CO₂ Dynamics and Heterogeneity in a Cave Atmosphere: Role of Ventilation Patterns and Airflow Pathways

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Abstract

Understanding the dynamics and distribution of CO₂ in the subsurface atmosphere of carbonate karst massifs provides important insights into dissolution and precipitation processes, the role of karst systems in the global carbon cycle, and the use of speleothems for paleoclimate reconstructions. We discuss long-term microclimatic observations in a passage of Postojna Cave, Slovenia, focusing on high spatial and temporal variations of $p\text{CO}_2$. We show 1) that the airflow through the massif is determined by the combined action of the chimney effect and external winds and 2) that the relationship between the direction of the airflow, the geometry of the airflow pathways, and the position of the observation point explains the observed variations of $p\text{CO}_2$. Namely, in the terminal chamber of the passage, the $p\text{CO}_2$ is low and uniform during updraft, when outside air flows to the site through a system of large open galleries. When the airflow reverses direction to downdraft, the chamber is fed by inlets with diverse flow rate and $p\text{CO}_2$, which enter via small conduits and fractures embedded in a CO₂-rich vadose zone. If the spatial distribution of inlets and outlets produces minimal mixing between low and high $p\text{CO}_2$ inflows, high and persistent gradients in $p\text{CO}_2$ are formed. Such is the case in the chamber, where vertical gradients of up to 1000 ppm/m is observed during downdraft. The results presented in this work provide new insights into the dynamics and composition of the subsurface atmosphere and demonstrate the importance of long-term and spatially distributed observations.

Introduction

Carbon dioxide (CO₂) is known to be an important greenhouse gas and its distribution between the atmosphere, oceans, and vegetation is well studied and documented. In karst areas CO₂ plays a crucial role in dissolution and precipitation of carbonates, which may play an important role in carbon budget (Liu et al. 2010; Jeannin et al. 2016). Therefore, a deeper understanding of CO₂ fate and transport in the vadose zone of karst is needed. In vadose caves, the exchange of CO₂ between the atmosphere and water films flowing on the rock surface drives precipitation and dissolution of calcite. The identification and understanding of CO₂ dynamics also provides crucial information on speleothem growth and decay, their use as paleoclimate proxies, occupational safety in show caves, and the role of karst areas in the global carbon cycle (Baldini et al. 2008, 2018; Serrano-Ortiz et al. 2010; Baldini 2010; Martin 2017; Liñán et al. 2018; Guirado et al. 2019).

The CO₂ concentration in cave air varies over a wide range of values, from around atmospheric concentrations (~410 ppm) to more than two orders of magnitude higher (Ek and Gewalt 1985; Batiot-Guilhe et al. 2007; Houillon et al. 2017). The instantaneous partial pressure of CO₂ ($p\text{CO}_2$) at each position depends on sources, sinks, and transport fluxes. The main sources of CO₂ in caves are: (1) the degassing of groundwater and dripping water, (2) advection and diffusion from the soil and epikarst zone, (3) decomposition of organic matter introduced into the cave or deep vadose zone, (4) anthropogenic or biogenic production, and (5) geogenic production (Baldini et al. 2006; Baldini 2010; Breecker et al. 2012; Milanolo and Gabrovšek 2015; Prelovšek et al. 2018). It is widely recognized that the

soil and epikarst CO₂ reservoir, which is constantly replenished by plant material decay, soil microorganism metabolism, and root respiration, is a major source of cave CO₂ (Appelo and Postma 2005; Baldini 2010; Breecker et al. 2012). Organic material can be transported deeper into the vadose zone and, when oxidized, become a source of CO₂. As a result, the CO₂ reservoir expands into a deeper vadose zone, where it is often referred to as a *subsoil carbon source* or *ground air* (Atkinson 1977; Serrano-Ortiz et al. 2010; Matthey et al. 2016; Baldini et al. 2018). This CO₂ reservoir is now well recognized through contemporary research of the karst vadose zone *p*CO₂ in boreholes (Benavente et al. 2010, 2015), direct measurements in the soil zone (Blecha and Faimon 2014; Garcia-Anton et al. 2017), carbon isotope records in speleothems (Noronha et al. 2015), hydrochemistry of drip water (Bergel et al. 2017), or case studies with long-term monitoring (Matthey et al. 2016, 2021; Bourges et al. 2020).

The secondary porosity of the karst vadose zone allows the underground storage of CO₂, but it also allows air circulation, which mediates the exchange of ground air with the outside atmosphere. Ventilation through caves and the entire vadose zone can make an important contribution to the net carbon balance of ecosystems (Serrano-Ortiz et al. 2010). The extent and relative importance of the mechanisms forcing ventilation depend on the geographical location and altitude, meteorological conditions, the number and orientation of cave entrances, and the general cave morphology (Borsato et al. 2015; Covington and Perne 2015). The driving forces of cave ventilation may act on a transient or periodic (diurnal or seasonal) time scale, with the seasonal being most common in the temperate zone, where the temperature difference between the cave and outer atmosphere is large enough to cause density-driven airflows (James et al. 2015). Short-term fluctuations in the prevailing cave airflow may be caused by variations in the external atmospheric pressure (Pflitsch et al. 2010) or by the wind-driven effect caused by strong winds over the surface topography (Kowalczyk and Froelich 2010).

