



CARBON ISOTOPE INVESTIGATION OF FRESHWATER TUFA PRECIPITATION IN KARST STREAMS OF BÜKK MOUNTAINS (HUNGARY)

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Abstract

Recent freshwater tufa precipitation and its parent water were investigated at Szalajka valley, Sebesvíz and Dobrica Spring (Bükk Mts., Hungary). The aim of the study is to analyse the carbon isotope dynamics of freshwater tufa precipitated in karstic streams between the spring water and the first significant tufa barrage using field measurements, water chemistry, and carbon isotope analysis. A further aim was to examine the fossil tufa precipitations in recently active areas and their neighbourhood to determine their age using the ¹⁴C method. Based on the ³H content the water samples are relatively young (<10 y). To calibrate the calendar age of older tufas, dead carbon proportion (dcp) were determined in the recently formed freshwater tufas. The lowest dcp of the recent freshwater tufas was estimated at Sebesvíz (9.6±1.3%), the highest at Szalajka (16.4±2.4%) and a moderate value at Dobrica Spring (13.8±2.2%). Due to the rapid decrease in atmospheric ¹⁴C level we have to compensate the atmospheric ¹⁴C drop between the water infiltration time and the deposition time of fresh carbonates to compensate the bomb-effect. The oldest fossil tufa age (BC 6421-6096) was found at Sebesvíz located around 20 metres away from the riverbed, while the youngest fossil tufa ages (a few years/decades old) were found in the recently active area at all sites.

Keywords: freshwater tufa carbonate, carbon dynamic, ¹⁴C

INTRODUCTION

Freshwater tufas are continental carbonate sediments formed under open-air conditions, precipitating from ambient, mostly cool temperature (karst) waters in areas of carbonate bedrock (Pentecost, 2005, Capezzuoli et al., 2014). Their formation is strongly influenced by changes in supersaturated-water dynamics, leading to intense physicochemical and/or biological process of CO₂ degassing in the hydrological regime. Freshwater tufa deposits are globally distributed from the tropics to the polar regions (Pentecost, 2005).

Since the precipitation of the ambient freshwater tufas are related to the open-air system, they respond quickly to environmental changes, climatic catastrophes (e.g. flood), human activities (deforestation, modified drainage networks, pollution, tourism, agriculture) (Horvatincic et al., 2006; Forbes et al., 2010; Liu et al., 2011). The human influence on tufa deposition has been so consequential during late historical times that it has been cited as the most common cause of the decline of freshwater tufa deposits (Capezzuoli et al., 2014). However, the open-air system also has benefits, as tufa formation is linked to environmental parameters which can be used as an indicator of past climatic and hydrological conditions. As a result of the fast sedimentation rate of tufa (mm to cm/y), tufa may be

suitable for high-resolution climate studies (up to weekly and/or monthly resolution layers can be studied, Matsuoka et al., 2001). Thus, chemical (e.g. trace elements, stable isotopes) and fabric characteristics related to seasonal changes can be observed in detail (Kano et al., 1999, 2003; Matsuoka et al., 2001; Andrews and Brasier, 2005; Kawai et al., 2006, Hori et al., 2008). The oxygen isotopic composition of carbonate and its parent water provides an opportunity to calculate paleotemperature reconstruction using calcite-water oxygen isotope fractionation equations and/or based on $\Delta 47$ methods (Craig, 1965; Kim and O'Neil, 1997; Kele et al., 2015; Bódai et al., 2022).

The geological location, geomorphological position, size, shape and amount of the deposited carbonate and water all can provide information on the environmental conditions that prevailed at the time of their formation, which can be used as an analogy for fossil carbonates (Pedley, 2009). Water level changes, flow of the watercourses and their impact on the system, flood can be identified by the geomorphological position and/or material content of deposits (Luzón et al., 2017). To better understand the results and the process behind freshwater tufa precipitation (or the system), both stable isotope

ratios (e.g. $^{12}\text{C}/^{13}\text{C}$, $^{18}\text{O}/^{16}\text{O}$) and radioactive isotopes (e.g. ^{14}C , ^{238}U) methods can be used.

Since the deposited carbonate (and any organic material) has atmospheric carbon content, their radiocarbon (^{14}C) dating is possible (Libby, 1955; Pentecost, 2005; Lowe and Walker, 2015). The method is based on the fact that while an organism is alive or an inorganic deposit is formed, it builds in carbon – in isotopic equilibrium with the atmosphere. However, after the death of the living organism or deposition is finished, ^{14}C continues to decay, and if the decay rate of ^{14}C is known, the age of the death can be determined from measured/residual ^{14}C by considering other factors e.g. origin of carbonate or pollution (Pazdur, 1988; Horvatincic et al., 2000, 2003; Molnár et al., 2006ab, 2007; Tombor, 2017).

The aim of our paper is to analyse the carbon isotope of freshwater tufa precipitated in karstic streams in the Bükk Mts. in order to 1) better understand the dynamics of tufa deposition between the spring orifice and location of the first significant tufa precipitation (shape: barrage/dam) a few hundred metres away, and 2) to determine the dead carbon proportion (dcp) inside the recently formed freshwater tufa, which could be later

applied to determine the age of older tufas. In order to get a more accurate interpretation of chronology of freshwater tufa deposits, tritium tests were also carried out on water samples to understand the composition of water.

GENERAL SETTINGS

Bükk Mountains

In the Bükk Mts. (Fig. 1/A) several recently forming freshwater tufa deposits can be found (Hevesi, 1972), mainly linked to morphological steps (i.e. cascades, rapids, dams) where the turbulence and related CO_2 degassing are intense. On the northern side of the Bükk Mts., water-bearing rocks overlie the Paleozoic formations, while in the southern part, towards the Great Plain, the water-bearing rocks go deep and are covered by Tertiary and Quaternary sediments (Aujeszky et al., 1974; Aujeszky and Scheuer, 1979). Due to the different hydraulic conductivity of rocks of the Bükk Mts., a multilevel karst system evolved (Aujeszky et al., 1974; Aujeszky and Scheuer, 1974). Springs (e.g. Harica Spring, Dobrica Spring) at the northern side of Bükk Mts. are located at relatively high altitudes (300–500 m), and characterised by significantly variable

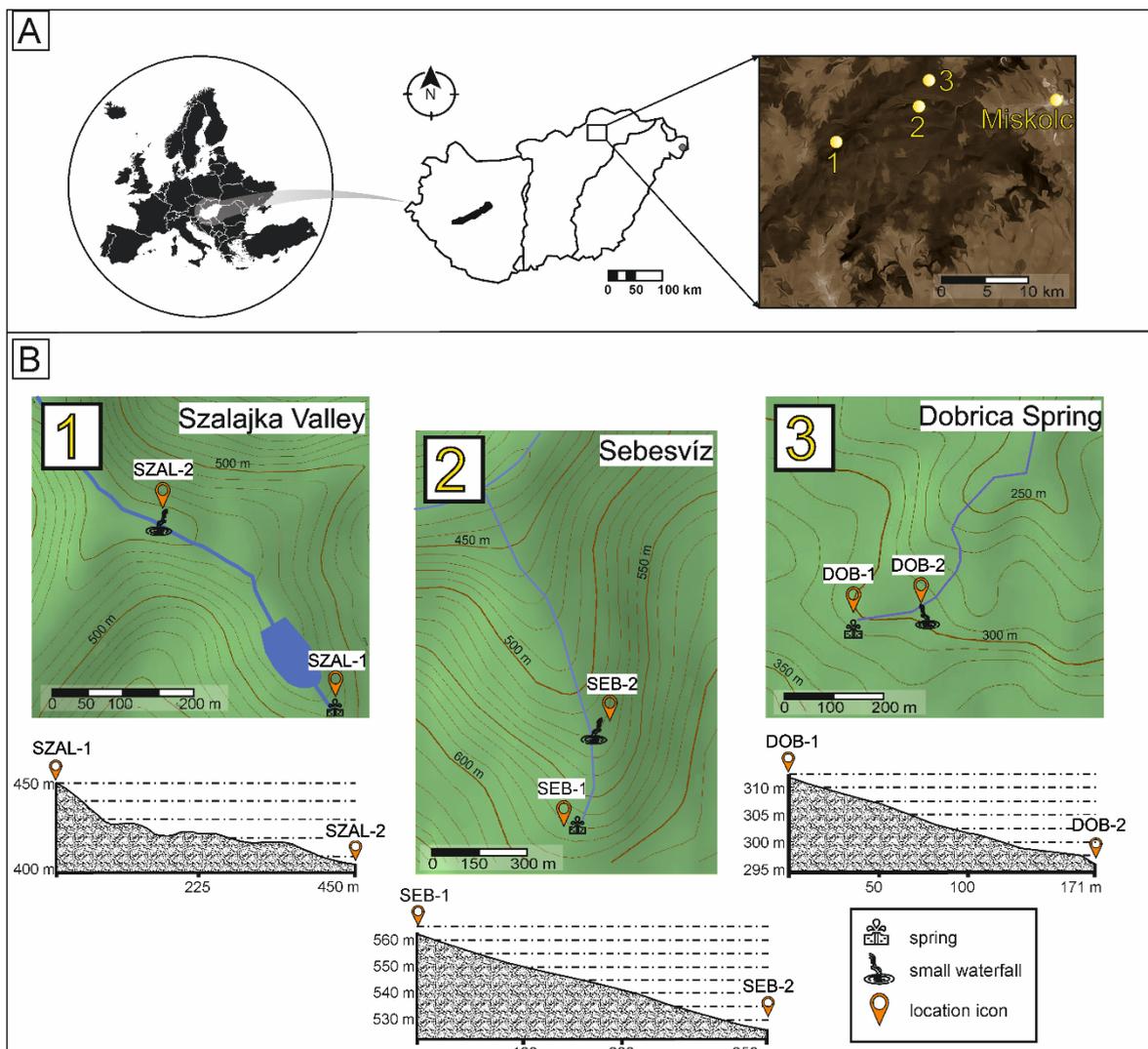


Fig. 1 A) Location of the studied areas in Hungary. B) Maps of the sampling sites, showing the altitude difference between the sampling points at each studied sites.

discharge and low temperature, and their aquifer is mostly Carboniferous-Permian and Upper Eocene limestone.

