

ANALYSIS OF DRIP WATER IN AN URBAN KARST CAVE BENEATH THE HUNGARIAN CAPITAL (BUDAPEST)

ANALIZA PRENIKLE VODE V URBANI KRAŠKI JAMI POD MADŽARSKO PRESTOLNICO (BUDIMPEŠTA)

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Abstract

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Katalin Fehér, József Kovács, László Márkus, Edit Borbás, Péter Tanos & István Gábor Hatvani: Analysis of drip water in an urban karst cave beneath the Hungarian capital (Budapest)

Our geological heritage is increasingly threatened by anthropogenic activity. This is especially true of the Pál-völgyi Cave System beneath Budapest. It is among the 150 longest and at the same time most endangered cave systems in the world. The aims of the study were (i) to set up a monitoring system in the cave, (ii) to track the daily changes in the quality and quantity of drip water, and (iii) to determine the exposure of the cave. Monitoring was conducted at two locations in a shallow area next to a fracture zone (site name: TG) and one lying in a tectonically less disturbed, geologically more homogeneous location 20 m deeper (site YC). The data obtained in respect of 13 variables were assessed using descriptive statistics, principal component- and periodicity analyses. At first glance, it was apparent that the eight water quality parameters differed in quantity between the two sites. Furthermore, using principal component analysis it was shown that in the fractured-shallow setting, anthropogenic activity (external urban pollution, e.g. de-icing, decrease of land cover etc.) is the driving process determining water quality. At the tectonically less fractured site (YC) external influences originating above ground may be

Izvleček

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Katalin Fehér, József Kovács, László Márkus, Edit Borbás, Péter Tanos & István Gábor Hatvani: Analiza prenikle vode v urbani kraški jami pod madžarsko prestolnico (Budimpešta)

Naša geološka dediščina je vse bolj ogrožena zaradi človekovih dejavnosti. To še posebej velja za jamski sistem Pál-völgyi pod Budimpešto. Sodi med 150 najdaljših in hkrati najbolj ogroženih jamskih sistemov na svetu. Cilji raziskave so bili (i) vzpostaviti sistem spremljanja izbranih parametrov v jami, (ii) spremljati dnevne spremembe kakovosti in količine prenikle vode, in (iii) določiti izpostavljenost jame onesaženju. Raziskava je bila izvedena na dveh lokacijah v plitvem območju blizu razpoklinske cone (ime vzorčnega mesta: TG) in na tektonsko manj pretrti in geološko bolj homogeni lokaciji 20 m globlje (ime vzorčnega mesta: YC). Pridobljeni podatki 13 spremenljivk so bili obdelani s pomočjo opisne statistike, analize glavnih komponent in periodičnostno analizo. Na prvi pogled je bilo očitno, da se je osem parametrov kakovosti vode kvantitativno razlikovalo med obema mestoma. Poleg tega se je s pomočjo analize glavnih komponent pokazalo, da je mesto v plitvem pretrtem območju pod velikim vplivom antropogenih aktivnosti (urbano onesnaženje, npr. sredstva proti zmrzovanju, zmanjšanje pokrovnih plasti, itd.), ki vplivajo na kakovost vode. Na tektonsko manj preoblikovanem mestu (YC) se zunanji vplivis površja mešajo z naravnimi kraškimi procesi.

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added to the natural karst-forming processes. The assessment of drip intensity and electric conductivity again highlighted the differences between the sites in terms of their reaction to precipitation. With regard to diurnal periodicity, although pH and Eh indicated a mature periodic behavior at both sites (covering 56–65 % of the total observed time), at site TG electric conductivity displayed diurnal periodicity over only 21 % of the total time, compared to 56 % at YC. All results pointed towards a conclusion that at site YC daily periodicity and water quality are much more connected to natural processes, while at site TG anthropogenic external influences suppress these.

Key words: cave drip water, hydrochemistry, karst, Pál-völgyi Cave System, time series analysis, urban pollution.

Ocena intenzivnosti kapljanja in električne prevodnosti je ponovno izpostavila razlike med vzorčnimi mesti v smislu njegovega odziva na padavine. V zvezi z dnevno periodičnostjo je vzorčno mesto TG kazalo dnevno periodičnost več kot 21 % celotnega časa, mesto YC 56 %, čeprav sta pH in Eh izkazali zrelo periodično obnašanje (56–65 % celotnega opazovanega časa) na obeh mestih. Vsi rezultati kažejo na sklep, da je na mestu YC dnevna periodičnost in kakovost vode veliko bolj povezana z naravnimi procesi, medtem ko jih na mestu TG antropogeni zunanji vplivi zadušijo.

Ključne besede: jamska prenikla voda, hidrokemija, kras, jamski sistem Pál-völgyi, analiza časovne vrste, urbano onesnaževanje.

INTRODUCTION

In the last 150 years, due to extensive urbanization and the appearance of vast metropolises, the landscape of their setting has changed drastically. With construction and mining activity, even the original relief conditions have been altered, and the indigenous flora has completely disappeared. Budapest, the capital of Hungary, has been no exception: land-use and the nature of the surface cover has changed from natural to e.g. garden-suburbs or blocks of flats, and together with this building a wide variety of services such as the laying of pavements and the construction of roads has been provided (Mari & Fehér 1999). Trends such as these on the surface should alert scientists to the need for an investigation of sub-surface water systems, since, as a direct result the amount of contaminants seeping into the ground has increased, eventually reaching the karst- and thermal waters and causing the deterioration of their water quality (Veni 1999).

With urbanization and its effects, geological riches (e.g. karst systems) are ever more under threat (Bolner *et al.* 1989; Brocx & Semeniuk 2007). This is especially true of those metropolises that are located upon remarkable geological sites. The Pál-völgyi Cave System, unique in the world, lies on the right bank of the Danube under Budapest. The cave system is 30.1 km length (Hungarian Cave Database 2016), the longest in Hungary and among the 150 longest in the world (Gulden 2016). More importantly, it is the recharge zone for the world heritage-designated thermal springs of Budapest. The problems discussed below are particularly important in a karst environment, especially in an urban environment such as the Pál-völgyi Cave system, the subject of the research (Fig. 1A, 1B).

If the cover soil is intact above the karst, it is able to filter pollutants arriving with the infiltrating waters. If, however, this upper surface is damaged by e.g. silviculture, construction, mining or agricultural activity,

these waters may reach the lower layers without facing any obstacles (Bolner 1995), guided mainly by the complex karst fracture system (Williams 2008). These waters will eventually manifest their anthropogenic origin in the sub-surface environment in drip water (Kern *et al.* 2009; Baldini *et al.* 2012; Hartland *et al.* 2012), or in speleothems (Kogovšek 2011; Siklósy *et al.* 2011; Baker & Fairchild 2012) in karst caves (Fairchild & Baker 2012). These characteristics typical of anthropogenic activity can be traced mainly in the elevated concentrations of ions (e.g. Na^+ , SO_4^{2-} , Cl^- , NO_3^-) present in the water and high electric conductivity values (Hem 1985) as “contaminants” with respect to the natural karst environment. The electric conductivity of drip water is one of the best indicators of pollution occasioned by anthropogenic activity in the hydrological system of such caves. Its analysis in terms of intensity and chemical composition already has a long history (e.g. Genty & Deflandre 1998; Baker & Brunsdon 2003). In an undisturbed setting, conductivity values should change together with bicarbonate concentrations. However, when the system is disturbed¹, e.g. by ions originating from sewage waters (Kogovšek 2011), conductivity does not change accordingly. If a whole cave is located in a geologically similar setting and large differences are observed in the drip water’s conductivity at different monitoring sites, it may be reasonably suspected that this is a result of external pollution and different sources of drip water. Generally, the least likely explanation is that these phenomena result from the geological setting.

Following the natural processes and tracking the changes induced by the previously discussed phenomena is quite straightforward. Local monitoring stations

¹ A system is disturbed when its natural regime is changed by anthropogenic influences.