The seasonality of cave ventilation is directly reflected in the *p*CO₂ values. *p*CO₂ maxima are often observed in warm periods when CO₂ production in the soil is highest and the cave air is static (e.g. formation of a cold trap in a descending cave) or when the airflow is directed from the soil zone and the surrounding karst massif towards the cave (Milanolo and Gabrovšek 2009; Faimon and Ličbinská 2010; Pla et al. 2016a; Peyraube et al. 2017; Covington et al. 2020). Minima are observed during strong circulation when the high inflow of outside air with low *p*CO₂ dilutes the cave air. In the absence of airflow, the *p*CO₂ of a cave balances with the *p*CO₂ of the surrounding vadose zone and reaches potentially extreme values (Houillon et al. 2017; Bourges et al. 2020). As an exception, CO₂ seasonality can be induced by winds in a tropical environment that may otherwise have no seasonal variations (Noronha et al. 2017), as suggested by James et al. (2015). In paleoclimate studies, CO₂ seasonality has been recognized as an important modulating factor introducing a seasonal bias in speleothem geochemistry (Spötl et al. 2005; Baldini et al. 2008; Kowalczyk and Froelich 2010; Sherwin and Baldini 2011; Cowan et al. 2013; James et al. 2015). However, spatially high-resolution CO₂ measurements in caves have rarely been carried out, although heterogeneity and steep CO₂ gradients may well be common. These ultimately influence drip water geochemistry on a micro-local scale within the cave environment

(Ek and Gewelt 1985; Baldini et al. 2006; Whitaker et al. 2009; McDonough et al. 2016). Finally, mineralization at karst springs has also been shown to be controlled by cave ventilation, which controls CO₂ levels in the vadose zone (Jeannin et al. 2017; Covington et al. 2021).

Contemporary research reveals additional, possibly universal CO₂ phenomena that are often neglected or simply not recognized due to sparse *p*CO₂ measurements—vertical gradients and local CO₂ accumulation behind constrictions, in fissures and depressions, and an increase in *p*CO₂ with distance from the entrance (Ek and Gewelt 1985; Baldini et al. 2006; Whitaker et al. 2009; Benavente et al. 2010; Breecker et al. 2012; Cowan et al. 2013; Ek and Godissart 2014; McDonough et al. 2016; Prelovšek et al. 2018; Bourges et al. 2020). In a conceptual model of CO₂ transport through the unsaturated karst zone, direct advection from the soil zone has become a preferred mechanism over diffusion to explain the spatio-temporal variation of CO₂ in caves (Covington 2016; Lang et al. 2017). However, the particular conditions of homogeneity or non-homogeneity of cave *p*CO₂, require further research.

The objective of this work is to show how different airflow pathways influence the spatio-temporal pattern of CO₂ within a cave environment and to explain certain specific phenomena related to CO₂, such as high-frequency temporal variation, spatially steep vertical gradients, and stratification. Over a period of three years, we continuously monitored the cave climate and, with high spatial resolution, frequently measured *p*CO₂ in a dead-end Pisani Passage of Postojna Cave (Slovenia). Based on these data we propose a general conceptual model of CO₂ transport through the karst vadose zone, which builds on the current understanding of CO₂ dynamics and transport in karst. The results imply the need for a thorough understanding of the cave environment in order to improve the reliability of paleoclimatic, geochemical, or similar research, and to ensure the safety of visitors in show caves.

Materials And Methods

2.1 Study site

Postojna Cave (abbr. PC; 45° 46' N, 14° 12' E) is a part of a 24 km long cave system in central Slovenia (Fig. 1). It is an active stream cave fed by the allogenic Pivka River (511 m a.s.l., $Q_{avg} \approx 5 \text{ m}^3/\text{s}$) and is hydrologically connected to Planina Cave where it discharges onto Planinsko Polje, a part of the catchment area of the Ljubljana springs (Blatnik et al. 2019; Šebela 2019). The cave has two different levels, a lower (epi)phreatic and an upper dry level that is visited by about 800,000 tourists per year. The cave system has three entrances connected by open passages, and two entrances, connected to other parts of the system by an artificial tunnel, which is closed by airtight doors. In addition, many “breathing holes” have been identified on the surface, whose connection to PC is confirmed or strongly suspected. The overburden between the upper level of the cave and the surface is between 34 m and 105 m (Šebela 2010). The configuration of many entrances at different altitudes enables year-round ventilation of the cave. The ventilation shows two different seasonal regimes, winter (typically upward) and summer (typically downward). In spring and fall there is a shorter transitional regime when the direction of airflow

fluctuates (Šebela and Turk 2011; Gregorič et al. 2014). The surface is largely covered by Dinaric beech and silver fir forests (Krajnc et al. 2017).

The easternmost and highest elevated passages of Postojna Cave are Pisani Passage (abbr. PP, slov. Pisani rov) and Brezimeni Passage (abbr. BP, slov. Brezimeni rov; Fig. 1). Pisani Passage (entrance at 529.5 m a.s.l.) is a 515 m long side-passage extending northwards and ending with breakdown related to the formation of the Velika Jeršanova collapse doline (Šebela and Čar 2000). It is formed within thin- and thick-bedded limestones of the Upper Cretaceous, which are strongly tectonically fissured in some places, creating the large collapse chambers (e.g. SC Hall (Šebela 1998), Fig. 1). Much of the passage is filled with clay-rich cave sediments and highly decorated with speleothems. While it is mostly developed horizontally, PP has several low-lying places, here called “depressions”, which we call First depression (FD), Ladder depression (LD), and Red Hall (RD). The vadose zone thickness above the passage is 100 m at the entrance and decreases to 30 m towards the end. The last part of the passage has two parts that are called Red Hall and White Hall (WH) which can be considered to be a single chamber with a volume of about 6800 m³. Brezimeni Passage is formed in similar lithology and extends ~400 m to the southeast, rising and branching towards the end. It is characterized by a large collapse chamber halfway along the passage and a high chimney about 30 m further down the passage, which is probably connected to the surface.

Although Postojna (533 m a.s.l.) is close to the Mediterranean Sea (20 km), it has a continental climate with cold winters and warm/hot summers. The average annual air temperature is 9.3°C, the coldest month is January with -0.1°C and the warmest July with 19°C (average of the period 1981-2010). The average annual precipitation for the same climate period is 1500 mm, with precipitation generally more concentrated in fall and in the colder months. During the 2017-2019 study period, average monthly mean air temperatures were above the long-term average, especially in the summer months, and warming in the range of 0.35–0.45°C per decade has been observed. There are two types of strong regional winds in Postojna – bora is a gusty, cold and generally dry katabatic wind blowing from the north-east, while jugo is a generally humid wind blowing from the south. As Postojna is surrounded by mountainous terrain (>1000 m a.s.l.) to the north and the east, it is mostly influenced by the north-eastern winds blowing from the interior over the Postojna Gate mountain pass. Winters are generally windier, while summers have a higher frequency of calm days (ARSO 2021).