Szalajka Valley Spring

The Szalajka Valley is located close to the village of Szilvásvár (Bükk Mts., NE-Hungary) (Fig. 1/B-1). The Szalajka Spring is the main source of the Szalajka stream (Pelikán, ed. 2005) with a mean annual discharge of ~4500 L/min. Its drainage area is the karstic Bükk Plateau (8–10 km²). The Szalajka Spring discharges at an altitude of 450 m (a.s.l.) (Hevesi, 1972) (Fig. 1/B-1), and the water reaches the surface at the border of the Triassic limestone layer and an impermeable clay shale (Aujeszky and Scheuer, 1979).

On the upper part of the Szalajka Valley, there is a significant amount of freshwater tufa of mostly unknown thickness in the depths. The Szalajka stream cut into this valley (Zsilák, 1960). In the bed of the Szalajka stream, numerous actively forming freshwater tufa deposits can be observed. The cold karstic water can keep the dissolved CO₂ in solution for a long time, so tufa precipitation starts later, further away from the spring. At about 450 m from the Szalajka spring, at the Fátöl Waterfall, one of the most spectacular tufa terraces of Hungary can be found. The smaller dams are 20–50 cm, the medium ones 50–100 cm, the larger ones 100–150 cm high, but the highest one is 205 cm. The width of the dams is 4–5 m.

Sebesvíz Spring

The spring of the Alsó-Sebesvíz belongs to the Garadna Valley system and is a contact spring of non-karstic rocks (Baráz, 2002) (Fig. 1/B-2). In the middle section of the valley, there is a cold, clear water spring called Huba with two orifices, one of that is blocked by a landslide (Fig. 1/B). The water discharge of the spring is extremely variable, averaging 800 L/min (Pelikán, 2005). About 350 m further from the spring (Fig. 1/B-2), a freshwater tufa barrage system begins forming a waterfall. The freshwater tufa forms an approximately 500 m long, 45 m wide, 8–10 m thick tufa dam deposition (Hevesi, 1972). In the steep slope, V-shaped valley, incision, and strong precipitation can be observed at the dams. The formed waterfalls and the freshwater tufa deposited on fallen tree trunks follow each other in irregular shapes in the waterbed. The water of the stream reaches the Garadna stream after about 1000–1200 m (Baráz, 2002).

Dobrica Spring

The Dobrica spring, located near the settlement of Varbó, at an altitude of 335 m (a.s.l.), is the left tributary of Gyertyán Valley (Fig. 1/B-3). The tufa precipitation begins to form ~170 m from the spring (Fig. 1/B-3). Compared to the right headwaters of Gyertyán Valley, where the Dobrica Spring is connected, there is a 15 m high elevation difference between the two valleys, which is the main reason for the tufa mound deposition (Hevesi, 1972). The Dobrica spring and its stream occur in a 60 m wide, 30 m long freshwater tufa fill, which is eroded in the middle. A 6 m high freshwater tufa mound is formed in it, and a cavity can be found inside the tufa mound/behind the waterfall.

Meteorological data of the studied sites

The climate of the area in the northern part of the Bükk Mts. is continental with seasonal contrast in temperature. The mean annual air temperature is ~10°C and the mean annual precipitation is ~860 mm (OMSZ, 2001).

The nearest meteorological station to the three studied sites, with monthly resolution data, is at Miskolc (131 m asl.), 28 km away from Szalajka Valley, 17 km away from Sebesvíz and 15 km away from Dobrica Spring (Fig. 1/A). The amount of annual precipitation changed between 749 and 790 mm, and the mean air temperature changed between 11.3–11.8°C, with the extremes exceeding 30°C in the summer (29.9–36.1°C in June–September) and around 0°C in the winter (0.5 to -1.5°C in January) during the measured period (from May 2019 to February 2021) (www.ksh.hu).

Hydrogeological units of the Bükk Mountains

The Bükk Mountains consist of rocks characterised by different water conductivity (Aujeszky and Scheuer, 1974; Pelikán, 2005). Thus, the mountain range can be divided into three major units based on the hydrogeological properties of the rocks. The Northern Unit consists of Carboniferous, Permian, Triassic, and Jurassic strata, the Middle Unit of Carboniferous, Permian, Triassic strata and the Southern Unit of Middle Triassic, Upper Jurassic strata (Fig. 2)

The Szalajka Spring belongs to the Southern Unit (Jurassic shale area between Szalajka Valley and Belpátfalva) (Fig. 2). According to the dip data, the Szentistvánhegyi metaandesite outcrops at the Fekete-sár and underlines at the Bükkfennsíki limestone, thus separating the water system of the Szalajka Spring from the rest of the Nagy Plateau.

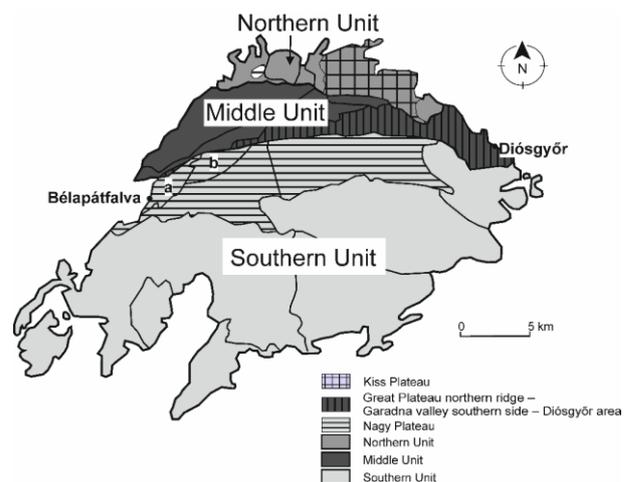


Fig. 2 The hydrogeological units of the Bükk Mts. based on Pelikán (2005). The Szalajka Spring belongs to the Southern Unit (shale area), the Sebesvíz Spring belongs to the Middle Unit (dolomite and limestone stripes) and Dobrica Spring belongs to the Northern Unit (Kis Plateau). Northern Unit: Kiss Plateau (Barátságkerti, Csókási, Kalapács sinkholes belong here) Middle Unit: Great Plateau northern ridge – Garadna valley southern side – Diósgyőr area (Száráz Valley and Felső-Sebesvíz belongs here) Southern Unit: Nagy Plateau: a) shale area between Szalajka Valley and Belpátfalva, b) area of Istállóskő (Fekete-sár belongs here).

The Huba Spring at Sebesvíz belongs to the Middle Unit (northern margin of the Nagy Plateau) (Fig. 2). This unit extends from Bélapátfalva to Diósgyőr and is practically formed by an east-west striking, steeply and locally uplifted of Hámori Dolomite, Szentistvánhegyi metaandesite, Fehérkői Limestone and Vesszősi Formation layers. The impermeable Szentistvánhegyi metaandesite is located between the two karstic lithological units but is missing in two sections for tectonic reasons (Szárász Valley, Felső-Sebesvíz).

The Dobrica Spring belongs to the Northern Unit (Kis Plateau) (Fig. 2). It is the largest karst unit in the area north of the Garadna Valley. The Triassic rock assemblage is composed of metaandesite and metabasalt, Kisfennsíki Limestone, Vesszősi Formation, Felsőtárkányi Limestone overlying Palaeozoic aquifer sediments. There are several sinkholes in the area (Barátságkerti, Csókási, Kalapács, etc.), which partly discharge the water they absorb into the low and medium yield springs in the north at an altitude of around 300 m asl.

METHODS

Field measurements and sampling

Seasonal measurements and sampling were carried out in 2019 and 2021 at all sites on seven occasions. Two sampling points (Fig. 3) were selected for every studied site, one at the spring orifice and a second a few hundred metres away from the spring, where there is a significant freshwater tufa deposition (Table 1) (Figs. 1, 3). At all points a Hanna HI98108 instrument (accuracy: $\pm 0.5^\circ\text{C}$, $\text{pH} = \pm 0.1$) was used to measure in situ water temperature and pH, whereas conductivity (EC) was determined with a Hanna HI98303 Dist3 pen (precision: $\pm 0.2\%$ of the total scale). At the studied tufa barrages, we have registered the water temperature in two different ways. We applied field temperature registers (Wire/iButton Temperature Logger, accuracy: $\pm 0.5^\circ\text{C}$) for longer time period measurements and we applied measurement by a Hanna HI98108 unit on the days of water sampling. Tufas were not detected at none of the springs. To collect fresh carbonate, plastic surfaces were placed in the stream bed and replaced seasonally. To get an overall picture of the age of the tufa outcrops based on field observations and the porous structure of the freshwater tufa, fossil freshwater tufa

samples were collected in the cross-section and along the longitudinal profiles where possible.

Radiocarbon dating was performed on a total of 17 fossil carbonate samples and 2 organic materials (plant remains) at all three sites (Szalajka Valley: 3, Sebesvíz: 8 + 1 organic, Dobrica Spring: 6 + 1 organic). Water and tufa samples (recens and fossil) were collected for water chemistry, stable isotope, tritium and radiocarbon laboratory analyses during each sampling field campaign. Water samples for used for the determination of anions were filtered and stored without additional treatments, whereas samples for the determination of cations and trace elements were acidified after filtration by the addition of Suprapur Nitric Acid. For isotope analyses, water samples were collected into clean plastic bottles and kept airtight closed, without headspace air in dark and cold conditions until the lab analyses.

Chemical and isotope analyses of karstwater and carbonate deposit samples

Water chemistry and isotope analyses were performed at the Isotope Climatology and Environmental Research Centre (ICER), Institute for Nuclear Research, Debrecen, Hungary.

Determination of major cations was carried out using an Agilent 4200 microwave plasma atomic emission (MP-AES) spectrometer. Elements were determined by their emission on wavelengths: Na 588.995 nm, K 766.491, Ca 422.673, Mg 279.553). Conditions of measurements were optimized. 0.1% CsCl was used as ionization buffer. Titration was applied for determining HCO_3^- and CO_3^{2-} ions (0.1 M HCl, indicators were methyl orange and phenolphthalein). Anions were determined by ion chromatography, using a Metrohm instrument (850 Professional IC). Total phosphorus was measured after digestion with potassium persulphate by spectrophotometry with molybdenum blue method. Total organic carbon was measured by total organic carbon analyzer (Shimadzu TOC-Vcpn). The laboratory run under ISO/IEC 17025: 2017 (NAH-1-1755/2018).

