

Stable isotopes and water chemistry in Čachtice Cave and Hladový prameň Cave in relation to karst topology, soil cover, and past land-use

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Abstract: The Čachtické Karpaty Mts. are the northernmost part of the Malé Karpaty Mts. The studied area belongs to the Čachtice Karst area built by Middle to Upper Triassic Wetterstein limestone and dolomite. The Hladový prameň and Čachtická caves represent two contrasting cave systems, which were formed along steeply dipping fault structures with N–S and NW–SE strikes, respectively. The stable isotopes of CO₂ in water samples from both caves point to microbially produced soil CO₂ as main source of carbon in dissolved bicarbonate. We observed lighter carbon in water of the Hladový prameň, probably due to thicker pile of decomposing leaf litter above the cave and thus more soil CO₂ production. The study of carbon isotopes in grasses and soils with different histories of land-use ruled out presence of grasslands dominated by C4 plant species producing heavier carbon. In speleothems, the lightest oxygen occurs in soda-straws, while in flowstones and helictites the oxygen is heavier due to evaporation prior to calcite crystallization. Dripwater sampled simultaneously in the Hladový prameň and Čachtická caves slightly differ, reflecting a lagged response to rainfall events due to much thicker overburden in the Čachtická Cave. According to chemical analyses, the spring water at the Hladový prameň Cave has developed in shallow circulating system within Wetterstein Limestone, without significant contact with underlying dolomites.

Key words: karst water, stable isotopes, tectonics, soil carbon, Čachtice Karst

1. INTRODUCTION

The karstification is a rather complicated process dependent on different external and internal factors, like climatic conditions, presence of plant cover, soil thickness and composition, hydrologic conditions, rock composition, presence of tectonic discontinuities, etc. Therefore it should be a proper approach to study karst phenomena in a multidisciplinary way. Following this principle, in this paper we are presenting a multidisciplinary approach of the karst phenomena research combining methods of water geochemistry, stable isotope study of cave drip-water, speleothems, soil and plants, as well as tectonic field study.

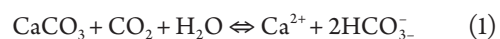
The research of a stable isotope could help to answer a wide range of questions regarding palaeoclimatic factors influencing karstogenesis. Carbon isotope composition of CO₂ in water percolating between the surface and the cave passages is influenced by presence of C3 and/or C4 plants (Pyankov et al., 2010; Bonafini et al., 2013) and microbial activity during organic detritus decomposition in the soil layer (Fessenden & Ehleringer, 2002; Boström, et al., 2007).

The isotope composition changes of C and O in speleothems are mirroring changes in palaeoclimatic and environmental conditions influencing cave evolution in the past (McDermott et al., 2006; Lachniet, 2008; Kacanski et al., 2011; Fairchild & Baker, 2012)

Karst processes are tied to rock types with high solubility in water, mainly carbonates. The initial karstification is often

dependent on predispositions in rock such as fissures, tectonic faults, bedding planes, joints, and shear fractures (Klimchouk & Ford, 2000). On the surface they are often represented by lines of sinkholes arranged along the cave passages located beneath the surface. Therefore, sinkhole mapping is an extremely useful method for their identification (Lačný et al., 2019).

These discontinuities are further widened by dissolution (eq.1), forming underground network of cavities.



The dissolution rate is controlled by concentration of dissolved CO₂, which saturates the rainwater in soil. Limestone dissolution may further proceed in open or closed system. The open system process happens when the CO₂ consumed by carbonate dissolution is continually resupplied by percolating water from a soil CO₂ reservoir where it is released by root respiration and/or organic bacterial decomposition of the organic detritus (Laursen, 1991). In opposite, the closed system dissolution occurs when the aquifer is isolated from the CO₂ reservoir, therefore it is not resupplied continually. In the former case the water is characterized by lower pH and higher TDS (Total Dissolved Solids) values, as the dissolution process is more effective comparing to the closed system (Appelo & Postma, 2006; Ford & Williamson, 2007). Carbon isotope values, which are initially around mid-point between light soil carbon (–20 to –30 ‰ PDB, Fairchild & Baker, 2012) and heavy limestone carbon (typically 0 to + 2 ‰

PDB Fairchild & Baker, 2012) are only weakly modified by limestone composition when passing fast through its porous network under open-system conditions. On a contrary, in closed system the solution is in prolonged contact with host limestone and gradually equilibrates with its composition, becoming progressively more positive. Drip-rate influences isotope composition in similar way though by different mechanism – longer dwelling time of terminal drop on the tip of stalactite/soda-straw causes increase in both O and C isotope values due to evaporation and CO₂ degassing, respectively.

2. STUDY AREA

Geological setting

The Čachtické Karpaty Mts. area are the northernmost part of the Malé Karpaty Mts. (Mazúr & Lukniš, 1980). They are located between villages Bzince pod Javorinou, Prašník, Čachtice, and Ivanovce (Fig. 1). The highest point is an elevation called Na Salaškách (588 m asl.). The plateau is divided into two parts by the Jablonka Valley, the northern part Nedze and the southern part Velký Plešivec.

The horst of Čachtické Karpaty Mts. is uplifted along normal faults from beneath Palaeogene sediments of Myjavská pahorkatina Hills in the west and Neogene sediments of Danube

Basin in the east. The Čachtické Karpaty Mts. consist of two Mesozoic lithostratigraphic units – the Jablonica Group (Triassic carbonates) and the Hrušov Group (Jurassic carbonates) of the Považie nappe of the Hronicum Unit (Havrila, 2011). The northern part of the Čachtické Karpaty Mts. is represented by younger members (mainly Jurassic), while middle part is composed of the Middle to Upper Triassic Wetterstein Limestone and Dolomite (Čachtice Karst Plateau) (Fig. 2), as well as the Upper Triassic Haupt Dolomite (Velký Plešivec karst area) (Began et al., 1984).

Mesozoic sediments are forming tectonic slices striking mostly to NE – SW with SE plunge. The central part of the mountain range is built up by the Middle and Upper Triassic Wetterstein Limestone and Dolomite (Salaj et al., 1987), hosting the Čachtice Karst with an area of 71 km² (Mitter, 1974). These carbonate rocks are forming an environment where the Čachtice Karst region was developed (Mitter, 1974).

The Wetterstein Limestone (Ladinian – Early Carnian) are mostly massive, near the eastern marginal faults they are bedded and steeply dipping. Except of boundary faults delimiting the karst area, there are also geomorphologically significant NW – SE crossing faults. While these faults play major role in the evolution of all surface flows, another NE – SW oriented fault system has of major importance in the development of an underground stream system (Mitter, 1974). Most cave systems in the study area were developed on these NE–SW faults.

