

## Chemical denudation dynamic based on hydrochemical measurements in the area of Drienovecká jaskyňa Cave basin (Slovak karst, Slovakia)

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**Abstract:** Denudation is a fundamental process for the development of karst relief. It has different intensity in different geological and climatic condition and beside this many other partial factors influence the intensity and dynamic of the process during the year. In karst systems, there is often a positive correlation between water partial pressure of CO<sub>2</sub> and denudation. The Drienovecká jaskyňa Cave spring represents typical active fluviokarstic spring and its catchment area is represented by Wetterstein and Waxenec limestones, and Drienovec conglomerates. This catchment study area is located at the contact of the continental and oceanic climate, in terms of altitude at the border between the lowland and mountain climate. During three hydrological years we measured main karst water parameters that helped us bring first results on chemical denudation in the catchment area. The water from the spring is of calcium-magnesium-bicarbonate type. Hydrogeochemical analyses indicate that it is mostly water from an open hydrogeological structure. Water of the cave spring is oversaturated with respect to calcite, which is documented by the saturation index of calcite, whose values are higher than the solubility product of calcite. During the studied period, the dynamic of the chemical denudation rate is clearly observable with peaks in spring months in year 2014 and 2016. The average value of denudation rate for the entire period is 21.06 mg Ca<sup>2+</sup>. Factors that influence chemical denudation include, for example, type of carbonate rock, CO<sub>2</sub> partial pressure, water and air temperature, chemical composition of the aqueous solution, activity of soil organisms, vegetation and others. Water from melted snow can also play a significant role in changes in water chemistry and thus chemical denudation.

**Keywords:** chemical denudation, denudation factors, Carbon dioxide, Slovak karst, Drienovecká jaskyňa Cave

### Introduction

Chemical denudation is a classic issue in karstology, and the primary process of karstification is uniform lowering or surface denudation. As chemical denudation plays a significant role in regulating atmospheric CO<sub>2</sub> balance, it is gaining more attention in research (Ran et al. 2017). The denudation rate is the measure of how fast a karst surface is being lowered by bedrock dissolution (Dreybrodt 1988, White 1988, Ford and Williams 1989). With the development of new methods and analyses, there has been a recent surge in detailed research in this field, including the advancement of quantitative and qualitative methods.

Corbel (1959) was one of the first researchers to describe the factors affecting denudation and observed that karst develops differently in various climatic regimes. Smith and Newson (1974) investigated dissolution rates based on chemical and mechanical erosion. Priesnitz (1974) found that limestone solubility and yield have a positive relationship, which was confirmed by Pulina (1974) and Gams (1966). In the Svartisen region of north Norway, Lauritzen

(1990) determined chemical denudation values in eight karst areas and found similarities with sites in northern Sweden and Canada. Appelo and Postma (2005) discussed the issue of karst denudation, and Gabrovšek (2007) presented a simple mathematical model of denudation rate in karst. Shopov et al. (2009) reconstructed the carbonate denudation rate based on temperature and precipitation, while Prelovšek (2012) studied speleogenetic processes dynamics in underground streams of Slovenia using various methods. Rzonca and Buczynski (2013) investigated intense karst denudation in crystalline basins with small deposits of marble in the Polish Sudetenland. An overview of chemical denudation from different regions of the world is given in tab 6. While the chemical dissolution of carbonates may not directly affect current environmental changes, the amount of CO<sub>2</sub> released into the atmosphere by chemical denudation cannot be ignored. It is important to know its volume to study other processes in the natural karst environment, and even though carbonate areas make up only 15.2% of the earth's surface (Goldscheider et al. 2020), global rock weathering contributes up to 60% of the overall uptake of CO<sub>2</sub> by the atmosphere (Amiotte-Suchet et al. 2003). A selection of important karst aquifers, karst water resources and caves present World Karst Aquifer map - WOKAM (BGR, IAH, KIT and UNESCO 2017). Therefore, knowledge of the chemical composition of waters and their character in karst areas is crucial (Maher and Chamberlain 2014), and research in various karst regions of the world in recent years has focused on this subject.

In Slovakia, Roda et al. (1986) conducted a study on monitoring denudation and corrosion around cave entrances. One of the pioneers in denudation research was Droppa (1996, 2013), who focused on determining denudation rates primarily in the karst basins of the Low Tatras. Lánczos and Filipčíková (2017) described geochemical processes that involve CO<sub>2</sub> reactions in the cave environment and water solution in selected caves of Malé Karpaty Mountains in western Slovakia. Gessert et al. (2021) utilized the ionic runoff method to quantify chemical denudation in the Jasovská planina Plateau area.

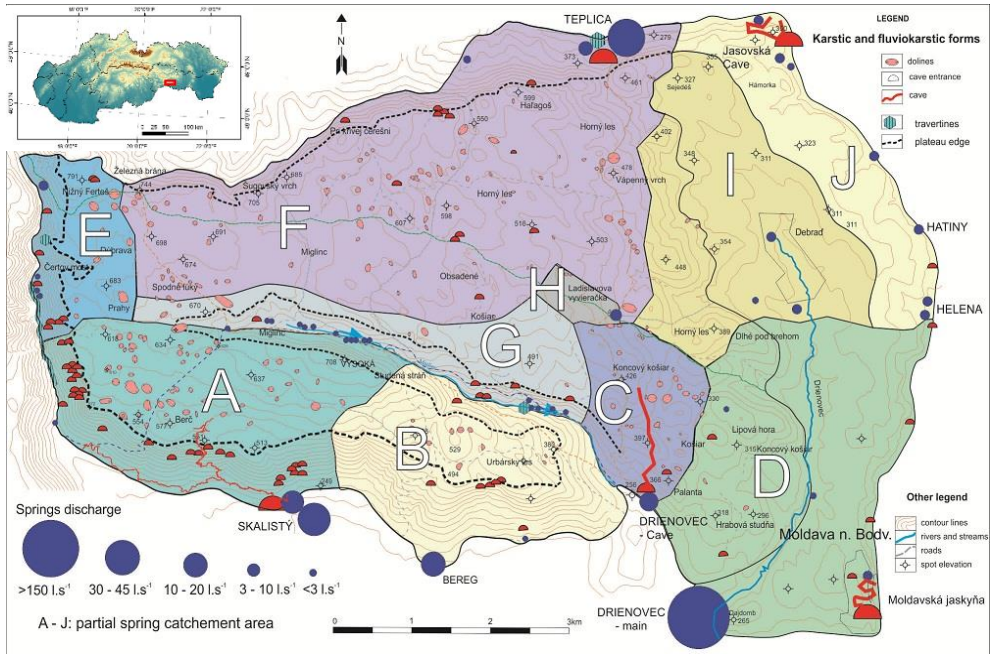
The Slovak Karst plateaus are known for their well-developed karst landscape, which is one of the best karstified in Europe. Situated at the transition between the continental and oceanic climates and at the altitude boundary of lowland and mountain climates, this region presents an ideal setting for studying denudation. Since the rate of denudation varies depending on the area and climatic zone, conducting research on denudation in this region would provide much-needed detailed information for this area. Furthermore, by comparing the results with other localities, we could gain insight into the similarities and differences in denudation processes.

The present study conducted comprehensive hydrochemical analyses of groundwater and chemical denudation in the Slovak Karst. The data was collected from the spring in Drienovec between November 2013 and October 2016, covering a period of three hydrological years. These are the first results of their kind for this karst area.

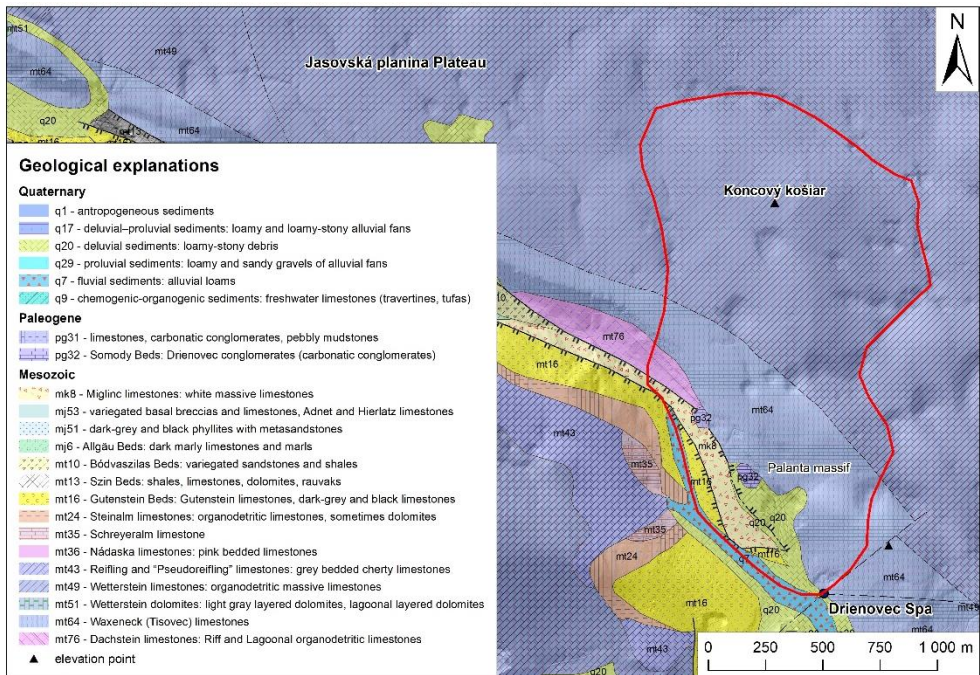
### **Position and physical-geographical conditions of the Drienovecká jaskyňa Cave catchment area**

The Drienovecká jaskyňa Cave can be found at the southern foothill of the Jasovská planina Plateau, situated on the southeastern edge of the Slovak Karst. It is a significant cave in the area, known for its active flow. The cave spans a length of 1348 m and has a general NE direction. It is a multi-level cave with three primary levels, spanning roughly 60 m vertically. Some of the cave passages have undergone changes due to a collapse. Based on prior research, literature review, and field observations, various potential catchment areas were identified on the Jasovská planina Plateau. These areas are drained by karst springs that have seasonally varying yields, as depicted in figure 1.

