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The impact of lithology in the recharge area on the hydrochemical properties of the Slatinski Izvor spring (North Macedonia)

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Abstract

The Slatinski Izvor spring is located in the Poreče basin, in the Slatinska Reka river valley in the central part of the Treska river basin. Hydrochemical characteristics of water from the karst spring Slatinski Izvor were analysed in the period between June 2013 and June 2014. The results showed that the lithology of the catchment area of the spring is reflected in the chemical composition of the water. All used methods showed that spring belongs to calcium bicarbonate water type. The spring had typical shallow and fresh water and short residence time of the water in the karst aquifer. All water samples had low concentration of nutrients and heavy metals and can be considered as potential for water supply and irrigation.

Key words: karst spring, hydrochemistry, Slatinski Izvor

Introduction

Karst aquifer hold significant amounts of groundwater, and since carbonate rocks cover 35% of the surface in Europe (COST Action 65 1995) they are an important source of drinking water. In addition to their quantity, the quality of karst waters is becoming increasingly important. Because of the specific nature and unique hydrogeological characteristics, karst aquifers require specific investigation approach such as hydrochemical methods implementation. Hydrochemical study provides significant information about water quality, but also insight into the functioning of the karst aquifers (Hunkeler & Mudry 2007), reflects the nature of the recharge area that feeds the spring (Palmer 2007), residence times, water-rock interactions, human impacts, etc.

Karst aquifers in North Macedonia are very important for water supply of several cities, such as: Skopje, Kičevo, Prilep, Ohrid, Gostivar, Kavadarci, Struga (Mircovski & Spasovski 2005). In the Poreče basin, which is the largest karst region in the country (Kolcakovski & Boskovska 2007, Temovski 2012), there are several karst springs, including the Slatinski Izvor spring. The present study present follow-up of the research on the basic hydrochemical properties of waters from the Slatinski Izvor spring (Gičevski et al. 2015). The main aim of the paper was to understand the impact of the lithology in the recharge area on the hydrochemical characteristics of the spring water.

Study area

The Slatinski Izvor spring is situated in the Poreče basin, in the river valley of Slatinska Reka which is created with the confluence of the rivers Kruševska Reka and Markoska Reka. This spring is 2.5 km downstream

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from the village Slatina, in the southeast direction. The study site is part of the protected area Monument of Nature Slatinski Izvor.

The wider area is built in pre-Cambrian dolomite marbles which are tectonically crushed and well karstified. Paleozoic quartz-sericite schists and metasandstones, metarhyolite tuffs, muscovite-chlorite-quartz schists and epidote-chlorite-amphibole schists prevail in the western part, which are moderately-permeable rocks with fissure porosity. Mesozoic aplitic granite with fissure porosity can be found between the marbles and the Paleozoic rocks. The carbonate rocks are covered with Pliocene sediments (gravel, sands, clay) which are highly-permeable rocks with intergranular porosity. Quaternary sediments are represented by moraines in the upper parts of Pesjak Mountain, and alluvium that fills the river bed of Slatinska Reka (Dumurdžanov et al. 1978, 1979) - both of these units have intergranular porosity.

The karst spring Slatinski Izvor is situated in the Pelagonian horst-anticlinorium tectonic unit which is separated from the Western Macedonian tectonic unit with a fault in NW-SE direction, traced for more than 50 km (Dumurdzanov et al. 2005). There is a covered fault on the river bed of Krušeska Reka in NW-SE direction (Fig. 1).

The lower part of the river Slatinska Reka has karst surface morphology and well developed underground karst relief represented by five caves. The spring Slatinski Izvor serves as an entrance for the cave Slatinski Izvor, and represents the main outflow of groundwater from this karst system (Petreska 2004; Gičevski & Hristovski 2015; Gičevski et al. 2016, 2017).

The karst spring Slatinski Izvor is the largest and the most important spring in the area, and it is captured for water supply. It is intermittent spring, which discharge varies between 0 and 100 L/sec.

Materials and methods

In order to identify the chemical characteristics of the spring water, field measurements and laboratory analyses were carried out. The water samples were collected every month between June 2013 and June 2014. Water temperature, pH and electrical conductivity were measured *in-situ* at the time of sample collection using the field type instruments, with a hand-held water quality meter. Samples were collected manually in polyethylene bottles.

