Abstract
Carbon dioxide (CO$_2$) concentration (CDC) plays an important role in karst processes, governing both carbonate deposition and dissolution, affecting not only natural processes, but also human activities in caves adapted for tourism. Its variations due to various controlling parameters was observed from 2017 to 2021 in two Croatian show caves (Manita peć and Modrič) where we examined inter- and within-cave correlation of internal aerology regarding the sources, sinks and transport mechanism of CDC in a karst conduit setting. In both caves, the main sources of CO$_2$ are: i) plant and microbial activity i.e. root respiration and organic matter decay within soil horizons and fractured epikarst, and ii) degassing from CO$_2$-rich percolation water. The main sink of CO$_2$ is dilution with outside air due to cave ventilation. Chimney-effect driven ventilation controlled by seasonal differences between surface and cave air temperatures shows winter (T$_{out}$<T$_{cave}$) and summer (T$_{out}$>T$_{cave}$) ventilation regime, which are modulated by the geometry of cave passages, the transmissivity of the overlying epikarst, and occasionally by the external winds, especially the gusty north-eastern bora wind. In these terms, the Modrič Cave appears to be more confined and less ventilated, with a substantial CDC difference between the left (550-7200 ppm) and right (1475->10,000 ppm) passages. The Manita peć Cave is, in contrast, ventilated almost year-round, having 7 months of CDC equilibrated with the outside atmosphere and the highest summer CDC values of ~1415 ppm. In both caves, at the current level of tourist use, anthropogenic CO$_2$ flux is not a matter of concern for cave conservation. In turn, in the innermost part of the right Modrič Cave passage visitors’ health might be compromised, but the tourists are allowed only in the left passage.

Sspeleothem growth rate, recognized as a useful palaeoenvironmental proxy for speleothem-based paleoclimate studies, strongly depends on CDC variations, so the high CDCs recorded in the Modrič Cave indicate the potential periods with no speleothem deposition due to the hampered degassing of CO$_2$ from the dripping groundwater. The opposite effect i.e. enhanced ventilation (that supports calcite precipitation) during the windy glacial/stadials, as well as substantial vegetation changes must also be taken into consideration when interpreting environmental records from speleothem calcite.

Keywords: show cave, CO$_2$, cave ventilation, anthropogenic impact, Croatia

1. INTRODUCTION
Caves are natural underground voids formed predominantly by the dissolution of soluble (mostly carbonate) bedrock and they act as natural windows to the Earth’s Critical Zone (ECZ). The ECZ is a relatively thin, but extremely heterogeneous zone that extends from the bottom of the groundwater body to the uppermost parts of the surface vegetation in which life can be sustained by coupled chemical, biological, physical and geological processes (BRANTLEY et al., 2007) and which is most exposed to environmental changes. The natural functioning of this system is strongly regulated by climate and associated hydrological and vegetational changes which can be reliably archived within speleothems (REGATTIERI et al., 2019). Therefore, speleothem-based research is increasing globally (COMAS-BRU et al., 2020), complemented by the monitoring of cave properties such as hydrogeology, hydrogeochemistry, microclimate, cave air composition, etc., the understanding of which is essential for the appropriate interpretation of the palaeoenvironmental signals recorded in speleothem carbonate.

Although it is just a trace gas in the atmosphere (416.49 ppm in May 2021, NOAA accessed on 30 August 2021), CO$_2$ plays an important role in the overall Earth system, especially when misbalanced from the natural state. On an incomparably smaller scale, CO$_2$ in cave air is, in an underground environment, also important and interesting for its various sources, sinks and effects that occur with or without human interaction. Generally, CO$_2$ partial pressure is one of the most important factors that controls both carbonate dissolution and speleothem deposition (DREY-BROD'T, 1999) and the understanding of CO$_2$ distribution and dynamics in the underground is essential for various aspects of cave science including the aforesaided speleothem-based palaeoclimate studies (BALDINI et al., 2008; COWAN et al., 2013; GREGORIČ et al., 2013). Cave air CO$_2$ concentration (CDC) is controlled by dynamic equilibrium between different CO$_2$ sources and sinks and their competing influences depending on both spatial and temporal particularities of the cave environment. The main natural sources of underground CO$_2$ are: i) diffusion of CO$_2$-rich air generated by root respiration and organic matter decay transmitted from the soil through the joints and fissures, ii) degassing from the groundwater which was enriched by CO$_2$ on its way through the soil and epikarst, iii) biological productivity i.e. decomposition (micro-organisms feeding on organic matter, usually guano) within the cave, and iv) deep-seated (thermal) geogenic sources (BALDINI et al., 2008; FAIRCHILD & BAKER, 2012; PRELOVŠEK et al., 2018). In addition to the aforementioned natural sources, show caves may receive extra...
anthropogenic CO₂-flux from visitors breathing (e.g. DRAGO-VICH & GROSE, 1990; LINÁN et al., 2008). The most substantial sinks of cave air CO₂ are: i) ventilation i.e. dilution of the CO₂-rich cave air with relatively CO₂-poor outside air, and ii) uptake by groundwater i.e. CO₂ dissolution in under-saturated cave water (COWAN et al., 2013).