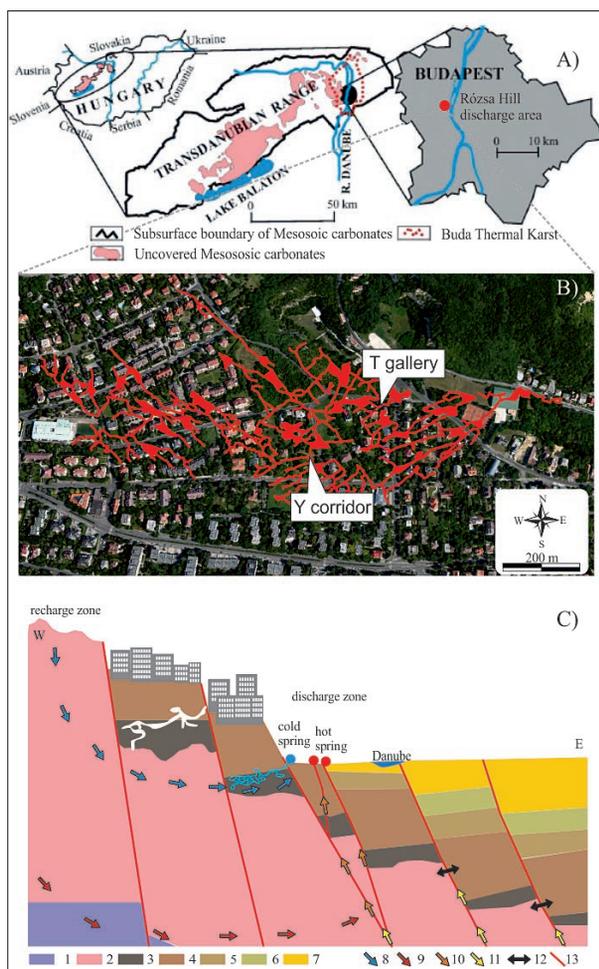


Fig. 1: Location of the Buda thermal karst and the study area in the Rózsa Hill in Budapest, Hungary A), the two sampling sites marked within the Pál-völgyi Cave System (red lines) B) and the conceptual model of the Rózsa Hill discharge area C), where 1: Permian-Lower Triassic evaporitic-carbonate strata; 2: Triassic carbonates; 3: 119 Szépvölgy limestone; 4: Buda marl; 5: Tard clay; 6: Kiscell clay; 7: Miocene formations; 8: local/intermediate flow systems; 9: regional flow systems; 10: regional karst + basinal fluids; 11: basinal fluids; 12: complex water-rock interaction; 13: structural elements (based on Eröss *et al.* 2012).

(See section 2.2) need to be set up to analyze the drip water (Kogovšek 2011; Baldini *et al.* 2012; Hartland *et al.* 2012; Kogovšek & Petric 2013; Liu & Brancelj 2014). In the area, systematic measurements of drip water quality have been carried out since the mid-1980s (Bolner *et al.* 1989; Mádl-Szőnyi *et al.* 2007; Fehér 2009). The results of these analyses indicate a continuous increase in the concentrations of various polluting components, again providing motivation for further, deeper inspection.

In the light of the preceding considerations the authors felt compelled to formulate the following goals: (i) the setting up of a monitoring system in the Pál-völgyi Cave System – subjacent to anthropogenic activity on the surface, (ii) the tracking of daily changes in the quality and quantity of drip water, and (iii) the determination of the cave's exposure, with the aim of providing an example for the further examination of other caves in such settings.

MATERIALS AND METHODS

SITE DESCRIPTION

The study area, The Buda thermal karst –and as a part of it the Pál-völgyi Cave System – was chosen to illustrate the exposure of caves to urban anthropogenic activity. It is one of Europe's largest functioning thermal karst systems, and a part of the main karst water reservoir of the Transdanubian Central Range (Fig. 1A). The Mesozoic carbonate sequence in certain parts of the range can reach a thickness of a couple kilometers, ensuring petrological continuity, and thus providing the hydrodynamic connection between the thermal karst and the other sub-areas (Mádl-Szőnyi & Tóth 2015). One of the regional discharge areas of the range's aquifers is the Buda thermal karst, and as part of this, the Rózsa Hill itself (Fig. 1A), the location of the study site. This is a hypogene karst system on the border of an emerged carbonate block and a sedimentary basin (Eröss 2010; Eröss *et al.* 2012; Mádl-

Szőnyi & Eröss 2013; Fig. 1C). The Buda thermal karst has developed in a regional discharge area of the aquifer system of the Transdanubian Range. However, the range of hills of which the Rózsa Hill area is a part serves as local recharge area, and this is where the Pál-völgyi cave is found.

On the Rózsa Hill, because of periglacial processes, the eroded rocks produce a vast amount of clastic rock. However, as a result of downhill creeping, the sedimented loess mixed with clastic rock, giving a diverse (fine/ coarse) cover on the karst strata. Thus, it can be concluded that the friable carbonate bedrock and the previously mentioned cover *in certain settings* functions as an epikarst and moderates infiltration/pollution (Virág *et al.* 2011). These Rózsa Hill coarse strata, only partially function as aquiclude layers, as supposed earlier by Mádl-Szőnyi *et al.* (2007). In the present case,

beneath the coarse strata a Buda Marl formation can be found (estimated macroporosity: 1.5 %; Kleb *et al.* 1993). Its hydrological characteristics are determined by faults (Gáspár *et al.* 2015) and beneath the marl a Szépvölgyi Limestone Formation (matrix porosity: 5–10 %; Albert 2010) can be found.

The Pál-völgyi Cave is located mainly in the previously mentioned limestone, but extends into the marl as well. Its system of passages follows the 25–30° dip of the limestone and marl. The thickness of the marl above the cave is 20–70 m in general (Gáspár *et al.* 2015) and 40–60 m above the sampling sites.

As discussed above, the land use – as is true of Budapest in general – has changed on the Rózsa Hill as well. In the 18th Century, approx. 40 % of its area was covered by forests and bushes; by the mid-1980s this had decreased to 8 %. In the meanwhile, the proportion of built-up area increased from 2 % to 85 %, reaching 90 % by the turn of the 21st Century (Mari and Fehér 1999; Fig. 1B).

Thus, caves beneath such areas function as unique natural laboratories to gather further information about the current hydrological characteristics (water retention/conductance) of the coarse cover strata.

SAMPLING SITES AND MEASUREMENTS

One possible way of determining the threat of pollution in the Rózsa Hill area is the chemical analysis of drip water. The physico-chemical composition of drip water in a sense functions as tracer, reflecting the characteristics of infiltrating waters of natural and/or anthropogenic origin, e.g. sewage waters coming from damaged drain pipes or other washed-down pollutants. The cave galleries are located halfway between the surface and the karst water table (average depth 50 m). This setting provides ideal conditions for the detection of possible pollution from the surface before it reaches the water table.

Two monitoring sites were chosen for the study. One is located in the Térképész Gallery (TG) 40 m beneath the surface, next to the tectonically fractured zone of Szép Valley, while the other is the Y Corridor (YC), 60 m deep, lying beneath a declivous pediment in a geologically more homogeneous location than TG (Fig. 1B; cross section: Fig. A1).

Based on research experience gained in the course of previous monitoring campaigns in the cave, a decision was made to commence the systematic measurement of a much wider set of parameters instead of the previous occasional sampling (Bolner *et al.* 1989; Fehér 2009). In this way, it should be possible to separate natural geochemical processes from the anthropogenic ones. Thus, the following monitoring strategy was developed.

The measurements can be categorized into two groups: (i) continuous high frequency (hourly) and (ii)

bi-weekly. In the first, pH, Eh (mV) and electric conductivity (EC; $\mu\text{S cm}^{-1}$) were measured, while in the course of the bi-weekly measurements water quality (Na^+ ; K^+ ; Ca^{2+} ; Mg^{2+} ; Cl^- ; HCO_3^- ; NO_3^- ; SO_4^{2-} (mg l^{-1}) and drip intensity (ml h^{-1}) measurements were performed on samples taken from the two sites. The hourly-measured data were retrieved during the collection of the bi-weekly samples. This was carried out for both sites from 15.07.2013 to 13.04.2014.

An ODEON Range data collector (Fig. A2) and the sampling instrument were set up so the drip water in the cave would fall into its funnel and, passing along a plastic tube, reach the bottom of the sampling cell. When the cell is full the water goes into the sampling bottle (Fig. A2). This way water circulation and the constant water coverage of the electrodes is ensured.

In addition to the collected data, the daily sum precipitation data (mm) of the Ferenchegy meteorological station (N47°31'01.22"; E19°00'56.06"; ELEV: 230 meters above Baltic Sea level; NLCO 1975), were acquired from the Hungarian Meteorological Service for the time interval 15.07.2013 to 13.04.2014. It should be noted that snow – only 1 cm – fell on only one day (01.02.2014), so the delay effect due to snow melt (i.e. a change in aggregate conditions) could be disregarded.

METHODS USED

The different sampling frequencies of the measured parameters clearly determined the set of methods that could be employed to assess their time series. On the one hand, in the case of the bi-weekly water quality samples it was sufficient to use principal component analysis (PCA) to find the driving processes of drip water quality (for details see the following section). On the other hand, the high frequency (hourly) time series complied with the requirements of the analysis of periodic/spectral components to investigate the different sites' exposure to anthropogenic effects.

