Dear Editor,

We are submitting a revised version of our manuscript *Transfer of environmental signals from surface to the underground at Ascunsă Cave, Romania*.

From the previous version we introduced a subsection (2.7) in the Methods section, regarding the statistical methods used in the manuscript. We also introduced subsection 3.6 in which we discuss the relevance of our work for the paleoclimate study of speleothems.

Moreover, we added the p-value for the correlation between different parameters.

Thank you for your time and consideration!

With best regards,

Virgil Drăgușin

Transfer of environmental signals from surface to the underground at Ascunsă Cave, Romania

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Abstract. We present here the results of a four year environmental monitoring program at Ascunsă Cave (SW Romania) designed to help us understand how climate information is transferred through the karst system and archived by speleothems. The air temperature inside the cave is around 7 °C, with slight differences between the upper and lower parts of the main passage. CO_2 concentrations in cave air have a seasonal signal, with summer minima and winter maxima. This might indicate the existence of an organic matter reservoir deep within the epikarst that continues to decompose over the winter, and are possibly modulated by seasonal differences in cave ventilation. The maximum values of CO_2 show a rise after the summer of 2014, from around 2000 ppm to about 3500 ppm, following a rise in surface temperature. Using two newly designed types of water/air equilibrators we were able to determine the concentration of CO_2 dissolved in drip water, by measuring its concentration in the equilibrator headspace and then using Henry's law to calculate its concentration in water. This method opens the possibility of continuous data logging using infrared technology, without the need of costly and less reliable chemical determinations. The local meteoric water line ($\delta^2H = 7.7 \ \delta^{18}O + 10.1$), constructed using monthly aggregated rainfall samples, is similar to the global one, revealing the Atlantic as the strongly dominant vapor source. The δ^2H excess values, as high as 17 ‰, indicate that precipitation has an important evaporative component, possibly given by moisture recycling over the European continent. The variability of stable isotopes in drip water is similar at all points inside the cave, suggesting that the monitored drip sites are draining a homogenous reservoir. Drip rates, as well as stable isotopes, indicate that the transfer time of water from surface is in the order of a few days.

1. Introduction

The large-scale monitoring of karst systems is mainly undertaken from the perspective of water resource management or conservation (e.g. White, 1988; Ford and Williams, 2013). However, with the use of speleothems

as tools for climate reconstruction, came the need for monitoring karst systems at a much finer spatial and temporal scale, where water/rock and water/atmosphere interactions have to be taken into account (Fairchild and Baker, 2012). In speleothem paleoclimatology, cave monitoring studies are used as tools for local, case by case calibration of speleothem proxies against climate parameters and were employed throughout the world: Gibraltar (Mattey et al., 2008), Belgium (Verheyden et al., 2008; Van Rampelbergh et al., 2014), France (Genty et al., 2014), Czech Republic (Faimon et al., 2012), Spain (Smith et al., 2016; Dumitru et al., 2017), Austria (Spötl et al., 2005), Germany (Riechelmann et al., 2013), USA (Onac et al., 2008; Feng et al., 2014; Meyer at al., 2016), Australia (Jex et al., 2012) or China (Hu et al., 2008; Duan et al., 2016). Such studies focus mainly on parameters such as cave air temperature and relative humidity, CO_2 concentration in drip water and cave atmosphere, or stable isotopes ratios in drip water and modern calcite. Lately, a series of review papers have detailed the systematics of stable isotopes in speleothems (McDermott, 2004; Fairchild et al., 2006; Lachniet, 2009), while the book of Fairchild and Baker (2012) offers an updated and detailed framework for speleothem paleoclimatology.

Water is the main carrier of information between surface climate and speleothems, thus the most used paleoclimate proxy is $\delta^{18}O$. The interpretation of speleothem $\delta^{18}O$ values is not usually straightforward because they are influenced by thermal and hydrological processes both at the surface and underground, sometimes in opposing ways. For example, at the surface, the altitude effect could be counteracted by a rain shadow effect, as evidenced in the Andes by Chamberlain and Poage (2000). Seasonal changes in the vapor source of rainfall or in conditions at the vapor source can modify the annual $\delta^{18}O$ values of rain water and represent an important issue in speleothem paleoclimate reconstructions. Information on the vapor source are usually inferred based on the meteoric water line and the δ^2H excess value in precipitation (Craig, 1961; Gat, 1996; Pfahl and Sodemann, 2014). When entering the soil-karst system, water can be subjected to evaporation in the soil, the epikarst or even in the cave, thus imprinting higher values to calcite than the original rainfall (Bar Matthews et al., 1996; Markowska et al., 2016; Dumitru et al., 2017). Finally, during calcite deposition, temperature dependent fractionation between drip water and calcite $\delta^{18}O$ is rarely following theoretical estimations, hence the need for the determination of fractionation equations for each speleothem under consideration.

While drip water $\delta^{18}O$ can be modified by evaporation inside the cave, another important environmental proxy, $\delta^{13}C$, can be kinetically altered by strong degassing of CO_2 from solution when the pCO_2 gradient between drip water and cave atmosphere is large (Hendy, 1971; McDermott, 2004). CO_2 concentration in cave air is generally a result of soil CO_2 input, modulated by cave ventilation (Atkinson, 1977; White, 1988). Higher concentrations of dissolved CO_2 are given by enhanced plant respiration and organic matter decomposition in the soil above the cave. Compared against cave air CO_2, it helps identify variations in cave ventilation, periods with increased calcite deposition or with increased kinetic fractionation of $\delta^{13}C$ (Spötl et al., 2005; Banner et al., 2007; Mattey et al., 2010). Thus, a careful characterization of pCO_2 gradients is an important element in cave monitoring. While cave air CO_2 concentrations are easily measured and recorded using infrared technology, dissolved CO_2 is usually modeled using the alkalinity and pH of water (Tooth and Fairchild, 2003; Spötl et al., 2005; Riechelmann et al., 2013). This approach is time consuming, costly, and offers only spot values.

Here we present the results of an ongoing monitoring study started in 2012 at Ascunsă Cave and, for comparison, at the nearby Isverna Cave. This study is designed to help us understand how climate information is archived by speleothems at Ascunsă Cave, in preparation for the publication of a series of new, high resolution stable isotope profiles from Holocene stalagmites from this cave and from several others in the Carpathian region.

Using isotopic analysis of rainfall, we try to identify the dominant vapor sources of precipitation, knowing that our region falls under the influence of both Atlantic and, to a lesser extent, Mediterranean air masses (Baltă and Geicu, 2008). Moreover, we want to detail the seasonal changes in precipitation $\delta^{18}O$, in order to see to which extent the drip sites respond to seasonal variability. Further, we check if modern calcite is deposited in equilibrium conditions or the isotopic values of oxygen and carbon are significantly modified by kinetic fractionation.

An important part of the present study was to develop and validate a new method for the more straightforward measurement of dissolved CO_2 using air/water equilibrators and open the way for high resolution data logging of drip water CO_2 using infrared technology.

2. Materials and methods

Ascunsă Cave is situated in the Mehedinți Mountains (SW Romania, Fig. 1), a region under a temperate-continental climate with Mediterranean influences (Bojariu and Paliu, 2001; Apostol, 2008; Baltă and Geicu, 2008). The cave is 671 m long, 145 m deep and its entrance is located at 1080 m above sea level (a.s.l.). This active cave, rich in speleothems, is developed mostly on the contact between wildflysch (mélange) and limestone.

A small river enters the main cave passage at the White Chamber coming through the Tributary Passage, while and outside river was draining inside the cave through the entrance. At the moment, the outside river is redirected along the valley and does not enter the cave anymore. Since 2012, a monitoring program was started and continuously developed at Ascunsă and Isverna caves, the latter situated at an altitude of 450 m a.s.l. and functioning as the main water collector of this karst system.

Inside Ascunsă Cave, several sites were equipped for monitoring (Fig. 2): POM Entr. (25 m from entrance, -7 m below the entrance level), POM A (100 m from entrance, -30 m), POM 2 (220 m from entrance, -80 m) and POM B (270 m from entrance, -90 m). Apart from these, we have also monitored the small river inside the cave, at a point close to POM A, as well as the outside temperature.

In Isverna Cave, a temperature logger was placed at ~200 m from entrance in the Intermediary Passage, sheltered from the possible influence of the large river flowing through the lower level of the cave. Air temperature, rainfall amount and the isotopic composition of precipitation were also monitored close to the cave (460 m a.s.l.). We note that due to local constraints we did not monitor outside temperature in standard siting conditions that are required from a meteorological station.

2.1. Air temperature, relative humidity and drip counting

Since 2014, Tinytag Plus2 temperature and relative humidity loggers as well as a Stalagmate drip counter were added to the monitoring setup. The logger that records outside temperatures at Ascunsă Cave (POM Ext.) was first placed in a fissure in the entrance area and then moved in December 2014 a few meters outside into another fissure and covered with litter. For this reason, the temperature recorded by it is only an estimates for atmosphere values; however, it better reflects conditions at the surface/subsurface interface.

Relative humidity in the two caves was difficult to measure for long periods of time. Condensing water vapor appears to saturate the sensors of data loggers, therefore we would consider RH to be close to 100 % at the two caves.

2.2. Rainfall amount, rain water and drip water stable isotopes

Rainfall amount was measured at Isverna village (460 m a.s.l.) using a Pluvimate rainfall logger. It should be taken into account that the rainfall logger is not optimized to measure snow fall and can only measure the water produced by melting snow already present in its funnel. Monthly composite rain water samples were collected at Isverna and Drobeta-Turnu Severin meteorological station (located 40 km to the south, at 77 m a.s.l.) in 5 L volumes primed with white paraffin oil to prevent evaporation. Cave drip water was collected during each visit, at roughly 6-8 weeks intervals, using 2 ml glass vials.

H-O stable isotopes were measured in rainfall and drip waters using Picarro L2130*i* cavity ring-down spectroscopy systems. For the period July 2012 - September 2013 they were measured at the Babeș-Bolyai University Stable Isotope Laboratory with a precision of 0.03‰ for $\delta^{18}O$ and 0.1‰ for δ^2H. Reproducibility between measurements of duplicate samples was ~0.08‰ for $\delta^{18}O$ and ~0.19‰ for δ^2H. All values are calibrated against VSMOW–SLAP.

Since September 2013 samples were measured at the Ștefan cel Mare University Stable Isotope Laboratory using a Picarro L2130*i*, coupled to a high precision vaporizer. Samples were manually injected in the vaporization chamber and the average of the last four injections for which the standard deviation was better than 0.02 for $\delta^{18}O$ and 0.2 for δ^2H was used in calculating the isotopic values. The raw values were normalized to the SMOW-SLAP scale using two internal standards (and a third one used as a control), the precision being better than 0.02 ‰ for $\delta^{18}O$ and 0.2 ‰ for δ^2H.

To investigate the possible vapor sources, we modeled the back trajectories of air masses that were present at our site during days with rainfall above 5 mm. We ran the Hysplit 4 model (Draxler and Hess, 1997; Draxler and Hess, 1998; Draxler, 1999; Stein et al., 2015) using the GDAS 0.5° data (DOC/NOAA/NWS/NCEP/EMC, 2001) for the coordinates of the pluviometer (44° 58' 48.26" N 22° 37' 15.13" E) at an altitude of 500 m above ground level.

2.3. Cave air CO_2

During our monitoring program we measured CO_2 concentration in the cave atmosphere at 6-8 weeks intervals. CO_2 concentration was measured since July 2012 using two Vaisala GMP222 probes with an accuracy of (1.5 % of range + 2 % of reading). Between July 2012 and December 2014 we used a probe calibrated for the range 0-2000 (2k) ppm. Since December 2014, a GMP 222 probe calibrated for the range 0-10000 (10k) ppm was used. Because in October 2014 we measured values as high as 3560 ppm, larger than the 2000 ppm calibrated range of the probe, we ran a standardization experiment using the two probes. Following this test we saw that the 2k probe can confidently measure samples up to 3200 ppm. The errors associated with this figures are 221 ppm for the 10k and 97 ppm for the 2k, giving us confidence that the field measurements are genuine.