Elevated cave air CDC, increased either naturally or anthropogenically, may affect the cave environment in several ways. First, when percolating groundwater (in which CO₂ is controlled predominantly by soil ρCO₂) reaches the air-filled voids, equilibration with lower ρCO₂ cave air occurs and degassing of CO₂ can cause calcite precipitation from the water saturated with respect to calcite (HOUILLON et al., 2017). However, elevated ρCO₂ in cave air can hamper degassing of CO₂ from the dripping groundwater resulting in either the absence or cessation of calcite deposition (BALDINI et al., 2006; 2008). Second, cave air CO₂ dissolved in water condensed within the cave produces carbonic acid which may dissolve bedrock or already crystallized speleant calcite, a process known as condensation corrosion (DUBLJANSKY & DUBLJANSKY, 1998; FAIMON et al., 2006; BALDINI et al., 2006; GABROVŠEK et al., 2010). Thirdly, high cave air CDC values are related to health issues, so already a CDC of 5000 ppm is regarded as the occupational exposure limit (ILO, 2006), and it must be considered for all visitors in show caves, including tourists, guides, cavers and scientists. The majority of caves have elevated CDCs, usually in summer, which in some cases reach extremely high values, such as ~14,000 ppm in the Romanian Ursišlo Cave (CONSTANTIN et al., 2021), ~22,000 ppm in Galleria das Láminas, Portugal (BENSON et al., 2021), ~35,000 ppm in Béke Cave, Hungary (CZUPPON et al., 2018), ~31,000 ppm in District Park Cave and ~38,000 ppm in Natural Bridge Caverns in the USA (COWAN et al., 2013), even up to >44,000 in Chauvet Cave (BOURGES et al., 2020) and ~60,000 ppm in Causse d’Aumelas (BATJOT-GUILHE et al., 2007) in France. In Croatia, the first records of elevated CDC were published by MALEZ (1954) and BOŽIČEVIĆ (1966), and afterwards numerous occurrences of high CDC have been reported by cavers, but systematic monitoring began only in 2016 within 5 show caves in the continental part of Croatia (BOČIĆ & BUZJAK, 2018).

Here, we present the first results of multi-year monitoring of the cave environment aimed at estimating spatial and temporal variations of cave air CDC in two show caves located in the coastal zone of the Dinaric karst in Croatia – the Manita peć and Modrič caves, both considered to be small and simple caves with relatively low numbers of visitors. The obtained data sets enabled us to: i) reveal cave ventilation dynamics in order to detect possible seasonal speleothem growth patterns crucial for palaeoenvironmental studies; ii) estimate the anthropogenic contribution to the cave CO₂ background levels and potential effects on the cave interior, and iii) assess the possible health hazard for the visitors from an elevated CDC.

2. STUDY SITE

The Dinaric karst in Croatia is characterized by relatively high mountain ranges (up to 1831 m) stretching parallel to the coast, one of which is Velebit Mountain – the host of the two studied caves. Modrič Cave is located in its foothill at 32 m a.s.l., while the entrance of Manita peć Cave is at 570 m a.s.l., on the side of the canyon perpendicular to the mountain range (Fig. 1). Given their geographical position and geological settings, some specific meteorological features (e.g. bora events) are expected to influence the cave atmospheres i.e. ventilation.

The Modrič Cave (44° 15’ N, 15° 32’ E) is situated 120 m from the shoreline on the SW slope of the central part of Velebit Mountain. The cave is formed within a 2.5 km wide fault zone, in well-bedded Upper Cretaceous limestone (MIKO et al., 2002), and consists of two, mostly horizontal, passages with a total length of 829 m and a single narrow entrance (KUHTA et al., 1999). Overlying bedrock is 1-27 m thick and vegetation cover above the cave is sparse trees, bush and grassland. Soon after its discovery in 1985 and an initial topographic survey, Modrič Cave came to the attention of various scientific disciplines and has since become one of the most investigated Croatian caves (SURJČ, 2018). Palaeontological research of Quaternary vertebrate faunal remnants (MALEZ, 1987; AGUILAR et al., 2004) was followed by a thorough speleological and geological survey and partial geochemical and hydrogeological investigations (KUHTA et al., 1999); the geochemical aspect was focused on sediments, percolating water and bat guano influences (MIKO et al., 2001; 2002). Because the cave has been open for adventure tourism since 2004, radon activity in the cave air was occasionally monitored (BUZJAK et al., 2010; SRSEN, 2019). For the purpose of palaeoclimate reconstruction, thorough microclimate monitoring, along with speleothem and dripwater stable isotope analyses, were conducted in several campaigns from 2003 onwards (SURJČ et al., 2010; 2017; 2020; RUDZKA et al., 2012).

