Characterising CO₂ carbon isotopic composition in a cave atmosphere at Havranická Cave, Malé Karpaty Mts.: A case study

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Abstract: This study provides the results of an investigation of the carbon isotopic composition in a CO₂ cave atmosphere at Havranická Cave, Malé Karpaty Mts., Western Carpathians. The measured concentrations and δ¹³C values range between near-atmospheric (~ 612 ppmV and –7.38 ‰ PDB) values and depleted (~1039 ppmV and –13,5 ‰) values suggesting mixing of two contrasting CO₂ sources. Other measured characteristics such as temperature, humidity and CO₂ concentrations show trends related to depth, where temperature and humidity remain constant and the CO₂ content increases with depth. We conclude that the carbon isotopic composition of cave air is a result of mixing of atmospheric and soil-derived CO₂, degassed from dripwater. The contribution of carbon from limestone bedrock is possible, however, it cannot be confirmed with the current dataset.

Key words: Malé Karpaty Mts. Havranická Cave, cave atmosphere, carbon dioxide, stable isotopes

1. INTRODUCTION

Caves represent a unique environment where one can study deeper parts of the vadose zone, its geochemical composition changes with changes of physical or chemical conditions, and transport of components between different phases (Breecker et al., 2012). Describing and monitoring of cave inner conditions is of high importance in characterizing site-specific microclimatic processes and seasonality of environmental variables. Changes in microclimatic conditions and the chemical composition of cave atmosphere and water are directly transferred into growing speleothemes, from which they may be interpreted as proxy information (Spötl et al., 2005; Fairchild et al., 2006 and references cited therein; Gázquez et al., 2016;). Isotope composition of cave air CO₂ is an important member in a very complex process from dissolution of host rock to precipitation of speleothem calcite accompanied by degassing. This information may refine the interpretation of speleothem proxy records. Mixing of different CO₂ sources entering the speleothem means biassing the extracted paleoclimatic information (Breecker et al., 2012), thus it is very helpful to have thorough knowledge on the composition and fluxes of all available CO₂ pools prior to any paleoclimatic investigations.

1.1 Specific properties of cave atmosphere in relation to CO₂ fluxes

Cave atmosphere is characterized by its physical properties such as temperature, humidity, partial pressure of gases, the cave's ventilation and velocity of the air flow. Temperature and humidity
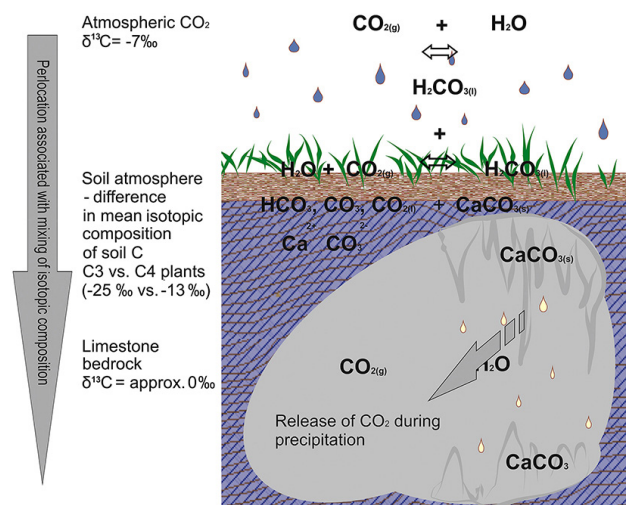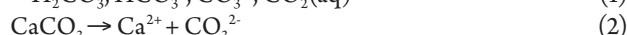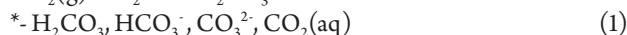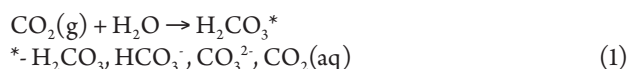
are usually nearly constant within a one-year period, especially in larger caves typified by their own microclimate. Previous studies (Spötl et al., 2005; Kowalczyk & Froelich, 2010; Breecker et al., 2012) showed evidence of seasonality in partial pressure of cave CO₂, which is tightly connected to the ventilation of caves.

Cave air ventilation was considered the primary mechanism of CO₂ removal from caves (de Freitas et al., 1982; Breecker et al., 2012 and others). From several possibilities, there are two dominant mechanisms that control cave ventilation, one is based on the temperature, density-driven air flow known as the chimney effect and the other is based on wind-driven air flow known as the Venturi effect (Wigley & Brown, 1976). In relation to carbon cycling in the vadose zone in epikarst, it is also important to study the possible sources of carbon dioxide in the cave atmosphere. The main sources of CO₂ in the cave atmosphere are: a) respiration of plants and soil microorganisms, b) exchange with atmospheric CO₂, d) host rock dissolution, e) degassing of CO₂ from supersaturated waters in the caves of hypogenic origin, f) decomposition of organic matter in caves and g) anthropogenic sources, which are considered mostly in show caves (Troester & White, 1984; Breecker et al., 2012; Gázquez et al., 2016). From all of those mentioned, soil respiration and atmospheric CO₂ are considered the dominant contributors of the composition of cave atmosphere in most caves.