2.4. Drip water CO_2

To study drip water pCO_2 we adapted the headspace method that is typically used to measure gases evolving from open waters or soils (see for example Broecker and Takahashi, 1966). Here we used two types of water/air equilibrators in which drip water was collected from stalactites via a tube and allowed to degas without having contact with the cave atmosphere (Fig. 3). Being isolated from the cave atmosphere, the CO_2 concentration values

of the confined atmosphere (pCO$_{2ca}$) are considered to be in equilibrium with those of the confined drip water (pCO$_{2cw}$), following Henry's law. The confined atmosphere evolved from degassing of the accumulated water was sampled and the concentration of CO$_2$ was measured using a Vaisala GMP222 probe. As CO$_2$ concentration values are affected by temperature and atmospheric pressure, these parameters were measured with a Vaisala

5 HMP70 temperature probe and a barometer (±5 hPa resolution). The concentration of CO$_2$ in infiltrating waters (CO$_{2cw}$) was calculated using Henry's law, based on the values measured in the confined atmosphere of the equilibrator headspace (CO$_{2ca}$) and considering the solubility of CO$_2$ in water (H^{cc}=c$_{cw}$/c$_{ca}$) as 0.83 (Sander, 2015). For the sampling itself, the GMP 222 probe was placed in a small volume attached to the equilibrator through a three-way closed valve. The probe volume was vacuumed using a manual vacuum pump also attached to the valve

10 and, after checking the stability of the vacuum to insure no leakage and contamination with atmospheric air, the valve was opened to allow air from the headspace to enter the probe volume. Throughout this time the handheld meter was turned off. After allowing enough time for the air sample to penetrate the probe's membrane, the handheld meter was turned on.

Type A equilibrator (Fig. 3, left) is comprised of two main parts: an inner cylinder which is open at the base, and

15 a slightly wider, outer cylinder which is open at the top and hosts the inner cylinder. Water accumulated in the inner cylinder drains through its bottom and then flows upwards towards the rim of the outer one, where it drains. This ensures that water accumulated from drips has a large surface that is opened only to the interior of the inner cylinder and degasses towards the headspace. In order to reduce CO$_2$ diffusion between cave air and the confined atmosphere through the accumulated water, the distance between the inner and outer cylinders has to be minimal,

20 thus reducing the surface exposed towards the cave atmosphere. The rim height of the outer cylinder controls the height of the water table, and thus the headspace volume inside the inner cylinder. The headspace volume is important in relation with the sample quantity needed for the measurement, if the measurement is done on grab samples.

Type B equilibrator (Fig. 4, right) is simpler, accumulating water in a single volume and draining it through a tube

25 mounted in its lower part. The upper level of this tube controls the water level inside the volume. In practice, we used a very long tube coiled around the exterior of the volume. The extended length of the tube has the role of hindering CO$_2$ degassing towards the cave atmosphere, thus maximizing the likelihood that the confined atmosphere remains in equilibrium with drip water.

When placing the equilibrators, care was taken in order for them to tap a stalactite with a drip rate high enough

30 that would allow for the confined water to be constantly refreshed. Thus, we tried to reduce the danger of CO$_2$ mobility through the whole water mass either towards or from the cave atmosphere.

At POM A we used a Type B equilibrator until November 2015, when we switched to Type A. Later, in November 2016, at POM B the Type B equilibrator was replaced with a Type A.

2.5.   Water chemistry

35 Drip water from the equilibrators described above, as well as water from nearby pools, were sampled from POM A, POM 2 and POM B. Using a WTW Sentix 41 electrode we measured the temperature and pH of cave waters, the latter after calibration with two buffer solutions with values of 7 and 10 that were left to equilibrate with the cave temperature. Electrical conductivity (EC) was measured using a WTW TetraCon 325 EC electrode. Total carbonate hardness was determined by titration using a Merck MColortest water hardness test.

Water samples collected during each visit were stored in Nalgene HDPE bottles. The complete chemical analysis of all water samples was conducted in the Hydrogeochemistry Laboratory of the Emil Racoviță Institute of Speleology (Bucharest, Romania) on a Perkin Elmer NexIon 300S Q-ICP-MS. All determinations were conducted in compliance with the US-EPA 6020B method (EPA, 2014). Calibrations were checked against NIST 1640a and NIST 1643e water standards.

2.6. Modern calcite stable isotopes

Modern calcite was precipitated on glass plates and analyzed for O and C stable isotopes at the site of the published POM 2 stalagmite (Drăgușin et al., 2014) and on the top of the actively growing POM X stalagmite. Results for the period prior to April 2013 were reported by (Drăgușin et al., (2014). Calcite farmed after this period was measured at CEA-CNRS-LSCE (France) on a VG-OPTIMA mass spectrometer. All values are reported in ‰ relative to VPDB. The error is better than 0.08 ‰ for $\delta^{18}O$ and 0.05 ‰ for $\delta^{13}C$.

2.7. Statistical methods

In order to study the relationship between different parameters we performed linear regression analysis using the least squares method and determined both the determination coefficient (R^2) and its significance (p-value). The correlation between rainfall and drip rate was determined following the methodology described in Mangin (1984) and using the STOCHASTOS v3.0 software of d'Hulst (1994).

3. Results and discussion

3.1. Temperature regime of Ascunsă and Isverna caves

For better comparison we use data logged continuously between February 2015 and February 2017 while all the logs overlap. The external temperature at the two caves has a good correlation, Ascunsă values showing lower daily amplitude, related probably to its subsurface location and in a forested area. The mean value over this period was 6.77 °C (SD=6.45 °C) at Ascunsă and 14.01 °C (SD=7.70 °C) at Isverna. Using temperature values from the European Climate Assessment (ECA) (Klein Tank et al., 2002) for Drobeta-Turnu Severin meteorological station (average 14.07 °C, SD=9.14 °C), we see that temperature variability in our area was similar to regional one (Fig. 4).

Based on the good correlation between our site and the Drobeta meteorological station, we could use data from the latter in order to get more insight into the relative temperature variability over the whole monitored period at our site. Annual temperature at Drobeta decreased from an average of 13.7 °C in 2012 to a value of 13.3 °C in 2014, only to rise to 14.1 °C in 2015. In 2016 it dropped to 13.6 °C (Fig. 5). At seasonal scale, we see a more complex image. Average winter values increased constantly between 2012 (0.5 °C) and 2016 (4.6 °C), while spring temperatures generally decreased. Summer and autumn values were coupled, both showing a decrease between 2012 and 2014, a rise in 2015 and a large drop in 2016, which resembles the variability of annual temperature. Thus, it appears that the summer/autumn couple controls the annual temperature values.

At Ascunsă Cave, POM2 and POM A have a stable temperature regime (Fig.6). While the average at POM2 is 7.33 °C (SD=0.06 °C) at POM A it is 7.05 °C (SD=0.06 °C). At the same, time POM Entr. shows higher variability

(average 5.74 °C, SD=0.86 °C) due to its proximity to the entrance and to the steep morphology of the passage, which allows cold air to easily reach this point. Such a dynamic behavior was described, for example, at Obir Cave (Austria) by Spötl et al. (2005). The resemblance between POM Entr. and POM A, with steady warming during summer and sharp decreases during late winter, shows that annual temperature variability is felt at POM A, but the amplitude is less than 0.2 °C. Because the variability at POM A and POM 2 is so small and would not affect any isotopic calculations that could be performed, we will not discuss it further.

Inside Isverna Cave the average temperature was 10.22 °C (SD=0.25 °C) between 2015 and 2017, with relatively stable conditions until February 2016. Temperature began to rise from ~10.1 °C in February 2016 to ~11.1 °C in March 2017. This disruption might reflect the 2015 warming recorded at the surface. As cave air temperature usually reflects long term mean annual values of surface air (Wigley and Brown, 1976) we can use the values from Isverna and Ascunsă caves to calculate a local lapse rate that should be taken into account when discussing the altitude effect on $\delta^{18}O$. Given a 2.8 °C difference between Isverna and Ascunsă (POM 2) for the relatively stable period of 2015-2016, we calculated a value of 6.1°C km^{-1}, in agreement with the global value of 6.4 °C km^{-1} (Brunt, 1933).

3.2.   Rainfall amount and drip rate variability

According to data extracted from the ECA database (Klein Tank et al., 2002), the annual rainfall amount at Drobeta was unusually high in 2014 (1169 mm) in comparison to the 1961-2000 average of 662 mm (Dragotă and Baciu, 2008). Values decreased to 674 mm in 2015 and rose to 746 mm in 2016. At Isverna we recorded similar values for 2015 (702 mm) and 2016 (725 mm).

Following the general trend in rainfall amount, drip rate values diminished over the recorded period, from >30 drips min^{-1} at the beginning of the record to 8 drips min^{-1} in early 2017 (Fig. 7). The higher drip rates recorded at the beginning of our study might reflect increased recharge from the previous months of 2014. During 2014-2015, the time series is punctuated by sharp rises to values as high as 90 drips min^{-1}, linked to rainfall events (Fig. 3), a behavior that indicates a fracture recharge of the karst system (White, 2002; Ford and Williams, 2013).

Although the drip log is not continuous, spectral analysis can help reveal how it responds to precipitation. We performed Fourier transform analysis of average daily drip rates and daily rainfall amounts on three continuous time slices: 18 August 2014 – 30 November 2014, 05 July 2015 – 30 November 2015 and 01 April 2016 – 30 November 2016. The results show there is a close link between them for the period 2014-2015, while during 2016 there seems to be a weaker relationship (Fig. 8).

Cross-correlation analysis of the two datasets shows a similar picture: a very weak correlation in 2016 but a good correlation in 2014 and 2015. During the three periods analyzed, the strongest correlation is found three days after rainfall events. In 2014 and 2015 the r_k values for a three day lag are similar (0.44 and 0.43, respectively), while in 2016 it is only 0.07 (Fig. 9). Interestingly, during 2015 the analysis indicates a second peak in drip rate 8 days after rain events (r_k=0.39). Based on these two peaks, we could speculate that the reservoir discharging through the POM 2 drip site might be fed, at times, via two routes: a fast one characterized by open fractures and a slower one, possibly buffered by an epikarst reservoir (Mangin, 1994).

3.3. CO_2 concentration in cave air and drip water

The variability of cave atmosphere CO_2 (CO_{2atm}) at POM Entr. is in close relation with outside temperature ($R^2=0.66$, p value < 0.05), reaching over 2500 ppm during the warm season but close to 500 ppm in winter (Fig. 10). This might reflect a seasonal input of soil derived CO_2 which is stronger in summer and weak during the cold
5   season, combined with stronger winter ventilation (Wigley and Brown, 1976; Spötl et al., 2005; Banner et al., 2007). Air temperature at this site is between 5 and 7 °C during summer, much colder that outside air, and between 4 and 6 °C during winter, warmer than outside air. The winter setting could lead to stronger convective air circulation (Spötl et al., 2005; Fairchild and Baker, 2012), efficiently ventilating the entrance part of the cave. The winter mode is shorter than the summer one, covering the period November - December to March - April, and the
10   transition between the two is sharp.

At the other three monitoring sites inside Ascunsă Cave, CO_{2atm} records show similar trends: high values in October and low in April. The CO_2 concentrations vary between 700 and 2100 ppm over the period July 2012 to July 2014 but rose following the summer season of 2014 and reached a maximum of 4040 ppm in March 2016. While the higher CO_{2atm} recorded during 2014-2016 could be easily explained by enhanced biological activity
15   following the temperature increase (Lloyd and Taylor, 1994), we cannot rule out a possible weakening ventilation. Even though limestone thickness is different between the upper and the lower parts of the cave (40 m at POM A and 100 m at POM 2 and POM B), the CO_{2atm} signal remains the same. This striking resemblance could be due to similar transfer times of soil CO_2 through the epikarst and karst and to similar ventilation processes throughout the cave.