Karst massifs are subject to heat exchange between rock, air, and water (Luetscher and Jeannin 2004). Although the fluids penetrating the massif exhibit daily and seasonal cycles and long-term trends, the massif establishes an equilibrium temperature (Badino 2005), which can be detected in thermally very stable (non-ventilated) parts of cave systems and in deep groundwater and water trickles that percolate through the vadose zone (Badino 2010). In the Postojna region, temperatures between 8.5°C and 9°C are typically measured in such situations.

2.2 Microclimatic monitoring

Microclimatic monitoring in Postojna Cave was established to obtain general patterns of cave microclimate and to assess the impact of tourist visits. The backbone of the monitoring network was established in the period of 2009–2012 at four sites (1, 4, 7, and 8 in Fig. 1). The stations were installed along the main airflow pathways (sites 1 and 8), in the places where the greatest impact of tourists was expected (site 7), and in the remote, unvisited parts of the cave (sites 2, 3–6). All instruments are connected to data loggers, additionally, stations 1, 3, 5, and 7 are or were also connected to the web server via the existing optical line or DTN protocol. Details about the measurement system, data acquisition, transmission, and storage are given by Gabrovšek et al. (2014). The stations record with a resolution of 10 min an ambient temperature at three vertical positions with Pt100 temperature sensors (resolution 0.01 °C; accuracy ± 0.1 °C), a CO₂ concentration (Vaisala GMP222 and GMP252 probes; measuring range 0–10.000 ppm; accuracy $\pm 1.5\%$ of full scale and $\pm 2\%$ of reading for GMP222, and $\pm 2\%$ of reading for GMP252), and wind speed and direction (ultrasonic Gill Windsonic anemometer; resolution 0.01 m/s; accuracy $\pm 2\%$ at 12 m/s; directional accuracy $\pm 3^\circ$ at 20 m/s). The original network was extended by additional wind speed (Gill Windsonic), temperature (HOBO MX2203 TidbiT; resolution 0.01 °C, accuracy ± 0.2 °C), and CO₂ instruments, mostly in Pisani Passage and Brezimeni Passage ($T_1 - T_3$). Here, the wind speed time series has been modified to include the direction for each station—positive values for an updraft (typical winter situation) and negative values for a downdraft (typical summer situation). Monitoring in the farthest chamber of the Pisani Passage (i.e., Red Hall, abbr. RD, slov. Rdeča dvorana) started in 2012, but the older data are sparse due to energy shortage and related instrument failures. Since 2016, the station has been connected to the cave's power line via a UTP cable, which is also used to transmit the data. The station receives three temperature inputs and two CO₂ measurements, which are marked as CO₂ floor and CO₂ ceiling, positioned 6.5 m above the latter (Fig. 2c). Ventilation in the PP is monitored at its entrance (site 3), while sites 4 and 6 are discontinuous, and airflow data are only available for shorter periods. Additional temperature HOBO loggers were installed in PP at sites 3, 4, and 6 in 2019.

2.3 Spot CO₂ measurements

The spot CO₂ concentrations were measured with a Vaisala portable CO₂ meter (GM70) with GMP222 or GMP252 probes. All measurements were automatically compensated to the standard temperature and pressure (298 K, 1013 hPa). Occasionally, the readings were compared between several Vaisala meters, calibrated at different times, to detect potential drift. The differences were within the range of the expected uncertainty. Spot $p\text{CO}_2$ measurements were carried out with an equilibration time of at least 2 minutes with unattended automatic recording to eliminate interference from respired CO₂. Longitudinal CO₂ profiles along PP were obtained by spot measurements of $p\text{CO}_2$ at 26 predefined positions ~ 1 m above the ground (completely marked on Fig. 1 and Fig. S1 and partially marked in Fig. 2c). The procedure was repeated on average 28 times at all sites over several seasons and ventilation regimes (from 13 September 2017 until 16 January 2020). The vertical CO₂ profile in RD was obtained by setting up a Tyrolean traverse with a pulley system, which allowed an exact horizontal and vertical positioning of the CO₂ instrument (location marked in Fig. 1). In this way, a grid of CO₂ values was created twice, on 30

May 2018 and 7 August 2018, along the entire horizontal and vertical span of the cross section. As the profiles showed uniform values in the horizontal direction and high gradients in vertical direction, the following seven surveys were carried out at a single horizontal position. For more details, see section S2 in the supplementary material.

2.4 Other data sources

Meteorological and climatic data of external conditions (air temperature and pressure, wind speed and direction, precipitation, and snow cover) were obtained from the national meteorological stations of the Slovenian Environmental Agency in Postojna 1.2 and 2 km SSW from the main entrance of the PC representative of typical meteorology above the cave (ARSO 2021). The extended profiles and cross-sections in the PP were accurately drawn using data from the 3D laser scanning survey carried out in 2013 by Sven Philipp and Jan Will from the Darmstadt University of Technology, Germany, and Franjo Drole from the Karst Research Institute ZRC SAZU, Slovenia. Similarly, the surface proximity was acquired from the LiDAR DEM data (ARSO 2020).

Results And Discussion

3.1 Microclimatic characteristics of the Postojna Cave System

The ventilation pattern shows typical seasonal and diurnal variations, which are characteristic for a dynamically ventilated cave system with several entrances (Fig. 3a). In winter, cold outside air flows into the cave through the main entrance at the base of the structural escarpment. The air, heated by the massif, is then driven by buoyancy through the cave passages and numerous small but open airflow pathways connecting the cave with the topographic surface above. In summer the situation is reversed. The air enters the massif at inlets on the surface, cools down in contact with the massif, and flows along largely unknown pathways to the cave and along the cave towards the main entrance (Fig. 2a and b). During the transition regimes, the outside temperature rises above and below the cave temperature daily, so that diurnal changes from updraft to downdraft are observed (typically in spring and fall). In all graphs negative values for the airflow velocity are used for the downdraft situation and positive for the updraft situation. Although the chimney effect is the dominant driving factor of cave airflow, external wind also drives subsurface ventilation, as will be discussed in Section 3.3. However, a detailed analysis of wind-induced cave airflow in Postojna Cave is provided in another paper (Kukuljan et al., 2021).