The stable isotope composition of water, dissolved inorganic carbon (DIC) and carbonate deposits were analyzed using an automated GASBENCH II sample preparation device attached to a Thermo Finnigan DeltaPLUS XP mass spectrometer (Vodila et al., 2011).

Table 1 Location and coordinates of the sampling points in the Bükk Mts., indicating downstream distances from the spring orifices (Szalajka Valley, Sebesvíz and Dobrica Spring)

Location	Code	Distance from the spring (km)	Coordinates	
Szalajka V.	SZAL-1	-	N48° 04' 22.26"	E20° 24' 54.27"
Szalajka V.	SZAL-2	0.46	N48° 04' 33.74"	E20° 24' 36.59"
Sebesvíz	SEB-1	-	N48° 06' 29.37"	E20° 33' 14.69"
Sebesvíz	SEB-2	0.35	N48° 06' 31.69"	E20° 33' 16.01"
Dobrica Spring	DOB-1	-	N48° 08' 28.89"	E20° 35' 36.94"
Dobrica Spring	DOB-2	0.17	N48° 08' 30.57"	E20° 35' 45.73"

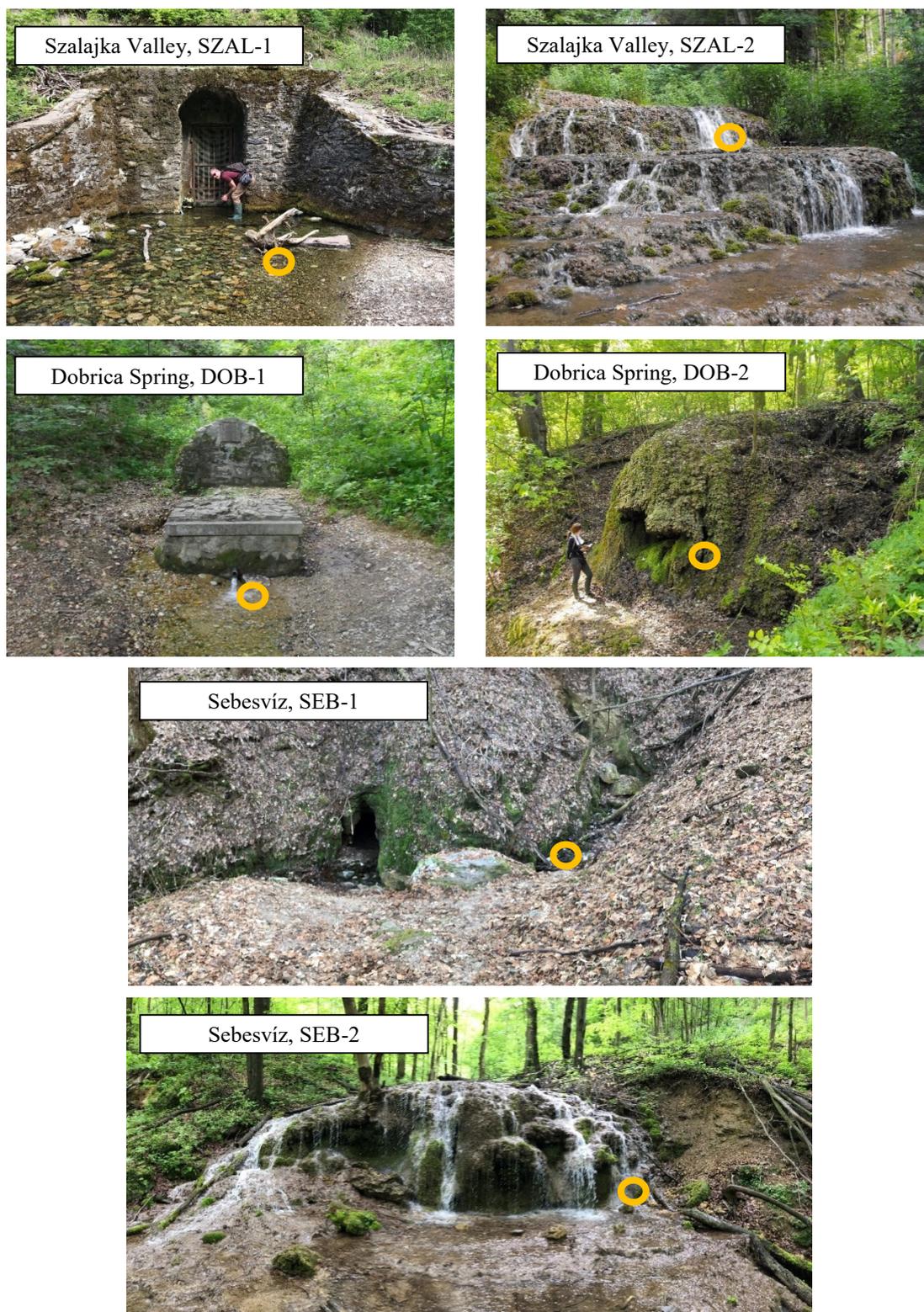


Fig.3 Field photos of the sampling points (spring and tufa deposit from karstic streams) at the studied sites

Hydrogen and oxygen isotope compositions of the water are given as $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values relative to V-SMOW, and DIC carbon isotope values are expressed as $\delta^{13}\text{C}$ relative to V-PDB. The precision of the measurements is better than ± 0.15 ‰ for $\delta^{18}\text{O}$, ± 2 ‰ for $\delta^2\text{H}$, and ± 0.08 ‰ for $\delta^{13}\text{C}$. Tritium (^3H), the radioactive isotope of hydrogen with a 12.32 year half-life. This environmental isotope as a natural tracer is used to describe circulation patterns in hydrology, hydrogeology and limnology

research. It is usually measured in Tritium Units, where 1 TU is defined as the ratio of 1 tritium atom to 10^{18} hydrogen atoms (Jenkins and Smethie 1996). Karst water samples have been analysed for tritium using the ^3He -ingrowth method with a special ^4He isotope dilution technique (Palcsu et al., 2010; Papp et al., 2012). The uncertainty of the method is 0.1–0.3 TU in the range of 5–10 TU. This ^3H analyses process involves four steps: distilling a water sample, removing dissolved gases

through vacuum pumping, allowing the sample to produce ^3He atoms from tritium decay over a few weeks or months, and finally analyzing the helium isotopes abundance using a noble gas mass spectrometer. By measuring the ^3He , the tritium concentration in the sample can be determined (Palcsu et al., 2010; Papp et al., 2012).

Radiocarbon analyses of karstwater samples and carbonate deposits

About 20 mg of the carbonate samples were treated with 85% orthophosphoric acid in a vacuum tight digestion reactor and kept for 1 hour at 70°C to release the DIC as CO_2 gas into the reactor headspace. The liberated CO_2 was subsequently purified and trapped cryogenically by means of a customized vacuum line (Molnár et al., 2013a). In addition, fossil marble, as blank standard material (IAEA-C1, 0.0 pMC) and a known age travertine reference material (IAEA-C2, 41.14 pMC) was also treated as control samples for the CO_2 extraction step, to determine if any modern/fossil carbon contamination is introduced during the extraction or graphitisation procedure. Preparation of water samples (up to 50 mL/sample) was prepared in similar way as the carbonates, except the water was injected by a sterile plastic syringe into the prevacuumed digestion reactor vessel through a septum-sealed cap. A 0.45 μm pore size membrane filter was attached to each plastic syringe to filter the particles from water samples during injection. After the acidic digestion of DIC and solid carbonates or sealed tube oxidation of cellulose samples, the reaction vessels were connected to a dedicated gas handling line where the CO_2 can be recovered and purified by a cryogenic method. The water vapor is trapped first at -70 °C (isopropyl alcohol – dry ice) and the CO_2 is frozen at -197 °C (liquid N_2). After the remaining junk gases were evacuated, the purified CO_2 was expanded to a known volume and its quantity was measured with high precision Baratron® 626B pressure sensor (range: 0-500 mbar) (Molnár et al., 2013a).

Finally, the recovered CO_2 samples were converted to graphite by the sealed tube graphitisation technique (Rinyu et al., 2013). The ^{14}C activities of the graphite targets were measured by an EnvironMICADAS AMS at ICER laboratory (Molnár et al., 2013b). The overall measurement uncertainty was calculated by including counting statistics, background subtraction and normalisation (Synal et al., 2007). The results were corrected for the $\delta^{13}\text{C}$ isotopic fractionation using the Bats software (Stuiver and Polach, 1977; Wacker et al., 2010). The corrected conventional ^{14}C ages were calibrated to a calendar age using Calib 8.1 and CaliBomb softwares, depending on the age range.

Dead carbon proportion analyses

The percentage of inactive carbon or dcp (dead carbon percent) in carbonate deposits is expressed by the following formula (Genty et al., 1999):

$$\text{dcp}_{\text{past}} = [1 - (a^{14}\text{C}_{\text{carb}} / a^{14}\text{C}_{\text{air}})] * 100\%$$

where $^{14}\text{C}_{\text{carb}}$ is the specific radiocarbon activity of the carbonate, $^{14}\text{C}_{\text{air}}$ specific radiocarbon activity of atmospheric modern CO_2 during carbonate precipitation. The dcp value of a carbonate deposit is used for correction of its initial ^{14}C content in order to obtain a realistic age estimate for the precipitation time.

RESULTS

Field observations

Szalajka Valley

The water temperature at the SZAL-1 (spring) sampling point changes seasonally between 11.3 and 7.9°C (Fig. 4/A). At the SZAL-2 point (Fátyol Waterfall, the distance from the spring is about 462 m), the maximum value is 14.8°C, the minimum value is 4.9°C. The pH values increased downstream (Fig. 4/B). The changes in pH along the longitudinal profile is in a range from 8.58 to 7.03. The lowest value at SZAL-1 sampling point is 7.03 and the maximum value is 8.08. At the SZAL-2 sampling point, the minimum value is 7.27 and the maximum value is 8.58 (Supplementary Table1). The EC values decrease from the spring to the waterfall, varying between 650 and 448 $\mu\text{S}/\text{cm}$ (Fig. 4/C). At SZAL-1 sampling point the max value is 650, the min is 461 $\mu\text{S}/\text{cm}$ (average: 508 $\mu\text{S}/\text{cm}$). At SZAL-2, the max value is 505, and the min is 448 $\mu\text{S}/\text{cm}$ (average: 471 $\mu\text{S}/\text{cm}$) (Supplementary Table 1).