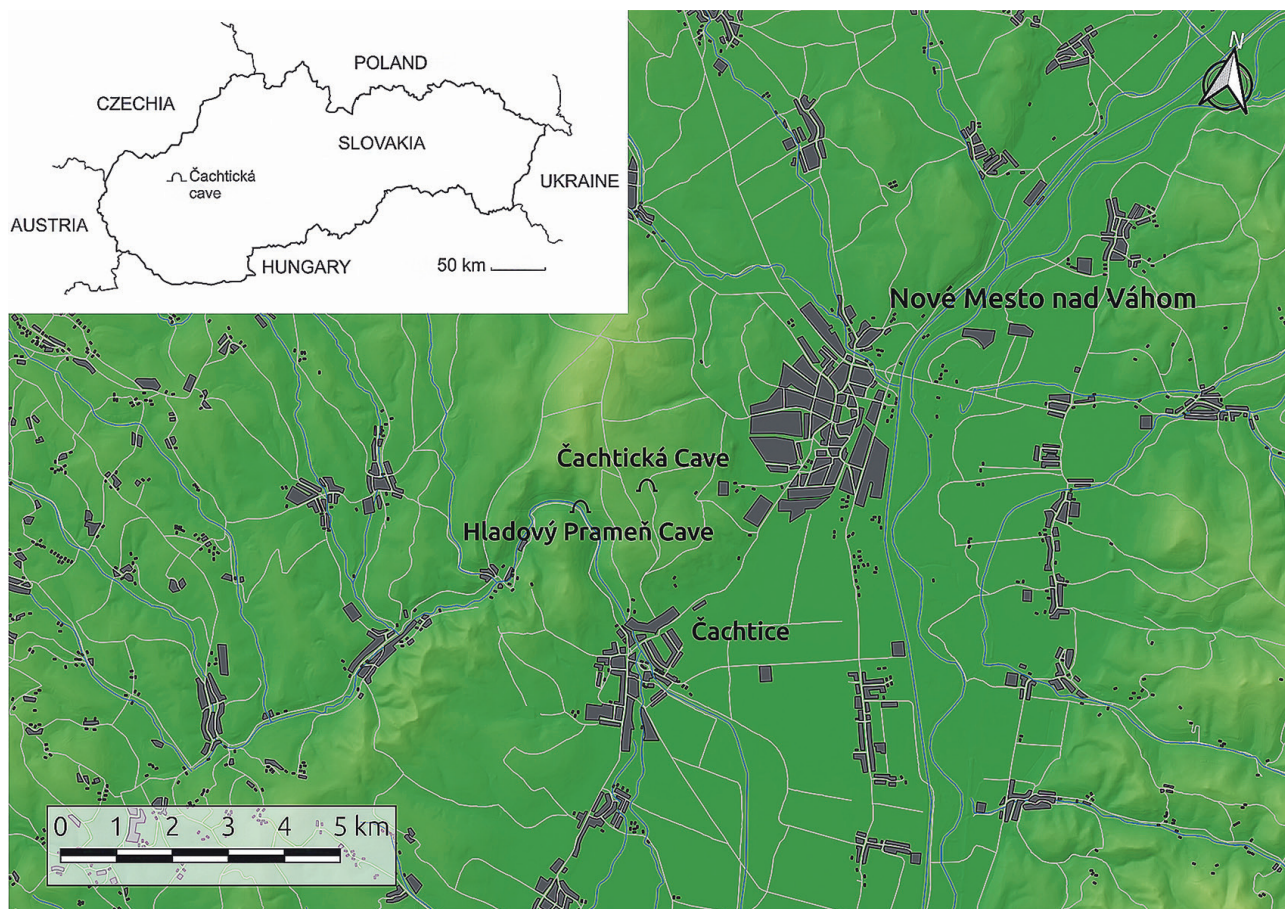


Fig. 1. Location of the Čachtická Cave and Hladový prameň Cave.