The Drienovecká jaskyňa Cave basin (fig. 2) extends into the Palanta massif (336 m), composed of light lagoon-like Waxenec limestones and partially Drienovec conglomerates (Mello et al. 1996). The Silicium Nappe is present in the area, represented by Triassic and Jurassic rocks, Upper Cretaceous and tertiary and quaternary sediments.



**Fig. 1.** Potential catchment areas of Jasovská planina Plateau springs, by the letter C is designated catchment area of Drienovec Cave with the cave ground plan  
 Source: Hochmuth and Gessert (2017)



**Fig. 2.** Geological map section, catchment area of Drienovecká jaskyňa Cave delineated by red line (ŠGÚDŠ 2017, adapted)

The Triassic rocks make up a significant part of the karstified carbonates, including Gutenstein, Steinalm, Wetterstein riff and lagoon limestones, Waxenec and Dachstein limestones. Jurassic rocks consist of Adnet and Hierlatz limestones, with small local occurrences in the nearby Miglinc valley, where Cretaceous Miglinc limestones are also found. The Paleogene period is represented by the Šomod formation and Drienovec conglomerates, which interfere with the base of the Neogene period.

The Drienovecká jaskyňa Cave and its catchment area are situated at the intersection of two significant regional tectonic lines: The Rožňava deep fault, which runs in a northwest-southeast direction, and the fault on which the eastern valley of the Bodva River (an extension of the Darnó fault line) is located. The latter fault is clearly visible in the Miglinc valley and acts as the boundary between two partial tectonic structures. The formation of the Turňa basin and its separation from the Mesozoic Jasov Plateau are attributed to several faults running in an east-west direction. Therefore, dislocation structures of downward, displacement, and rearward character have a significant impact on the area (Zacharov, 2008). Orvan (1974) suggested that the springs surrounding Drienovec primarily drain the southern tectonic unit, known as the Hačava-Jasov, which slopes towards the south.

The average annual temperature of the Slovak Karst area, according to the Atlas of the Slovak Republic (Slovak environmental agency 2002), ranges from 8-9 °C, with spring temperatures averaging 9-10 °C, summer temperatures averaging 18-19 °C, autumn temperatures averaging 8-9 °C, and winter temperatures averaging -1 to -2 °C. The area receives an average total precipitation of 601-700 mm per year, with spring receiving 151-200 mm, summer receiving 201-250 mm, autumn receiving 119-150 mm, and winter receiving 59-100 mm. The average duration of snow cover is 60-80 days between November and March. The Drienovec catchment area, located in the Slovak Karst, is characterized by a dense land cover, consisting mainly of beech forests that thrive primarily on leptosols and rubified rendzinas.

## Methods and materials

During the hydrological years 2013-2016 (for 34 months, monthly) discharge rate (using the FP 11 current meter, Global water), temperature, pH, conductivity (Hanna HI 98129) and alkalinity (using the titrimetric kit Aquamerck Alkalinity Test 1.11109.0001) were studied in the field. Water samples were taken for further laboratory analyses in order to study the chemical composition. Major ion concentrations were analyzed on a Shimadzu UV-2600 UV-VIS spectrophotometer and a Metrohm TitrIC 7 chromatograph. Complete results of separate measurement are in Tab. 3.

For karst water characterization we are using coefficients represent an auxiliary criterion in solving the genesis of the chemical composition of water  $rMg / rCa$ ,  $r(Na + K) / r(Ca + Mg)$ , for waters with carbonate organic mineralization,  $rHCO_3/rCl$  to determine the depth coefficient and  $rNa/rCl$  to determine the origin of sodium. We also illustrated the chemical composition of water using a Piper diagram (fig. 3).

Based on chemical analysis, saturation indices (SI) were calculated for calcite, dolomite and gypsum, as well as ion activity products for the mentioned minerals (fig. 6-8). The PHREEQC program (Parkhurst and Appelo, 1999) was used for the calculation of SI and  $pCO_2$ .

The relationship is between the concentration of  $Ca^{2+}$  ions and the partial pressure of  $CO_2$ , which is derived from the equation for calculating the equilibrium constant of the calcite dissolution reaction (Appelo and Postma 2005, in Fľaková, Ženišová 2012). Using this equation, it is possible to determine potential the rate of denudation, which can be characterized as decalcification - the release of  $Ca^{2+}$  ions into the solution:

$$m_{Ca^{2+}} = \sqrt[3]{\frac{10^{-6} \cdot pCO_2}{4}} \quad (1)$$

where  $m_{Ca^{2+}}$  is the molar concentration of  $Ca^{2+}$  ions,  $pCO_2$  is the partial pressure of  $CO_2$ .

$LOG = (S/(C+Na))$  and  $LOG = (C+Ca)/(Cl+Na)$ , are commonly used to describe the chemistry of groundwater in open hydrogeological systems in karst (Pačes 1983).  $LOG = (S/(C+Na))$ , represents the logarithm of the ratio of the concentration of dissolved solids (S) to the sum of the concentrations of cations (C) and sodium (Na) in groundwater.  $LOG = (C+Ca)/(Cl+Na)$ , represents the logarithm of the ratio of the sum of calcium (Ca) and cation concentrations to the sum of chloride (Cl) and sodium (Na) concentrations in groundwater. This expression is often used to evaluate the mixing of groundwater with different sources.

To assess the role of cation exchange and reverse ion exchange in the aquifer system, we used the chlor-alkaline indices (CAI-I and CAI-II) as proposed by Schöller (1967).

CAI – I (1):

$$CAI - I = \frac{Cl^- - (Na^+ + K^+)}{Cl^-} \quad (2)$$

CAI – II (2):

$$CAI - II = \frac{Cl^- - (Na^+ + K^+)}{SO_4^{2-} + HCO_3^- + CO_3^{2-} + NO_3^-} \quad (3)$$

where all ions are articulated in meq/L.

## Results and discussion

The results of flow and chemical analysis of individual water samples are presented in tab. 1. Based on the characterization coefficient  $r(Na + K) / r(Ca + Mg)$ , it can be stated that karst water originates from a clearly karstic subsoil (coefficient less than 0.1). In four terms from our study period, the  $rMg / rCa$  coefficient is greater than 0.1 and in two is 0.1 (Tab. 2), indicating water from dolomitic limestone or mixed circulation. However, in most cases it is less than 0.1, which means that the water comes from pure limestone.

We observe slightly lower alkalinity in the spring and autumn months compared to other months of the study period. These months also had higher precipitation than usual. Therefore, we consider in this case the change of the catchment area boundary over time and thus also the chemical composition of water, which is related to the facial diversity of the studied area and the potential occurrence of dolomites or dolomitic limestone in the lens positions. Also changes of coefficients over time indicate changes in the catchment area during the year, which is significantly dependent on climatic conditions (amount and form of precipitation, temperature, phenological phase, etc.)

The depth coefficient  $rHCO_3/rCl$  and  $LOG = (S/(C+Na))$  and  $LOG = (C+Ca)/(Cl+Na)$  indicate that it is predominantly an open hydrogeological structure (Tab.1). The ratio of calcium and cations to chloride and sodium can provide an indication of the greater contribution from shallow groundwater or surface water (fig. 3). Sodium is mostly bound in NaCl, in three samples it is also bound as NaHCO<sub>3</sub>. According to Franko et al. (1975), the HCO<sub>3</sub> anion is a feature of the lithogenic-meteoritic component of water; It is believed that it originates mainly from the dissolution of carbonate and aluminosilicate rock-forming minerals by infiltrating rainwater. In most of the study, however, Na<sup>+</sup> is bound to Cl and carries only the fossil marinogenic (stagnant) water component.

The water from the spring is of calcium-magnesium-bicarbonate type (Gessert et al. 2021). In all samples weak acids predominate over strong acids and alkaline earth metals predominate on alkaline metals and the carbonate hardness (secondary alkalinity) exceeds 50%.