1.2 Application of carbon isotope ratios to constraining different sources

If the dominant sources of the cave atmosphere CO₂ are considered to consist mostly of two end-members, the atmospheric

(average –7.8 ‰ Sharp, 2007; Hoefs, 2009) and the soil CO_2 (wide range of values, but approx. from –25 ‰ to –12 ‰ depending on dominance of C3 or C4 plants, respectively), which comes to the cave by degassing of hydrogencarbonate of dripwater, the final composition of the cave air is indeed a mixture of these end-members (Breecker et al. 2012). However, since the theory of processes of soil respiration, decay of organic matter, etc. are much more difficult, we refer to Cerling 1984 and Cerling et al. 1991 for further detail. Processes of water percolation through soil and bedrock, involving dissolution of host rock and precipitation of speleothem calcite might also involve some recombination of oxygen, and this is described by equations 1–4 and Fig. 1, where one can figure out the ratio of recombination.

$$CO_2(g) + H_2O \rightarrow H_2CO_3{}^*$$
$$*\text{- } H_2CO_3, HCO_3{}^-, CO_3{}^{2-}, CO_2(aq) \tag{1}$$
$$CaCO_3 \rightarrow Ca^{2+} + CO_3{}^{2-} \tag{2}$$
$$CaCO_3 + H_2CO_3{}^* \leftrightarrow Ca^{2+} + 2HCO_3{}^- \tag{3}$$
$$2HCO_3{}^- + Ca^{2+} \rightarrow CaCO_3 + CO_2(g) + H_2O \tag{4}$$

Fig. 1: Illustration of processes which occurs in atmosphere, soil, after contact of aggressive solution with bedrock and when solution reaches the cave interior.

Precipitation of a certain amount of calcite may occur before the solution reaches the interior as dripwater, and this process influences the isotopic composition of expelled gas and crystallizing calcite, as well as residual water chemistry (Fairchild et al., 2000, Genty et al., 2001). Both carbon and oxygen have distinct interpretative values in isotope geochemistry of CO_2 and carbonates. Stable isotope ratios of carbon are used to distinguish source and fluxes in the carbon cycle, especially when describing the evolution and shifts of vegetation cover on the surface in the cave studies. The main difference is between inorganic (carbonate) and organic source of carbon, as presented in table 1 (Sharp, 2007).

Oxygen isotopic data are commonly used for studying variations of the climate in the past due to strong dependence on the temperature of the isotopic composition of the materials. Sources of oxygen in the geosystem are mostly inorganic (water,

Tab. 1: Average values of $\delta^{13}C$ in different reservoirs and fluxes of carbon in the carbon cycle, selected materials most relevant for cave studies, according to Sharp (2007).

Reservoir	Average $\delta^{13}C$ (‰ vs. PDB)	Flux (10^{15} g.yr^{-1}) and direction
Atmosphere	from –6 to –7	102 (to ocean) 122 (to land biota)
Land plants and soil humus C3	–25	
Land plants and soil humus C4	–12	
Carbonate sedimentary rocks	from 0 to 1	0.17 (to dissolved bi-carbonate deep ocean) 0.03 (to atmosphere) 0.? (to mantle)

silicates, oxides, atmospheric O_2 etc.), so there is no „biological pump present to exhaust a preferentially lighter isotope (Sharp et al., 2007).

2. THE GEOGRAPHICAL, GEOLOGICAL AND ENVIRONMENTAL SETTING OF THE SURROUNDINGS OF HAVRANICKÁ CAVE

Entrance to the Havranická Cave is situated on the ridge of the Havranica hill (717 m a. s. l.) near the Havrania skala cliff in the Malé Karpaty Mts of south-western Slovakia (Fig. 2). The overall known length of the cave is 174 m and its denivelation is 51 m below the entrance. The geological surroundings (Fig. 1) consist mostly of Gutenstein limestones of the Hronikum unit. Several tectonic features were identified here, the main speleogenetic predisposition is a major fault with a N-S strike and subvertical dip. (Lánczos et al., 2013).

The ridge has steep slopes covered by a sparse deciduous forest dominated by beech and maple trees. Soil cover is relatively thin due to the strong exposure to the erosion processes. The cave extends steeply downwards through a narrow passage to the first larger space, which is approximately in the middle of the recently known part of the cave called the "Zbojnícka chamber". After this chamber, the cave narrows into a passage once more, ending with a 7 metre deep shaft with a small chamber known as the „Zasintrená hall" on its bottom. The main passage is branched into several short narrow holes (Fig. 3). The main path through the Havranická Cave is also characterized by its ventilation. In the cave, there are also three side branches with different altitudes and lengths, with no permanent air flow observed. Cave passages are without any recent flowstone features, and only in the Zbojnícka chamber and the Zasintrená hall can be found two places with secondary autochtonous fillings, fed by an active water supply. We sampled the cave air at 5 sampling sites in order to characterize the entire cave, where we measured temperature and air humidity concurrently (Fig. 3).