PRINCIPAL COMPONENT ANALYSIS

Although the water quality indicators correspond to temporally changing processes, the less frequent bi-weekly measurements do not show any detectable temporal structure: the consecutive samples can be considered as being independent of each other; thus, the conditions for the application of PCA are satisfied (Hatvani *et al.* 2015; Kovács *et al.* 2015). The choice of PCA over factor analysis is explained by the fact that the latter decomposes the covariance structure, while PCA breaks the full variance down into principal components without loss of information (Abdi & Williams 2010). Since the amount of contaminants and other water quality indicators is highly relevant, it would be meaningless to scale them to unit

variance. Hence a covariance matrix is preferred in PCA over the correlation matrix. It should be noted that PCA does not automatically decide how many principal components should be considered satisfactory in the aim of representing variability (Kaiser 1960).

PERIODICITY ANALYSIS

The high frequency (hourly) sampling provided an opportunity for periodicity analysis. A multitude of methods is suitable for the determination of a periodic or spectral component of a time series. Stationary time series can be relatively easily analyzed using a standard Fourier transformation; this method is, however, incapable of telling us when those frequencies occurred. The simple Fourier analysis presupposes the permanent presence of oscillating components with constant amplitude. However, in a propagating process the amplitude of a spectral component is not necessarily invariable over time. This fact calls for time-frequency analysis of the power spectra, in order to study the temporally localized behavior of a time series in the frequency domain. Some of the most frequently used procedures are the Short Term Fourier Transform (STFT), in which the traditional Fourier Transform is multiplied by a fix-sized sliding window, or multi-resolution analysis or wavelet analysis, which may also be regarded as the enhancement of the STFT (Gröchenig 2001).

As discussed by Kaiser (1994), the STFT, as with other windowed Fourier transformation techniques, represents an inaccurate and inefficient method of time-frequency localization, as it imposes a window length or “response interval” on the analysis. For analyses where a predetermined scaling may not be appropriate, because of a wide range of dominant frequencies, a method of time-frequency localization that is scale-independent, such as wavelet analysis, should be employed. Wavelet transformation was established in order to further the quest for balance in time and frequency resolution (Torrence & Compo 1998). The wavelet approach is localized in time and scale (frequency), resulting in a time-scale (time-frequency) decomposition of the signal using scaled localized oscillating functions, the wavelets. By fragmenting the data into short dampening “wavelets” instead of infinitely oscillating long sine waves, the wavelet transform can be used to analyze time series that contain nonstationary power at different frequencies (Daubechies 1990).

In the first attempt, the applied STFT signaled clearly that the presence of the diurnal component is not permanent (for details, please see Appendix 3). In order to refine the results and utilize significance levels

for the more exact detection of the periodic components, wavelet spectrum analysis (WSA) was used. One of the frequently used basic wavelets also employed in the computations is the Morlet wavelet (Morlet *et al.* 1982), obtained by localizing a complex sine wave with a Gaussian envelope (Fig. 2). The wavelet transformation $W_n(s)$

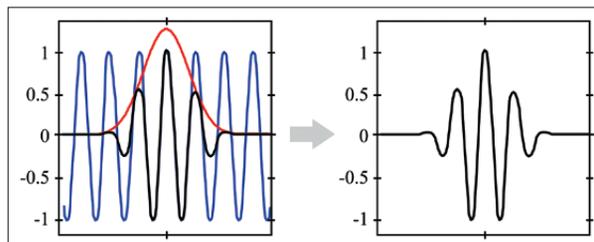


Fig. 2: Graph of the Morlet wavelet.

may be defined as the convolution of the data and the wavelet function (1):

$$W_n(s) = \sum_{n'=0}^n X_{n'} \Psi^* \left[\frac{(n'-n)\delta t}{s} \right] \quad (\text{Eq. 1})$$

in which the asterisk (*) represents the complex conjugate, ‘ X_n ’ the original data stream, ‘ s ’ the scale, ‘ ψ ’ the basic (mother) wavelet function and ‘ δ ’ the degree of the resolution. “The mother wavelet provides a source function to generate daughter wavelets, by scaling and translating it. This way it creates a self-similar structure, and as a result the data’s periodic component over time can be examined” (Kovács *et al.* 2010). This enables the computation of the proportion of the presence/detectability of the daily periodic component in the observation days. Note here that the output graphs of WSA have edge artifacts, since the wavelet is not completely localized in time. Therefore, as is the general practice in wavelet analysis (Torrence & Compo 1998) a cone of influence (COI; i.e. the region where edge effects cannot be ignored meaning that wavelet power estimation is reliable) is introduced.

Before applying wavelet spectrum analysis, it was necessary to get rid of any trend contamination by removing it using a locally estimated scatterplot smoothing (LOESS) (Cleveland 1979; Cleveland & Devlin 1988). This removed the large, long-term fluctuations, while preserving the daily oscillations.

All mathematical and statistical computations were performed using R 3.2.3 (R Core Team 2013), IBM SPSS 20 and the saturation indices were calculated using Phreqc for Windows. For the visualizations of the results, CorelDRAW Graphics Suite X7 and MS Office 2013 were used.

RESULTS

WATER QUALITY ANALYSIS ON THE DATA
BETWEEN JULY 2013 AND APRIL 2014

Overview on groundwater chemistry

As a first step, clear differences were brought out regarding their hydrogeochemical characteristics by plotting the main ion composition of the drip-water at the two sites on Piper diagrams (Piper 1944). It turned out that the samples of drip water taken at site TG belong to the Na-Ca and Cl-SO₄ facies (Fig. 3A), while those from site YC belong to the Ca-Na and Cl-SO₄-HCO₃ facies (Fig. 3B) according to the nomenclature of Back (1966).

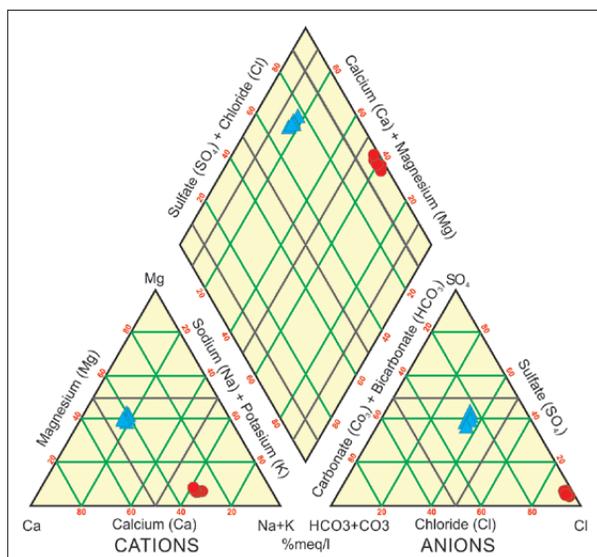


Fig. 3: Facies categorization of the drip water at sites TG red dots and YC blue triangles.

In other words, at site TG Na and Cl, while at site YC Ca and Mg, and SO₄ and HCO₃ are dominant. Therefore, in the case of site YC the concentration of ions resembles that of a karst system better. The most explicit difference between the sites is that the concentration of most of the anions and cations was higher at TG (Tab. 1A) than at YC (Tab. 1B) even if considered in mmol l⁻¹ (Tab. 1), e.g. the chloride and sodium content was more than one magnitude higher at TG (Fig. A4).

If the saturation indices are calculated, the difference between the two sites is again explicit. Site TG is close to the equilibrium state regarding calcite with slight over-saturation (SI_{cc}: 0.05–0.08). At YC, however, again, slight, but higher over-saturation is seen in the case of calcite (SI_{cc}: 0.14–0.48), dolomite (SI_{do}: 0.2–0.9) and aragonite (SI_{ar}: 0.3), than at TG.

As a result of the nine month long sampling campaign and the following laboratory analysis,

it was found that conductivity at site TG varied between 5,300–6,000 μS cm⁻¹, while at site YC between 900–1,100 μS cm⁻¹ (Fig. 4B). The difference between the two sites could also be observed in the case of drip intensity ranges (TG: 30–80 ml h⁻¹, YC: 20–60 ml h⁻¹; Fig. 4B respectively). It may also be inferred from the graphs (monotone decreasing trend from the beginning of the measurements), that EC was higher in summer, although measurements were not available for it during that time.

At both sites, the changes in EC and drip intensity in general followed each other. When drip intensity decreased, so did EC and vice-versa. In the time period assessed, two events can be brought up as examples of the parallel increase of both parameters. The first (Event 1) occurred in November–December 2013 and the second (Event 2) in January–February 2014. The volume of change significantly differs at the two sites (Fig. 4). In the case of EC, at site TG the change was only 200 μS cm⁻¹ during the first and 600 μS cm⁻¹ during the second event, while at site YC it was only 10 μS cm⁻¹ and 30 μS cm⁻¹ respectively. A similar case was observed in drip intensity as well, where again bigger changes were observed at site TG (15 & 25 ml h⁻¹) than at site YC (5 ml h⁻¹) during both events.