The Manita peć Cave (44°18’ N, 15°28’ E) is located on the steep flank of the Velika Paklenica canyon carved perpendicularly into the Velebit Mountain. It is a simple, 175 m long, descending spacious chamber formed in Upper Jurassic limestone, with a height up to 38.5 m and total volume of 67,510 m³ (KUHTA, 2010). The overburden is up to 80 m thick and heavily fractured. Ground surface cover is sparse patches of terra rossa, shrubs and grass. Scientific interest for this cave had already begun in 1900 with the first biospeleological investigation, followed by geological and speleological surveys in 1929, which also included preliminary notes on its microclimate and hydrogeology. Due to its rich speleothem formations, in 1937 it was adapted for visitors with construction of the first pathway and a new artificial entrance (Action Plans National Park Paklenica, 2007). In the following decades the cave has been the site of occasional environmental research projects, one of which was the monitoring of radon activity in the cave atmosphere (RADOLIČ et al., 2012). This was fundamental for assessing the health and safety of visitors and guides. Although both caves are open for visitors, there is a significant difference in the approach to touristic management between them. Modrič Cave is available for individually arranged visits year-round, but the peak numbers of visitors occurs between April and October, with an annual maximum of 727 visitors in 2019. Organized as an adventure tour with caving equipment, visitors in groups of up to 30 people spend approximately 1.5 to 2 hours within the left passage of the Modrič Cave. Manita peć Cave operates as a “classical” show cave with guided tours and no need for special equipment. According to the current timetable, during the summer (July, August, September), Manita peć Cave is open every day, then three days a week through the late spring and early autumn (May, June, October), finally in April only one day per week. It is closed for visitors during the winter season, except for organized groups on demand. In order to minimize anthropogenic impact, it has been open just for 4 hours per day. A maximum of ~13,000 visitors per year was reached in 2017. The usual visiting time in Manita peć Cave is up to 30 minutes for groups of 25-30 visitors.
3. METHODS

Monitoring of cave air CDC was conducted in Modrič Cave from March 2017 to March 2021 in the right passage and from July 2018 to March 2021 in the left passage. In Manita peć Cave CDC monitoring covered the period between January 2018 and March 2021. Measurements were performed on a monthly basis using a 7755 AZ Handheld CO₂ & Temperature & Relative Humidity Meter (CO₂ range 0-9999 ppm; resolution 1 ppm; accuracy ±50 ppm or ±5% of reading (0-2000 ppm); air temperature range -10-60 °C; resolution 0.1 °C; accuracy ±0.6 °C). The measurements were carried out at the beginning of each month, on the same day in both caves. Along with regular monthly monitoring, CDC was measured on several occasions before and after tourist group visits (usually 20-30 people) in spring and summer, to assess anthropogenic impact on the cave air properties. Eight measurement points were established in Manita peć Cave, and 7 in Modrič Cave, distributed at approximately even distances from the entrance to the innermost parts, with additional measurement points in front of each cave (Figs. 1c &1d).

Additionally, in the Modrič Cave’s right passage, air temperature and relative humidity were also continuously recorded (1-hour intervals) using Onset Hobo® PRO-V2 U23-001 data loggers (T range -40 to 70 °C; accuracy ±0.25 °C from -40 to 0 °C; ±0.2 °C from 0 to 70 °C; resolution 0.04 °C; RH range 0 to 100%, accuracy ±2.5% from 10% to 90% RH, ±5% <10% or >90% RH, resolution 0.05%). External temperatures and precipitation data were obtained from the Croatian Meteorological and Hydrological Service (CMHS) for the station in Starigrad Paklenica (ca. 4 km SW of the Manita peć Cave and ca. 9 km NW of the Modrič Cave) for 1992-2018: a) air temperature and precipitation; b) difference between precipitation and potential evapotranspiration (Croatian Meteorological and Hydrological Service /CMHS/, 2021); c) east-facing entrance of Manita peć Cave and the plan with measurement points; d) north-facing entrance of Modrič Cave and the plan with measurement points. Water balance (potential evapotranspiration) was calculated using the Thornthwaite evapotranspiration model (THORNTHWAITE, 1948; MCCABE & MARKSTROM, 2007).
km SE from Manita peć Cave and ca. 8 km S from the Modrič Cave) was used instead. Both stations share similar topographic location and climate properties, so no significant changes in data representativeness are expected.

4. RESULTS

4.1. Spatio-temporal variations of the cave air CO\(_2\) concentration

Spatial and temporal variations of Modrič Cave air CDC are presented in Fig. 2 and the complete data set is provided in Tab. 1A in the Appendix. At the first measurement point M00 in front of the cave, during the period between March 2017 and March 2021 we recorded CDCs from 350 ppm to 590 ppm. Cave air CDC of the main passage measured at points M11 and M22 varied between 412 ppm and 6868 ppm; similar to that in the left passage, values between 480 ppm and 7228 ppm were recorded at points T13, T14 and T15. Meanwhile, along the right passage, at measurement points M31 and M32, the CDC range was from 994 ppm to >10,000 ppm (i.e. it exceeded the measurement limit of instrument).

Spatio-temporal variations of cave air CDC in the Manita peć Cave between January 2018 and March 2021 are given in Fig. 3 and in Tab. A2 in the Appendix. The first measurement point (MP 01) was ~100 m away from the cave entrance at the most exposed part of the mountain slope, at the lookout, and provides values of the outside CDC, while point MP 02 was at the very entrance of the cave, right in front of the gate bars with a CDC range of 339-664 ppm (Fig. 4). The remaining measurement points (MP 03 – MP 09), which were distributed evenly along the descending channel, had CDC values ranging between 325 ppm and 1415 ppm.