The hydrochemical characteristics were analysed at the Institute of Biology, Faculty of Natural Science and Mathematics, Ss. Cyril and Methodius University in Skopje. All water samples were filtered within 12 hours of collection and analysed within 3-4 days. Sulphate was determined by photometric method of Dèvai *et al.* (1973) and chlorides by Mohr's method (Škunca-Milovanović *et al.* 1990). All of the major cations: calcium (Ca), magnesium (Mg), sodium (Na) potassium (K), as well as minor cations and trace elements: copper (Cu), manganese (Mn), zinc (Zn), iron (Fe) were analysed by wet acid digestion followed by atomic absorption spectrometry on Agilent 55Z or graphite furnace Agilent 240Z (Allen 1989). All of the values are presented in mass concentrations (mg/L).

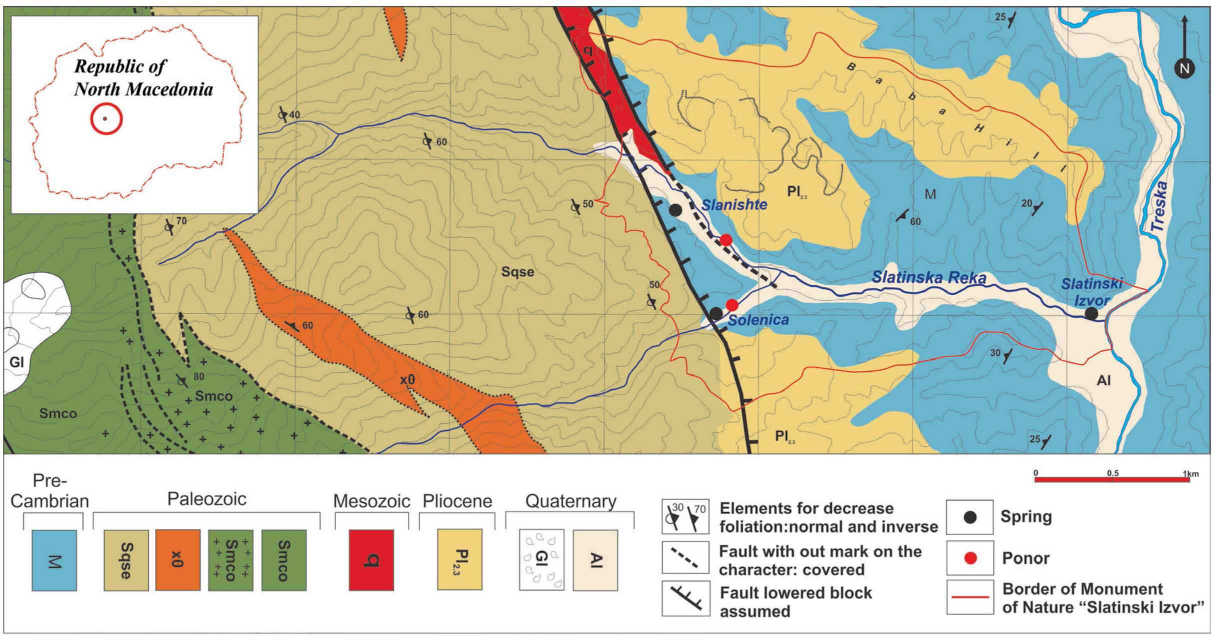

Figure 1. Hydrogeological map of the study area.

Legend: M-dolomite marbles, Sqse-quartz-sericite schists and metasandstones, xΘ- metarhyolite tuffs,Smco-muscovite-chlorite-quartz schists, Smco- epidote-chlorite-amphibole schists, q-aplitic granite, $Pl_{2,3}$-pliocene sediments, Gl-moraines, Al-alluvium.

The Mg/Ca ratio was calculated based on values of respective ions expressed in meq/L.