20   Although the production of soil CO_2 peaks in the warm season (Lloyd and Taylor, 1994; Breecker et al., 2012), the fact that we recorded the highest CO_{2atm} values in winter could be explained by the existence of regions of CO_2 production deep within the epikarst, as theoretically proposed by Atkinson (1977) and later recognized in different settings by Benavente et al. (2010), Mattey et al. (2010), Breeker et al. (2012) or Faimon et al. (2012). Recently, Noronha et al. (2015) used radiocarbon to trace the origin of speleothem carbon and suggested the
25   possibility that this is dominated by carbon resulted from the decomposition of dissolved organic matter deep within the karst system. At Ascunsă Cave this The existence at Ascunsă Cave of a deep seated carbon reservoir seems to be supported by the observation of a ventilation event in January 2016 which was expressed at all three inner sites as a ~1000 ppm reduction in CO_2 concentration following a drop of 10°C in outside air temperature. Together with the subsequent rise in values, this event implies the existence of a steady CO_2 flux towards the
30   cave, compatible with a winter production deep within the karst system.

In Fig. 11 we see that, with no exception, CO_{2ca} (and, by extension, CO_{2cw}) was always greater than CO_{2atm} by a few thousand ppm. Nevertheless, as opposed to CO_{2atm}, CO_{2ca} shows differences between the three sites. At POM A CO_{2ca} has the highest values, reaching over 11000 ppm, close to theoretical concentrations in soil atmosphere (Atkinson, 1977 and references therein; Brook et al., 1983), and shows a similar profile to CO_{2atm}. Supported by
35   the resemblance between CO_{2atm} and CO_{2ca} at POM A, we can state that the change in equilibrator type at POM A in November 2015 did not seem to affect the measured values of CO_{2ca}. At POM 2 CO_{2ca} has slightly lower values, while POM B recorded the lowest values of the three points. This different behavior shows that the CO_2 input via drip water is not similar throughout the cave and suggests that there are either different sources of CO_2 feeding the system or different pathways toward these drip sites. The ventilation event of January 2016 appears

to have slightly affected POM A CO_{2ca} too, indicating that ventilation occurs at some extent on the CO_2 pathway to this site.

The difference observed between CO_{2cw} and CO_{2atm} is also seen between the modeled partial pressure in pool waters ($pCO_{2fw\ model}$) that are considered to be in equilibrium with the cave atmosphere and the modeled pCO_2 of the confined water ($pCO_{2cw\ model}$) calculated using the PHREEQC program (Fig. 12a). Nevertheless, the modeled values of the confined water are different, at times, from those based on the direct measurements ($pCO_{2cw\ measure}$) (Fig. 12b). This might be due to a range of uncertainties inherent from the different physical and chemical measurements of cave waters that were not considered here (e.g.: the determination of hardness or alkalinity by titration or the determination of pH). Using only the measured pCO_{2ca} to calculate pCO_{2cw} limits the intervening errors just to the straightforwardly known measurement error and to that associated with the empirical determination of Henry's law constant.

In support of the robustness of our method there are visible differences in other characteristics of the confined and pool waters. For example, the confined water is always more acidic (Fig.13a). A clear difference is also seen in total carbonate hardness and electrical conductivity, with confined waters having always greater values in both parameters (Fig. 13b and c). These differences could be explained by the higher content of dissolved CO_2.

3.4. Rain and drip water stable isotopes

3.4.1. Rainfall isotopic signature

At Isverna, between September 2014 and June 2016 $\delta^{18}O$ values in precipitation show seasonal variability, between a minimum of -14.68 ‰ in January 2016 and a maximum of -4.75 ‰ in April 2015 (Fig. 14). The weighted average $\delta^{18}O$ and δ^2H values of January-December 2015 are -9.36 ‰ and -62.09 ‰, comparable to weighted annual means derived from GNIP (IAEA/WMO, 2016). During 2015, weighted averages at Drobeta were -8.31 ‰ and -53.56 ‰, respectively. These values are consistent with those measured by Bojar et al. (2017) at Dumbrava, some 60 km SE of Isverna.

The local meteoric water line (LMWL) at Isverna is defined as $\delta^2H=7.7\delta^{18}O + 9.7$, for January - December 2015, and $\delta^2H=7.7\delta^{18}O + 10.1$ for September 2014 to June 2016, an equation similar to the global meteoric water line (GMWL; Craig, 1961). At Drobeta, the 2015 LMWL is defined as $\delta^2H = 7.9\delta^{18}O + 9.5$ and δ^2H excess values varied between 4 ‰ and 16 ‰ (Fig.15a).

While we would expect a Mediterranean contribution to precipitation brought via the winter cyclones (Bojariu and Paliu, 2001), the LMWL equation seems to indicate the Atlantic Ocean as a heavily dominating vapor source. Knowing that the equation of the Mediterranean meteoric water line is $\delta^2H = 8\delta^{18}O + 22$ ‰ (Gat and Carmi, 1987), any mixing of the two sources would modify the LMWL.

The δ^2H excess values fall between 11 ‰ and 15 ‰, outside the range predicted by GNIP and characteristic of a region with enhanced evaporation (Dansgaard, 1964; Gat et al., 2003; Delattre et al., 2015). At Dumbrava (Bojar et al., 2017) and Drobeta they have similar values and variability (Fig. 15b), indicating a regionally consistent setting.

Between August 2014 and August 2016 there were 104 rainy days with at least 5 mm of rain and we modeled the five day back trajectories of the air masses present at our site during these days (Fig. 16). These trajectories appear to fall within four categories: Atlantic, Mediterranean, E European/W Asian and a more local one, not spreading much outside the Carpathian-Balkan region. Nevertheless, it can be seen that some of the East European

trajectories are in fact deflections of Atlantic pathways. Thus, the majority of the air masses arriving at our site during rainy days appears to be of Atlantic origin, with only a restricted number originating or passing over the Mediterranean. As the origin of an air mass is not definitive evidence for the origin of moisture that condensed when it arrives at a site, it is still an indication of the vapor source. We note that it is not within the scope of this paper to detail the exact moisture content of each air mass whose trajectory we modeled, but that it should be the aim of further study. As we see that the Mediterranean was a minor contributor to local precipitation, the evaporative component implied by the δ^2H excess could indicate that rainfall included an important element of recycled moisture over the European land-mass (Aemisegger et al., 2014).

In December 2015 an unusually high $\delta^{18}O$ value of -9.04 ‰ was recorded. Throughout the whole month, we recorded a single rain episode of 6 mm on 01 December 2015. This event started in the afternoon when the air temperature was 12 °C and ended at midnight when temperatures were still as high as 9 °C. The air mass present at our site during this day appears to have travelled through Central Europe, across the Adriatic and into the Thyrrenian Sea, from where it returned to mainland Europe. This complicated pathway makes the air mass prone to accumulate both continental and Mediterranean moisture. We suggest that the high isotopic value is also linked to the abnormally high air temperature for this season that promoted higher continental evaporation and is not representative for seasonal variability.

3.4.2. Drip water stable isotopes

At Ascunsă Cave drip water $\delta^{18}O$ shows almost the same variability at all sites (Fig. 17), but with a muted signal when compared to that of rain water, an indication of a well-mixed aquifer (Riechelmann et al., 2011; Smith et al., 2016). A similar variability is seen in drip water at the Green Lake in Isverna Cave too, although here the values are higher, an expected result of the altitude effect. This gives us confidence that this signal at Ascunsă Cave is not site related and that it is indeed representative for the surrounding area. Drip water $\delta^{18}O$ at the two caves rose in the summer of 2014. For example, at POM2 the 2012-2014 average $\delta^{18}O$ was -10.65 ‰, whereas the following period had an average of -10.19 ‰. Here, the 2012-2016 water line is defined as $\delta^2H = 5.0\delta^{18}O - 16.8$ (Fig. 18a). For the period August 2013 – August 2016, drip water at the Green Lake in Isverna Cave has a water line defined as $\delta^2H = 6.1\delta^{18}O - 5.2$ and δ^2H excess values around 12 ‰ -13 ‰, with an exception in September 2014, when we recorded 7.95 ‰.

The September 2014 values and, at other drip sites, those from August 2014 too, have an outlier character in both $\delta^{18}O$ and δ^2H. On 17 August 2014 we measured values as high as -9.62 ‰ at POM 2, while on 17 September 2014 we measured -9.18 ‰. Compared to the whole δ^2H excess record at POM 2 which runs between 13 ‰ and 16 ‰, their values stand out for being very low (9.5 ‰ and 6.8 ‰, respectively). Such anomalous values, recorded at all drip sites appear to be linked to the advection of air masses from around the Caspian Sea (Fig. 16). For that region, the weighted August and September $\delta^{18}O$ values stand between -6 ‰ and -2 ‰ and the weighted δ^2H excess around 0 (IAEA/WMO, 2016). An enriched moisture source would explain both the $\delta^{18}O$ and δ^2H excess values recorded during these events. After discarding the enriched values of August and September 2014 but also those of March 2015, the ground water line (GWL) at POM 2 is $\delta^2H = 7.9 \delta^{18}O + 13.6$ and δ^2H excess values fall between 13 and 15.5 ‰. At the Green Lake, after discarding the September 2014 values, the GWL becomes $\delta^2H = 8.0 \delta^{18}O + 12.7$.

The September 2014 event, with $\delta^{18}O$ values as high as -8.72 ‰, is replicated in both caves, and follows a high intensity precipitation episode that took place a week prior. At Drobeta it peaked at a total of 157 mm on 14 and 15 September 2014 (Klein Tank et al., 2002), while at Isverna we recorded 104 mm during these two days. The study of these two rain events and their reflection in the cave is interesting from two points of view: first of all it indicates that the transfer time of water from surface to the cave is on the order of days, as also indicated by drip rate response to rainfall. Secondly, the lack of any strong peaks in the drip log at this time could be assigned to the fact that these events did not contribute too much to reservoir recharge, or some of the signal was buffered by the epikarst. At POM 2, a declining trend in drip rate was present before the September event, probably associated with summer drought. On 18 September 2014, three days after the rain event, the drip rate started to rise from 28 drips min^{-1} and peaked two days later at only 31 drips min^{-1}. For comparison, a rain event from 22-23 October 2014 totaling 116 mm produced a rise in drip rate from 21 to 90 drips min^{-1}. This was followed by a long period when drip rates remained above 30 drips min^{-1}.

After discarding the August-September 2014 values, we recalculated the groundwater lines from our drip sites and compared them to the LMWL. From Fig. 18b we can see that they all have intercept values above 10. This could be due to processes that take place after the precipitation reaches the ground, most probably evaporation in the soil/epikarst as observed, for example in semi-arid regions by Bar-Matthews et al. (1996) or Markowska et al. (2014). We can also see that the GWL at the Green Lake inside Isverna Cave is closest to the Isverna LMWL, while all the Ascunsă Cave plot the highest.

3.5.   Farmed calcite stable isotopes

Average $\delta^{18}O$ values of farmed calcite at POM 2 (-8.07 ‰) and POM X (-7.88 ‰) show similar variability throughout the monitored period, with the POM X samples having, in general, higher values (Fig. 19). A large difference between drip water and cave atmosphere pCO_2, as determined at Ascunsă Cave, is a prerequisite for out of equilibrium processes (Hendy, 1971). A slower drip rate, as observed at POM X in comparison to POM 2, would promote longer degassing times, thus increasing the kinetic effects and leading to higher calcite isotopic values (Dreybrodt, 2008). Using the equations of Kim and O'Neil (1997) and Tremaine et al. (2011) we calculated the theoretical $\delta^{18}O$ equilibrium values of the farmed calcite at POM2 and POM X, at 7.2 °C. The input value for drip water $\delta^{18}O$ was considered as the average of samples bracketing the farming period. The measured $\delta^{18}O$ values plot above the Kim and O'Neil (1997) predictions and below those predicted by the equation of Tremaine et al. (2011).

