. These data were compared with earlier tracer tests that were conducted in this catchment. Joint dissolution secondary porosity prevails in karst areas, which results from a combination of tectonic activity and carbonate dissolution. The size of cavities ranges from smaller fissures and joints, in which the flow is similar to the flow in rocks with intergranular porosity, up to broad conduits and speleological objects, in which rapid and turbulent flow is present.

The area under consideration belongs to the Croatian Dinaric karst. It is situated in the Lika region, which represents the hilly karst, with karst poljes (Fig. 1 – detail). The Croatian karst region is part of the Adriatic carbonate platform – of palaeogeographic structure, which existed from

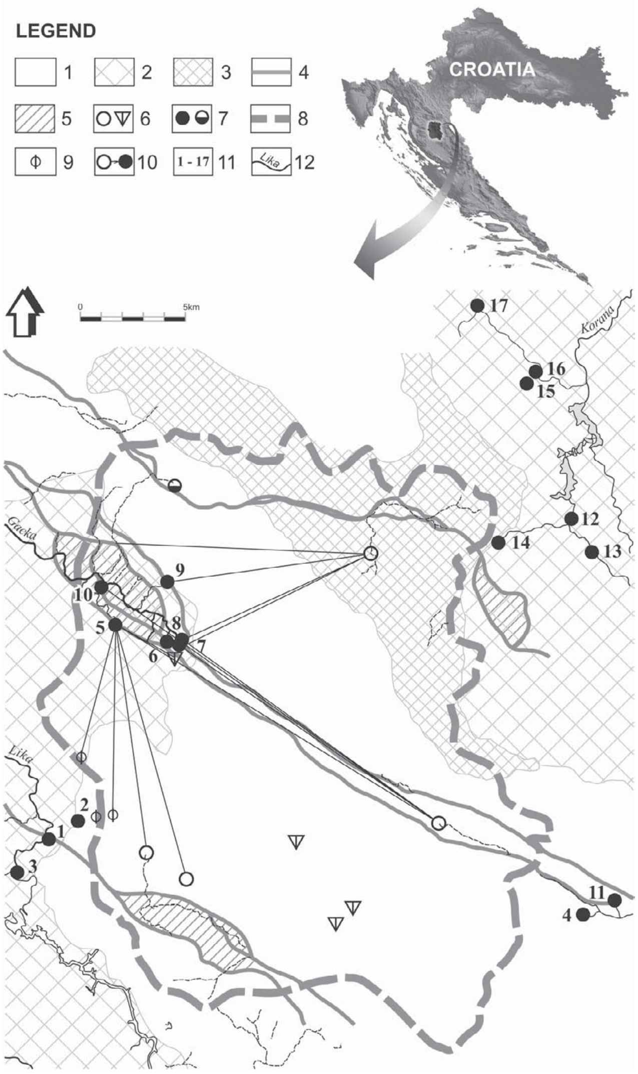

Figure 1: Schematic hydrogeological map of the study area, with the sampling sites (position of the study area in the detail). 1 – very permeable rocks, 2 – predominantly permeable rocks, 3 – predominantly impermeable rocks, 4 – most important faults, 5 – extension zone, 6 – swallow hole (ponor) and vertical cave (pit), 7 – spring: permanent and intermittent, 8 – groundwater divide, 9 – borehole, 10 – groundwater connection (tracer test), 11 – sampling point, 12 – river.

the Lower Jurassic until the end of the Cretaceous, representing a substantial part of the karst Dinarides (VELIĆ, 2007; VLAHOVIĆ et al., 2005). The karst relief includes approximately 46% of the Croatian state territory. The systematic research of karst has a long history of more than two hundred years. This region, with its numerous well-developed and diverse karst forms; both on the surface and underground, is unique in the world, a 'locus typicus'. Furthermore, geological scientists from all over the world, when referring to the Dinaric karst, call it the 'classical karst'. Terms such as ponor, dolina, polje, and jama, which relate to karst phenomena in this region, are used in the international geological vocabulary, confirming this unique status. (GOTTSTEIN MATOČEC et al., 2002).

Similar investigations in the Lika and neighbouring regions were carried out by many authors (BONACCI, 2001; HORVATINČIĆ et al., 1986). Studies were also conducted in other types of karst areas all over the world (SIMSEK et al., 2008; AZZAZ et al., 2008). The investigations and results presented here are parts of an extensive hydrogeological study used for writing a master's thesis (LUKAČ REBERSKI, 2008). Newly published hydrological researches suggest an underground connection between the river Lika (Fig. 1), streams and some of the Gacka river springs (BONACCI & ANDRIĆ, 2008). These theories are possible, but were not researched within the presented program, but will be considered in future research.

2. GEOLOGICAL, HYDROGEOLOGICAL, AND STRUCTURAL-TECTONIC CHARACTERISTICS

The investigated area is composed mostly of carbonate rocks, belonging to the Jurassic and Cretaceous Ages, and clastites of the younger Paleogene (the so-called Jelar deposits), which exist around Gacko polje. Jelar deposits indicate very dynamic conditions at the time of their formation, and they are represented as lime breccias with unsorted fragments of Jurassic, Cretaceous, and Palaeogene sediments. Lithostratigraphic members enable the separation of rocks according to hydrogeological characteristics (Fig. 1). The rocks are divided according to permeability as follows:

- **Very permeable** carbonate rocks are the most common types, in which limestones prevail;
- **Predominantly permeable** rocks are represented by Jurassic and Cretaceous carbonates and Palaeogene clastites, i.e. Jelar deposits. Jelar deposits show about 50% less permeability than the carbonates of the Jurassic and Cretaceous, which surround them (BAHUN & FRITZ, 1975);
- **Predominantly impermeable** rocks-comprising dolomites of Jurassic and Cretaceous periods;
- **Impermeable deposits** – found in a very small area in the eastern part of the investigation area;
- Quaternary deposits are sorted out as a separate group with **alternate properties,** because their permeability varies depending on the thickness and composition. They are mostly represented in the depressions of karst poljes.

By studying the neotectonic activity of the Dinarides, PRELOGOVIĆ (1989) indicated the neotectonic phases and classified the active structures and faults. He separated the seismically active zones and described the tectonic movements in these areas. The recent dynamics of these areas causes the formation of new structures of the pull-apart type, which morphologically correspond to karst poljes and great sink-holes.

Lithological, morphological, and hydrogeological properties of rocks, the spatial and hypsometric position, and tectonics, influence the hydrogeological function of the area. Using this approach, the complete barriers, incomplete barriers, and permeable areas can be distinguished.

To determine the size of the catchment areas, the apparent velocities, and groundwater-flow directions, several tracings were carried out using the artificial tracer Na-fluorescein. Because of the relatively monotonous lithology, the groundwater-flow directions depend more on the structural relationships than on the lithological characteristics. The area

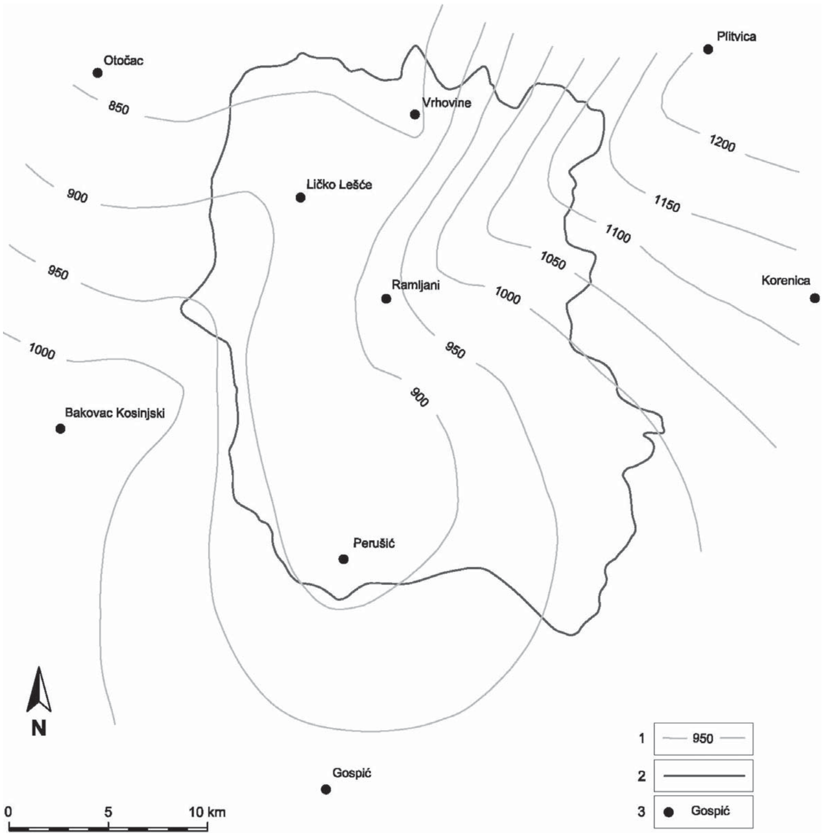

Figure 2: Arrangement of isohyets in the catchment area of the spring zone of the Gacka River. 1 – isohyet; 2 – groundwater divide; 3 – rain gauge station.

under study is characterized by the dinaric strike of the structures (NW–SE). The tracings showed that the groundwater-flow direction in the greater part of the catchment area is parallel to the structures. This is due to the position of the main boundary faults, favourable to the stress direction (20°–45°) and along which the right transcurrent shifts appear, as apart from the opening up of spaces and appearance of structures of a pull-apart type (PRELOGOVIĆ, 1989). These fault sections play the most important roles in creation of the hydrogeological conditions in this area. In contrast, an unfavorable direction of the fault to stress direction leads to local compression by closing of the space and possible prevention of water flow.

3. HYDROLOGICAL CHARACTERISTICS

The river Gacka is characterized by favourable hydrological conditions. The flow regime is standardized in comparison to other karst rivers, and considerable alterations of the flow quantities through its river bed do not occur. The ratio of the lowest, medium, and highest discharge is 1:4:20, whereas the ratio of the neighboring Lika river is 1:100:800 (BONACCI, 1987), which shows its vividly torrential character.

The quantity of rainfall is one of the most important climatic factors with direct influence on the formation of underground and surface waters. Although the entire Lika region is characterized by a high quantity of rainfall, distinctive spatial differentiation in rainfall occurs. The areas with high relief (mountains) are characterized by greater rainfall than the lower areas (karst poljes). In the catchment areas of the spring zone of the river Gacka and in its direct neighborhood, there are nine rain-gauge stations for measuring rainfall.

On the basis of the collected hydrological data, the balance calculation was completed using the method based on quantity of runoff. The balance has been calculated both for the hydrological year 2002/2003 and for a period of thirty years. One hydrological year in the observed climate extends from the beginning of October to the end of September the next year. According to previous research, the surface of the Gacka springs catchment area is 487 km^2; 94% is underground runoff, and 6% is surface runoff. Due to the significant heterogeneity and unpredictability of karst systems, and a need for difficult and expensive research, together with the variations in size of the catchment depending on hydrological conditions, the defined catchment area can vary in size to a certain degree. In order to determine the average rainfall in the catchment area, a method based on isohyets was used. The isohyets were obtained by the interpolation of values of rainfall quantities in the observed hydrological year, reported by the 9 rain-gauge stations located in the catchment area and its neighbourhood (Fig. 2). The quantity of annual rainfall for the hydrogeological year 2002/03 calculated according to this method was 924 mm. For the balance calculation, the value of the total catchment runoff was used, which was obtained by measurement of the daily discharge by the water-gauge station located about 8 km downstream from the spring zone. The supposition is that, along this flow, there are neither considerable inflows nor runoffs. According to these data, the annual discharge for the observed hydrological year was 14.15 m³/s. The runoff coefficient is calculated according to the formula:

$$\alpha = \frac{Q_{AVG}}{H} \qquad (1)$$

where α is the runoff coefficient, Q_{AVG} is the runoff volume in m³, H is the rainfall volume in m³ over the catchment area in the observed hydrological year.

The runoff coefficient, calculated according to the runoff quantity, is unnaturally high superficially. Its value calculated according to this method is 0.99; thus, it implies that 99% of the total annual rainfall infiltrates underground and that evapotranspiration almost does not exist. The runoff coefficient for the period of thirty years, calculated by the same method is 0.72, i.e. 72% of precipitation infiltrates into the karst underground, from which it is apparent that the balance calculation for only one year does not produce relevant data. The main reason for such variation is masked by numerous influences, such as karstification, cavity size, epikarst zone properties, air temperature, snow cover, terrain slope, and intraannual rainfall distribution. The quantities of rainfall have the greatest influence on the runoff quantities, and their annual collection is decisive if the rainfall quantities are considerably lower than the possible annual evapotranspiration. In this manner, from the example of the water-regime study of the karst spring situated in Hungary, it was shown that for the same quantity of annual rainfall, underground infiltration ranges from 7% to 70% (STEPINAC, 1969).

Because of the significant heterogeneous characteristics of the karst aquifers, the quantitative data obtained either by pumping or by tracing refer to a narrow local area around the investigation site, and obtained values can rarely be average values that refer to the entire system (TERZIĆ et al., 2007, 2008). In contrast, the runoff hydrograms of springs refer to the total response of aquifers to rainfall (PADILLA et al., 1994).

The recession diagram of Gacka was prepared on the basis of the hydrogram of the discharge of the river Gacka for the period from 01.02.2002. to 31.12.2003. From the runoff hydrogram, two recession periods can be identified. The first recession period extends from 15.04.2002. to 22.09.2002, and the second from 12.04.2003. to 20.10.2003. The drainage characteristics of the aquifer are better expressed in the second recession period, and this portion of the hydrogram is considered for the calculation of the recession coefficient (Fig. 3) and runoff quantities from the water-bearing system. During the recession period, weaker rainfall was recorded. The hydrogeological year 2002/03 represented a dry year with reference to the previous ones, and hence it was suitable for observing the drainage characteristics of the water-bearing system.