Sebesvíz Spring

At Sebesvíz the water temperature changes from 11.6 to 6.5°C within the studied period (Fig. 4/A). The water temperature at the spring (SEB-1) changes between 9.1 and 8.0°C (the change at the spring is 1.1°C). At the SEB-2 point (the distance from the spring is about 350 m), the maximum value is 11.6, the minimum value is 6.5°C (Supplementary Table 1). The pH values increased downstream. The changes in pH along the longitudinal profile is in a range from 8.52 to 7.04 (Fig. 4/B). The lowest value at SEB-1 sampling point is 6.49 and the maximum value is 8.00. At the SEB-2 sampling point, the minimum value is 7.04 and maximum value is 8.52. The EC values show a decrease from the spring orifice to the waterfall and varied between 558 and 424 $\mu\text{S}/\text{cm}$ (Fig. 4/C). At SEB-1 sampling point the maximum value is 558, and the minimum value is 508 $\mu\text{S}/\text{cm}$ (average: 526 $\mu\text{S}/\text{cm}$). At SEB-2, the maximum value is 525, while the minimum value is 424 $\mu\text{S}/\text{cm}$ (average: 471 $\mu\text{S}/\text{cm}$) (Supplementary Table 1).

Dobrica Spring

The water temperature at the DOB-1 (spring) sampling point changes between 10.8 and 9.1°C (the change at the spring is 1.7°C) (Fig. 4/A). At the DOB-2 point (the distance from the spring is about 171 m), the maximum value is 12.9, and the minimum value is 5.5°C (Supplementary Table1). The pH values increased downstream along the longitudinal profile. The change in pH is between 8.30 and 6.36 (Fig. 4/B). The highest value at DOB-1 sampling point is 8.15 and the lowest value is

6.36. At the DOB-2 sampling point, the maximum value is 8.30 and the minimum value is 6.94. The EC values show downstream decrease and varied between 730 and 476 $\mu\text{S}/\text{cm}$. At DOB-1 sampling point the maximum value is 730, the minimum is 480 $\mu\text{S}/\text{cm}$ (average: 639 $\mu\text{S}/\text{cm}$). At DOB-2, the maximum value is 683, the minimum is 476 $\mu\text{S}/\text{cm}$ (average: 571 $\mu\text{S}/\text{cm}$) (Fig. 4/C) (Supplementary Table1).

The spring water temperature changes in a narrower range at the studied sites (Fig. 4/A) and the water temperature changed seasonally downstream at all studied sites. The pH values increased downstream along the longitudinal profile between the spring and the tufa barrage at all sites (Fig. 4/B). This can be caused by the

CO_2 release due to the tufa precipitation. EC values show downstream decrease between the spring and the tufa barrage (Fig. 4/C).

The registers recorded the water temperature 4-6 times per day (every 6-8 hours) from July 2019 to October 2019 and from January 2020 to May 2020 at the studied tufa barrages (SZAL-2, SEB-2, DOB-2) (Fig. 1/B and Fig. 3).

The measured water temperature values are plotted as daily averages in Figure 5 (the water temperature measurement at Sebesvíz was not successful between July 2019 and October 2019). The temperature values measured by registers show a good correlation with the in situ measured temperatures. There are small differences

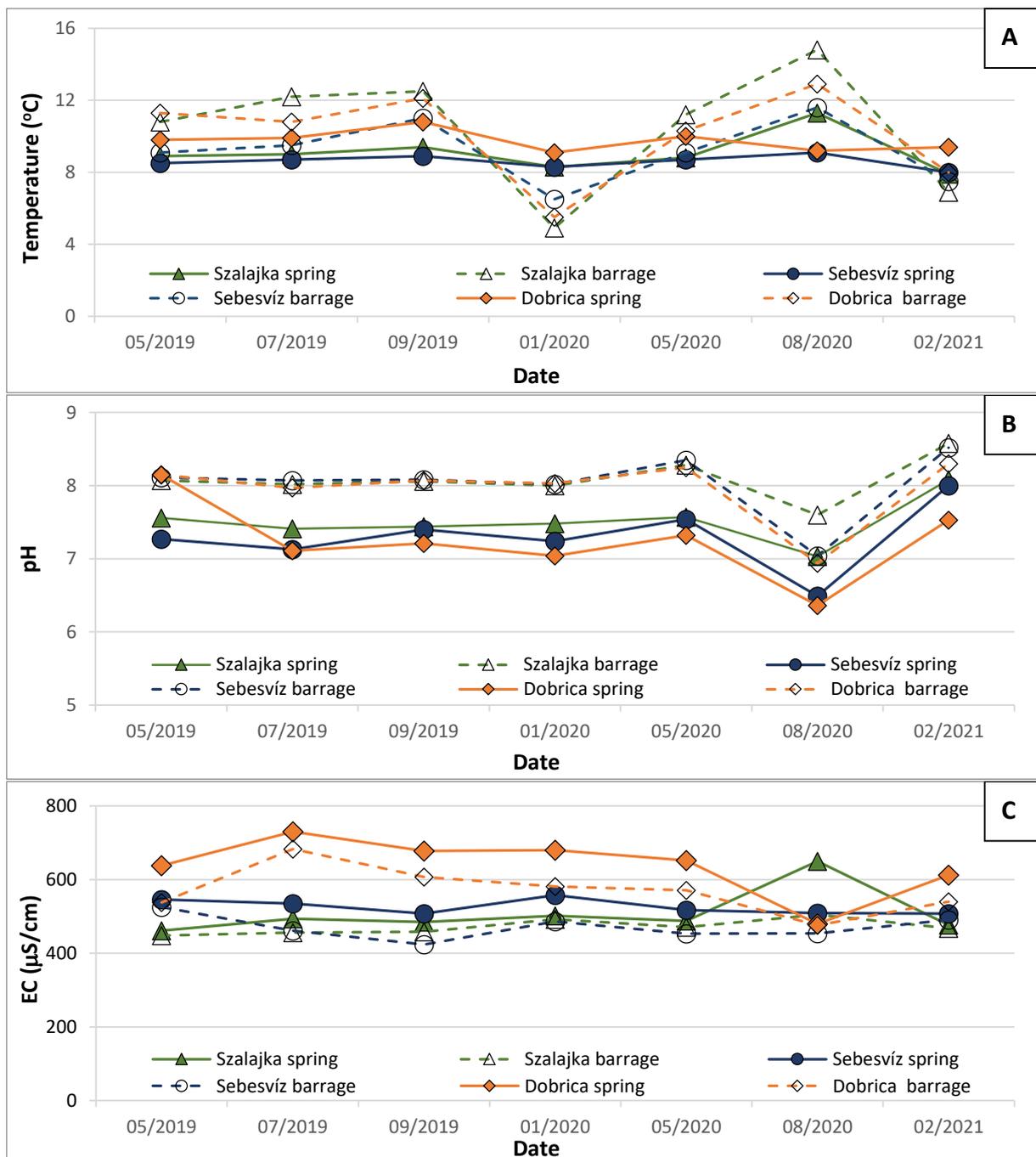


Fig. 4 In situ, seasonally measured temperature (A), pH (B) and EC parameters (C) of water in the Szalajka Valley, Sebesvíz and Dobrica spring (Bükk Mts.)

between the two types of temperature data on a given day because temperature registers record daily averages. In contrast, our occasional measurements last for only a few minutes during the sampling.

Hydrochemistry of the karst water

At the three sampling sites, water was sampled for water chemistry analysis at the spring orifices and at the dams on a summer (August 2022) and on a winter (February 2021) day.

The Ca^{2+} and HCO_3^- content of the water decreased significantly (by 5–25%) from the spring to the barrage in both seasons (Fig. 6), which can be interpreted as a result of the combined effect of the downstream deposition and

the accompanying CO_2 degassing (Supplementary Table 1).

The total dissolved organic carbon content (TDOC) at Szalajka Valley decreased from an average summer value (1.1–1.3 mg/l) by 20–30% in winter (0.89 mg/l) (Supplementary Table 1), while at the other two sites (Dobrica spring, Sebesvíz) the summer (1.11±0.08 mg/l) and winter (1.14 ±0.03 mg/l) TDOC values were within ±10% range around the mean value. The Cl^- content was quite variable for the three springs in the summer period (Szalajka: 1.42±0.02 mg/l; Sebesvíz: 2.21±0.02 mg/l; Dobrica: 3.56±0.11 mg/l), with a significant decrease (20–25%) in the winter period in all cases. The SO_4^{2-} content also showed a different pattern at the three sites in summer