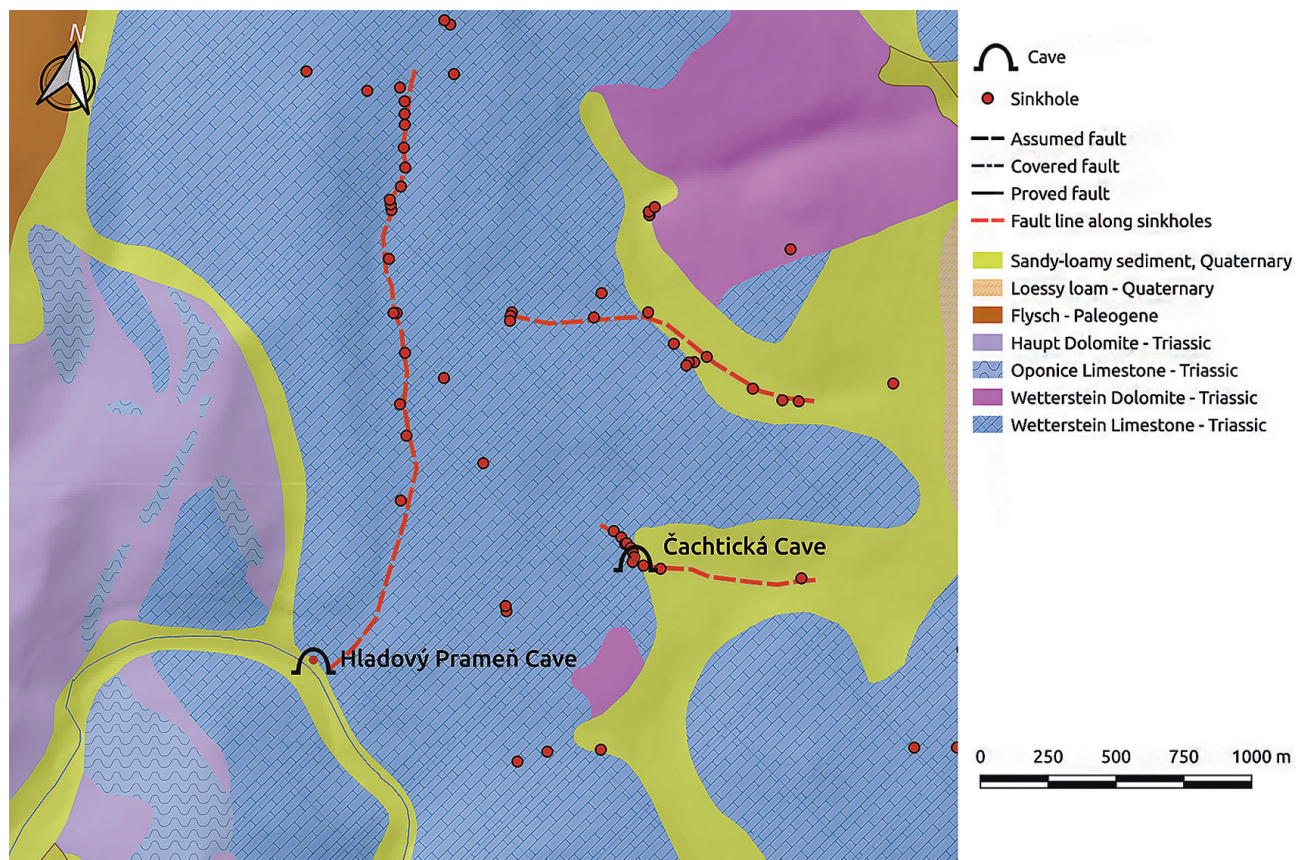


Fig. 2. Geological map of the studied area with location of sinkholes and studied caves according to Began et al. (1984) and Lačný et al. (2019).

2.2 Hydrogeology

The dominant hydrogeological features are developed on fault tectonics of the investigated area (Kullman et al., 1994). The NW – SE fault system forms a predisposition for surface water streams. Streams in the northern part of the mountain range, mainly Bošáček, Klanečnica, and Kamečnica, have an important role in the recharge of hydrogeological structures. In this case, they represent a significant proportion of groundwater, unlike most of the karst-crack hydrogeological structures of the Western Carpathians, which are mostly replenished by the infiltration of precipitation water (Kullman et al., 1994). On the other hand, the stream of Jablonka drains the hydrogeological structure especially at high water levels. Hydrometric measurements and significant loss of water in surface streams (Kullman et al., 1994) are showing possible existence of open and high-capacity water-bearing faults. However, the NE – SW boundary fault system limiting the mountain range from the eastern side has the main groundwater draining function (Kullman et al., 1994). From the point of view of the groundwater discharge of the carbonate aquifer, the Čachtické Karpaty Mts. are characterized by a very small number of karst-fissure springs. Groundwater is discharging into seven karst-fissure springs, partly forming linear or areal discharges located on the eastern edge of the mountain. The only spring located inside the hydrogeological structure is the occasional resurgence the Hladový prameň Cave in the Jablonka Valley.

2.3 Location of caves

2.3.1 The Čachtická Cave

The entrance to the Čachtická Cave (Fig. 3) is situated in one of the sinkholes of a larger old depression on Čachtice Karst Plateau. The known length of the cave system is 3865 m and depth is 110 m (Sluka, 1983). The cave is a complicated system of mostly vertical fissure spaces, chimneys and domes paralleled/connected by corridors. Thin vertical passages were created mostly by corrosive widening of cracks and fissures in more than one phase (Mitter, 1974; Sluka, 1983). The bottom of the cave is at approximately 226 meters a. s. level and is filled by clayey – sandy sediments occurring almost in every spaces of the cave. The argillaceous material was transported by flood water from the surface, or deposited by groundwater from surrounding areas during flood events, but no signs of an active water flow were observed (Mitter, 1974). The cave evolved during the first phase of speleogenesis in the phreatic to epiphreatic zone. In the second phase, after water level decrease the evolved in the vadose zone. Therefore it is a hypergenous dissolution cave according to methodology of Bella (2016).

2.3.2 The Cave Hladový prameň

This cave (Fig. 4) was discovered in 1952 by Ján Majko (Majko, 1961), it is located between Višňové and Čachtice villages at the easternmost part of Hrabutnice Valley. Its length is 88 m and ends with small fissure lake. The cave walls are formed mostly by



Fig. 3. The corridor map of Čachtická Cave (Sluka et al., 1999) with sampling sites.

the Wetterstein Limestone without larger speleothems, except few soda-straws and flowstones. At the present time we have not enough information to exactly define its genetic type. It is a resurgence cave, which probably evolved in the phreatic to epiphreatic zone, similarly to the Čachtická Cave (Bella, 2016).

3 METHODS AND SAMPLES

Measurements of geological deformation structures both on the surface and in the underground were carried out by standard geological survey methods using the Freiberg geological compass. The OpenStereo software was used for plotting and geometric analysis of planar structural elements (Grohmann & Campanha, 2010).

A structural analysis was carried out in the vicinity and in the Cave Hladový prameň, by means of the geometric and kinematic analysis of faults and cracks. The aim of the investigation was to determine, which structures played an important role in cave speleogenesis and to identify them as possible surface phenomena, such as fracture structures and/or sinkhole linear distribution.

Two water samples were taken from the Hladový prameň karst spring for the purpose of chemical analysis. During field sampling measurements of pH, electrolytic conductivity, oxidation-reduction potential, temperature, and dissolved oxygen content measurements were performed by the Aquamater field device equipped with the Aquaread electrode unit. The

alkalinity and acidity were determined by the acid-base titration method using repetitive pipette. The alkalinity was measured by titration of 0.1 M HCl per 100 ml sample with mixed indicator (bromocresol green and methyl red). The acidity was measured by titration of 0.1 M NaOH per 100 ml of the sample, as indicator phenolphthalein was used. Immediately a water sample was taken, Ca^{2+} , Mg^{2+} , Al^{3+} , Fe, SO_4^{2-} and NO_3^- were determined by photocolourimetric method using the Merck® Spectroquant Move field analyzer. This method is not suitable for alkali metals determination, but in not contaminated karst waters their concentrations are rather low. Therefore, the total dissolved solids (TDS) values mentioned in this text are computed without alkali metals concentrations.

Thermodynamic equilibria including saturation indices related to mineral phases in the water sample were calculated using the USGS PHREEQC software (Parkhurst & Appelo, 1999).