A previous monitoring study (Lánczos & Filipčíková, 2016) showed that below the depth of 30 m in the cave, humidity and
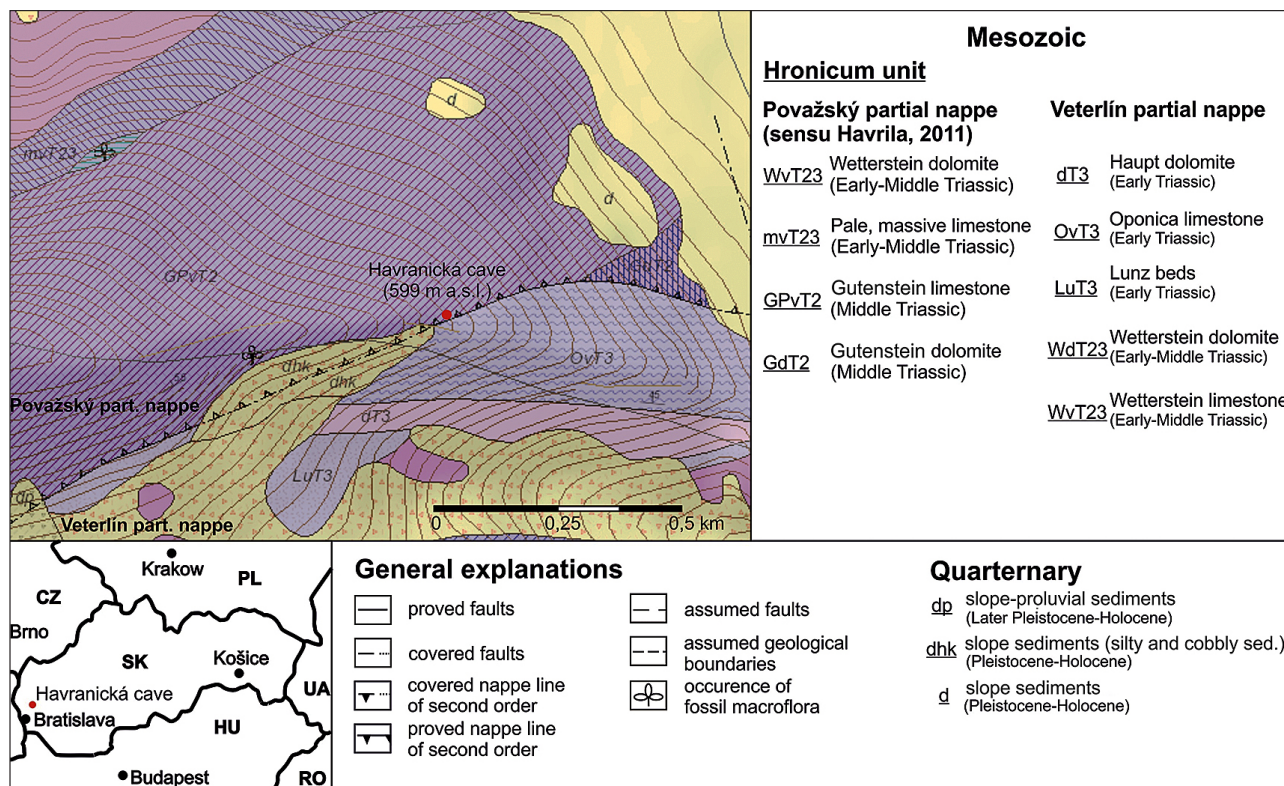
Fig. 2: Localization and the geological setting of Havranická Cave. Geological map available at http://apl.geology.sk/gm50js. http://apl.geology.sk/gm50js
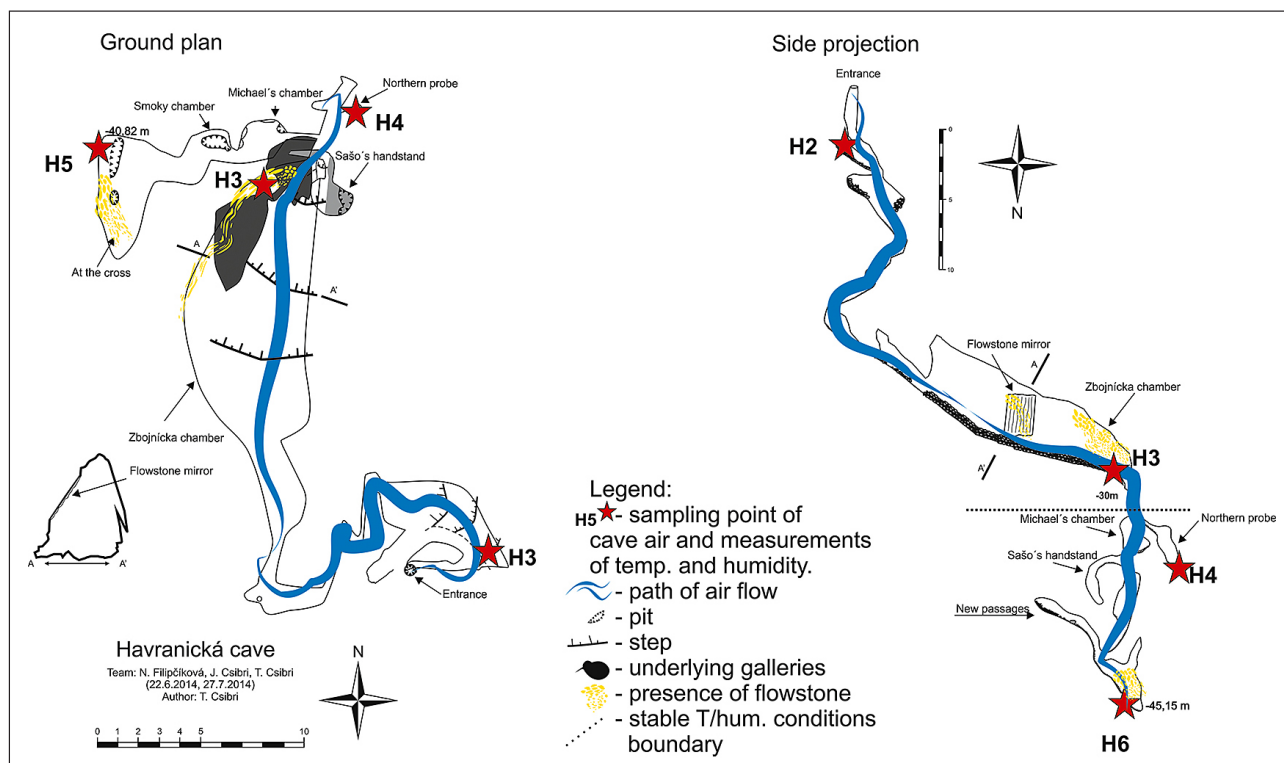