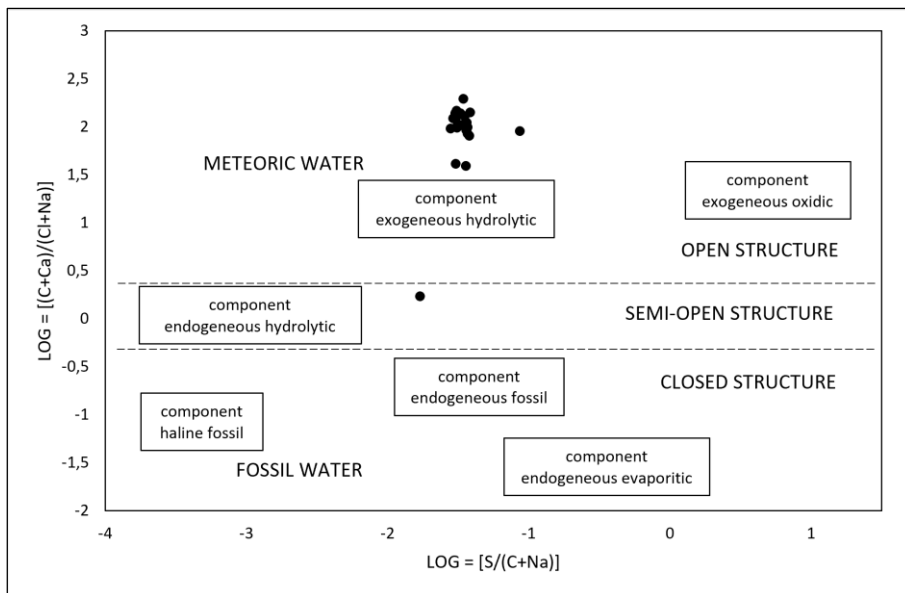
Based on the Piper plot (according to Fláková and Ženišová 2020, fig. 4), we can conclude that water from all samples is of calcium-magnesium-bicarbonate type. All samples have a high content of Ca<sup>2+</sup> and HCO<sub>3</sub><sup>3-</sup>, which is a consequence of the constant dissolution of carbonate rocks. The content of other elements (especially Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup> and Cl<sup>-</sup>) is more variable. This indicates that the water was not always in contact with the rocks containing the given elements (e.g. dolomite, magnesium calcite, etc.).

**Tab. 1. Results of chemical analysis of water samples**

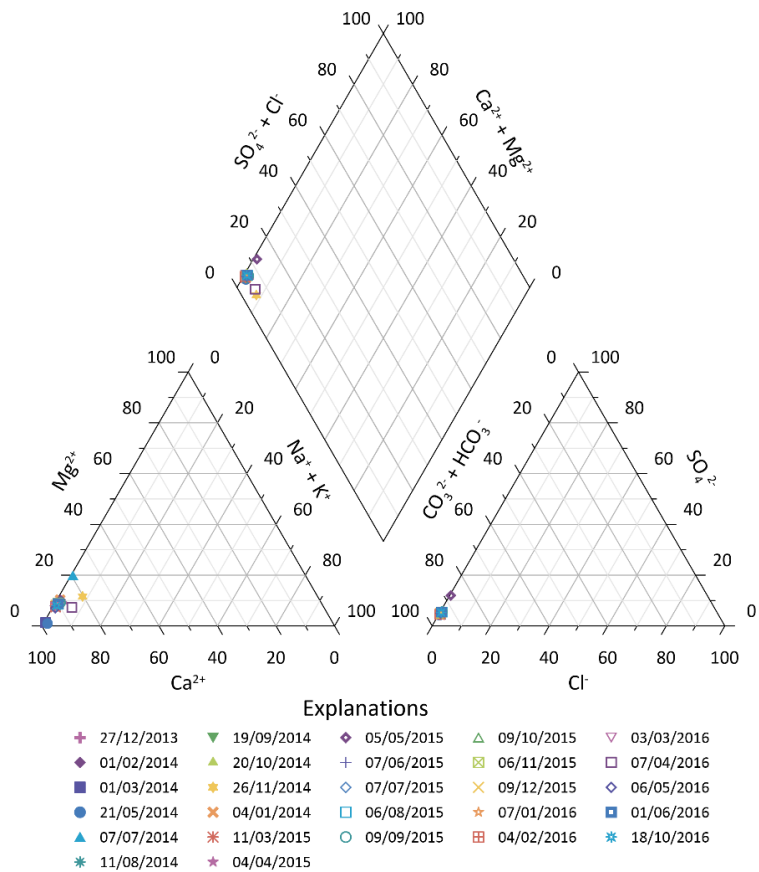
Date	Q (l/s)	Na <sup>+</sup> (mg/l)	K <sup>+</sup> (mg/l)	Ca <sup>2+</sup> (mg/l)	Mg <sup>2+</sup> (mg/l)	NH <sup>4+</sup> (mg/l)	F <sup>-</sup> (mg/l)	Cl <sup>-</sup> (mg/l)	NO <sub>2</sub> <sup>-</sup> (mg/l)	NO <sub>3</sub> <sup>-</sup> (mg/l)	PO <sub>4</sub> <sup>3-</sup> (mg/l)	SO <sub>4</sub> <sup>2-</sup> (mg/l)
27/12/2013	11.4	1.8	1.2	115.4	11.9	0.1	0.1	2.9	0.1	6.4	0.5	23.9
01/02/2014	42.0	0.4	0.3	117.0	10.0	0.1	0.1	1.7	0.2	60.4	0.5	21.0
01/03/2014	49.0	0.5	0.2	122.2	1.7	0.1	0.1	2.3	0.3	83.1	0.5	17.4
21/05/2014	109.0	1.5	0.9	151.3	1.4	0.1	0.1	1.5	0.1	6.1	0.5	17.6
11/08/2014	15.6	1.3	0.8	125.9	11.9	0.1	0.1	1.7	0.1	6.9	0.5	21.2
19/09/2014	13.7	1.3	0.9	127.7	12.5	0.1	0.1	1.4	0.1	8.4	0.5	21.1
20/10/2014	13.8	0.4	0.4	126.9	12.1	0.1	0.1	1.6	0.2	8.2	0.5	22.2
26/11/2014	18.4	4.1	5.0	91.2	13.2	0.1	0.1	1.7	0.1	7.4	0.5	21.5
04/01/2015	15.0	0.8	0.5	104.4	12.1	0.1	0.1	1.8	0.1	6.8	0.5	23.8
11/03/2015	59.0	0.8	0.6	132.3	10.6	0.1	0.1	1.7	0.1	6.0	0.5	20.2
04/04/2015	26.5	0.9	0.6	131.9	11.4	0.1	0.1	1.8	0.1	6.0	0.5	22.0
05/05/2015	18.1	1.2	0.5	120.0	13.9	0.1	0.1	2.0	0.1	2.9	0.5	58.6
07/06/2015	11.8	0.1	1.0	123.0	10.6	0.5	0.0	1.7	0.5	5.8	0.2	22.7
07/07/2015	9.2	0.9	1.5	126.0	12.0	0.1	0.1	2.9	0.1	9.6	0.5	25.5
06/08/2015	7.4	0.9	1.0	123.0	11.9	0.1	0.1	2.9	0.1	10.1	0.5	25.6
09/09/2015	5.6	0.9	1.3	113.0	11.7	0.1	0.1	3.0	0.1	9.6	0.5	26.0
09/10/2015	4.5	1.3	0.4	124.0	12.4	0.1	0.1	1.9	0.2	6.3	0.5	24.0
06/11/2015	11.9	1.0	0.4	117.0	11.8	0.2	0.1	1.8	0.1	9.3	0.5	23.0
09/12/2015	12.8	0.4	0.4	110.0	10.0	0.1	0.1	1.8	0.1	7.7	0.5	22.0
07/01/2016	48.5	0.4	0.4	110.0	9.5	0.1	0.1	1.9	0.1	7.8	0.5	22.0
04/02/2016	31.5	0.4	0.4	115.0	9.8	0.1	0.1	2.0	0.1	7.4	0.5	22.0
03/03/2016	104.0	0.8	0.4	128.0	10.7	0.1	0.1	1.9	0.1	7.7	0.5	21.0
07/04/2016	36.5	4.5	5.4	129.0	10.8	0.1	0.1	2.1	0.1	7.7	0.5	24.0
06/05/2016	19.4	1.1	0.6	135.0	10.2	0.1	0.1	2.0	0.1	7.5	0.5	23.4
01/06/2016	19.0	0.8	0.6	109.0	10.6	0.1	0.1	1.9	0.1	6.9	0.5	22.3
18/10/2016	9.0	0.9	0.5	122.0	10.5	0.1	0.1	1.8	0.1	8.8	0.5	21.8

**Tab. 2. Results of characterization coefficients**

Date	rMg/rCa	r(Na+K)/r(Ca+Mg)	rHCO <sub>3</sub> /rCl	rNa/rCl	Date	rMg/rCa	r(Na+K)/r(Ca+Mg)	rHCO <sub>3</sub> /rCl	rNa/rCl
27/12/2013	0.103	0.012	2.433	0.618	07/07/2015	0.095	0.008	2.453	0.301
01/02/2014	0.085	0.003	4.089	0.242	06/08/2015	0.096	0.007	2.476	0.296
01/03/2014	0.014	0.003	2.533	0.223	09/09/2015	0.104	0.009	2.363	0.290
21/05/2014	0.009	0.008	4.215	0.943	09/10/2015	0.100	0.006	3.632	0.658
07/07/2014	0.249	0.329	3.960	91.106	06/11/2015	0.100	0.005	3.889	0.550
11/08/2014	0.094	0.008	4.202	0.765	09/12/2015	0.091	0.003	3.889	0.244
19/09/2014	0.098	0.008	4.761	0.902	07/01/2016	0.086	0.003	3.421	0.211
20/10/2014	0.096	0.003	3.725	0.273	04/02/2016	0.085	0.003	3.800	0.210
26/11/2014	0.145	0.044	4.184	2.406	03/03/2016	0.084	0.005	3.177	0.438
04/01/2015	0.116	0.005	3.830	0.439	07/04/2016	0.084	0.035	3.301	2.184
11/03/2015	0.080	0.005	4.148	0.478	06/05/2016	0.076	0.006	3.706	0.533
04/04/2015	0.087	0.005	4.198	0.504	01/06/2016	0.097	0.006	3.264	0.430
05/05/2015	0.116	0.006	3.450	0.591	18/10/2016	0.086	0.005	3.575	0.486
07/06/2015	0.086	0.004	4.032	0.029					