Total hardness, TH (as mg/L $CaCO_3$) of spring water samples was calculated by using the following equation (White 2010):

$$TH = 100.09\left(\frac{Ca\,(mg/L)}{40.08} + \frac{Mg\,(mg/L)}{24.305}\right)$$

Piper diagram (Piper 1944) was used for the interpretation of the chemical analyses of the water samples. The major cations and anions are plotted in milligram per litter, in each triangle, then the plotting from triangular fields was extended further into the central diamond field. The trilinear Piper diagram was used to identify the water composition type and rock types of the aquifer.

D'Amore *et al.* (1983) determined six parameters for distinguishing water groups based on the geological characteristics of the main reservoir crossed by each water sample. Hydrochemical parameters are marked by letters from A to F:

$$A: \frac{100}{\Sigma\,(-)}(HCO_3^- - SO_4^{2-})$$

$$B: 100\left(\frac{SO_4^{2-}}{\Sigma\,(-)} - \frac{Na^+}{\Sigma\,(+)}\right)$$

$$C: 100\left(\frac{Na^+}{\Sigma\,(+)} - \frac{Cl^-}{\Sigma\,(-)}\right)$$

$$D: 100\left(\frac{Na^+ - Mg^{2+}}{\Sigma\,(+)}\right)$$

$$E: 100\left(\frac{Ca^{2+} + Mg^{2+}}{\Sigma\,(+)} - \frac{HCO_3^-}{\Sigma\,(-)}\right)$$

$$F: 100\left(\frac{Ca^{2+} - Na^+ - K^+}{\Sigma\,(+)}\right)$$

Parameters define the ratio between dissolved species where brackets represent concentrations in meq/L, and range from +100 to -100 meq/L. Sum Σ represents the sum of cation and anion concentrations. Parameter A helps to differentiate between water circulation in calcareous soils and those in evaporitic rocks. Parameter B distinguishes between sulphate-enriched water that circulates in evaporitic soils and sodium-enriched water that encounters marly, clayey sedimentary soils. Parameter C distinguishes between waters that originate from ‚flysch' or ‚volcanites' and those that originate from carbonate-evaporite series or from a regional quartzitic shale rock. Parameter D differentiates between waters that have circulated in dolomitized limestone. Parameter E distinguishes between circulations in carbonate aquifers and those in sulphate-containing aquifers. Parameter F indicates the increasing K^+ concentration in the water samples.

Sodium absorption ratio (SAR) is commonly used as an index to determine water quality for irrigation purposes. SAR is an important parameter to measure the sodium hazard for water having high bicarbonate concentration. Therefore, water quality of the collected water samples was evaluated by determining SAR. SAR was calculated by the following equation (Wilcox 1955):

$$SAR = \frac{Na}{\sqrt{(Ca + Mg)/2}}$$

where concentrations are expressed in meq/L.

Results and discussion

Hydrochemical properties of the spring water and water-rock interaction

Tab. 1 gives the general hydrochemical characteristics of water samples. The Slatinski Izvor spring showed small temperature variation, ranging from 8°C to 10.4°C. All water samples belong to the

Table 1. Hydrochemical data from the spring Slatinski Izvor.

Parameters	Min	Max	Mean	Number of samples	WHO guideline values (WHO2011)	Macedonian guideline values (OGRM 2006)
Temp. (°C)	8.0	10.4	9.64	13		
pH	7.2	8.2	7.82	13	6.5-8.5	
EC (µS/cm)	200	300	243.07	13	1500	
Ca^{2+} (mg/L)	12.69	35.83	23.02	12	75	150
Mg^{2+} (mg/L)	5.75	11.91	8.67	13	50	50
Cl^- (mg/L)	10.4	21.6	14.61	13	250	200
Na^+ (mg/L)	2.64	5.258	3.77	13	200	200
K^+ (mg/L)	0.76	1.603	1.04	13	12	
SO_4^{2-} (mg/L)	12.83	34.94	23.36	13	250	200
HCO_3^- (mg/L)	176.9	250.1	222.41	13	500	600
NO_3^- (mg/L)	0.00	1.69	0.84	13	50	50
NO_2^- (mg/L)	0.00	1.41	0.22	13		0.1
NH_4^+ (mg/L)	0.12	0.61	0.36	13		
TH (mg/L)	73.56	132.51	92.27	13	500	

water group with alkaline reaction, with pH oscillating from 7.2 to 8.2. The electrical conductivity (EC) values varied from 200 µS/cm to 300 µS/cm that is attributed to the short residence time of water in the karst aquifer.

