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Hydrological and hydrochemical characteristics of the lower part of the river basin of Slatinska Reka, Republic of North Macedonia

Хидролошки и хидрохемиски карактеристики во долниот дел од речниот слив на Слатинска Река

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Abstract:

The lower part of the river basin of the Slatinska Reka river is protected in the category of Monument of Nature and it is placed on the tentative list of UNESCO World Heritage Sites. The chosen locations in which sampling were done are situated within the karstic part of the river basin.
The hydrological method applied on the surface streams, points out that the karstification has strong influence on the discharges along the streams. The losses of water are constantly increasing in downstream direction. In order to understand the hydrochemical properties of the surface streams, water samples were taken monthly from four points between December 2011 and November 2013. For all water samples, the measurements included temperature, pH and electrical conductivity, as well as mass concentrations of major ions of calcium, magnesium, bicarbonate, chloride, sulfate, potassium, sodium, nitrate, nitrite, ammonium and trace elements (Zn, P, Mn, Fe, Cu, Cd, Pb, Co). HCO_3^- and SO_4^{2-} were dominant dissolved species in all water samples. The hydrochemical results showed that the lithology of the area is reflected in the chemical composition of the waters and the anthropogenic impact is very low. In agreement with the current Macedonian Regulations of Natural Mineral Water the overall water quality of Slatinska Reka fits into the 1st quality class.

Keywords: Slatinska Reka river, daily discharge, physical properties, water chemistry, water quality

Долниот дел од речниот слив на Слатинска Река е заштитен во категоријата споменик на природата и се наоѓа на тентативната листа на подрачја од светското наследство на UNESCO. Истражувањето беше спроведено во карстниот дел од речниот слив.
Истражувањата на површинските води укажуваат дека карстификацијата има силно влијание врз протокот на реката, при што загубите на вода се зголемуваат низводно по течението.

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Примероци од вода беа собирани месечно во периодот декември 2011 – ноември 2013 година од четири точки со цел да се утврдат хидрохемиските карактеристики. Притоа, следните параметри беа анализирани: температура, pH, спроводливост, концентрација на главните јони (Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, SO_4^{2-}, K^+, Na^+, NO_3^-, NO_2^-, NH_4^+), како и концентрација на елементи во трагови (Zn, P, Mn, Fe, Cu, Cd, Pb, Co). HCO_3^-и SO_4^{2-} беа доминантните анјони во сите анализирани примероци вода. Хидрохемиските резултати покажаа дека литологијата на подрачјето се рефлектира во хемискиот состав на водите, додека антропогеното влијание е многу ниско. Според македонската класификација, водите од Слатинска река припаѓаат на I класа.

Клучни зборови: Слатинска Река, дневен проток, физички карактеристики, хемиски состав, квалитет на вода

Introduction

Karst terrains have complex characteristics and they represent a unique environment due to their specific morphology, hydrology and biota. People have been living on karst for millennia, and therefore it is important to study and understand the processes in the karst and protect it as these terrains are vulnerable to environmental impacts. Unfortunately, distortion of the ecological balance of the karst systems results from different activities of people (Williams, 1993; Kranjc, 1995). Exploitation of karst water can constitute a positive socio-economic force, but also the exploitation is often accompanied by a negative impact which affects the environment.

Because karst waters have unique and specific nature, they require specifically adapted research methods. In this paper some hydrological and hydrochemical results are presented. A monitoring network was combined with regular sampling for major and trace elements analysis.The data from two-year period (December 2011 - November 2013) were analyzed. The main purpose of the paper is to understand the impact of the karstification to the