The springs are recharged by resources from the aquifer during the recession, which are accumulated in the hydrogeological basin during the recharging period. The shape of the curve depends on the hydrodynamic properties of the aquifers, such as hydraulic conductivity (K), storage coefficient (S), and hydraulic gradient (I), in addition to the geomorphological characteristics of the catchment area, such as geometry, slope, length, and karst-channel distribution. The following factors also have an important role: (a) season and climate, (b) the nature, thickness, spatial arrangement, and level of soil saturation. Maillet's formula (DEWANDELA et al., 2003) is used for defining the recession component of the discharge hydrogram:

$$Q_t = Q_0 \text{ x } e^{-at} \qquad (2)$$

– where Q_t denotes the runoff quantity at a particular moment "t", Q_0 is the runoff quantity at the beginning of recession, α is the recession coefficient, and "t" is the time.

Maillet's exponential equation only approximately represents the analytical solution. There are other solutions that are used for defining the recession curve; these represent the exact analytical solutions from which it is possible to obtain the quantitative data of parameters of the water-bearing sys-

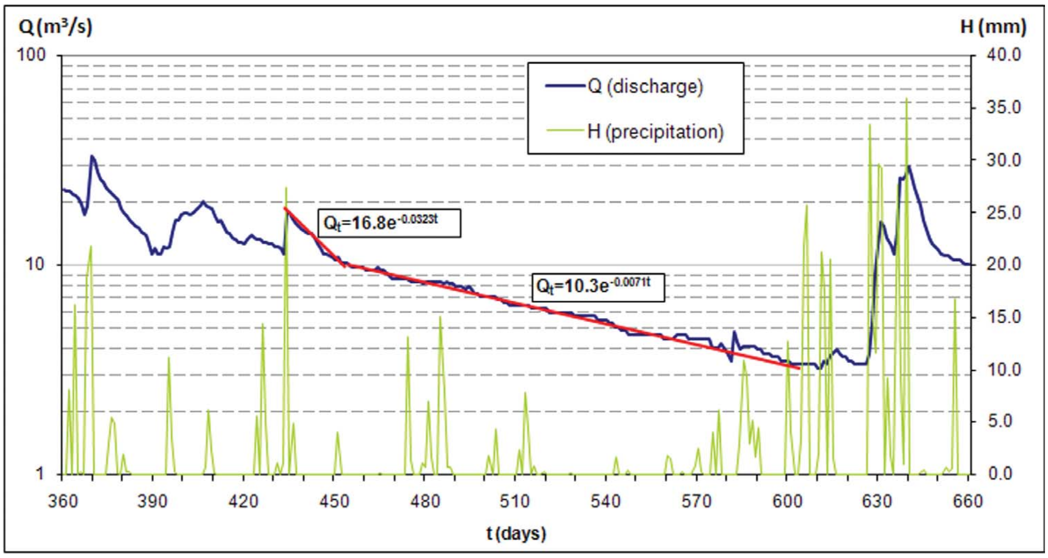

Figure 3: Comparative presentation of the Gacka River discharge, (semi-logarithmic scale) and the daily quantities of rainfall (Lukač Reberski, 2008). The period shown is from 27.01.2003. to 23.11.2003.

tem. Analyzing the particular segments of the curve between the 436th and 611th day, it is obvious that 18 days after the aquifer starts to empty changes in the conditions influencing runoff appear. This occurrence is apparent from the change of the slope direction by which the runoff curve is approximated after being transformed into the semilogarithmic scale, that is, from the change of the recession coefficient. In the beginning, the channels and larger joints are emptied, after which the smaller joints follow, which is shown in the milder slope of the curve. At the beginning of the recession, the slope of the curve is steep, with a calculated recession coefficient of $\alpha = 0.0323$ day^{-1}. Then, a significant curve slope change occurs with a recession coefficient of $\alpha = 0.0071$ day^{-1}, which indicates an aquifer of heterogeneous permeability, typical for karst aquifers. It was calculated that during the observed recession period that lasted 175 days, 99 x 10^6 cubic meters of water were discharged.

4. SAMPLING, ANALYSIS METHODS, AND DATA PROCESSING

Water samples were collected from 17 sites every month for one hydrogeological year, from September 2002 to September 2003 (Table 1). The sampling locations comprised the upper flow region of the river Gacka and its spring zone and boundary-catchment areas. Toward the south of the river Gacka, the catchment area of the river Lika; to the northwest, the catchment area of the river Korana; and to the south-east, the catchment area of the river Una were also considered in this study. In the catchment area of the river Gacka, the locations were springs Tonkovića vrelo (7), Majerovo vrelo (9), Knjapovac (6), Klanac (8), Jaz (10), and Pećina (5). In the catchment area of the river Lika are the Dežmino vrelo (1) and Mlakvena greda (2) springs, and the Krušćica accumulation (3). In the catchment area of the river Korana, there are the springs of the Crna (13) and Bijela (14) rivers and the Plitvica (15) and Sartuk springs (17). The Begovica (4) and Pećina-Korenica (11) springs are located in the catchment area of the river Una. Matica (12) belongs to the surface flow on a site where the Bijela and Crna streams join, and Rodić (16) is on the confluence of the Plitvice and Sartuk streams. Some of these springs are temporary ones drying up in the summer months, when it is not possible to obtain samples. These are Mlakvena greda, Dežmino vrelo, and Pećina-Korenica (Fig. 1).

The values of water temperature, pH, electrolytic conductivity (EC value), and total dissolved solids (TDS) were measured in situ. The analyses for determining the basic chemical parameters, such as alkalinity, calcium hardness, total hardness, nitrates, sulfates, and phosphates, were carried out in the laboratory. The processes of preparation and measurements of samples were the usual methods in hydrochemistry, and the chemicals used for sample preparations and standard solution were products of the HACK company. EC and TDS were measured by the WTW conductivity meter, model LF340/SET, calibrated with a standard solution of 0.01 mol/l KCl. It is very important to determine the concentration of hydrogen ions because it is the most important parameter during calculation of the saturation (APPELO & POSTMA, 1994). Moreover, it is best to measure the pH immediately in situ because, during the sampling for laboratory analyses, it is impossible to avoid the loss of carbon dioxide (CO_2) from water (gas removal), which leads to an increase in pH and sedimentation of $CaCO_3$. Thus, the results of the chemical analyses in the laboratory become erroneous. In addition, during sampling, the oxidation of some ions occurs, which can cause sedimentation of the mineral under study. The concentration of hydrogen ions and the temperature were measured by a 43800-00 model pH meter (HACH). The instrument was calibrated in situ by applying standard buffer solutions of pH 7, 8, and 9. The instrument had a temperature compensator to avoid errors in pH measurements caused by the huge temperature difference between the spring and surface waters. Alkalinity of the water samples was measured by titration with H_2SO_4 using bromocresol green-methyl red indicator. Calcium and magnesium levels were determined by complexometric titration with EDTA, according to standardized procedures. The concentrations of sulfides, nitrates, and phosphates were measured colorimetrically using a spectrophotometer (DR/2010, HACH). All the afore-mentioned parameters were determined by the standard additive method, according to the procedures described in the instructions. The only variation was that the isotopic analyses of the stable isotopes $\delta^{18}O$ and $\delta^{2}H$ were carried out on 24 samples (Table 2). The isotopic analyses were conducted in the "Enviromental Isotope Laboratory", Institute of Water Resources Management, Graz, Austria. For the year under study, the hydrological data were collected from the State Hydrometeorological Institute in order to correlate the hydrogeological and hydrogeochemical parameters. The computer program NETPATH (US Geological Survey, PLUMMER et al., 1994), was used to model the geochemical reactions along a flow, and determine the balance of ions and the saturation state. It is evident from these calculations that particular minerals dissolve or are deposited under the conditions that dominate in the water medium. In this context, the saturation indices were calculated in relation to the minerals calcite (SI_C), aragonite (Si_A), and dolomite (Si_D); the partial pressure of CO_2 (pCO_2), and TDS, and the concentrations of the main ions were calculated from the concentration unit mg/l by conversion into mol/l.

Multivariate cluster analysis was used to determine the extent to which the measured indicators of the hydrochemical system of the spring waters have similar affinities, i.e. similar behaviour and origin. The cluster method aided interpretation of the geochemical data and served to strengthen the bonds between the samples (DAVIS, 1986). Its application has already shown its usefulness in the investigation of the morphometric and structural characteristics of water and soils in Croatia (GRGIĆ, 1990; KAPELJ et al., 1999; PEH & MIKO, 2003; MARKOVIĆ et al., 2006). The basic principle of cluster analysis is the hierarchical arrangement of samples according to their similarity, i.e. the similarity of their attributes, into groups or clusters. Most often they are the correlation coefficients. Each hierarchical level within the dendrogram is a consequence of the degree of homogeneity within one group (cluster) and, therefore, the sample

Table 1: Results of measurements of hydrogeochemical indicators in spring and groundwater.

LOCATION (number) – month – year	T (°C)	EC (µS/cm)	pH	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^{+} (mg/l)	K^{+} (mg/l)	HCO^{3-} (mg/l)	Cl^{-} (mg/l)	SO_4^{2-} (mg/l)	NO_3N (mg/l)	PO_4^{3-} (mg/l)
MLAKVENA G. (2) -09-02	12.6	370	7.46	92	2.2	2.40	0.58	283	1.7	1	0.1	0.16
KRUŠĆICA (3) -09-02	20.2	260	8.22	50	5.4	1.80	0.44	173	1.1	0.1	0.1	0.06
PEĆINA (5) -09-02	9.6	328	7.72	87	3.9	1.90	0.12	269	1.1	2	1.0	0.06
KNJAPOVAC (6) -09-02	10.1	340	7.45	90	5	3.55	0.71	275	4.2	15	0.4	0.15
TONKOVIĆA V. (7) -09-02	9.9	338	7.4	89	5.9	3.72	0.88	271	3.2	15	0.3	0.12
KLANAC (8) -09-02	9.9	338	7.27	88	1.2	3.11	0.81	260	2.8	13	0.4	0.23
MAJEROVO V. (9) -09-02	9.1	313	7.52	64	18	1.92	0.51	260	1.2	5	0.7	0.13
JAZ (10) -09-02	10.1	340	7.41	89	5.4	3.44	0.67	277	4.0	15	0.3	0.11
DEŽMINO V. (1) -10-02	9.7	358	6.91	100	3.2	2.21	0.49	323	1.8	1	0.2	0.14
MLAKVENA G. (2) -10-02	8.7	342	7.18	88	7.8	2.55	0.56	317	1.9	1	0.2	0.25
KRUŠĆICA (3) -10-02	13.9	216	6.5	38	13	1.20	0.35	183	1.5	1	0.3	0.28
BEGOVICA (4) -10-02	9.3	333	6.97	70	16	1.28	0.51	295	0.3	1	0.5	0.33
PEĆINA (5) -10-02	9.2	347	7.32	53	30	1.97	0.68	320	1.3	1	0.5	0.1
KNJAPOVAC (6) -10-02	9.9	354	7.37	45	36	2.58	0.71	314	1.3	9	0.5	0.19
TONKOVIĆA V. (7) -10-02	9.8	352	7.3	54	32	2.35	0.70	316	1.2	8	0.5	0.17
KLANAC (8) -10-02	9.4	339	7.39	47	34	2.41	0.83	308	1.5	5	0.6	0.17
MAJEROVO V. (9) -10-02	8.9	317	7.44	67	20	1.68	0.43	291	1.2	1	0.6	0.19
JAZ (10) -10-02	9.9	357	7.21	63	26	2.34	0.61	314	1.9	9	0.5	0.16
PEĆ.-KOR. (11) -10-02	9.4	327	6.91	52	26	1.30	0.21	287	1.0	1	0.4	0.18
DEŽMINO V. (1) -11-02	9.3	363	7.32	78	1.2	1.50	0.38	253	1.1	0.1	0	0.01
MLAKVENA G. (2) -11-02	9.7	379	7.19	52	7.5	1.55	0.91	231	0.8	1	0.1	0.03
KRUŠĆICA (3) -11-02	10.8	231	7.57	36	17	1.99	0.75	193	1.1	1	0.2	0.02
BEGOVICA (4) -11-02	9.1	327	6.77	51	9	1.02	0.33	205	0.5	0.1	0.3	0.12
PEĆINA (5) -11-02	9.1	334	7.35	78	2	2.00	0.95	269	1.2	1	0.3	0.03
KNJAPOVAC (6) -11-02	9.8	374	7.25	57	18	1.85	0.90	270	1.0	1	0.4	0.07
TONKOVIĆA V. (7) -11-02	9.6	372	7.17	66	8.8	2.11	0.77	250	1.4	1	0.5	0.01
KLANAC (8) -11-02	9.2	334	7.24	71	1.5	2.07	0.81	240	1.2	1	0.3	0.01
MAJEROVO V. (9) -11-02	8.7	323	7.27	77	1.9	3.20	0.97	256	1.6	1	0.5	0.03
JAZ (10) -11-02	9.8	374	7.21	78	3.6	1.69	0.63	285	1.4	1	0.4	0.05
PEĆ.-KOR. (11) -11-02	8.9	331	6.95	57	3.1	2.05	0.58	194	1.1	1	0.3	0.08
MATICA (12) -11-02	7.8	298	7.39	54	19	1.50	0.44	265	0.7	0.1	0.7	0.05
CRNA (13) -11-02	7.6	277	7.59	66	7.1	1.61	0.32	238	0.4	0.1	0.5	0.02
BIJELA (14) -11-02	7.5	310	7.26	92	4.6	1.33	0.55	287	0.6	1	0.7	0.01
PLITVICA (15) -11-02	7.4	302	7.79	58	14	2.14	0.49	248	1.1	1	0.9	0.02
RODIĆ (16) -11-02	7.4	303	7.6	63	11	2.25	0.72	251	1.1	1	0.8	0.01
SARTUK (17) -11-02	8.2	312	7.35	73	7.1	2.35	0.67	261	1.1	1	0.9	0.05
DEŽMINO V. (1) -12-02	9.2	353	7.3	95	0.2	1.57	0.42	291	0.9	1	0	0.01
MLAKVENA G. (2) -12-02	9.4	374	7.15	106	1.5	1.15	0.48	341	0.5	0.1	0	0.06
KRUŠĆICA (3) -12-02	7.5	230	7.33	61	3.7	1.02	0.51	209	0.4	1	0.2	0.01
BEGOVICA (4) -12-02	9.1	329	6.87	96	6.8	2.09	1.00	314	1.1	1	0.3	0.19
PEĆINA (5) -12-02	8.5	337	7.22	104	5.1	3.90	0.87	328	1.6	1	0.4	0.02
KNJAPOVAC (6) -12-02	9.5	364	7.27	104	5.4	4.10	0.88	331	2.0	1	0.3	0.04
TONKOVIĆA V. (7) -12-02	9.5	363	7.27	106	3.7	2.31	0.76	327	1.1	1	0.3	0.12
KLANAC (8) -12-02	9	334	7.4	98	5.1	2.22	0.80	311	1.1	1	0.4	0.02
MAJEROVO V. (9) -12-02	8.7	321	7.27	89	6.8	2.90	0.85	292	1.5	0.1	0.6	0.04
JAZ (10) -12-02	9.6	366	7.31	104	5.1	2.11	0.64	332	1.2	1	0.3	0.04