Fig. 3: The map of Havranická Cave with sampling and measurments spots (H2-H6). The main path of the air flow through the cave is indicated in blue colour.

temperature remain constant with increasing depth, which was considered as "stable inner cave climatic conditions". An observed general increase in concentrations of cave atmosphere CO_2 with depth and specific trends in the amount of the measured CO_2 were attributed to seasonality and the related change of air flow direction (Lánczos & Filipčíková, 2017).

3. MATERIALS AND METHODS

The field work was conducted on the 6th and 8th of July, 2016. The weather was sunny and there was a light wind, 15 % clouds and no rain. Air temperature was 19,6°C at 11:00 AM, and the direction of airflow through the cave was in a downwards direction, which is usual in the summer regime. Sampling was conducted from the deepest accessible parts of the cave in an upwards direction (Fig. 1), and 5 samples were taken in total.

CO_2 concentration was measured using a Testo 535 Monitor (precision +/- 50 ppm) and the air humidity and temperature using TFA 31.10 28 DTH Dewpoint Pro. Both were measured concurrently. The sampling procedure was performed with the highest care to avoid contamination by breath, fractionation after change of the temperature and possible subsequent condensation of air humidity inside the sampling bag after leaving the cave. Cave atmosphere was sampled into 3 liter Tedlar® gas sampling bags (Restek). In order to remove water, we developed a special
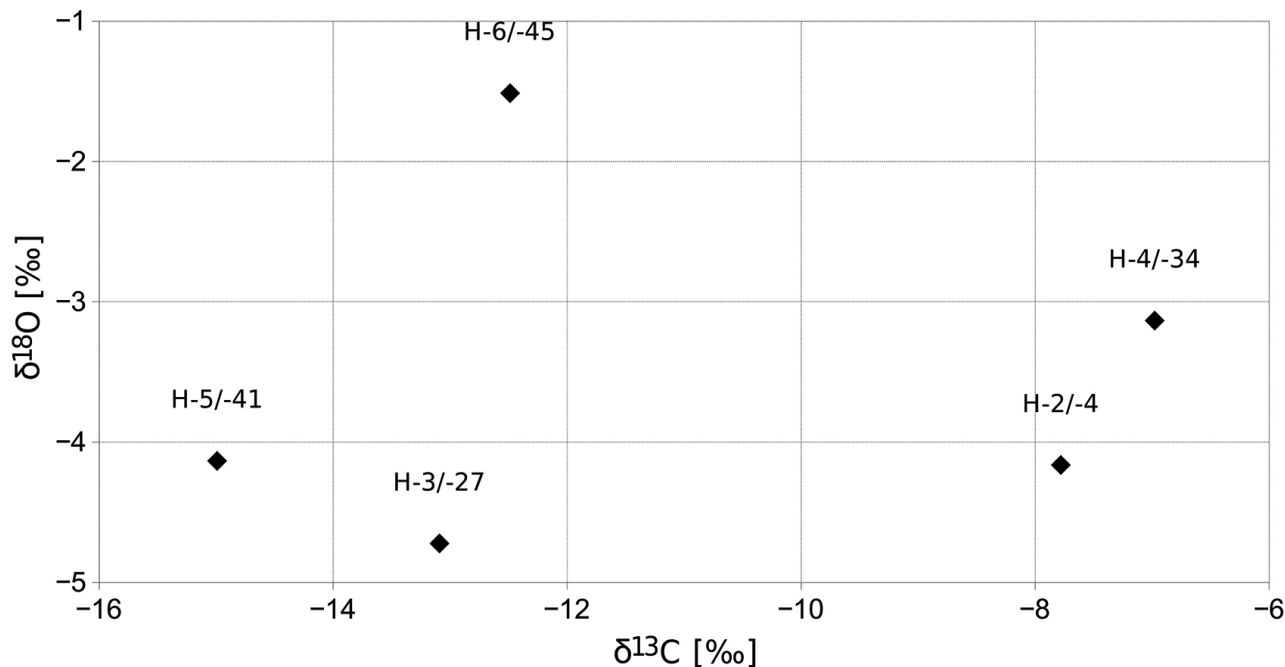