Water was sampled into 2 ml glass vials sealed by gas-tight cap with PTFE/silicon septa using syringes. Values of pH and EC were measured using the Extech Exstik II device in some samples, where the amount of the sampled water allowed the measurement. The H and O isotope analysis was performed on FlashHT device coupled to isotope-ratio mass spectrometer (ITMS) MAT2S2 via a continuous flow interface Conflo IV (Thermo). A volume of 0.5 microliter of water was injected by syringe into glassy carbon pyrolysis reactor heated to 1400 °C where conversion of water to H_2 and CO takes place on carbon, the produced gas is separated on GC column and pure gases

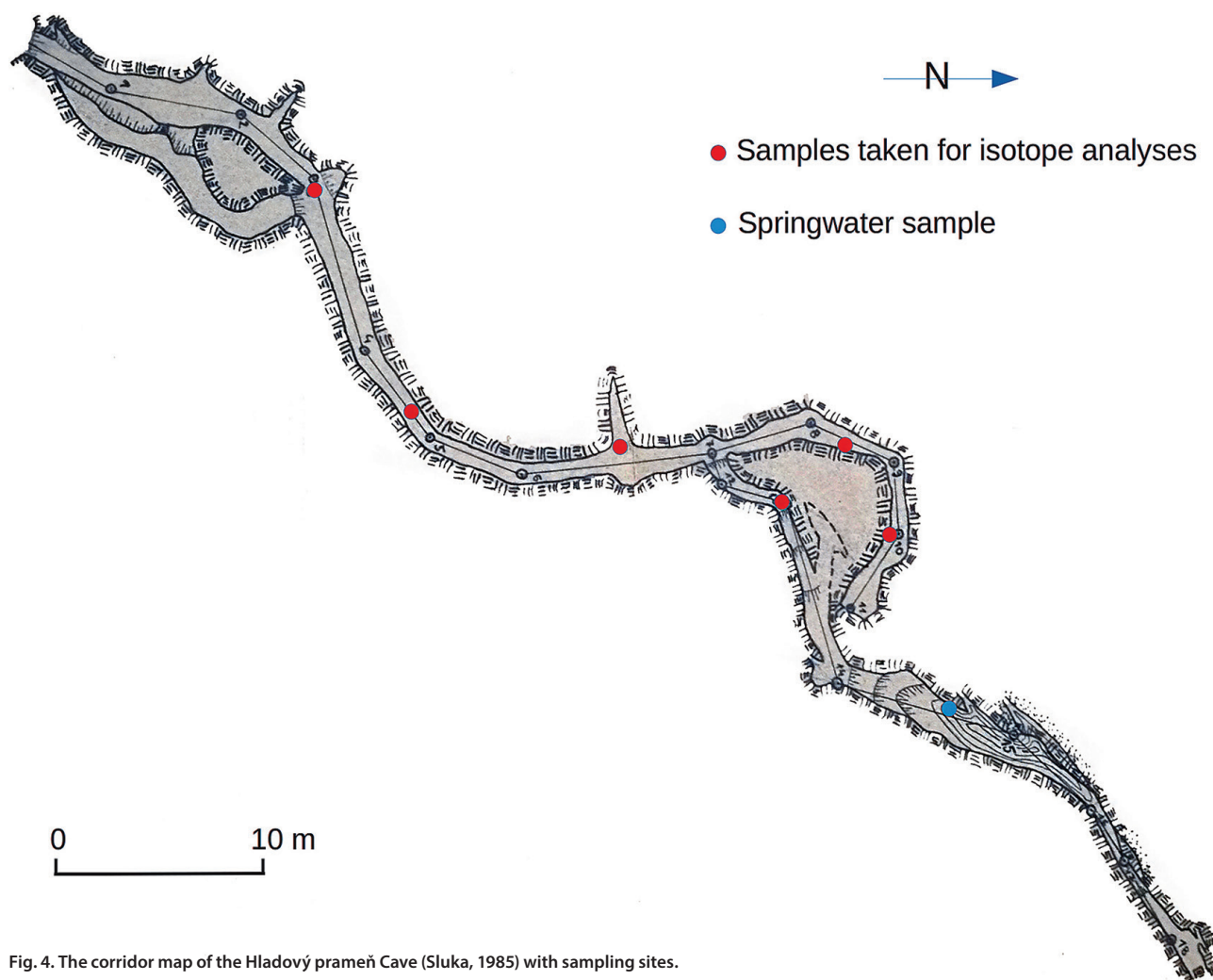


Fig. 4. The corridor map of the Hladový prameň Cave (Sluka, 1985) with sampling sites.

enter the IRMS separately, measured against reference gases H_2 and CO_2 . Raw measurements are calibrated by international reference materials VSMOW2 and SLAP2 with δD 0.30 ‰ and -427.50 ‰ and H and $\delta^{18}O$ 0.02 ‰ and -55.50 ‰, respectively. These standards were bracketing the sample sequence, no drift of isotope values was observed. All the values are reported in permil vs. SMOW, precision of measurement is ca. 1.2 ‰ for hydrogen and 0.2 ‰ for oxygen. The samples were measured in triplicate, first analyses of each triad were omitted in order to avoid possible memory effects and two later values were averaged.

In summer 2018 we collected samples of carbonates and water for analyses of stable isotopes of C-O and H-O, respectively. From the Hladový prameň Cave we got samples of wallrocks limestone and water from small lake at the end of the cave. From the Čachtická Cave we collected samples of wallrocks, flowstone from the floor, soda-straws and helictite. All the samples were collected near the measurement point 274 in Veľká Kaplnka hall.

In spring 2019, we sampled soil from horizons A and B at 22 localities, as well as 7 different grasses for analysis of stable C isotopes. The horizon A is an uppermost soil layer in depth of 2–5 cm consisting of decomposed leaf litter, the horizon B is a deeper soil part from 15 to 25 cm. The sampling sites were selected to cover four scenarios of changing land use between

1950 and 2019 based on historical orthophotographs from 1950 (TUZVO/Geodis, 2017) and present-day aerial images (www.mapy.cz): 1) forest to steppe; 2) steppe to forest; 3) steppe unchanged; 4) forest unchanged.

All the stable isotope ratios were measured on isotope-ratio mass spectrometer (IRMS) MAT 253 (Thermo Scientific). The C and O isotopes of carbonates and waters were measured in continuous-flow regime using Gasbench III preparation device coupled to IRMS. Finely ground samples of about 60 micrograms of carbonate were loaded into glass vials (Labco) and flushed with helium to remove atmosphere. Water samples were injected into helium pre-flushed vials. The subsequent acid digestion (McCrea, 1950) took place at 40 °C overnight, acid was dosed into vials by needle through rubber septa. The evolved CO_2 was analysed by IRMS against reference CO_2 gas. Raw isotope ratios were calibrated using international reference material NBS18 with $\delta^{13}C = +5.014$ ‰, $\delta^{18}O = -23.2$ ‰ and two working standards with $\delta^{13}C = +2.48$ ‰, $\delta^{18}O = -2.40$ ‰ and $\delta^{13}C = -9.30$ ‰, $\delta^{18}O = -15.30$ ‰, respectively. Typical precision of measurement is 0.1 ‰ for carbon and 0.2 ‰ for oxygen. Isotope values are reported as permil vs. PDB.