Table 1: continued

LOCATION (number) – month – year	T (°C)	EC (µS/cm)	pH	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^{+} (mg/l)	K^{+} (mg/l)	HCO^{3-} (mg/l)	Cl^{-} (mg/l)	SO_4^{2-} (mg/l)	$NO_3^{-}N$ (mg/l)	PO_4^{3-} (mg/l)
PEĆ.-KOR. (11) -12-02	7.7	305	6.75	84	7.3	2.44	0.68	292	1.4	1	0.3	0.03
DEŽMINO V. (1) -01-03	9.4	343	7.35	99	4.6	1.20	0.34	315	0.8	0.1	0	<0.01
MLAKVENA G. (2) -01-03	7.1	317	7.72	99	0	1.35	0.40	294	1.2	0.1	0	<0.01
KRUŠĆICA (3) -01-03	2.2	186	7.64	60	5.4	1.10	0.57	204	0.9	1	0	0.01
BEGOVICA (4) -01-03	9	326	7.08	91	0.5	1.40	0.52	269	0.7	0.1	0	0.14
PEĆINA (5) -01-03	8.1	324	7.3	99	1	1.77	0.68	295	0.9	0.1	0	<0.01
KNJAPOVAC (6) -01-03	9.4	361	7.19	82	5.1	2.92	1.20	267	1.5	1	0	<0.01
TONKOVIĆA V. (7) -01-03	9.5	360	7.26	100	6.1	4.11	1.40	314	2.0	8	0	<0.01
KLANAC (8) -01-03	9.1	335	7.24	100	0.2	3.89	1.25	293	1.8	1	0	<0.01
MAJEROVO V. (9) -01-03	8.6	311	7.76	104	2.9	4.03	0.98	311	2.0	7	0	<0.01
JAZ (10) -01-03	9.4	362	7.26	98	0.5	2.51	0.52	301	1.2	8	0	<0.01
TITPEC-01-03	7.1	297	7.13	83	0.2	2.29	0.61	261	1.4	0.1	0	<0.01
DEŽMINO V. (1) -02-03	10.4	325	7.57	90	5.1	1.22	0.38	307	0.7	3	0.1	0.01
MLAKVENA G. (2) -02-03	4.3	284	7.66	106	0.2	1.25	0.40	311	0.5	1	0.1	0.01
KRUŠĆICA (3) -02-03	0.9	157	8.07	53	2.7	1.13	0.25	168	0.6	2	0.1	0.02
BEGOVICA (4) -02-03	8.9	261	7.41	93	0.2	1.08	0.26	272	0.4	1	0	0.13
PEĆINA (5) -02-03	8	323	7.52	95	1.9	1.28	0.51	296	1.1	1	0	0.02
KNJAPOVAC (6) -02-03	9.4	360	7.3	104	2.2	1.97	0.68	316	1.1	1	0	0.04
TONKOVIĆA V. (7) -02-03	9.5	358	7.33	102	2.7	2.58	0.71	311	4.2	1	0	0.04
KLANAC (8) -02-03	9.1	338	7.32	96	3.4	2.35	0.70	297	3.2	1	0	0.04
MAJEROVO V. (9) -02-03	8.7	313	7.33	83	7.3	2.41	0.83	279	2.8	1	0	0.04
JAZ (10) -02-03	9.6	362	7.54	104	2.9	1.68	0.43	317	1.2	1	0.1	0.05
PEĆ.-KOR. (11) -02-03	5.2	280	7.77	85	5.6	2.34	0.61	276	4.0	0.1	0.1	0.04
MATICA (12) -02-03	6.5	284	8.36	57	26.6	1.30	0.21	297	1.8	1	0	0.05
CRNA (13) -02-03	7.8	276	7.66	67	11.5	1.50	0.38	249	1.9	0.1	0	0.06
BIJELA (14) -02-03	7.5	311	7.92	61	20	1.20	0.34	275	1.5	1	0	0.05
PLITVICA (15) -02-03	7.2	295	7.01	59	22.4	1.35	0.40	281	1.1	1	0	0.07
RODIĆ (16) -02-03	5.7	282	7.83	61	21.5	1.10	0.57	280	1.1	1	0	0.04
SARTUK (17) -02-03	3.3	265	7.49	58	25.4	1.40	0.52	291	1.5	0.1	0.1	0.03
DEŽMINO V. (1) -03-03	10.1	335	7.3	93	3.4	1.77	0.68	287	1.2	3	0.2	0.01
MLAKVENA G. (2) -03-03	8	312	7.33	98	1.7	1.28	0.51	296	1.4	1	0.1	<0.01
KRUŠĆICA (3) -03-03	5	196	7.89	59	3.4	1.97	0.68	187	0.8	1	0.3	<0.01
BEGOVICA (4) -03-03	6.7	286	7.21	89	1.2	2.58	0.71	266	1.2	0.1	0.4	0.15
PEĆINA (5) -03-03	8.7	329	7.48	97	2	2.35	0.70	293	0.9	0.1	0.5	0.03
KNJAPOVAC (6) -03-03	9.5	358	7.28	101	3.9	3.56	1.10	303	1.6	10	0.4	0.01
TONKOVIĆA V. (7) -03-03	9.5	356	7.3	98	4.6	2.11	0.75	302	1.1	9	0.4	0.01
KLANAC (8) -03-03	9.1	331	7.48	95	3.4	1.69	0.63	295	1.5	0.1	0.4	0.02
MAJEROVO V. (9) -03-03	8.6	309	7.25	84	4.9	2.05	0.58	268	2.0	0.1	0.6	0.01
JAZ (10) -03-03	9.5	359	7.41	104	0	1.50	0.44	301	1.8	11	0.3	0.03
PEĆ.-KOR. (11) -03-03	8.9	313	7.53	89	1.22	1.61	0.32	266	2.0	1	0.4	0.01
MATICA (12) -03-03	7.9	289	8.26	64	18.1	1.33	0.55	275	1.2	0.1	0.8	0.03
CRNA (13) -03-03	7.7	279	7.77	67	11	2.14	0.49	248	4.0	0.1	0.6	0.06
BIJELA (14) -03-03	7.5	313	7.58	60	24.4	2.25	0.72	289	1.8	0.1	1.1.	0.05
PLITVICA (15) -03-03	7.2	284	7.65	62	19.5	2.35	0.67	269	1.9	1	1.3.	0.04
RODIĆ (16) -03-03	7.6	287	7.24	61	20	1.57	0.42	271	1.5	1	1.3.	0.04
SARTUK (17) -03-03	6	287	7.81	55	26.3	1.15	0.48	282	1.1	1	1.1.	0.02

Table 1: continued

LOCATION (number) – month – year	T (°C)	EC (μS/cm)	pH	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^{+} (mg/l)	K^{+} (mg/l)	HCO^{3-} (mg/l)	Cl^{-} (mg/l)	SO_4^{2-} (mg/l)	NO_3N (mg/l)	PO_4^{3-} (mg/l)
DEŽMINO V. (1) -04-03	10.8	337	7.52	88	6.1	1.02	0.51	277	1.1	9	0.3	0.01
MLAKVENA G. (2) -04-03	10.3	363	7.31	93	0	2.09	1.00	270	1.5	1	0.2	0.01
KRUŠĆICA (3) -04-03	12.3	234	7.36	55	5.6	1.35	0.40	187	1.2	0.1	0.3	0.01
BEGOVICA (4) -04-03	9.1	322	7.27	93	0	1.10	0.57	272	1.4	0.1	0.4	0.14
PEĆINA (5) -04-03	9.1	336	6.63	98	0	1.40	0.52	285	0.8	0.1	0.6	0.01
KNJAPOVAC (6) -04-03	9.6	353	7.26	98	0	1.77	0.68	286	1.2	1	0.4	<0.01
TONKOVIĆA V. (7) -04-03	9.5	349	7.35	101	1.5	1.28	0.51	293	0.9	7	0.4	0.01
KLANAC (8) -04-03	9.6	332	7.63	94	2.7	1.97	0.68	287	0.7	0.1	0.4	0.01
MAJEROVO V. (9) -04-03	8.7	306	7.22	84	6.6	2.58	0.71	275	0.9	0.1	0.6	0.02
JAZ (10) -04-03	9.7	353	7.34	98	2.9	2.35	0.70	304	1.5	1	0.4	0.02
PEĆ.-KOR. (11) -04-03	9.6	310	7.43	87	3.9	2.41	0.83	278	2.0	1	0.3	0.02
MATICA (12) -04-03	9	300	8.19	62	17.8	1.68	0.43	270	1.8	0.1	0.8	0.02
CRNA (13) -04-03	7.7	276	7.83	68	10.2	2.34	0.61	247	2.0	0.1	0.6	0.02
BIJELA (14) -04-03	7.6	314	7.65	61	24.2	1.30	0.21	291	1.9	1	1.0	<0.01
PLITVICA (15) -04-03	7.6	286	7.86	60	19	1.28	0.51	263	1.0	0.1	1.4	0.01
RODIĆ (16) -04-03	8	291	7.08	63	18.9	1.97	0.68	271	1.1	1	1.3	0.02
SARTUK (17) -04-03	9.4	318	8.24	50	29	2.58	0.71	282	0.8	1	1.0	0.02
DEŽMINO V. (1) -05-03	11	335	7.77	87	7.32	2.35	0.70	279	1.1	13	0.3	0.04
MLAKVENA G. (2) -05-03	13.3	377	7.23	92	3.4	2.41	0.83	281	0.5	4	0.1	0.02
KRUŠĆICA (3) -05-03	20	272	8.07	50	6.8	1.68	0.43	181	1.2	1	0	0.12
BEGOVICA (4) -05-03	9.6	328	7.41	94	0.7	1.69	0.63	277	1.0	1	0.5	0.10
PEĆINA (5) -05-03	9.3	328	7.42	92	3.2	2.05	0.58	280	1.4	1	0.9	0.01
KNJAPOVAC (6) -05-03	9.5	343	7.48	94	5.1	1.50	0.44	289	1.2	8	0.4	<0.01
TONKOVIĆA V. (7) -05-03	9.5	342	7.4	97	3.7	1.61	0.32	298	1.6	2	0.4	<0.01
KLANAC (8) -05-03	9.3	334	7.34	93	4.9	1.33	0.55	286	1.4	8	0.3	<0.01
MAJEROVO V. (9) -05-03	8.9	308	7.24	78	11.5	2.14	0.49	281	1.1	1	0.7	0.13
JAZ (10) -05-03	9.8	346	7.3	95	5.1	2.25	0.72	291	1.1	8	0.4	0.01
PEĆ.-KOR. (11) -05-03	10.7	312	7.71	79	9	2.35	0.67	273	1.5	1	0.3	<0.01
MATICA (12) -05-03	9.3	311	8.21	61	21	1.57	0.42	279	1.2	0.1	0.9	<0.01
CRNA (13) -05-03	7.9	281	7.54	65	14.6	1.15	0.48	259	1.4	0.1	0.7	<0.01
BIJELA (14) -05-03	7.5	310	7.47	60	27	1.69	0.63	301	0.8	1	1.2	0.14
PLITVICA (15) -05-03	7.3	301	7.99	63	21.2	2.05	0.58	282	1.2	1	1.3	<0.01
RODIĆ (16) -05-03	8.7	310	8.27	65	22	1.50	0.44	290	0.9	1	1.2	0.01
SARTUK (17) -05-03	9.9	321	8.49	65	21.7	1.61	0.32	290	0.7	1	1.1	<0.01
MLAKVENA G. (2) -06-03	20.1	422	7.53	98	1.5	1.33	0.55	293	0.9	1	0.1	0.05
KRUŠĆICA (3) -06-03	26.5	272	8.27	45	5.4	2.14	0.49	162	1.5	1	0.2	0.01
BEGOVICA (4) -06-03	9.9	327	7.27	92	2.9	2.25	0.72	281	2.0	1	0.6	0.11
PEĆINA (5) -06-03	9.7	318	7.46	85	3.4	2.35	0.67	261	1.8	1	0.8	0.05
KNJAPOVAC (6) -06-03	9.7	336	7.21	94	4.4	3.28	0.42	279	2.0	13	0.3	0.01
TONKOVIĆA V. (7) -06-03	9.8	335	7.25	94	4.4	1.15	0.48	278	1.9	14	0.5	0.01
KLANAC (8) -06-03	10.3	338	7.09	95	4.4	2.96	0.44	283	2.4	12	0.4	0.06
MAJEROVO V. (9) -06-03	9.1	308	7.19	78	12	1.61	0.32	282	1.1	1	0.8	0.01
JAZ (10) -06-03	9.9	338	7.46	96	4.9	3.59	0.81	286	1.9	14	0.5	0.01
MATICA (12) -06-03	10.6	322	8.16	55	31	2.14	0.49	309	1.1	1	0.7	0.01
CRNA (13) -06-03	7.9	279	7.57	62	17	2.25	0.72	261	0.5	1	0.5	0.01
BIJELA (14) -06-03	7.5	307	7.15	62	24	2.35	0.67	291	1.2	1	1.2	0.01