For the deposition period June-August 2014 we used only the drip water $\delta^{18}O$ value at the beginning of the deposition interval and not the average of the samples bracketing the whole period, as the enriched drip water from August 2014 would predict an unreasonable value of -6.77 ‰ / -7.70 ‰.

The POM X $\delta^{13}C$ values appear to be affected too by the slow drip rate and the increased kinetic fractionation that accompanies it. The values are higher than at POM2 and more variable. When compared to the available drip rate recorded at POM2, we see that two low $\delta^{13}C$ values (-10.54 ‰ and -11.03 ‰) occur during periods with average drip rates of 33 and 43 drips min^{-1}, respectively (September/December 2014 and December 2014-February 2015), while a third one (-9.65 ‰), was measured from a period with an average of 13 drips min^{-1} (July-August 2015). Moreover, when POM X $\delta^{13}C$ values are compared with average air temperatures from Drobeta (ECA dataset, Klein Tank et al., 2002), there seems to be a good correlation between the two, except for two periods: November

2012 - February 2013 and August - September 2013. If these two samples are omitted from the calculation, the value of R^2 is 0.74 (p value < 0.05). We note that we also calculated the precipitation amount for the same periods and their correlation with $\delta^{13}C$ or $\delta^{18}O$ is weaker: $R^2 = 0.06$ (p value > 0.05) for $\delta^{13}C$ and 0.35 (p value > 0.05) for $\delta^{18}O$. The same test was applied for POM2 farmed calcite and it returned an R^2 value of 0.05 (p value > 0.05) for

5      $\delta^{13}C$ and 0.14 for $\delta^{18}O$ (p value >0.05).

A direct correlation between calcite $\delta^{13}C$ and outside air temperature is counterintuitive, as common knowledge states that warmer periods are characterized by lower calcite values due to the input of more depleted $\delta^{13}C$ via organic activity (see for example the review of McDermott, 2004). Such a direct correlation could be induced by a full seasonal delay in the transfer time of the surface signal, but this is contradicted by the common variability

10   of $\delta^{18}O$ at both POM 2 and POM X. Besides, as this $\delta^{13}C$ anomaly is not replicated at POM 2, it could mean that it is a process specific to POM X. A likely explanation would be that it is the result of kinetic fractionation during periods with increased pCO_2 gradients between drip water and cave atmosphere, a process further enhanced by low drip rates (Mattey et al., 2010; Mayer et al., 2014). Assuming that higher air temperature is transposed into higher drip water CO_2 via increased organic activity, we calculated, for the periods with available $\delta^{13}C$ data,

15   average air CO_2 at POM 2 as well as the average temperature values from Drobeta. Further, we normalized the resulting values and subtracted CO_2 from temperature. We then plotted the resulting values in Fig. 20, considering that larger differences represent steeper CO_2 gradients between drip water and air, while lower differences represent gentler gradients. We can see that there is good correlation between the two data sets, except for the periods November 2012 – February 2013 and August – September 2013. If these two samples are omitted from

20   the calculation, the value of R^2 is 0.54 (p value < 0.05).

~~While POM 2 and POM X have similar $\delta^{18}O$ behaviors, the POM X $\delta^{13}C$ might prove helpful in extracting information on the past kinetic fractionation strength and its controls: cave air CO_2/ventilation and drip water CO_2/outside temperature.~~

25   **3.6.** Relevance for speleothem paleoclimate studies

Rainfall isotope data presented here show that Ascunsă Cave and its surroundings are nowadays mostly influenced by recycled Atlantic moisture, with a reduced Mediterranean contribution. Nevertheless, by analyzing $\delta^{18}O$ data from stalagmite POM 2, Drăguşin et al. (2014) demonstrated that this stalagmite recorded during the Holocene

30   millennial scale hydrological changes that took place in the Eastern Mediterranean. This suggests that calcite at Ascunsă Cave is continuously deposited under different climate settings, thus making speleothems from this cave useful for the study of past atmospheric circulation (Cruz et al., 2006; Lachniet, 2009). Moreover, the stable microclimate conditions inside the cave indicate that $\delta^{18}O$ values of speleothems are not kinetically altered and are representative for surface climate conditions (Baldini et al., 2006; Dreybrodt and Scholz, 2011).

35   At the same time, when the difference between drip water and cave air pCO_2 is coupled with slow drip rates, it can induce important changes in calcite $\delta^{13}C$ through degassing (Dreybrodt and Scholz, 2011; Riechelmann et al, 2013), as we saw in the case of stalagmite POM X. While POM 2 and POM X have similar $\delta^{18}O$ behaviors, ~~the~~ POM X $\delta^{13}C$ might prove helpful in extracting information on the past kinetic fractionation strength and its controls: cave air CO_2/ventilation and drip water CO_2/outside temperature.

40

4.   Conclusions

We presented here the characteristics of a series of chemical and physical parameters recorded in air, water and modern calcite at Ascunsă and Isverna caves, as a prerequisite for speleothem paleoclimate proxy calibration. Carbon dioxide levels in cave air rose after the warm season of 2014, almost doubling their concentration from around 2000 ppm to about 4000 ppm. Using two specifically adapted types of air/water equilibrators, we were able to determine dissolved CO_2 concentrations in drip water more easily and reliably than using the classical approach which depends on costly chemical analysis. We showed that drip water CO_2 at the three monitored points is always greater than and not as homogenous as in cave air and can reach values as high as 11000 ppm. Our approach opens the way to cost effective logging of cave water CO_2 that could be applied in speleothem science but also in show cave monitoring, where visitors are an important source of CO_2. Moreover, these equilibrators could be used to sample any dissolved gas for concentration or stable isotopic measurements.

Studying monthly collected rain water samples at Drobeta and Isverna, we brought new isotope data from a region scarcely covered by the Global Network of Isotopes in Precipitation (GNIP). The $\delta^{18}O$ monthly values varied between -15 ‰ in winter and -4 ‰ in summer, while the 2015 weighted mean was -9.36 ‰ at Isverna and -8.31 ‰ at Drobeta. These values are comparable to weighted annual means for this region derived from GNIP data. The local meteoric water line is similar to the global one and δ^2H excess values reach up to 16 ‰, much higher than those interpolated from GNIP. Modelling of back trajectories shows that most of the air masses that were present at our site during rainy days are of Atlantic origin, with reduced input from the Mediterranean. This suggests that the elevated δ^2H excess values are mostly the result of Atlantic moisture being recycled over the European continent.

Drip water $\delta^{18}O$ from Ascunsă Cave indicates the existence of a single, homogenous reservoir. Two enriched isotopic events in August and September 2014, as well as drip logging, indicate that water transfer time at Ascunsă Cave is on the order of days, via fracture flow.

Farmed calcite stable isotope analysis showed that the POM 2 site is not visibly affected by kinetic fractionation (as compared to the nearby POM X), making the stalagmite that formed here a good candidate for regional paleoenvironmental reconstruction.

Author contribution

V. Drăguşin designed the study, V. Drăguşin, S. Balan, I. Mirea, L. Tîrlă, M. Vlaicu performed fieldwork, V. Drăguşin and S. Balan designed the water/gas equilibrators, D. Blamart, V. Drăguşin F. L. Forray, I. Mirea, V. Nagavciuc and A. Perşoiu performed isotopic analysis, C. Marin and A. Tudorache performed chemical analysis, V. Drăguşin and L. Tîrlă modeled back-trajectories of air masses, I. Orăşanu performed statistical analysis. V. Drăguşin prepared the manuscript with contributions from all co-authors. The authors declare that they have no conflict of interest.

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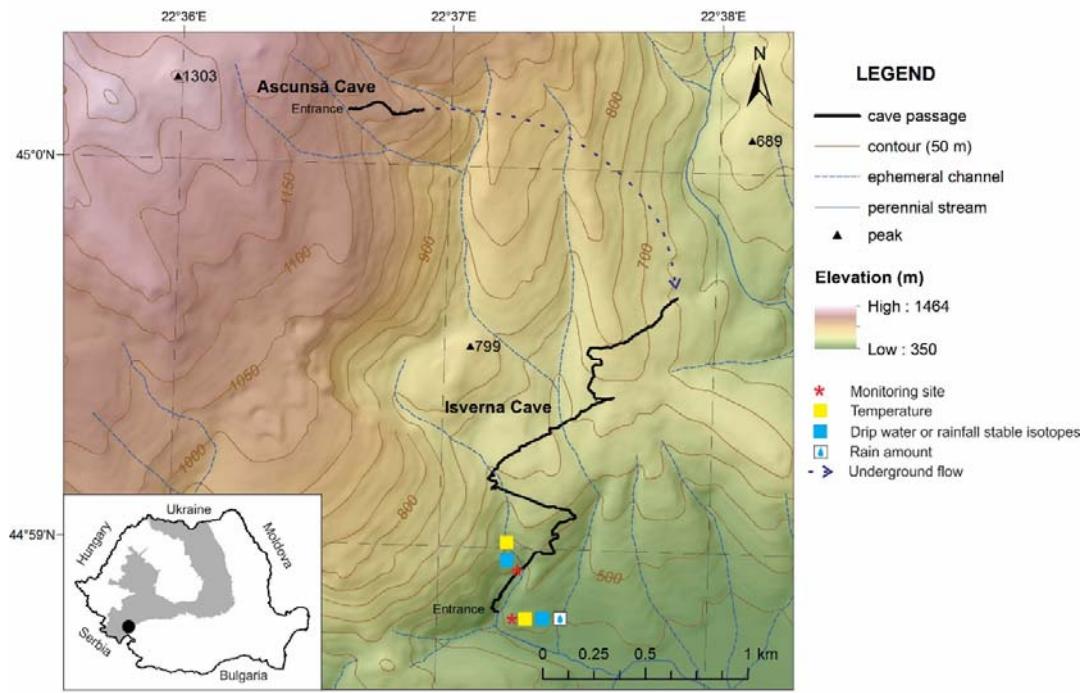


Figure 1. Location of Ascunsă and Isverna caves within the region

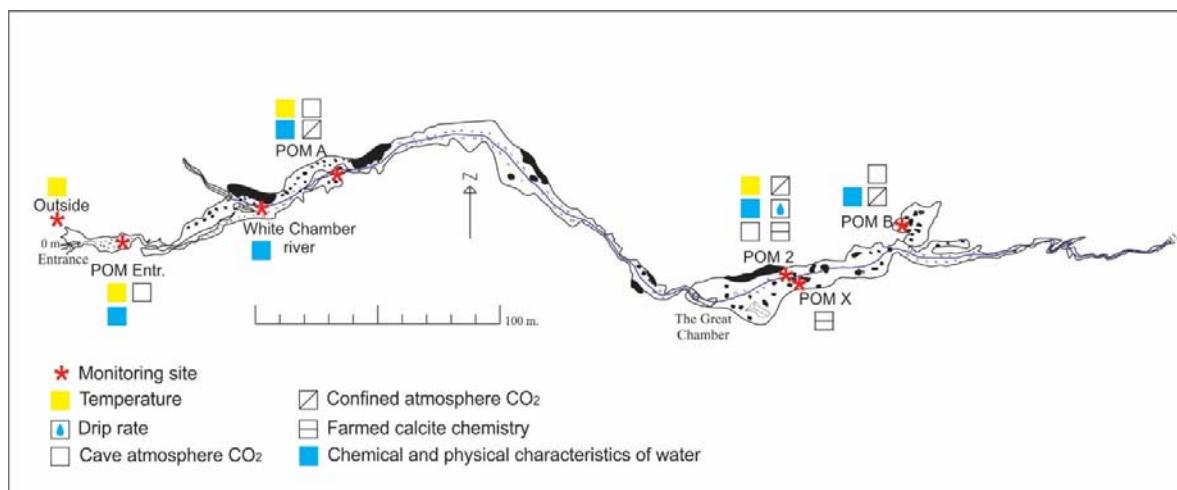



Figure 2. Map of Ascunsă Cave with location of monitoring sites (below).