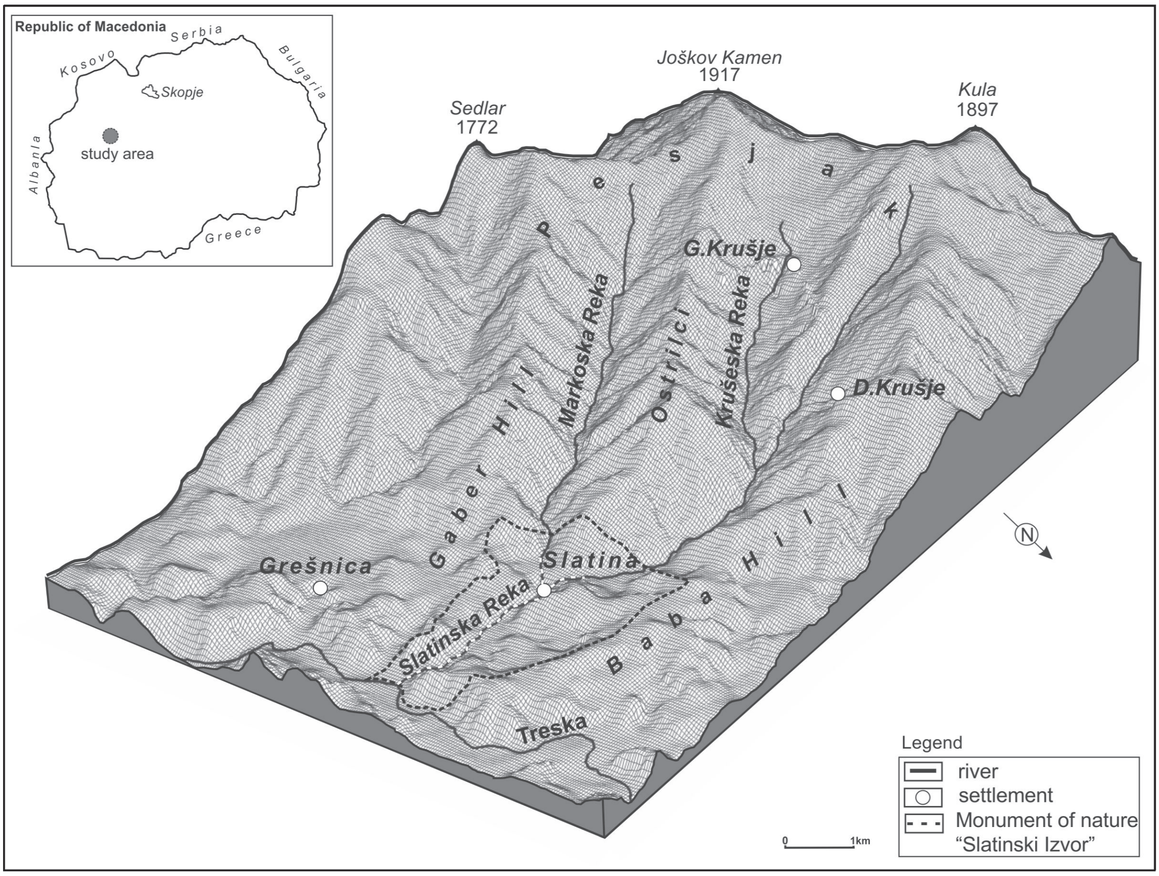

Fig. 1. Geographical location of the research area

discharges along the Slatinska Reka river, and to determine the hydrochemical characteristics of the surface water.

Study area

The river valley of Slatinska Reka is located in the Poreče basin of western part of the country, in the middle part of the Treska river drainage basin (Fig. 1). Slatinska Reka, a left tributary of the Treska river is created with the confluence of the rivers Kruševska Reka and Markoska Reka. The springs of these two streams are located on Pesjak mountain at 1740 and 1530 m a.s.l., respectively. Both streams confluence downstream near the Slatina village. Slatinska Reka is flowing in W-E direction. The river is 9.8 km long with an average gradient of 126.5 ‰. The river basin has an area of 30.170 km^2, and the confluence with the Treska river is at 500 m a.s.l.

The lower part of the river valley is composed of Precambrian dolomite marble which is tectonically crushed and well karstified. Carbonates cover 4.96 km^2 of Slatinska Reka drainage basin. Ca and Mg are the dominant major elements in the carbonate rocks, whereas B, Sr and V are the dominant trace elements (Gičevski et al. 2015). Paleozoic quartz-sericite schists and metasandstones, metarhyolite tuffs, muscovite-chlorite-quartz schists and epidote-chlorite-amphibole schists prevail in the upper part, which are moderately-permeable rocks with fissure porosity. Between the marble and the Paleozoic rocks, Mesozoic aplitic granite with fissure porosity can be found. 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 on the upper parts of Pesjak mountain and alluvial deposits which fill the river bed of Slatinska Reka - both of these units have intergranular porosity.

Karst surface morphology in the river valley is influenced by the incision of Slatinska Reka, developing fluviokarst surface morphology a through valley with allogenic river. The underground karst is well developed, and it is represented by five caves which have "normal" epigenic development.

The sources of the sinking streams of Slatinska Reka and its trubitaries Kruševska Reka and Markoska Reka are in a non-carbonate environment. At the contact with carbonate rocks, the streams sink underground as a point input into the karst system, and continue to flow underground. Nowadays, the karst spring Slatinski Izvor which serves as an entrance of the same cave, represents the main outflow of groundwater from this karst system (Petreska 2004; Gičevski & Hristovski 2015; Gičevski et al. 2016).

In the river valley, there are three small, almost depopulated settlements (Slatina, Gorno Krušje, Dolno Krušje), with rudimentary agriculture economy. The lower, karst part of the river valley is protected as a Monument of Nature "Slatinski Izvor" and it is placed on the tentative list of UNESCO World Heritage Sites.

The recharge of the Slatinski Izvor spring is a combination of both, allogenic and autogenic recharges. Sinking stream Kruševska Reka provides the allogenic recharge. The rapid circulation of groundwater within the karst system and the connection between the surface stream Kruševska Reka and the spring Slatinski Izvor is confirmed by a natural tracer (flood pulses) and an artificial tracer (Gičevski et al. 2016). The autogenic recharge is represented by precipitation which infiltrates through and is stored in the vadose zone, and subsequently recharges the phreatic zone (Gičevski et al. 2017).