Table 1: continued

LOCATION (number) – month – year	T (°C)	EC (µS/cm)	pH	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^{+} (mg/l)	K^{+} (mg/l)	HCO^{3-} (mg/l)	Cl^{-} (mg/l)	SO_4^{2-} (mg/l)	NO_3N (mg/l)	PO_4^{3-} (mg/l)
PLITVICA (15) -06-03	7.4	297	7.31	63	21	1.57	0.42	283	1.0	1	1	0.01
RODIĆ (16) -06-03	10	315	7.71	59	22	2.58	0.71	275	1.4	1	1.2	0.01
SARTUK (17) -06-03	14.7	353	8.16	52	25	2.35	0.70	270	1.2	1	1	0.01
DEŽMINO V. (1) -07-03	11.3	366	8.11	90	6.8	4.21	0.83	276	2.1	16	0.4	0.01
KRUŠĆICA (3) -07-03	25.8	318	8.7	43	8.3	1.68	0.43	164	1.4	1	0.2	0.04
BEGOVICA (4) -07-03	10.7	316	7.38	92	4.8	1.69	0.63	285	1.1	2	0.7	0.21
PEĆINA (5) -07-03	9.4	315	8.11	87	6.3	2.05	0.58	279	1.1	1	1.2	0.02
KNJAPOVAC (6) -07-03	9.9	336	7.79	96	3.9	4.25	1.10	279	2.2	16	0.7	0.15
TONKOVIĆA V. (7) -07-03	9.8	335	7.57	97	6.3	1.61	0.32	293	1.2	15	0.6	0.01
KLANAC (8) -07-03	9.5	330	7.64	99	2.9	1.33	0.55	285	1.4	14	0.7	0.31
MAJEROVO V. (9) -07-03	9	307	7.81	79	11	1.61	0.32	279	0.8	3	1	0.13
JAZ (10) -07-03	10	339	7.76	98	4.9	2.32	0.79	290	2.0	16	0.6	0.03
MATICA (12) -07-03	11.8	329	8.91	55	28	2.14	0.49	293	0.9	2	0.9	0.06
CRNA (13) -07-03	7.9	280	8.28	63	22	2.25	0.72	283	0.7	3	0.9	0.06
BIJELA (14) -07-03	7.5	307	8.34	62	22	2.35	0.67	285	0.9	1	1.2	0.06
PLITVICA (15) -07-03	7.4	298	8.78	64	24	1.57	0.42	297	1.5	1	1.2	0.22
RODIĆ (16) -07-03	8.7	306	9.02	60	23	2.58	0.71	282	2.0	1	1.3	0.05
SARTUK (17) -07-03	13	342	9.14	51	25	2.35	0.70	264	1.8	2	1.2	0.01
KRUŠĆICA (3) -08-03	24.2	272	8.56	44	6.3	2.41	0.83	160	2.0	1	0.5	0.16
BEGOVICA (4) -08-03	10.9	340	7.97	92	4.4	1.68	0.43	289	1.9	1	0.3	0.28
PEĆINA (5) -08-03	10.3	315	8.41	87	11	1.69	0.63	307	1.0	1	0.5	0.07
KNJAPOVAC (6) -08-03	10.1	335	7.84	98	3.4	3.60	0.75	281	1.8	17	0.3	0.08
TONKOVIĆA V. (7) -08-03	9.8	330	7.7	94	4.4	4.20	0.33	273	2.3	18	0.3	0.01
KLANAC (8) -08-03	9.9	332	7.4	95	4.9	3.14	0.95	281	1.1	16	0.3	0.04
MAJEROVO V. (9) -08-03	9.7	311	7.63	76	15	1.85	0.90	291	0.5	2	0.5	0.01
JAZ (10) -08-03	10.1	337	8.06	96	4.9	3.11	0.82	281	2.1	18	0.4	0.06
MATICA (12) -08-03	9.6	310	9.17	62	22	2.07	0.81	285	1.0	2	0.7	0.02
CRNA (13) -08-03	7.9	280	8.74	67	14	1.99	0.75	264	1.4	1	0.4	0.03
BIJELA (14) -08-03	7.4	307	8.77	66	22	1.02	0.33	295	1.2	2	0.8	0.01
PLITVICA (15) -08-03	7.5	299	8.4	65	23	2.00	0.95	295	1.6	3	0.6	0.01
RODIĆ (16) -08-03	9	305	8.83	60	25	1.85	0.90	293	1.4	2	0.5	0.05
SARTUK (17) -08-03	14.2	346	9.07	52	30	2.15	0.71	290	3.0	4	0.8	0.06
KRUŠĆICA (3) -09-03	17.6	229	8.62	49	8	2.07	0.81	183	2.8	1	0.2	0.01
BEGOVICA (4) -09-03	9.9	336	7.94	91	3.9	3.20	0.97	284	1.2	1	0.6	0.08
PEĆINA (5) -09-03	9.3	332	8.11	76	3.4	2.25	0.72	233	4.0	2	0.9	0.07
KNJAPOVAC (6) -09-03	9.9	331	7.75	94	8.3	4.42	0.95	289	2.1	19	0.5	0.01
TONKOVIĆA V. (7) -09-03	9.9	332	7.83	92	12	4.35	0.79	301	2.0	19	0.6	0.01
KLANAC (8) -09-03	13.9	328	7.84	81	5.9	2.58	0.71	251	1.5	17	0.5	0.02
MAJEROVO V. (9) -09-03	9.3	305	7.77	76	15	2.35	0.70	290	1.2	2	0.7	0.01
JAZ (10) -09-03	10.1	336	7.92	94	12	3.58	0.91	305	2.8	21	0.5	0.01
MATICA (12) -09-03	9.6	308	8.21	66	22	1.68	0.43	296	1.3	2	0.8	0.01
CRNA (13) -09-03	7.8	282	8.21	68	18	1.69	0.63	284	1.0	1	0.6	0.08
BIJELA (14) -09-03	7.4	308	7.95	60	24	2.05	0.58	286	1.1	1	1	0.01
PLITVICA (15) -09-03	7.4	287	7.98	62	22	1.50	0.44	283	1.5	1	1.2	0.01
RODIĆ (16) -09-03	8.1	290	8.76	65	20	1.61	0.32	282	1.2	1	1.2	0.08
SARTUK (17) -09-03	9.5	304	9.01	63	21	1.33	0.55	281	1.4	1	1.1	0.01

Table 2: Results of the measurements of stable isotopes.

LOCATION (number) – month – year	$\delta^{2}H$	$\delta^{18}O$
DEŽMINO V. (1) -11-02	–53.6	–8.04
PEĆINA (5) -11-02	–52.1	–7.91
TONKOVIĆA V. (7) -11-02	–59	–8.78
MAJEROVO V. (9) -11-02	–63.5	–9.12
PEĆ.-KOR. (11) -11-02	–58	–8.83
PLITVICA (15) -11-02	–66.3	–9.85
DEŽMINO V. (1) -01-03	–54.6	–8.46
PEĆINA (5) -01-03	–55.7	–8.35
TONKOVIĆA V. (7) -11-02	–61	–8.93
MAJEROVO V. (9) -01-03	–63.6	–9.53
PEĆ.-KOR. (11) -01-03	–63.7	–9.34
PLITVICA (15) -01-03	–71.8	–10.36
DEŽMINO V. (1) -04-03	–60.2	–8.9
PEĆINA (5) -04-03	–59.3	–8.64
TONKOVIĆA V. (7) -04-04	–60	–8.98
MAJEROVO V. (9) -04-03	–65.9	–9.72
PEĆ.-KOR. (11) -04-03	–67	–9.74
PLITVICA (15) -04-03	–69.4	–10.49
DEŽMINO V.(1) -07-03	–59.1	–8.86
PEĆINA (5) -07-03	–57.4	–8.45
TONKOVIĆA V. (7) -07-04	–58.2	–8.81
MAJEROVO V. (9) -07-03	–66.1	–9.89
PEĆ.-KOR. (11) -07-03	–64.1	–9.87
PLITVICA (15) -07-03	–69.6	–10.48

can only belong to one group. The coefficient of distance is the similarity measure, the values of which are between 0 and ∞. The value 0 represents total similarity. In processing the chosen data, Pearson's "r" distance was used, and Ward's method was applied for connecting the measured data,. Ward's method is based strictly on classification demand, according to which data groups are formed such that the distance among particular members of the group is the least possible.

5. HYDROGEOCHEMICAL MEASUREMENT RESULTS AND THEIR INTERPRETATION

5.1. Temperature

The temperature of groundwater is a well-known natural indicator, which serves to determine groundwater origin, underground retention time, and its dynamics. The water temperature at the spring is in accordance with the annual air temperature of the spring recharge area. Consequently, the groundwater that is recharged from hypsometrically higher areas with lower annual average air temperatures will have a lower temperature. Generally, the groundwater temperature in karst varies from 4.9 °C–17.8 °C (BONACCI, 1987). In the karst areas where quick and turbulent groundwater flow prevails, the water temperature of a spring can be considerably influenced by seasonal changes of air temperature. During such quick groundwater flow, the retention time of the fresh infiltrated water in the underground zone is short; hence, the annual oscillation of temperature in the spring will be greater. The temperature of the groundwater that flows near the surface varies considerably, in contrast to the flow in the deeper parts (GUNN, 1982). Water that sinks deep into the vadose zone and that is retained underground for a relatively long period has a homogeneous temperature with time.

From the diagrams of temperature (Fig. 4) measured in the springs, it can be observed that the greatest temperature alterations are noticed in the surface waters of the Krušćica accumulation and in the Mlakvena greda and Sartuk springs. The Krušćica accumulation is the surface flow of the Lika river; Mlakvena greda and Sartuk have low diffuse discharge; in these places, the water temperature is under the influence of the air temperature. The least temperature variations are noted in the springs of the Crna and Bijela rivers (Black and White rivers) and in the Plitvica spring, all belonging to the catchment area of the Korana. Small variations are measured in the Tonkovića vrelo, Knjapovac, and Jaz from the catchment area of the river Gacka. This could be the result of homogenization of temperatures because of underground retention, i.e. because of the nonexistence of greater channel systems. The temperature variations are greater in the Pećina spring, which is probably caused by the smaller surface of the catchment area of that spring. Temperatures of the springs in the catchment area of the river Gacka are somewhat higher (about 2 °C) than those in the catchment area of the river Korana, which is in accordance with the average annual air temperature of the recharging area for these springs.

5.2. Negative logarithm of the hydrogen ion concentrations (pH value)

The activity of hydrogen ions in water solutions is controlled by the reactions in which the hydrogen ions are consumed or produced. It is very sensitive to weathering and mineral dissolution; however, as the concentration of the hydrogen ions is under the influence of numerous processes, it is difficult to attribute their values to different surroundings. The value of the pH of the spring waters is a useful indicator of the equilibrium reaction state. H^+ ions are mostly obtained from H_2CO_3, which is formed by the dissolution of CO_2 in water and is independent of other variables. Therefore, hypotheses about the conditions in the catchment area are not proposed on the basis of H^+ ions, but from the measured pH factor and alkalinity. The partial pressure of CO_2 (pCO_2) is calculated, on the basis of which conclusions are derived and hypotheses are proposed.

According to the measured pH values, the spring waters of the investigated area are neutral to weakly alkaline. The lowest values of pH are predominantly found in the winter months, and they gradually increase during the warmer months (Fig. 5). The highest values are achieved in summer. The smallest variations of pH are in the catchment area of the Gacka river.

In addition to the temperature variations, the values of pH, hydrogen carbonate alkalinity, and the basic ionic com-

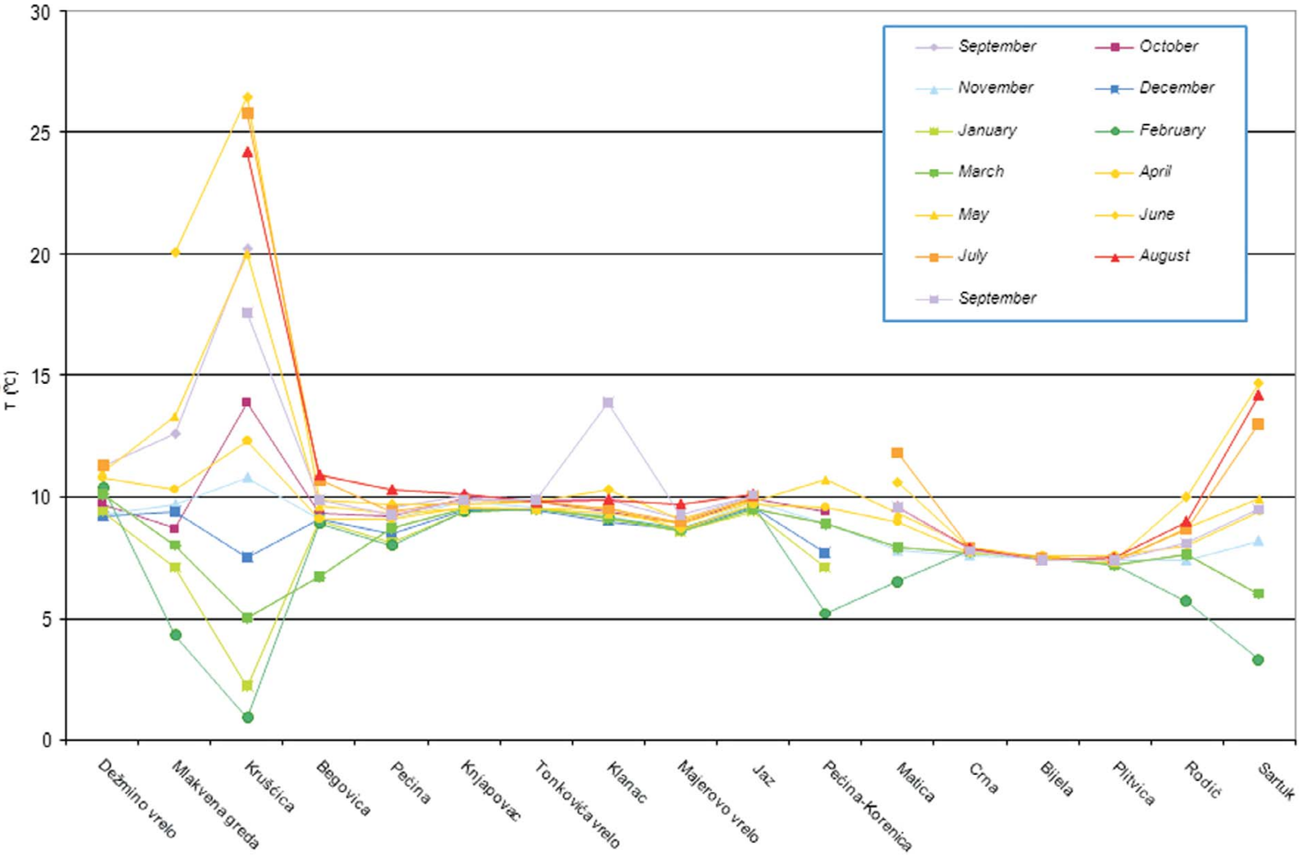

Figure 4: Temperature of the spring and surface waters.

