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RESEARCH ARTICLE

Cave monitoring in Hungary: An overview

GYÖRGY CZUPPON[1,2]*, ATTILA DEMÉNY[1], SZABOLCS LEÉL-ŐSSY[3], JÓZSEF STIEBER[4], MIHÁLY ÓVÁRI[5], PÉTER DOBOSY[6], ÁGNES BERENTÉS[1] and RICHARD KOVÁCS[7]

[1] Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, Eötvös Loránd Research Network, Budapest, Hungary

[2] Department of Hydrogeology and Engineering Geology, Institute of Environmental Management, University of Miskolc, Miskolc, Hungary

[3] Department of Physical and Applied Geology, Eötvös Loránd University, Budapest, Hungary

[4] Stieber Environmental Ltd., Budapest, Hungary

[5] Nuclear Security Department, Centre for Energy Research, Eötvös Loránd Research Network, Budapest, Hungary

[6] Institute of Aquatic Ecology, Centre for Ecological Research, Eötvös Loránd Research Network, Budapest, Hungary

[7] Duna-Ipoly National Park Directorate, Budapest, Hungary

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ABSTRACT

In this study, already published and new monitoring data are compiled from the Baradla and Béke caves in the Aggtelek Karst, from the Vacska Cave in the Pilis Mountains as well as from the Szemlőhegy and Pálvölgy caves in the Buda Hills. Recent investigations (2019–2020) include monitoring of climatological parameters (e.g., temperature, CO_2) measured inside and outside the caves, and the chemical, trace element and stable isotopic compositions of drip waters. In the Baradla Cave, the main focus of the investigation was on the stable isotope composition and the temperature measurements of drip water. In the Vacska Cave, which belongs to the Ajándék-Ariadne cave system, CO_2 measurements and drip water collection were conducted in order to perform chemical and stable isotope measurements. In the Szemlőhegy and Pálvölgy caves, the chemical and stable isotope compositions of drip waters at six sites were determined. These datasets were used to characterize the studied caves and the hydrological processes taking place in the karst, and to trace anthropogenic influences. Climatological investigation revealed seasonality in CO_2 concentration related to outside temperature variation, indicating a variable ventilation regime in the caves. In addition, the contributions of the winter and summer precipitation to the drip water were also estimated, in order to evaluate the main infiltration period. The knowledge of these parameters plays a crucial role in constraining the carbonate precipitation within the cave. Thus, the dataset compiled in this study can provide a basis for the interpretation of speleothem-based proxies.

KEYWORDS

Baradla, Béke, Szemlőhegy, Pálvölgy, Ajándék-Ariadne cave system, stable isotope, water chemistry, climatological parameters, Hungary

*Corresponding author. Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, Hungarian Academy of Sciences, Budaörsi út 45., H-1112 Budapest, Hungary.
E-mail: czuppon@geochem.hu, czuppon.gyorgy@csfk.org

INTRODUCTION

The number of publications focusing on cave monitoring has been increasing in recent decades. One of the main reasons for this trend is the recognition of the importance of the results obtained from monitoring activities for the interpretation of speleothem-based proxies and for climate reconstructions (Fairchild et al., 2000; Spötl et al., 2005; Riechelmann et al.,

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2011; Czuppon et al., 2018a, 2018b). In order to utilize the stable isotope ratios, trace element compositions, and petrographic characteristics of cave carbonate deposits (e.g., stalagmites, flowstones), it is necessary to determine the complex interaction and relationship between climate parameters and the response within the cave (e.g., Riechelmann et al., 2011). Such an investigation may include the monitoring of various parameters outside and inside the cave (e.g., Tremaine et al., 2011, 2013). In this study, we present a compilation of monitoring data from the Baradla and Béke caves (Aggtelek Karst), the Vacska cave which is part of the Ajándék-Ariadne cave system (Pilis Mountains), as well as from the Pálvölgy and Szemlőhegy caves (Buda Hills) (Fig. 1). The basic information of these caves is summarized in Table 1, while Table 2 includes the type of monitoring activities which were conducted in each cave. The temperature, hydrogen and oxygen isotope compositions of drip water and the CO_2 concentration were measured at the Nehéz-út site in Baradla Cave in order to provide a dataset for characterization of speleothem formation. The investigations in Vacska Cave endeavored to characterize the isotopic and chemical composition of drip water and climatological parameters. The main aim of the monitoring performed in the Pálvölgy and Szemlőhegy caves is to trace anthropogenic influences by measuring the chemical and the stable isotope compositions of the drip waters. In the present study we focus on cave climatology (e.g., temperature variation, ventilation) and the relationship between the isotopic composition of the drip water and precipitation (e.g., seasonality, contribution of winter and summer precipitation to the drip water) as well as on the anthropogenic influences in the Pálvölgy and Szemlőhegy caves. In addition, part of the dataset and the results presented in this study provide the basis for a chapter within the book entitled "Cave and Karst Systems of Hungary" to be published by Springer (Czuppon et al., 2022).

EXPERIMENTAL DESIGN, MATERIALS AND METHODS

Monitoring – Baradla Cave

In Baradla Cave the same site (the "Nehéz-út", NU site, Fig. 2) was chosen in the present campaign as that monitored during 2013–2015 (Czuppon et al., 2018a). The drip water used for stable isotope measurement was collected regularly (every two months during visits to the caves) at two locations at the NU site located 10 m from each other. In addition, the temperature of the drip water was also recorded continuously by a Tiny Tag Plus 2 temperature data logger (TGP-4020) manufactured by Gemini Data Loggers (UK) Ltd. The flying lead thermistor was attached directly to the glass plate placed under the drip sites in order to minimize the effect of the cave air on the drip water temperature measurement (Fig. 3). In addition, the glass plates were also utilized to collect recent carbonate precipitates formed from the drip water (Fig. 3) in order to determine their stable isotope composition (Demény et al., 2021).

The CO_2 concentration at the NU site was also monitored using a portable CO_2 meter (Testo 535; uncertainties: ±3% of the value). The same device was used in the previous monitoring campaign (Czuppon et al., 2018a). The cave air pCO_2 has been determined every season (winter, spring, summer, autumn) since 1994.

Monitoring – Vacska Cave

Vacska Cave belongs to the Ajándék-Ariadne cave system which includes several other caves: Legény, Leány, Ariadne, Rejtekút, Indikációs, Ősi and Ajándék (Fig. 4). In Vacska Cave the drip waters (Fig. 4, blue circles) were collected at several sites for the performance of stable isotope and