Materials and methods

The float method was used for the measurement water discharge of surface streams. This method requires little time and equipment. Under favourable conditions and with repeated observations, float measurement may be accurate to within an error margin of 10%, whereas in non-uniform sections or where wind is excessive, measurements may be in error by 25% or more (Gordon et al. 2004). The distance between the two points was measured and calculated the average cross-sectional area by multiplying the stream width by its average depth. The stream velocity was calculated as a ratio between the distance of the two stream points and the time required for a floating object to be carried the length of the stream segment. Such measurements give only the surface velocity and a correction factor must be applied to assess the average velocity over a depth. A factor of 0.7 is recommended for a flow of approximately 1 m depth (Shaw 1994). The discharge (Q) is related to the average flow velocity (v) and the cross-sectional area of flow (A) in the following equation:

$$Q=vA$$

A method described by Bonacci (1987)

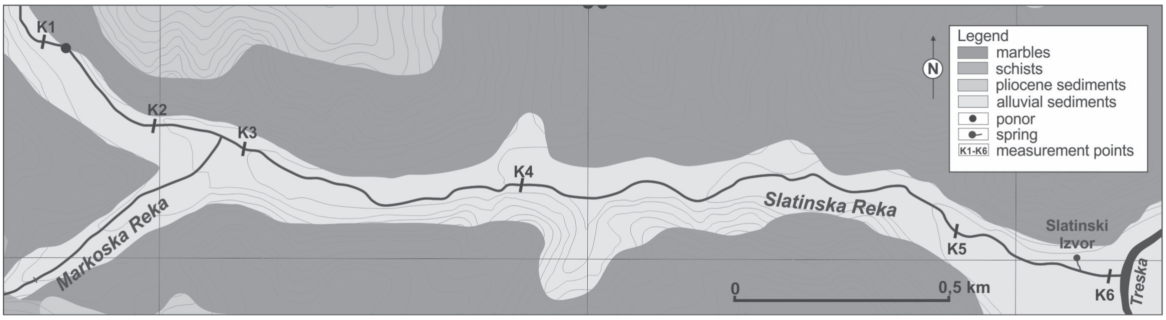

Fig. 2. Locations of the measurement points of discharges in Slatinska Reka basin

was used to show how the karstification affects the discharges along the surface river. The average daily discharges of the downstream station of the section are plotted on the ordinate, whereas the discharge difference between the downstream and upstream section for the same day is plotted on the abscissa. Negative values for the difference in discharges indicate water loss into the karst underground on the analyzed section, whereas positive values indicate a gaining river. The intersection point where a curve crosses the axis is called a "limit discharge" which represents a very important hydrological parameter. The area defined by the curve and the ordinate axis in the negative domain represents an indication of the quantity of losses. When the limit discharge is exceeded it may mean that the aeration zone becomes saturated and groundwater level has risen to the river (Bonacci 1987).

There were six measurement points (K1-K6) with K1 before the ponor and K6 at the confluence of Slatinska Reka with Treska (Fig. 2). Discharge measurements were made between 1st and 7th July 2013.

In order to identify the chemical characteristics of the river waters, field measurements and laboratory analyses were carried out. These were the first continuous analysis for this river basin. The water samples were collected every month between December 2011 and November 2013. A total of 69 water samples were collected from all surface streams (fig. 3). A total of 40 water samples were collected from the stream Markoska Reka, which were taken at two sampling points: the first one at 150 m upstream from the salt spring Solenica (Markoska Reka 1, MR1), and the second one at 100 m downstream from the same spring (Markoska Reka 2, MR2). A total of 19 water samples were collected from the Kruševska Reka immediately before the active ponor, and 10 water samples from Slatinska Reka before the inflow into Treska. The num-