As a rough estimate, it can be seen that in the case of Event 1 it took about ~1 day for TG and ~2 days for YC to respond to the effect of the precipitation of the previous days, while in the course of Event 2 such a distinction cannot be made because of the lack of outlying precipitation peaks. It should be noted that in the case of the other precipitation events no explicit change was seen in either the EC or the drip intensity parameters. However, it is suspected that in the course of both Event 1 & 2, the previously seeped-down water had not yet exited the system, so the prolonged and/or smaller precipitation events – especially in the case of Event 2 – reached an already water-saturated system, causing a response in drip intensity and EC. The only explicit exception may be January 2014 (Fig. 4), when at site TG there was an increase in drip intensity, but without the expected decrease afterwards, probably because of the effect of the precipitation in Event 2.

The driving processes of water quality

To explore the determining background parameters of water quality in the drip water datasets of the two sites PCA was used. The first principal component (PC) in the case of site TG explained 77 %, the second PC, however, only 21 % of the total variance. In the case of site YC these figures were 83 % and 13 % respectively, meaning that the

Tab. 1: Descriptive statistics of cations and anions at TG (number of samples: 17) A) and YC (number of samples: 15) B) (15.07.2013–13.04.2014). M: mean, MED: median, SD: standard deviation, CV: coefficient of variation, MIN: minimum, MAX: maximum.

A)									
TG Statistic / Parameter	Measurement unit	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	K ⁺	Mg ²⁺	Ca ²⁺	Na ⁺	NO ₃ ⁻
M		117.8	208.5	1739.1	6.6	50.7	308.3	766.2	66.4
MED		116.7	213.4	1719.3	6.4	48.6	305.4	754.5	66.7
SD	(mg l ⁻¹)	6.6	12.5	79.7	0.4	6.4	10.6	55.4	1.2
CV		6 %	6 %	5 %	6 %	13 %	3 %	7 %	2 %
MIN		105.1	176.0	1648.4	6.2	41.7	297.7	709.4	64.0
MAX		128.4	220.6	1878.9	7.3	66.0	328.3	954.5	68.4
M	(mmol l ⁻¹)	1.9	2.2	49.1	0.2	2.1	7.7	33.3	1.1
B)									
YC									
M		162.7	171.2	112.0	3.7	49.5	75.7	32.0	77.9
MED		157.6	168.8	109.9	3.4	48.6	74.4	32.0	78.6
SD	(mg l ⁻¹)	20.7	13.6	6.0	0.4	2.6	5.1	1.6	2.0
CV		13 %	8 %	5 %	12 %	5 %	7 %	5 %	3 %
MIN		140.1	155.3	106.4	3.3	45.2	68.7	29.2	72.8
MAX		198.5	215.8	124.1	4.3	53.3	84.0	34.8	80.1
M	(mmol l ⁻¹)	2.7	1.8	3.2	0.1	2.0	1.9	1.4	1.3

remaining variance explained by the further PCs was less than 2 % and 4 % for TG and YC respectively, indicating that these subsequent factors may be ignored (Fig. 5).

At site TG, chloride and sodium were much more determining than all the other components. Site YC is, contrastingly, clearly bicarbonate dominated, with chloride and calcium also being important in both PCs (Fig. 5B). In addition, sulfate is only important in the second PC at site YC. Thus, the most notable difference between the two sites is to be found in the parameters related to natural karst processes, since at site YC bicarbonate has large factor score in the first PC, while at site TG neither bicarbonate nor calcium has any significance in the determination of the first two PCs.

Periodicity analysis of the data between October 2013 and January 2014

Prior to periodicity analysis, the long-term variability was removed from the pH, Eh and EC time series of the two sites using LOESS. The characteristic shorter fluctuations were thus preserved intact, while the “masking” trend was omitted (e.g. see Fig. A5). As the next step, a time-frequency analysis concentrating on diurnal periodicity was conducted for the time series of pH, Eh and EC measured at both observation sites using WSA (e.g. Fig. A6). For each series, time intervals were sought in which the 24 hour period was detectable. Then the proportion

of the number of days with daily periodicity to the overall number of observation days was calculated for each time series, and the two observation sites characterized and compared using these figures. It may be conjectured that the obtained characterization is indicative of the transfer of contaminating substances.

The proportion of time with a daily period present vs. the full time period was calculated (as in Kovács *et al.* 2010), and found to be of similar magnitude at both sites for pH and Eh. EC, however, was peculiar in this sense, since at site TG it indicated daily periodicity over a much smaller portion of time than at YC (Tab. 2).

Tab. 2: The presence of a daily period in percentages compared to the total assessed time.

	pH	Eh (mV)	EC (µS cm ⁻¹)
TG	61.8 %	56 %	21 %
YC	65 %	59.9 %	56 %

As a final step, the daily mean course was determined by averaging out the fluctuations for each hour of the day (Fig. 6). In the case of all three parameters, the first and most explicit difference is that at site TG the amplitude of the daily period is much larger than at YC, approx. 5.5, 3, and 3 times larger for pH, Eh, and EC, respectively. In addition, in the case of pH and Eh there is a clear shift between the minima and maxima. At YC the

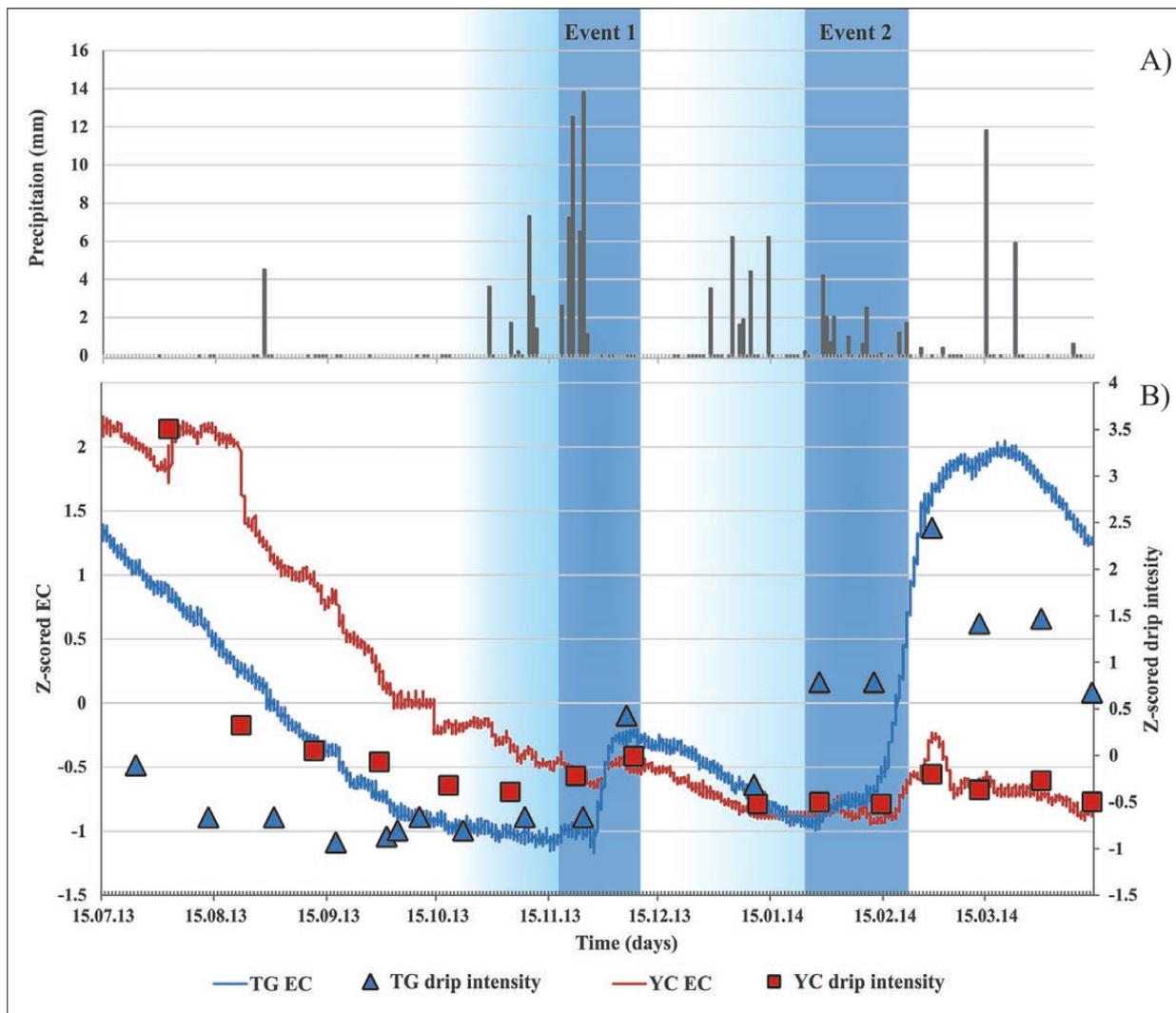


Fig. 4: Precipitation events (mm) A) along with the Z-scores of EC and Drip intensity at sites TG (blue triangle) and YC (red square) B) for 15.07.2013 to 13.04.2014. The light blue vertical bands indicate the precipitation events that started filling up the karst and the dark blue ones the precipitation events that triggered the change in EC and drip intensity.