Stable carbon isotopes of organic matter were measured after decomposition of soil and grass samples in elemental analyzer

Flash2000 HT Plus coupled to IRMS. Organic residues after digestion in hydrochloric acid of about 60 – 100 micrograms were wrapped into tin cups and combusted at 1000 °C in quartz tube packed with chromium oxide, electrolytic copper and silvered cobaltous/cobaltic oxide. The CO₂ gas was further purified chromatographically and leads into IRMS in a stream of helium. Raw isotope ratios measured against CO₂ reference gas were calibrated to PDB scale using two international reference materials (USGS24 carbon, USGS41 glutamic acid) and two working standards (IVA urea, SUERC carbon) with δ¹³C values –16.05 ‰, +37.76 ‰, –39.79 ‰, –25.60 ‰, respectively. All the values are reported in permil PDB, precision is 0.1 ‰.

Water samples of 0.5 microliter were injected into pyrolysis reactor of elementary analyser Flash2000 HT Plus where they decomposed to H₂ and CO at 1400 °C. These gases were measured by IRMS and their stable isotope composition was recalculated using calibrations standards (VSMOW2 and SLAP2 with δD = +0.30 and –427.50 ‰ SMOW and δ¹⁸O = +0.02 and –55.50 ‰ SMOW, respectively) measured along the samples. All the values are reported in permil against SMOW, precision of measurement is 0.12 ‰ for oxygen and 0.57 ‰ for hydrogen.

4. RESULTS

4.1 Structural analysis

A total of 24 planes were measured, of which ten planar structures were in the cave itself. Planes on the basis of field research were classified into 2 categories (S₀, S₁) with respect to their genetic and intersection relations. The planes measured in the cave form a separate reference layer. The S₀ planes represent primary bedding (red great circles) and generally they are inclined westwards at 50° in average. The second group of planar structures consists of discontinuities (S₁, blue great circles) generally oriented in the NE–SW direction with steep inclination to the NE or SW. The dataset also includes the W–E striking discontinuities, because of their low frequency and subvertical dip. The S₁ planes were also significantly observed on the surface outcrops.

Following the measurements of planar structures in the cave (green great circle) and the rose diagram prepared on the basis of structural measurements, it can be stated that the cave origin was significantly influenced by the NE–SW oriented planes (S₁ group). On the surface, this trend of planes were significantly observed and measured, in particular near the assumed fault NE–SW direction, located north-east of the cave (Fig. 5).

In conclusion, the Hladový prameň Cave was formed on the NE–SW fault structure. The most significant cave of the Čachtice Karst – Čachtická Cave was also formed on the fault structures of the same trend. The bedding planes (S₀) in the previously known parts of the cave are not significant in terms of their speleogenesis.

4.2 Water sample chemical analyses

Two water samples were taken from the Hladový prameň Cave in July 2018 and in March 2019 (Tab. 1). When the first sample

was taken, the water level was extremely low, the water formed a small pond with an area of approx. 1.5 m² and a depth of about 80 cm, approx. 60 m far from the cave entrance. Water is flowing to the pond through the debris from the side opposite the entrance and is leaving through the debris on the opposite side. The pH value of 7.07 is unusually low for the karst springs of the Western Carpathians, in the karst springs of Slovakia pH values lower than 7 occur rarely, on the contrary, there are no rare values close to 8 or higher (as it comes from yet unpublished data of more than 200 karst water analyses done by one of the authors). Such a low pH is due to a relatively high concentration of CO₂, which results in a high total dissolved solids content (TDS, 611.9 mg.l⁻¹) due to the more intensive dissolution of carbonate rock minerals. The TDS consists mainly of calcium cations and hydrogen carbonate anions, which can be inferred that the main mineralization process is the dissolution of calcite in limestone. In March 2019, when the second sample was taken, the water level was probably more than 1.2 – 1.5 m higher, the length of the pond was approx. 6 – 7 m, the width was 1.2 m. However, the main difference was in extremely high concentration of NO₃⁻ (504.64 mg.l⁻¹), considerably lower HCO₃⁻ (229.42 mg.l⁻¹) and Ca²⁺ (91 mg.l⁻¹) as well as TDS (886.79 mg.l⁻¹). The pH value was even lower than in July 2018 (6.8).

Tab. 1. Results of chemical analysis and in situ measurements of water samples from the karst spring of Hladový prameň Cave.

Date	July 27.2018	March 27.2019	July 27.2018	March 27.2019	
T _{water} [°C]	10.35	10.5	Eh [meV]	82.9	-
pH	7.07	6.8	O ₂ [mg.l ⁻¹]	9.57	-
EC [µS.cm ⁻¹]	714	656	O ₂ [sat. %]	87.2	-
CO ₂ [mg.l ⁻¹]	67.46	61.61	SiO ₂ [mg.l ⁻¹]	7.36	5.73
TDS [mg.l ⁻¹]	611.9	886.79			
	Cations [mg.l ⁻¹]		Anions [mg.l ⁻¹]		
Ca ²⁺	135	91	SO ₄ ²⁻	20	32
Mg ²⁺	11.9	11.7	NO ₃ ⁻	3.98	504.64
Fe ²⁺	0.04	0.28	HCO ₃ ⁻	433.21	229.42
Al ³⁺	41	9	⁹ rMg ²⁺ /rCa ²⁺	0.15	0.21
Saturation indices					
Calcite	-0.19	0.17	Dolomite	-1.31	-0.42

4.3 Stable isotopes

Average carbon stable isotopes analyses in water from soda-straws are 12.48 ‰ in the Čachtická Cave and 14.93 ‰ in the Hladový prameň Cave. The value in the Hladový prameň spring is –17.35 ‰, in siphon is –11.39 ‰ and in veil is –11.40 ‰.

Average values of stable isotope analyses of flowstones in ČČ: δ¹³C is –5.94 ‰, δ¹⁸O is –6.16 ‰. For the wallrock in the Čachtická Cave is the mean value δ¹³C 2.72 ‰, δ¹⁸O is 5.14 ‰ and in the Hladový prameň Cave: δ¹³C is 0.43 ‰, δ¹⁸O is –5.97 ‰. For soda-straws the average values for ČČ are: δ¹³C –8.90 ‰, δ¹⁸O –9.38 ‰ and for helictite: δ¹³C –7.27 ‰, δ¹⁸O –7.08 ‰.