Seasonal/daily temperature variations depend strongly on the relative position with respect to the main ventilation pathway and the distance from the entrances. Points near the main entrances and along the main ventilation pathways show much higher seasonal temperature variations ($\pm 3.5^{\circ}\text{C}$ at OC), which decrease towards the cave interior ($\pm 0.4^{\circ}\text{C}$ at BC) and towards the most distant dead-ends ($\pm 0.1^{\circ}\text{C}$ at PP). The average air temperature in the system is between 9°C and 11°C and a phase delay between the outside and seasonal average cave temperature reaches several months (Šebela and Turk 2011). In some places, especially in BC, the presence of tourists interrupts the typical cave temperature for a short time (Šebela et al. 2015).

The seasonality of the ventilation is also reflected in the composition of the cave atmosphere. In summer, the air enters underground at a topographically higher surface, passes mostly through smaller openings and enters the main cave system. Downdraft seasonally coincides with increased biogenic CO₂ production during the warm season, resulting in increased $p\text{CO}_2$ values in the cave (Lang et al. 2017). During updraft, outside air enters the cave through large entrances and dilutes the CO₂ throughout the entire cave system (Fig. 3c). $p\text{CO}_2$ along the main ventilation pathways can decrease to atmospheric levels. Various circumstances can lead to a substantially uneven distribution of $p\text{CO}_2$ in the cave. In a poorly ventilated passage, the $p\text{CO}_2$ in the cave is nearly in equilibrium with the $p\text{CO}_2$ of the surrounding vadose zone. In the case of Pisani Passage, high $p\text{CO}_2$ values were considered to be the result of poor ventilation (Prelovšek et al. 2018). The main proposed sources of CO₂ were direct seepage of CO₂-enriched air from the vadose zone and degassing of the percolating water, which showed equilibrium $p\text{CO}_2$ values similar to those measured in the cave air. Gregorič et al. (2013) found similar fluctuations in another trace gas, radon, whose activity concentration reached extremely high values (up to 45 kBq/m³, annual mean ~25 kBq/m³). The authors suspect that in addition to stagnating summer air conditions, thick soil layers, surface proximity and clay-rich cave sediments could be responsible for such extremes. The Pisani Passage is, therefore, an ideal candidate to study the CO₂ dynamics of PC.

3.2 Microclimatic observations in the Pisani Passage

3.3 Cave airflow

The airflow velocity into/out of the Pisani Passage is measured at its entrance, where the passage is limited to a cross-sectional area of 1.42 m². The air flow rate is shown in Fig. 4b. In general, the airflow follows the ventilation regimes typical of Postojna Cave, updraft for $T_{\text{cave}} > T_{\text{ext}}$ (typically in winter, positive values) and downdraft for $T_{\text{cave}} < T_{\text{ext}}$ (typically in summer, negative values, Fig. 4a and Fig. 4b). The PP, thus presents an airflow pathway that connects the inner part of the cave (OC) with the higher-lying surface. However, there are no physically known connections between the PP and the surface, suggesting that the air mainly follows a network of small conduits and fractures. Most of these airflow pathways are too small to be localized exactly, but a site of detectable, seasonally reversible airflow was found at the far end of PP (PP_{end}), suggesting that the entire passage is ventilated.

The temperature records in Fig. 4c show small differences at different vertical position in the Red Hall and in the PP_{end}. Similar temperatures were recorded in the Ladder Depression (LD)(Fig. 4c), During downdraft the temperature span along the entire Pisani Passage is less than 0.4 K (8.5°C-8.9°C).

In Fig.4b one can observe a steady dominant downdraft in warm periods and updraft in cold periods. In cold periods, however, clear intervals of downdraft can also be observed, which is contrary to the forcing of the chimney effect. The correlation of the direction of the cave airflow with various possible drivers showed that such downdrafts are caused by the external wind gusts. Fig. 5a shows the airflow velocity at OC and PP in relation to the outside wind during one such a cold period. Note that for visual clarity, the

wind speed has been oriented and colored depending on the prevailing direction; positive values for winds of 0–90° and 270–360° (winds 0–90° are colored red and marked NE), and negative values for 90–270° (winds 135–225° are colored blue and marked S). The decrease of an updraft or the complete reversal of the airflow to a downdraft occurs during periods of the northeastern external wind, especially with gusts of >10 m/s (marked by the red arrow). In some periods these reversals occur despite of the fact that T_{cave} is more than 10°C above T_{ext} . On the other hand, an increase of updraft (blue arrow) is observed when the wind is blowing from a S direction. The effect is similar in the warm period (Fig. 5b), where the typical downdraft ($T_{\text{cave}} < T_{\text{ext}}$) is reduced or reversed by a S wind or increased by a NE wind. These effects occur throughout all seasons, as the outside winds do not have a clear seasonality. During the high summer or high winter season, however, the chimney effect is predominant and only the strongest gusts of wind cause a change in the direction of airflow.

The importance of the wind-driven effect is also demonstrated in Fig. 6, which shows the relation between the cave airflow velocity and the external temperature for the 2018 and 2019 time series. Red dots present the complete dataset, while blue and green dots show only data points when the external wind gusts were below 3 m/s and 1 m/s, respectively. By excluding the wind effect (blue and green points on Fig. 6), a typical picture of the chimney effect relationship emerges, where cave airflow velocity has a square root dependence on the difference between external and internal temperature. The black line in Fig. 6 shows the square root fit to the green point cloud (Badino 2010).