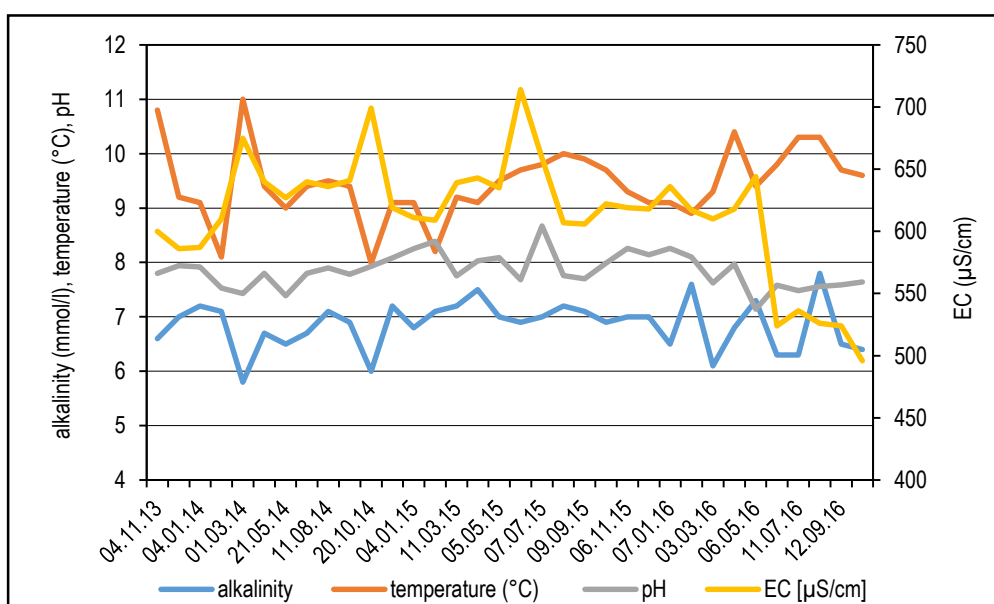
**Fig. 3.** Hydrochemical field of Drienovecká jaskyňa Cave basin



**Fig. 4.** Piper plot of Drienovecká jaskyňa Cave spring

The water temperature affects the solubility of CO<sub>2</sub> and affects the aggressiveness of the water (Roda et al. 1986). In general, as the temperature of water increases, the solubility of CO<sub>2</sub> decreases. When karst water is colder, it can hold more dissolved CO<sub>2</sub>, which can lead to increased acidity and the potential for chemical dissolution of the carbonate bedrock. Conversely, when karst water is warmer, it can hold less dissolved CO<sub>2</sub>, which can reduce the acidity and the potential for chemical dissolution. From the temperature graph we see fluctuations 8 - 11°C.

The relationship between alkalinity and temperature (fig. 5) in karst water can be complex and is influenced by a variety of factors. Generally, the alkalinity of karst water tends to decrease as temperature increases, although the magnitude of the effect can vary depending on the specific characteristics of the aquifer and the water chemistry (Jeannin et al. 2016). Decrease in alkalinity with increasing temperature was due to the decreased solubility of calcium carbonate and the increased consumption of alkalinity by microbial processes.



**Fig. 5.** Main water parameters - alkalinity, temperature, pH and EC

We found a weak positive correlation between EC and temperature and moderate negative correlation between pH and temperature, but the relationship varied depending on the time of year (tab. 3). The relationship was influenced by factors such as the geology of the aquifer and the amount of rainfall (Li et al., 2018, Tao et al. 2012).

**Tab. 3.** Pearson correlation coefficient between main water parameters – alkalinity, temperature, pH and EC

parameter	alkalinity	temperature (°C)	pH	EC (µS/cm)
alkalinity	1.00	-0.16	0.16	0.04
temperature (°C)	-0.16	1.00	-0.46	0.39
pH	0.16	-0.46	1.00	-0.13
EC (µS/cm)	0.04	0.39	-0.13	1.00



According to Prelovšek (2012), the level of chemical denudation can be estimated based on the electrical conductivity (EC) value of karst water, as this provides an indication of the amount of dissolved solids present. However, in this particular study, there was not a strong correlation between conductivity and chemical denudation.

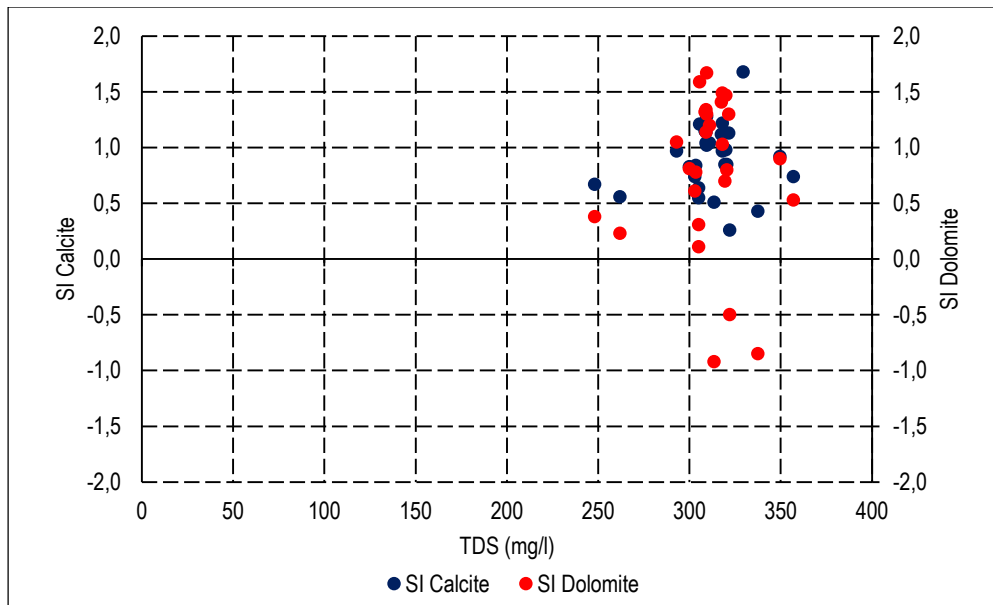
Based on the values of saturation indices and ion activity (tab. 4), we can evaluate the carbonate balances of the karst system of the Drienovecká cave basin. Solving these balances allows us to assess the state of saturation of the water flowing out of the Drienovec Cave spring with respect to calcite, dolomite and gypsum. According to Pačes (1983), the system is in equilibrium if the SI value is from the interval -0.5 to 0.5. In our case, the average SI values of calcite are higher than 0.5, which implies that the system is oversaturated with respect to calcite, which is also documented by the log IAP of calcite (fig. 7A), whose values are higher than the solubility product of calcite. The supersaturation with respect to calcite is not a surprise, as it is water flowing from the cave, which during its activity underground dissolved carbonate minerals and thus became saturated with  $\text{Ca}^{2+}$  ions. The SI values of dolomite as well as the log IAP of dolomite point to oversaturation of most samples with respect to dolomite. Only three cases indicate non-saturation with respect to dolomite. In the mentioned cases, a low value of magnesium was detected by chemical analysis, probably caused by the fact that the water is "younger" (detected by tritium analysis, Palcsu et al. 2021), stayed in the massif too short, and thus did not have time to dissolve the dolomite, or enrich yourself with magnesium. We also constructed a graph of water saturation against calcite and gypsum (fig. 7B). In all cases, the water is saturated with respect to calcite but not saturated with respect to gypsum.

The relationship between calcite and dolomite saturation indices and total mineralization can provide information about the chemical equilibrium in the karst system and may be used to infer the dominant processes occurring within the aquifer.

**Tab. 4.** Saturation indices for Drienovec Cave spring

		SI calcite	SI dolomite	SI aragonite	SI gypsum	log IAP calcite	log IAP dolomite	log IAP aragonite	log IAP gypsum
Year 2014	min	0.43	-0.92	0.28	-2.14	-7.98	-17.61	-7.98	-6.74
	max	0.98	1.47	0.83	-1.98	-7.43	-15.24	-7.43	-6.57
	median	0.85	0.81	0.69	-2.04	-7.56	-15.91	-7.56	-6.64
	average	0.78	0.49	0.62	-2.04	-7.63	-16.22	-7.63	-6.64
Year 2015	min	0.74	0.53	0.58	-2.15	-7.67	-16.18	-7.67	-6.75
	max	1.68	2.46	1.52	-1.64	-6.73	-14.26	-6.73	-6.23
	median	1.03	1.25	0.88	-2.01	-7.38	-15.46	-7.38	-6.61
	average	1.04	1.19	0.88	-1.99	-7.37	-15.52	-7.37	-6.59
Year 2016	min	0.26	-0.50	0.10	-2.07	-8.15	-17.21	-8.15	-6.67
	max	1.28	1.67	1.12	-1.98	-7.13	-15.04	-7.13	-6.58
	median	1.04	1.14	0.89	-2.04	-7.37	-15.60	-7.37	-6.64
	average	0.88	0.82	0.73	-2.04	-7.52	-15.89	-7.52	-6.64
Whole period	min	0.26	-0.92	0.10	-2.15	-8.15	-17.61	-8.15	-6.75
	max	1.68	2.46	1.52	-1.64	-6.73	-14.26	-6.73	-6.23
	median	0.95	0.97	0.79	-2.03	-7.47	-15.73	-7.47	-6.63
	average	0.91	0.85	0.75	-2.02	-7.50	-15.86	-7.50	-6.62

Our samples showed medium TDS (250-350 mg/l), while in three samples the water is undersaturated with respect to dolomite (fig. 6). This suggests that there is potential for the water to dissolve more dolomite, as the concentration of dissolved dolomite in the water is lower than its solubility under the current conditions of temperature, pressure and chemical composition. SI of calcite and dolomite does not show a significant correlation with TDS.