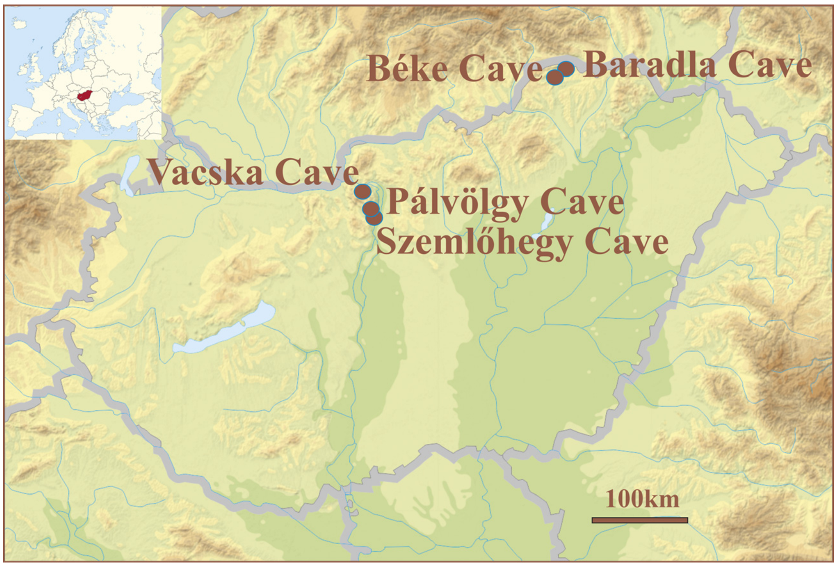


Fig. 1. Monitored caves presented in this study

Table 1. Monitored parameters of the selected caves in Hungary

Cave							Climate	
Name	Location	Host Rock: Formation	Rock type	Total length [km]	Vertical extend [m]	Number of entrance	Mean Annual Air Temperature [°C]*	Total Annual Precipitation [mm]*
Béke	48°29′ N, 20°31′ E	Gutenstein limestone Steinalm limestone Wetterstein limestone	Limestone with dolomitic layers	~6	97	3	8–9	650–700
Baradla	48°28′ N, 20°30′ E	Gutenstein limestone Steinalm limestone Wetterstein limestone	Limestone with dolomitic layers	~22	112	5	8–9	650–700
Vacska**	47° 41′ N, 18°50′E	Dachstein Limestone	Limestone	9.3	206.1	1	8–9	600–650
Szemlőhegy	47° 31′ N, 19°01′E	Szépvölgy limestone Budai Marl	Limestone Marl	2.23	50.4	4	9–10	550–600
Pálvölgy***	47° 31′ N, 19°00′E	Szépvölgy limestone Budai Marl	Limestone Marl	16.3	112	2	9–10	550–600

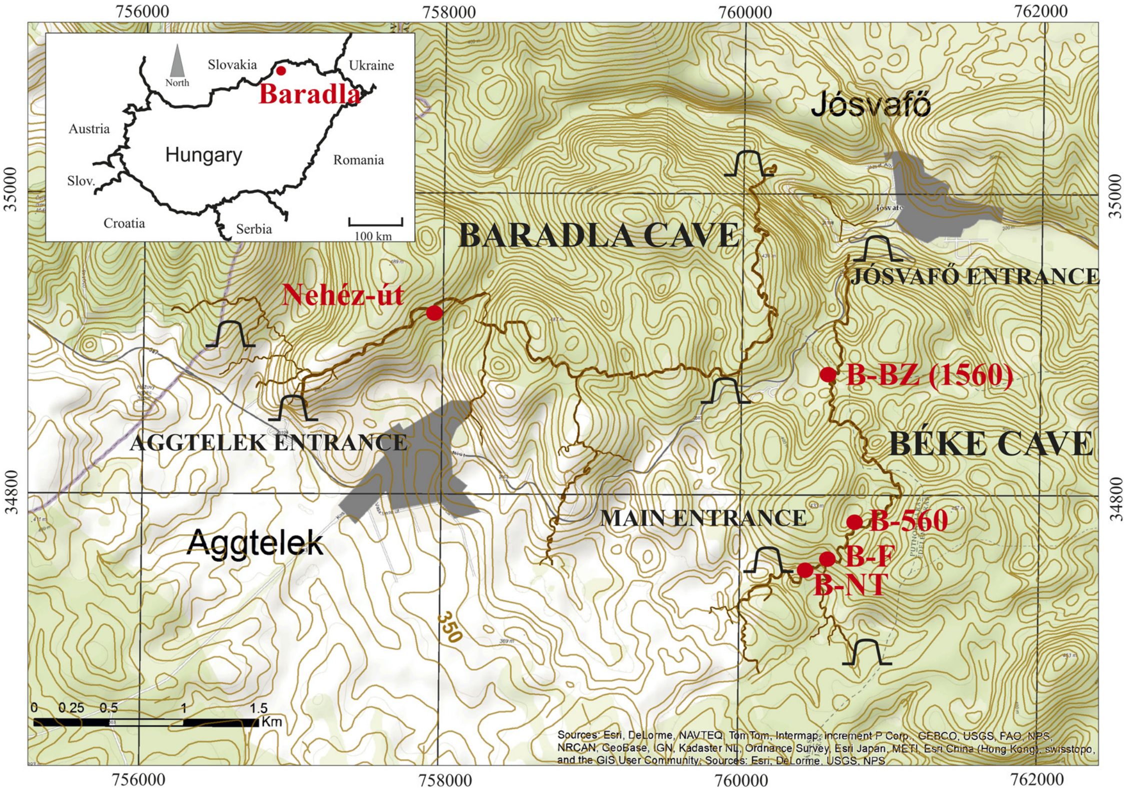
**Data source*: www.met.hu. The values in the table are for the reference period of 1971–2000.

**Vacska Cave is part of the Ariadne cave system (Ariadne cave system includes 8 caves, total length: 20 km; vertical extend: 206.1 m; entrances: 9).

***Pálvölgy Cave is part of the Pálvölgy cave system (Pálvölgy cave system includes, total length: 32 km, vertical extend: 122.6 m; entraces: 10).

Table 2. Monitored parameters of the selected caves in Hungary

		Cave climatology		Drip water			Fresh carbonate		
Name of the cave	Monitoring period	Temperature	CO_2 concentration	δD, $\delta^{18}O$	Chemistry	Temperature	$\delta^{13}C$, $\delta^{18}O$	Clumped isotope	Publications
Béke	2013–2016	√	√	√	√		√		Czuppon et al. (2018a)
Baradla	2013–2016	√	√	√	√				Czuppon et al. (2018a) Demény et al. (2016)
Baradla	2019–2020		√	√		√	√	√	Demény et al. (2021), present study
Vacska	2019–2021	√	√	√	√	√	√	√	present study
Szemlőhegy	2019–2021			√	√	√			present study
Pálvölgy	2019–2021			√	√	√			present study



Sources: Esri, DeLorme, NAVTEQ, TomTom, Intermap, increment P Corp., GEBCO, USGS, FAO, NPS, NRCAN, GeoBase, IGN, Kadaster NL, Ordnance Survey, Esri Japan, METI, Esri China (Hong Kong), swisstopo, and the GIS User Community, Sources: Esri, DeLorme, USGS, NPS

Fig. 2. Studied sites in the Baradla (Nehéz-út, NU site) and Béke caves (B-NT: Nagy-tufa; B-F: Felfedező-ág; B-560: 560 site, B-BZ: Buzogány Hall). Modified after Czuppon et al. (2018a)

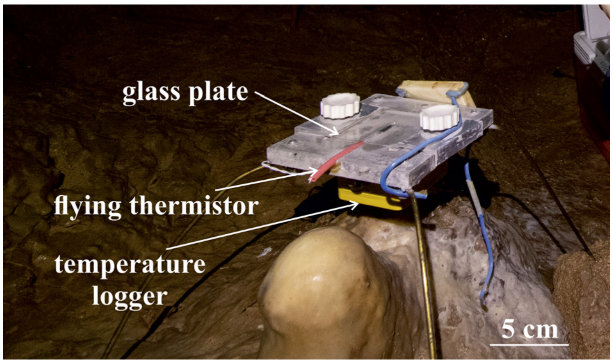


Fig. 3. The temperature logger with flying thermistor used at NU site (Baradla Cave) to record the temperature of drip water. The glass plate was placed above the temperature logger to collect fresh carbonate precipitation

chemical analyses: Rózsát-terem (RT); Mérfőldkőháti-terem (MK); Cseppköves-hasadék (CS); Nyeregponti-terem (NYP) and pond waters fed by drip waters: Mérfőldkőháti-terem (MK); Fennkőháti-terem (FK). In order to collect the drip waters a funnel attached to a plastic bottle was used (Fig. 5). The electrical conductivity and pH value of the waters were determined at the sites using the WTW pH/cond. 3320 device (temp.: ±0.1°C in the range between −5°C and +105°C; pH: ±0.01 between −2 and +14; conductivity: ±1μS cm^{-1} between 0–2000). The results of electrical conductivity and pH are given after temperature correction.

