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THE INFLUENCE OF SEASONAL FACTOR ON CHEMICAL DISSOLVING OF LIMESTONE VARIABILITY IN SVRLJISKA VALLEY

Abstract: How big is the influence of climatic factor on the intensity of rocks dissolving (limestone) in Serbia? Previous investigations of rivers water chemistry changes have shown it insignificance. This investigation shows significant collective influence of climatic elements contained in "seasonal factor".

Key words: chemical erosion, climate, season, limestone, Svrljiska valley

Садржај: Колики је утицај климатског фактора на интензитет растварања стена (кречњака) у Србији. Досадашњим истраживањима промене хемизма воде речних токова закључено је да је он миноран. Овим истраживањима уочен је значајан уплив збирног утицаја климатских елемената садржаних у "сезонском фактору".

Кључне речи: хемијска ерозија, клима, сезона, кречњаци, Сврљишка котлина.

Introduction

Svrljiska valley is located in South-Eastern part of Serbia. The most of the rim is consisting of limestone while bottom is covered by Neogene sediments. These lithologic relations cause great number of springs which are located in contact of these two litological units. At the other hand, tectonic structure caused different forms of ground waters: siphon spring, descendent and normal karst springs. Most of them are typical example of hydrological situation in the condition of dammed karst.

Springs in limestone are of great anthrop-geographic significance in this region. Population of limestone areas stand the lack of surface water but there are abundance of ground water in various forms of springs using for needs of population and cattle rising. The same occurrence is in Svrljiska valley but because of climatic condition there are springs of low abundance that are scattered. Considering that, this kind of springs is real fortune. Settlements are formed around these springs supplying them with water. In this region all important springs are caped, using for local population but its claims to be a problem for geomorphologists and hydrologists which are in impossibility to determine the value of abundance.

The aim of this investigation is to establish the influence of variable seasonal climatic elements on the intensity of chemical dissolving in limestone. Essential physico-geographical and chemical parameters are observed on 5 (localities) limestone springs in Svrljiska valley during one year, precisely, in the period from 01 January 2005 up to 31 January 2006.

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Physico-geographical characteristics of the terrain

In accordance with purpose of this investigation, only parameters of great importance for examined phenomenon are processed. Those are: litologico-tectonic relations, precipitation, essential physico-geographical parameters of waters; unfortunately temperature data are missing.

Location, dimension, boundaries

Svrljiska valley is an individual geographical entirety in Eastern part of Serbia. This valley as also one of the most remarkable transversal valleys in Karphato-Balkan region of Eastern Serbia, as well as one of the largest valleys in Serbia at all.

This region includes predominant part of river basin of the Svrljiski Timok which is left component of river Beli Timok. It extends in East-West direction as the mountain range in surroundings. Svrljiska valley is a part of Svrljiska area which includes Palilulska valley and Budzak area. The valleys are surrounded by typical limestone mountains which outstanding, lonely peaks are over 1200 m. The lowest point is on 335m and the highest point is at 1334m. There are three different parts in regional physiognomy: 1) high, presented by lukovsko-okoliska plateau, 2) narrower, Svrljiska valley, 3) spacious depression in North foothill of Svrljiska Mountain. Small vertical division is of great importance for natural characteristics of Svrljiska area. Although it is limited in most of the area, Svrljiska valley is not completely closed. It's especially opened in the direction of West and South-West, to Aleksinacka valley and to Golak area (Timok). Over the curve Gramada connections with Niska valley in neighborhood are made easier (Petrovic J., 2001).

Geological composition

Svrljiska valley, actually Svrljiska syncline, is located in the South rockiest part of Carpatho-Balkanian Mountains range. The valley is mostly consisting of Mesozoic carbonate rocks while flysch is presented by two narrow, mostly divided zones. The bottom of the valley is covered by Neogene sediments. Magmatic rocks and recent sediments are irrelevant feature in geological structure of the valley.