The Ca^{2+}, Mg^{2+} and Na^{+} were the dominant cations, whereas HCO_3^-, SO_4^{2-} and Cl^- were the dominant anions in the spring water. The mean concentrations of the chemical parameters were: Ca^{2+}= 23.02 mg/L, Mg^{2+}= 8.67 mg/L, Na^{+}= 3.77 mg/L, HCO_3^-= 222.41 mg/L, SO_4^{2-}= 23.36 mg/L, Cl^-= 14.61 mg/L. All water samples had low concentrations of Na^+ (3.77 mg/L) and K^+ (1.04 mg/L). HCO_3^- and SO_4^{2-} were the dominant dissolved species in the water, indicating the predominant carbonate and sulphate rocks in the catchment area.

The presented chemical composition of the water samples (Tab. 1) is very similar to the results from previous investigation conducted in the period 2011-2013 (Gičevski et al. 2015).

Cation and anion concentrations are presented on Piper diagram (Fig. 2). Water is reach in Ca^{2+}, Mg^{2+} and HCO_3^- and is the plot area of water of temporary hardness. The hydrochemical facies suggest that dissolution processes of the carbonate rocks control the hydrochemistry of spring water. The hydrochemical type of Slatinski Izvor spring was Ca-HCO_3 which resulted mainly from dissolution of dolomite in the catchment area. This type of water is typical of shallow and fresh waters.

Water-rock interaction

The calculated values of the parameters A-F for the water samples of the Slatinski Izvor spring are plotted in rectangular D'Amore diagram (Fig. 3). The spring water belongs to β type which is characterized by typical Ca-HCO_3 type of water. The high values of the A parameter point out to a water circulation within carbonate terrains. The negative values of the B parameter point out to the sodium enriched water that encountered clay sediments, whereas the values of the C parameter exclude the essential influence of flysch and clayey sediments. The negative values of the D parameter point out to a water circulation within dolomite limestone. The values of the E parameter indicate that the water circulates through rock that contain sulphates. The high values of the F parameter show that the calcium concentration is dominant in relation to sodium and potassium.

The Mg/Ca molar ratio in the collected water samples provides information on water-rock interaction in the catchment area. The Mg/Ca is a useful parameter providing the lithological composition of carbonate rock through which the water circulates (White 1988). A ratio Mg/Ca=1 is for dissolved water from dolomite, whereas a ratio Mg/Ca=0 is for dissolved water from pure calcite. A ratio Mg/Ca of 0.5 indicates an equilibrium between calcite and dolomite. All water samples (Fig. 4) are above the line of 0.5 or near below it, suggesting dominant dissolution of dolomitic limestone or dolomite in the catchment area.

Four trace elements (Cu, Mn, Zn, Fe) were studied (Tab. 2). Their concentrations in spring water depend on aquifer mineralogy and on chemical rock-water interaction. The concentrations of trace elements (heavy metals) in the water samples were low and they are not a significant contaminant of the spring. The