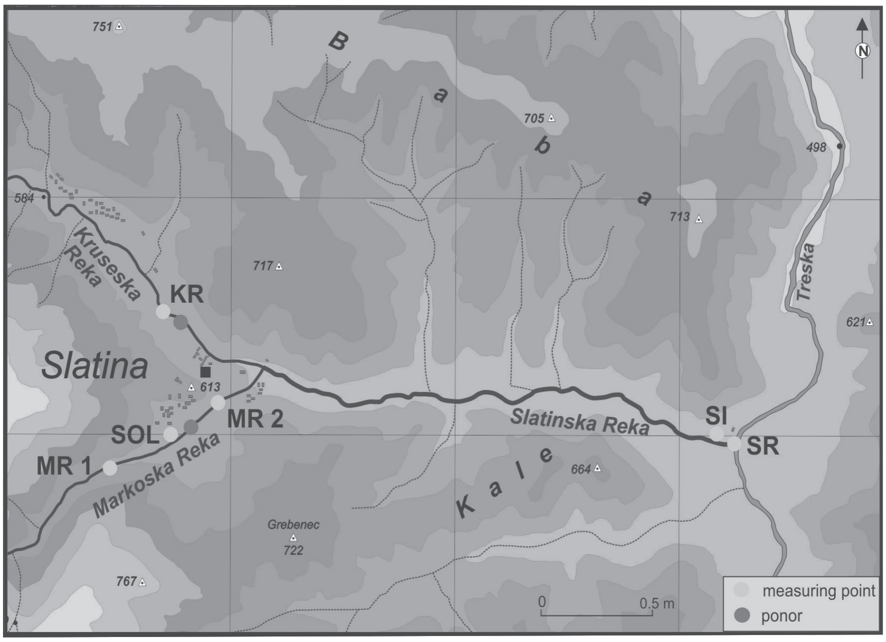

Fig. 3. Map of surface rivers with measuring points marked

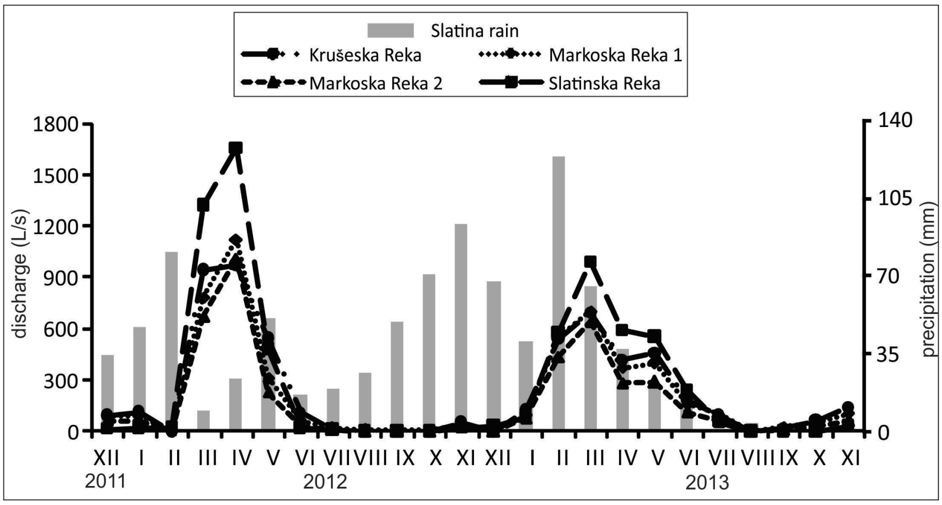

Fig. 4. Discharges of the rivers (measured once a month) in the study area versus precipitation, in the time period between December 2011 - November 2013

bers of water samples depended on the hydrological conditions. Water temperature, pH and specific electrical conductivity (EC) were measured *in-situ* at the time of sample collection using a handheld field instrument Lovibond CHECKIT Micro. Samples were collected manually in polyethylene bottles.

The hydrochemical properties were analyzed at the Institute of Biology, Faculty of Natural Sciences and Mathematics, Ss. Cyril and Methodius University in Skopje. All water samples were filtered within 12 hours of collection and analyzed within 3-4 days. Sulphate (SO_4^{2-}) was determined by the photometric method of Dévai et al. (1973) and chlorides (Cl^-) by the Mohr's method (Škunca-Milovanović et al. 1990). All of the major cations: sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}) as well as minor cations and trace elements: copper (Cu), cadmium (Cd), cobalt (Co), lead (Pb), manganese (Mn), zinc (Zn), iron (Fe) were analyzed by wet digestion followed by atomic absorption spectrometry on Agilent 55Z or graphite furnace Agilent 240Z (Allen 1989). Total phosphorus was determined in the same digested material by the method of Fiske & Subarow (1925). All of the values are presented in mass concentrations ($mg \cdot L^{-1}$).

Piper diagram (Piper 1944) and Chadha diagram (Chadha 1999) were used for the interpretation of the chemical analyses.

The chemical water types in the study area were determined based on their chemical composition using the trilinear Piper diagram (Piper 1944). The major cations and anions are plotted in $mg \cdot L^{-1}$, in each triangle, then the plotting from triangular fields was extended further into the central diamond field. The Piper diagram was used to identify the water composition type and rock types of the aquifer.

In the Chadha diagram (Chadha 1999) the difference in milliequivalent percentage between alkaline earth metals (calcium plus magnesium) and alkali metals (sodium plus potassium), expressed as percentage reacting values, is plotted on the X-axis, and the difference in milliequivalent percentage between weak acidic anions (carbonate plus bicarbonate) and strong acidic anions (chloride plus sulphate) is plotted on the Y-axis. The milliequivalent percentage differences between alkaline earths and alkali metals, and between weak acidic anions and strong acidic anions, would plot in one of the four possible subfields of the proposed diagram. The square or rectangular field describes the overall character of the water.

Results and discussion

Hydrological characteristics of the Slatinska Reka river

The hydrological characteristics of Slatinska Reka are not regularly monitored. For the purpose of this paper, we measured once a month discharges at four positions.

For the first observation year, Kruševska Reka and Markoska Reka had the highest discharges in April, and for the second year in March. This is as a consequence of snow melting on Pesjak Mountain, as well as the rain events (Fig. 4). During August, September and October 2012, and August 2013, their river beds were dry. Slatinska Reka had the highest water levels in April 2012 and in March 2013, while during August, September and October in both years, the river bed was dry. Actually, the river bed downstream of the Slatinski Izvor spring had small amount of water due to the feeding of the spring, while the upstream parts from the spring were dry.