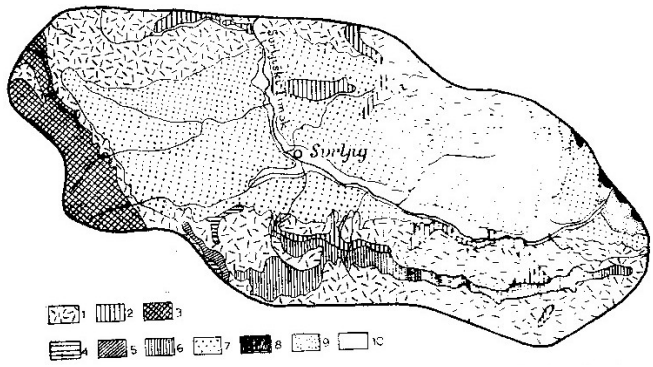

Figure 2 Geological map of Svrljiska valley

Legend: 1) Permian massive limestone; 2) Otrivian limestone and dolomites; 3) Permian red sandstones; 4) Otrivian dolomites; 5) Senon limestone; 6) Devonian slates and sandstones; 7) Mio-Pliocene sediments (clays, marls, conglomerates); 8) andesites; 9) Paleogene limestone and conglomerates; 10) alluvium. (Source: Geological map of Sr Srbia, 1968)

Climatic characteristics

According to its position Svrljiska valley is very exposed to influences of cold continental masses from South-Eastern direction, primarily during the winter. The low Tresibaba Mountain is weak obstacle to penetration of cold winds from the Wallacho-Pontic basin; this is also because of deep carved gorge of Svrljiski Timok. At the other hand, over the low curve Slivlje, Svrljiska valley is wide opened to penetration of worm and moist air masses from South-Western direction, from Pomoravlje over the Toponicka River, as well as over the curve Gramade.

Svrljiska valley, like the other valleys in South-Eastern Serbia, is not characterized by spacious and wide bottom, but has narrow alluvial plain of Svrljiski Timok. Mountainous surrounding is presented by plains 1100-1200 m high in the South and 900-1000 m high in the North. Sunny side is divided by numerous valleys, long and narrow beams while the shady side is steep and vertical in places. This is the main reason why there is no known vertical air flows in the valley, that characterize summer period of year in other valleys.

Precipitation

Svrljiska valley is located in driest area in the South-East of Serbia. Rain gage located in Svrljig is founded 80 years ago. The averaged monthly and yearly amounts of precipitation, according to data of Hydro-Meteorological Institute of Serbia, for the period 1995-2005, have had following values:

Table 1. Averaged yearly amount of precipitation for the period 1995-2005

Month	J	F	M	A	M	J	J	A	S	O	N	D	Year
Precipitation (mm)	41	36	31	60	54	51	47	47	68	52	52	56	595

The averaged yearly amount of precipitation on rain gage Svrljig (375m) of 595 mm has unequal distribution during the year. Maximal amount of precipitation is secreted on September and minimal on March. Distinctions in the amount of precipitation per seasons are insignificant. In the spring 55 mm of precipitation is fallen, in summer 54 mm, autumn 53mm and in the winter 36 mm.

Snow usually falls on the bottom of the valley from the end of November to the beginning of March. On the mountains in surrounding first snow begins in the middle October. In recent decades snow cover lasting is reduced.

During 2005, the annual amount of precipitation was 708 mm this is 19% above average of many years. Winter months were especially moist (sum of precipitation from January to March was 178 mm). Considering the absolute height of limestone terrains and temperature, those precipitations were extracted mostly as a snow. From point of view of rocks chemical dissolving dynamics, precipitations extracted during the August are vary important in condition of low moisture of ground, high temperature and great potential of evaporation.

Table 2. The averaged yearly amount of precipitation for 2005

Month	J	F	M	A	M	J	J	A	S	O	N	D	Year
Precipitation (mm)	57	76	45	72	54	50	41	115	18	40	64	76	708

Spring capacity as a function of ground water supply in limestone-dolomite terrains is in connection with annual sum and distribution of precipitation.

Vegetation

Svrljiska region is one of afforested areas in Eastern Serbia. It has great areas under the deciduous forest which belongs to sub-province of sub-Mediterranean-Balkan forests that is under the province of European deciduous forest: cerris, hornbeam, cinnamon

strawberry, beech and black locust. Deciduous vegetation slows down water draining and sinking of atmospheric precipitation, in the first place in limestone terrains. Conifer forests are widely-spaced distributed only in artificial gardens on limestone base, in the height of 1000m where are the forests of black pine tree.