Figure 4: Isotopic composition of CO_2 in the atmosphere of the Havranická Cave.
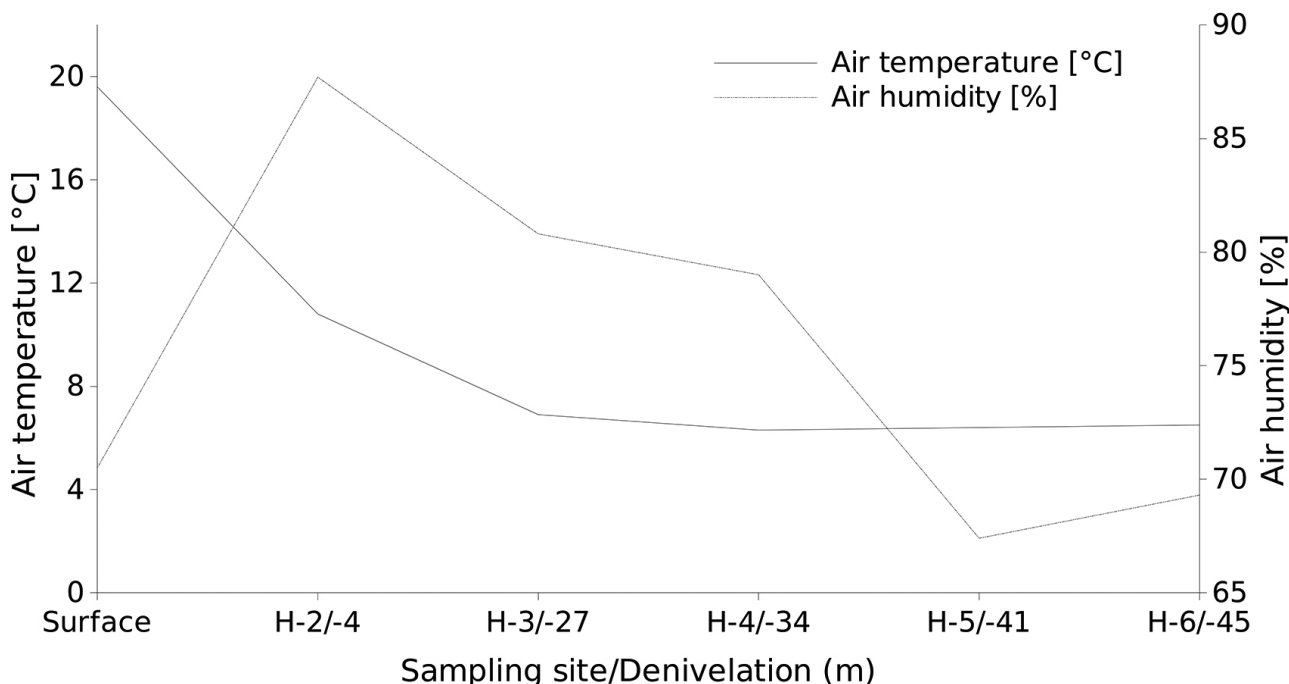

Figure 5: Temperature and humidity dependencies to depth.

sampling device consisting of a pump made from a gas-tight syringe with two one-way valves, and a plastic tube filled with silica-gel orange SGO50 /2-5mm/ (Mikrochem) as a dehydration agent. The air is sampled through a 1,5 m long silicone hose terminated by a mucus aspirator in order to enable sampling from a safe distance which was out of reach of breath. Samples were delivered to a laboratory of the Earth Sciences Institute of the Slovak Academy of Sciences in the city of Banská Bystrica in a thermostable case. In the laboratory, the bags were connected to a vacuum purification line where CO_2 was prepared for stable isotope analysis. After removal of water vapour on magnesium perchlorate, carbon dioxide was cryofocused in stainless steel tubing at -192°C in a liquid nitrogen bath, and after total freezing, the trap was heated in ethanol to ca -110°C. After pumping-out methane and permanent gases, the CO_2 was released into a sample bellow of a dual inlet system of the mass spectrometer MAT 253 (Thermo) and measured against in-house reference gas. The resulting $\delta^{13}C$ values are reported as permil vs. VPDB, standard deviations were 0.007 ‰ to 0.067 ‰, with a mean of 0.013 ‰.