Figures 4b and 6 also show that for the same ΔT the wind speed is stronger in downdraft. While the reasons for this asymmetry have not yet been investigated in our case, such an observation is not so rare (Covington and Perne 2015). Reasonable assumptions would be that it is due to the geometry of the airflow pathways or to a disequilibrium between the outside temperature range and the temperature of the massif, which presents a long-term average. The use of virtual temperature, which includes the influence of relative humidity and $p\text{CO}_2$ on air density, may also explain the shift (Kowalski and Sánchez-Cañete 2010). However, these discrepancies are not crucial for this work.

The air temperature inside Pisani Passage has a very stable value of 8.8°C, which is on average lower than in the adjacent parts of Postojna Cave for the same period 2017–2019 (10.8°C in BC). Annual temperature fluctuations below 0.1°C were recorded at all measuring sites in the passage. This includes the PP_{end} site, which is only ~30 m from the surface and has a detectable airflow almost all year round. Therefore, it can be expected that the air is in thermal equilibrium with the massif when it reaches the cave. While the annual temperature fluctuation of a given location is rather small, there are systematic differences between them. This can be seen between $T_1 - T_3$ in RD where the span increases in summer and greater variability is observed in winter (Fig. 4d). These differences have not yet been investigated in detail. Records since 2012 show a gradual temperature increase of about 0.08°C/year, starting from 8.5°C in 2012 and reaching 8.9°C at the end of 2019. At present, we cannot yet confirm whether this is a trend following the warming of the exterior indicated by Domínguez-Villar et al. (2015), whether it is related to

the change in the surface vegetation cover, increasing number of visitors, or whether is it due to another reason. Warming has also been observed in other parts of Postojna Cave (Šebela et al. 2015).

3.4 The longitudinal gradient of CO₂

Spot $p\text{CO}_2$ measurements were carried out during different seasons and ventilation regimes to investigate the general dynamics and possible gradients of CO₂ across Pisani Passage. As already observed by Prelovšek et al. (2018), an increasing trend with distance from the entrance is confirmed, independent of the ventilation regime (Fig. 7). However, this rule does not apply to the Red Hall at the far end of PP nor to other weakly ventilated or unventilated sites, which apparently protect the CO₂ from advection. We have found that all CO₂ rich sites are located in morphological depressions (see Fig. 1, Fig. 3c, and Fig. S1). The seasonal differences are seen as changes in the size and slope of the longitudinal CO₂ gradient from the entrance to the inner cave—the winter gradient is the gentlest and the summer gradient the steepest. These gradients are similar to those measured in Ste-Anne Cave (5.3 ppm/m (Ek and Gewalt 1985)) or in Srednja Bijambarska Cave (0.2–2.2 ppm/m (Milanolo and Gabrovšek 2009)).

3.5 Temporal CO₂ dynamics in the Red Hall

In general, the seasonal variation of $p\text{CO}_2$ in Pisani Passage corresponds to the variations in other sections of the Postojna cave system; low values in cold periods due to strong dilution by the outside air, and high values in warm periods due to advection from the CO₂-rich vadose zone. A closer look, however, reveals an interesting phenomenon in the final chamber of PP (Red Hall), where during the downdraft the $p\text{CO}_2$ is significantly higher near the floor than at the ceiling (Fig. 4d). The $p\text{CO}_2$ at the floor station can even exceed 10,000 ppm, while the maximum daily value at the ceiling probe is only 3200 ppm. The differences between floor and ceiling can reach almost 8000 ppm during the summer season, indicating a permanent, drastically different air composition within only 6.5 m of vertical difference. Both values and their difference show a gradual increase from mid-May to mid-October, when $p\text{CO}_2$ in the soil and the epikarst is expected to increase as well. During the updraft, the air in the RD is well mixed and the $p\text{CO}_2$ can fall well below 1000 ppm. This apparent “stratification” will be discussed further in the next section.

The $p\text{CO}_2$ fluctuations in Red Hall are directly related to the airflow in Pisani Passage, which is not only driven by the chimney effect, which explains the seasonal dynamics, but also by the wind effect. The wind-driven effect on cave ventilation is explained in another paper (Kukuljan et al., 2021), here we present the effect on $p\text{CO}_2$. An example of a winter period (18 days) is shown in Fig. 8, where the chimney effect forces an updraft. During most of the period, the $p\text{CO}_2$ on the floor and the ceiling of Red Hall are almost equal and low (~1000 ppm). However, during periods of strong NE wind, the direction of the airflow reverses towards downdraft, whereupon the floor and ceiling $p\text{CO}_2$ curves are immediately separated. The floor $p\text{CO}_2$ increases, while the ceiling $p\text{CO}_2$ even shows an initial decrease, followed by a moderate increase. When the outside wind direction and thus the airflow direction along the PP is reversed, the updraft situation with the mixed atmosphere is restored within a few hours. This effect also

occurs during the rest of the year. However, in the high summer season, it is suspected that a maximum CO_2 flux from the karst massif is reached, so that the NE wind only increases the speed of the airflow, while the CO_2 concentration remains the same or even decreases slightly. The southerly wind causes a temporary mixing of the air in RD or, if it lasts long enough, a decrease of the total $p\text{CO}_2$, regardless of the season or the ventilation regime.

3.6 Vertical CO_2 profile

To investigate the phenomenon of apparently vertically stratified air in Red Hall in full spatial detail, we measured vertical CO_2 profiles. This was done by gradually lowering the instrument from the ceiling to the floor at different horizontal positions. Two complete grid profiles of 8 m in height and 20 m length were created to confirm that the stratification is present in the entire cross-section of the chamber (Fig. 9). After uniform values were found in the horizontal position, only one position (14 or 16) was selected for the subsequent profiles (for more details on profile setup, see section S2 in the supplementary materials). The $p\text{CO}_2(\text{height})$ curves show two distinct gradients with maximum values at the floor of the hall and minimum values at the ceiling.