Location and basic characteristics of the investigated springs

In the period from 01.01.2005 up to 31.01.2006 once a week were taken the samples of the water from 5 limestone sources. Physico-chemical analyze is made by classical methods of analytical chemistry in the Laboratory of physical geography of the Faculty of Geography in Belgrade (Manojlovic, 1992). Unfortunately great number of springs is caped so we could only guess about its capacity. Limestone sources are located at the rim of Svrljiska valley. Four sources are on the Northern slopes of Svrljiska Mountain, and one is on the Southern slopes. The names of the springs given in tables and figures will be reduced and marked by numbers from 1 to 5. Those springs are: spring in Drajince (**1**), Beloinjsko spring (**2**), Crniljevacko spring (**3**), also "9 Jugovica" (**4**) and "Dobrez" (**5**), both of them in Lalince.

Spring in Drajince- Located at the Southern rim of Tresibaba Mountain, on 530m. Spring come to the surface in contact of conglomerates, sandstones and sands with limestone. This spring is of small capacity and downstream from capping there is almost no water.

Beloinjsko spring-This spring comes to the surface below Boloinjska peak at the height of 460m in Beloinje village in contact of limestones, clayey limestones and argillites. The source is in a small rocky pommel carved at right side of Beloinje brook. In sourced pommel of Beloinje spring come to the surface several springs: one permanent, three periodical. The permanent spring flows out right near the bottom of the pommel from several cracks, so it has broken distribution. Periodical springs flow out above permanent one. Considering the quantity of water Beloinjsko spring is in group of poor quantity limestone springs on Northern slopes of Svrljiska Mountain and water capacity varies. Temperature of water varies, too. Winter temperatures are around 5.5°C and summer temperatures are over 12°C.

Crnoljecacko spring-comes to the surface from Vrelska cave on 48 m directly above Crnoljevica village in contact of limestone, sandstone and argillites. Vrelska cave branches off in three vertical canals. Lower canal is under the water permanently, middle only during the period of water maximum and the highest is never inundated which is in agreement with landing of a ground water in limestone. Capacity of water varies; maximum is in autumn and spring while minimum is during the summer and at the beginning of spring. During the rain showers springs stir. According to conditions of lowing out, temperature considerable varies from 7.7°C up to -11.8°C.

"9 Jugovica"-This spring is located in center of Lalince village on 420m and comes to the surface in contact of limestone and clayey limestone with argillites. It is caped as a faucet with 9 pipes. It has a great capacity which is independent of season. Temperature moves from 7.5°C to 12.5°C.

"Dobrez"-Located in Lalince village in different location then previous on 420m. Also comes to the surface in contact of limestone and clayey limestone with argillites. Because of discordance of temperature and water capacity as well as determined physico-chemical parameters these two springs located in Lalince comes from different collectors. Temperature varies from 8.1°C up to 12.2°C.

Methodology of the investigation

Physico-chemical analyze of water was convenient for the purpose of this paper. Concentration of calcium, magnesium, and hydro-carbonates are measured as well as

temperature, conductivity and pH. On that base we acquired conditions for establishing possible influence of seasonal factor on chemical dissolving in limestone of Svrljiska valley. It was examined by total hardness of water, partial pressure CO_2 as well as by index of water saturation by calcite and dolomite.

Method of examination of Ca^{2+} and Mg^{2+} is based on volumetric, more exactly on titration with EDTA (ethylene two amine tetra acetic-acid). Concentration of HCO_3^+ ions is calculated after the titration of sample with HCl of low molarities with combined indicator (bromo-cresol green and methyl red in ethanol). After conducted analyzes calculations were done by standard methods of physical chemistry (Manojlovic, 1992).