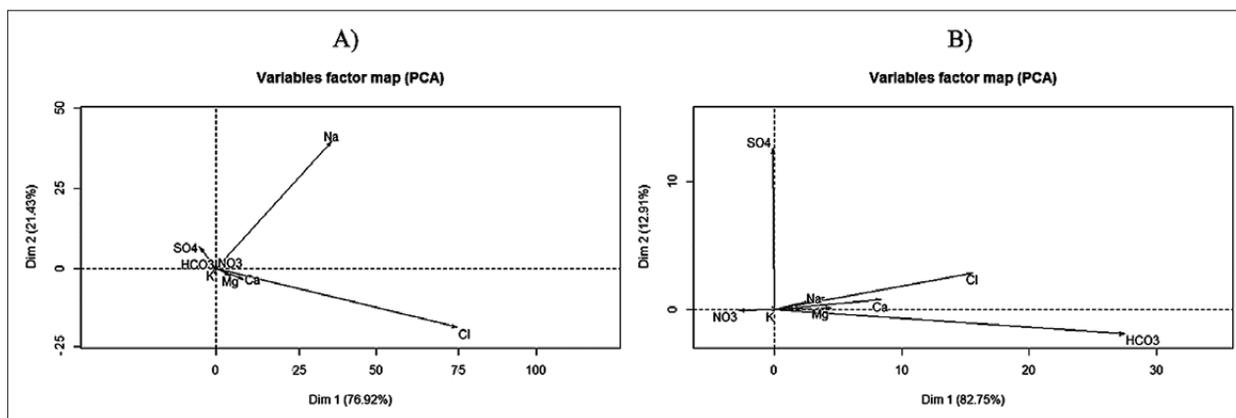


Fig. 5: Results of PCA at site TG A) and YC B).

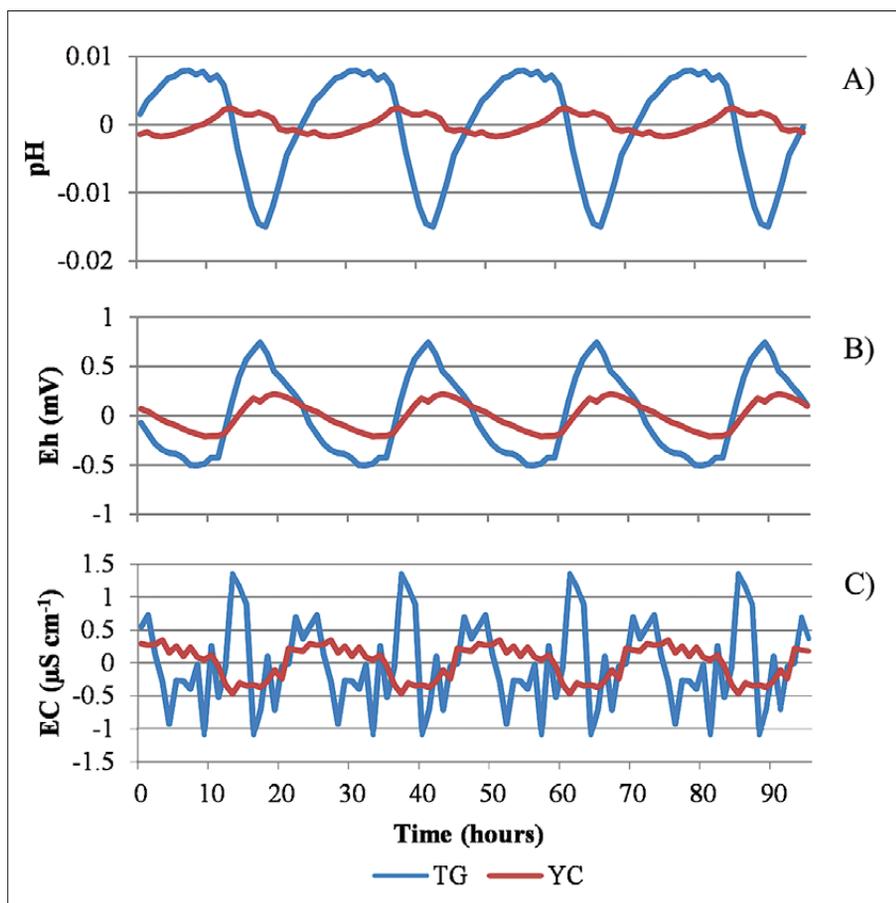


Fig. 6: pH A), Eh B), and EC C) average daily fluctuations of the de-trended time series, repeated four times for better visualization, at the two sites.

peaks of the curves occur 6h (pH) and 2h (Eh) later than at TG. As for EC, a clear and mature daily period is only present at YG. Such comparisons between the time lags would thus be inappropriate. As an additional observa-

tion, pH and EC show clearly opposing patterns. When pH decreases, EC increases, and vice-versa at both sites (Fig. 6).

DISCUSSION

On the basis of the presented analyses significant differences may already be observed between the two monitoring sites at the level of the descriptive statistics. This is particularly interesting since both are located in the same geological formation, albeit in different tectonic settings: TG is situated near the fracture zone of the Szép Valley 40 m below ground, with water reaching it quickly via seepage from the surface, while YC is located in a much less fractured rock, under a declivous pediment at a depth of 60m (Fig. A1). Therefore, water seeps down slower and in smaller quantities. In general, besides the local differences, the observed values were clearly way above what might reasonably be considered as natural for both the

cations and anions. The values in our study area, e.g. for (i) chloride were 2 to 30 times more, and (ii) sulfate ~3.5 to 4 times more (at sites YC and TG respectively) than the maxima in the Postojna cave (Slovenia), which is known to be affected by the residues (chlorides, nitrates, sulfates and phosphates) of the nearby military facilities. This is noteworthy even if we consider that the Pál-völgyi Cave System has a marl cover (Fig. 1C). Interestingly, the nitrate values were higher in the Postojna Cave than in the Pál-völgyi Cave System, indicating the fecal origin of the pollution (cesspools) in the previous case (Kogovšek 2011).

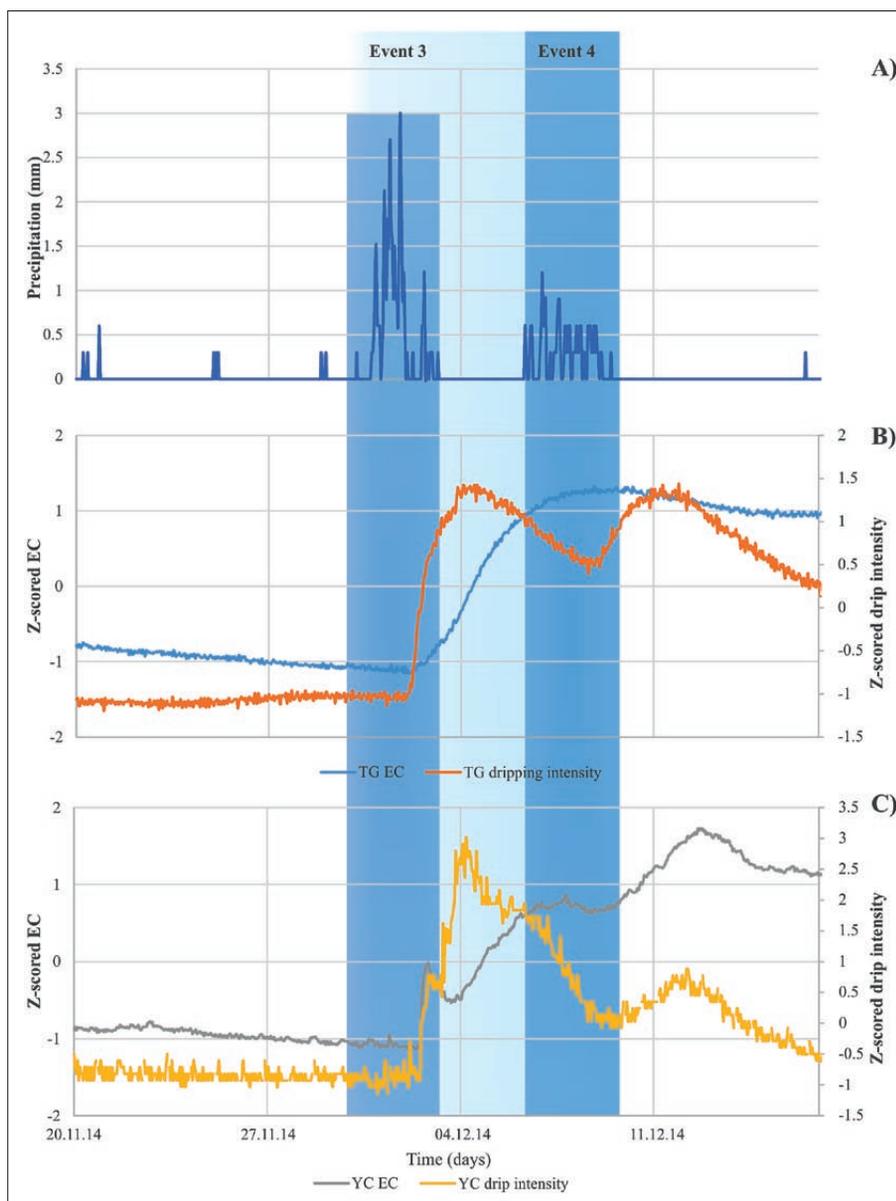


Fig. 7: Precipitation events (mm) A) along with the Z-score transformed EC and Drip intensity at sites TG B) and YC C) for 20.11.2014 to 17.12.2014. The light blue vertical bands indicate the precipitation events that started filling up the karst and the dark blue ones the precipitation events that triggered the change in EC and drip intensity.