Temporal variations of CDC in both caves are seasonal, with the highest values in summer/autumn, and the lowest during the winter/spring, which is the opposite of natural atmospheric CDC fluctuations (Pearman & Hyson, 1981). Namely, due to the phytoplankton bloom and plant photosynthesis in the warmer part of
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the year, CO$_2$ is absorbed from the atmosphere, so the CDC in the northern hemisphere decreases, while in autumn decaying plants release their CO$_2$ back into the atmosphere, which along with elevated fossil fuel consumption leads to an atmospheric CDC increase. Surprisingly, the CDC variations in the surface air in front of our studied caves at M00 and MP 01 do not follow that pattern. Instead, they coincide with in-cave CDC variations, as demonstrated in Fig. 4, showing the influence of the in-cave environment on the nearest surroundings.

4.2. Visitor numbers and their impact on cave air CO$_2$ concentration

The total annual numbers of visitors in the caves are given in Figs. 5a and 5c, and the monthly distribution of the Manita peć Cave visitors is presented in Fig. 5b. The highest annual values reached in 2017 and 2018 are due to the prolonged working hours (4 hours per day instead of 3 hours) of Manita peć Cave, and the sudden decrease of visitor numbers in both caves is a direct response to the COVID-19 pandemic.

Measurements of CDC before and after groups of tourists were conducted in spring and summer season at the sites where the visitors pause for the sightseeing or explanations, and the results are given in Table 1. During the spring season, the increase of CDC measured immediately after the groups was 14-22% and 20-28% for Manita peć Cave and Modrič Cave, respectively. However, due to the relatively low initial CDC, absolute values after the visitors are still within safety limits. High CDCs in the summer season remained after the visitors at similar levels, ~1250 ppm in Manita peć Cave and ~5100 ppm along the left passage of Modrič Cave. The exception was measurement point MP03 in Manita peć Cave with an increase of 66% (from 740 ppm to 1230 ppm), but due to its location near the entrance, the CDC probably quickly reduced to the previous values.

5. DISCUSSION

Distribution and variations of cave CO$_2$ are controlled by an interplay of different sources and sinks and their spatial and temporal evolution, which are in the case of Modrič and Manita peć caves, relatively simple. There are no underground rivers or geogenic sources of CO$_2$, and in-cave decomposition of organic matter does not play an important role, since there are no large de-
posits of organic matter such as guano. The main factors controlling CDC are transport of CO$_2$-rich air from the soil horizon and epikarst, along with CO$_2$ degassing from drip water, and its dilution by the external CO$_2$-poor air, i.e. cave ventilation (EK & GEWELT, 1985). Cave ventilation dynamics follow several patterns controlled predominantly by seasonal temperature variations, cave morphology, and potentially by anthropogenic CO$_2$-flux, while the ventilation itself is mainly triggered by differences between outside (T$_{out}$) and cave air (T$_{cave}$) temperatures (SPÖTL et al., 2005; BALDINI et al., 2006), and wind (RIECHELMANN et al., 2019; KUKULJAN et al., 2021). These particular features are discussed below.

5.1. Impact of cave morphology and epikarst structure on spatial CDC variations

Substantial differences between the Modrič and Manita peć cave morphology are depicted in their cross sections (Fig. 6). Modrič Cave is almost horizontal except for the small descent near the entrance, and a short ascent at the beginning of the right passage. Although relatively similar in dimensions, the two passages differ by their accessibility. Along the left passage during the winter time, there are only small variations of CDC, with values <100 ppm higher that those outside the cave (Fig. 7a). Similarly, CDC values are also relatively evenly distributed in the summer-autumn season (Fig. 7b), which is likely caused by unobstructed movement of the air through the left passage due to its larger dimensions compared to the right one. In the right passage, CDCs are substantially higher both during the warm and cold seasons, and spatial variations are more pronounced. The entrance section of the right passage (after M22) is only slightly ascending, but obviously enough to prevent or at least mitigate the inflow of the cool outside air during the cold season. Additionally, the more diverse morphology of the right passage with several smaller chambers connected by narrow corridors makes this passage more constrained. An abrupt increase in CDC occurs ca. 50 m inside the passage, which is in accordance with the findings of BALDINI et al. (2006) and MILANOLO & GABROVŠEK (2009) who generally recorded such sudden increases in CDC right after constrictions in their studied caves.

There is another difference in the spatial distribution of CDC between the two passages in the Modrič Cave. The left one has evenly distributed either summer (higher) or winter (lower) CDC values throughout the whole passage, while in the right passage the CDC values increase towards the end (Fig. 7). This partially reflects the structure of the overlying bedrock, which is apparently more fractured, and hence easily ventilated, due to the fault zone along the left passage. The sets of small stalactites and sodastraws in the second part of this passage additionally point to the matrix porosity (FAIRCHILD & BAKER, 2012) of that part of the cave and can be regarded as a macrofissural network cf. BOURGES et al. (2006), defined as fissures of less than 1 mm aperture which transfer both rainwater and CO$_2$-rich soil air towards the cave. Conversely, the bedrock of the right passage is more compact, or maybe even sealed by the spelean carbonate which is also reflected in more homogeneous drip rates, sometimes unresponsive to surface rain events (SURIĆ et al., 2018). The apparent differences of the atmospheric regimes in the relatively similar passages underline that the volume of the critical zone involved in the control of in-cave atmosphere is much larger than the volume of the underground chambers and includes also the voids of the surrounding karstified bedrock (BOURGES et al., 2006).