In addition, cave air CO_2 concentration was also monitored between 14 May 2019 and 29 November 2020 at the MK site. The pCO_2 was measured every three hours using a portable CO_2 meter (ENVIRO 100 by STIEBER Ltd.; range between 0 and 30,000 ppm; ±3% of the value). The temperature was measured inside (MK site) and outside the cave between 14 March 2020 and 16 January 2021 using Tinytag Plus 2 loggers manufactured by Gemini Data Loggers (UK) Ltd (TGP-4500 and TGP-4017).

Monitoring – Szemlőhegy and Pálvölgy Caves

The monitoring activities in the caves under the capital city of Budapest included collection of drip waters at four sites in Szemlőhegy Cave (Csengő-terem: CSE, Pettyes-terem: PE, Óriás-terem: ORI, Örvény-folyosó: OR) and at two sites in Pálvölgy Cave (Meseország-1: ME-1, and Meseország-2: ME-2) for stable isotope and chemical analyses (Fig. 6). The temperature, pH and electric conductivity were always measured at the sites using the WTW pH/cond. 3320 device (temp.: ±0.1 °C in the range between −5 °C and +105 °C; pH: ±0.01 between −2 and +14; conductivity: ±1μS cm^{-1} between 0–2000). The results of electrical conductivity and pH are given following temperature correction.

Analytical methods

Stable hydrogen and oxygen isotope analyses of the water samples were carried out using a Liquid-Water Isotope Analyser-24d, manufactured by Los Gatos Research, at the

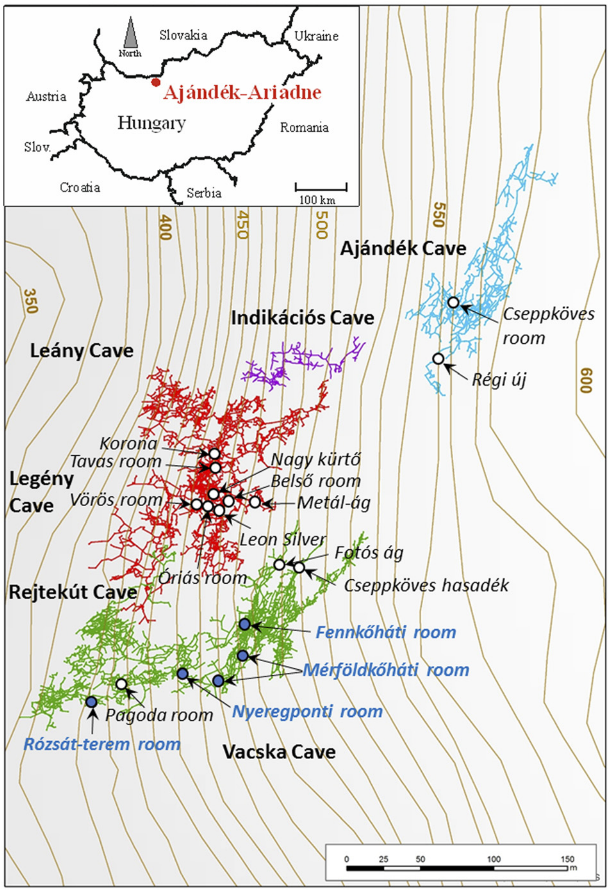


Fig. 4. Sampling sites for drip waters in Vacska Cave (blue circles) which is part of the Ajándék-Ariadne cave system. The sites from where carbonate samples were collected are also shown. Modified after Czuppon et al. (2022)

Fig. 5. Collection of drip water in Vacska Cave

Institute for Geological and Geochemical Research (IGGR) in Budapest, Hungary. This instrument was also used in the previous monitoring campaign (2018a). The isotopic compositions of the water samples are expressed as δD and $\delta^{18}O$ in ‰ relative to V-SMOW (Vienna Standard Mean Ocean Water; Coplen et al., 1996). The precision is better than 1.0‰ and 0.15‰ for hydrogen and oxygen isotope ratios, respectively. More details of the stable isotope analyses are described in Czuppon et al. (2018a).

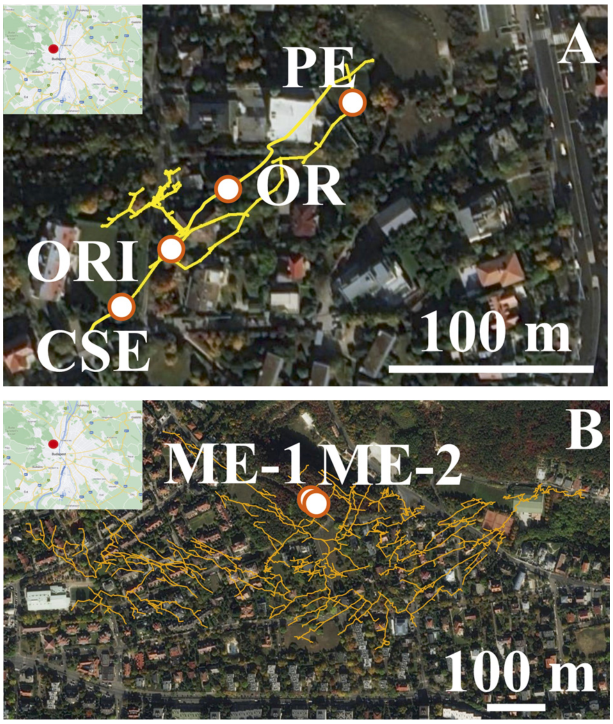


Fig. 6. Location of sampling sites in Szemlőhegy Cave (A) and Pal-völgy Cave (B). Both caves are located on the west side of the capital city of Hungary (Budapest), marked by red circles on the small map

Trace element concentration measurements were conducted at the Institute of Chemistry, Eötvös Loránd University, Budapest, Hungary. About 10 mg of powdered carbonate sample was weighted into high purity 15 ml polypropylene centrifuge vials using an ultra-micro balance, then dissolved in 12 ml, 0.5 mol dm^{-3} nitric acid (Suprapure grade, E. Merck, Darmstadt, Germany). For the quantification 120 µl of 1 mg dm^{-3} indium internal standard solution was added. The analysis was carried out using an Element 2 inductively coupled plasma sector field mass spectrometer (Thermo-Finnigan, Bremen, Germany) (see Demény et al., 2017 for more details).

The concentrations of anions (chloride, bromide, nitrate, sulfate) and cations (ammonium, calcium, magnesium, sodium, potassium) were determined using a Dionex ICS 5000+ dual channel ion chromatography system (Thermo Fischer Scientific, USA) at the Institute of Aquatic Ecology. Alkalinity was determined by the standard titrimetric method (Eaton et al., 2005). Total organic carbon (TOC) and total nitrogen (TN) concentrations were measured using a Multi N/C 3100 TC–TN analyzer (Analytik Jena, Germany).

RESULTS

Baradla Cave

Cave air temperature and CO_2 concentration have been monitored at the NU site on a seasonal base since 1994. The data between 1994 and 2013 have already been published in Czuppon et al. (2018a). In this study, the data between 2013 and 2020 are presented (Table S1). The temperature of the cave air at this site ranges from 9.8 to 10.5 °C for the entire period (1994–2020) showing small seasonal variation. The winter is generally characterized by lower values (10.1 ± 0.1 °C), and the summer by higher values (10.4 ± 0.1 °C). The CO_2 concentration shows similar seasonal variability, as described by Czuppon et al. (2018a): lower values (2,060 ± 200 ppm) can be observed during the winter, while higher values (3,780 ± 160 ppm) during the summer.