**Fig. 6.** Calcite and dolomite saturation indices in relationship to the total mineralization

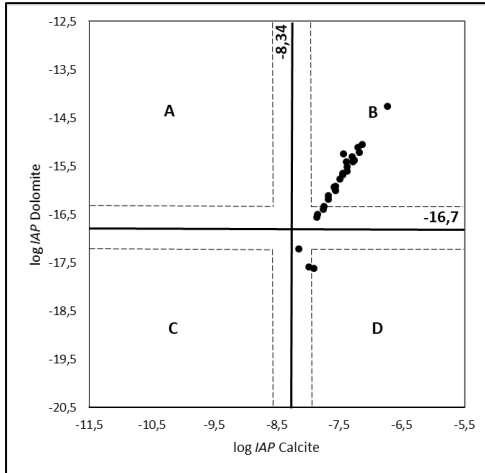
Despite the complicated geological structure of the cave's catchment area, supersaturation with respect to gypsum or gypsum and calcite (fig. 7B) was not demonstrated, but expected supersaturation with respect to calcite and dolomite and in three samples undersaturation (fig. 7A). We assume that this undersaturation is probably related to mixing with surface water and an increased amount of precipitation (high discharge during the measurements in the spring months).

Based on the Gibbs diagram (Gibbs 1970), the studied samples are located in the rock-dominated zone (fig. 8). This process represents decalcification, or in our understanding chemical denudation. This zone is typically associated with regions where the water interacts with rock formations such as limestone or dolomite, and is often found in karstic aquifers.

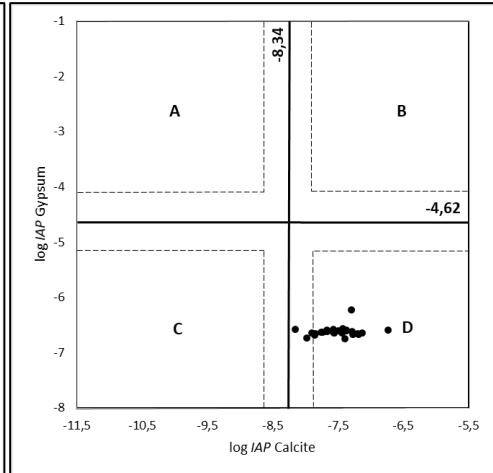
The negative CA index (basic ion exchange process) indicates the exchange of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions from the groundwater with  $\text{Na}^+$  and  $\text{K}^+$  ions from the aquifer material (El-Rawy et al. 2023). High values of CAI-I (greater than 1.0) suggest that the dissolved ions in the karst water are predominantly derived from atmospheric precipitation (fig. 9). This can occur in areas with high rainfall and limited exposure of the water to rock formations, such as in humid tropical regions. Our values are less than 1.0 what suggest a greater contribution from rock weathering.

Negative values of CAI-II (fig. 9) in the range of -0.01 to -0.04 can indicate the presence of dissolved sulfide minerals, such as pyrite, in the karst aquifer. These minerals can release sulfuric acid when they react with oxygen and water, leading to a decrease in pH and an increase in sulfate concentration in the water. This process can result in the dissolution of calcium carbonate minerals and a decrease in calcium and alkalinity concentrations, leading

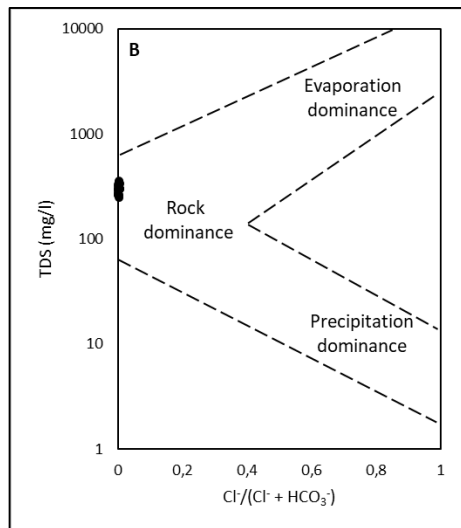
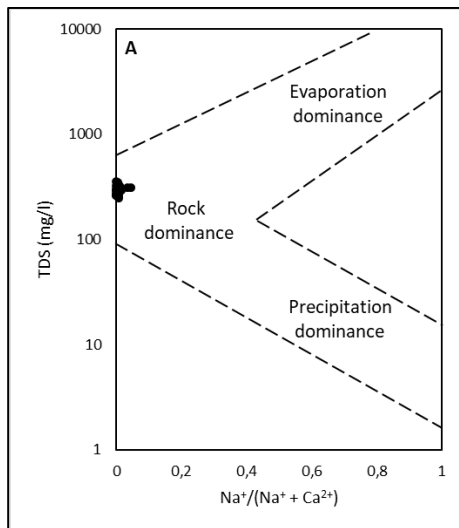
to negative CAI-II values (Gao et al. 2023). However, it's important to note that the exact interpretation of these values can vary depending on the specific geologic and hydrologic conditions of the karst system.



**Fig. 7A.** Water saturation with respect to dolomite and calcite. Supersaturation with respect to (A) dolomite, (B) calcite and dolomite, (D) calcite, (C) undersaturation with respect to calcite and dolomite



**Fig. 7B.** Water saturation with respect to gypsum and calcite. Supersaturation with respect to (A) gypsum, (B) gypsum and calcite, (D) calcite, (C) undersaturation with respect to calcite and gypsum



**Fig. 8.** Gibb's Diagram of the water quality

There is often a positive correlation between  $p\text{CO}_2$  and denudation in karst systems. This is because as  $\text{CO}_2$  dissolves in water, it forms carbonic acid which can react with the surrounding rock and cause chemical weathering. The resulting increase in dissolved ions can contribute to higher denudation rates. The table 5 provided shows the values of  $p\text{CO}_2$  and

denudation (measured in mg) for each year between 2014 and 2016, as well as the overall values for the entire period.

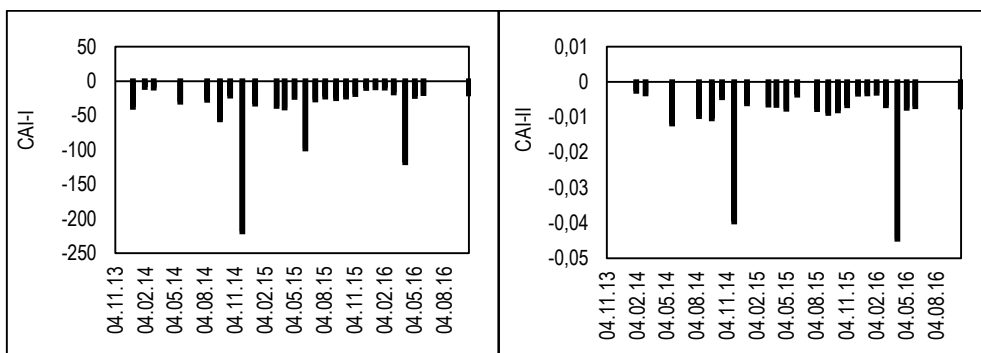
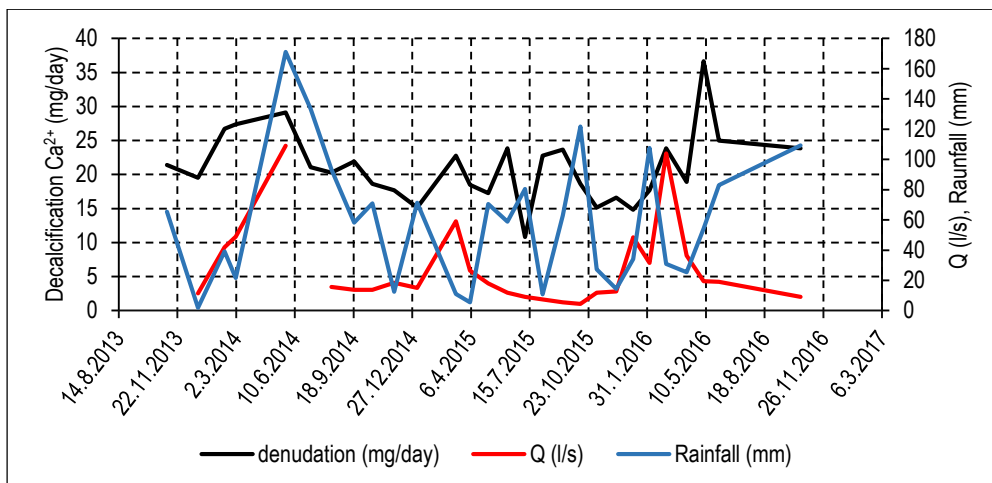


Fig. 9. CAI-I and CAI-II indices

The dynamic of chemical denudation is evident from fig. 10. The highest value of denudation was recorded in May 2016, the lowest in July 2015. It can be stated that higher values of denudation occur mainly in the spring to summer period, lower values are more likely in winter, or autumn season. The cause must be found in the factors that affect the amount of available CO<sub>2</sub> in the water. Fluctuations in CO<sub>2</sub> concentration have been shown to cause temporal variability in dissolution rates in karst springs (Covington and Vaughn 2018).