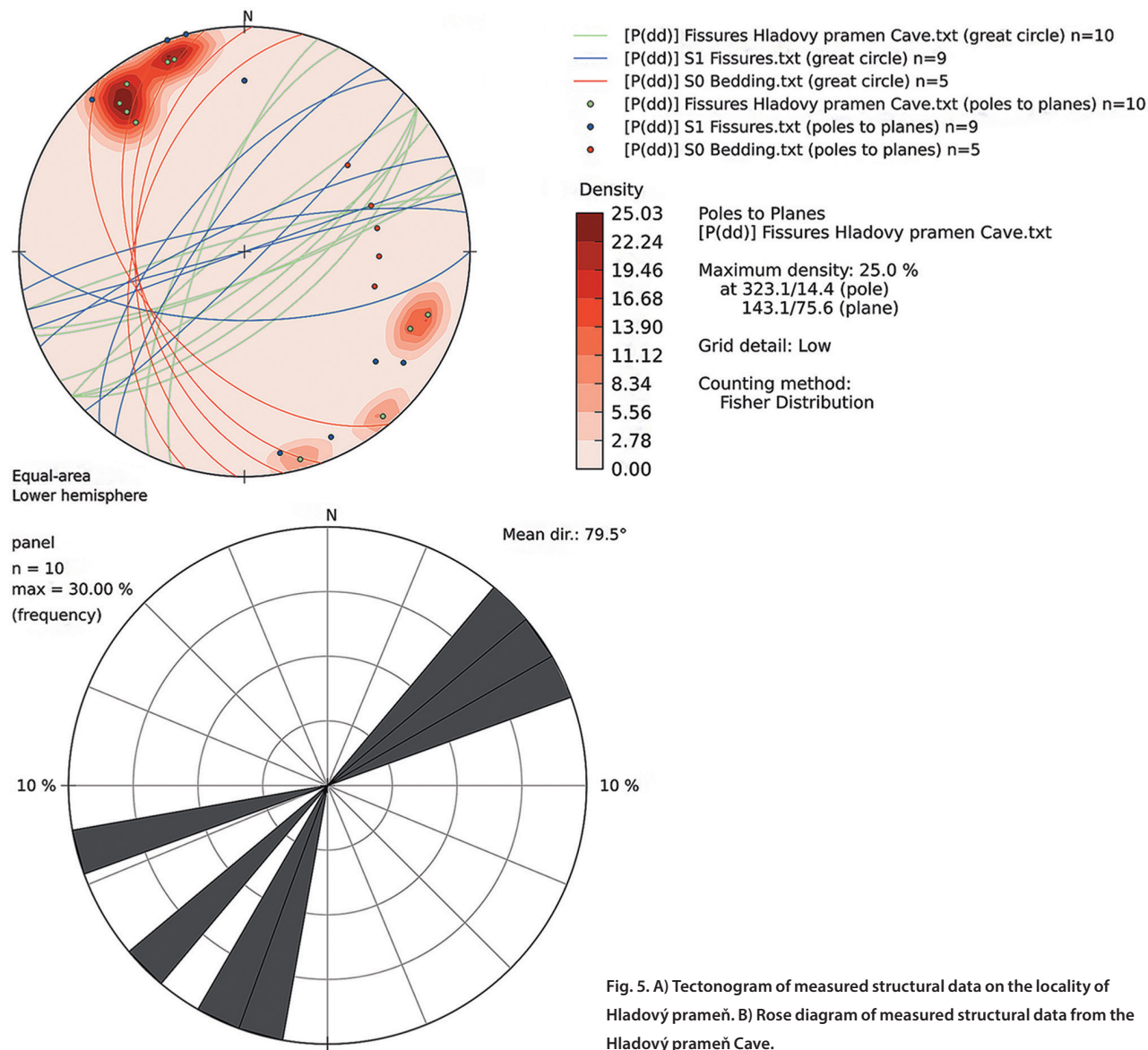


Fig. 5. A) Tectonogram of measured structural data on the locality of Hladový prameň. B) Rose diagram of measured structural data from the Hladový prameň Cave.

For water isotope measurements (C, H, O) we collected 12 samples of dripwater from soda-straws and water from the Hladový prameň Cave. The variability of values is shown in the $\delta^{13}\text{C} - \delta^{18}\text{O}$ plot and in the Tab. 2. We can observe different values for $\delta^{13}\text{C}$ in the Hladový prameň Cave and the Čachtická Cave. Parallel with sampling we also measured pH and EC values, but only in cases there was enough collectable water amount.

For stable isotope measurement we collected and measured totally 14 samples – helictite, flowstones, soda-straws, and wall-rocks for analyses of carbon and oxygen stable isotopes. In the Tab. 3 we can see the enrichment in heavy oxygen in direction: soda-straw – flowstones and helictites – wallrock.

5. DISCUSSION

Comparing the results of the analysis of water sampled in 2018 – 2019 with the results from 1980s' of the Hladový prameň

Tab. 2. Isotope analyses of water from the Hladový prameň Cave and Čachtická Cave collected in summer 2018.

Sample	$\delta^{13}\text{C}_{\text{PDB}}$ (‰)	$\delta\text{D}_{\text{SMOW}}$ (‰)	$\delta^{18}\text{O}_{\text{SMOW}}$ (‰)	pH	EC [$\mu\text{S}\cdot\text{cm}^{-1}$]
HP- spring	-17.35	-70.10	-10.42	6.8	656
HP- siphon	-11.39				
HP- veil	-11.40			8.17	729
HP- soda-straw	-17.71	-63.08	-9.19		
HP- soda-straw	-10.26				
HP- soda-straw	-16.82			8.17	920
ČČ- soda-straw	-13.86	-73.75	-10.58		
ČČ- soda-straw	-14.29				
ČČ- soda-straw	-11.40				
ČČ- soda-straw	-10.73				
ČČ- soda-straw	-12.16				
ČČ- soda-straw	-12.45			7.99	628

Tab. 3. Values of stable isotope analyses of helictite, flowstones, soda-straws, and wallrocks, collected in summer 2018.

Sample	$\delta^{13}\text{C}_{\text{PDB}}$ (‰)	$\delta^{18}\text{O}_{\text{PDB}}$ (‰)
ČC - helictite	-7.27	-7.08
ČC- soda-straw	-9.23	-8.82
ČC- soda-straw	-9.43	-11.16
ČC- soda-straw	-8.66	-9.98
ČC- soda-straw	-8.24	-7.99
ČC-soda-straw	-8.95	-8.96
ČC-wallrock	2.85	-5.1
ČC-wallrock	2.59	-5.18
ČC- flowstone	2.66	-4.67
ČC- flowstone	-10.06	-7.62
ČC- flowstone	-10.13	-8.24
ČC- flowstone	-6.59	-5.22
ČC- flowstone	-5.61	-5.09
HP - wallrock	0.43	-5.97