The temperature of the drip water was monitored between 4 December 2019 and 29 May 2020. This varied between 9.6 and 11.4 °C (Table S2). This range overlaps those observed for cave air in the period between 1994 and 2020.

The stable isotope compositions of drip waters display a relatively small variation during 2020 (Table S3); the δD values range between −60 and −56‰, while the $\delta^{18}O$ varies between −8.8 and −8.1‰ (Fig. 7/B).

Vacska Cave

The CO_2 concentration (Table S4) was measured at the MK site in Vacska Cave between 14 May 2019 and 29 November 2020. The cave air pCO_2 displays a seasonal variation similar to Baradla Cave, showing higher values (9,700 ppm) in summer and lower in winter (550 ppm) (Table 3). However, the amplitude of the seasonal variation is much greater (9,100 ppm) than that observed at NU-site (1,700 ppm). The temperatures measured at the MK site (Table S5) are characterized by very stable values (8.8±0.007 °C). The temperature outside of the cave varies seasonally (Table S6) according to the regional climate.

The isotopic compositions of the drip water collected in Vacska Cave can be divided into two groups (Fig. 8/A); those characterized by more positive values were sampled at

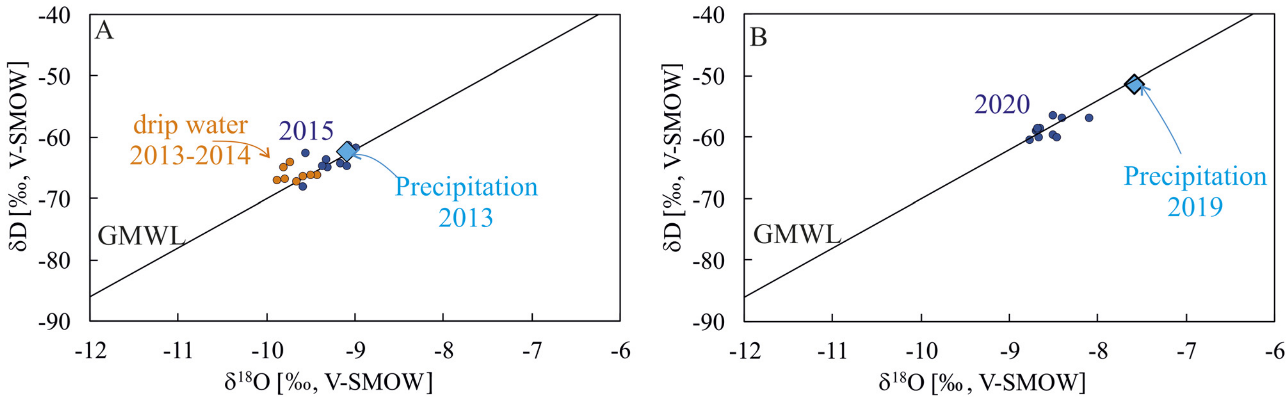


Fig. 7. Stable isotope composition of drip waters collected at the NU site in Baradla Cave in 2013–2015 (data source: Czuppon et al., 2018a) (A) and 2020 (B). The isotopic composition of the amount-weighted annual precipitation is shown by the light blue rhombus. The Global Meteoric Water Line (GMWL, Craig, 1961) is also indicated

Table 3. Temperature and CO_2 concentration variation in the selected caves in Hungary

Cave sites	a.s.l. [m]	T average [°C]	T min [°C]	T max [°C]	CO_2 average [ppm]	CO_2 min [ppm]	CO_2 max [ppm]
*Béke Cave (2013–2015)**	*338*						
Nagytufa (BNT)		9.8 ± 0.3	9.2	10.7	11,472	700	26,480
Felfedező-ág (BFE)		10.1 ± 0.4	9.3	10.8	12,719	800	32,010
Site of 560 (B560)		10.2 ± 0.3	9.6	11.0	14,088	1,100	33,065
Buzogány Hall (BBU)		10.4 ± 0.3	9.7	11.2	21,188	2,572	34,290
Baradla Cave	*332*						
Nehéz-út (BNU)		10.2 ± 0.2	9.6	10.5	2,924	1,600	4,200
Vacska Cave	*450*						
Mérföldkőháti (MK)		8.800 ± 0.007	8.784	8.827	4,164	550	9,700
Szemlőhegyi Cave	*219*						
Pettyes-terem (PE)		12.5 ± 0.1	12.4	12.8			
Örvény-folyósó (OR)		13.4 ± 0.1	13.3	13.7			
Csengő-terem (CSE)		13.6 ± 0.1	13.5	13.7			
Óriás-terem (ORI)		13.4 ± 0.1	13.2	13.7			
Pálvölgy Cave	*205*						
Meseország-1 (ME-1)		10.6 ± 0.7	9.5	12.7			
Meseország-2 (ME-2)		11.0 ± 0.8	10.5	14.0			

**Source*: Czuppon et al. (2018a).

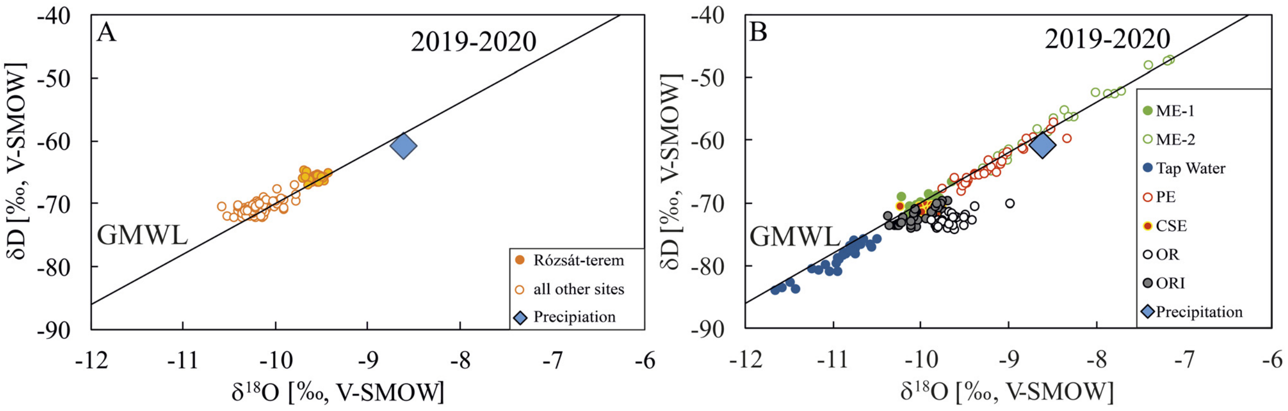


Fig. 8. Stable isotope composition of drip waters collected in Vacska Cave (A) and Pálvölgy Cave (ME-1: Meseország-1; ME-2: Meseország-2) and Szemlőhegy Cave (PE: Pettyes-terem; CSE: Csengő-terem; OR: Örvény-folyosó; ORI: Óriás-terem) (B). The isotopic composition of the amount-weighted annual precipitation is shown by the light blue rhombus. The Global Meteoric Water Line (GMWL, Craig, 1961) is also indicated

RT (filled orange circle in Fig. 8/A), while the others, which show more negative values (empty orange circle), were collected in the other part of the cave (MK, CS, NYP, FK). The Sr concentration of the RT site differ also from other sites, showing lower values than those at the MK, CS, NYP and FK sites. The sulfate (SO_4^{2-}) concentrations range at the RT site between 40 and 50 mg l^{-1}, while the nitrate (NO_3^-) concentration varies between 9 and 12 mg l^{-1}. At other sites the nitrate and sulfate concentration show greater values (SO_4^{2-} up to 230 mg l^{-1}; NO_3^-: up to 59 mg l^{-1}. All chemical compositions are presented in Table S7.