Tab. 5. Partial pressure of CO<sub>2</sub> (MPa) and denudation (mg/day) calculated by PHREEQC

	pCO <sub>2</sub>	Date	Denudation (mg)			
			Ca <sup>2+</sup>	Date		
Year 2014	min	4.03*10 <sup>-4</sup>	20. 10. 2014	min	18.65	20. 10. 2014
	max	1.53*10 <sup>-3</sup>	25. 5. 2014	max	29.11	25. 5. 2014
	median	6.10*10 <sup>-4</sup>	-	median	21.41	-
	average	8.03*10 <sup>-4</sup>	-	average	22.90	-
Year 2015	min	7.86*10 <sup>-5</sup>	7. 7. 2015	min	10.81	7. 7. 2015
	max	8.42*10 <sup>-4</sup>	7. 6. 2015	max	23.84	7. 6. 2015
	median	3.98*10 <sup>-4</sup>	-	median	18.58	-
	average	4.89*10 <sup>-4</sup>	-	average	19.11	-
Year 2016	min	2.02*10 <sup>-4</sup>	7. 1. 2016	min	14.81	7. 1. 2016
	max	3.06*10 <sup>-3</sup>	6. 5. 2016	max	36.64	6. 5. 2016
	median	4.22*10 <sup>-4</sup>	-	median	18.94	-
	average	7.97*10 <sup>-4</sup>	-	average	21.39	-
Whole period	min	7.86*10 <sup>-5</sup>	7. 7. 2015	min	10.81	7. 7. 2015
	max	3.06*10 <sup>-3</sup>	6. 5. 2016	max	36.64	6. 5. 2016
	median	5.51*10 <sup>-4</sup>	-	median	20.69	-
	average	6.89*10 <sup>-4</sup>	-	average	21.06	-



**Fig. 10.** Chemical denudation as decalcification ( $Ca^{2+}$ ) in hydrological years 2014, 2015 and 2016

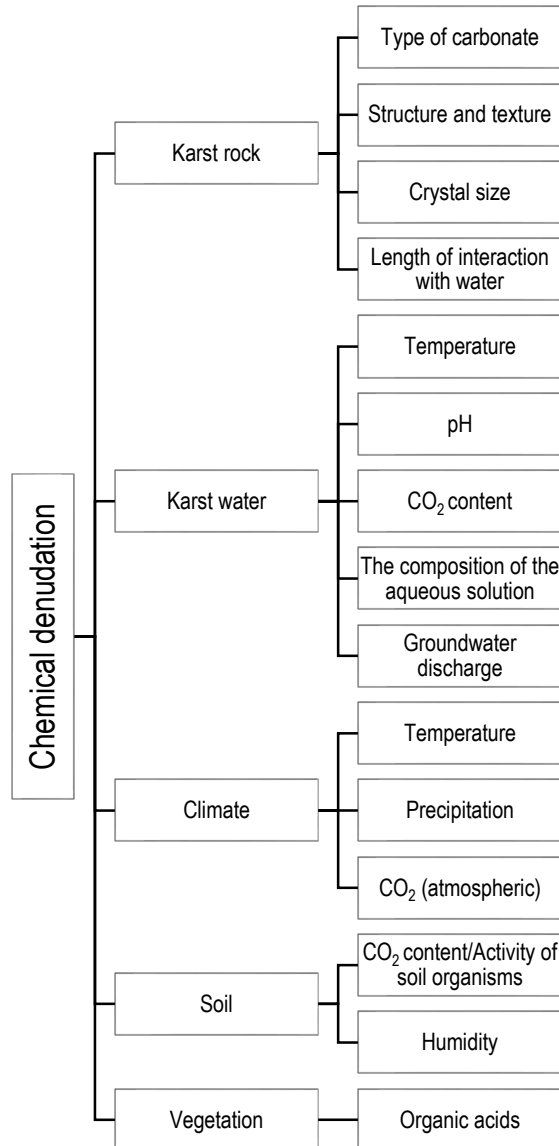
Factors of chemical denudation include: type of carbonate rock (structure and texture, crystal size, length of interaction with water),  $CO_2$  (partial pressure), water and air temperature, chemical composition of the aqueous solution, activity of soil organisms, vegetation and others (fig. 11).

a) type of carbonate (structure and texture, crystal size, length of interaction with water)  
Carbonates have different solubility. In the case of calcite, it is higher than in the case of dolomite, but smaller than in the case of aragonite (Pitter 2009). In our territory, there are mainly limestones formed by calcite. Wetterstein limestones are grainy and have a rougher surface, so they can also be subject to frost weathering (Jakál 2005). In the case of dolomites, chemical denudation is inhibited by increased magnesium content. The size of the crystals has a great influence on the solubility of minerals. Fine-grained minerals are more soluble than large crystals, since the most weakened places are the edges and corners of crystals, the number of which is higher in fine-grained minerals (Krauskopf and Bird 1995).

b) carbon dioxide and its fluctuations during the year  
The fluctuation of  $CO_2$  levels in soil during different seasons is impacted by several factors, such as temperature, moisture, plant activity, and microbial activity. When the growing season is underway, plants engage in photosynthesis and absorb  $CO_2$  from the soil, resulting in a decrease in its concentration. Conversely, during the non-growing season, when plants are dormant and microbial activity is diminished, the  $CO_2$  concentration in the soil tends to increase. Moreover, temperature and moisture levels can influence soil respiration rates, further contributing to the seasonal variations in  $CO_2$  levels. Generally, the winter months witness higher  $CO_2$  concentrations in soil, while the summer months experience lower concentrations.

c) water temperature  
In general, chemical denudation is dependent on the amount of water flowing through the system, the chemical composition of the water, and the time it spends in contact with the rock. However, temperature can also be a factor, as it can affect the solubility of minerals in the water and the rate at which chemical reactions occur. Higher temperatures can lead to increased solubility of minerals such as calcite, leading to higher rates of chemical denudation. Additionally, warmer temperatures can increase the activity of microbes, which can also contribute to chemical weathering and denudation.

The influence of snow melting water on chemical denudation can be significant (Bodiš et al. 2000). As snow melts, it generates large volumes of water that can transport dissolved carbon dioxide (CO<sub>2</sub>) and other chemical compounds into the soil and bedrock. The melting of snow increases the infiltration of water into the soil and can accelerate the dissolution of minerals such as calcite and dolomite. This is because the water is often acidic due to the presence of dissolved CO<sub>2</sub>, which can react with minerals and cause chemical weathering. Additionally, the influx of snowmelt water can also increase the amount of organic matter in soils, which can lead to the production of organic acids that enhance chemical weathering. Therefore, snow melting water can have a significant impact on the rate of chemical denudation in areas with seasonal snow cover.



**Fig. 11.** Main factors affecting the chemical denudation

#### d) chemical composition of water

The solubility of an acid salt decreases in the presence of a acid salt that has an anion or cation in common with the given acid salt. For example gypsum reduces the solubility of calcite but increases the solubility of dolomite. The increasing concentration of  $\text{Ca}^{2+}$  ions during the dissolution of gypsum leads to the precipitation of calcite. A decrease in the concentration of  $\text{CO}_3^{2-}$  due to the precipitation of calcite causes the dissolution of dolomite and an increase in the concentration of  $\text{Mg}^{2+}$  in the water. An increase in the concentration of  $\text{Mg}^{2+}$  causes an increase in the concentration of  $\text{Ca}^{2+}$  until the equilibrium of water with both minerals is established (Appelo and Postma 2005). The presence of other ions in the solution such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  causes the ionic strength effect. In general, the solubility of minerals increases with the total mineralization of water. Higher mineralized waters have a higher ionic strength of the solution (Freeze and Cherry 1979). The solubility of carbonates is also increased by the presence of  $\text{H}_2\text{S}$  and organic acids present in soils. The presence of inorganic acids such as  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$  significantly increases the solubility of carbonates, as their influence causes a double dissolution effect. In the first phase, dissolution occurs under the influence of acid, and then dissolution continues under the action of released  $\text{CO}_2$ . During the dissolution of minerals, in addition to free ions, complexes are also formed, and their presence in the solution increases the solubility of calcite and dolomite (Pitter 2009).

#### e) soil organism activity

The most important role here play acids and the already mentioned  $\text{CO}_2$ , which is accumulated in the soil from min. three biogenic sources. Firstly, root respiration of higher plants contributes to  $\text{CO}_2$  accumulation. Secondly, microorganisms (microbiota) contribute to the decomposition of soil organic matter, leading to  $\text{CO}_2$  release. Lastly, there are other decomposition processes unrelated to microbial activities that also contribute to  $\text{CO}_2$  production (Zámbó et al. 2001). These factors have a significant influence on karst corrosion, which subsequently affects the chemical composition of karst waters.

#### f) vegetation

In tropical areas, the influence of vegetation is clear. In densely forested areas organic acids resulting from the decomposition of organic residues accelerate the dissolution of limestone. In our climate, the influence of vegetation on karstification is not entirely clear. Based on a study by Kang et al. (2020) we can conclude that the process of the cycle of water and carbon binding in the area of karst forests can not only support the growth of vegetation, but also strengthen the processes of chemical weathering of carbonate rocks to absorb more  $\text{CO}_2$ . Some of the  $\text{CO}_2$  produced by forest respiration diffuses into the atmosphere as a carbon source, and the rest dissolves in groundwater, increasing corrosion.