The profiling was repeated in different ventilation regimes to obtain a temporal resolution of the CO_2 profiles as shown in Fig. 10. A typical winter regime with updraft is characterized by an almost uniform CO_2 distribution, while during downdraft the curves take on a characteristic shape and in extreme cases reach gradients of almost 1000 ppm per vertical meter. The maximum difference resulting from the available time series of the fixed floor and ceiling stations corresponds to a gradient of 1200 ppm/m (daily average). Similar curves were reported from borehole measurements in a karstic environment by Benavente et al. (2010, 2015).

The stratification in Red Hall is built up on the time scale of hours to days after the reversal of the airflow from updraft to downdraft regime. We have observed that our movement in the lower part of the chamber disturbs the stable stratification, but the characteristic profile restores within a few hours (few examples are available in Fig. S4b). To study this phenomenon in more detail, we deliberately force-mixed the air by stirring it with flat panels in RD for 20 min so that CO_2 was distributed almost evenly throughout the chamber. During this experiment we deployed two additional CO_2 meters at intermediate heights between the CO_2 stations on the floor and the ceiling. Fig. 11a shows the vertical profile before and after the mixing, and Fig. 11b shows the recordings of four CO_2 probes during the restoration of the characteristic profile. The experiment was performed in the summer ventilation regime (i.e., $T_{\text{cave}} < T_{\text{ext}}$), where we expected constant downdraft conditions. While the relaxation curve at the ceiling shows a typical exponential decrease almost immediately after the mixing, the concentrations at other positions begin to change 12 hours later. The comparison with the external wind data showed that the delay occurred during a southerly wind, which may have temporarily restricted the accumulation and relaxation of the lower probes. As soon as the wind changed direction, the accumulation and relaxation processes continued. However, this was a rather surprising situation, since the simultaneous separation of the $p\text{CO}_2$ curves is

much more common (visible in time series in Fig. 8 and Fig. S4). The reason for these apparent differences in responses has not yet been found.

The characteristic response times for CO₂ curves were investigated by fitting the data points to an exponential function. For the experiment of 17th of September 2019, the accumulation rates were 5.00 h for the lower (temporary) CO₂ instrument and 7.14 h for the floor CO₂ station. The relaxation times were shorter, from 1.41 to 4.00 h, for the ceiling CO₂ station and the upper instrument. The short characteristic time needed for restoration of a distinct CO₂ profile can only be explained by advective inflow of CO₂-rich and CO₂-poor air (Covington 2016; Lang et al. 2017). A plausible explanation is that there are several inputs with different CO₂ concentrations and that their flow distribution is such that the mixing is negligible. A pronounced CO₂ input is located at the far end of PP at 533 m a.s.l., 4 meters below the ceiling CO₂ station (marked PP_{end}, Fig. 2c). It is a narrow passage with a measurable airflow showing typical downdraft volume flow rates of about 0.05 m³/s and low *p*CO₂ values (1350–5180 ppm, average 2000 ppm, *n* = 30), which is comparable to the ceiling CO₂ station. The volume flow at the PP_{end} is about 14% of the volume flow that is discharged out of PP during downdraft.

Several places with extreme CO₂ levels have been located in Red Hall, White Hall and at the Ladder depression, although none of them has detectable airflow. One of them is a small flowstone-covered depression in the White Hall (Fig. S5a). We have performed similar mixing tests as described above where the air in depression was well mixed with the surrounding low-CO₂ air. After mixing is stopped, a high concentration is restored with a characteristic relaxation time of 0.02–0.07 h in a warm period and an order of magnitude slower in a cold period (Fig S5b). Such a rapid increase during the downdraft indicates an advective inflow with a small volume flow rate but high *p*CO₂. Based on these measurements and observations we propose a conceptual model of CO₂ transport in the Red/White Hall, which explains the observed phenomena.

4 The conceptual model of CO₂ transport

The advection driven by the chimney or wind effect is the main mechanism for CO₂ transport and the reason for the observed fluctuations of CO₂ concentration in the Pisani Passage atmosphere. Throughout the year an average of 0.54 m³/s of air is exchanged with the surface. Although it is an important ventilation pathway in the Postojna Cave system, the temperature in the passage is very stable, indicating an efficient heat exchange between the rock mass and the air. This indicates that the air enters and exits the passage through many small pathways (such as solutionally enlarged fractures and small conduits) that provide a high ratio of rock surface area to air volume required for efficient heat exchange. The entire area of Postojna Cave is strongly tectonised with numerous faults, fractures and crushed zones. These elements were also mapped along the entire Pisani Passage (Šebela 1992, 1998).

Figure 12 shows a conceptual model of airflow and CO₂ dynamics between the outside atmosphere and PP. During the updraft regime, air with low *p*CO₂ coming from the main entrance through the Old Cave

dominates along the entire Pisani Passage and exits to the surface along open pathways (blue arrows in Fig. 12a). During the downdraft regime the air enters the passage from the surface through many pathways with different aeraulic conductivities (red arrows in Fig. 12a). One can imagine a complex flow network of fractures and conduits along which the air flows from the surface to the cave (Fig. 12b). The air can enter the network enriched with soil CO₂ to varying degrees, depending on the soil thickness, the CO₂ production rate, and the porosity of the soil and the airflow network (Pla et al. 2016b). Furthermore, CO₂ may enter the airflow by diffusion from poorly ventilated compartments of the massif and reach the junctions with high $p\text{CO}_2$ pathways. Generally, pathways with high flow rate are expected to be less enriched with CO₂ once entering the cave, compared to poorly ventilated pathways. An example of a fast flow pathway is PP_{end} in Red Hall, the only inflow with a detectable airflow, and where the overall lowest $p\text{CO}_2$ values were observed in the Red Hall. The inflows with the highest CO₂ concentration cannot currently be detected because the air velocity is too low, but we can locate areas with high CO₂ concentrations and estimate the flux (Fig. S5). It has already been shown that the updraft in PP during cold periods contributes significantly to the soil CO₂, thus obviously requiring the existence of an underground CO₂ reservoir (Krajnc et al. 2017). Similarly, Faimon et al. (2020) found a clear relationship between updraft (UAF) and downdraft (DAF) modes of subsurface ventilation and the CO₂ concentration and $\delta^{13}\text{C}$ isotopic composition of soil air fluxes at the breathing spot above the probable cavity in Hranice Karst (Czech Republic). The concepts presented in that paper agree well with the concept presented here.