4. RESULTS

The key feature in the Havranická Cave is dynamic ventilation, in which its direction changes with the seasons. During the summer, cold cave air descends through the entrance of the cave to its deep inaccessible parts. During the cold season, the airflow direction reverses, and during periods with equilibrated temperatures between the cave interior and the surface, the air in the cave stagnates.

Concentrations of CO_2, its $\delta^{13}C$ and $\delta^{18}O$ values, temperature and humidity of cave atmosphere measured in this study are presented in Table 2 and Fig. 4, Fig. 5 and Fig. 6. The $\delta^{13}C$ ranged from –14.99 ‰ to –6.97 ‰; $\delta^{18}O$ ranged from 1.51 ‰ to –4.72 ‰ and concentrations of CO_2 ranged from 361 ppm to 1,940 ppm. The concentrations of cave air CO_2 increased with depth.

Obtained isotopic data related to the spatial characteristics in the cave (Fig. 2), are represented by two distinct groups. The first group consists of three samples (H3, H5 and H6) with

Table 2: Results of measurements of the cave atmosphere and isotopic values of δ¹³C and δ¹⁸O in CO₂ from air samples from Havranická Cave. Standard deviations are in brackets.

Identifier	t (°C)	Humidity (%)	CO₂ (ppm)	δ¹³CPDB (‰)	δ¹⁸OPDB (‰)
Surface	19.6	70.5	361	–	–
H2	10.8	87.7	543	-7.78 (0.067)	-4.16 (0.039)
H3	6.9	80.8	683	-13.09 (0.017)	-4.72 (0.040)
H4	6.3	79.0	682	-6.98 (0.041)	-3.13 (0.040)
H5	6.4	67.4	493	-14.99 (0.007)	-4.13 (0.034)
H6	6.5	69.3	1940	-12.49 (0.013)	-1.51 (0.014)
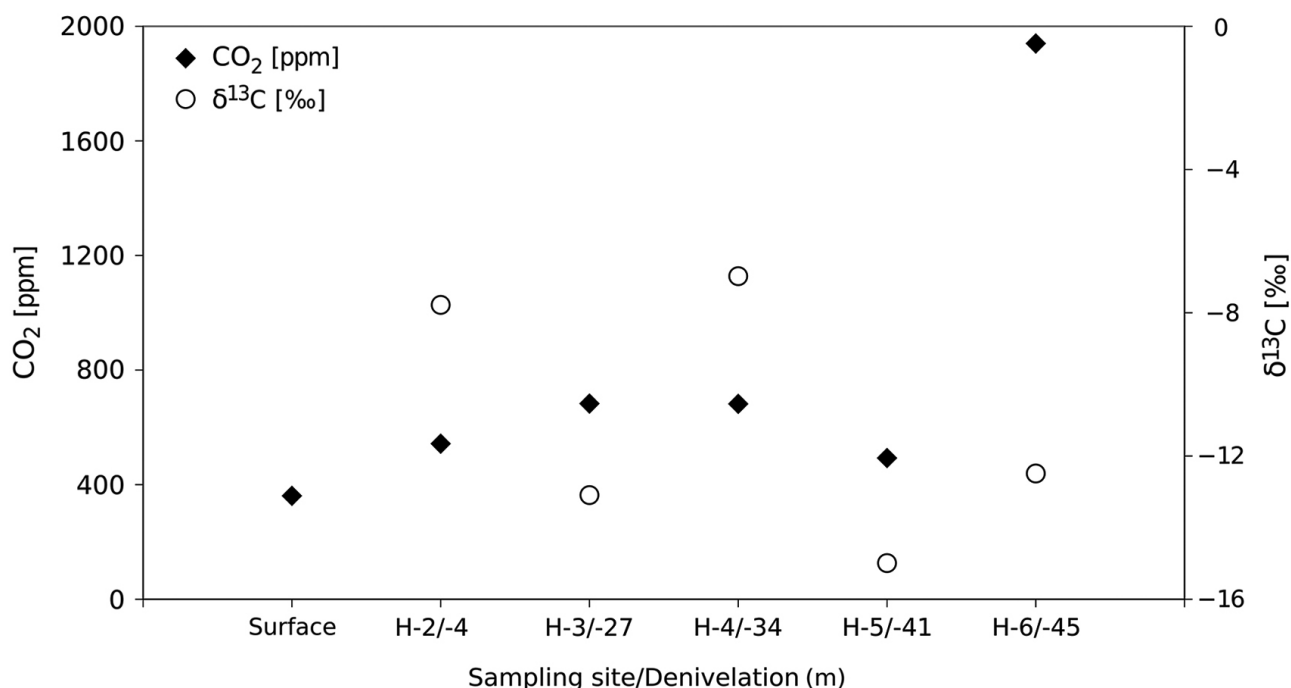
Figure 6: Dependence of δ¹³C of CO₂ to CO₂ concentration in cave atmosphere.

depleted values of δ^{13}C-CO_2 (–12.49 ‰ to 14.99 ‰) obtained from sites which are unique due to the presence of bulk flowstone deposits (Fig. 3) and are on the path of the air flow. The second group consists of the samples H2 and H4 with higher values of δ^{13}C-CO_2 (-7.78 ‰ and -6.98 ‰.) in comparison with the values of the previous group. The sample H2 was taken near the cave entrance and the sample H4 was obtained from one of the side branches called the „Northern probe".