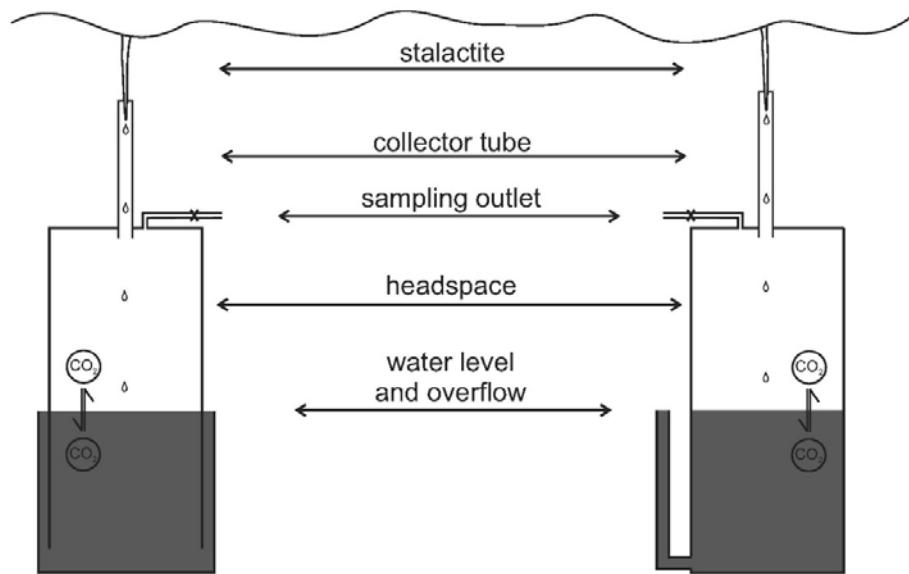



Figure 3. Schematic of the two water/air equilibrators used for

the measuring of drip water CO_2: Type A (left) and Type B (right).

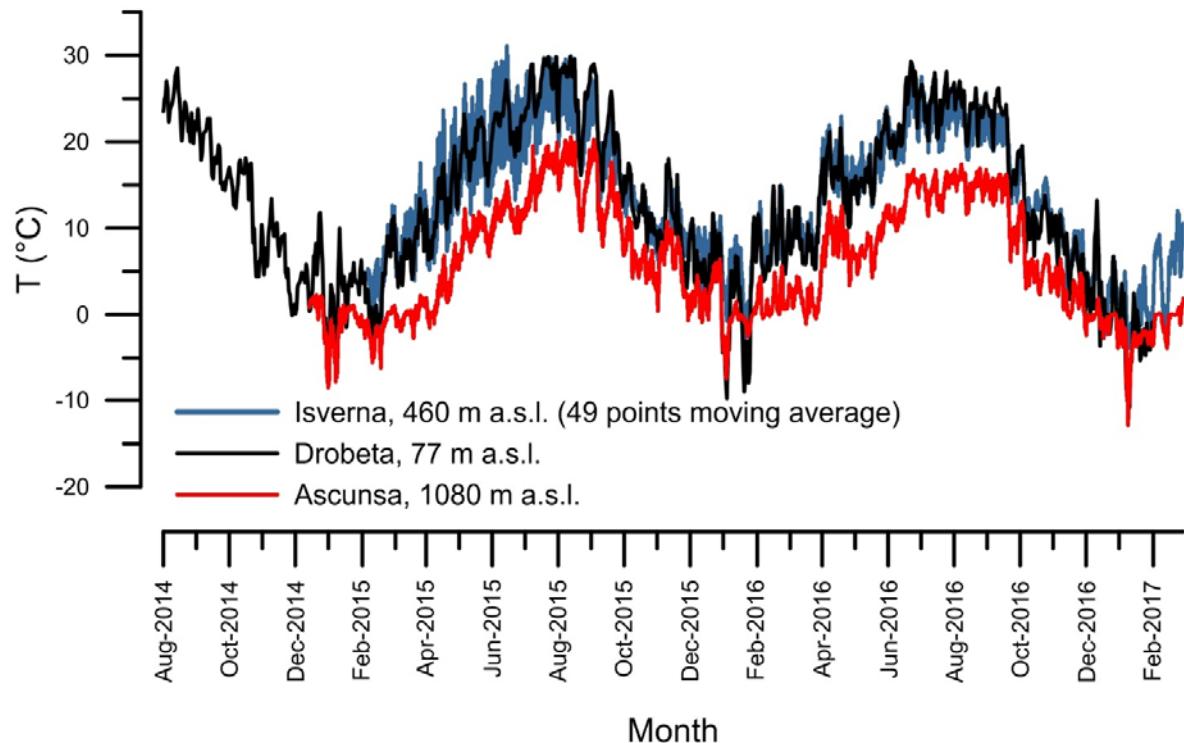



Figure 4. Temperature variability at Ascunsă Cave, Isverna and Drobeta. At Isverna the original data was logged at 30 minutes intervals and we smoothed the dataset using a 49 points moving average.

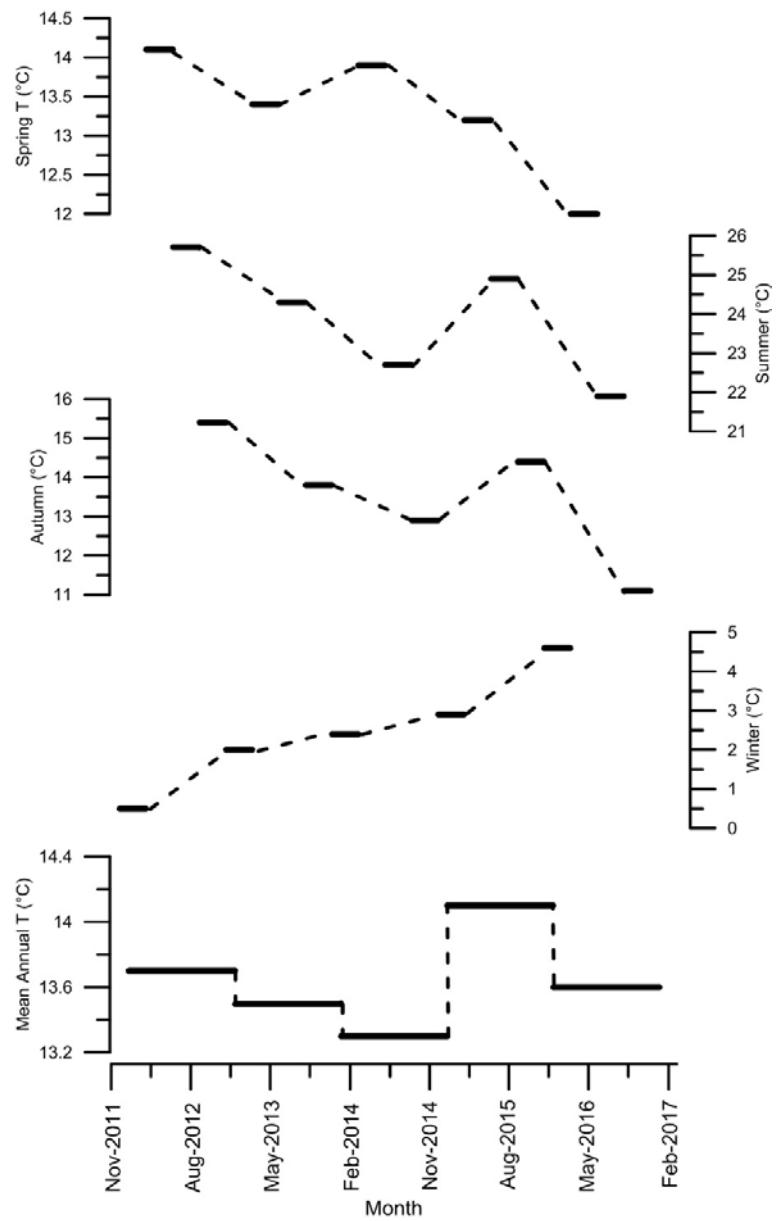



Figure 5. Annual and seasonal temperature averages at Drobeta since 2012.

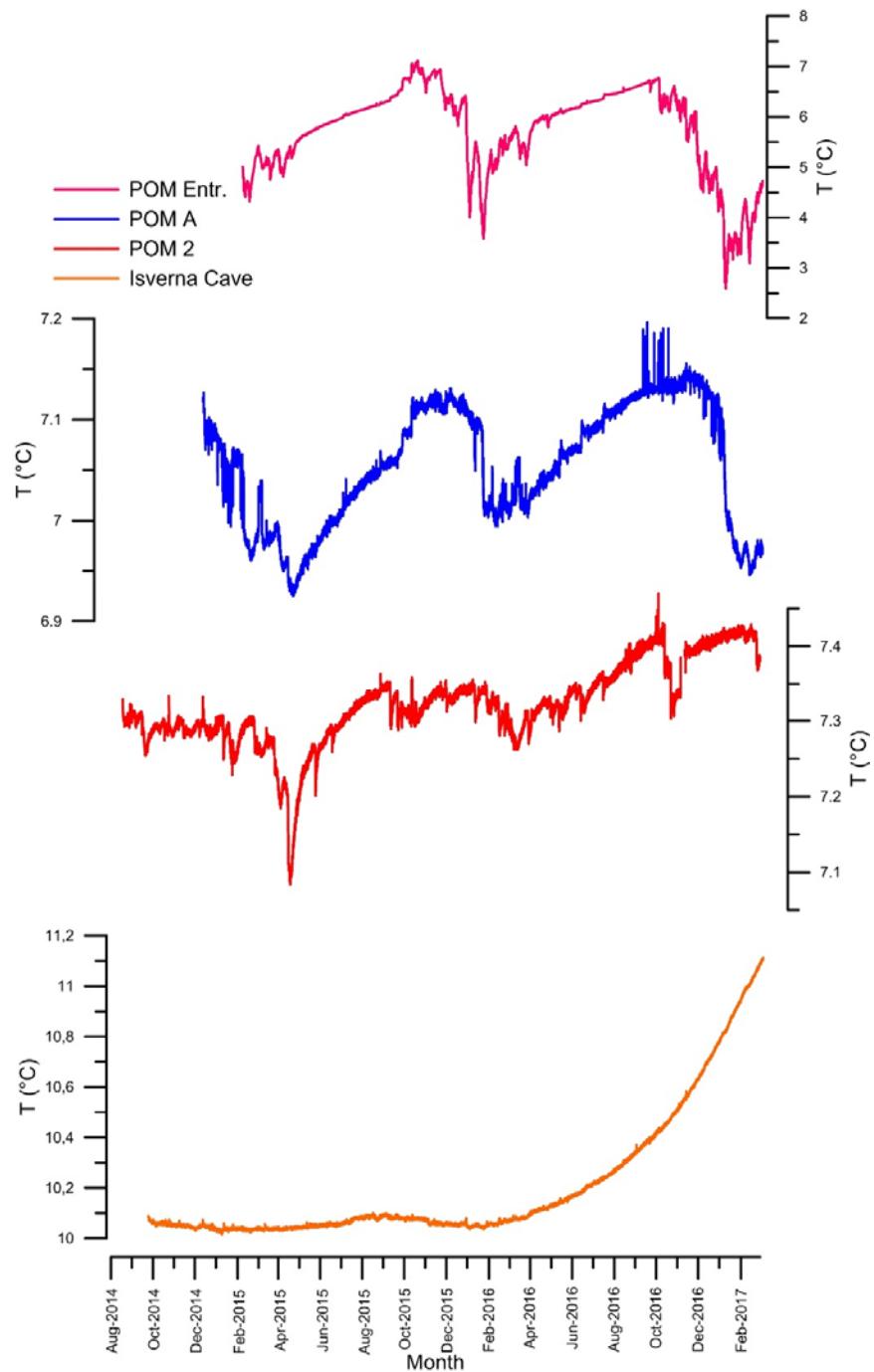



Figure 6. Temperature variability inside Ascunsă and Isverna caves.