Regarding saturation, the system is slightly over-saturated in general. The natural processes (e.g. carbonate-equilibrium reactions) dominating at YC (Fig. A4) are able to manifest themselves. For example in the process when the drip water exits the rock and gets in touch with the cave air – in the water collector – and its equilibrium CO_2 exits the water and the becomes slightly more over-saturated. In the case of TG, however, because of the higher anthropogenic influence the carbonate-equilibrium reactions are suppressed, as seen from the lower bicarbonate values as well.

The bi-weekly drip-intensity drove EC values, reflecting the well-known phenomenon that fallen precipitation seeps in through the epikarst, bringing with it substances from the surface. This, in turn, tends to

lead at first to a swift increase EC, followed by a diluting of the water (Ford & Williams 2007; Liu & Brancelj 2014). The speed of the decay was different for the two sites during/after two precipitation events (Events 1 & 2 in Fig. 4), but due to the lack of continuous drip intensity measurements, only estimations were made. Unfortunately, measurements as dense as those found in Liu & Brancelj (2014) were not available for the examined period to trace the impact of precipitation on drip intensity on a finer scale. However, an additional special set of data was available with continuous drip intensity measurements (20.11.2014 to 17.12.2014) from the area examined (Fig. 7).

Therefore, the lag between the precipitation events and the increase in drip intensity and EC could be de-

terminated exactly. In the course of Event 3, drip intensity started to increase at TG after 34 h and at YC after 44 h, while the change in EC followed it one hour later at both sites (at TG after 35 h and at YC after 45 h). In the course of Event 4, the previously seeped-down water (starting with Event 3) had not yet exited the system, so the prolonged and smaller precipitation events reached an already water-saturated system, causing an even slower response in drip intensity (TG: 68h; YC:81h). This was somewhat similar to the phenomena shown in Fig. 4. This is the same phenomenon that presumably took place in the course of Event 2 (Fig. 4). As for EC in Event 4, at TG it took the system 290 h to respond, probably due to the fact that the high amount of substances that reached the karst during Event 3 ($6,700 \mu\text{S cm}^{-1}$) had not yet exited the system, and at the time of Event 4 it only decreased a $100 \mu\text{S cm}^{-1}$, while at YC it started to increase parallel to drip intensity, due to the already known differences between the two sites (Fig.7).

Although, measurements did not cover summer, the starting points of the EC graphs at both sites are in line with the documented phenomenon that conductivity is higher in summer (Batiot *et al.* 2003).

As seen, the EC values were different for the sites, indicating a greater degree of anthropogenic influence at TG. Compared, however, with a cave in a pristine alpine site (Austria) 60 m below ground (as is site YC), the EC values recorded even at site YC were a minimum 3.5 times higher, and in some cases more than 25 times higher (Kern *et al.* 2011). This indicates the in general higher degree of disturbance and exposure of the explored section of the Pál-völgyi Cave System, although latter has a marl cover (Fig. 1C). At the same time, EC was found to be on the same scale as in another disturbed cave system in Slovenia (Kogovšek 2011). As for drip intensity, it was more variable at site TG, this originating from the difference in the settings of the sites, i.e. TG is closer to the fracture zone and located closer to the surface ($\delta h=20$ m).

STOCHASTIC REALTIONSHPIS

With the stochastic analyses, the parameters explaining most of the variance were sought, and consequently connected to the main processes governing the quality of the drip waters. In general, the presence of sodium and chloride might be the result of natural processes, such as weathering, but then again, large differences in concentrations within a cave located in a uniform geological setting alert us to the possible presence of external pollution. These may include, for example NaCl, used for de-icing for decades (Granato 1996), or the residues of detergents, disinfectants etc. On the other hand, elevated sulfate concentrations in drip water may be connected to

natural processes of the soil (Hem 1985), or to the decomposition of organic matter of anthropogenic origin. Nitrate, however, is always an indicator of human activity in the area, originating as it does in fertilizer usage or sewage waters, for example (Hem 1985; Lerner *et al.* 1999; Motyka *et al.* 2005).

In the present situation and study, these parameters were indeed related to anthropogenic and/or natural karst processes, as described in the study of Daoxian and Cheng (2009), though to a different degree at the two sites. In the case of site TG, it became evident that the parameters combined in the first two PCs are in close relationship with external urban pollution. The most pronounced were sodium and chloride originating from de-icing materials and/or domestic sources, reaching the subsurface flow (Panno *et al.* 2006). Natural processes do not seem to have a relevant role here at all.

On the contrary, site YC's first PC is bicarbonate dominated – representing the natural karst processes (Ford & Williams 2007) – but chloride is also present, again indicating an external influence from the surface, such as sulfate in the second PC (Kogovšek 2011). The reason for this lies in the setting of the sites, meaning that at YC there is a much greater chance for rock-water interaction to take place due to the slow seepage caused by the more consolidated environment, while in the case of TG the water does not have time to dilute the substances from the rock (Fig. A1).

PERIODIC BEHAVIOR

The periodicity analysis of the pH and Eh time series indicated high variability and a diurnal periodic behavior detectable over a substantial part of the observation period at both sites. The slight difference in the degree of detectability as well as the lag between the peaks of the periods at the two monitoring sites may be due to their geological settings, as previously described. After examining the results more closely, it became apparent that pH and EC were in anti-phase. The pH rose and EC dropped during daytime at both sites, as has been observed elsewhere in a karst underground river (Daoxian & Cheng 2009). These opposing patterns in the cases of pH and EC were found to hold in the bi-weekly data as well (Fig. 8A). Higher CO_2 content (i) decreased pH, and (ii) increased the solution capability, total dissolved solids (TDS, Fig. 8B, calculated from the measured cation and anion concentrations), and as a result, EC as well (Fig. 8 inset table).

The similarity of pH and Eh and the difference of EC in terms of daily periodic behavior at the two monitoring sites closely reflects the situation described in the Introduction in detail, thus providing evidence of the presence of anthropogenic influence on the area. At the