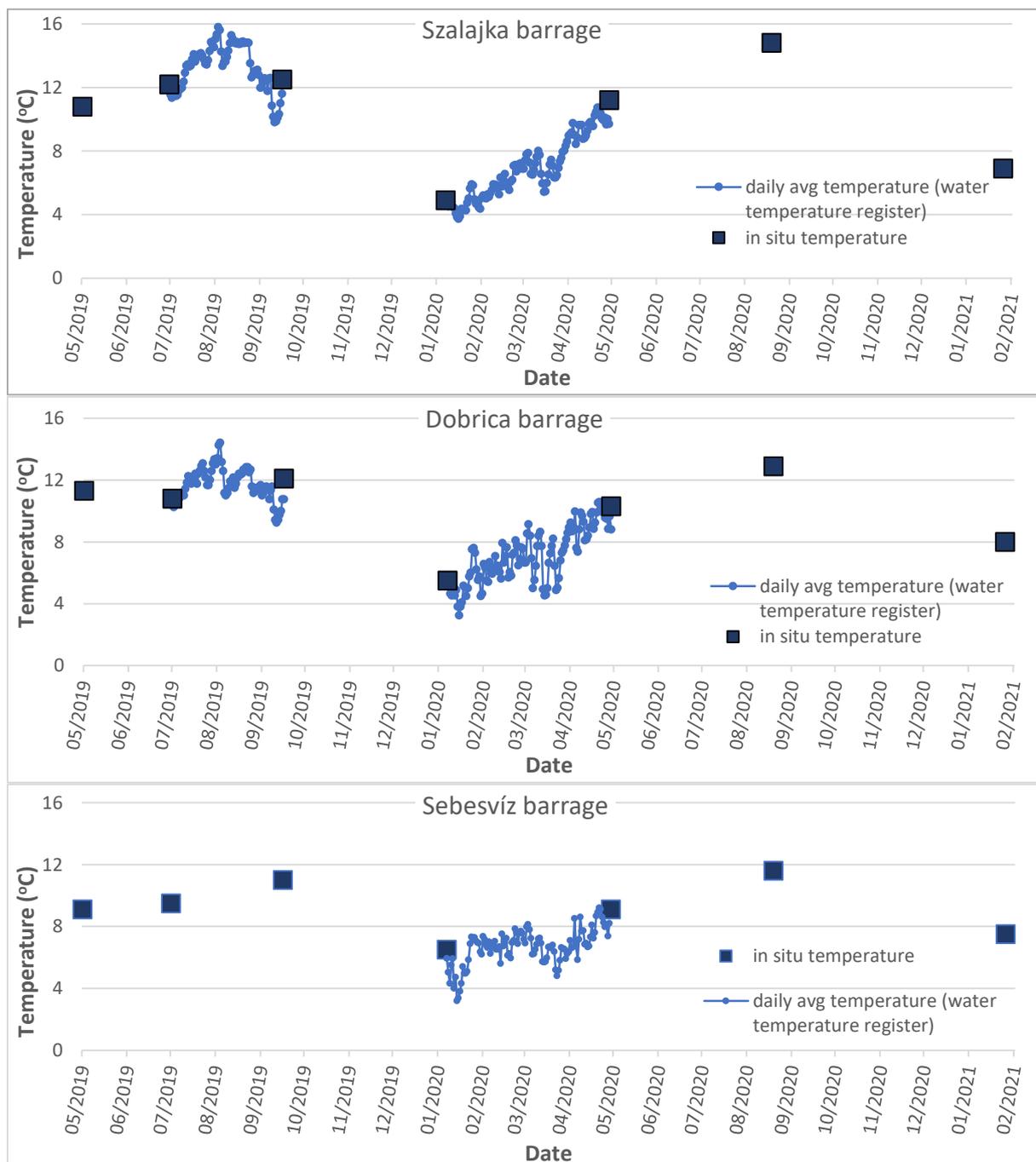


Fig. 5 Comparison of data obtained by a temperature logger and occasional temperature measurements made during water sampling

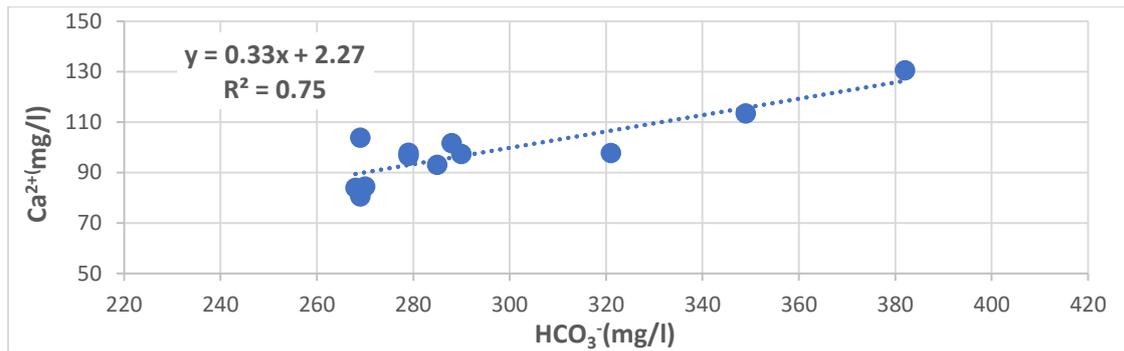


Fig.6 Correlation between the Ca²⁺ and HCO₃⁻ content of water at all the tree sites

(Szalajka: 13.61±0.01 mg/l; Dobrica: 42.73±0.79 mg/l; Sebesvíz: 14.87±0.04 mg/l), which remained similar in winter at one site (Dobrica), while it decreased remarkably (by 13–14%) at the other two sites. The water of Dobrica has higher Cl⁻ and SO₄²⁻ content than the Sebesvíz and Szalajka springs. Szalajka shows much lower concentrations of Mg²⁺ (summer: 1.04±0.04 mg/l; winter: 0.96±0.01 mg/l) than Dobrica (summer: 3.05±0.07 mg/l; winter: 2.52±0.07 mg/l) and Sebesvíz (summer: 3.98±0.30 mg/l; winter: 3.92±0.04 mg/l) (Supplementary Table 1). The K content shows a variable pattern (mean summer: 0.57±0.19 mg/l), which increases by 30–45% in winter (mean: 0.76 ±0.23 mg/l). Similarly, the Na content is also very variable in the comparison of the three sites, with a significant decrease (70%) in summer (mean: 1.38 ±0.72 mg/l). The NO₃⁻ content also varies significantly between sources (averages: Szalajka: 8.88±0.67 mg/l; Sebesvíz: 3.99±0.21 mg/l; Dobrica: 10.91±0.61 mg/l), which remain constant with ±10% variation between summer and winter. There was no detectable content of F⁻, NO₂⁻, and PO₄³⁻ in any of the water samples.

Tritium in water samples and infiltration time interval identification

The ³H content of the collected water samples at the

springs (-1) and also at the tufa deposits (-2) at each location (DOB-, SEB- and SZAL-) were analysed (Fig. 7).

The overall average of all the samples was 5.88 ± 0.59 TU, showing that all the water samples are relatively young, with relatively short (<10 y) residence time since they arrived into the karst system as rainwater.

Rain water ³H content data for Hungary are used from Palcsu et al. (2021) and were presented as decay corrected values (³H half-life: 12.32 y) for the sampling dates (Fig. 8). According to the observed ³H content in the spring water at the three investigated locations, it was possible to estimate the corresponding time of precipitation using the precipitation ³H time series. We have applied a piston flow model (as a basic approach) (Bethke and Johnson, 2008), without significant mixing effect of different rain waters in the karst system. The corresponding infiltration times are indicated in Figure 8. for the 3 different spring water samples (DOB: from 09/2011 to 04/2013; SEB: 03/2014 to 03/2016; SZAL: 11/2012 to 09/2013). As it is shown in Figure 8. in the last decade precipitation ³H content has rather complicated variations. It does not apply that the lower ³H content means the older infiltration age in this time period.

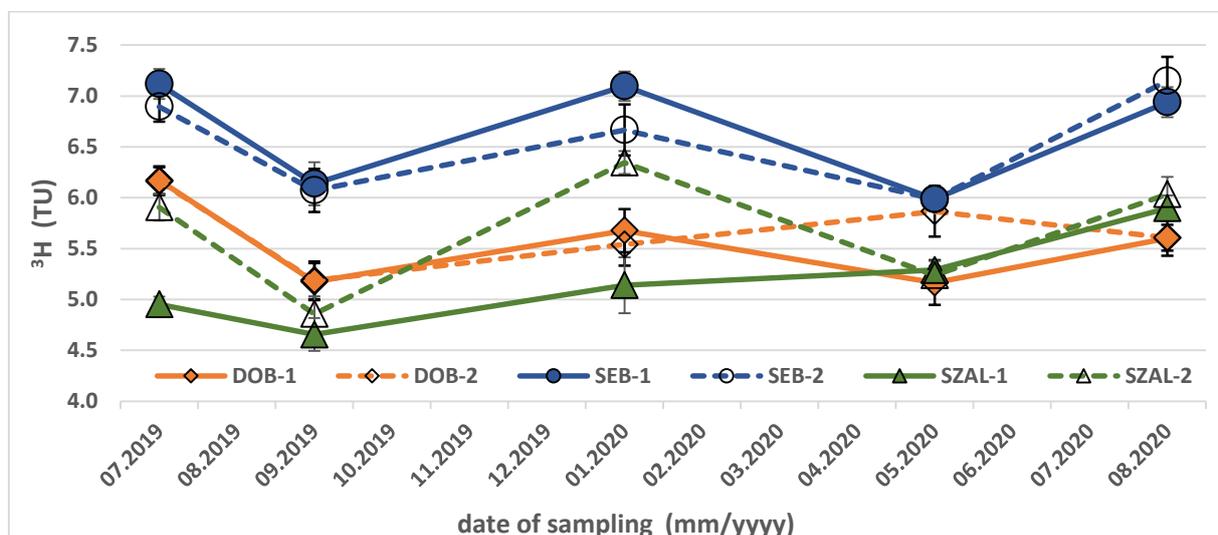


Fig.7 Measured water ³H content at the springs (-1) and at the tufa deposits (-2) at the different sampling campaigns.

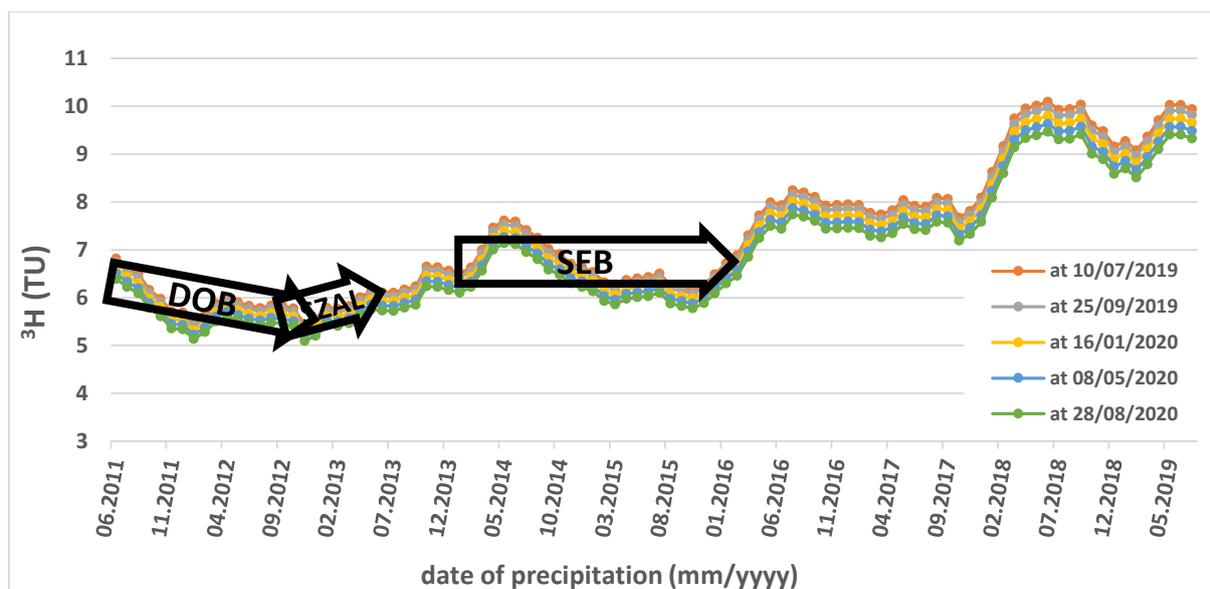


Fig.8 Rainwater ^3H time series in Hungary (after Palcsu et al., 2021), decay corrected for the water sampling dates (different colours correspond to the different sampling dates used for decay correction). Possible time of infiltration (represented by arrows) of the water samples into the karst system according to their ^3H content at the time of the sampling campaigns. Location codes of arrows: DOB: Dobrica; SEB: Sebesváz; SZAL: Szalajka.