Impact of the karstification on the river discharge

Average daily discharge measurements are presented in Tab. 1. All of the measured daily discharges dropped in the period from July 1st to July 7th, 2013 with K3 showing the highest decrease.

Figure 5 is a graphic presentation of the results obtained during the analysis. The first

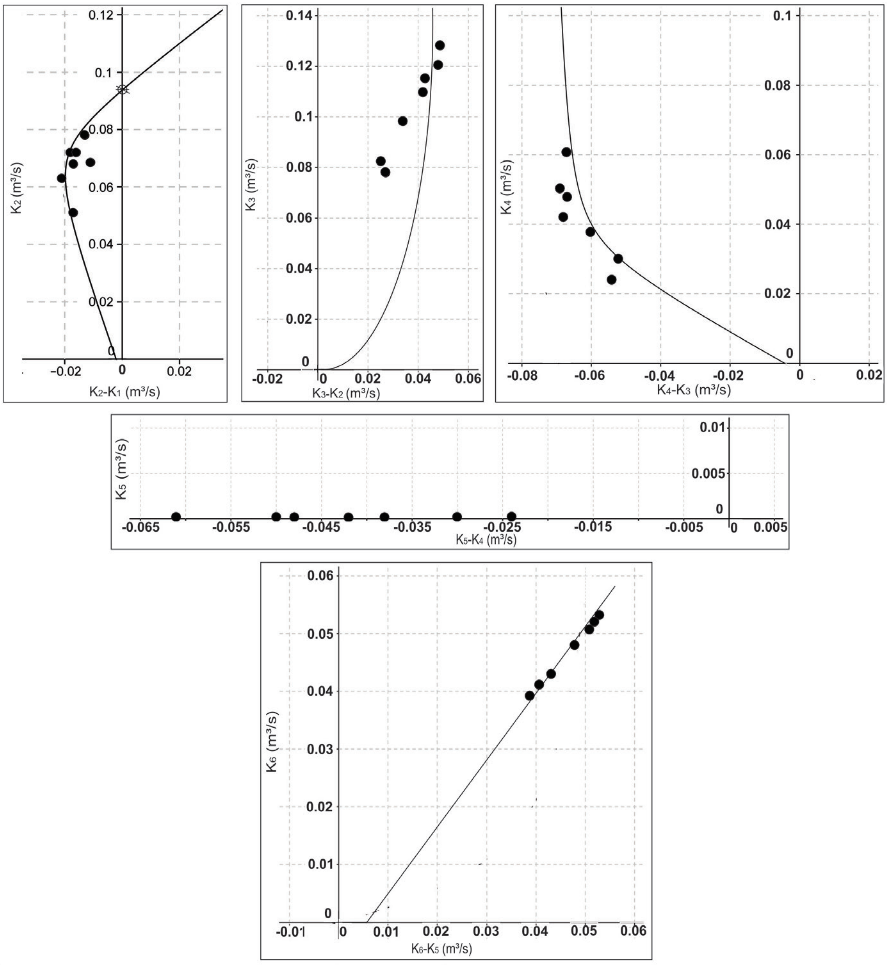

Fig. 5. Flow and discharge properties of different sections of the Slatinska Reka river basin

Table 1. Average daily discharge measurements (m^3/s) on the Slatinska Reka river, from July 1st to July 7th, 2013

	K1	K2	K3	K4	K5	K6
01.07.2013	0.091	0.078	0.128	0.061	0	0.053
02.07.2013	0.090	0.072	0.120	0.050	0	0.051
03.07.2013	0.088	0.072	0.115	0.048	0	0.052
04.07.2013	0.085	0.068	0.110	0.042	0	0.048
05.07.2013	0.085	0.063	0.098	0.038	0	0.043
06.07.2013	0.079	0.057	0.082	0.030	0	0.041
07.07.2013	0.068	0.051	0.078	0.024	0	0.039
Distance (m)	2742	2417	2206	1486	418	0

Table 2. Hydrochemical properties of the surface streams in the Slatinska Reka river basin, for the period December 2011 – October 2013. CV-coefficient of variation, n - number of water samples