As the oxygene isotopic composition is strongly dependent on equilibration processes with air humidity, the interpretation of our δ^{18}O values is extremely difficult. For this reason, we are presenting them for illustration purposes only.

The temperature ranged from 19.6 °C to 6.3 °C, and in spatial terms, decreased with increasing depth and did not change at approximately -30 m. Humidity ranged in a close interval from 87.7 % to 67.4 % with no distinct spatial pattern (Fig. 5).

5. DISCUSSION

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Karst is a unique terrain where a set of processes occurs influencing the genesis and evolution of karstic features. Our results are used to identify the source of carbon in the cave atmosphere CO_2 and to better understand the role of the carbon cycle within the epikarst and cave interior., The composition of carbon isotope is a reflecting contribution of at least two different sources, the atmospheric (~ 612 ppm and -7.38 ‰ δ^{13}C PDB) and the light end-member (~1039 ppm and -13.5 ‰ δ^{13}C, PDB). The identification of atmospheric CO_2 as one of the end-members is supported by evidence of increased values of carbon isotope characteristic for atmospheric composition according to existing literature (Sharp et al., 2007) and evidence of ventilation. Similar conclusions were presented also by other authors (Spötl et al., 2005; Breecker et al., 2012). The light end-member were identified as a contribution of soil CO_2, which may consist of CO_2 from decay of organic matter or from the root respiration and metabolism of soil biota (O´Leary, 1981).

The close relationship between the type of vegetation cover and the isotopic composition of the δ^{13}C in the soil CO_2 is widely accepted. Soil atmosphere is a major source of CO_2 for the meteoric waters percolating through bedrock to the cave interior. Two distinct groups of plants are known according to their photosynthetic pathway and consequently their carbon isotope composition: C3 plants, with typical values around -26 ‰, and C4 plants, where the average is -13.5 ‰ (Sharp et al., 2007). Percolating water from the surface contains CO_2, which is a mixture of initial atmospheric CO_2 (based on Henry´s law its content is 0.66638 mg.l^{-1}) and an indeterminate (up to 21 % of CO_2 according to Ford & Williams, 1989), but dominant amount of isotopically light CO_2 comes from the soil atmosphere. Such solution is in symmetry with respect to calcite, by dissolving this mineral the solution will obtain carbon and oxygen from the bedrock as well, which is isotopically much heavier (about 0 ‰ – 4 ‰) than other possible sources (Sharp et al., 2007). After reaching the cave interior, where the partial pressure of CO_2 is lower than in this solution, the carbon dioxide will degas from the solution and the solution

automatically becomes supersaturated with respect to calcite immediately followed by its precipitation. According to Lánczos & Filipčíková (2017), the saturation indices for calcite computed from the chemical analyses of the 5 samples taken in the Zbojnícka Chamber oscillated within the interval of 0.22 to 0.68, indicating calcite precipitation. This process causes the deposition of flowstone. The final composition of the atmosphere may reflect the mixture of the mentioned sources with respect to stable C and O isotopes of carbon dioxide (Dreybrodt & Romanov, 2016).

One possible explanation of the source of CO_2 in the group of samples with depleted values of δ^{13}C-CO_2 (samples H3, H5 and H6) is the soil atmosphere. Under circumstances of moderate climatic conditions, with the dominance of C3 plants, the expected values of δ^{13}C should be within -30 ‰ and -22 ‰ (Cerling, 1984). Our data was between -15 ‰ and 7 ‰, which is typical for C4 plants that dominate under dry and hot climatic circumstances (Cerling, 1984). Therefore, we rather consider mixing of different sources, probably during processes of dissolution of bedrock and precipitation of the cave speleothemes (Dreybrodt & Romanov, 2016). The inlet path for the gas of this origin may be related to the fractures network, however, according to the resulting values, we consider rather the processes of mixing during percolation of saturated water and creation of secondary autochtonous filling in the cave. We did not observe any correlationf of CO_2 concentration with carbon isotopic values, which might be due the small number of samples and sparse sampling grid.

The isotopic values of the second group of the samples are showing the atmospheric composition, which is obvious in the case of H2, the sample taken near the cave entrance. The sample H4 obtained at the depth 34 m below the entrance should been influenced by atmosphere minimally. It is not at the main passage through the cave and has no obvious signs of air flow and no flowstone features are present.

6. CONCLUSIONS

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Isotopic composition of the atmosphere in the Havranická Cave was studied in order to constrain the main sources of CO_2. We identified two distinct sources of cave air, one with a clear relationship with the atmospheric air and the other one with signs of mixing atmospheric and soil CO_2 with a possible contribution of carbon coming from bedrock and released during processes of dissolution and precipitation.