Analyze of results

Because of great number of analyses and obtained parameters its impossible to present them in tabular form, in original. For this reason that could be perceived through graphic analyze. The fact about total mineralization is given by specific electric conductivity. On the base of parallel realizing of data from whole 5 springs, two facts could be noticed: there is quite good agreement of trend, more exactly of conductivity changes during the year, but also big differences between same springs.

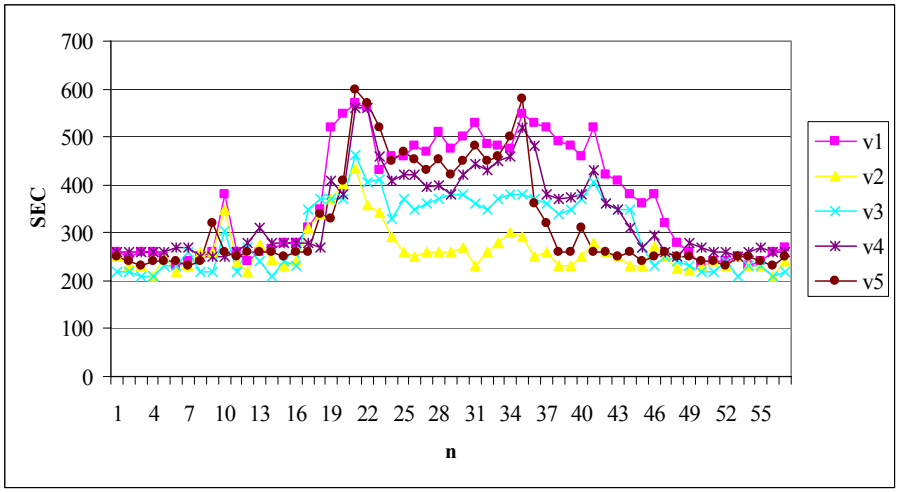

Figure 5 Change of Specific Electric Conductivity (SEC) during the time

The biggest averaged value of conductivity has spring 1 (in Draince), and the lowest spring 2 (Beloinjsko). These springs simultaneously have the biggest, more exactly lowest coefficient of variability. It means that area of feeding or mechanism of flowing out is not identical. According to lithologic conditions, first of all condition of dam in limestone for spring with lowest values, we could say that its gravitational spring whit water that little mixes below the level of dam. Second spring has completely different situation. Other springs are in range of extreme values.

Concentrations of established elements are different on different springs during the time. The biggest averaged concentration of Calcium is on spring 2 (Boloinjsko) and the lowest value is on spring 5 (Dobrez). The last spring is one of extreme springs according to variability of Calcium concentration; coefficient of variability near Dobrez village is 11.7 while near Draince village the value is 38.6. It means that spring in Dobrez has uniform regime of flowing out, while fluctuations in Draince are significant. As compensation of that spring in Dobrez has the highest concentration of Mg (31.5mg/l) but with less fluctuation during the time.

Table 3. Parameters of the concentration changes of main cat-ions in 2005

spring	1		2		3		4		5	
	Ca^{2+}	Mg^{2+}	Ca^{2+}	Mg^{2+}	Ca^{2+}	Mg^{2+}	Ca^{2+}	Mg^{2+}	Ca^{2+}	Mg^{2+}
X	100.8	22.9	111.3	11.7	73.0	27.1	63.7	25.2	58.0	31.5
S	38.9	5.4	32.6	2.4	18.2	8.9	14.2	18.9	6.8	6.2
min	48.9	14.7	58.9	8.0	46.9	11.3	45.5	5.1	48.9	21.6
max	152.0	31.3	210.0	18.5	112.0	48.0	102.0	72.6	74.0	45.3
max/min	3.1	2.1	3.6	2.3	2.4	4.2	2.2	14.2	1.5	2.1
V	38.6	23.5	29.3	20.2	24.9	32.7	22.4	75.1	11.7	19.6

Legend: X-arithmetic mean of 57 samples of water; S-standard deviation of parameter; min, max- minimal and maximal established concentration (mg/l); V-coefficient of variability

Concentrations of Ca and Mg only together shows trend of mineralization changes during the time. Those changes are expressed in German degrees on the base of the formula:

$$^{0}dH=0.1399*mg/l\ Ca^{2+} + 0.2315*mg/l\ Mg^{2+}.$$

The average hardness of spring water in Draince is 19.4, Beloinjsko 18.3, Crnoljevacko 16.5, "9 Jugovica" 14.7 and on spring Dobrez 15.4. Observing united concentrations of Ca and Mg the biggest variability in water hardness shows spring "9 Jugovica" (1:39), but the least is on spring Dobrez with coefficient of variability 14.8.