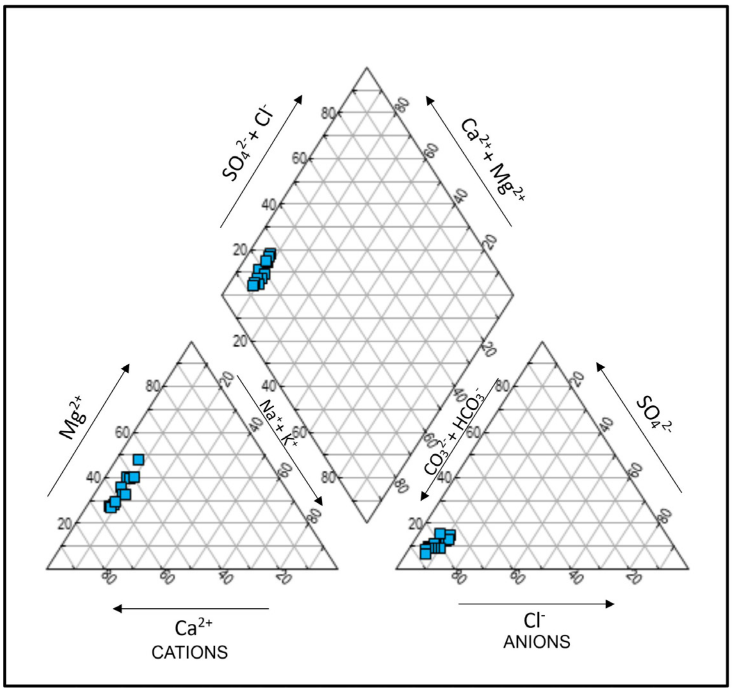

Figure 2. Piper diagram of water of spring Slatinski Izvor.

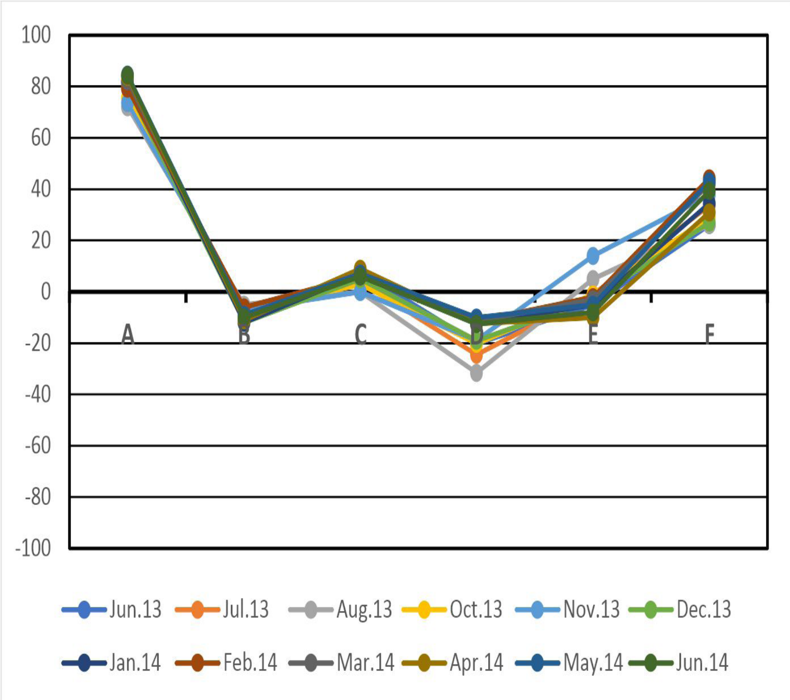

Figure 3. D'Amore diagram for the Slatinski Izvor spring.

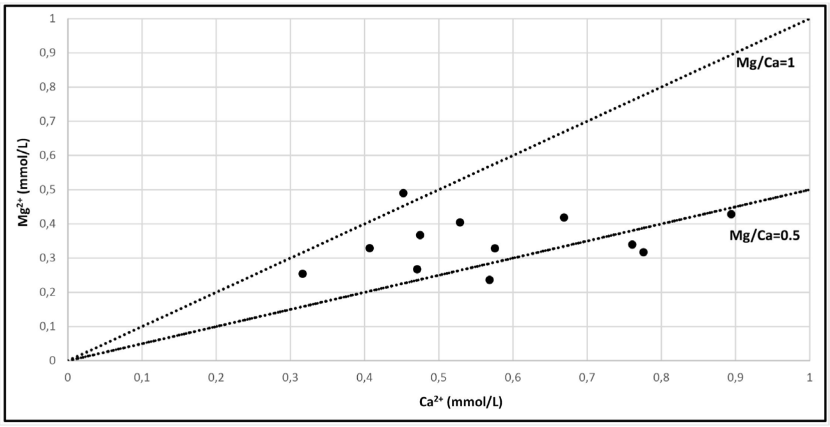

Figure 4. Molar ratio of magnesium to calcium in the spring Slatinski Izvor.

highest concentration had Cu, which with Mn can be derived from dissolution of carbonates and oxidation of sulphides (Kilchmann *et al.* 2004).