	Krušeska Reka (n=19)	Markoska Reka 1 (n=21)	Markoska Reka 2 (n=19)	Slatinska Reka (n=10)
t/°C				
Range	0-20	0-23	0-21	0-17
Mean	8.47	9.85	8.71	9.6
CV	0.67	0.66	0.68	0.61
pH				
Range	7.0-8.3	7.0-8.1	7.0-8.3	7.1-8.2
Mean	7.68	7.60	7.63	7.77
CV	0.06	0.05	0.05	0.05
EC /$\mu S \cdot cm^{-1}$				
Range	100-160	80-150	100-150	150-250
Mean	121	107	118	178
CV	0.17	0.17	0.15	0.18
TDS /$mg \cdot L^{-1}$				
Range	64-102.4	51.2-96	64-96	96-160
Mean	77.67	68.75	75.78	113.92
CV	0.17	0.17	0.15	0.18
$\gamma(Ca^{2+})/mg \cdot L^{-1}$				
Range	4.34-21.60	5.00-19.26	3.94-25.15	7.50-31.96
Mean	10.91	8.90	13.79	15.82
CV	0.41	0.41	0.45	0.47
$\gamma(Mg^{2+})/mg \cdot L^{-1}$				
Range	0.48-2.13	0.25-1.90	0.30-1.84	0.90-9.37
Mean	1.21	0.97	1.09	3.73
CV	0.34	0.40	0.32	0.67
$\gamma(Cl^{-})/mg \cdot L^{-1}$				
Range	6.4-18.8	4.6-8.0	7.2-59.2	6.4-16.0
Mean	10.14	5.94	24.92	9.87
CV	0.33	0.16	0.64	0.31
$\gamma(Na^{+})/mg \cdot L^{-1}$				
Range	1.47-4.95	1.39-2.84	2.09-17.02	1.37-4.03
Mean	3.03	1.94	8.61	2.55
CV	0.33	0.19	0.72	0.28
$\gamma(K^{+})/mg \cdot L^{-1}$				
Range	0.44-0.91	0.49-0.99	0.55-1.23	0.41-0.85
Mean	0.65	0.75	0.89	0.67
CV	0.22	0.17	0.24	0.17
$\gamma(SO_4^{2-})/mg \cdot L^{-1}$				
Range	15.11-52.53	12.53-101.67	9.58-75.12	15.85-31.79
Mean	29.82	35.41	36.50	24.11
CV	0.31	0.62	0.41	0.22
$\gamma(HCO_3^{-})/mg \cdot L^{-1}$				
Range	274.5-298.9	250.1-292.8	256.2-292.8	256.2-286.7
Mean	281.56	282.22	280.22	271.45
CV	0.01	0.02	0.03	0.03
$\gamma(NO_3^{-})/mg \cdot L^{-1}$				
Range	0.00-1.53	0.00-3.28	0.00-1.19	0.00-1.12
Mean	0.39	0.54	0.25	0.28
CV	1.07	1.56	1.32	1.18
$\gamma(NO_2^{-})/mg \cdot L^{-1}$				
Range	0.00-0.123	0.00-0.19	0.00-0.19	0.00-0.17
Mean	0.03	0.04	0.04	0.05
CV	1.12	1.25	1.07	1.18
$\gamma(NH_4^{+})/mg \cdot L^{-1}$				
Range	0.03-0.73	0.00-2.17	0.02-0.82	0.02-1.02
Mean	0.28	0.33	0.32	0.22
CV	0.72	1.45	0.67	1.19

section (K2-K1) represents an indication of the quantitative loss of water. The limit discharge along this section is nearly 0.09 m^3/s. At an increase of the discharge beyond the limit, the ground water starts to recharge the water quantities in Slatinska Reka. The second section (K3-K2) shows inflow which is caused due to the inflow of Markoska Reka at this section. The next two sections (K4-K3 and K5-K4) show that the losses of water are constantly increasing along the downstream profile, and the ground water levels are below the surface riverbed. The discharge of the point K5 of the section K5-K4 is equal to zero. The riverbed at the last section (K6-K5) is supplied with water only from the spring Slatinski Izvor. The shape of the curves in the last two situations is influenced by the fact that the discharge of the point K5 is zero (Fig. 5).

Physical characteristics

The results for the analysis of samples collected from four sampling points in surface streams are given in Tab. 2. All surface waters reflected the outer temperature and their seasonal variations. Average temperature of the stream Kruševska Reka was 8.47°C, of the point Markoska Reka 1 was 9.85°C, of the point Markoska Reka 2 was 8.71°C, and for Slatinska Reka was 9.6°C. The pH values did not change as much by sampling points. The values showed that all water samples belong to waters with alkaline reaction. When all values were taken into consideration, it was observed that all sampling points had 1st class water regarding the water quality according to the Macedonian Regulations of Natural Mineral Water (Official gazette of the Republic of Macedonia, No. 32/2006). The EC values in the surface waters were low, with the mean of 121 for Kruševska Reka, 107 at Markoska Reka 1, 118 at Markoska Reka 2 and 178 $\mu S \cdot cm^{-1}$ at Slatinska Reka. The relatively higher values of EC at Markoska Reka 2 compared to Markoska Reka 1 can be attributed to the impact of the salt spring Solenica. The saline water from the spring has very high EC values (7310.45 $\mu S \cdot cm^{-1}$). This is most probably a deep ancient ground water, which had been retained in the pores of the sediments and has spent a relatively long time in contact with the rocks of the aquifer (Gičevski et al. 2015).