The geometry of the system seems to be important for the formation of the vertical CO₂ profile. Significant vertical differences discovered during the measurements (Fig. 9 and Fig. 10) support the idea of dividing the Red/White Hall chambers into at least two, vertically stratified, microclimatic compartments. The upper compartment is efficiently ventilated by the inflow of CO₂-poor air from PP_{end}, while the lower compartment is filled with slow seepage of CO₂-rich air, emerging from cracks in the walls or from the floor (Fig. 12b). The boundary between these compartments is between 533 and 535 m a.s.l., which coincides with the height of the outflow from RD/WH, and the height of the inflow at PP_{end} (Fig. 2c and Fig. 9). The spatial characteristics of the CO₂-rich pathways are not yet clear. Although we have not found high-CO₂ inflows at or near the ceiling, it is likely that they surround the entire cave perimeter as illustrated in Fig. 12b. Airflow near the ceiling could mask these sources. Further work on the analysis of the spatially variable $\delta^{13}\text{CO}_2$ signals within the cave could provide further insights (Mandić et al. 2013; Krajnc et al. 2017).

The CO₂ dynamics for the rest of the Pisani Passage is presented as a longitudinal profile in Fig. 7. A positive gradient is expected in the cold season, when the outside air enters the cave through the large main entrances. Along the flow towards the interior of the massif the air is enriched with (mainly) remnant CO₂ and CO₂ degassing from the calcite precipitating trickles. An inverse gradient would be expected in the warm period, which is not the case in PP. There, the air enters the passage along many small hardly detectable pathways enriched with vadose CO₂ to different degrees. The change of $p\text{CO}_2$

along the passage depends on the longitudinal distribution, flow rate and $p\text{CO}_2$ of the inlets. Decrease of $p\text{CO}_2$ along the flow path indicates increasing contribution of inlets with lower $p\text{CO}_2$.

In order to clarify the hypothesis of low flow high- CO_2 and fast flow low- CO_2 pathways, a comparison with observations in the Brezimeni Passage (BP) can be made, which connects to the Old Cave 50 m from Pisani Passage (Fig. 1). The passage is similar in length to PP but has a smaller cross-section on average. The decisive element for the airflow dynamics of this passage is the high chimney in the middle section, as shown schematically in the Supplement (Fig. S6). Although we have not yet located the exact surface opening, it is assumed that it is connected by an efficient airflow pathway. This is indicated by an average airflow rate of $3.44 \text{ m}^3/\text{s}$, which is almost 7 times that of the PP ($0.54 \text{ m}^3/\text{s}$). Further on, its role is particularly reflected in the annual temperature records at three different positions in the passage (Fig. S7a). The amplitude of the seasonal variations at two sites (T_1 and T_2) along the dominant airflow pathway between the chimney and the OC is more than 2°C , while the temperature recording away from the dominant pathway (T_3) shows a variation (0.25°C) that is one order of magnitude smaller. The typical diurnal variation is also visible in the time series of the airflow velocity (Fig. S7b). The dominant airflow pathway is also evident in the $p\text{CO}_2$ data, where values of only 515 ppm were measured during the downdraft below the chimney and over 3000 ppm further away from the chimney (Sept 2018; Fig. S8). In summary, strong inlets/outlets like the chimney in BP, dominate the dynamics and composition of the cave atmosphere and obscure the contribution of smaller pathways that certainly exist. Such a dominant pathway is not present in PP, which makes the contribution of smaller pathways more obvious. The results could also be discussed in terms of the concepts proposed by Lang et al. (2017). They emphasized the importance of advective flows from the epikarst (abbreviated *AIFE*) for CO_2 concentration in caves. Therefore, Pisani Passage can be considered as a cave with geometry A (sensu Lang et al. (2017)) with an open lower entrance and “hidden” upper entrances. Although the Brezimeni Passage has no known upper entrance, it falls into geometry C based on airflow dynamics, with two open entrances with weak sources from soil/epikarst. While in Pisani Passage the *AIFE* plays a crucial role in the resulting CO_2 concentrations, in Brezimeni Passage it is obscured by the concentrated airflow entering through the chimney.

The effect of the external wind on cave airflow in Postojna Cave and thus on $p\text{CO}_2$ is clearly visible in the data (Figs. 4–6). A detailed analysis and quantitative assessment of the relative importance of the chimney effect and the wind-driven effect, supported by CFD simulations, is discussed by Kukuljan et al. (in review), so we give only a brief outline here. The surface above PC is characterised by karstified terrain with many dolines, while the main entrance is located on a south-facing scarp. Wind flow over a rough topography induces a variable pressure field at the surface and at the cave openings. External winds induce differential pressure between different entrances and “blowholes” (air inlets and outlets). Therefore, the relative orientation and position of entrances is important. In warm periods, NE winds enhance the downdraft driven by the chimney effect in OC and PP, while the S winds oppose the chimney effect and diminish the cave airflow. Conversely, in cold periods, the NE winds oppose the updraft driven by the chimney effect and can even reverse it to downdraft causing an increase in $p\text{CO}_2$ values, as

discussed in Section 3.3. The southerly wind increases the updraft in the cave, which is especially noticeable at the OC site, which is closest to the main cave entrance. Figs. 5a and 5b show how the high-frequency variation in the outside wind also affects the high-frequency variation in the time series of the cave airflow. Similar wind-driven cave ventilation has been studied in a cave in Florida (Kowalczyk and Froelich 2010) and in a tropical cave on the island of Guam, where seasonal density-driven airflows are otherwise unexpected (Noronha et al. 2017).