On the other hand, the Manita peć Cave consists of one large descending chamber that begins with two relatively large openings (1.7×2.5 m and 1.3×2.0 m), and the height difference from the entrances to the lowest point of the cave is 35 m. In addition, heavily fractured overlying bedrock detected in some places by the immediate rain fracture-flow infiltration (SURIĆ et al., 2017),
enables considerable air circulation via epikarst. Given the fulfilled prerequisites for significant ventilation, the spatial variations of CDC remain relatively minimal, particularly during the winter when cold air descend into the cave and CDC values within the cave are practically equal to the external ones (Fig. 8a). Summer spatial CDC variations are also relatively small (the maximum recorded value was 1415 ppm), specifically when compared to those in Modrič Cave. For the summer CO₂ distribution, the vertical dimension of the cave plays the leading role, with the inflow of the outside air being obstructed by the cold and dense air trapped at the cave bottom. This phenomenon has already been identified in the Manita peć Cave by the pocket of cold air having a year-round stable temperature of 9.0 °C (1σ=0.4 °C), while the external mean annual air temperature (MAAT) in front of the cave was 13.7 °C (2014-2015) (SURIĆ et al., 2017). Such a stable thermal stratification during warm periods in aerodynamically closed cold trap systems has been discussed in e.g. BOURGES et al. (2006), LUETSCHER et al. (2008), MILANOLO & GABROVŠEK (2009) etc.

5.2. Temporal controls of the cave air CO₂ concentration

Temporal variations of CDC given in Tabs. A1 and A2 and presented in Figs. 2 and 3 point to the strong seasonal mode in both studied caves. Given the constant air cave temperature, during the warm season the cave air temperature is lower than outside, and during the cold season the situation is the opposite. Correlation between ΔT (Tout − Tcave) and CDC implies that air temperature differences govern the air density gradients between the outside and cave air and also control air exchange i.e. ventilation (FAIRCHILD & BAKER, 2012). Studies conducted in caves with a comparable temperature regime and morphology in Germany (Bunker Cave; RIECHELMANN et al., 2019), Puerto Rico (Cueva Larga; VIETEN et al., 2016) and Bosnia and Herzegovina (Srednja Bijambarska Cave; MILANOLO & GABROVŠEK, 2009) revealed the same driving mechanism of seasonal CDC variations; that is ventilation driven by an air density gradient between external and cave air. Such circulation is known as a chimney effect, usually ascribed to the caves with two or more entrances at different altitudes (FAIRCHILD & BAKER, 2012). During the summer, warm surface air enters the cave via an upper entrance, cools down and with increased density it descends and emerges at a lower entrance as cold cave air. In winter time, cold dense outside air inflows through the lower entrance, warms up and, because it is less dense, appears at the upper opening (SPOTL et al., 2005). Despite the fact that our studied caves have only one passable entrance, the chimney effect can be attributed to them, particularly to the Modrič Cave since it has only 2-30 m overburden thickness of faulted and heavily fractured limestone bedrock, which practically acts as an upper entrance. Therefore, we identified two ventilation regimes and associated CDC variation patterns:

- summer: with Tout>Tcave – warm surface air on its way through the epikarst is enriched by CO₂, downdraft occurs and cool cave air flows outwards from the caves, as proven by measured elevated CDC in front of the caves (Fig. 4).
- winter: with Tout<Tcave – cool CO₂-poor outside air flows into the cave and decreases CDC within the caves, leading even to the complete equalization of CDC throughout the whole Manita peć Cave for seven months (Fig. 3).

Variations of temperatures and CDCs shown in Figs. 9 and 10 provide an insight into the periods of transition between Tout>Tcave and Tout<Tcave considered to be crucial for the behaviour of the cave CDC (LIÑÁN et al., 2018), additionally modulated with some site-specific features related to the geometry of the caves, wind etc. Generally, such thermal convective instability (BOURGES et al., 2006) with changes in cave air CDC was argued to occur rapidly and at precisely the time when the difference in temperature between the surface and cave air reverses sign (FRISIA et al., 2011). However, in the Postojna Cave it was shown that reversal from updraft to downdraft airflow occurs even while Tcave is more than 10 °C higher than Tout (KUKULJAN et al., 2021). In the Modrič Cave, in autumn when Tout drops below Tcave the decreasing trend of the CDC closely follows that of the Tout, apparently due to the strong inflow of the dense external CO₂-poor air into the cave. However, spring conversion displays an evident lag of the CDC peaks behind Tout maximum (Fig. 9). This might be because biological activity (the main driving mechanism of the CDC increase) increases more slowly than the temperature, which is particularly the case with deciduous plants which take time to grow leaves in the spring. The highest CDCs (>10,000 ppm) were recorded during the late summer of 2019 which was the coolest summer between 2017–2020, but the long-lasting warmth with above-average precipitation in July (CMHS, 2021) obviously triggered intensive biological activity inducing the CDC increase.

The aforementioned impact of different morphology of the left and right passage in the Modrič Cave is also evident when considering temporal variations in CDC distribution. Namely, the sudden drop in CDC values recorded in the left passage during the autumn/winter transition period (e.g. November and December 2018) with CDC values decreasing from >5000 ppm to 500-600 ppm (Fig. 9 & Tab. A1) coincides with the drop of the...
T_{out} below T_{cave}, which usually occurs during October and November and triggers the inflow of the CO$_2$-poor outside air into the cave. At the same time, the decrease of the CDC in the right passage is much smoother as values drop from ca. 5000-6000 ppm to 3000-4500 ppm owing to the right passage’s tight spots preventing the rapid inflow of cooler outside air, but also because of apparently more compact bedrock and therefore reduced outflow.