Hydrochemical properties

The major ions in all water samples of the streams Kruševska Reka, Markoska Re-

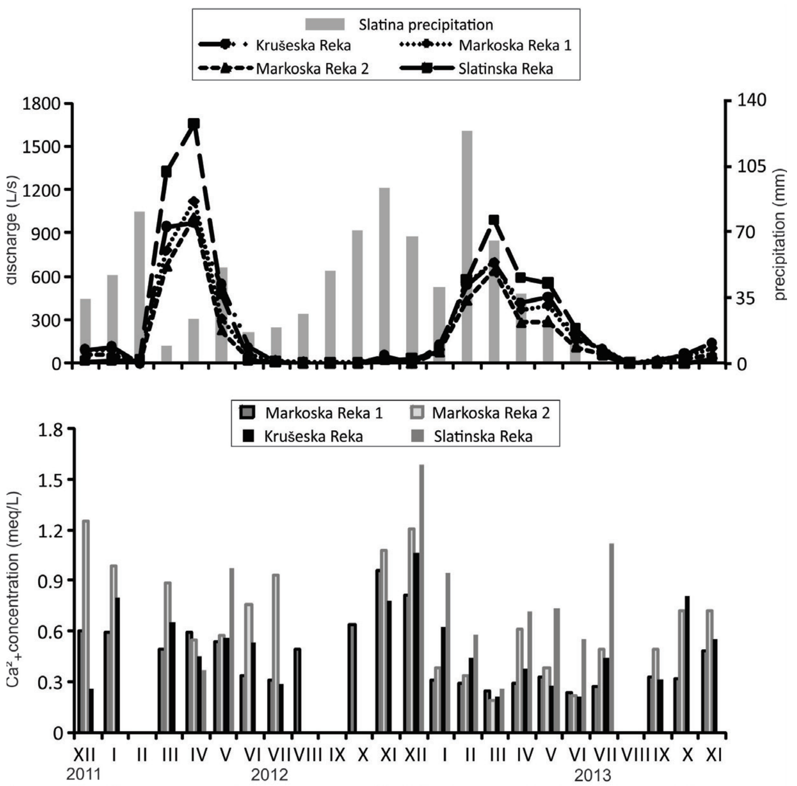

Fig. 6. Ca^{2+} concentration in the surface streams versus stream discharge and precipitation in the Slatinska Reka river basin

Table 3. Trace elements in the water samples of the surface waters in the Slatinska Reka river basin

	concentration range (µg·L^{-1})			
	Kruševska Reka	Markoska Reka 1	Markoska Reka 2	Slatinska Reka
Cu	1.386-8.438	1.525-15.750	1.375-7.000	1.625-6.500
Cd	nd-0.042	nd-0.134	nd-0.046	nd-0.041
Co	nd-0.433	nd-0.171	nd-0.319	nd-0.179
Pb	nd-0.168	nd-0.134	nd-0.341	0.004-0.078
	concentration range (mg·L^{-1})			
	Kruševska Reka	Markoska Reka 1	Markoska Reka 2	Slatinska Reka
Mn	0.001-0.011	0.002-0.023	0.002-0.008	0.001-0.007
Zn	0.002-0.011	0.003-0.019	0.003-0.023	0.003-0.010
Fe	0.016-0.232	0.026-0.491	0.022-1.589	0.020-0.141
P	0.000-0.106	0.002-0.062	0.000-0.102	0.001-0.040

ka 1 and Markoska Reka 2 were dominantly $Ca^{2+}>Na^{+}>Mg^{2+}$ for the cations and $HCO_3^{-}>SO_4^{2-}>Cl^{-}$ for the anions (Tab. 2). The major ions in the Slatinska Reka river were dominantly $Ca^{2+}>Mg^{2+}>Na^{+}$ for the cations and $HCO_3^{-}>SO_4^{2-}>Cl^{-}$ for the anions. HCO_3^{-} and SO_4^{2-} were dominant dissolved species in all water samples.

The quantity of dissolved carbonate increased downstream the streams (Fig. 6). During the higher discharges, there were small concentration of dissolved species in the water, whereas during the low discharges, the concentrations of the dissolved species were higher. Iron is present in the wider area (Gičevski et al. 2015), so sulfate may derive from the oxidation of iron sulphides which can leach into the watercourses.

The average hardness of the water samples of Kruševska Reka, Markoska Reka 1, Markoska Reka 2 and Slatinska Reka were 31.02, 25.77, 37.45 and 53.94 mg·L^{-1}, respectively. This parameter shows that the quantity of dissolved carbonate increased downstream the streams.

All surface waters from the area displayed good quality during the investigation period. The concentration of nitrate, nitrite and ammonium showed small seasonal fluctuation. The low values of potential water contaminants (NO_3^{-}, NO_2^{-}, NH_4^{+} and PO_4^{3-}) in Kruševska Reka and Markoska Reka point out to the low anthropogenic activity in the catchment area during both the dry and the wet periods of the year (Tab. 2). Their average values classify the water into 1st class.

Also, the concentrations of minor and trace elements (Cu, Cd, Co, Pb, Mn, Zn, Fe) in all surface waters were low (Tab. 3). Cu, Co and Fe were present in higher concentrations in comparison to other trace elements because of the water-rock interactions. It can be concluded that the concentration of all of the eight trace elements does not exceed the limit values of the 1st quality class.

Hydrochemical facies

In the Piper diagram (fig.7), most of the samples are plotted in the $Ca\text{-}HCO_3$ field, whereas several water samples taken downstream of the stream Markoska Reka showed $Ca\text{-}Na\text{-}HCO_3$ type. The results show that carbonate rocks have major influence on the water chemistry of the surface streams, and the salt spring Solenica impacts the water quality downstream of Markoska Reka.