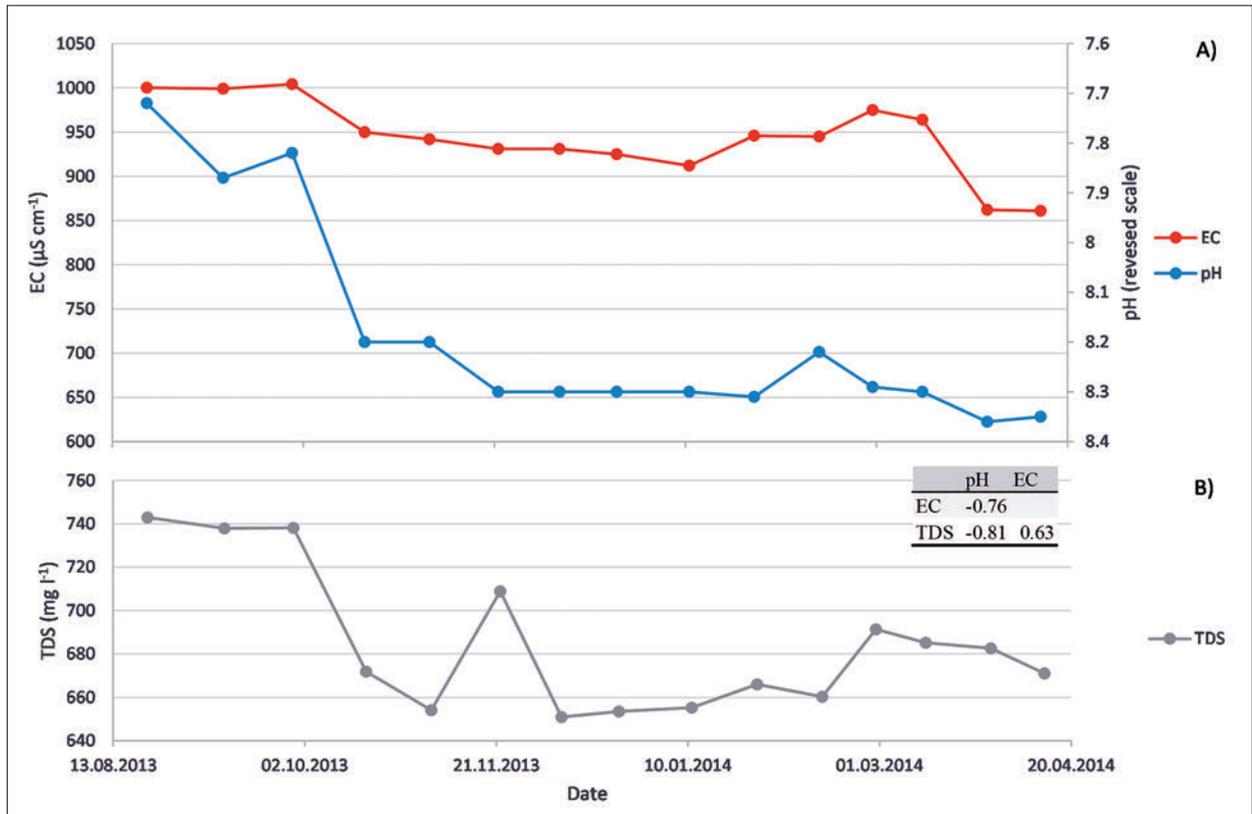


Fig. 8: Bi-weekly measurements for pH, EC A) and TDS B) at YC and their correlation matrix (inset table).

un-fractured YC site, the karst processes drive periodicity, while in the shallower TG, located next to the fracture zone, it is likely to be the topsoil and vegetation. However, it is suspected that the non-periodic patterns and the decreased daily periodicity seen in the case of EC at TG (wavelet results, Tab. 2) are the results of (i) anthropogenic contamination, and (ii) the fact that in the fractured zone next to TG (Fig. A1), water seeps down quite fast, (iii) as a result gathering the substances from a larger area/watershed and in a more concentrated way than at YC.

Another reason for the periodic patterns of the continuously measured parameters may be attributed to biological activity (root/rhizosphere respiration and soil organic matter decomposition; Zámbo *et al.* 2001; Meyer *et al.* 2014) in the soil lying over the area. Jakucs (1971), observing the atmosphere in the soil, found that CO₂ has a daily periodicity in different bio- and climate-specific karst micro areas (Szalai 2008), and so does carbonate in covered karst during continuous and prolonged seepage (Zámbo & Telbisz 1999). Both considered the solution of bicarbonate and the CO₂ concentration of the seep-water

as a main factor of “soil effect”, clearly determining the chemistry of the seeping water, consequently determining the pH of the water seeping into the karst. These processes and the anthropogenic effects are superimposed on the periodic patterns at sites TG and YC.

Although measurements have been conducted for drip water in the Pál-völgyi cave by Bolner *et al.* (1989), Bolner (1995) and Fehér (2009), and in other caves in Budapest by Mádl-Szőnyi *et al.* (2007), these only involved periodic/intermittent sampling campaigns. Thus, comparing the results of the unique continuous campaign presented here with their findings would not give a meaningful picture.

It should be noted that similar, continuous drip water collection has been performed in other Hungarian caves outside the capital, mainly for stable isotope composition and water chemistry in e.g. the Csodabogyós Cave (Czuppon *et al.* 2013, 2014), but this took place in areas located in an anthropogenically undisturbed setting. In addition, continuous climate- (Stieber & Leél-Össy 2015), and spring runoff measurements (Végh *et al.* 2005) are also available from natural karstic areas.

CONCLUSIONS

Exploring urban caves is equally important from the perspective of tourism, as well as therapeutic and scientific uses, and is a highly important task in protecting our geological heritage. For one thing, urban caves are much more affected than ones in areas remote from human activity by factors such as increases in the proportion of built-up areas, cracks in the drainage system, the lack of natural topsoil etc. in changing the behavior of natural karst processes. With the presented study, the explicit differences between the anthropogenically much more affected site (TG, near a fracture zone) and the tectonically un-disturbed site (YC) were highlighted. The processes at site TG were found to be different from the natural karst ones in operation at YC in the following ways. At TG, (i) Its water quality parameters reflected urban activity from both a descriptive and stochastic point of view to higher extent in other anthropogenically effected sited de-

scribed in literature; (ii) EC and drip intensity responded more swiftly and dynamically to precipitation; and (iii) as for periodicity, the external pollution inputs originating the urban environment, and as a minor factor, the lack, for example, of natural topsoil coverage disturbed and masked the periodic behavior which might be expected from such a karst environment. This was most explicit in the case of EC. The Pál-völgyi Cave System is of particular importance since it is a key recharge zone of the thermal springs of Budapest. This way continuous monitoring of its environment if of exceptional importance. Because the infiltrated polluted waters may change (i) the natural karst environment of the cave, (ii) its formations and minerals and (iii) the aerosols in it as well and consequently have a direct impact on its exploitation for therapeutic purposes and endanger the cave as a geological heritage.

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APPENDICES

APPENDIX 1

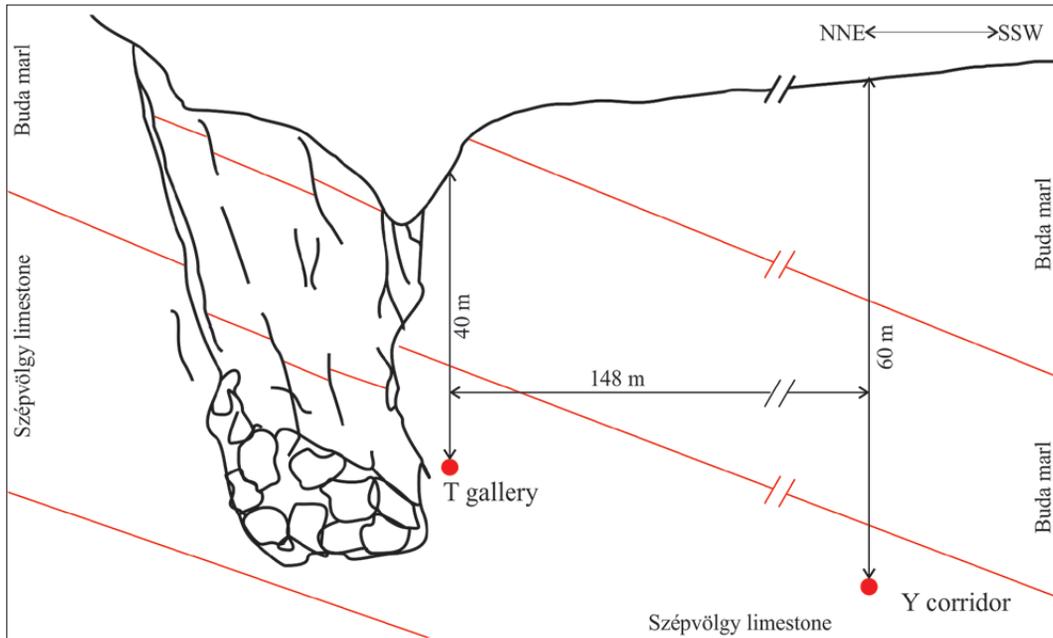


Fig. A1: Cross section of the studied area of the Pál-völgyi Cave System with the location of the two sampling sites, the T galley (TG) and the Y corridor (YC).

APPENDIX 2

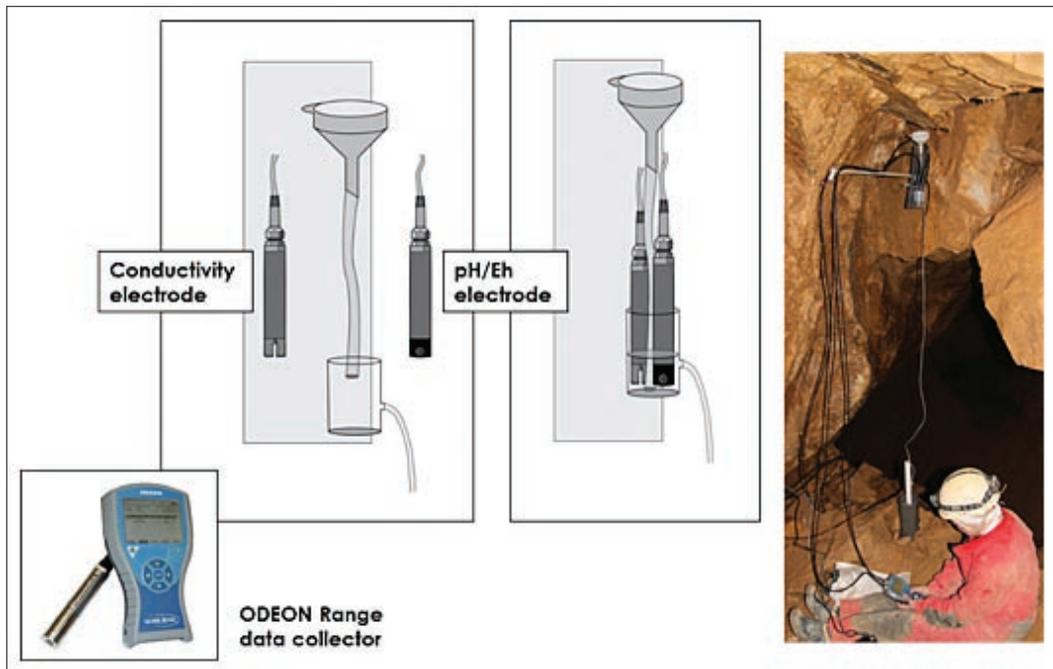


Fig. A2: Build-up of the ODEON data collector and sampling on site (photograph on the right).