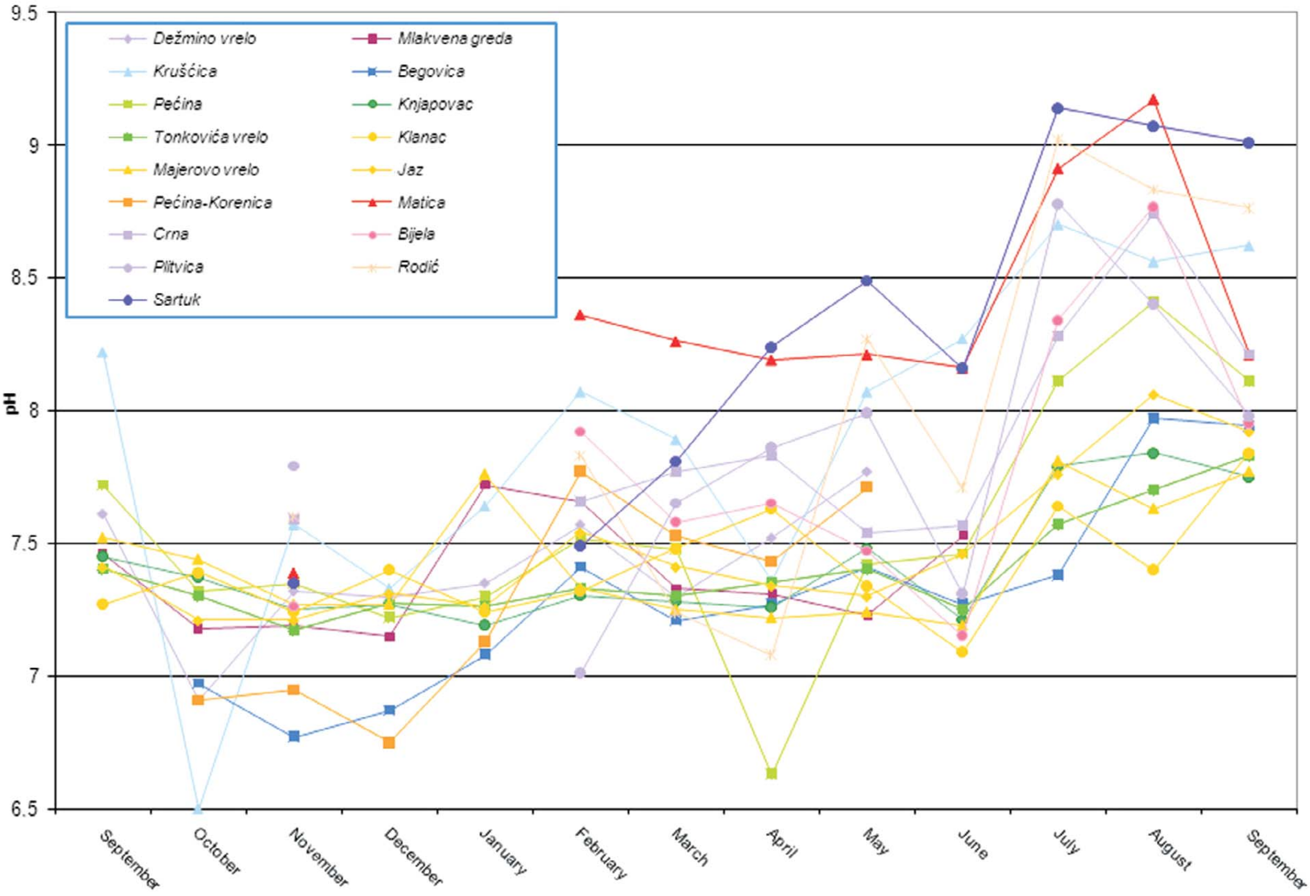

Figure 5: Variations of pH in spring and surface waters.

position in the spring and surface waters are the reflections of the seasonal vegetation and hydrological conditions (APPELO & POSTMA, 1994; HEM, 1985). In cases where there is strong mixing of each new contribution into the karst aquifer with the pre-existing groundwater, where the groundwater flow is predominantly diffuse, seasonal changes of temperature, pH, and TDS are generally small. Greater aberrations are present in springs where discharges oscillate considerably during the year (PAVIČIĆ et al., 2003; DREVER, 1985).

5.3. Partial pressure of carbon dioxide (pCO2)

Atmospheric pCO_2 is constant – $10^{-3.5}$ atm (32 Pa), i.e. 0.03 vol.% in the air; nevertheless, in the root zones where respiration processes occur, it varies depending on the depth and seasonal changes. At a depth of about 8–9 m, the value is increased 10 times (Fig. 6, 7). The main source of CO_2 in soil is plant respiration or the oxidation of organic substances. Agricultural soils have the highest content of CO_2. They are followed by grasslands and woodlands, the latter having the smallest CO_2 value. In open systems, in which a constant equilibrium of the pCO_2 of water with the atmospheric CO_2 is enabled, it remains constant, and the concentrations of carbonate and bicarbonate ions change according to the pH.

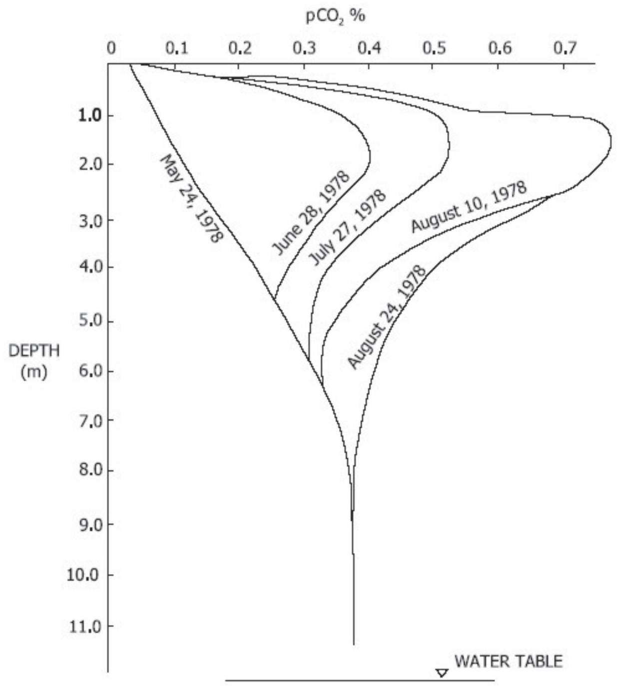

Figure 6: Seasonal alteration of pCO_2 in the soil in unsaturated medium (APPELO & POSTMA, 1994).

In systems where carbonates prevail, such as in the catchment areas of the river Gacka, the equations of the balanced reactions that occur in a water solution can serve as the basis for determining the formation of carbon dioxide. The pH and alkalinity are necessary for this calculation, and the value of initial pCO_2, e.g. from the air present in the soil, is obtained (HEM, 1985). From the pCO_2 and pH values, in addition to the saturation state, it is possible to estimate the conditions in which the reactions took place. As the values

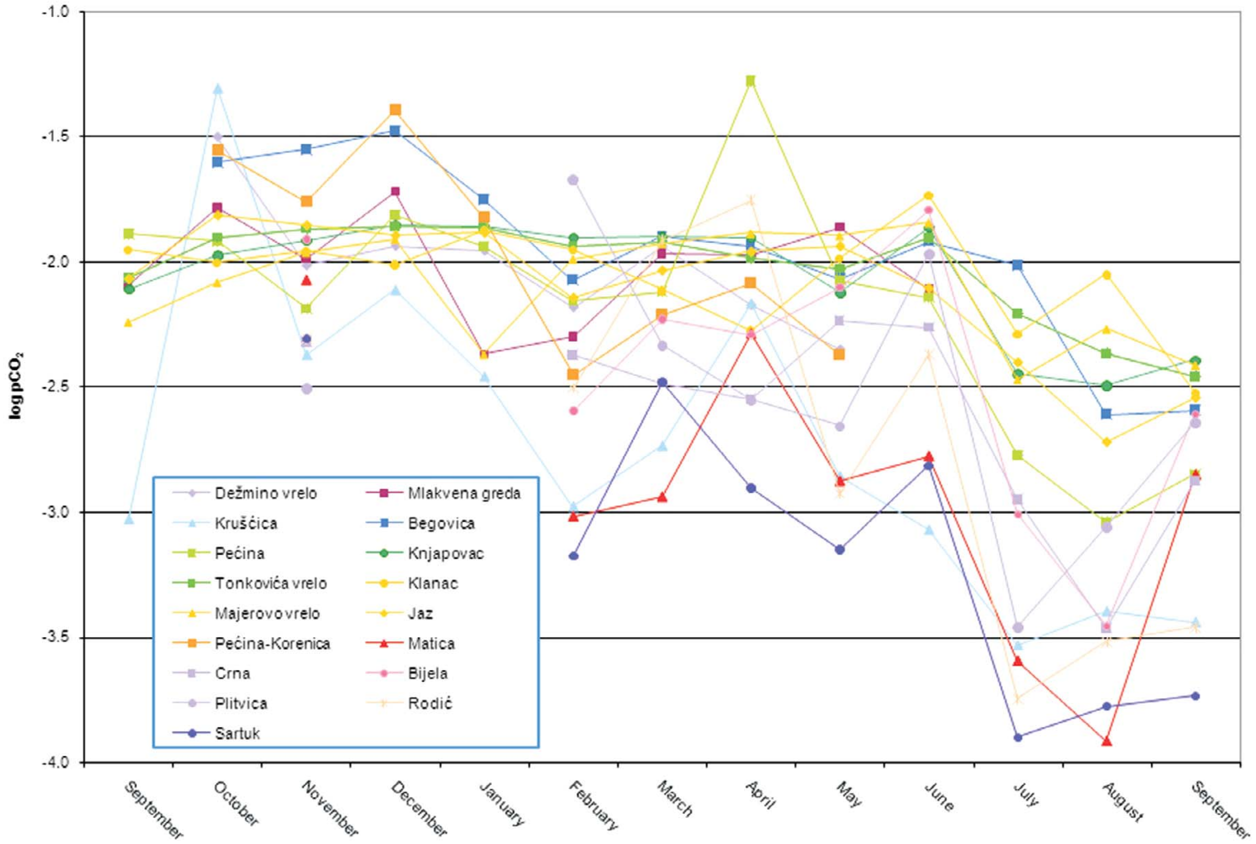

Figure 7: Values of the log pCO_2 on the observed sites.

of pCO_2 are very small, it is usual to express them in the logarithmic scale. They are calculated using the NEPTAH software package (PLUMMER et al., 1994).

The lowest values were obtained in the Krušćica surface accumulation as expected, because near the surface, a constant equilibrium with atmospheric pCO_2 was enabled, which is considerably lower than the one in the soil, where the variations of these values are the greatest (Fig. 7). Low values were recorded in the springs in the catchment area of the river Korana, and the reason was probably the deforestation of almost the entire catchment areas of these springs.

The values of pCO_2 are highest in the winter months (Fig. 7). They gradually decrease and reach the lowest values in summer. Although the highest values of partial pressure are expected in summer because of the respiratory processes of plants, it does not occur, because rainfall is very rare in summer and there is no water that could bring CO_2 by infiltration through the surface. The first autumn rains bring the dissolved CO_2 from the root zone; hence, values are the highest in autumn.

5.4. Electrical Conductivity (EC) and Total Dissolved Solids (TDS) evaluation

The EC value of pure water is low, but with the increase of TDS in water, the conductivity increases. Therefore, TDS and EC are correlated. The values of EC in the springs Knjapovac, Tonkovića vrelo, and Jaz from the catchment areas of the river Gacke are almost identical: from September to November, they are increased, and thereafter they gradually decrease (Fig. 8). After low water levels, heavy rains precipitate and wash out large quantities of dissolved substances from the soil and the epikarst zone, thus increasing these levels. In Klanac, they are somewhat lower and uniform throughout the year and in Majerovo vrelo, they are even lower. In the catchment areas of the river Korana, lower values were measured than in the catchment area of the Gacka, most probably because of the lower average temperatures. In dilute solutions, a temperature increase of 1°C causes an increase in conductivity of about 2% (HEM, 1985). Another reason for the lower values of EC in the catchment area of the river Korana could be the greater representation of dolomites in this catchment area, which are less soluble than limestones. The time needed to reach 95% saturation for dolomites is 100 times longer than that for limestones under similar conditions (APPELO & POSTMA, 1994).