Table 4. Basic parameters of total water hardness on five springs in Svrljiska valley

	v1	v2	v3	v4	v5	Average
X	19.4	18.3	16.5	14.7	15.4	16.9
s	6.7	5.0	4.4	6.3	2.3	4.5
min	10.4	10.3	9.5	7.7	12.5	11.1
max	28.2	33.7	26.8	29.9	20.4	26.7
max/min	2.7	3.3	2.8	3.9	1.6	2.5
V	34.3	27.4	26.7	42.7	14.8	26.7

Aggressiveness or incrustiveness of water is a parameter of its instantaneous capability to dissolve, actually to extract certain quantity of $CaCO_3$ ($MgCO_3$). As the most part of Ca^{2+} and Mg^{2+} in water is in equilibrium with hydro-carbonate, and HCO ion arise with one part from CO_2, that interaction of this gas with water solution considers the most significant parameter of its aggressive or incrustive character. Change in quality of CO_2 in water influences on carbon dioxide equilibrium.

Table 5. Basic parameters of partial pressure of CO_2 in spring water of Svrljiska valley

	v1	v2	v3	v4	v5	Average
X	0.0028	0.0026	0.0036	0.0013	0.0020	0.0025
S	0.0013	0.0006	0.0012	0.0005	0.0006	0.0004
min	0.0011	0.0010	0.0014	0.0004	0.0013	0.0019
max	0.0097	0.0038	0.0058	0.0039	0.0043	0.0037
Max/min	8.70	3.51	4.09	9.52	3.26	1.90
V	46.3	23.4	32.8	42.7	33.0	16.4

Quantity of CO_2 in water could be divided on two parts: one, presented as bicarbonate (tied or half tied) and the other which is free (balanced and aggressive CO_2). Concentration of free CO_2 is important for solution stability of Calcium-bicarbonate-$Ca(HCO_3)_2$. It should be certain quantity of balanced CO_2 in order to keep quantity of Calcium and Magnesium bicarbonates in solution. If balanced CO_2 is equal to free, total than water is in equilibrium. If the value of aggressive CO_2 is positive then water is aggressive contrary water is incrustive. All those united values are stated as partial pressure CO_2 (pCO_2). Its values

during 2005 are showed on Table 5. Concentration of CO_2 is increased on the beginning and at the end of the year.

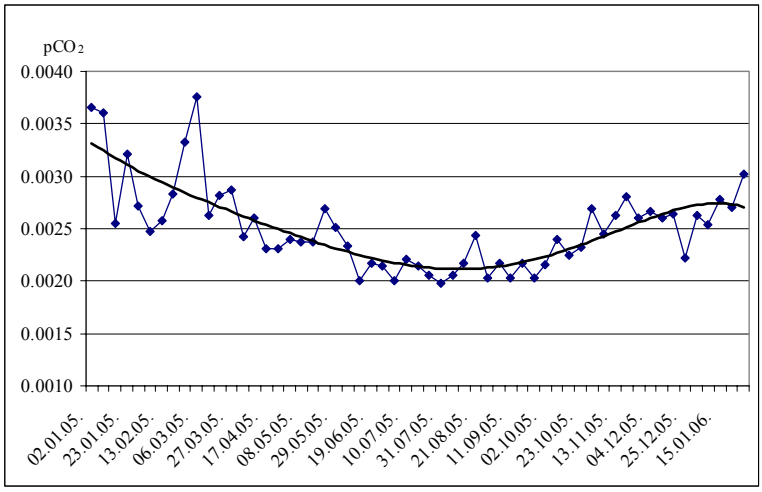

Figure 6 Change of average value of pCO_2 during the time and trend line

Calculation of Water Saturation Index has a great importance in studding influence of seasonal factor on limestone dissolving; it contains all important elements that determine its importance. Index of calcite (Sic) and dolomite (Sid) Water Saturation was important for this investigation. By this Index we could establish if investigated sample is saturated or oversaturated with Calcium-bicarbonate in existing condition (temperature of water, total quantity of dissolved mineral substances and concentration of Ca^{2+}, HCO^{3-} and H^{+} ions, actually pH). If SI=0 investigated sample is in equilibrium; negative values shows that water is unsaturated and positive refers to over saturation.