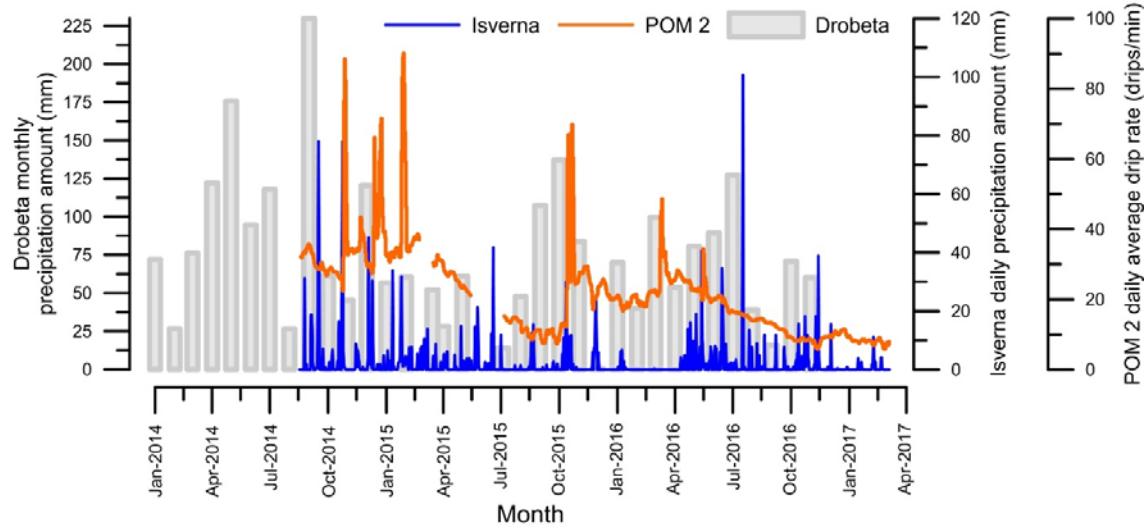



Figure 7. Comparison between monthly precipitation amount at Drobeta, daily precipitation amount at Isverna and POM 2 average daily drip rate.

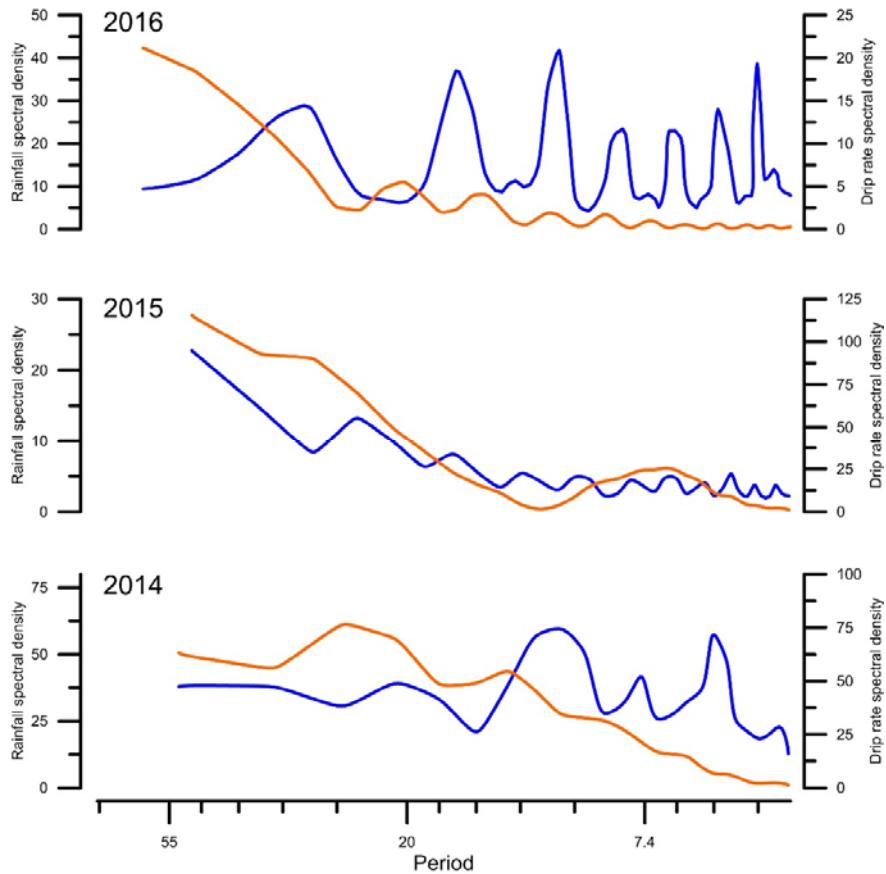



Figure 8. Results of the Fourier transform analysis of daily rainfall amount at Isverna and daily average drip rate at POM 2. For better visualisation, the period axis is expressed in natural log and does not show values higher than 74 and lower than 4.

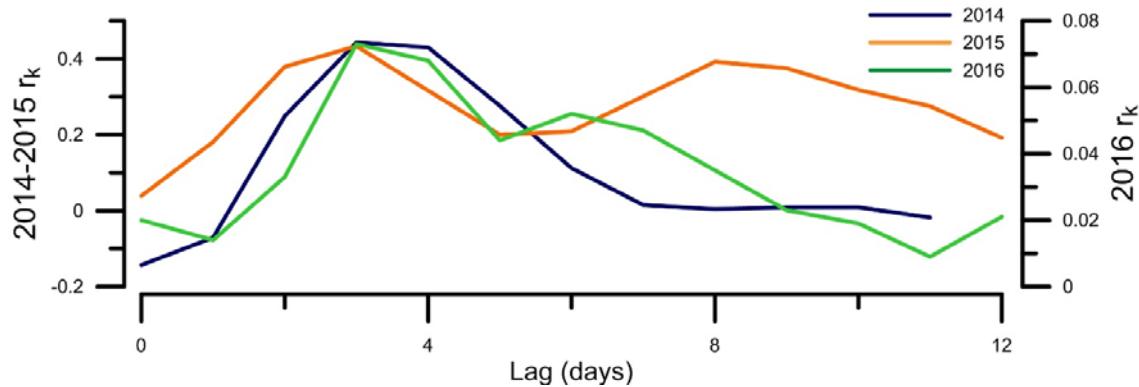



Figure 9. Cross-correlation coefficients between Isverna rainfall and POM 2 drip rate for the three periods analysed. For better visualization, the 2016 values were plotted on a separate axis.

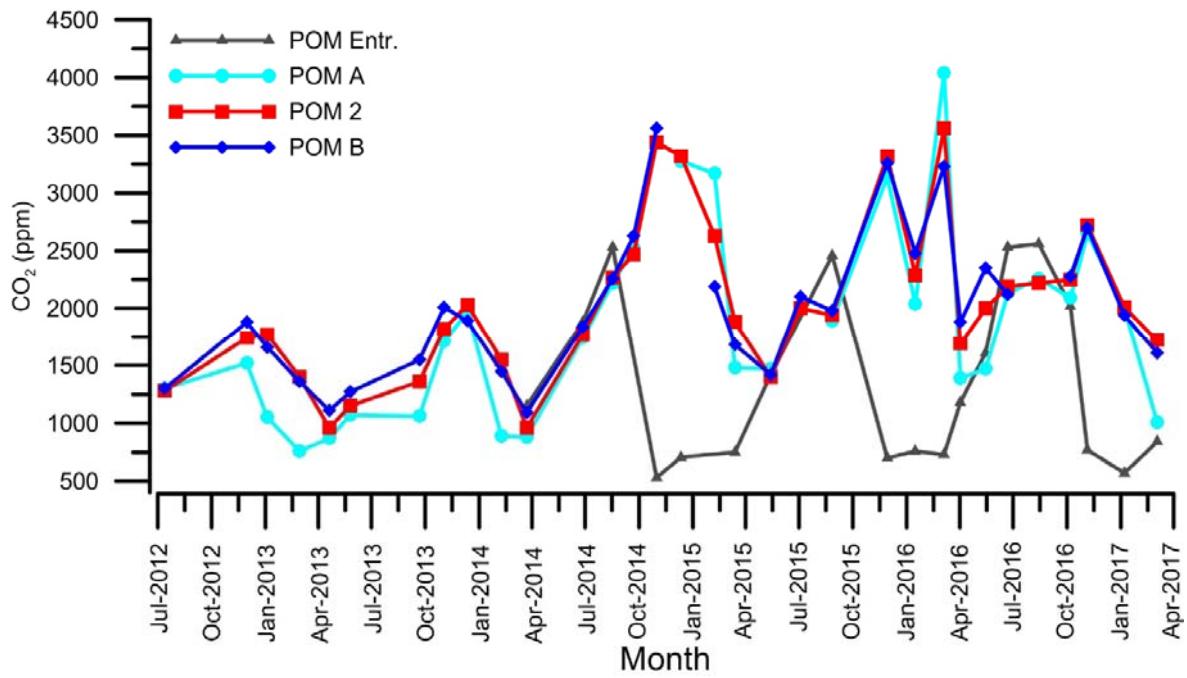



Figure 10. Cave air CO_2 concentrations at Ascunsă Cave.

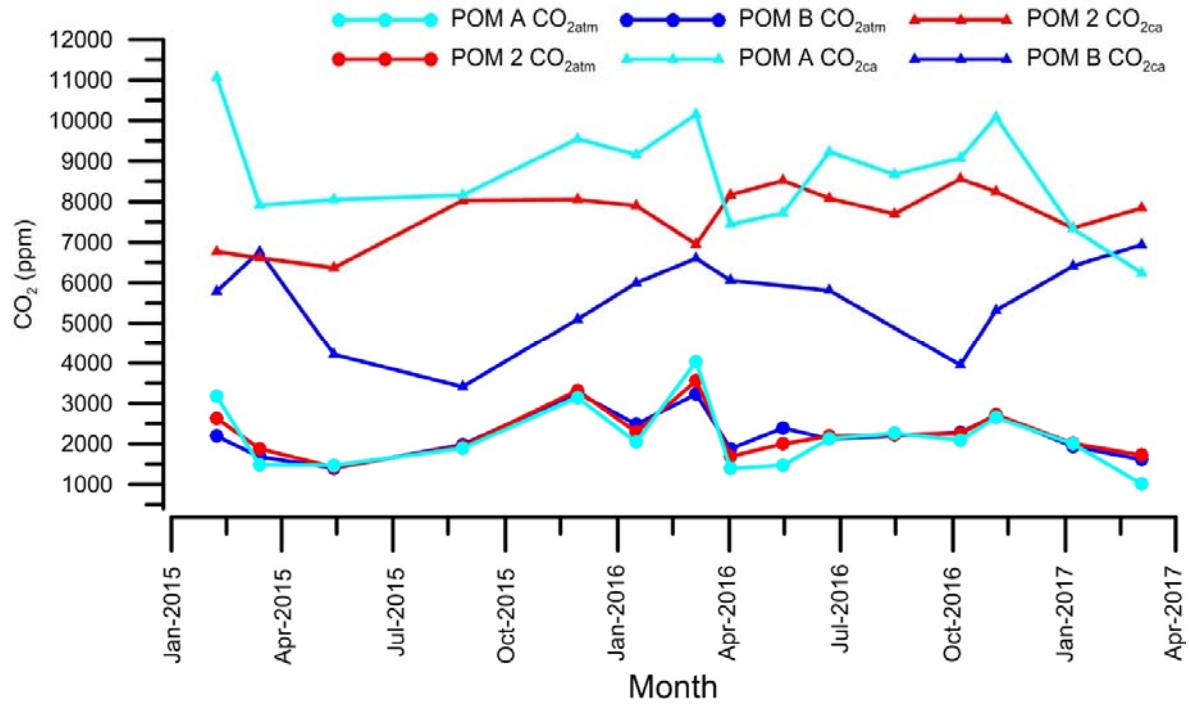



Figure 11. Measured concentrations of CO₂ at Ascunsă Cave in

the free atmosphere (CO₂atm) and in the confined atmosphere of the equilibrators (CO₂ca).