Among all the spring zones that are under considerable influence of the surface (Sartuk, Mlakvena greda, Dežmino vrelo, and the Krušćica accumulation), the highest values were measured in August and the smallest in February. A similar situation occurs in the springs from the catchment area of the river Una. In the winter months, the discharge is much greater, the dilutions are greater, and the EC is lower than in the summer periods. In the Krušćica accumulation,

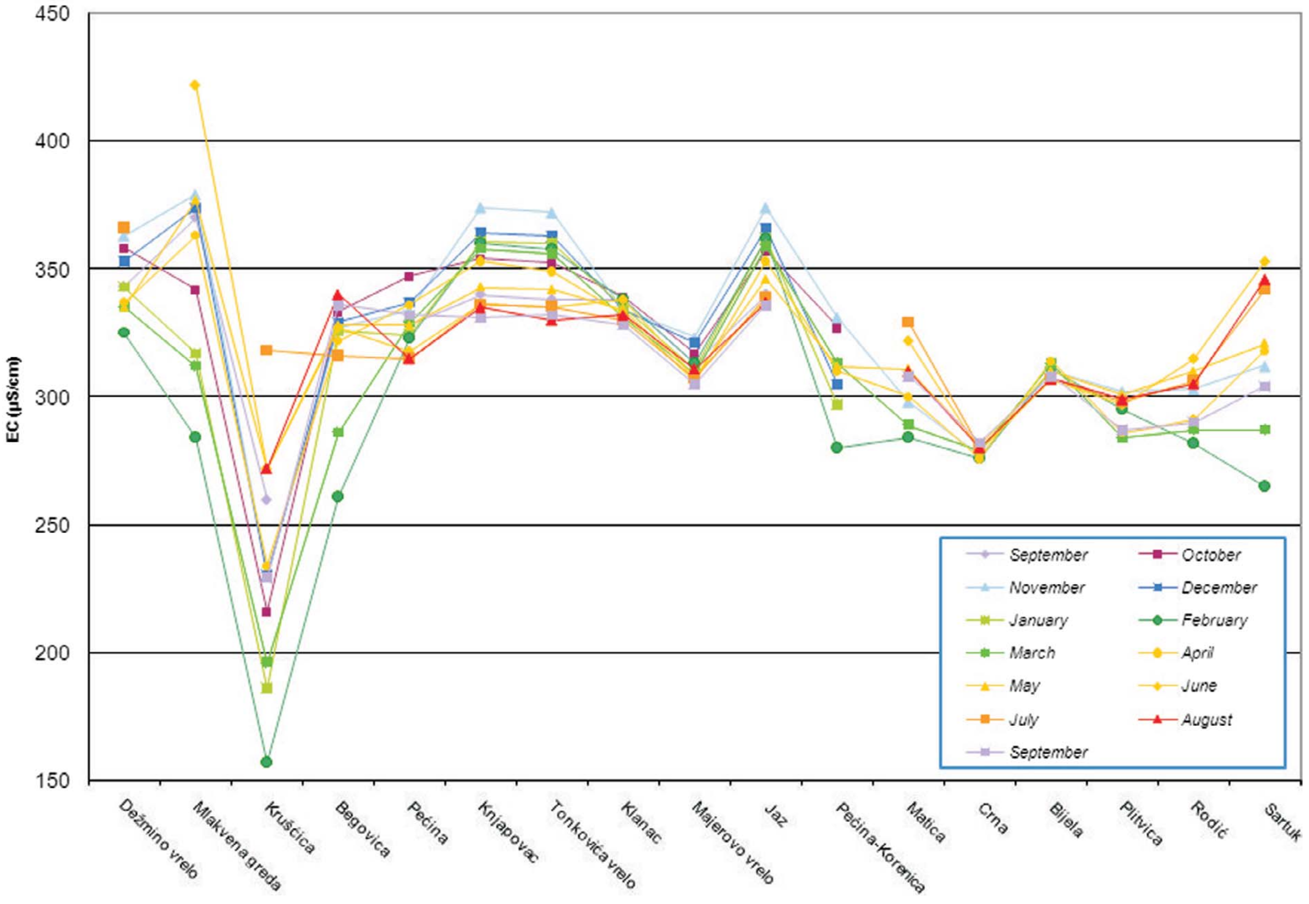

Figure 8: The distribution of EC values.

the values are considerably lower and deviate from all other sampling locations, but this was expected because the surface water is diluted owing to the direct influence of rainfall.

5.5. Alkalinity

Alkalinity of the water sample is equal to the number of equivalents of the dissociated weak acids; i.e. it represents the capacity of the dissolved substances in the solution to react with the acid and neutralize it. It is determined by titration with a strong acid, and the final point is the pH at which all the dissolved substances that contribute to alkalinity begin to be reactive. Although it is possible to find other weak acids in the solution, in practice, only the dissolved carbonate acid has quantitative importance for determining the alkalinity. The alkalinity is equal to:

$$Alk = m_{HCO_3^-} + 2m_{CO_3^{2-}} \qquad (3)$$

– where Alk denotes the alkalinity expressed in the concentration unit, and m is the molar concentration [mmol/l].

At the values of pH < 8.3, less than 1% of carbonate acid is present as CO_3^{2-} and, in this situation, the concentrations of hydrogen and carbon are the only important ones. The main source of carbonate, which influences the alkalinity of the surface and underground waters, is CO_2 present in the atmosphere, in soil, and in the unsaturated medium. The carbonic acid is formed by dissolution of CO_2 in water, and it is separated into two stages in which the hydrogen carbonate and carbonate ions are formed, which is presented in the following reactions:

$$CO_{2(g)} + H_2O \rightarrow H_2CO_3 \qquad (4)$$

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \qquad (5)$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-} \qquad (6)$$

The concentrations of the hydrogen carbonate ions in natural water range within a moderate interval because of the influence of the carbonate balance. Most of the surface water bodies contain less than 200 mg/l hydrogen carbonate, whereas in groundwater, somewhat higher values are usually present.

The lowest concentrations of hydrogen carbonate ions were measured in November. The reason for this could be the greater dilution that occurs at the beginning of the rainy season (Fig. 9). Bunsen's coefficient of CO_2 solubility is considerably greater at lower temperatures, and in accordance with this, the production of carbonic acid is greater, which dissociates to yield hydrogen carbonate ions.

In the catchment area of the river Gacka, there are greater differences between the minimum and the maximum values than in the catchment area of the river Korana, probably because of the same reasons as in the case of homogenization of the temperature of the surface and underground waters. In the Krušćica Reservoir, the lowest values were recorded because of the direct exposure to rainfall and, hence, greater dilution of the constituents.

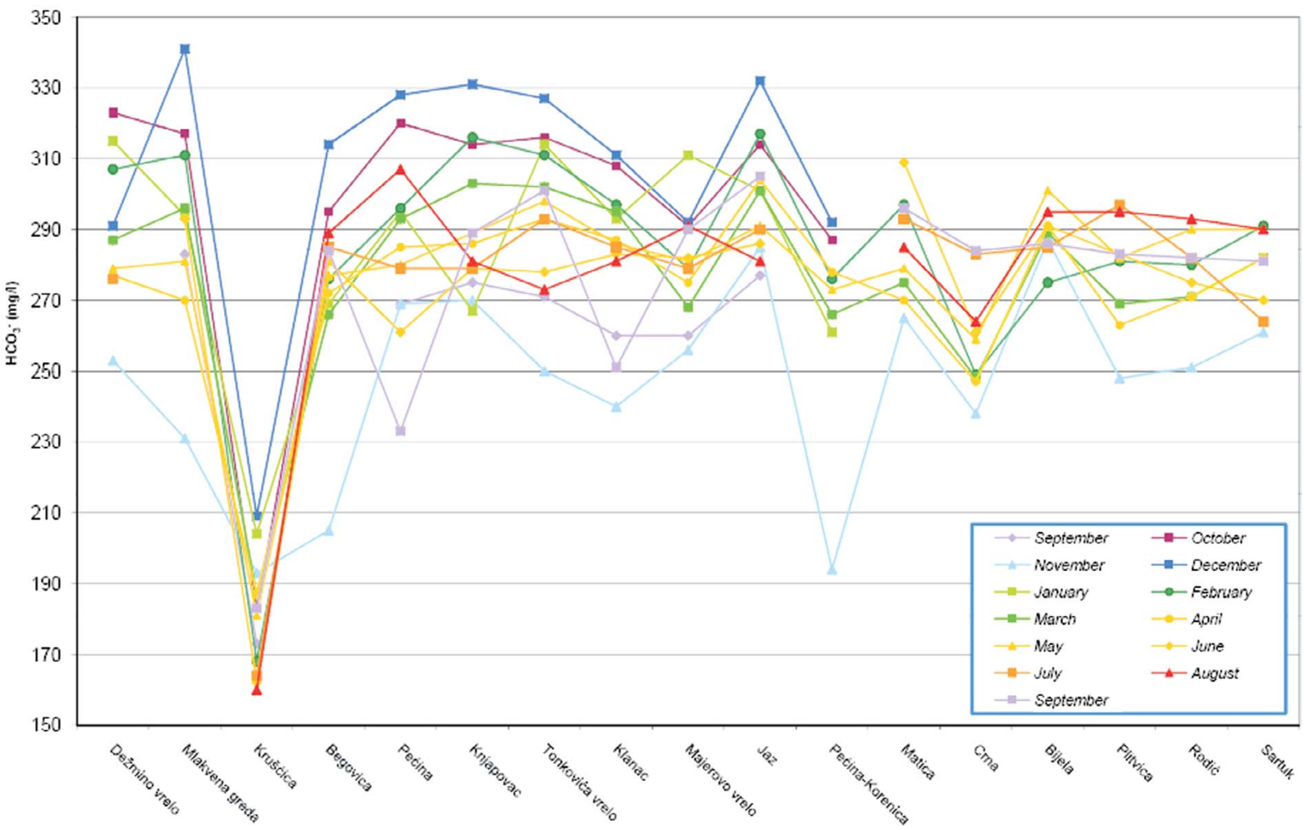

Figure 9: Hydrogen carbonate alkalinity of the springs and surface waters.

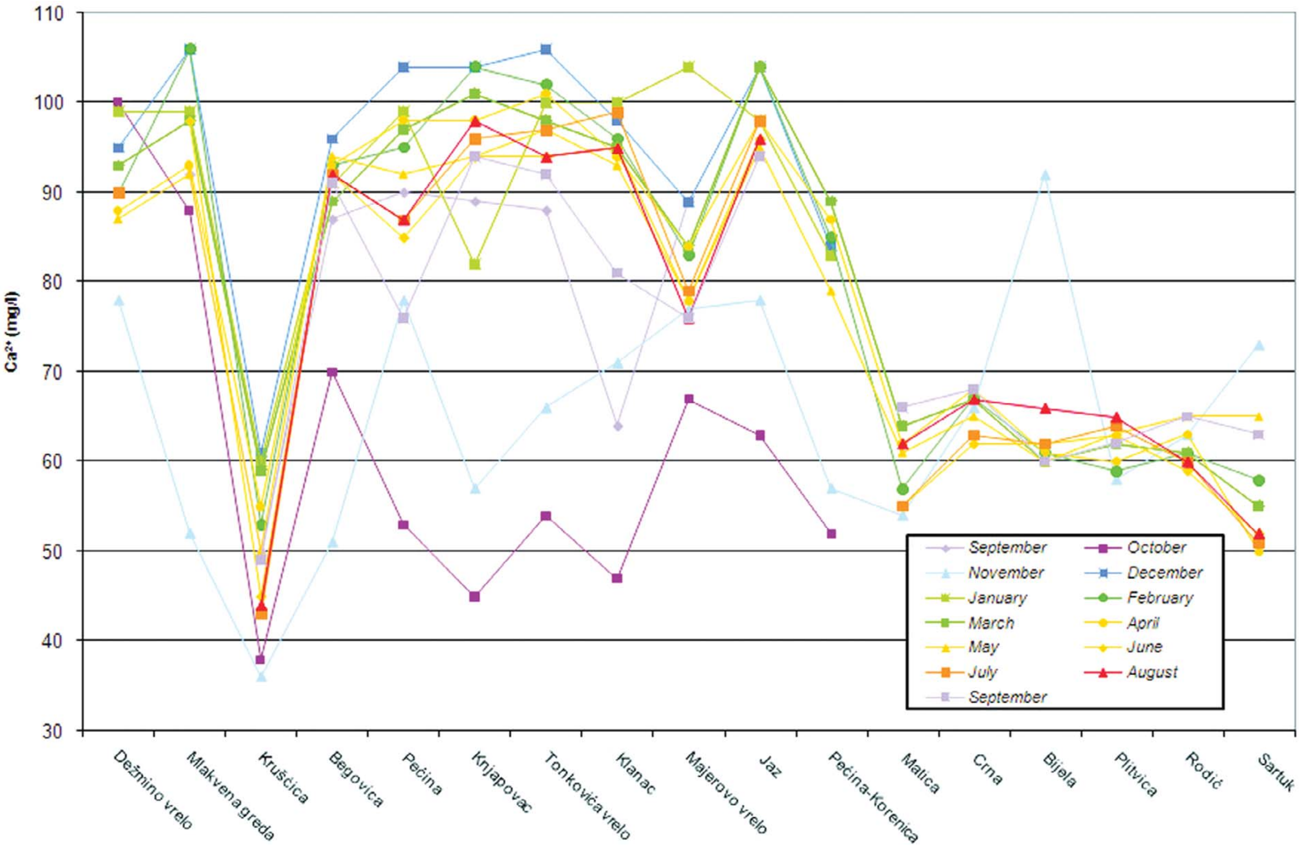

Figure 10: Distribution of calcium ions.