The transition between higher summer and lower winter CDC values in the Manita peć Cave (Fig. 10) is governed by both the chimney effect and the cold trap responsible for the cave’s site-specific temperature regime. The cold trap is present during most of the year, so T_{out} remains below T_{cave} only relatively briefly during the winter (December to February/March). Still, the innermost part of the cave retains unchanged CDC until May/June when T_{out} increases to approximately 15-17 °C (Fig. 10). Presumably, because of the large volume of that part of the cave (cave ceiling is ca. 30 m high), it takes a longer time for the CDC to increase. Also, the surface above the cave is over 600 m a.s.l., so increased biological activity in the soil lags behind that on the surface above the Modrič Cave.

5.3. Impact of specific meteorological events

Occasionally, ventilation can be further modulated, and more rapid changes in CDC values are expected during specific meteorological episodes such as strong winds (RIECHELMANN et al., 2019; KUKULJAN et al., 2021) and intense precipitation events (BOURGES et al., 2020). Modrič and Manita peć caves have northward- and eastward-facing entrances, respectively, exposed to the north-eastern bora – a gusty downslope windstorm characteristic for the eastern Adriatic coast (GRISOGONO &
BELUŠIĆ, 2009). During the bora episodes, which are particularly frequent in March (e.g. IVANČAN-PICEK & VUČETIĆ 1990; COLUCCI & PUCILLO 2010), we observed, anecdotally, three in a row, chimney circulation is disturbed in the Modrič Cave and surface air is pushed into the caves through the fractured bedrock due to the pronounced barometric high. Similar reversed airflow is recorded in the Postojna Cave during the strong NE wind with gusts of >10 m/s (KUKULJAN et al., 2021). If airflow is not measured, such events can be distinguished by sudden decreases of cave air relative humidity, as recorded in March 2015 in Manita peć and two other adjacent caves (SURJIĆ et al., 2017). An immediate lowering of CDC can be revealed by continuous daily measurement as it was conducted e.g. in Bunker Cave during the strong southern winds (RIECHELMANN et al., 2019), while our monthly measurement registered only the slight decrease of CDC after the onset of the warm season increase (5/2017, 4/2018, 5/2019, 3/2020) (Tab. A1). Impact of the south-eastern scirocco wind was not perceived, but probably might be instrumentally measured, similar to the Postojna Cave where the southern wind increases the winter updraft (KUKULJAN et al., 2021). In fact, these reversal and/or amplifying effects can occur in all seasons, but the predominant chimney effect can be overridden only by the strongest wind gusts (KUKULJAN et al., 2021). This secondary wind-induced ventilation may have ramifications for speleothem record interpretation when it comes to dry and windy glacial periods in which summer high CDC could have been suppressed, enabling speleothem precipitation.

An opposite effect, i.e. an increase of CDC, may be related to intense precipitation that increases groundwater infiltration in the cave, which in turn elevates the CO₂ concentration through degassing from the drip water (HOULLON et al., 2017; BOURGES et al., 2020). Although two extreme rain events occurred during the monitoring period (daily precipitation of 229 mm on 11 Sept 2017 and 151 mm on 5 Jun 2020), increased CDC values were not observed during the monthly visit. This implies that short-term rain (and infiltration) events do not affect CDC on a monthly scale in terms of consequent growth cessation, particularly when site-specific settings of the aquifers are considered. Stalagmate® drip logger data point to a wide range of flow regimes (BAKER et al., 1997), from an immediate response due to fracture flow in the Manita peć Cave (SURJIĆ et al., 2017) to practically unresponsive homogenised drip rates in the right passage of the Modrič Cave (SURJIĆ et al., 2018).

5.4. Influence of visitors on cave CDC and/or the opposite impacts

Any human presence in the caves can elevate air temperature, relative humidity and dust content in the air, as well as disturb its chemical composition which can all potentially threaten speleothem formation. Upon cessation of the use of open fire and acetylene lighting in show caves (in Modrič Cave it was part of an adventure offer until 2015), breathing remains the only direct human influence on the cave air chemical composition. In exhaled human breath, CO₂ concentration is ~20,000-58,000 ppm (BYRNES et al., 1997), and in specific circumstances in the caves, it appears to serve as a high-concentration source of CO₂ (PRELOVŠEK et al., 2018). Individual production, i.e. CO₂ exhalation rate, depends on a person’s age and physical activity. Some estimated and calculated values are: 0.2-1.2 L CO₂ min⁻¹ person⁻¹ (DRAGOVICH & GROSE 1990), 0.39 ± 0.11 L CO₂ min⁻¹ person⁻¹ (FAIMON et al., 2006) and 0.35-0.45 L CO₂ min⁻¹ person⁻¹ (MILANOLO & GABROVŠEK, 2009). The contribution of CO₂ from human breathing (ΔCO₂) can be calculated by the expression (1) (PRELOVŠEK et al., 2018):

$$\Delta CO₂ = J_A \times t \times n_v / V_{est}$$

where ΔCO₂ is change of CDC due to the exhalation (in ‰), J_A is CO₂ production (exhalation) rate (in L CO₂ min⁻¹ person⁻¹), t is the residence time of the visitor (in minutes), n_v is number of visitors, and $V_{est}$ is estimated volume of the cave/Passage (in m³).