Table 2. Trace elements in the water samples of the Slatinski Izvor spring (mg/L).

Parameters	Min	Max	Mean
Cu	1.75	9.75	3.54
Mn	0.00	0.02	0.00
Zn	0.003	0.051	0.01
Fe	0.03	0.112	0.15

Drinking water quality and irrigation water quality

The concentration of major ions in the spring water samples and their comparison with the World Health Organization (WHO) (2011) and Macedonian Regulations of Natural Mineral Water (Official gazette of the Republic of Macedonia, No. 32/2006) are presented in Tab.1. In general, the concentration of major ions of water samples were within acceptable limits of both WHO and Macedonian drinking water standards. All water samples from the Slatinski Izvor spring showed good quality, especially regarding the low values of maximum recorded concentrations of nitrate (1.69

mg/L), nitrite (1.41 mg/L), and ammonium (0.61 mg/L). The Slatinski Izvor spring is suitable for water supply.

Based on total hardness values, four types of water are classified: < 75 mg/L $CaCO_3$ as soft; 75-150 mg/L $CaCO_3$ as moderately hard; 150-300 mg/L $CaCO_3$ as hard; and > 300 mg/L $CaCO_3$ as very hard (EPA 1986). Both extreme degrees of soft (< 75 mg/L as $CaCO_3$) and very hard (> 300 mg/L as $CaCO_3$) are considered as undesirable properties of waters. Waters with hardness over 500 mg/L are not suitable for most domestic purposes. The total hardness values of the Slatinski Izvor spring are presented in Tab. 1. All samples had hardness values below the allowable limit for domestic use. However, most of water samples fall into moderately hard, and only two water samples belonged between soft and moderately hard.

Water having high sodium absorption ratio (SAR) values is not suitable for irrigation because it can damage the soil structure and create permeability problem. If the SAR value < 10, the water is safe for irrigation (Wilcox 1955). The SAR values of the Slatinski Izvor spring were all less than 0.27, which indicates excellent quality for irrigation purposes.

Conclusion

The results showed that the lithology of the catchment area of the Slatinski Izvor spring is reflected in chemical composition of the spring water. Hydrochemical analyses of water samples pointed out the predominant carbonate and sulphate rocks in the catchment area. The study area represent a contact karst where the water comes from a non-carbonate area which has lesser impact on water chemistry. The water sinks at the contact between non-carbonate and carbonate rocks and flows through the karst system. The karst lithology of the catchment area has a major influence on the hydrochemical composition of the spring water.

The spring water hydrochemical facies was classified as calcium bicarbonate ($Ca\text{-}HCO_3$) type suggested that the dissolution of dolomite rocks in the catchment area is controlling water chemistry. This type of water is typical of shallow and fresh waters.

The electrical conductivity values were attributed to the short residence time of water in the karst aquifer.

The concentrations of trace elements in the water samples were low and they are not a significant contaminant of the spring. Their concentration can be derived from dissolution of carbonates and oxidation of sulphides.

Low concentrations of nitrates, nitrites, and ammonia show low anthropogenic impact and low pollution. All water samples can be considered at potentially suitable for water supply and irrigation purposes.

References

Allen, S.E. (ed.) (1989). *Chemical analysis of ecological materials*. Blackwell scientific publication, pp. 368, Oxford-London-Edinburgh-Boston-Melbourne.

COST Action 65 (1995). *Hydrogeological aspects of groundwater protection in karstic areas*. Final report. European Commission, Directorate-General XII, Science, Research and Development, Report EUR 16574 EN.

D'Amore, F., Scandiffio, G., Panichi, C. (1983). Some observations on the chemical classification of ground water. *Geothermics*, **12**: 141-148.

Dèvai, I., Horváth, K., Dèvai, G. (1973). Sulphate content determination of natural waters and description of a new photometric procedure. *Acta. Biol. Debrecina*, **10-11**: 129-142 (in Hungarian).

Dumurdžanov N., Stojanov R., Petrovski K. (1978): General Geological map of SFRJ in 1:100 000: sheet Kruševo (K 34-91). Federal Geological Survey, Beograd, 58 p.