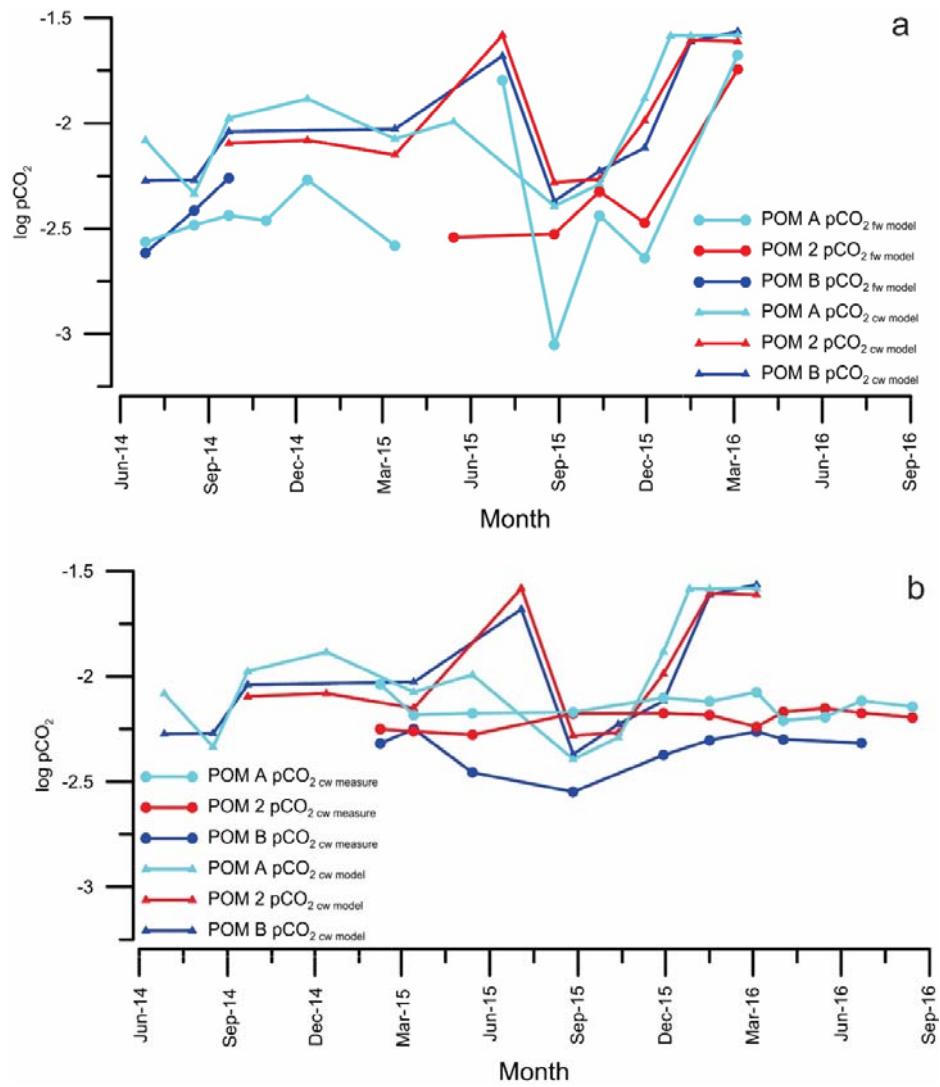



Figure 12. Comparison between (a) $CO_{2fw\ model}$ and $CO_{2cw\ model}$ and (b) $CO_{2cw\ model}$ and $CO_{2cw\ measure}$.

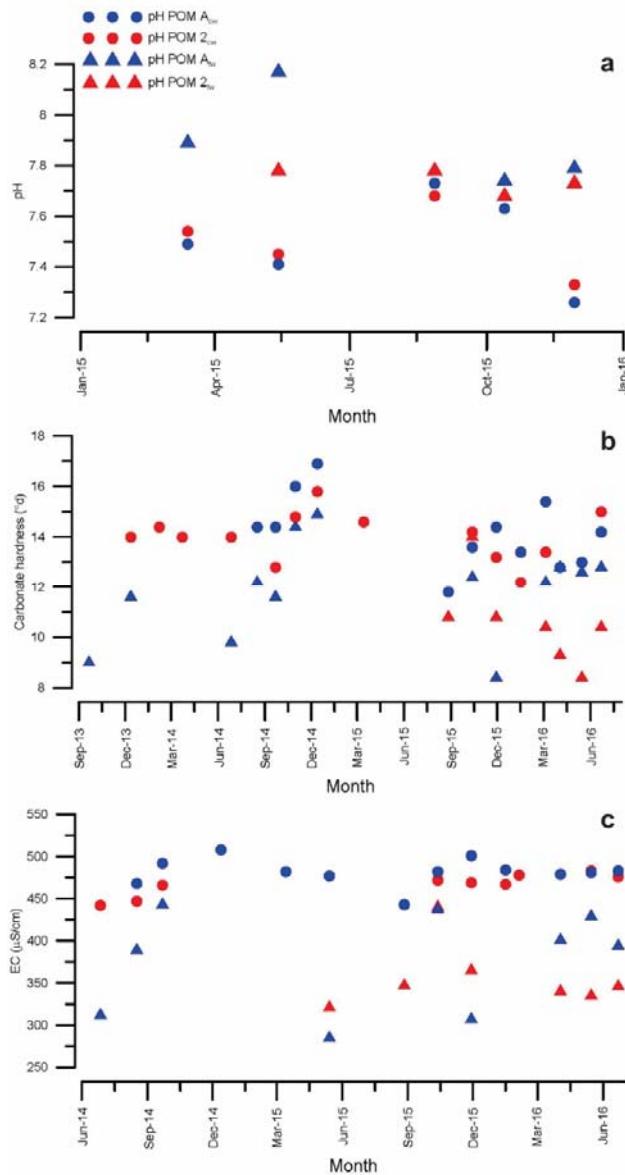



**Figure 13. Comparison between pool and confined waters: (a) pH,
(b) carbonate hardness and (c) electrical conductivity.**

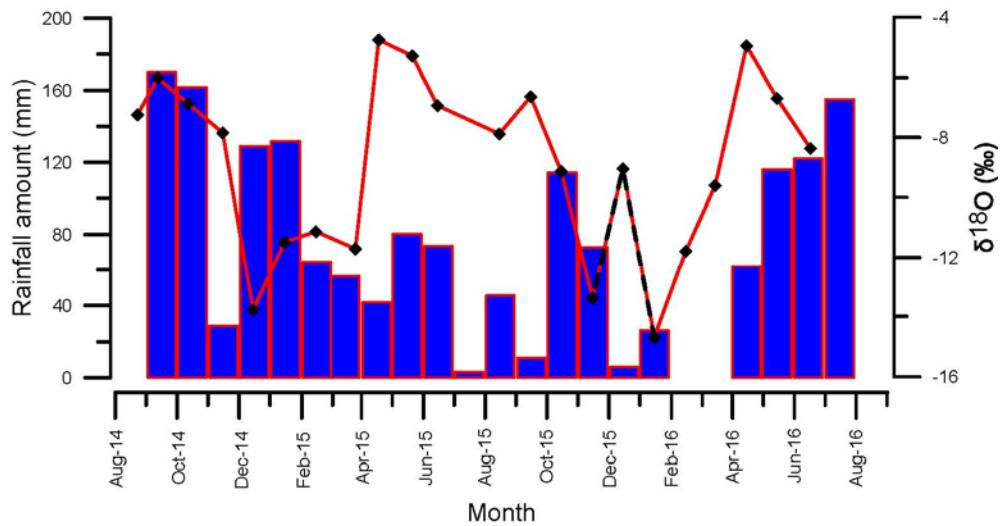



Figure 14. Monthly rainfall amounts and δ¹⁸O values at Isverna. The red-black line highlights the anomalous character of the December 2015 isotopic value.

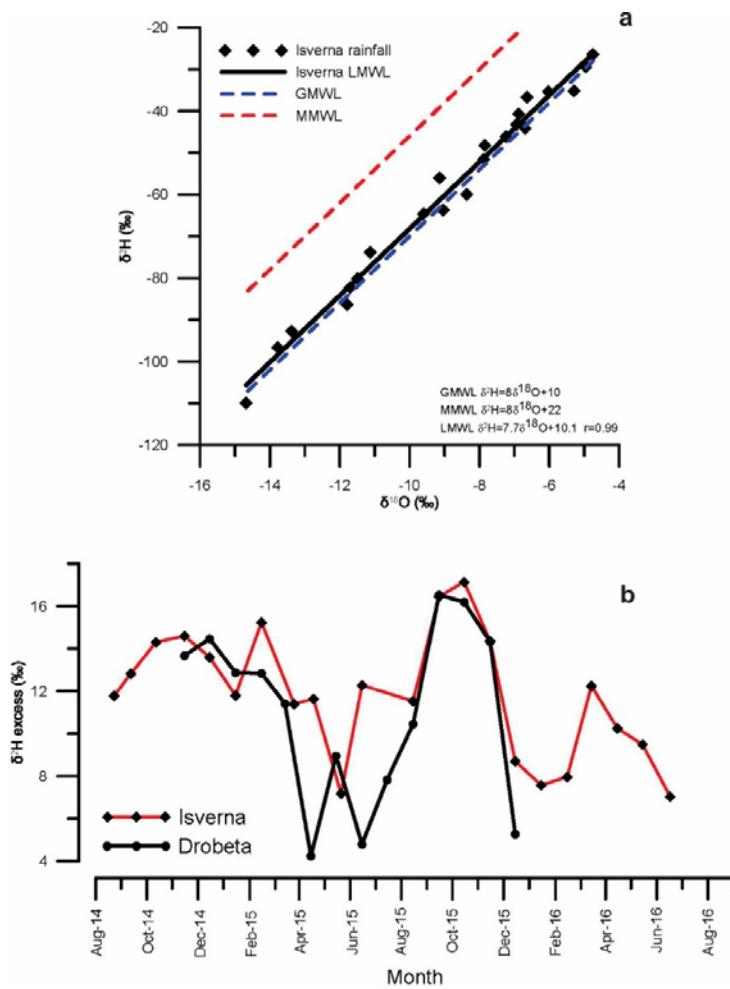



Figure 15. Comparison of (a) the GMWL (Craig, 1961), MMWL (Gat and Carmi, 1970) and LMWL and (b) δ2H excess values at Isverna and Drobeta.