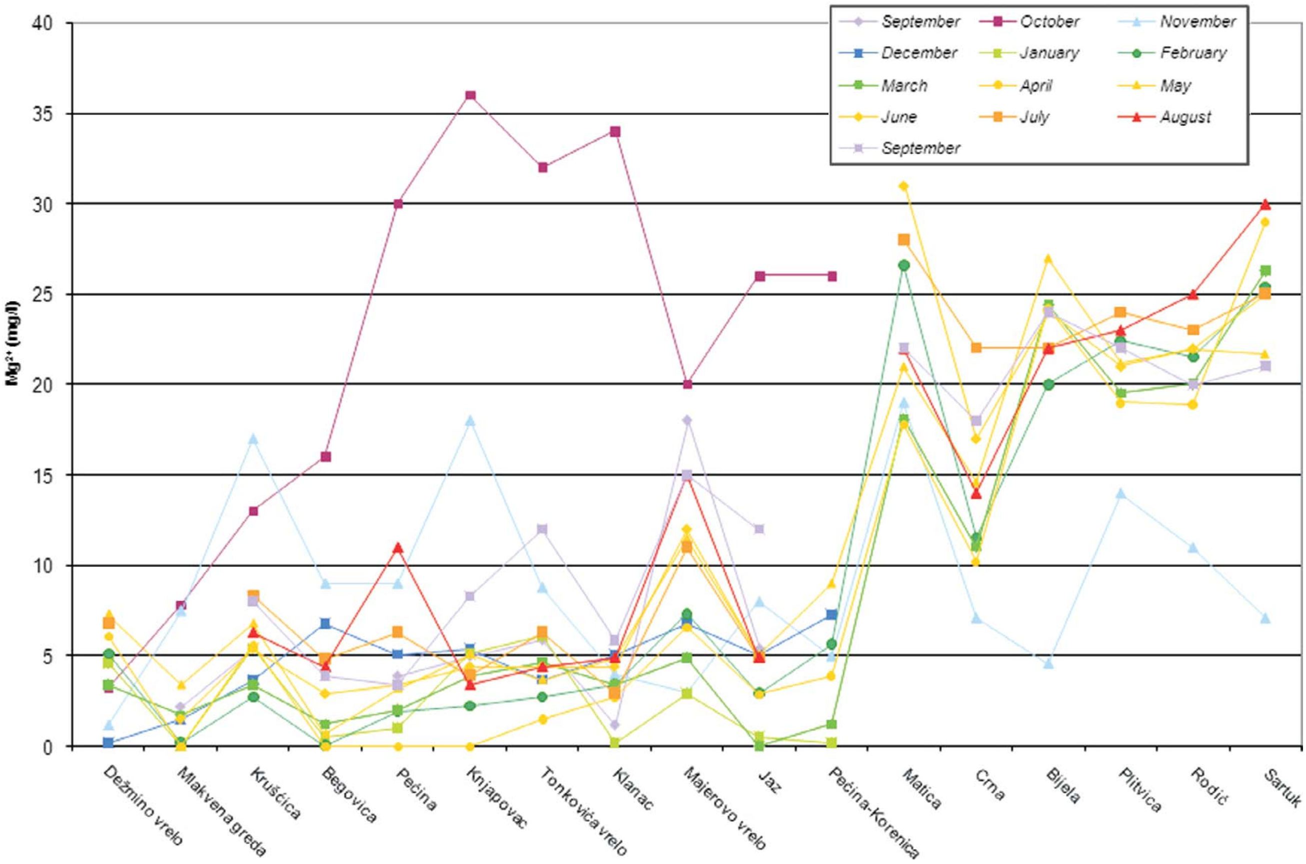

Figure 11: Distribution of magnesium ions.

5.6. Calcium and magnesium

The lowest values of Ca concentrations were measured in October and November. In the catchment area of the river Korana, the concentrations were considerably lower than in other catchments. In the Krušćica surface accumulation, the lowest values were measured (Fig. 10). In contrary to Ca, the concentrations of Mg ions were higher in October and November, after which period they decreased. The lowest values were measured in the winter months and, in the warmer summer months, they gradually increased (Fig. 11). In the catchment area of the Korana, they were considerably higher than in other catchment areas. As the carbonates are distinguished by their greater solubility in relation to other minerals, it can be expected that the basic anion and cation composition of water is a good reflection of the environment through which the groundwater flows. From the molar ratio of magnesium and calcium (Fig. 12), it is apparent that this ratio is considerably higher in the catchment area of Korana than in other catchments, which indicates the aquifer being situated in rocks with a predominantly greater constituent of dolomites. Moreover, the molar ratios of Mg/Ca measured in October was much higher than the ratios in other months because of the first autumn rains, which wash out calcium, magnesium, and hydrogen carbonate ions from both the soil and the weathering zone in the surface parts of the area composed of dolomite-bearing rocks. This is also the explanation of the low values of calcium ions and high values of magnesium ions in October and November. During the warmer months in the Majerovo vrelo, lowering of water levels, results in greater ratios of magnesium, which could indicate the presence of dolomites in the deeper parts of the aquifer. In other springs, this ratio is similar and indicates that these springs are recharged mostly from limestones.

5.7. Saturation conditions with calcite and dolomite

Equilibrium is rare in nature. The solution is in most cases too saturated with reference to some minerals, which suggests the process of deposition; or it is unsaturated, which implies that dissolution of the mineral is in progress. The saturation index shows the direction in which the reaction takes place. The kinetics of carbonate dissolution are rapid enough to reach equilibrium in soils that contain fragments of $CaCO_3$, and the circulation of air through the bare rock can be so rapid that the water entering the inner fissures of the rock mass is still unsaturated, which is necessary for calcite dissolution. To be able to calculate if the solution is in thermodynamic equilibrium, data about the activities of the various types of dissolved ions that represent a particular mineral are necessary, in association with the temperature of the solution. The state of saturation is expressed by the ratio of the ionic activity products in the solution and the activity product in a state of equilibrium. Very often, the saturation index is used, which is the logarithm of the above ratio (HEM, 1985).

$$SI = \log IAP/K \tag{7}$$

– where SI denotes the saturation index, IAP denotes the product of ionic activity, and K is the product of solubility.

If SI = 0, it implies that an equilibrium exists between the mineral and the solution, SI < 0 points to lack of satura-

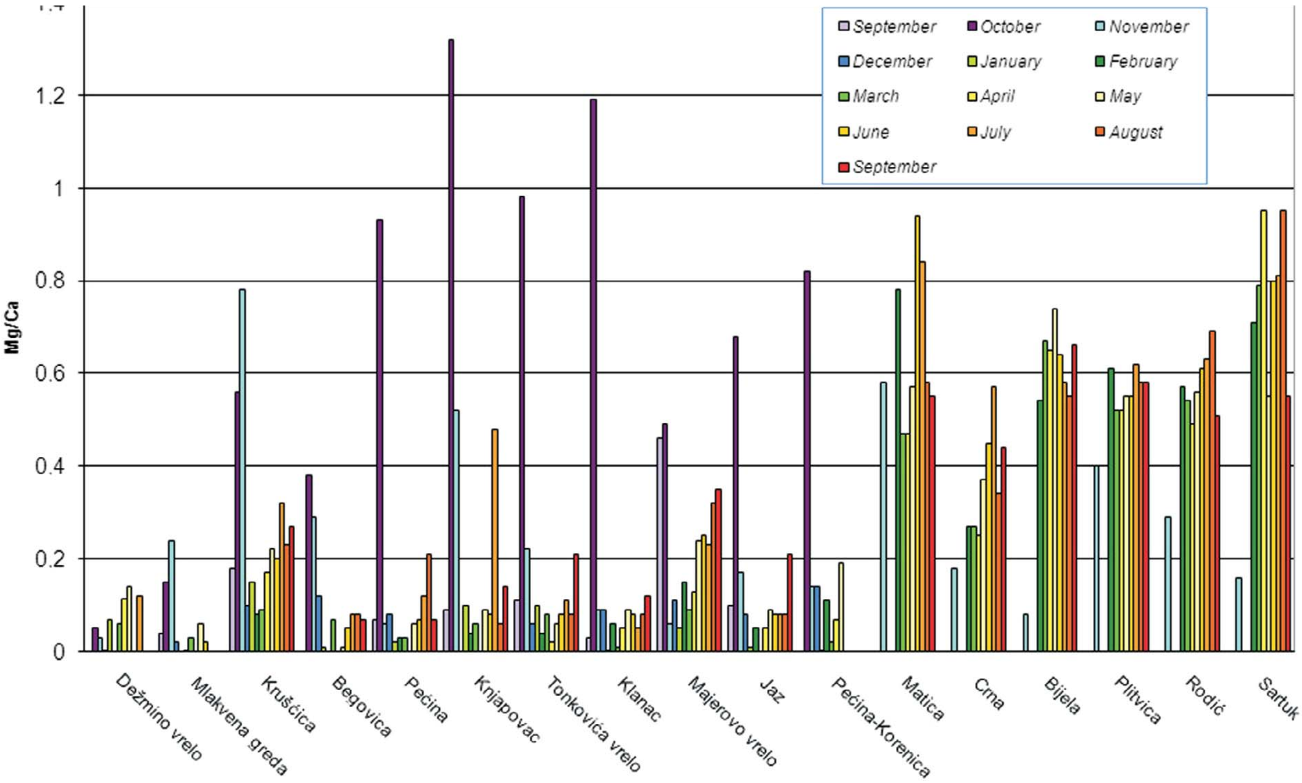

Figure 12: Molar ratios of Mg/Ca of the spring and surface waters.

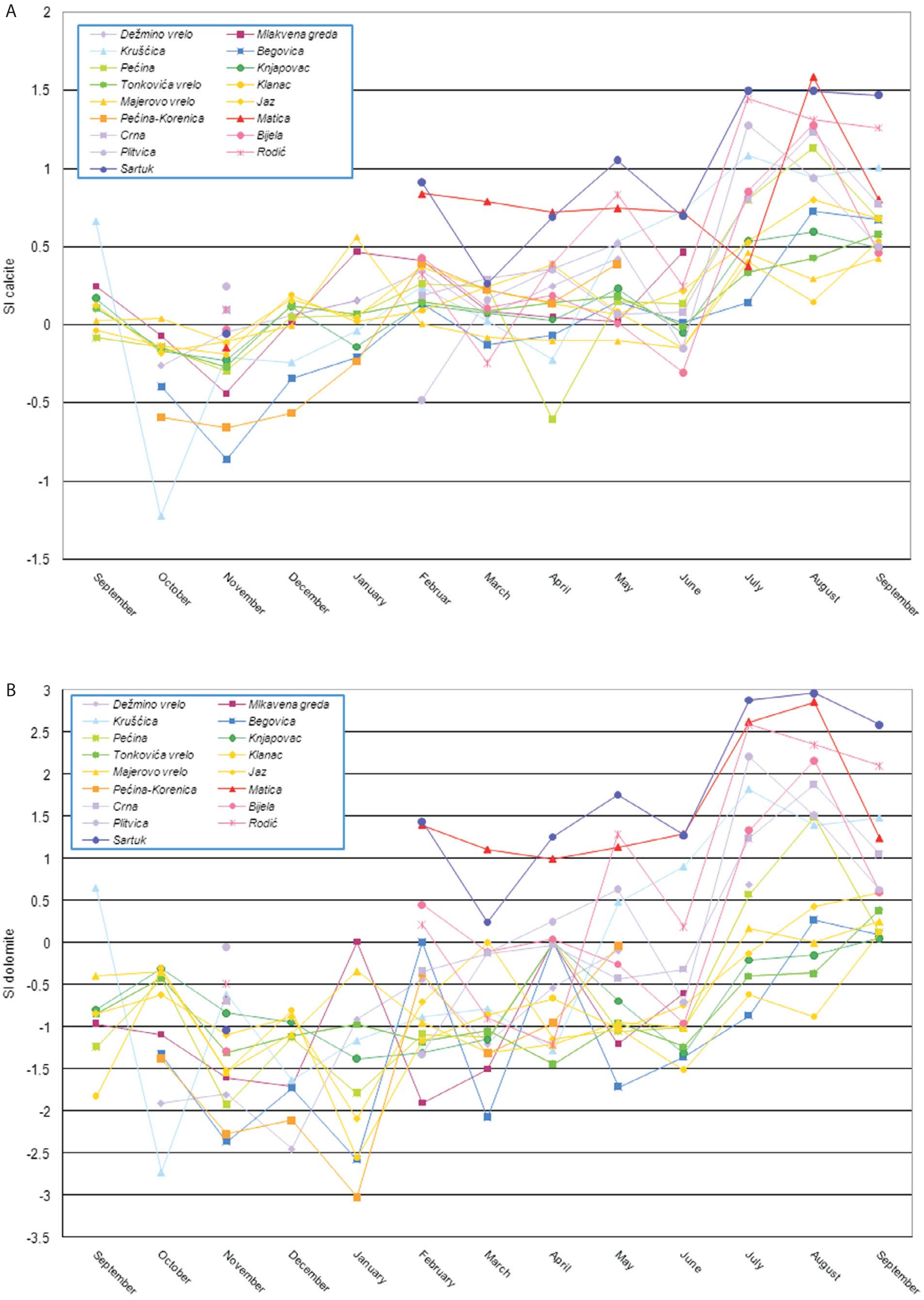

Figure 13: Values of the saturation indexes for calcite (a) and dolomite (b).

tion, and $SI > 0$ indicates the oversaturation of the solution with reference to the mineral. Both saturation indices (for calcite and dolomite) indicate the lowest values in October, after which values increase to reach their maxima in the summer months (Fig. 13). Saturation indices in relation to calcite are approximately close to the equilibrium conditions of samples from the springs in the catchments of the rivers Gacka and Lika, whereas greater saturation was recorded in the summer months in samples from the springs of the catchments of the rivers Korana and Una. Saturation with dolomite ranges from the equilibrium state to the lack of saturation in the catchment areas of Gacka and Lika to oversaturation in the catchment areas of Korana. The catchment of the river Korana is composed predominantly of carbonates, in which dolomites prevail. In the catchments of the rivers Gacka and Lika, limestones prevail, which was confirmed by the data obtained.

5.8. Sulfates, nitrates, and phosphates

Spring waters in the Lika region usually have low contents of sulfates. Important sources of sulfates can be the melting of gypsum, oxidation of metal sulfides (most often, pyrite), mixing of groundwater with seawater in some coastal zones (PAVIČIĆ et al., 2006), acid rain, and fertilizers. Sulfates can also be formed as a result of human influence such as pollution by wastewater; e.g., waters from cement factories or pollution caused by fuel burning. In all the springs from the Gacka catchment, in Dežmino vrelo from the catchment of the river Lika, and in the Begovica spring from the catchment of the river Una, sulfates are present in considerably lower concentrations than in other samples. In the catchment area of the river Korana, the values are low. The highest concentrations were measured in the summer months. In samples from the springs belonging to the catchment area of the rivers Gacka and Dežmino vrelo, the increased contents of sulfates probably originated from the factory manufacturing calcite products.

Nitrates in the groundwater can be of different origins, such as septic tanks, oxidation of organic nitrogen, and the growing problem of extensive usage of fertilizers in agriculture. The maximal permitted concentration (in Croatia) of nitrates in water is 50 mg/l (which corresponds to 11 mg/l NO_3^--N).

Phosphates are the only type of phosphorus complexes in the majority of water systems. They are good indicators of pollution because they are used in the production of detergents, and fertilizers and because they are present in faeces as the product of metabolic processes. The orthophosphate ion, $PO_4^{3},^{-}$ is the final product of dissociation of phosphoric acid. It represents the most stable form of phosphates and is often found in natural waters. The lowest values of nitrates were measured in the catchment areas of the river Lika (< 0.4 mg/l), whereas in other places they were higher; however, they did not exceed 1.4 mg/l, which are very low values. Orthophosphate ions range from < 0.1 to 0.31 mg /l PO_4^{3-}. Regardless of the seasonal variations, the concentrations of phosphates and nitrates are generally very low (Table 1), which indicates the superior quality of the groundwater.