Szemlőhegy and Pálvölgy Caves

Drip waters were collected at four sites in Szemlőhegy Cave and at two sites in the Pálvölgy Cave for chemical and stable isotope analyses (Table S8 and S9). In addition, tap waters were also sampled in the visitor center above Szemlőhegy Cave. The stable isotope compositions of drip waters show relatively large variations at the PE site in Szemlőhegy Cave and the ME-2 site in Pálvölgy Cave, revealing strong seasonality (Figs 8/B and 9). The chemical composition of the drip waters was also determined (Table S8–S9). The nitrate (NO_3^-) and sulfate (SO_4^{2-}) concentrations show high values in Szemlőhegy Cave, where they can exceed 380 mg l^{-1} and 330 mg l^{-1}, respectively. In Pálvölgy Cave the nitrate concentration is relatively low, while the sulfate concentrations are high (up to 170 mg l^{-1}), similarly to Szemlőhegy Cave. The concentration of chloride (Cl^-) and sodium (Na^+) ions in the drip waters in both caves display elevated values (Cl^- up to 1,500 mg l^{-1}, Na+ up to 650 mg l^{-1}).

DISCUSSION

Cave climate

Among the factors that can control speleothem formation, cave climatological parameters, such as air temperature, humidity, and CO_2 concentration, are especially important (e.g., Spötl et al., 2005). These parameters show various patterns in the recently and previously monitored caves in Hungary (Czuppon et al., 2018a; Stieber, 2018, Stieber and Leél-Őssy, 2019). The lowest temperature was observed at

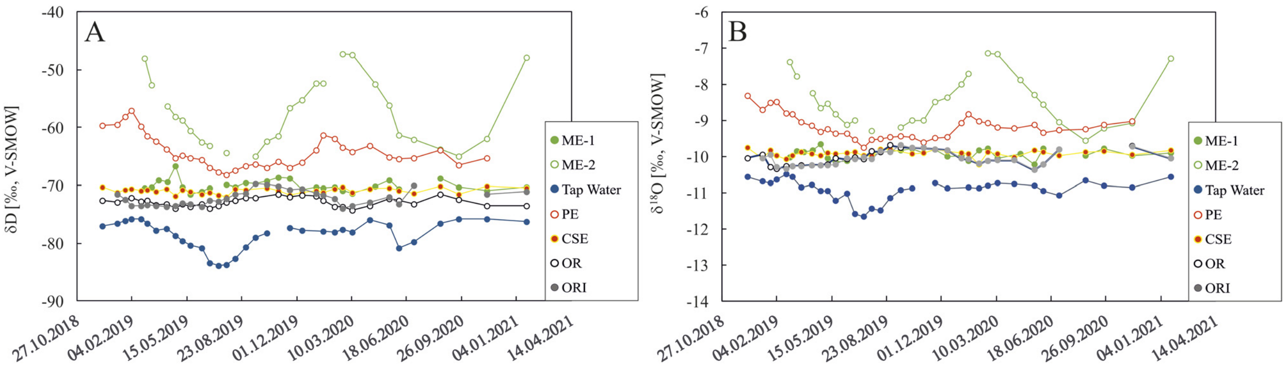


Fig. 9. δD (A) and $\delta^{18}O$ (B) time series of tap water and drip waters collected in Pálvölgy Cave (ME-1: Meseország-1; ME-2: Meseország-2) and Szemlőhegy Cave (PE: Pettyes-terem; CSE: Csengő-terem; OR: Örvény-folyosó; ORI: Óriás-terem). Modified after Czuppon et al. (2022)

the MK site in Vacska Cave, while the highest was found in the caves located in Budapest (Szemlőhegy and Pálvölgy caves) (Table 3). Although the observed differences in the temperature values can be partly attributed to elevation differences, the elevated temperatures in the Pálvölgy and Szemlőhegy caves are assumed to be due to the influence of warm air from lower chambers related to warm water in the karst (Stieber, 2018). The temperature variations are generally small in all studied caves. Especially the MK site in the Vacska Cave displays remarkable stability (8.800 ± 0.007 °C). This feature is most likely related to the morphology of the cave passages (i.e., narrow) and the relatively large distance of the site from the cave entrance (200 m). Small seasonality in temperature could only be revealed at the NU site in Baradla Cave (Czuppon et al., 2018a).

Cave temperature has a direct impact on the oxygen isotope fraction (e.g., O'Neil, 1986) during speleothem formation as the fractionation has a temperature dependency (e.g., Sharp, 2017; Fairchild and Baker, 2012). In addition, it also has an indirect effect because the relative difference between air temperature inside and outside the cave governs ventilation in addition to cave morphology and outside pressure conditions (Mattey et al., 2008). Ventilation can cause a significant kinetic effect on the isotopic compositions of the precipitating carbonate (speleothem) resulting in a positive shift in both δ^{18}O and δ^{13}C values. The strength of the ventilation can be traced by the variation of CO_2 concentration in the cave air. Weak ventilation results in high CO_2 concentration while strong ventilation lowers the CO_2 concentration. In the monitored caves, the annual variation of CO_2 concentration generally follows the same trend, showing high values during summer and low values in winter. Moreover, the amplitude (the difference between the low and high values) can vary from cave to cave (Table 3) and can change with time depending on the evolution of the cave, affecting the connections among the passages, chambers and the accessibility of cave entrances. In the case of Béke Cave dramatic change has been observed in 2013 and in the following years, when extremely high concentrations were found in both the summer (26,000–34,000 ppm) and winter periods (700–2,500 ppm). The rapid and relatively large increase in CO_2 concentration occurred by blocking of the cave passage between two entrances (main and Jósvafő entrances), resulting in limited ventilation (Czuppon et al., 2018a; Stieber and Leél-Őssy, 2019). Moreover, before the cave was explored in 1953, it is assumed that the CO_2 level was lower (<20,000 ppm). In addition, in the period between 1953 (exploration of the cave) and 2013, the CO_2 concentration was significantly lower (1,400–3,800 ppm) based on sporadic measurements (Stieber and Leél-Őssy, 2019). Thus, it is reasonable to envision that similar changes in ventilation (and CO_2 concentration) took place in the past, also as a result of natural processes, and occurred recently due to extensive cave exploration. Therefore, it is important to take into account these possibilities during the interpretation of the stable isotope composition of speleothems.

Nevertheless, some seasonality in CO_2 has always been observed in the monitored caves, independently of the absolute concentration values. The change between high and low CO_2 content generally takes place when the temperatures outside and inside the cave are equal (Figs 10 and 11). Thus, in Hungary this shift typically occurs during spring and autumn. Apparently, the switches are relatively rapid, especially in Béke Cave, where they take place within one to two months (Fig. 10).

The variabilities in CO_2 concentration can also affect the carbonate precipitation rate, as the high CO_2 concentration in the cave air can prevent CO_2 degassing from the drip water. In contrast, a low CO_2 level, which implies enhanced ventilation, induces rapid degassing and hence increased calcite precipitation (Mattey et al., 2008).

In summary, we can conclude that during the summer half-year (when ventilation is weaker and CO_2 concentration is higher), there is expected to be a lower carbonate precipitation rate and a smaller kinetic effect on the isotopic composition. In contrast, during the winter half-year an enhanced kinetic effect on the isotopic composition of precipitating carbonate likely takes place, as in Vacska Cave (Czuppon et al., 2022). Moreover, it should be noted that in Béke Cave the CO_2 concentration remained at a relatively high level even during the winter half-year; thus, the effect of ventilation might be minimal in this period as well (Czuppon et al., 2018a).