In the Manita peć Cave, with its relatively short working hours, in August there are only ~130 visitors per day (2020 not taken in account due to COVID-19 pandemic), and with their average residence time of 30 minutes in the total cave volume of 67,510 m³, they contribute to the overall CDC with 12-26 ppm per day. Seasonal peak attendance in the Modrič Cave is 30 visitors per day and their trip takes place in the left passage, roughly estimated at 10,000-13,000 m³ of total volume. During the 2-hour tour, their contribution to the natural CDC is approximated to 55-162 ppm, which is six times higher than in Manita peć Cave. Both of these estimations are calculated with a theoretical absence of ventilation. A similar increase of 5.6 to 28 ppm per adult-equivalent person per hour was measured in the Grotta di Ernesto (FRISIA et al., 2011). Our calculated values corroborate the measurements given in Tab. 1 and reflect prudent management of both caves in the sense of environmental protection.

An opposite effect, i.e. the impact of high cave air CDC on visitors, can be expected in summer since the high tourist seasons coincides with the period of the elevated naturally occurring CO₂ (Figs. 2a, 3 and 5b). In the Manita peć Cave, the highest recorded CDC value of 1415 ppm has no influence on visitors, as that is around the level commonly reached indoors, but values that occur along the Modrič Cave tourist path are already 20-25 times higher than those of the outside atmosphere. Luckily, CDC peaks are reached only in September, after the tourists’ peak in August. Potentially harmful CDCs >10,000 ppm that can cause increased respiratory rate, respiratory acidosis, metabolic stress, increased brain blood flow and increased minute ventilation (AZUMA et al., 2018) have been recorded in the right passage which is only of scientific interest and not visited by tourists. However, there is an additional health risk in that part of the cave. It relates to the radioactive gas radon which is emitted from the deeper Earth’s crust without any surface input. According to preliminary observation (SRŠEN, 2019), given its good correlation with CDC, and dependence of its concentration exclusively on dilution with surface air, we may expect potentially dangerous values during the summer season in the right passage.

5.5. Potential impact of long term natural and anthropogenic environmental changes to the surface on speleothem-based palaeoclimate interpretation

Contemporary vegetation cover that consists of scrubby Mediterranean maquis-like plants has been subject to permanent natural, and more recent human-induced, changes that result in pro- or degradation of the soil horizon and plant density – the main source of CO₂ in our studied sites. On decadal to centennial scales, the earliest anthropogenic impact manifested by enhanced erosion due to deforestation can be detected in marine sediment from Modrič Bay back to 1715 cal BP, with maximum at 160-265 BP (HASAN, 2017). Velebit woodlands across the wider region experienced drastic changes, as they were overused during the 16th-17th c. not only by the Venetians, Habsburgs and Ottomans (ŠTEFANEK, 2000), but also by the growing local population
(RUKAVINA, 1990). This also coincided with the Little Ice Age with increased demands for firewood (KUŽIĆ, 1999). Under the French government starting at 1805, and with ameliorated climate conditions, erosion and/or deforestation declined (HASAN, 2017). Organized reforestation began in the late 19th century (KASER, 1987) and was intensified during the ban on goat breeding in 1954-1982, but the recovery has been relatively slow. Evident changes of vegetation cover on the decadal scale have been documented by aerial photography (Fig. 11). Bare karst scenery that dominated in 1959 and 1973 was partially changed by planned reforestation (recorded in 1989), followed by natural (and occasional anthropogenic) forestation during the last three decades. Each of these soil or/and vegetation alterations might have left an imprint in CO2-controlled speleothems growth rate.

Going farther back into the past, beyond human interference, climate changes at the centennial to millennial scale controlled environmental settings in terms of temperature and/or humidity variations and hence cave ventilation, which, in turn, forced or ceased speleothem precipitation. Throughout the glacial periods, commonly regarded as cold, dry and windy, in ice-covered and some periglacial regions, speleothem deposition completely ceased (BAKER et al., 1995; LOWE & WALKER, 1998). This was due to the lack or negligible input of pedogenic CO2 into the karst system because of the absence of a soil cover (SPÖTL et al., 2006; LI et al., 2021). However, that was not the case in littoral Croatia, as evidenced in currently submerged speleothems that precipitated during the Last Glacial Maximum (SURIĆ & JURACIĆ, 2010), and particularly in speleothems from the Manita peć Cave where sufficient pedogenic CO2 sustained karst processes, including speleothem deposition, throughout the last glacial cycle (SURIĆ et al., 2021). Presumably, the possibility of growth cessation caused by a diminished gradient between pCO2