5.9. Statistical processing of the hydrogeochemical indicators

Statistical analysis using multivariate cluster analysis of R-modality, provided an insight into the mutual affinity of the measured hydrogeochemical indicators in the spring waters. The chosen variables were sorted into three basic groups (Fig. 14). Two of them could be considered as lithogeochemical (C1 and C3), and one as human-induced (C2). C1 is named “limestone dissolution”, which implies karstification. It is highlighted by three parameters (Ca^{2+}, HCO_3^-, and EC). The C2 cluster is most probably a consequence of road-salting during the winter time, and four indicators are emphasized (Na^+, K^+, Cl^-, and SO_4^{2-}). This cluster is anthropogenic and is called the “human impact”. The C3 group is again lithogeochemical and based on Mg^{2+} and NO_3^--N levels. This cluster is most probably connected with the erosion and leaching of the soil and the epikarst belt, usually in the beginning of the rainy season. Mg^{2+} ions are extracted in this group because of the weak solubility of the mineral dolomite in comparison with calcite. Therefore, these ions are released from the rock fragments in the soil and the epikarst zone dur-

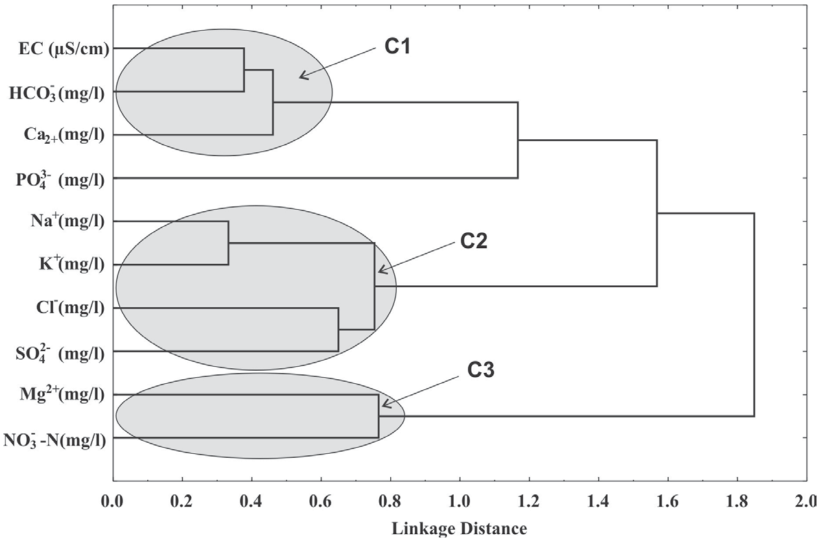

Figure 14: Dendrogram of the geochemical affinities of the measured hydrogeochemical indicators. Tree diagram, Ward’s method, 1 – Pearson r (Statistica 7.0).

ing the dry periods by vegetation, and then washed out by the first rains. Nitrates are also accumulated in the soil cover, mostly in karst poljes, and are also washed out by rainwater.

5.10. Stable isotopes of oxygen ($\delta^{18}O$) and hydrogen (δ^2H)

Stable hydrogen and oxygen isotopes are useful for establishing the origin of groundwater in areas where waters of diffrent origins, ages, and evolutions are present (GUAY at al., 2006). The ratio of these isotopes of oxygen and hydrogen is used in the investigation of karst hydrogeological systems to determine the recharge areas and for the investigation of the hydrodynamic conditions in aquifers. The oxygen and hydrogen isotopes are the components of the water molecule ($HD^{16}O$, $H_2{}^{16}O$, $H_2{}^{18}O$), and in natural conditions, their concentrations vary from 180 to 340 ppm for deuterium (D) and from 1880 to 2010 ppm for ^{18}O. The variations are the consequences of the so-called isotopic fractionation during the phase transitions of water. During evaporation, the lighter isotopes are separated, and the vapour becomes poor in heavy isotopes, in comparison with water. The fractionation depends on pressure, composition of steam, and the most important factor of all, the temperature of the phase transition. The lower the temperature of the phase transition is, the higher the fractioning effect, and vice versa. The isotopic composition of water is reflected as the relative aberration (δ) of the ratio between the heavier isotopes and lighter ones in the sample (R_{uz}) compared to the ratio of these isotopes in the standard (R_{stand}), and it is expressed per thousand (δ x 1000):

$$\delta = \frac{R_{uz} - R_{s\tan d}}{R_{s\tan d}} \qquad (8)$$

A sample of seawater obtained at a depth of 50 m in the ocean was used as the standard; Ratio in standard mean ocean water (SMOW) for oxygen, $R_{SMOW} = (2005.20 \pm 0.45) \times 10^{-6}$, and for deuterium, $R_{SMOW} = (155.76 \pm 0.05) \times 10^{-6}$. There is a correlation between the quantities of the stable isotopes ^{18}O and ^2H in both rainfall and groundwater. At meetings of the International Atomic Energy Agency (IAEA) in Vienna and the World Meteorological Organization (WMO), data were presented about the quantities of isotopes in rainfall as measured by the network of meteorological stations all over the world (IAEA, 1981, 1983). Linear dependence of the ratios of the isotopes $\delta^{18}O$ and δ^2H on rainfall can be represented by the equation of the line:

$$\delta^2H = (8.17 \pm 0.08)\,\delta^{18}O + (10.56 \pm 0.64)\ \text{‰} \qquad (9)$$

– with the correlation coefficient r = 0.997, and standard error of determination of $\delta^2H = \pm 3.35$‰.

The obtained line is called the “Meteoric Water Line”. This line is valid for waters and rainfall that do not evaporate very much. The ratio of the stable isotopes in water samples is measured using the technique of mass spectrometry. In the chosen springs from which water was collected for the isotope analyses; (Dežmino vrelo, Pećina, Tonkovića vrelo, Majerovo vrelo, Pećina-Korenica, and Plitvice), the influence of the high-altitude effect can be observed for all the periods of sample collection (autumn, winter, spring, and summer) (Fig. 15). According to these data, the elevation above sea level of the predominant recharge of the Plitvice spring is the highest, followed in order by the other springs: Majerovo vrelo, Pećina-Korenica, Tonkovića vrelo, Dežmino vrelo, and Pećina. Plitvica and Majerovo vrelo partially drain the same area, although Plitvica has more negative values because its catchment is at a higher elevation and further inland. The effect of seasons on the expected response in the springs under study is significant. The values of the ratios are more positive in the autumn (November 2002) when the water is discharged, in which a part of the summer rainfall is expressed more, whereas in April, lower values of the ratio are noticed as a consequence of melting of snow, which is of greater influence than winter precipitation.

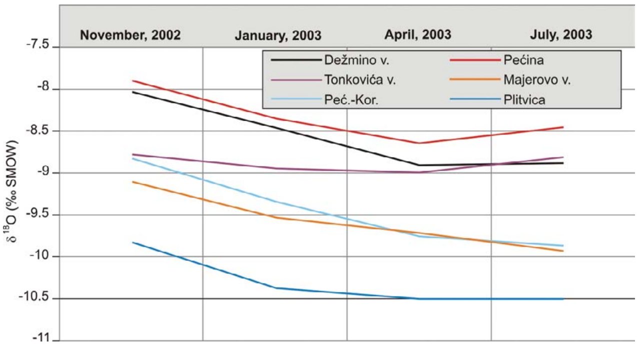

Figure 15: Changes of the ratio of $\delta^{18}O$ in samples of spring and surface waters.

CLARK & FRITZ (1997) estimated that the isotope gradient, also called the high-altitude effect, is about 0.15 to 0.5‰ for each 100-m increase in elevation above sea level for $\delta^{18}O$, and for deuterium, it is about –1 to –4‰ for the same gradient (in Europe and Africa). In the broader area of Croatia, the gradient is between 0.26, for coastal station, to 0.37 ‰, for continental observation station (KRAJCAR BRONIĆ et al., 2004; KRAJCAR BRONIĆ et al., 2003). In accordance with this estimation, the elevations above sea level of the predominant recharge areas of the investigated springs were measured. The Živulja spring, with a small catchment area and with constant discharge, was chosen as the referential source. However, the obtained values were too high for the Plitvice spring; therefore, a reasonably greater gradient was used: 0.4‰/100-m elevation above sea level (Fig. 16). In spite of the small number of data (only four sam-

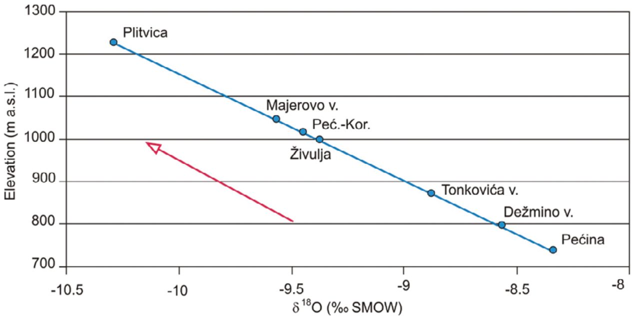

Figure 16: Representation of elevations above sea level of the predominant recharge areas.

pling times per year), this can be explained by the fact that the recharge area of the Plitvice spring in comparison with other springs is mostly under the influence of continental precipitation.

6. CONCLUSION

The investigation area is characterized by very poor surface hydrography, which is characteristic of all the karst areas. Precipitation infiltrates very quickly into the water table, and the springs are mostly situated in contact with the fault zones between the permeable and impermeable deposits. The rocks are mostly represented by carbonates (limestones and dolomites). Structural-tectonic relationships are the main factors for creating the preferential groundwater-flow directions and the occurrence of springs (PRELOGOVIĆ, 1989). The rock-mass division was carried out according to their hydrogeological characteristics. The hinterland of the Gacka spring zone is chiefly composed of very permeable Cretaceous limestones, Palaeogene breccias (Jelar), and impermeable dolomites, alternating with dolomitic limestone or dolomitic breccias to a certain extent. The Jelar breccias are approximately 50% less permeable (BAHUN & FRITZ, 1975) than the Jurassic and Cretaceous carbonates. The Jelar breccias are sorted into the less permeable deposits. Complete barriers, incomplete barriers, and permeable areas can be distinguished based on the rock-mass characteristics. On the basis of the geological, structural-tectonic, hydrogeological, tracer, and hydrological data, the catchment area of the river Gacka was defined as an area extending to 487 m^2. The existing observation network of climatological, rain-gauge, and water-gauge stations in the entire catchment was not satisfactory. The processing of year-long series of hydrological data showed that calculating the balance for only one year does not yield relevant results for the runoff coefficients. The reason for this is the existence of the huge retention space (ŽUGAJ, 1981) in the hinterland of the spring zone, which enables the formation of vast water supplies that flow out in springs and recharge the flow of the river Gacka during the drier period. This is also the reason for the homogenous flow of the river Gacka in which there is no considerable change in the discharge even during years with the most extreme drought conditions.

By analysis of the hydrograms of discharge and precipitation in the period from 01.02.2002. to 31.12.2003., the recession period was chosen, from which the recession coefficients and the approximate runoff quantities from the water-bearing system were calculated (Fig. 3). The calculated recession coefficients led to the conclusion that this is a typical karst aquifer in which, after the period of rainfall, the channel systems and greater fracture zones (quick flow) are emptied first and, subsequently, all smaller joints within the rock mass are emptied. Finally, the shape of the curve increasingly suggests a similarity with the diffuse flow in an intergranular medium (basic flow). It was calculated that during the observed recession period that lasted 175 days, 99 x 10^6 cubic meters of water were discharged. This result corresponds to the analysis of the Gacka river system made by ŽUGAJ (1981), according to which, the average volume of water filling and emptying from the underground retention zone was 103.2 x 10^6 m^3.

Interpretation of the hydrogeochemical data and the statistical processing of field and laboratory data, allowed the hydrogeochemical facies to be determined, and the results obtained aided decision making about both the origin of the groundwater and the characteristics of aquifers. Statistical processing of the hydrochemical data using multivariate cluster analysis of R-modality, resulted in the chosen variables being grouped into three, which could be associated with the three most important processes in this sensitive karst system (Fig. 14):

(1) C1 is the group of all three indicators, two of which belong to limestone dissolution (Ca^{2+} and HCO_3^-). The third indicator in C1 is EC, which practically indicates that karstification has the greatest impact on EC, and therefore, on mineralization of the tested water samples;

(2) C2 is the human-induced factor, or pollution, which mostly originates from the salt used for melting the ice from roads and motorways within the catchment area; and

(3) C3 is again a natural lithogeochemical factor, associated with the washing out of the soil and the epikarst zone; nevertheless, the interpretation level is less clear than from the first two clusters, because it has only two parameters (Mg^{2+} and NO_3^-). Compounds that are washed out by the first heavy rains in the beginning of the rainy season are natural (Mg^{2+}, from dolomite rock fragments) or nitrogen transformation (NO_3^-, nitrification caused by agriculture and plant-respiration processes).

Hydrochemical analyses identified characteristics of particular springs and their mutual similarities and differences. In the springs from the Korana catchment, the ratios of Mg and Ca ions are considerably higher than in the springs of other catchments, which suggests that the aquifer is situated predominantly in the midst of dolomites. In the catchment of the river Gacka on Majerovo vrelo, greater concentrations of Mg ions were measured than in other Gacka springs. It appears that the recharge area of this part of the catchment is characterized by dolomites in the deeper zones of the karst aquifer. The nitrate and phosphate concentrations are very low, which shows the superior quality of groundwater.

The ratios of the stable isotopes of oxygen and hydrogen enabled the determination of the average elevation of the recharge areas of particular springs. On the basis of these data, it was concluded that the recharge area of the Plitvice spring has the highest elevation. It is followed by Majerovo vrelo, Pećina-Korenica, Tonkovića vrelo, Dežmino vrelo, and Pećina, in order of decreasing elevation (Fig. 16). For more precise results, the sampling should be undertaken more often. These results were obtained on the basis of only four samplings during the observed hydrological year, in which rainy and snowy months prevailed, and at these times, the precipitation was enriched with the lighter isotopes.

A multidisciplinary approach, with a special reference to hydrogeochemical and isotopic data, allowed a better understanding of this complex karst system and its catchment boundaries.

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