Natural and anthropogenic processes recorded in the drip water

Relationship between the precipitation and drip waters. The stable isotope compositions of drip waters in the monitored caves are generally characterized by narrow ranges (Table 4). Only the ME-2 site in Pálvölgy Cave and the PE site in Szemlőhegy Cave show a relatively larger variation in δD and δ^{18}O values (Fig. 9). At these sites the differences between the highest and lowest values exceed 10‰ and 1‰ for hydrogen and oxygen isotope composition, respectively. At other studied sites, the amplitudes of the isotopic values are relatively small, showing no seasonality during the year. This observation implies that the infiltrations are generally slow and the aquifer in the epikarst above the cave sites is well mixed. The lack of seasonality indicates that the residence time is longer than one year. Moreover, in the case of the Nehéz-út site in Baradla Cave, drip waters were also collected in 2019–2020 after the first monitoring campaign (2013–2015), and the isotopic composition of drip water showed a positive shift (from −9.43 ± 0.28‰ to −8.56 ± 0.19‰, see Fig. 12, Table 4) relative to the previous period. A similar shift was also observed in the amount-weighted isotopic compositions of the precipitation (Fig. 12, Table 5), as well as in farmed calcites precipitated from drip waters at the Nehézút site (from $\delta^{18}O_{V\text{-}SMOW} = 23.0 \pm 0.1$‰, Demény et al., 2016, to $\delta^{18}O_{V\text{-}SMOW} = 24.0 \pm 0.3$ ‰, Demény et al., 2021). These findings indicate that slight changes in the precipitation

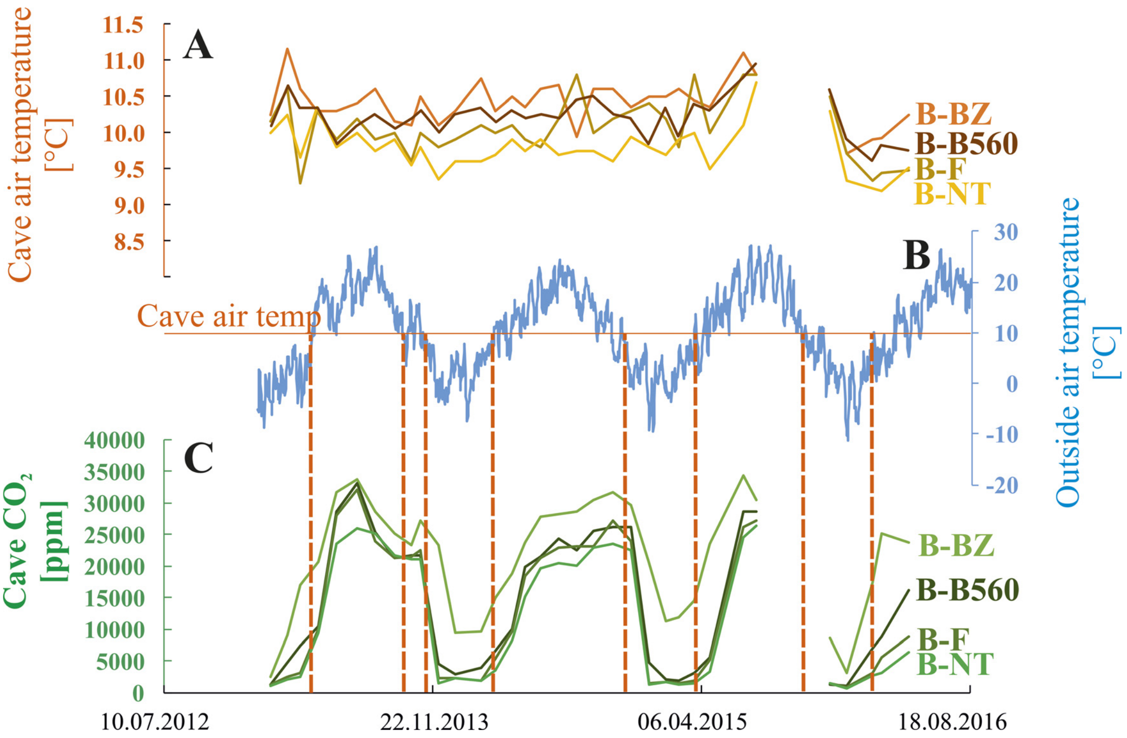


Fig. 10. Cave air temperature (A), outside temperature (B) and CO$_2$ concentration (C) measured in Béke Cave. (B-NT: Nagy-tufa; B-F: Felfedező-ág; B-560: 560 site, B-BZ: Buzogány Hall). The dashed lines indicate the time when the outside and inside temperatures were equal and when the ventilation direction changed inducing a shift between low and high CO$_2$ regimes

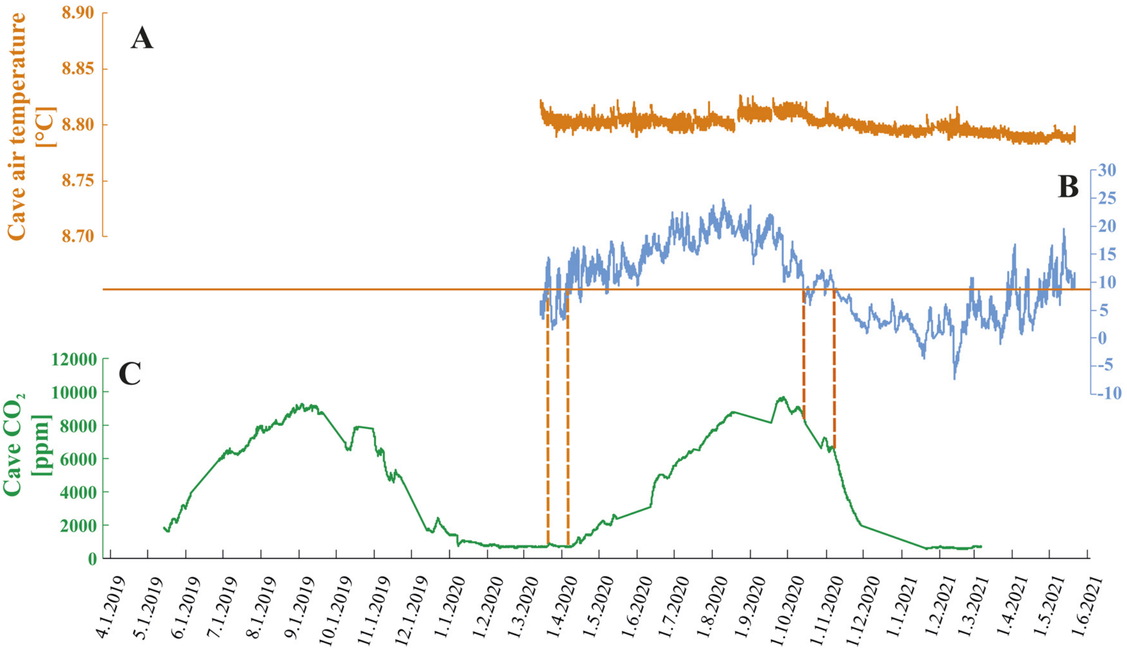


Fig. 11. Cave air temperature (A), outside temperature (B) and CO$_2$ concentration (C) measured at the MK site in Vacska Cave. The dashed lines indicate the time when the outside and inside temperatures were equal and when the ventilation direction changed inducing a shift between low and high CO$_2$ regimes

over the years can be reflected in the composition of the drip waters. Thus, it can be concluded that, although the seasonal isotopic signal observed in precipitation is generally not transmitted to drip water, inter-annual variability can be recorded in drip water and hence in the precipitating carbonate (e.g., speleothem).