Carbon isotopes in water

The three study areas present a very consistent radiocarbon picture, despite being located at relatively distant points in the Bükk karst region, on different sides, with different spring-barrage distances and belonging to different aquifers. The average radiocarbon value (for 7 different occasions) taken at the sampling points of the three sites is 89.2 ± 2.8 pMC. The individual and temporal trends for each site are presented in Table 2 and Figure 9.

All water samples were analysed for ^{14}C (at three locations and 7 sampling campaigns). The values measured at the spring of Sebesváz cover a narrower range. Here, the average ^{14}C value of the spring water was 91.9 ± 1.6 pMC, while the value of the water at the barrage, 350 m away, was slightly higher, 92.1 ± 1.3 pMC (Fig. 9/C). The average ^{14}C value of Dobrica spring was 89.0 ± 2.0 pMC, while the average ^{14}C value at the barrage, 171 m away, was 89.2 ± 1.6 pMC (Fig. 9/B). The average ^{14}C value at the Szalajka spring was 86.1 ± 2.0 pMC, and the average ^{14}C value at the Fátyol Waterfall's barrage, 462 m away, was 89.4 ± 2.7 pMC (Fig. 9/A).

We have investigated the presence of atmospheric CO_2 isotope exchange from the air into the water during its transport between the spring orifice and the tufa barrier. Our results have shown there was no significant ^{14}C content change for the Sebesváz and Dobrica spring according to the spring-barrage pair based on our measurements.

There was an average 0.21 ± 0.83 pMC ^{14}C increase from the spring to the barrage at Sebesváz (Fig. 9/B) and 0.22 ± 1.07 pMC at Dobrica spring (Fig. 9/C). In the case of Szalajka spring – Fátyol Waterfall, where the spring-barrage distance is the largest (462 m), an increasing ^{14}C value was detected (Fig. 9/A). The ^{14}C value increase at the Fátyol dam 0.85 ± 0.54 pMC.

Out of the three studied systems, the water from the Szalajka spring contains the lowest proportion of modern carbon and ^{14}C with an average of 86.1 ± 2.0 pMC.

The Szalajka spring water dissolved inorganic carbon has an average $\delta^{13}\text{C}$ value of $-12.8 \pm 1.1\text{‰}$ (V-PDB), which is the closest to the $\delta^{13}\text{C}$ value of air (-8‰) (www.gml.noaa.gov), thus its $\delta^{13}\text{C}$ value is less sensitive for the possible interaction with airborne CO_2 . There is a shift in the $\delta^{13}\text{C}$ stable isotope ratio of the water DIC from spring to barrage: $1.8 \pm 0.7\text{‰}$ (V-PDB) at Sebesváz and $2.2 \pm 1.4\text{‰}$ (V-PDB) at Dobrica spring (Fig. 9). The $\delta^{13}\text{C}$ isotopic fractionation rate at the Szalajka spring – Fátyol Waterfall pair is the smallest among the three studied systems (the $\delta^{13}\text{C}$ shift rate is $1.2 \pm 1.5\text{‰}$ (V-PDB)). At the sites of Sebesváz and Dobrica springs, we have seen a systematic $\delta^{13}\text{C}$ stable isotopic shift from the spring to the barrage in the dissolved inorganic carbon fraction. It appears that the water flow at Sebesváz and Dobrica springs show a more pronounced positive directional stable isotope fractionation and less shift is visible at Szalajka.

Carbon isotopes in carbonate deposit

The average values of $\delta^{13}\text{C}_{\text{carb}}$ ($\delta^{13}\text{C}$ value of the recent/freshwater tufa carbonate deposit) for the three studied sites are the following: Sebesváz $-10.6 \pm 0.4\text{‰}$ (V-PDB), Dobrica spring $-10.3 \pm 0.4\text{‰}$ (V-PDB) and Szalajka spring $-10.0 \pm 0.5\text{‰}$ (V-PDB).

For each studied site, the tufa carbonate is slightly more positive in stable ^{13}C isotope ratio relative to the parent water (Fig. 9).

Age determination of flowstone sediments

To determine the age of the tufa deposits, it is necessary to determine and correct the apparent ^{14}C age at the time of deposition. To estimate the apparent age in the past (when a deposit formed), we measured the apparent age

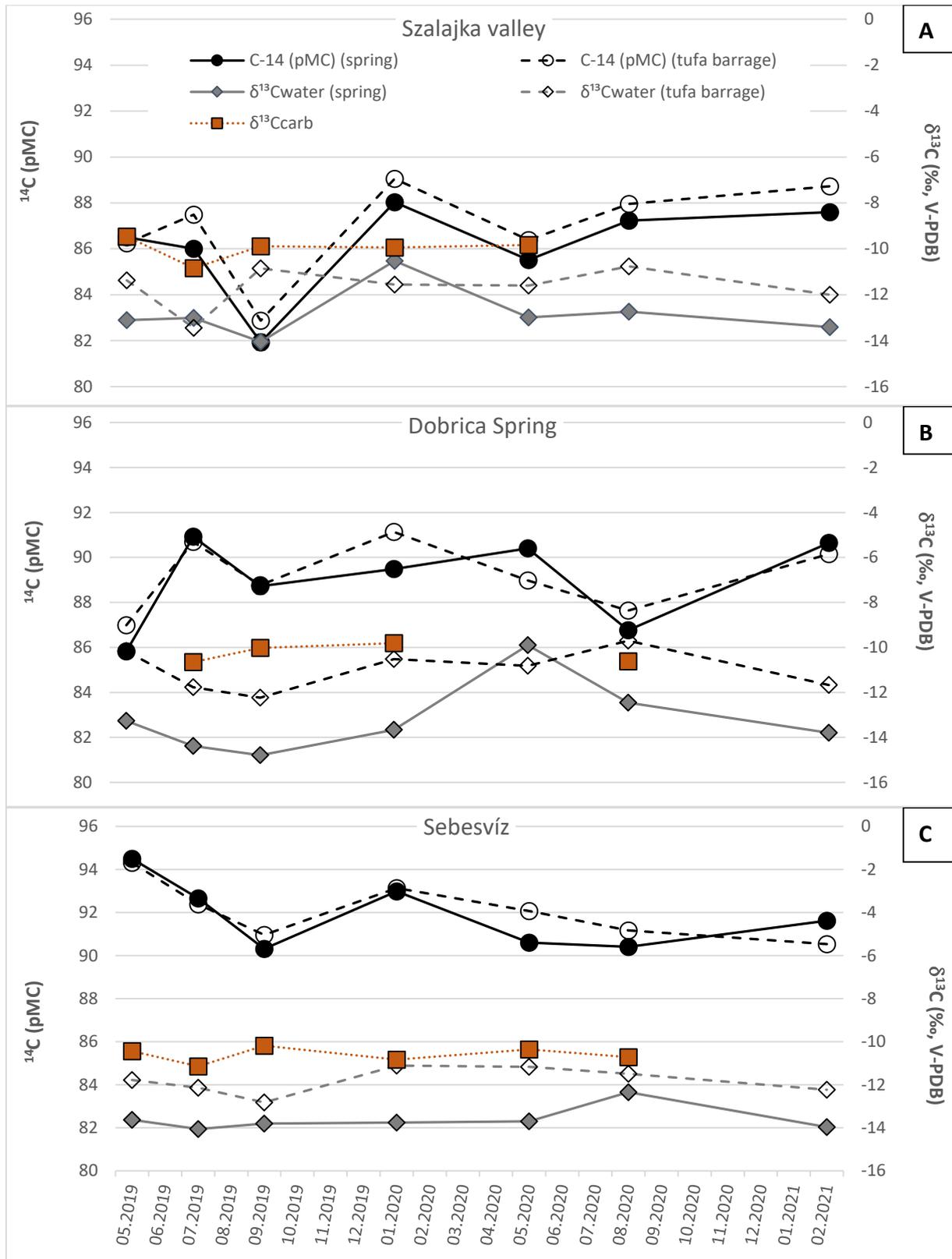


Fig. 9 Seasonally measured ¹⁴C, δ¹³C values of the water and δ¹³C values of the tufa

of fresh carbonate deposits. For this purpose, fresh tufa carbonates were collected at each sampling site. The measured (recent) apparent ¹⁴C age values were used as a correction of the measured conventional ¹⁴C age of the investigated old tufa samples.