Figure 11. Natural and anthropogenic environmental transformations on the surface above the Modrić Cave between 1959 and 2020. Modrić Cave plan is given in red.
in drip water and cave air was compensated by enhanced wind activity (WACHA et al., 2013; DURN et al., 2018; KOVACIČ et al., 2013) which promotes cave ventilation (RIECHL-MANN et al., 2019). As for the past interglacials, likewise today, growth interruptions due to enhanced biological activity, elevated CDCs and hindered degassing have been possible in the Modrič Cave. Given that the potential growth cessation occurs only seasonally, the winter signal may dominate in other speleothem climate-related properties and proxies driven by CO₂-flux, as well (GENTY et al., 2001; BALDINI et al., 2008; FRISIA et al., 2011). One such commonly used proxy is δ¹³C, which increases with vegetation decline related to climate deterioration, accompanied finally by the cessation of speleothem growth (FRISIA et al., 2011). In addition, cave ventilation forces degassing of CO₂ from dripwater, prior to any calcite precipitation onto the stalagmites (FRISIA et al., 2011). Prior calcite precipitation leads to ¹³C-enrichment in the speleothems (FAIRCHILD & BAKER, 2012) during deposition within the cave atmosphere obviously favourable for their growth. These similar signals, but supported by opposite conditions, underscore the importance of a multiproxy approach to verify palaeoclimatic interpretations.

6. CONCLUSIONS

We presented the results of multiyear monitoring of CDC in the Modrič and Manita peć show caves, which was conducted in order to identify spatio-temporal CDC variations, their controlling mechanisms and potential mutual influence and interrelationships between cave atmosphere and visitors.

i) The main sources of CO₂ in both caves are plant- and microbial-derived CO₂ produced in the soil horizon by root respiration and decay of organic matter that is transported downward, and in-cave CO₂ degassing of the dripping groundwater. Underground streams are absent and CO₂ production by cave biota is considered negligible. The sink for the cave air CO₂ is dilution with outside air due to the cave ventilation which is governed by air density differences derived from different air temperature, and by occasional wind-induced air flow.

ii) General ventilation patterns are seasonal and mimic the chimney-type circulation with associated CDC variations: the winter mode includes inflow of cold, dense CO₂ rich chimney-type circulation with associated CDC variations: the and by occasional wind-induced air flow. radiative forcing drives convective transport of outside air due to the cave ventilation which is governed by the same dynamic (seasonal) ventilation patterns, underscore the importance of a multiproxy approach to verify palaeoclimatic interpretations.

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ii) General ventilation patterns are seasonal and mimic the chimney-type circulation with associated CDC variations: the winter mode includes inflow of cold, dense CO₂-rich air into the caves due to the \( T_{\text{out}} < T_{\text{cave}} \), while in summer mode, warm surface CO₂-rich air enters into the caves during \( T_{\text{out}} > T_{\text{cave}} \). The key events are abrupt transitions from \( T_{\text{out}} > T_{\text{cave}} \) to \( T_{\text{out}} < T_{\text{cave}} \) followed by a sudden CDC drop. Occasionally, NE bora wind-induced air flow, as a secondary ventilation pattern, overprints the primary ventilation model, while the influence of wind-driven ventilation of the SE scirocco was not noticed.

iii) Superimposed upon the ventilation driven by air density gradient are circulation effects controlled by cave geomorphology and epikarst architecture, so the similar seasonal ventilation patterns result in large differences between absolute CDC values in the inclined and spacious Manita peć Cave, and the horizontal and more confined Modrič Cave. Moreover, within the same cave, the right and left Modrič Cave passages are ventilated differently due to the fractured fault zone of passable left passage (more ventilated) and more constrained right one (less ventilated).

iv) Although these caves are only 8 km apart, belong to the same type of climate (Cfa) and vegetation zone (Mediterranean), and spatio-temporal CDC variations within them are generally controlled by the same dynamic (seasonal) ventilation patterns, the magnitude of CDC variation appears to be site-specific. Due to the dependence of calcite precipitation on CDC variation, careful selection of the samples for speleothem-based palaeoenvironmental studies is essential. In particular, the Manita peć Cave generally does not experience major CO₂ fluctuations, so neither deterioration by condensation corrosion of the already deposited calcite, nor growth inhibition due to the CDC fluctuations is expected. On the other hand, the very high summer-autumn CO₂ concentration within Modrič Cave could reduce CO₂ degassing from the dripwater and thus hamper calcite precipitation.

v) Due to the low number of visitors, anthropogenic impacts on cave CDC is negligible even in the confined Modrič Cave passages, when compared to the natural CO₂ input which is higher by two orders of magnitude. In the Manita peć Cave episodes with slightly elevated human-induced concentrations are occasional and temporary short-duration events, with insignificant contribution to the natural CO₂ content.

vi) Conversely, given the site-specific nature of CDC and known temporal patterns, cave management should maintain the same practice of short visits of small groups in Manita peć Cave and the left passage of Modrič cave, while the right one should be avoided at least in late summer and during autumn.

vii) Elevated CDC values and similar preliminary results of radon measurements urge high-resolution (daily to hourly) monitoring of both parameters, measurement of velocity and the direction of air flow, along with collection of modern calcite to assess its precipitation in relation to the ventilation dynamics.

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REFERENCES


Surić et al.: Spatio-temporal variations of cave-air CO\textsubscript{2} concentrations in two Croatian show caves: natural vs. anthropogenic controls


Table A1. Modrić Cave air CO₂ concentration (in ppm) measured during the 2017-2021 period. April 2020 data are missing due to the COVID-19 pandemic lockdown. For the measurement points, reader is referred to the Fig. 8.

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