The chemical denudation results calculated by us represent the rate of  $\text{Ca}^{2+}$  cations that are released from the solid rock into the solution during the dissolution process. Since during the dissolution process other chemical elements (depending on the composition and purity of the rock) of which the given carbonate rock is composed also pass into the solution, our results cannot be considered complete. Given that  $\text{Ca}^{2+}$  cations represent a relatively large part of carbonate rock (e.g. in limestone it is 40%, the rest is  $\text{CO}_3^{2-}$ ), we think that the results give an idea of the size of chemical denudation in the researched area. This is data from one spring where karst water flows out of a potential watershed. Its size can be changed, or its extent is not fully known, since no dyeing tests were conducted in the area. For this reason, we did not recalculate the data to the area of the basin, and therefore it is more difficult to compare them with known data from Slovakia and the world (tab. 6). The data calculated by us on the amount of chemical denudation represent a different approach to its research and we think that they can be a supplement to the classic methods represented by e.g. Gams (1966) or Pulina (1974).

**Tab. 6.** Chemical denudation rate in karst regions located in different climatic zones

Type of climate/locality	State	Denudation rate (m <sup>3</sup> .km <sup>-2</sup> .year <sup>-1</sup> )	Source
<b>Warm humid climate</b>			
Rio Bueno	Jamaica	51.0	Biro et al. (1967)
Rio San Vicente	Cuba	46.0	Lehman et al. (1956)
Sierra de los Organos	Cuba	52.9 – 136.1	Pulina and Fagundo (1992)
Sierra del Rosarion	Cuba	59.0 – 92.0	Pulina and Fagundo (1992)
Kissimmee River, Florida	USA	27.0	Douglas (1962)
<b>Moderate climate</b>			
Punkva, Moravian karst	Czech Republic	6.0 – 25.4	Corbel et al. (1964), Raušer, Štelcl and Vlček (1965), Štelcl, Vlček and Piše (1969)
Rička	Czech Republic	9.1 – 12.0	Himmel (2000), Ondráček (1982)
Jedovnický potok river	Czech Republic	6.0	Raušer, Štelcl and Vlček (1965)
Horná Morava	Czech Republic	24.6 – 85.7	Panovský (1976)
Kentucky	USA	64.0	Douglas (1962)
Lee, Essex	United Kingdom	63.0	Douglas (1962)
Areuse, Switzerland's Jura	France	89.0	Burger (1959)
Muotatal, Waldkarst	Switzerland	91.0	Bögli (1971)
Kirchberg am Wechsel (Hermannshöhle Cave)	Austria	48.0	Pavuzá (1997)
Demánovská dolina valley, Nízke Tatry Mts.	Slovakia	46.8 – 55.3	Droppa (1976)
Jánska dolina valley, Nízke Tatry Mts.	Slovakia	28.7 – 42.8	Droppa (1978)
Nízke Tatry – north part	Slovakia	17.8	Droppa (2013) (in years 1974 – 1978)
Drienovecká jaskyňa Cave	Slovakia	15.0	Gessert and Sládek (2022)
<b>Subarctic and arctic climate</b>			
Muotatal, holokarst	Switzerland	71.0	Bögli (1971)
Spitsbergen	Norway	3.0 – 20.0	Pulina (1977)

## Conclusions

Denudation plays a crucial role in the formation of karst topography and has occurred at varying rates throughout different climatic periods in the past. In our research paper, we focus on the present climatic conditions and the dynamics of denudation. This process exhibits considerable variability and is primarily influenced by the geological characteristics of the specific area and the meteorological conditions experienced throughout the year. In the Slovak karst region, denudation is also influenced by factors such as snowfall and water retention, which gradually or rapidly enter the karst system during the spring months. Fluctuations in temperatures near freezing often lead to the swift melting of some or all of the snow cover. During the studied period, the dynamic of the chemical denudation rate is clearly observable with peaks in spring months in year 2014 and 2016. The average value of denudation rate for the entire period is 21.06 mg Ca<sup>2+</sup>. While the exact extent of the underground water flow basin remains somewhat uncertain, we can still consider the calculated denudation values as representative for this region and comparable to similar values observed in other areas of Europe.



## References

- AMIOTTE SUCHET, P., PROBST, J.-L., LUDWIG, W. 2003: Worldwide distribution of continental rock lithology: Implications for the atmospheric/soil CO<sub>2</sub> uptake by continental weathering and alkalinity river transport to the oceans. *Global biogeochemical cycles*, 17, 10378. DOI: <https://doi.org/10.1029/2002GB001891>.
- APPELO, C. A. J., POSTMA, D. 2005: *Geochemistry, groundwater and pollution*. London (CRC Press). DOI: <http://dx.doi.org/10.1201/9781439833544>.
- BGR, IAH, KIT, UNESCO 2017: *World Karst Aquifer Map, 1:40 000 000*. Berlin, Reading, Karlsruhe, Paris.
- BIROT, P., CORBEL, J, MUXART, R. 1967: Morphologie des regions calcaires à la Jamaïque et à Puerto Rico. *Comptendu de deux missions subventionnées par le Comité Nat. Recherche Sci.* 335-392.
- BODIŠ, D., LOPAŠOVSKÁ, M., LOPAŠOVSKÝ, K., RAPANT, S. 2000: Chemické zloženie snehovej pokrývky na Slovensku – výsledky 25-ročného pozorovania. *Podzemná voda*, 6, 2, 162-173.
- BÖGLI, A. 1971: Karstdenudation – das Ausmass des korrosiven Kalkabtrages. *Regio Basiliensis*, 12(2), 352-361.
- BURGER, A. 1959: Hydrogeologie du Bassin de l'Areuse. These. *Bull. Soc. neuch. Géogr.*, 52(1), 304 p.
- CORBEL, J. 1959: Erosion en terrain calcaire. *Annales de Géographie*, 68, 9-120.
- CORBEL J. 1964: L'erosion terrestre, etude quantitative (Methodes. Techniques. Resultats). *Ann. geogr.*, V. 73 (398), 385-412.
- COVINGTON, M. D., VAUGHN, K. A. 2018. Carbon dioxide and dissolution rate dynamics within a karst underflow-overflow system, Savoy Experimental Watershed, Arkansas, USA. *Chemical Geology*, 527, 118689. DOI: <https://doi.org/10.1016/j.chemgeo.2018.03.009>.
- DOUGLAS, I. 1962: *An Evaluation of so used in the Study of landforms with special Limestone Areas*. Unpublished thesis. Oxford (University of Oxford).
- DREYBRODT, W. 1988: *Processes in karst*. Berlin-Heidelberg (Springer-Verlag).
- DROPPA, A. 1976: Intenzita korózie krasových tokov v Demänovskej doline. *Slovenský kras*, 14, 3-30.
- DROPPA, A. 1978: Intenzita korózie tokov v Jánskej doline. *Slovenský kras*, 16, 39-67.
- DROPPA, A. 1996: Vplyv ročných období na koróziu demänovského krasu. In Lalkovič, M. ed. *Kras a jaskyne, výskum, využívanie a ochrana*, pp. 63-70.
- DROPPA, A. 2013: Koróznny účinok krasových tokov na severnej strane Nízkyh Tatier. *Slovenský kras*, 51, Suppl. 1, 100 p.
- EL-RAWY, M., FATHI, H., ABDALLA, F. et al. 2023: An Integrated Principal Component and Hierarchical Cluster Analysis Approach for Groundwater Quality Assessment in Jazan, Saudi Arabia. *Water*, 15, 1466. DOI: <https://doi.org/10.3390/w15081466>.
- FLAKOVÁ, R., ŽENIŠOVÁ, Z. 2012: *Učebné texty z hydrogeochémie*. Bratislava (Slovenská asociácia hydrogeológov), 161 p.
- FLAKOVÁ, R., ŽENIŠOVÁ, Z. 2020: *Chemická analýza vody v hydrogeológii*. Bratislava (Slovenská asociácia hydrogeológov), 167 p.
- FRANKO, O., GAZDA, S., MICHALÍČEK, M. 1975: *Tvorba a klasifikácia minerálnych vôd Západných Karpát*. Bratislava (GÚDŠ – Geological institute of Dionýz Štúr).
- FREEZE, R. A., CHERRY, J. A. 1979: *Groundwater*. New Jersey (Prentice-Hall, Inc.).
- FORD, D. C., WILLIAMS, P. W. 1989: *Karst Geomorphology and Hydrology*. London (Chapman and Hall).
- GABROVŠEK, F. 2007: On Denudation Rates in Karst. *Acta Carsologica*, 36(1), 7-13.