APPENDIX 3. STFT RESULTS

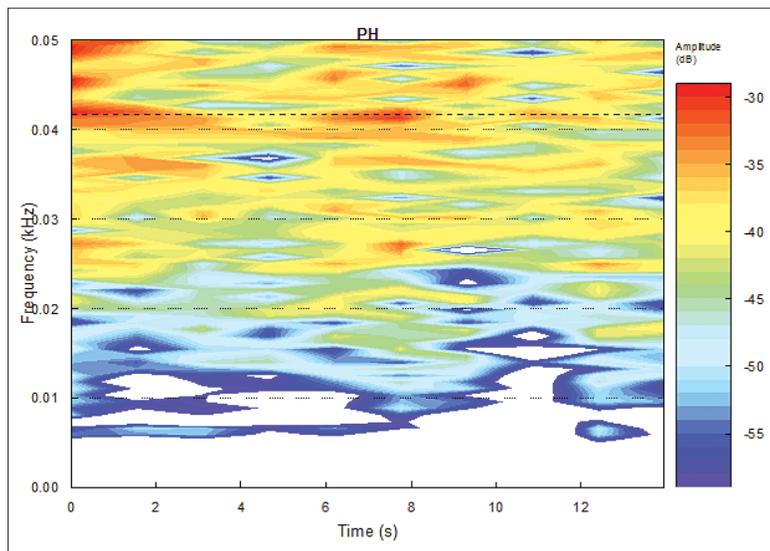


Fig. A3: STFT results of pH at site YC.

STFT was applied first to the series, using Bartlett window and window width 200 data points (Fig. A3).

High amplitudes can be observed along the 24 hourly periods (0.0417 frequency, broken line) and its close neighborhood in the majority of the time-domain. It is very difficult however to distinguish, whether it is an effect of the choice of the window width, or a result of a genuine diurnal period. It would be straightforward to narrow the window width but then due to the poor separation of frequencies the 24 hourly period would disap-

pear in the whole last third of the time domain. To the contrary, by widening the window, the 24 hourly period would completely fill in the full time domain as if it were detectable any time. Further, to our best knowledge no statistical test is available for assessing the significance of the estimated amplitude at a given time, therefore the required proportion of days with periodic behavior could not be found with prescribed reliability. This necessitates a further analysis, when time and frequency resolutions do not change at the expense of each other.

APPENDIX 4

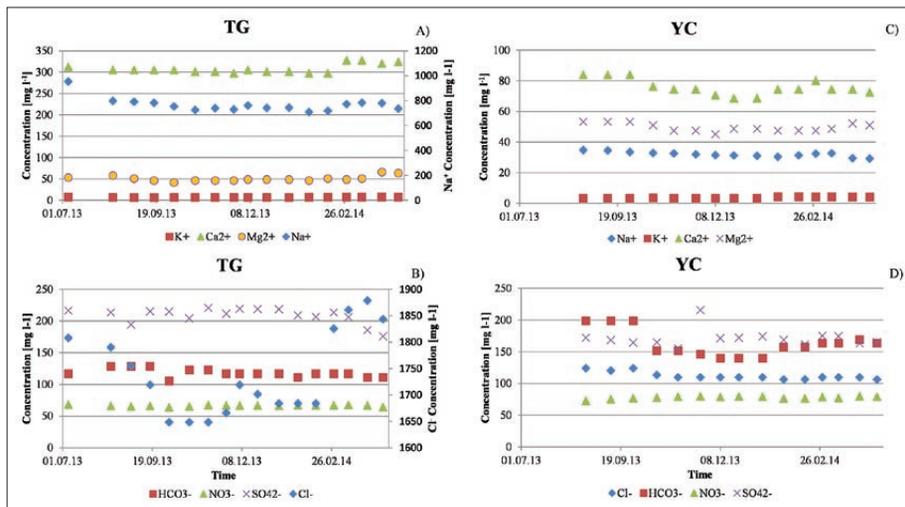


Fig. A4: Cation concentrations at TG A) and YC B) and anion concentrations at TG C) and YC D).

APPENDIX 5

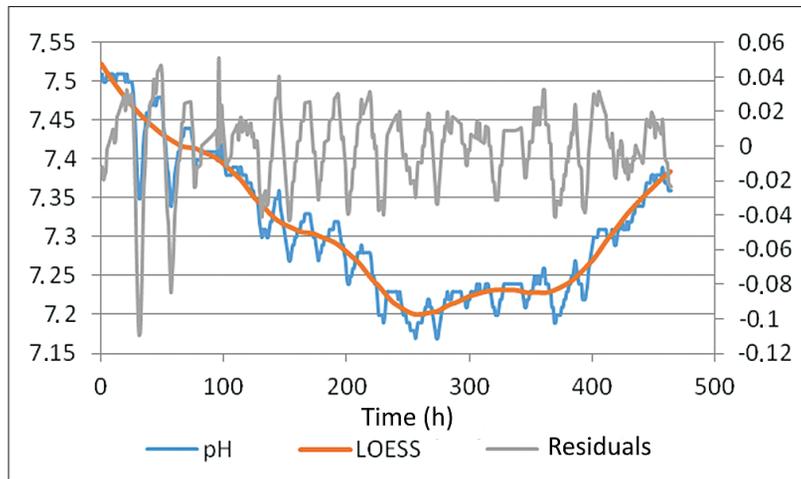


Fig. A5: Example on LOESS on pH at site TG with the original data the smoothing curve and the residuals.

APPENDIX 6

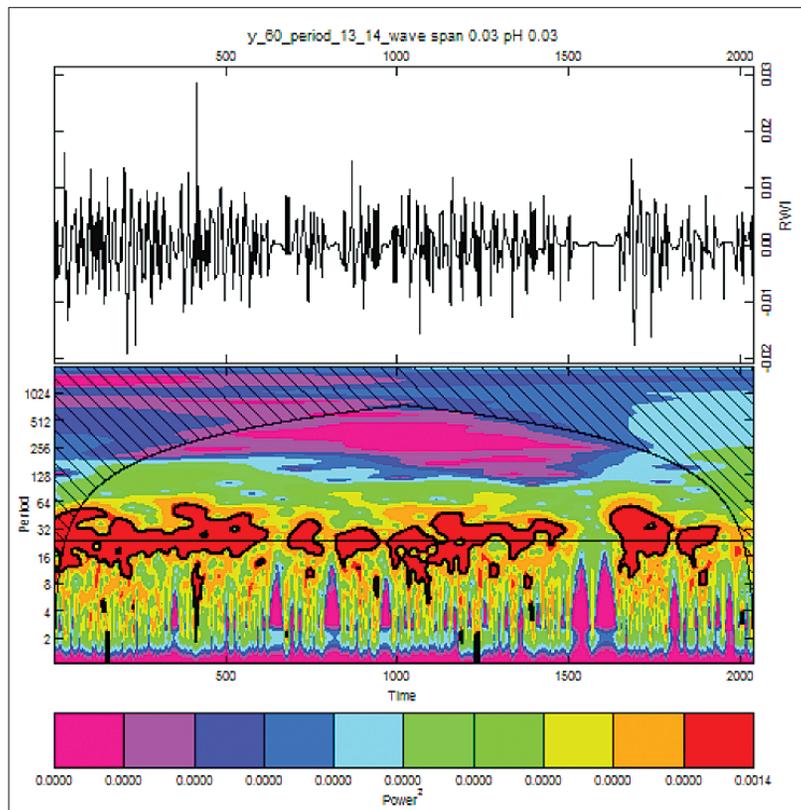


Fig. A6: Z-score standardized pH values (upper graph) and daily periodicity (lower graph) at site YC. The domain of the 5% significance level against red noise are colored by red and marked with a thick black contour. The dashed areas outside the thin black line mark the COI. The black horizontal line indicates the approximated place of the daily period.