For further research that could lay the groundwork for more accurate interpretations, we recommend performing regular monitoring of the cave atmosphere composition in order to obtain season – specific data, as well as setting up a denser sampling grid inside the cave. It will be also necessary to include the sampling of in situ soil CO_2 for both CO_2 concentration and isotope composition, as well as the analysis of dripwater.

References

Breecker D. O., Payne A. E., Quade J., Banner J. L., Ball C. E., Meyer K. W. & Cowan B. D., 2012: The sources and sinks of CO2 in caves under mixed woodland and grassland vegetation. *Geochimica et Cosmochimica Acta,* 96, 1 November 2012, 230–246.

Cerling T. E., 1984: The stable isotopic composition of modern soil carbonate and its relationship to climate. *Earth and Planetary Science Letters*, 71, 2, 229–240.

Cerling T. E., Solomon D. K., Quade J. & Bowman J. R. 1991: On the isotopic composition of carbon in soil carbon dioxide. *Geochimica et Cosmochimica Acta*, 55, 11, 3403–3405.

de Freitias C. R., Littlejohn R. N., Clarkson T. S. & Kristamnent I. S., 1982: Cave climate: Assessment of airflow and ventilation. *International Journal of Climatology*, 2, 4, 383–397.

Dreybrodt W. & Romanov D., 2016: The evolution of ¹³C and ¹⁸O isotope composition of DIC in a calcite depositing film of water with isotope exchange between DIC and CO₂ containing atmosphere, and simultaneous evaporation of the water. Implication to climate proxies from stalagmites: a theoretical model. *Geochimica et Cosmochimica Acta*, 195, 15 December 2016, 323–338.

Fairchild I. J., Borsato A., Tooth A. F., Frisia S., Hawkesworth C. J., Huang Y., Mc Dermott F. & Spiro B., 2000: Controls on trace element (Sr-Mg) compositions of cave waters: implications for speleothem climatic records. *Chemical Geology*, 166, 3–4, 255–269.

Fairchild I., Smith C. L., Baker A., Fuller L., Spötl Ch., Mattey D., Mc Dermott F. & E.I.M.F., 2006: Modification and preservation of environmental signals in speleothems. *Earth-Science Reviews*, 75, 1-4, 105–153.

Ford D. & Williams P., 1989: Karst Geomorphology and Hydrology. Chapman & Hall, London, 601 p.

Gázquez F., Quindós-Poncela L., Sainz-Fernández C., Fernández-Villar A., Fuente-Merino I. & Celaya-Gonzalez S., 2016: Spatiotemporal distribution of δ¹³C-CO₂ in a shallow cave and its potential use as indicator of anthropic pressure. *Journal of Environmental Management*, 180, 15 September 2016, 421–432.

Geologická mapa Slovenska M 1:50 000 [online]. Bratislava: Štátny geologický ústav Dionýza Štúra, 2013. Dostupné na internete: http://apl.geology.sk/gm50js.

Genty D., Baker A. & Vokal B., 2001: Intra- and inter- annual growth rate of modern stalagmites. *Chemical Geology*, 176, 1-4, 191–212.

Hoefs J., 2009: Stable Isotope Geochemistry, Springer–Verlag, Berlin Heidelberg, 285 p.

Kowalczyk A. J. & Froelich P. N., 2010: Cave air ventillation and CO2 outgassing by radon-222 modeling: how fast do caves breathe? *Earth and Planetary Scientific Letters*, 289, 1–2, 209–219.

Lánczos T., Lačný A., Jánošík M. & Feketeová Z., 2013: Speleogenesis of the Havranická Cave as an important phenomenon of the Plavecký Karst (Malé Karpaty Mts.) *Acta Geologica Slovaca*, 5, 1, 83–96. [in Slovak with English summary]

Lánczos T. & Filipčíková P., 2016: Geochemical factors of karst phenomena formation and development on the site of Havrania skala (Malé Karpaty Mts.). *Aragonit,* 20, 1, 63

Lánczos T. & Filipčíková P., 2017 : Speleogenetic importance of CO₂ for development of selected caves of Plavecký karst area in the Malé Karpaty Mts. *Acta Carsologica Slovaca*. 55, 1, 5–22. [in Slovak with English Summary]

O´Leary M. H., 1981: Carbon isotope fractionation in plants. *Phytochemistry*, 20, 4, 553–567.

Sharp Z. 2007: Principles of stable isotope geochemistry. Pearson Education, Inc., Upper Saddle River, NJ 07458, 344 p.

Spötl Ch., Fairchild I. J. & Tooth A. F., 2005: Cave air control on dripwater geochemistry, Obir Caves (Austria): Implications for speleothem deposition in dynamically ventilated caves. *Geochimica et Cosmochimica Acta*, 69, 10, 2451–2468.

Troester J. W. & White W. B., 1984: Seasonal fluctuations in the carbon dioxide partial pressure in cave atmosphere. *Water Resources Research*. 20, 1, 153–156.

Wigley T. M. L. & Brown M. C., 1976: The physics of caves. In: Ford, T. D., & Cullingford, C. H. D. (Eds.): The Science of Speleology. Academic press, London, pp. 329–345.