spring water quality monitoring (Kullman et al., 1994, see Tab. 5), it is evident that the chemical composition of the water has not substantially changed and is not influenced by water discharge of the resurgence. The differences are in the higher pH value and higher free CO_2 concentration in 1980s' established under the regime observation. The saturation index values against calcite indicate a state not too far from the equilibrium, although the sample of water taken from us shows a slightly undersaturated state ($\text{SI}_{\text{calcite}} = -0.19$) and the saturation index calculated from the average values of the chemical observations of the mode observation state slightly supersaturated ($\text{SI}_{\text{calcite}} = 0.11$). The chemical composition of the water was obviously affected by the dissolution of limestones without a substantial amount of dolomites, which results from the molar ratio $\text{rMg}^{2+}/\text{rCa}^{2+}$ (0.15, 0.21, and 0.16 respectively; Rapant & Vrana, 1985 see Tab. 4) We can conclude that the chemical composition of karst spring water is affected only minimally by dolomite dissolution, which is also associated with lower values of saturation indices against dolomite dissolution ($\text{SI}_{\text{dolomite}} = -1.31, -0.42, -0.22$, respectively). The water sample taken in March 2018, when the water level was higher, also the chemical composition is considerably different, mostly because the extremely high NO_3^- concentration (Tab. 1). This analysis was repeated three times, to avoid mismeasurement. As we are not aware of any anthropogenic contamination sources within the supposed infiltration area, the high nitrate concentration was probably caused by flushing a bat guano deposit in an unknown cavern upstream of the Hladový prameň Cave, maybe as a consequence of snowmelt during spring months. Abnormally high nitrate concentration in karst water was observed also in the water sample taken in the PP2 Cave in the Plavecký Karst of the Malé Karpaty Mts. (Slovakia) by Láncoz & Filipčíková (2017). However, in that case the influence of a bat guano accumulation was evident.

5.1 Stable isotopes in carbonates

On the plot (Fig. 6) the lightest oxygen occurs in soda-straws, probably because of least evaporation at this entry point of water into the cave. The heavier oxygen in flowstones and helictite may be explained by larger exposition and prolonged time to evaporation of thin water film and capillary water, respectively, and precipitation of enriched calcite after removal of a larger amount of isotopically light water into vapour. The same effect probably shows $\delta^{13}\text{C}$ values, while light carbon is degassing, residual solution is progressively enriched in ^{13}C . However, the flowstone crust records much larger time span than the soda-straw and thus changing climate and environmental parameters may be also pronounced in its isotope composition, such as temperature and vegetation cover.

5.2 Stable isotopes in water, soil and grass

The differences in H and O isotopic composition in dripwater between soda-straw and spring water at the Hladový prameň Cave (Tab. 2) may reflect different hydraulic response of porous network versus open fissures. Stagnant waters in the spring are probably averaging the rainfall compositions over longer period, while soda-straw may reflect individual precipitation events. The isotopic composition seems to respond to the events differently (probably more readily) at the Hladový prameň Cave (25 m) with its thinner overburden than the Čachtická Cave at a depth of 75 m, yielding different water isotope values at the same sampling time.

Carbon isotope composition of water at the Hladový prameň Cave is slightly lighter than in the Čachtická Cave (averagely -14.16 ‰ vs. -12.48 ‰). Carbon isotope variations are often explained in terms of changing ratio of C3 and C4 vegetation, the latter being isotopically heavier by ca. 14 permil (Pyankov et al., 2010). The area is nowadays largely forested; however, historical aerial photographs from 1950 show dramatic change in land use – sixty years ago the area was dominated by steppe and pastures over the Čachtická Cave and shrubby steppe and open forest above the Hladový prameň Cave (TUZVO/Geodis, 2017). The soil carbon may still inherit the past $\delta^{13}\text{C}$ composition

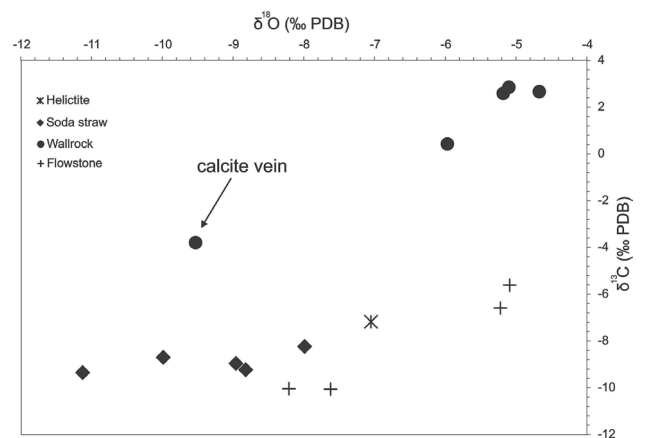


Fig. 6. Stable isotope analyses of helictite, flowstones, soda-straws, and wallrocks.

Tab. 4. Values of carbon stable isotopes from soil and grass soil.

No	Lat.	Long.	Horizon	Depth [cm]	2019	1950	δ ¹³ C
1	48°44'16.71	17°46'20.34	A	5	F	F	-26.62
			B	25	F	F	-25.78
2	48°44'22.08	17°46'26.03	A	5	F	F	-25.89
			B	25	F	F	-25.12
3	48°44'21.48	17°46'34.35	A	5	F	S	-27.14
			B	25	F	S	-25.07
4	48°44'18.91	17°46'35.17	A	5	S	S	-24.37
			B	25	S	S	-24.67
5	48°44'15.46	17°46'38.99	A	5	S	S	-26.55
			B	25	S	S	-25.33
6	48°44'22.41	17°46'42.66	A	5	F	S	-26.93
			B	20	F	S	-25.30
7	48°44'24.75	17°46'51.65	A	5	F	F	-27.67
			B	25	F	F	-26.44
8	48°44'24.77	17°47'12.18	A	5	F	F	-27.27
			B	20	F	F	-25.48
9	48°44'28.69	17°47'9.70	A	5	F	S	-26.90
			B	15	F	S	-25.71
10	48°44'30.94	17°47'4.80	A	5	F	S	-27.24
			B	10	F	S	-25.91
11	48°44'34.57	17°46'55.65	A	5	F	S	-27.17
			B	10	F	S	-26.48
12	48°44'38.59	17°46'39.89	A	5	S	S	-27.21
			B	10	S	S	-26.07
13	48°44'35.76	17°46'36.68	A	5	S	S	-26.33
			B	20	S	S	-25.69
14	48°44'38.47	17°46'31.45	A	5	F	S	-27.51
			B	25	F	S	-25.23
15	48°44'40.65	17°46'27.87	A	5	F	F	-27.28
			B	15	F	F	-25.73
16	48°44'42.24	17°46'20.96	A	5	S	S	-26.66
			B	20	S	S	-25.93
17	48°44'40.12	17°46'15.18	A	5	F	F	-25.93
			B	25	F	F	-25.34
18	48°44'28.57	17°46'12.72	A	3	F	F	-26.72
			B	30	F	F	-24.90
20	48°43'55.67	17°47'1.03	A	5	S	S	-26.66
			B	20	S	S	-25.43
21	48°44'2.74	17°47'4.17	A	5	F	S	-26.86
			B	20	F	S	-25.48
22	48°43'56.86	17°47'14.33	A	5	S	S	-26.62
			B	15	S	S	-26.36
Grass							
1	48°44'18.91	17°46'35.17	G	na	S	S	-27.41
2	48°44'18.91	17°46'35.17	G	na	S	S	-27.81
3	48°44'22.41	17°46'42.66	G	na	F	S	-31.60
4	48°44'22.41	17°46'42.66	G	na	F	S	-31.38
5	48°44'22.41	17°46'42.66	G	na	F	S	-29.31
6	48°44'38.59	17°46'39.89	G	na	S	S	-28.43
7	48°44'38.59	17°46'39.89	G	na	S	S	-29.50