All water samples of the streams were also plotted on a Chadha diagram (Fig. 8), and they fall in the 5th sub-field. This indicates that the alkaline earths and weak acidic anions exceed both alkali metals and strong acidic anions, respectively. Such waters have temporary hardness. A few water samples from the stream Markoska Reka fall in the 3th sub-field. This indicates that weak acidic anions exceed strong acidic anions.

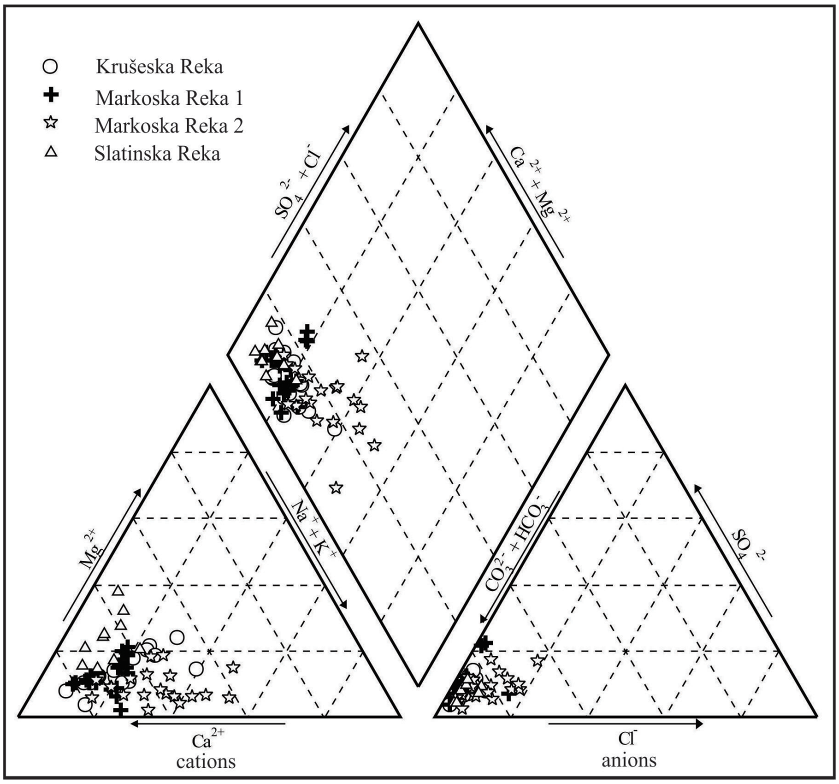

Fig. 7. Piper diagram of the surface waters in the Slatinska Reka river basin

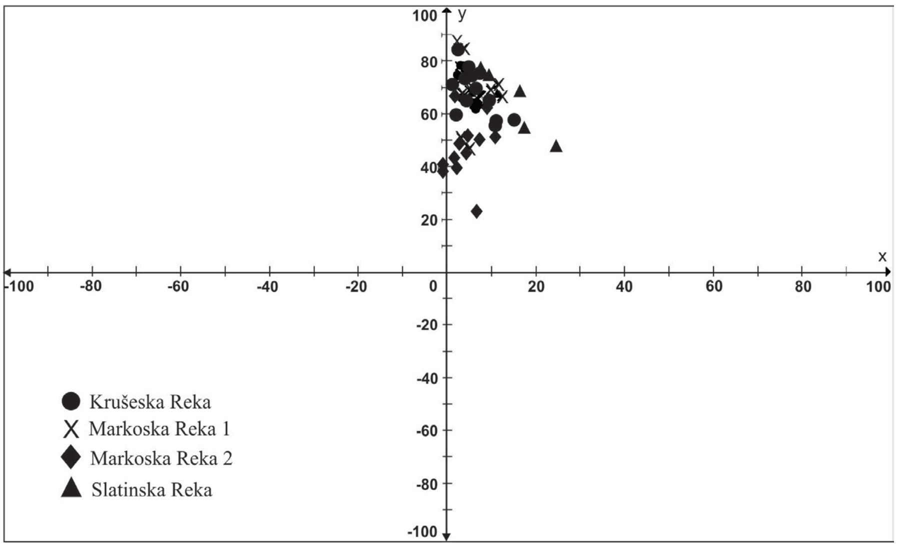

Fig. 8. Chadha diagram of the surface waters in the Slatinska Reka river basin

Conclusion

The catchment of Slatinska Reka is composed of both carbonate and non-carbonate part, each producing a different hydrological response. Investigation of the discharge measurements (during low waters) of the surface streams has shown that, at the contact between non-carbonate and carbonate rocks, the capacity of the ponors is low (nearly 0.09 m^3/s), whereas downstream the river, the losses of water constantly increase.

The results of the hydrochemical analysis point out that carbonate rocks have high influence on the water chemistry of the surface streams, with salt spring Solenica having an impact on the water quality downstream of Markoska Reka. The quantity of dissolved carbonate increased downstream the streams.

All water samples showed good quality because of the low anthropogenic activity in the catchment area. According to the results obtained during the analysis, all surface waters can be used as reference points for further ecological investigations.

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