The average ¹⁴C content of recent freshwater tufa carbonates measured in the Szalajka Valley is 92.54±1.10 pMC, at the Dobrica spring, 89.36±2.28 pMC and at the Sebesvíz, 86.20±2.47 pMC (Table 2). In order to correct the measured values of the fossil carbonates, we obtained dcp-corrected ¹⁴C conventional ages, which can be

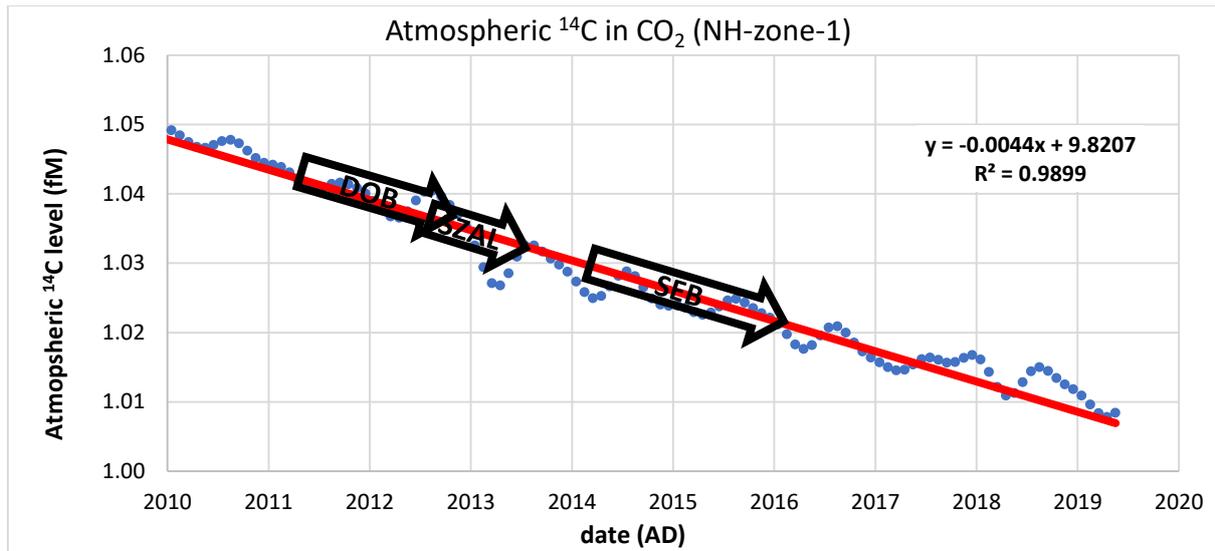


Fig.10 Atmospheric ¹⁴C levels (after Hua et al. 2021). The arrows in the figure indicate the time of water infiltration.

calibrated to calendar ages. The ¹⁴C content of the air was taken as 100.46±0.20 pMC based on direct atmospheric ¹⁴C observations from Hungary (Major et al, 2018). Thus, the dead carbon percentage (dcp) of the recent freshwater tufa at Szalajka Valley is 7.9±1.3%, at Dobrica well 11.1±2.3% and at Sebesvíz 14.2±2.5% in their total carbon content.

The presented dcp (%) (normal) values in Table 2. correspond to the original definition of dcp by Genty et al. (1998), where the actual atmospheric ¹⁴C level at the time of sampling is applied in the dcp calculation. But after the ¹⁴C bomb peak, the atmospheric ¹⁴C content decreases relatively fast from around 200 pMC (top value) to close

to the natural 100 pMC level (before bomb-peak actual level). This fast atmospheric ¹⁴C level change (decrease) disturbs the use of dcp concept by Genty et al. (1998) as it means about 0.44 pMC drop per year as it is presented by the linear fit on the atmospheric ¹⁴C level of the last decade Figure 10. It means along the bomb-peak period atmospheric ¹⁴C was rather different (higher) at the time of water infiltration than a few years later, when water flows out from the spring and samples are collected/deposited.

It would be expressed as “negative” dcp fraction, without any physical meaning, just as an artefact result because the above effect from the bomb-spike. Thus the

Table 2 Summary table of ¹⁴C and dcp data of recens tufas

Location	Date	¹⁴ C (pMC)	¹⁴ C (age BP)	dcp (%) (normal)	dcp (%) (bomb corrected)
Dobrica spring, DOB-2	01.02.2019.	87.28 ± 0.22	1093± 20	13.1	15.8
Dobrica spring, DOB-2	01.06.2019	91.79 ± 0.33	688 ± 26	8.6	11.4
Dobrica spring, DOB-2	28.08.2020	89.01 ± 0.16	935 ± 14	11.4	14.1
		89.36 ± 2.28		11.1 ± 2.3	13.8 ± 2.2
Atmospheric CO ₂ ¹⁴ C pMC (2011-2013) (NH Zone-1)					103.65 ± 0.48
Szalajka Valley, SZAL-2	01.02.2019.	83.60 ± 0.21	1439 ± 21	16.8	18.9
Szalajka Valley, SZAL-2	01.06.2019	88.52 ± 0.33	980 ± 27	11.9	14.1
Szalajka Valley, SZAL-2	28.08.2020	86.50 ± 0.29	1165 ± 27	13.9	16.1
		86.20 ± 2.47		14.2 ± 2.5	16.4 ± 2.4
Atmospheric CO ₂ ¹⁴ C pMC (2012-2013) (NH Zone-1)					103.07 ± 0.26
Sebesvíz, SEB-2	2019.02.01	92.58 ± 0.22	619 ± 19	7.8	9.6
Sebesvíz, SEB-2	2019.06.01	93.69 ± 0.32	524 ± 26	6.7	8.5
Sebesvíz, SEB-2	2020.05.08	92.83±0.29	598 ± 25	7.6	9.3
Sebesvíz, SEB-2	2020.08.28	91.05 ± 0.15	753 ± 14	9.4	11.1
		92.54 ± 1.10		7.9 ± 1.3	9.6 ± 1.3
Atmospheric CO ₂ ¹⁴ C pMC (2014-2016) (NH Zone-1)					102.38 ±0 .28

bomb-effect could cause significant underestimation of the real dcp if it is derived from ^{14}C analyses of modern carbonate deposits (after the bomb-peak). To avoid the bomb-effect consequences during dcp estimation and have a better, more realistic dcp analyses, we have to compensate the atmospheric ^{14}C drop between the water infiltration date and the deposition time of recent carbonates. Atmospheric ^{14}C level record from Hua et al (2021) are presented in Figure 10 and water infiltration time period is indicated by the arrows on the figure. The estimated infiltration periods were calculated according the water sample ^3H analyses in Section 4.3. for dcp calculation. We have applied the atmospheric CO_2 ^{14}C pMC (NH-Zone1) record, corresponding to the time of infiltration, instead of the sampling years.

The bomb-effect corrected dcp values are presented in the last columns in Table 2. The difference between the conventional (Genty et al., 1998) and the bomb-effect corrected dcp values are between 1.7–2.7% in the investigated three karst spring system. Thus, the inactive carbon content (dcp) of the recent freshwater tufa at Szalajka Valley is $9.6 \pm 1.3\%$, at Dobrica well $13.8 \pm 2.2\%$ and at Sebesviz $16.4 \pm 2.4\%$, when a detailed bomb-effect

correction is applied as described above. This bomb-corrected dcp are useful for conventional ^{14}C age corrections to help better calendar age estimation of older carbonate deposits.

For the samples taken in the Szalajka Valley (SZAL-a, b) (Supplementary Fig. 1), we can see that the tufa samples are just a few years or decades old (2012–2019, 2005–2019, 1997–2019) (Table 3) (Supplementary Fig. 1).

The tufa samples were taken in the middle (DOB-d) and the upper (DOB-b) section of the fossil peripheral carbonate and the furthest fossil tufa outcrops from source (DOB-c) (Supplementary Fig. 3). The field observations at Dobrica spring suggest that the freshwater tufa precipitation was once much more intense, based on the fossil peripheral carbonate surrounding the recently active freshwater tufa deposition (DOB-b, d) and the carbonate outcrops further away from the source (DOB-c).

At the active freshwater tufa precipitation, the youngest age (1996–2019) was obtained in the small cavity (DOB-a) inside the waterfall, where leaking water forms small stalactites (Supplementary Fig. 3/A/1). We also measured ages in the upper section of the inactive

Table 3 Summary table of dcp data and calculated ages of fossil tufas (negative ages means after 1950 AD, after the bomb peak as the result of the Libby (1955)'s equations of conventional ^{14}C age without physical meaning as age).

Code	Location	Material	dcp bomb corrected ^{14}C pMC (1s)	dcp bomb corrected ^{14}C age (yr BP) (1s)	Calibrated age (1s)
DeA-19272	SZAL -a/1	carbonate	100.65±2.81	-52±235	2012–2019
DeA-19273	SZAL -a/2	carbonate	102.05±2.85	-163±235	2005–2019
DeA-19274	SZAL -b	carbonate	104.50±2.92	-350±235	1997–2019
DeA-19230	SEB -a/1	embedded plant remains	107.98±0.28	-617±21	AD 2001–2003
DeA-19275	SEB -a/2	carbonate	104.26±1.48	-335±119	2007–2014
DeA-19276	SEB -a/3	carbonate	103.71±1.47	-292±119	2008–2016
DeA-19277	SEB -b	carbonate	73.38±1.04	2487±120	BC 774–480
DeA-19278	SEB -c/2	carbonate	92.54±1.31	622±120	AD 1279–1421
DeA-19279	SEB -c/1	carbonate	83.39±1.18	1459±120	AD 434–670
DeA-19280	SEB -d/1	carbonate	101.14±1.43	-91±119	2012–2019
DeA-19281	SEB -d/2	carbonate	103.71±1.47	-293±119	2008–2016
DeA-19282	SEB -e	carbonate	39.70±0.56	7422±123	BC 6421–6096
DeA-19266	DOB-a	carbonate	105.01±2.61	-392±209	1996–2019
DeA-19267	DOB-b/1	carbonate	89.50±2.23	891±209	AD 898–1299
DeA-19268	DOB-b/2	carbonate	87.86±2.19	1040±209	AD 775–1211
DeA-19269	DOB-b/3	carbonate	88.02±2.19	1025±209	AD 775–1218
DeA-19270	DOB-c	carbonate	88.65±2.21	968±209	AD 888–1266
DeA-29733	DOB-d/1	embedded plant remains	75.41±0.38	2267±41	BC 393–230
DeA-19271	DOB-d/2	carbonate	81.60±2.03	1634±209	AD 225–641

part (DOB-b), located downstream, left side in the cross-section near the recent active barrage. The sample (DOB-b) contained layers which are visible, so a horizontal age analysis was attempted in the inner (DOB-b/1), middle (DOB-b/2) and outer (DOB-b/3) parts of the sample, spaced 4–6 cm apart horizontally (Supplementary Fig. 3/A/2). The measured ages were as follows; in the inner part (DOB-b/1) AD 898–1299, in the middle part (DOB-b/2) AD 775–1211 and in the outer part (DOB-b/3) AD 775–1218 (Table 3). Due to the very similar ages, which are within error of each other, it is difficult to make a horizontal growth rate estimate, but it can be concluded that the successive layers were probably formed very rapidly (within 300–500 y).