- GAMS, I. 1966: Faktori in dinamika korozije na karbonatnih kameninah slovenskega, dinarskega krasa. *Geogr. Vestnik*, 38, 11-68.
- GAO, M., LI, X., QIAN, J. et al. 2023: Hydrogeochemical Characteristics and Evolution of Karst Groundwater in Heilongdong Spring Basin, Northern China. *Water* 15, 726. DOI: <https://doi.org/10.3390/w15040726>.
- GESSERT, A., SLÁDEK, I., STRAKOVÁ, V. et al. 2021: Ionic Runoff as a Way to Determine the Degree of Karst Denudation (Case Study Jasov Plateau, Slovak Karst, Slovakia). *Water*, 13(11), 1449, p. 1-21. DOI: <https://doi.org/10.3390/w13111449>.
- GESSERT, A., SLÁDEK, I. 2022: Factors and chemical denudation dynamics in the area of Drienovec Cave basin. *Geografické informácie*, 26, 2, 79-90.
- GIBBS, R. J. 1970: Mechanisms controlling world water chemistry. *Science*, 170, 1088-1090.
- GOLDSCHIEDER, N., CHEN, Z., AULER, A. S. et al. 2020: Global distribution of carbonate rocks and karst water resources. *Hydrogeological Journal*, 28, 1661-1677. DOI: <https://doi.org/10.1007/s10040-020-02139-5>.
- HIMMEL, J. 2000: Intenzita krasovění vápencu zóny vertikální krasové cirkulace v Moravském krasu. *Speleo*, 29, 12-18.
- HOCHMUTH, Z., GESSERT, A. 2017: The Jasov Plateau in the Slovak karst as an experimental area for the denudation dynamic research. In Moore K., White S. eds. *Conference Handbook: 17th International Congress of Speleology*. Sydney (Australian Speleological Federation), pp. 34-38.
- JAKÁL, J. 2005: Vlastnosti geologickej štruktúry a ich odraz v usmernení procesov krasovania. *Geomorphologia Slovaca*, 5, 2, 16-22.
- JEANNIN, P.-Y., HESSENAUER, M., MALARD, A., CHAPUIS, V. 2016: Impact of global change on karst groundwater mineralization in the Jura Mountains. *Science of the Total Environment*, 541, 1208-1221. DOI: <http://dx.doi.org/10.1016/j.scitotenv.2015.10.008>.
- KANG, Z., CHEN, J., YUAN, D. et al. 2020: Promotion function of forest vegetation on the water & carbon coupling cycle in karst critical zone: Insights from karst groundwater systems in south China. *Journal of Hydrology*, 590, 125246. DOI: <https://doi.org/10.1016/j.jhydrol.2020.125246>.
- KRAUSKOPF, K. B., BIRD, D. K. 1995: *Introduction to Geochemistry, 3rd edition*. New York (McGraw-Hill), 227 p.
- LÁNCOŠ, T., FILIPČIKOVÁ, P. 2017: Speleogenetický význam CO<sub>2</sub> pre vývoj vybraných jaskýň Plaveckého krasu v Malých Karpatoch. *Slovenský kras*, 55(1), 5-22.
- LAURITZEN, S., E. 1990: Autogenic and allogenic denudation in carbonate karst by the multiple basin method: An example from Svartisen, North Norway. *Earth surface processes and landforms*, 15(2), 157-167. DOI: <https://doi.org/10.1002/esp.3290150206>.
- LEHMANN, H., KRÖMMELBEIN, K., LÖTSCHERT, W. 1956: Karstmorphologische, geologische und botanische studien in der Sierra de los Organos auf Cuba. *Erdkunde*, Bd. 10, H. 3, 185-204.
- LI, Q., WU, P., ZHA, X. et al. 2018: Effects of mining activities on evolution of water chemistry in coal-bearing aquifers in karst region of Midwestern Guizhou, China: evidences from  $\delta^{13}\text{C}$  of dissolved inorganic carbon and  $\delta^{34}\text{S}$  of sulfate. *Environmental Science and Pollution Research*, 25, 18038-18048. DOI: <https://doi.org/10.1007/s11356-018-1969-3>.
- MAHER, K., CHAMBERLAIN, C., P. 2014: Hydrological Regulation of Chemical Weathering and the Geologic Carbon Cycle. *Science*, 343, 1502. DOI: <https://doi.org/10.1126/science.1250770>.
- MELLO, J., POLÁK, M., ELEČKO, M. et al. 1996: *Geologická mapa Slovenského krasu 1:50 000*. Bratislava (Ministerstvo životného prostredia Slovenskej republiky).

- ONDRÁČEK, S. 1982: Vliv Moravského krasu na některé chemické a fyzikální vlastnosti vod v točích v povodí Říčky. *Československý kras*, 33, 35-51.
- ORVAN, J. 1974: *Hačavsko-jasovská hydrogeologická štruktúra*. Žilina (IGHP – geological and hydrogeological survey).
- PAČES, T. 1983: *Základy geochemie vod*. Praha (Academia).
- PALCSU, L., GESSERT, A., TÚRI, M. et al. 2021: Long-term time series of environmental tracers reveal recharge and discharge conditions in shallow karst aquifers in Hungary and Slovakia. *Journal of Hydrology: Regional Studies*, 36, 100858. <https://doi.org/10.1016/j.ejrh.2021.100858>.
- PARKHURST, D. L., APPELO, C., A., J., 1999: User's Guide to PHREEQC (version 2) – a Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. *US Geological Survey Water-Resources Investigations Report 99-4259*, 312 p.
- PAVUZA, R. 1997: Hydrologische Aspekte der Hermannshöhle bei Kirchberg am Wechsel. In Hartmann, H. W., Mrkos, H. eds. *Die Hermannshöhle in Niederösterreich - „Die Höhle“*, 50. Wien (Wiss. Beiheft z. Z.), pp. 147-166.
- PITTER, P. 2009: *Hydrochemie*. Praha (Vysoká škola chemicko-technologická).
- PRELOVŠEK, M. 2012: *The dynamics of the present-day speleogenetic processes in the stream caves of Slovenia*. Ljubljana – Postojna (Založba ZRC).
- PRIESNITZ, K. 1974: Losungsraten und ihre geomorphologische Relevanz. *Abhandlungen Akademie der Wissenschaften in Göttingen, Mathematisch-Physikalische*, 29(3), 68-84.
- PULINA, M. 1974: *Prace geograficzne 105: Denudacja chemiczna na obszarach krasu węglanowego*. Warszawa (Wydawnictwo Polskiej akademii nauk), 159 p.
- PULINA, M. 1977: Uwagi o zjawiskach krasowych w południowej części Spitsbergenu. *Kras i Speleologia*, 10(1), 104-129.
- PULINA, M., FAGUNDO, J. R. 1992: Tropical karst and chemical denudation of western-Cuba. *Geographia Polonica*, 60, 196-216.
- RAN, L., LI, L., TIAN, M. et al. 2017: Riverine CO<sub>2</sub> emissions in the Wuding River catchment on the Loess Plateau: Environmental controls and dam impoundment impact. *J. Geophys. Res. Biogeosci.*, 122 (6), 1439-1455. DOI: <https://doi.org/10.1002/2016JG003713>.
- RAUŠER, J., ŠTELCL, O., VLČEK, V. 1965: Principal Characteristic of Karst Water in the Central European area. According to the Results of Research from the Moravian Karst. *Problems of the Speleological Research*. Academia (Praha), 85-105.
- RODA, Š., RAJMAN, L., ERDŐS, M. et al. 1986: *Vznik a vývoj sintrových foriem v piatich jaskyniach Slovenského krasu*. Osveta (Martin).
- RZONCA, B., BUCZINSKI, S. 2013: Intense karst denudation in a crystalline basin with a small share of carbonate rocks (Sudety Mountains, SW Poland). *Catena*, 107, 154-164.
- SCHÖLLER, H. 1967: Qualitative Evaluation of Ground Water Resources. In Schöller, H. ed. *Water Resource Series No. 33: Methods and Techniques of Groundwater Investigation and Development*. Paris (UNESCO), pp. 44-52.
- SHOPOV, Y., STOYKOVA, D., SANKOV, L. T. et al. 2009: Past Annual Variations of the Karst Denudation Rates. In Durán, J. J., Andreo, B., Carrasco, F. eds. *Publicaciones del Instituto Geológico y minero de Espana. Serie: Hidrogeología y aguas subterráneas, no. 18*. Madrid (Instituto Geológico y Minero de España), 487- 494.
- SLOVAK ENVIRONMENTAL AGENCY 2002: *Atlas of the Slovak Republic*. Banská Bystrica (Slovak Environmental Agency). [cit. 2023-02-02]. Retrieved from: <https://app.sazp.sk/atlassr/>.

- SMITH, D. I., NEWSON, M. D. 1974: The dynamics of solutional and mechanical erosion in limestone catchments on the Mendip Hills, Somerset. In Gregory K. J., Walling D. E. eds. *Fluvial processes in instrumented watersheds*. London (Institute of British Geographers), pp. 155-167.
- ŠGÚDŠ 2017: *Geological map of Slovakia 2017*. Bratislava (ŠGDÚŠ – State Geological Institute of Dionýz Štúr). [cit. 2023-02-02]. Retrieved from: <https://apl.geology.sk/gm50js/>.
- ŠTELCL, O., RAUŠER, J., PÍŠE, J. 1969: Limestone Solution Intensity in the Moravian Karst. *Studia Geographica*, 5, 71-86.
- ŠTELCL, O., VLČEK, V., PANOVSÝ, K. 1976: Intenzita koroze různých typů karbonátových hornin v ČSR. *Československý kras*, 28, 29-48.
- TAO, X., WU, P., TANG, CH. et al. 2012: Effect of acid mine drainage on a karst basin: a case study on the high-As coal mining area in Guizhou province, China. *Environmental Earth Sciences*, 65, 631-638: DOI: <https://doi.org/10.1007/s12665-011-1110-0>.
- WHITE, W. B. 1988: *Geomorphology and Hydrology of Karst Terrains*. New York, Oxford (Oxford University).
- ZACHAROV, M. 2008: Geologické a tektonické pomery Drienovskej jaskyne v Slovenskom krase. *Slovenský kras*, 46(1), 41-52.
- ZÁMBÓ, L., HORVÁTH, G., TELBISZ, T. 2001: Investigations of microbial origin of karst corrosion of soils depending on different temperatures. *Chinese Science Bulletin*, 46, 28-32.

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