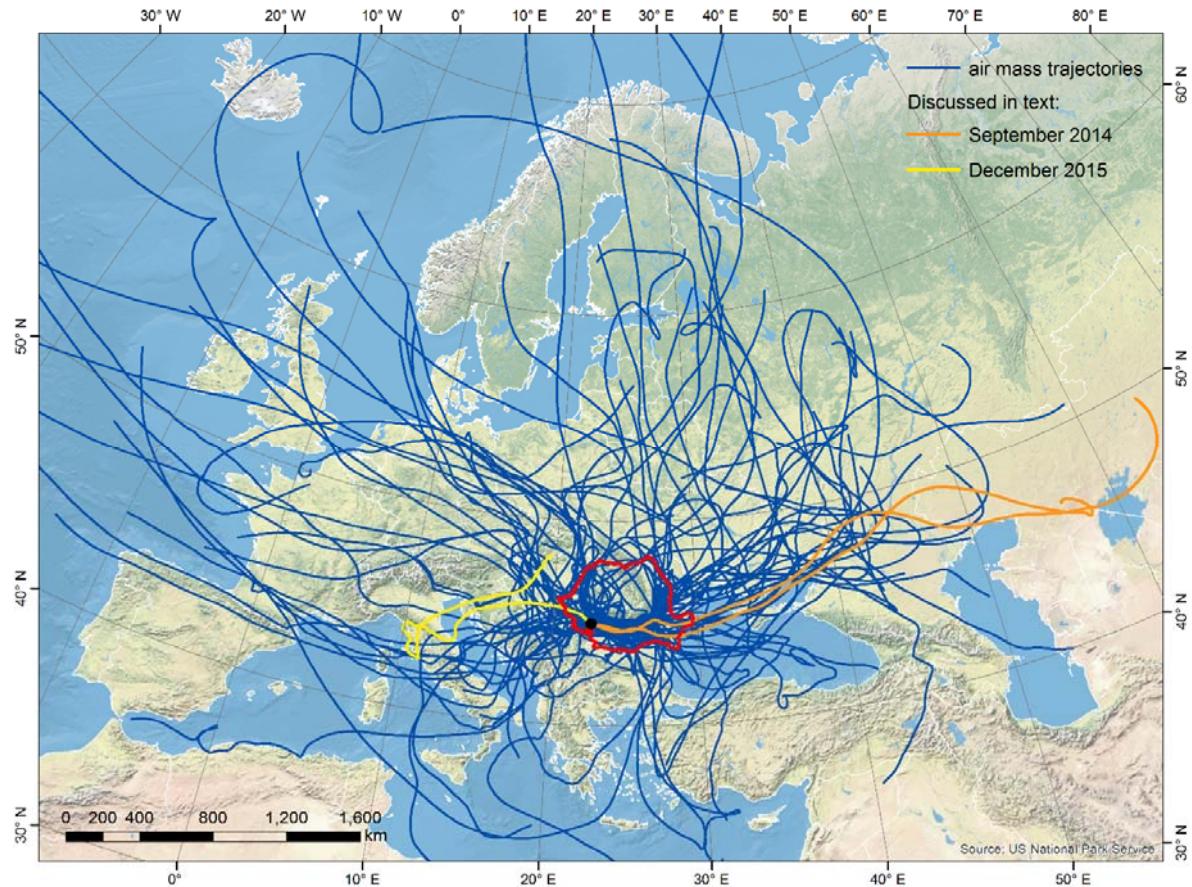
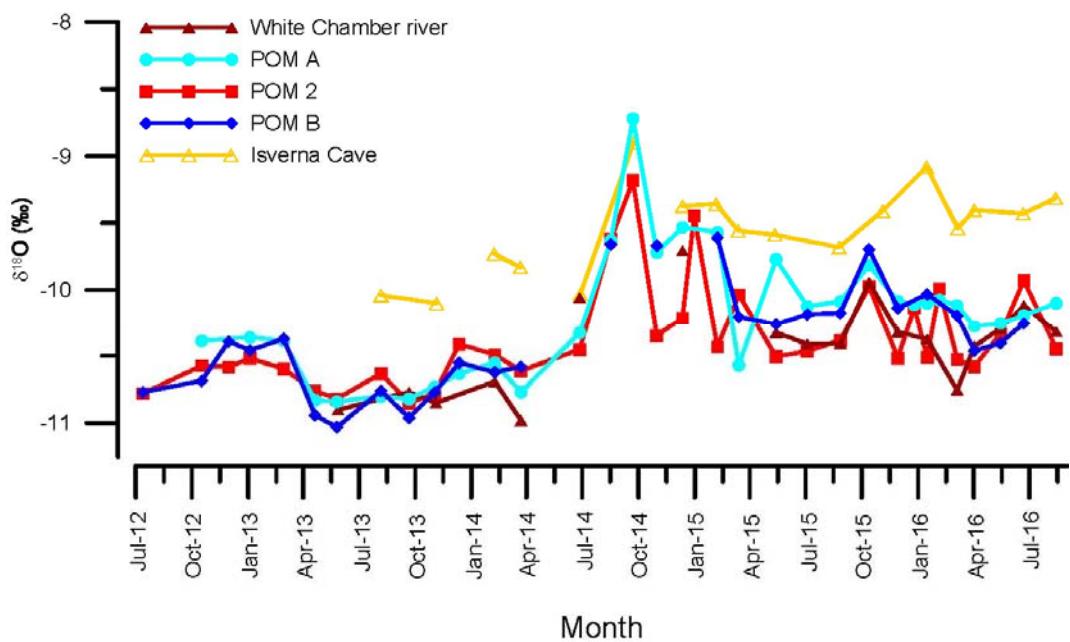



Figure 16. Air mass trajectories reconstructed using the Hysplit 4 model.

 Figure 17. Drip water δ¹⁸O variability at Ascunsă and Isverna caves.

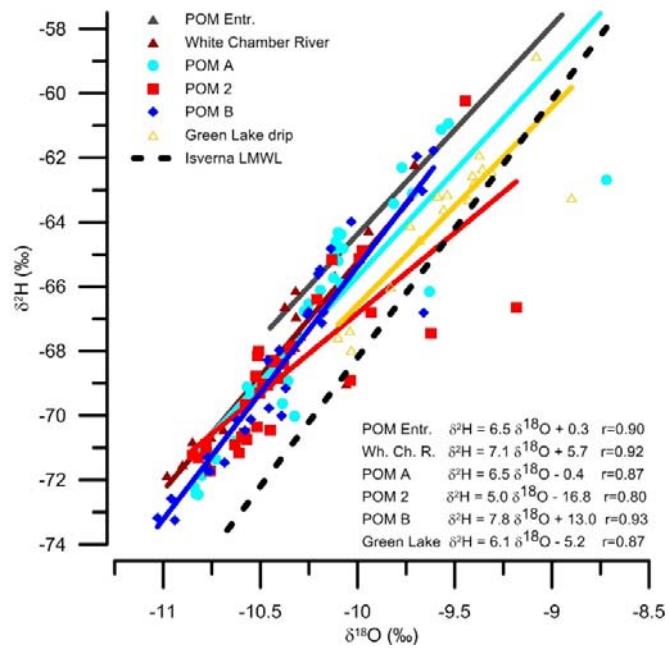
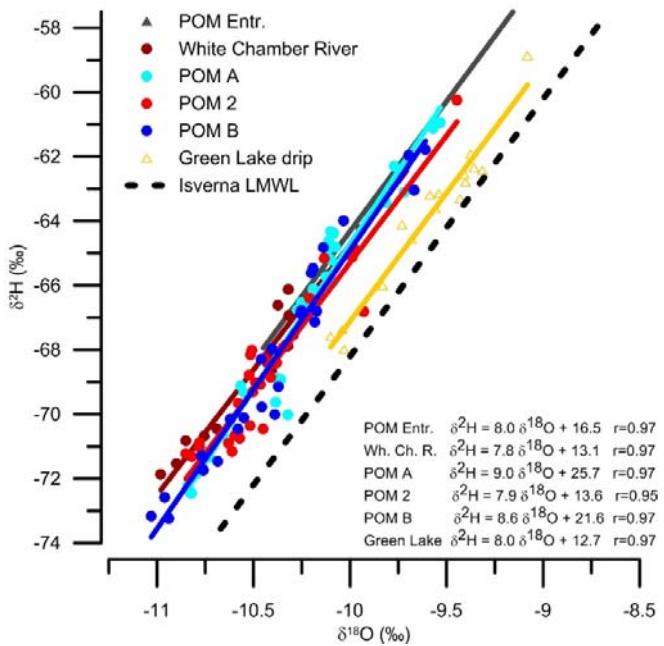



Figure 18. Water lines of drip points from Ascunsă and Isverna caves compared to the Isverna LMWL for the whole monitoring period (a) and after discarding anomalous values (b).

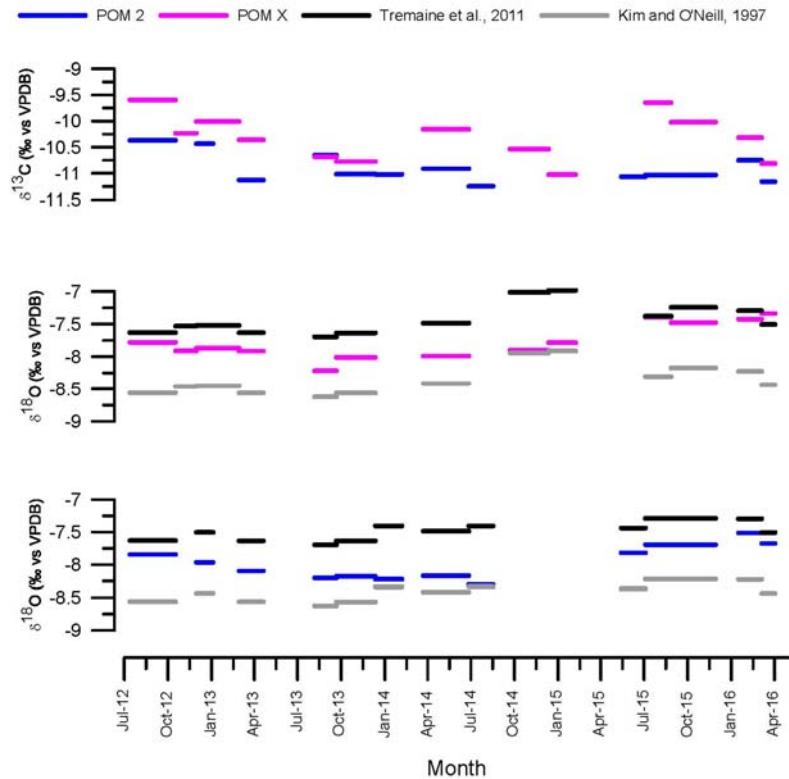



Figure 19. Stable isotope values of calcite farmed at POM 2 and POM X.

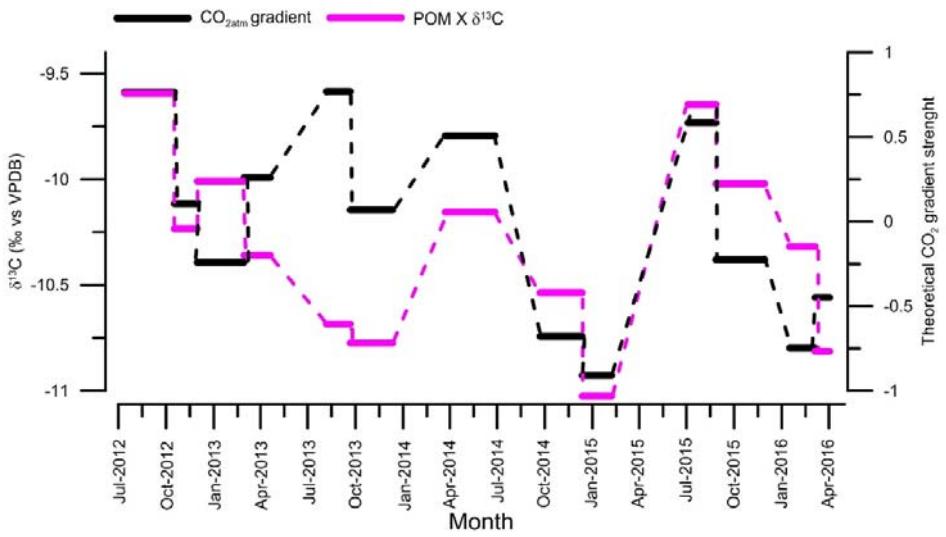



Figure 20. POM X δ¹³C variability and its relationship with degassing gradients.