Moving downstream, another fossil tufa sample was taken on the left side of the fossil tufa outcrops (DOB-d) a few 10 m from the sampling point DOB-b (Supplementary Fig. 3/A/1). In this case, the age of the organic material found in the tufa sample was calibrated to BC 393–230, and the age of the surrounding carbonate as AD 225–641. At the farthest sampling point downstream, there is a separate fossil tufa block (DOB-c). The age of this sample, AD 888–1266, is similar to the sample taken in the upper section of the fossil tufa mound (DOB-b) (Table 3). This point is located at the junction of the Dobrica spring and the Gyertyán Valley. These two fossil freshwater carbonate deposits (DOB-b, DOB-c) according to their age, accumulated approximately at the same time within a few decades of each other. At the Dobrica spring, the oldest age was measured in the tufa sample taken in the middle section of the older, peripheral tufa mound (DOB-d), suggesting that strong, concentrated precipitation took place here in the past as well, due to the local geomorphological conditions. The earlier tufa deposit is eroded over the time and the Dobrica Spring cuts itself into the fossil tufa deposit and still forms new tufa there (DOB-a) (Supplementary Fig. 3/A).

Similar observations were made at Sebesvíz as at the Dobrica spring, with inactive freshwater tufa outcrops present alongside still active deposits.

Tufa samples were taken at the highest amount of recently active freshwater tufa deposits (Supplementary Fig. 2). Three measurements were carried out in this tufa sample, one of which was organic material. The age of the organic material (SEB-a/1) was dated AD 2001–2003, the age of its surrounding carbonate (SEB-a/2) was dated AD 2007–2014, while the age of the outer surface of the sample (SEB-a/3) was dated AD 2008–2016 (Table 3) (see Supplementary Fig./2), consistent with the assumed (inside-out) mode of formation of the sample. On the left side of this outcrop (SEB-b), a few metres away, in an apparently inactive section, we obtained age of BC 774–480 years, while on the right side, a few 10 m away, inactive outcrops are much older, BC 6421–6096 years (Table 3) (see Supplementary Fig. 2/A). Thus, the oldest age was measured here.

We also sampled farther downstream with a few hundred meters and about 1 m wide fossil freshwater tufa block (SEB-c) (Supplementary Fig. 3/B/1). Two age determinations were done on the sample (inner and upper side) (Supplementary Fig. 3/B/2). The age determined in

the inner part of the sample (SEB-c/1) was AD 434–670, while the outer part (SEB-c/2) was AD 1279–1421 (Table 3). This block is located in the immediate vicinity of the watercourse but is inactive nowadays. Since there is no such large-scale outcrop near it, it is possible that it was detached from an upper part and drifted here or that there was a core around which carbonate was deposited in the past. A sampling point (SEB-d) located in the waterbed about 50 m downstream of the active outcrop (SEB-a) (Supplementary Fig. 3/C) also confirms a recent age (2012–2019 and 2008–2016), which is consistent with this being a currently active area.

DISCUSSION

Carbon isotope in water and freshwater tufa

Among the three studied system, Szalajka spring water exhibits the highest proportion of dissolved dead carbonate, as its ^{14}C specific concentration (average: 86.1 ± 2.0 pMC) deviates the most from the atmospheric ^{14}C specific concentration (~ 100 pMC). For the same reason the $\delta^{13}\text{C}$ value of its dissolved inorganic carbon ($-12.8 \pm 1.1\text{‰}$, V-PDB) is the most positive relative to the other 2 springs. As a result of more dissolved dead carbonate Szalajka water has the closest to the $\delta^{13}\text{C}$ value of the atmospheric CO_2 (-8‰) (www.gml.noaa.gov). In contrast, the dissolved inorganic carbon found in the Dobrica spring and Sebesvíz predominantly consist of modern carbon, indicating a higher proportion of biogenic carbon originating from the soil, and a lesser contribution from old limestone origin. However, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the studied Hungarian tufa fits well to stable isotope composition of tufas from the neighbouring countries (Andrews, 2006) and represent intermediate values between Western and Eastern Europe, reflecting increasing continentality in climate from west to east.

When we investigate the carbon isotope signal change along the water flow from the springs to the barrages, a noticeable shift in the $\delta^{13}\text{C}$ value of dissolved inorganic carbon (DIC) is observed in two cases of the studied systems. At Sebesvíz, the $\delta^{13}\text{C}$ shift is $1.8 \pm 0.7\text{‰}$ (V-PDB), while at Dobrica spring, it is $2.2 \pm 1.4\text{‰}$ (V-PDB) along the water flow (Fig. 9). This unambiguous positive $\delta^{13}\text{C}$ shift can be interpreted as a result of isotope fractionation due to the continuous outgassing of its dissolve inorganic carbon into the air as isotope exchange is less likely, due to the fact no significant ^{14}C intake was detected during the flow.

In comparison, the $\delta^{13}\text{C}$ isotopic shift between the Szalajka spring and Fátyol Waterfall pair is the smallest among the three studied systems ($1.2 \pm 1.5\text{‰}$). It is in good agreement with the fact that we measured the smallest decrease in HCO_3 content along the Szalajka flow.

In each of the investigate sites, $\delta^{13}\text{C}$ stable isotope ratio of the tufa carbonate is slightly more positive compared to the DIC of the parent water (Fig. 9). It is likely due to the isotopic fractionation in the deposition processes while the heavier isotope is slightly more preferred. Carbon isotope exchange can also occur

between the air and the precipitate, and it might also generate some positive stable isotope ratio shift in the carbonate precipitate as atmospheric origin CO₂ has a more positive δ¹³C (-8 ‰, V-PDB).

Tufa ages

The recent carbonate deposits at our sites demonstrate higher values than the average dcp values found in stalactites measured in Baradla Cave (5.1±1.5%) (Aggtelek Karst, Hungary) (Molnár et al., 2006a), in the Ajándék cave (0–5%) (Pilis Mts., Hungary; Tombor, 2017) and in Béke Cave (5.0±0.3%) in the Hungarian Aggtelek Karst (Demény et al., 2019). On the other hand, dcp values of the studied three sites fit well to those of modern stalagmites from SW France (9±1.5%) (Genty and Massault, 1999), from Belgium (12.2±1.5%; Genty et al., 1998) and from Slovenia (11.6±1.5%) as described by Genty et al. (1999). To understand the reasons of resemblance with dcp values of modern stalagmites outside of Hungary further investigations are needed.

In the Szalajka Valley, the tufa samples (SZAL-a, b) (Supplementary Fig. 1) show relatively young ages, they are only a few years/decades old (Table 3). The possible reason for the measured young ages could be that the barrage structure at the Fátyol Waterfall is very porous, water still flows through it today, which could affect the parts in the lower layers, thus fresh carbon could be incorporated there. It means, within this porous system, there is potential for carbonate rejuvenation by fresh carbon and ¹⁴C intake. Thus, there is a chance that the system has not become fully closed and ¹⁴C value of the deposit has not been completely preserved due to the influence of water flowing through it.

The field observations at Sebesvíz and Dobrica spring indicate that the freshwater tufa precipitation was more intense in the past, based on the large area of the fossil peripheral carbonate surrounding next to the recently active, but less extent freshwater tufa deposition (SEB-e, b; DOB-b, d). The more intense carbonate precipitation areas are connected to rather steep slopes at our study sites (SEB-a; DOB-c).

CONCLUSION

The aim of our study was to analyse the carbon isotope dynamics of freshwater tufa between the spring and the first significant tufa depositions and to determine the age of older tufas in three karstic streams (Szalajka Valley, Sebesvíz, Dobrica spring) in the Bükk Mts.

The ³H content shows that all the water samples are relatively young, with relatively short (<10 y) residence time. According to the water ³H analyses estimated infiltration periods have been calculated.

Szalajka Spring water shows the highest proportion of dissolved dead carbonate, as its ¹⁴C specific concentration (average: 86.1±2.0 pMC) deviates the most from the atmospheric ¹⁴C specific concentration (~100 pMC). The Szalajka spring water has an average δ¹³C value (-12.8 ±1.1‰ V-PDB) closest to the δ¹³C of air (-8‰) and consistent with the fact that it has the highest proportion of the past dead carbonate content suggesting

that the carbons of Dobrica Spring and Sebesvíz have modern carbon.

At Sebesvíz and Dobrica Spring, the δ¹³C shift of waters was higher relative to Szalajka Valley along the water flow. This positive δ¹³C shift can be interpreted as a result of isotope fractionation by the continuous outgassing of dissolved inorganic carbon into the air as isotope exchange is less likely, due to the fact that no significant ¹⁴C intake was detected.

For all three studied sites, the δ¹³C of tufa is more positive at the barrages than in its parent water likely due to isotopic fractionation processes or carbon isotope exchange can also occur between the air and the precipitate.

The lowest amount of inactive carbon content (dcp) of the recent freshwater tufas was measured at Szalajka Valley (9.9±1.3%), the highest at Sebesvíz (16.4±2.5%) and at Dobrica spring the dcp was 13.8±2.2%. These dcp values were higher to the average dcp value of the measured stalactites from Hungary, although fits well to the dcp values of the modern stalagmites of Europe (Genty et al., 1999). The bomb-corrected conventional ¹⁴C ages provide better estimation older carbonate deposits.

The age of tufa samples in the Szalajka Valley is just a few hundred years old (AD 1442–1957) probably influenced by water still flowing through the porous structure of the deposit. At the Sebesvíz and Dobrica spring, the youngest ages (AD 2009–2019) were dated in the recent active area or near the watercourses. At both sites, the age of the studied organic matter and its surrounding carbonate are in good correlation. The oldest age (BC 6467–6252) was measured at Sebesvíz of all three studied sites, at the fossil tufa outcrop (in cross-section) is the farthest here from the barrage.

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