Tab. 5. Results of the water quality monitoring of the water of the Cave Hladový prameň - average values (Kullman et al., 1994)

Twater [°C]	10.07	EC [µS.cm ⁻¹]	714
pH	7.3	CO ₂ [mg.l ⁻¹]	137.57
TDS [mg.l ⁻¹]	609.5		
Cations [mg.l ⁻¹]		Anions [mg.l ⁻¹]	
Na ⁺	1.5	Cl ⁻	4.9
Ca ²⁺	129.8	SO ₄ ²⁻	17.7
Mg ²⁺	13.2	NO ₃ ⁻	1.8
rMg ²⁺			
rCa ²⁺	0.16	HCO ₃ ⁻	431.7
Saturation indices			
Calcite	0.33	Dolomite	-0.22

due to possible occurrence of C4 grasses in the steppe-dominated area on the plateau above the Čachtická Cave called Drapliak (heavier carbon in dripwater) and their absence in bushland/forest (Hladový prameň Cave – lighter carbon in dripwater).

We tested this option by 1) searching for C4 grasses in modern vegetation of the area, and 2) investigation of carbon isotopes in soils with different land-use histories. Pilot inspection of grass species from the Čachtice Plateau and their isotope measurements (Tab. 4) showed no presence of C4 grasses in present-day biotopes. Therefore, we examined the variations in C isotopes in soils in places where 1) biotope changed from forest to steppe or vice-versa, and 2) the biotope remained unchanged – either steppe or forest.

From Tab. 4 and Fig. 7 it is obvious that there are no significant contrasts in C isotopes in soils between places with different vegetation cover. C isotope ranges largely overlap and thus the distribution of biotopes cannot account much for variations in δ¹³C in cave dripwaters. The only systematic variation is the ¹³C enrichment in B horizon against A horizon, probably due to bacterial preference for light carbon during fermentation of

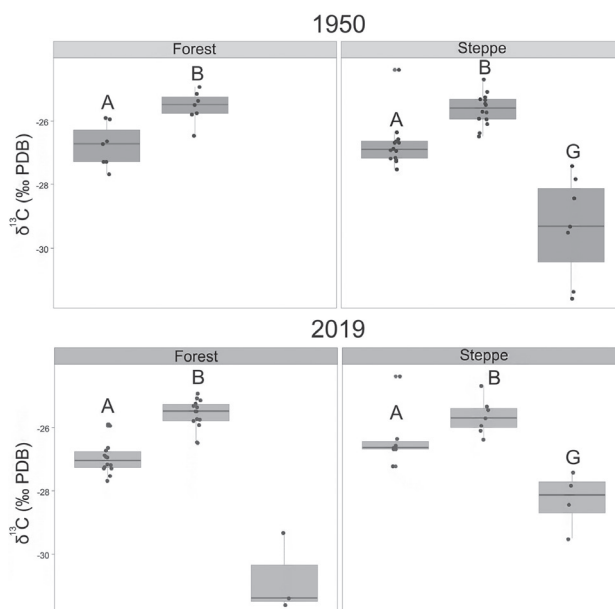


Fig. 7. Measurements of stable carbon isotopes from soil and grass: A – shallow horizon; B – deeper horizon; G – grass.

soil organic matter (Fessenden & Ehleringer, 2002; Boström, et al., 2007). Isotopes in unidentified grasses show depletion in ^{13}C by about 3 ‰ in the samples from forest against those from open steppe biotopes, which is consistent with canopy effect (Bonafini et al., 2013). These grasses contribute negligibly to the soil carbon budget comparing too much higher loads of leaf litter from trees. No grasses show values typical for C4 metabolism (Pyankov et al., 2010)

More plausible explanation of striking depletion in $\delta^{13}\text{C}$ at the Hladový prameň Cave follows from excessive CO_2 content in water. Source of such massive enrichment may only be the microbially produced active soil CO_2 . The relatively high CO_2 content and low pH values of the water samples taken from the spring in the Hladový prameň Cave could be explained by decay of thick leaf litter layers accumulated in the sinkholes in the Jesenského duby sinkhole lineage north of the cave (Lačný et al., 2019). Main fissures that formed the Hladový prameň Cave are subvertical and oriented generally in the NE–SW direction. We suppose that these fissures are related to recent neotectonic movements as a result of an extension during the Late Pleistocene and Holocene (Vojtko et al., 2008; Littva et al., 2015).

6. CONCLUSIONS

Summarizing our results, we can conclude that the two investigated caves represent different endokarst systems. Both caves could be connected to the faults proposed on sinkhole lines documented by Lačný et al. (2019). The Čachtická Cave is probably genetically linked to the NW–SE oriented fault, while the Hladový prameň Cave is connected with the N–S fault (see Fig. 2).

The thick epikarst at the Čachtická Cave effectively averages the infiltrating water composition, resulting in more uniform isotope values in dripwater, in contrast to much thinner epikarst at the Hladový prameň Cave where larger temporal variations in isotopes probably reflect individual precipitation events.

The lighter carbon isotope in the spring water sample of the Hladový prameň Cave is probably due to large accumulations of leaf litter in sinkholes of the N–S oriented fault, which is apparently its main infiltration source.

In the soil samples no influence of C4 vegetation was found, thus the isotope variations in dripwater and speleothems cannot be explained in terms of variable C3/C4 biomass. The minor depletion in ^{13}C by ca. 3 ‰ in forest grasses against those in grassland is due to canopy effect.

Differences in land-use and forest advance into grassland during last 70 years also did not prove significant effect on carbon isotopes in dripwater.

The complexity of the various factors (geomorphology, tectonics, petrology, pedology, vegetation, etc.) forming the karst features requires complex research approach combining different scientific methods to unveil processes influencing the karstogenesis.

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