Dumurdžanov N., Stojanov R., Petrovski K. (1979): Explanatory notes for the General Geological map of SFRJ: sheet Kruševo. Federal Geological Survey, Beograd, 58 p.

Dumurdzanov, N., Serafimovski, T., Burchfiel, B. C. (2005). Cenozoic tectonics of Macedonia and its relation to the South Balkan extensional regime. *Geosphere*, **1**(**1**): 1-22.

EPA (1986). Quality criteria for water 1986. US Environmental Protection Agency, EPA 440/5-86-001. Washington, DC 20460.

Gičevski, B., Hristovski, S. (2015). Hydrochemical properties of cave lake and ground water flow in the cave of Slatinski Izvor in the dry period of the year. *Contributions, Section of Natural, Mathematical and Biotechnical Sciences, MASA*, **36**(**1**): 19-26.

Gičevski, B., Hristovski, S., Mirčovski, V., Boev, B. (2015). Hydrochemical properties of springs Slatinski Izvor and Solenica (Republic of Macedonia). *Acta carsologica* **44**(**2**), 215–226.

Gičevski, B., Petrič, M., Kogovšek, J. (2016). Interpreting groundwater character from flood pulses and artificial tracer test – A case study of the Slatinski Izvor spring (Republic of Macedonia). *Third Congress of Geologists of Republic of Macedonia*, 67-76.

Gičevski, B., Hristovski, S., Petrič, M. (2017). Drip water in cave Slatinski Izvor – hydrochemical properties and its influence on the discharge of the spring Slatinski Izvor during low waters. *Proceedings of the 5th Congress of Ecologists of Macedonia with International Participation*, Ohrid, 19-22 October 2016. Macedonian Eco logical Society, Skopje, 82-89.

Hunkeler, D., Mudry, J. (2007). Hydrochemical methods. In Goldscheider, N. & David, D. (eds). *Methods in Karst Hydrogeology.* Taylor & Francis, 93-121.

Kilchmann, S., Waber, H. N., Parriaux, A., Bensimon, M. (2004). Natural tracers in recent groundwaters from different Alpine aquifers. *Hydrogeology Journal*, **12**: 643-661.

Kolcakovski, D., Boskovska, G. (2007). Extension and age of carbonate rocks in Republic of Macedonia. *Bulletin of Physical Geography*, **3**/**4**: 77-82.

Mircovski, V., Spasovski O. (2005). Water supply from the karst aquifers in the Republic of Macedonia. International Conference "Water Resources and Environmental Problems in Karst", Belagrade-Kotor, 2005, 291-294.

OGRM (2006). Ordinance for special requirements of natural mineral water safety *Official gazette of the Republic of Macedonia*, **32**: 10-15.

Palmer, N.A. (2007). *Cave geology*. Cave Books, Dayton, Ohio, 454 pp.

Petreska, B. (2004). Slatina spring. *Bulletin of Physical Geography*, **1**: 87-95.

Piper, A. M. (1944). A graphical procedure in the geochemical interpretation of water analyses. *Transactions American Geophysical Union*, **25**: 914-923.

Škunca-Milovanović, S., Feliks, R., Đurović, B. (1990). *Voda za piće – Standardne metode za ispitivanje higijenske ispravnosti*. Savezni zavod za zdravstvenu zaštitu, Beograd, 844 pp.

Temovski, M. (2012). Površinska rasprostranetost na karstnite karpi vo Republika Makedonija, Geografski razgledi, Skopje, 46, 21–35.

Wilcox, L. V. (1955). *Classification and use of irrigation waters*. USDA Circ. 969, Washington, DC.

White, W. B. (1988). *Geomorphology and hydrology of karst terrains*. Oxford University Press, New York, 464 pp.

White, W.B. (2010). Springwater geochemistry. In: Kresic, N., Stevanovic, Z. (eds). *Groundwater Hydrology of Springs – Engineering, Theory, Management and Sustainability*. Elsevier, 231-268.

WHO (2011). Guidelines for drinking-water quality. World Health Organisation, 541 pp.