According to results we got in this paper we could conclude water from all five springs is mostly incrustive. Values given in Table 5 refer to this. As Index of water saturation with dolomite is high and limestone created from calcite we could conclude that magnesium mostly has origin in Neogene sediments, actually this is dissolving of substances in which structure magnesium sulfate takes part.

Table 6. Average values of Sic and Sid

	1	2	3	4	5	X
SIc	0.97	0.97	0.61	0.93	0.78	0.85
SId	1.84	1.84	1.12	1.75	1.46	1.60

Conclusion and discussion

Precipitation and temperature are in direct connection with total mineralization and water hardness. In cold part of year increased mineralization on springs in limestone is expressed as well as its hardness, partial pressure pCO_2 and decreased value of SI Index. All this is pointing out that influence of seasonal factor on mineralization change and the intensity of chemical dissolving in limestone at the rim of Svrljiska valley during 2005 was expressive. Unfortunately continuity of observing of water chemistry in 2-5 years is missed. With that we could speak with credibility about combination of seasonal climatic elements, process of rocks chemical dissolving with physico-chemical characteristics of ground waters.

Previous investigations of seasonal climatic factor influence on change of running waters chemistry in Eastern part of Serbia are not showed its big importance (Manojlovic, 1989, 1992, Manojlovic P., Dragicevic S., Mustafic S., 2003). This could be result of different influences of season on surface or ground waters in general or on concurrence of events that year in Svrljiska valley. Following investigations will show direction in solution of this problem.

LITERATURE

Petrovic B.J., (2001): **Nature of Svrljiska valley**. Novi Sad.

Manojlovic P. (1989**): The experimental investigation of intensity of corosion in karst in East Serbia**. Faculty of Natural Sciences and Mathematics, Belgrade.

Manojlovic P. (1992): **Chemical erosion as a geomorphologic process-theoretical, analytical and methodological approach**, Faculty of Natural Sciences and Mathematics, Belgrade.

Manojlovic P., Dragicevic S., Mustafic S., (2003): **Some chemical characteristics of Karst waters in eastern Serbia in the function of tourism development**. The development and potentials of ecotourism on Balkan Peninsula, volume II, Belgrade.

ПРЕДРАГ МАНОЈЛОВИЋ
МИЛИЦА ДАМЊАНОВИЋ РАКИЋ

Р е з и м е

УТИЦАЈ СЕЗОНСКОГ ФАКТОРА НА ВАРИЈАБИЛНОСТ ХЕМИЈСКОГ РАСТВАРАЊА КРЕЧЊАКА У СВРЉИШКОЈ КОТЛИНИ

Падавине и температура су у директној вези са укупном минерализацијом и тврдоћом воде. У хладнијем делу године изразита је повећана минерализација воде крашких врела, њена тврдоћа, парцијални притисак CO_2, а с тим у вези смањена вредност SI индекса. Све то указује да је током 2005. године утицај сезонског фактора на промену минерализације вода и интензитет хемијског растварања кречњака обода Сврљишке котлине био изразит. Нажалост, недостају континуелна праћења хемизма вода 2-5 година. Тиме би се могло много веродостојније говорити о комбинацији сезонских климатских елемената, процеса хемијског растварања стена са физичко-хемијским карактеристикама подземних вода.

Досадашња истраживања утицаја сезонских климатских фактора на промену хемизма текућих вода Источне Србије нису указала на толико велики њихов значај. То може да буде резултат или различитих утицаја сезона на површинске и подземне воде уопште, или на стицај околности те године у Сврљишкој котлини. Наредна истраживања указаће на правац у решавању овог проблема.