Another important feature characterizing the relationship between the precipitation and drip water is that

Table 4. Stable isotope composition of drip water from selected caves in Hungary

Cave sites	a.s.l. [m]	δD average [‰, V-SMOW]	δD min [‰, V-SMOW]	δD max [‰, V-SMOW]	δ^{18}O average [‰, V-SMOW]	δ^{18}O min [‰, V-SMOW]	δ^{18}O max [‰, V-SMOW]
*Béke Cave (2013–2015)**	*338*						
Nagytufa (BNT)		−64.21 ± 1.21	−68.07	−62.12	−9.30 ± 0.15	−9.56	−8.97
Felfedező-ág (BFE)		−65.80 ± 1.24	−68.11	−62.76	−9.50 ± 0.18	−9.89	−9.20
Site of 560 (B560)		−65.05 ± 1.66	−67.95	−60.55	−9.48 ± 0.25	−9.84	−8.85
Buzogány Hall (BBU)		−63.71 ± 1.13	−65.64	−60.86	−9.31 ± 0.16	−9.63	−9.00
*Baradla Cave (2013–2015)**	*332*						
Nehéz-út (BNU)		−64.75 ± 1.93	−68.04	−61.35	−9.43 ± 0.28	−9.88	−8.99
Baradla Cave (2020)	*332*						
Nehéz-út (BNU)		−58.59 ± 1.33	−60.36	−56.26	−8.56 ± 0.19	−8.77	−8.09
Vacska Cave (2019–2020)	*450*						
Rózsát-terem (RT)		−65.64 ± 0.55	−66.83	−64.49	−9.56 ± 0.07	−9.71	−9.42
Mérföldkőháti (MK)		−71.16 ± 0.62	−72.17	−69.28	−10.23 ± 0.12	−10.35	−9.90
Cseppköves-hasadék (CS)		−70.31 ± 0.49	−71.12	−68.89	−10.19 ± 0.12	−10.32	−10.01
Nyeregponti-terem (NYP)		−70.10 ± 1.23	−71.79	−66.91	−10.11 ± 0.17	−10.33	−9.77
Szemlőhegyi Cave (2019–2020)	*219*						
Pettyes-terem (PE)		−64.17 ± 2.85	−68.25	−57.06	−9.18 ± 0.34	−9.75	−8.34
Örvény-folyósó (OR)		−72.69 ± 0.91	−74.21	−70.18	−9.66 ± 0.17	−9.88	−8.98
Csengő-terem (CSE)		−70.94 ± 0.49	−72.05	−70.09	−9.92 ± 0.09	−10.23	−9.76
Óriás-terem (ORI)		−72.18 ± 1.28	−74.00	−69.77	−10.07 ± 0.19	−10.37	−9.69
Pálvölgy Cave (2019–2020)	*205*						
Meseország-1 (ME-1)		−70.00 ± 0.99	−71.54	−66.62	−9.93 ± 0.13	−10.22	−9.65
Meseország-2 (ME-2)		−57.50 ± 5.86	−65.03	−47.27	−8.46 ± 0.71	−9.56	−7.16

* Czuppon et al. (2018a).

generally, the δD and δ^{18}O values from drip water in the studied caves are lower than the values in the amount-weighted annual precipitation (Figs 7–8), indicating a higher contribution (60–70%) from precipitation falling in the winter half-year (Table 6). Although this general observation remains valid even if the absolute values of the drip water have shifted slightly over the years, the relative contributions of the "summer half-year" and "winter half-year" precipitation may vary (Table 6) with time and within the same cave. At the NU site (Baradla Cave) the relative contribution of winter precipitation shows an increase of 15–20% in 2020 relative to those values observed in 2013–2014 (Table 6).

In the case of Vacska Cave, the RT site is characterized by fewer negative values (Fig. 9/A) compared to others. Therefore, it is assumed that the infiltration of summer precipitation above this site is greater (contribution of summer precipitation is ~46%) relative to the infiltration at other sites (contribution of summer precipitation is ~20–30%, Table 6), and the residence time of the water is likely shorter compared to other drip sites. This is in line with the Sr concentration found in the drip water, which is lower at this site. Sr concentration depends on the residence time of the water in the karst, as the prolonged water-rock interaction favors incongruent carbonate dissolution, which induces more dissolution of Sr (e.g., McGillen and Fairchild, 2005; Borsato et al., 2016).

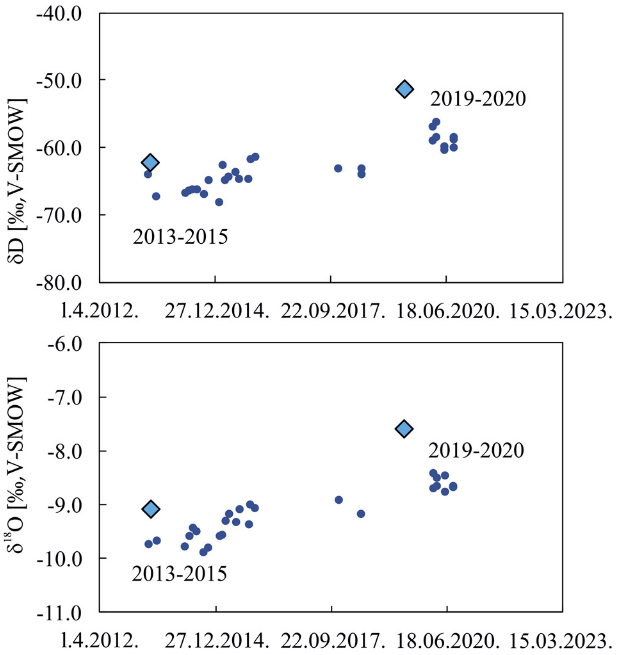


Fig. 12. Hydrogen (A) and oxygen isotope composition of drip water collected at the NU-site in Baradla Cave. The isotopic compositions of the amount-weighted precipitation are also shown by the light blue rhombus. Modified after Czuppon et al. (2022)

Table 6. Relative contributions of winter and summer half-years

Cave-sites	Relative contributions [%] **	
	Summer half year	Winter half year
*Béke Cave (2013–2015)**		
Nagytufa (BNT)	44	56
Felfedező-ág (BFE)	30	70
Site of 560 (B560)	34	66
Buzogány Hall (BBU)	45	55
*Baradla Cave (2013–2015)**		
Nehéz-út (BNU)	37	63
Baradla Cave (2020)		
Nehéz-út (BNU)	15	85
Vacska Cave (2019–2020)		
Rózsát-terem (RT)	46	54
Mérföldkőháti (MK)	25	75
Cseppköves-hasadék (CS)	28	72
Nyeregponti-terem (NYP)	29	71
Szemlőhegy Cave (2019–2020)		
Pettyes-terem (PE)	54	46
Örvény-folyósó (OR)	30	70
Csengő-terem (CSE)	30	70
Óriás-terem (ORI)	25	75
Pálvölgy Cave (2019–2020)		
Meseország-1 (ME-1)	32	68
Meseország-2 (ME-2)	79	21

**Source*: Czuppon et al. (2018a).
** Average values of the drip waters were taken from Table 4 and precipitation data from Table 5.

Table 5. Stable isotope composition of precipitation

Location	δD [‰, V-SMOW]*	δ^{18}O [‰, V-SMOW]*
Aggtelek: 2013–2014		
Annual	−62.29	−9.09
Summer half-year (April–September)	−57.58	−8.50
Winter half-year (October–March)	−69.25	−9.95
Aggtelek: 2019		
Annual	−51.29	−7.58
Summer half-year (April–September)	−45.83	−6.69
Winter half-year (October–March)	−60.08	−9.02
Budapest 2019		
Annual	−60.78	−8.61
Summer half-year (April–September)	−52.44	−7.55
Winter half-year (October–March)	−78.95	−10.94

*All values represent amount-weighted averages.

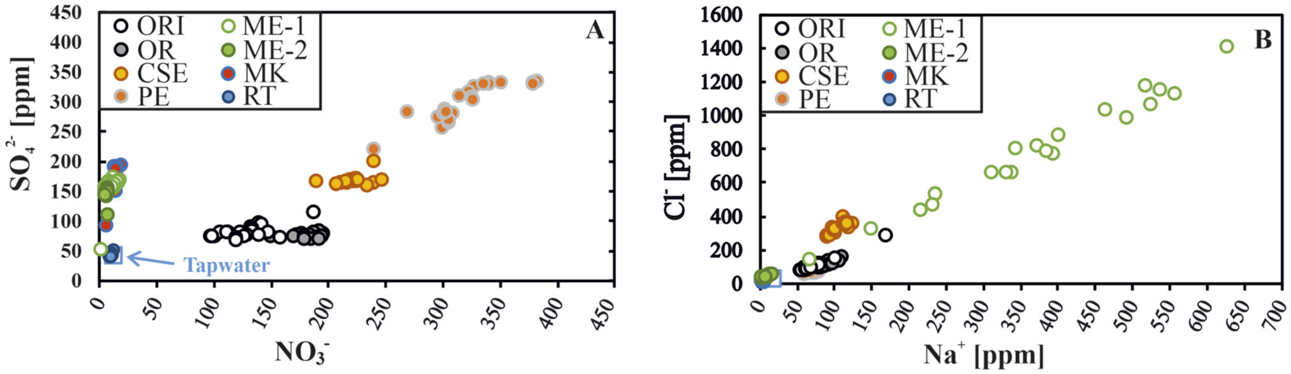


Fig. 13. Sulfate (SO_4^{2-}) vs. nitrate (NO_3^-) contents (A); and chloride (Cl^-) vs. sodium (Na^+) contents (B) of drip waters collected in Vacska Cave (MK, RT) and Pálvölgy Cave (ME-1,ME-2) and Szemlőhegy Cave (PE, CSE, OR, ORI). Modified after Czuppon et al. (2022)

Similarly to RT, the ME-2 site in Pálvölgy Cave and the PE site in Szemlőhegy Cave also show less negative isotopic composition relative to other drip sites. In addition, the stable isotope variabilities of these sites (ME-2 and PE) reveal relatively large seasonality (Fig. 9), suggesting shorter residence time. The significantly lower Sr concentration of the PE site (100 ± 10) relative to the CSE site (300 ± 50) in the same cave supports this explanation.

In summary, it can be concluded that the majority of drip waters in the monitored caves indicate infiltration with winter dominance (Béke Cave: 55–70%; Baradla Cave: 60–80%; Vacska Cave: 55–75%; Szemlőhegy: 70–75%, except for the PE site; Pálvölgy Cave 70%, except the ME-2 site) and presence of a relatively well-mixed aquifer in the epikarst.

Anthropogenic influence. In contrast to the Ajándék-Ariadne cave system in the Pilis Mountains and to the Béke and Baradla caves in the Aggtelek Mountains, the Pálvölgy and Szemlőhegy caves are located within the capital city of Hungary (Budapest, Fig. 6), surrounded by garden suburbs, blocks of flats, pavements and roads (Virág et al., 2009). Therefore, several studies have previously investigated the drip water compositions in order to trace anthropogenic influences (e.g., Fehér, 2011; Fehér et al., 2009, 2016; Fehér and Borbás, 2014; Takácsné Bolner, 2013; Virág et al., 2009; Virág and Mádl-Szőnyi, 2013). The most peculiar features of the drip waters collected in these caves are the high sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-) and sodium (Na^+) contents based on the recent (Table S10 and S11, Fig. 13) and previous studies (e.g., Fehér, 2011; Takácsné Bolner, 2013; Virág et al., 2009). Several reasons have been invoked to explain these high concentrations, such as pollution from water pipes, sewage system, road salt (which is used as a de-icing chemical during winter) and fertilizer (e.g., Fehér, 2011; Takácsné Bolner, 2013; Virág et al., 2009). Only in the case of sulfate was some contribution from the overlying marl (Buda Marl Formation) assumed, as it contains pyrite (and gypsum). Beside this natural contribution, contamination from the sewage system received great attention as a potential source.

In order to evaluate the role of the sewage system, stable isotope compositions of drip water were also measured. The δD and $\delta^{18}O$ time series of drip waters (PE site), which are characterized by the greatest concentration of sulfate and nitrate, show a similar pattern to those in tap water (i.e., negative values in summer and less negative values in winter; Fig. 9) implying that the drip water is influenced by the tap water. Although this observation apparently supports the contamination by the sewage system, the absolute values of stable isotope composition of this site (PE) differ most significantly from those of the tap water. Therefore, we argued that the contribution from pipelines or sewage system must be limited, and another source is required to explain the concomitant elevated sulfate and nitrate contents (Fig. 13A). Thus, the observed stable isotope characteristics are not related to the seasonality of tap water (Fig. 8/B and 9); instead, it might reflect the seasonality of precipitation at a smaller amplitude and shifted by six months. The amplitude of the seasonal variation of δD and $\delta^{18}O$ of precipitation generally decreases and disappears with the increase of the infiltration (residence) time of the percolating water due to dispersion. The Sr concentration can be used to trace this effect. The lower Sr concentration found in PE drip water compared with others suggests a lower residence time and hence relatively rapid infiltration.

This more rapid infiltration might imply a faster response to the hydrological changes and processes on the surface and hence greater sensitivity to surface contamination. Therefore, it is reasonable to invoke the usage of fertilizer as an alternative source for the elevated sulfate and nitrate concentration observed in drip waters (especially at the PE site). In addition, the elevated sodium and chloride concentrations (especially at the ME-2 site; Fig. 13/B) are likely also related to surface processes and anthropogenic activity (road salt).

CONCLUDING REMARKS

We compiled monitoring data from the Béke, Baradla, Vacska, Szemlőhegy and Pálvölgy caves. This compilation revealed some general features and trends in addition to site-specific characteristics. Most of the studied caves indicate strong seasonality in CO_2 concentration, showing high values in summer and low values in winter. This variation can influence the carbonate precipitation rate and reflect the magnitude of the ventilation, which has a direct effect on the stable isotope composition of precipitating carbonates. In addition, the investigation of the relationship of stable isotope composition of the drip waters and the amount-weighted precipitation indicated that the epikarst above the studied sites is generally well mixed and the dominant infiltration takes place during the winter half-year. Thus, the speleothems from these locations likely record multiannual winter-biased climate trends. Apart from these general features, all caves and sites have their own characteristics. These site-specific features play a key role in constraining the factors that influence the carbonate precipitation and the observed chemical and isotopic variations in speleothems. Thus, these observations reinforce the importance of cave-monitoring activities before interpreting speleothem proxy data. In addition, the monitoring of stable isotope and chemical composition of the drip water helped to constrain the anthropogenic and natural processes that effected the infiltrating water in the Buda karst.

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SUPPLEMENTARY MATERIAL

Supplementary materials (Table S1–S11) associated with this article can be found in the online version at https://doi.org/10.1556/24.2021.00109.

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