Although it appears that the chimney effect and wind effect control the CO₂ dynamics in PP, there may be other factors involved. In some cases, CO₂ dynamics in mature caves has been found to be controlled by variation of drip rate, water infiltration or saturation of vadose zone (Milanolo and Gabrovšek 2015; Bourges et al. 2020). Theoretically, airflow and infiltration water pathways are shared within a vadose zone, and in this way saturation with water can limit or block the gas exchange between the cave and the exterior (Cuezva et al. 2011; Garcia-Anton et al. 2014; Pla et al. 2016b). In the case of PP, however, we have not found that this effect is significant in the CO₂ dynamics studied (at the level of continuous variation of $p\text{CO}_2$ or the specific CO₂ phenomena described previously). A redistribution of the airflow through larger, open, and non-saturated pathways may obscure the significance of this effect. If it is present nevertheless, it may be more pronounced in the cold period, when more precipitation is normally recorded in Postojna and rates of evapotranspiration are lower. It is also expected that snow cover or freezing of the soil could restrict gas exchange, as only the larger openings would remain open due to the melting effect of the rising warm cave air. The longest period in the years 2017–2019 with continuous snow cover was February 2018, when the cold fronts brought about 30 cm of snowfall. This month-long period with a low average outside temperature of -2°C was characterized by a strong accumulation of CO₂, which reached a maximum of 2500 ppm at the floor station in the Red Hall. Although it is probable that the air discharge from the cave was blocked by the snow cover or the soil freezing, the same period is also characterized by the longest continuous NE wind event, which may also have limited the air discharge (i.e., expected updraft). Therefore, we could not study these effects in detail separately. As suggested by some recent studies in the Mediterranean (Cuezva et al. 2011; Garcia-Anton et al. 2014, 2017; Pla et al. 2016a), prolonged warm periods increase soil permeability and cause increased soil gas exchange. Although the long-term effects can only be speculated, we might expect that longer dry seasons would limit soil biogenic CO₂ production and reduce overall CO₂ flux due to increased ventilation. However, in our case we did not find this limiting threshold, but rather increasingly prolonged periods of high CO₂ in the RD (Fig. 4c). This behavior could be explained by the greater role of subsoil CO₂ sources, which are less affected by outside conditions (Mattey et al. 2016). The CO₂ dynamics were also compared with the change in atmospheric pressure, but did not show a significant correlation. Previous research in PC confirms that pressure equalization is practically instantaneous, so that no barometric airflow is expected (Šebela and Turk 2011).

Although the specific configuration of the airflow pathways in the Pisani Passage may be considered as local and hardly generalized, we believe that these observations are not unique and that such situations would be (or have been) recorded in other caves where the airflow system connecting the cave to the

surface consists of several non-dominant airflow pathways. In reality, there are many more caves with a single-entrance that are, nevertheless, better ventilated than caves with continuous, unobstructed passages between numerous entrances. A poorly mixed cave atmosphere would probably lead to high gradients of parameters (such as CO_2 and temperature) between different parts of the cave and microclimatic environments. These can be easily identified and investigated by denser and more careful measurements of $p\text{CO}_2$. Certainly such micro-local CO_2 environments also have an important influence on the hydrochemistry of dripping water and subsequent analysis for paleoclimate or similar research. This is already obvious in the case of the RD, where the floor underneath the drip spots shows a large number of characteristic dissolution features, so-called corrosion cups. While these are the subject of ongoing research, we postulate that high vertical CO_2 gradients during the downdraft profoundly alter the hydrochemistry of the drip water. In the upper air compartment, the drips equilibrate to a low $p\text{CO}_2$ level, while in the lower one they reach a much higher $p\text{CO}_2$ value and become corrosive. The kinetics and long-term effects of such a heterogeneous environment on the geochemistry of speleothems is still an important open research question.

Conclusions

Ventilation has a strong influence on the composition of the cave atmosphere. In the case of Postojna Cave, the ventilation is driven by the combined chimney and wind effects. During updraft, the fresh outside air enters through the main entrances and dilutes the cave atmosphere in terms of CO_2 . During downdraft, the air enters at higher elevations and is then enriched with CO_2 along different airflow pathways, crossing the CO_2 -rich soil, epikarst, and vadose zone. When reaching the cave, these pathways have inlets with different airflow rates and different $p\text{CO}_2$. In most situations, the air from different inlets mixes in the cave and individual contributions are not easily observed. We have found that in the case of Pisani Passage, a dead-end side passage of Postojna Cave, the specific configuration of the inlets and the position of the outflow from the Red Hall/White Hall terminal chamber produces vertically-stratified compartments with different airflow pathways well separated. The upper compartment has a high airflow rate and low $p\text{CO}_2$ inputs, while the lower compartment has low airflow rates and high $p\text{CO}_2$ inputs. This leads to a strong vertical gradient of $p\text{CO}_2$, which is quickly restored after forced or natural mixing caused by the reversal of the airflow direction. On cold days, there is usually strong air mixing in the chamber and the corresponding gradient is negligible. In exceptional cases, $p\text{CO}_2$ stratification may also occur during cold periods, which we have found to be related to the wind-pressure effect of north-easterly gusts. These strong gusts suppress the chimney effect and turn the updraft toward a downdraft, restoring the $p\text{CO}_2$ stratification. Outside winds also influence the larger-scale cave ventilation by increasing or decreasing cave ventilation depending on their direction and the direction of the air density-driven ventilation, which results in high frequency variations in the cave airflow time series. Our preliminary observations suggest that long periods of an environment with high- CO_2 content near the cave floor can have a large influence on the hydrochemistry of drip water. The results of this study imply the need for a thorough assessment of the cave environment at a micro-local level in order to increase the reliability of paleoclimatic,

geochemical or similar cave research, but also to ensure the safety of visitors in frequently visited show caves.

Declarations

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Conflicts of interest/Competing interests

Not applicable.

Availability of data and material

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Code availability

Not applicable.

Authors' contributions

Lovel Kukuljan, Franci Gabrovšek and Vanessa E. Johnston designed the study, collected data, and maintained the instruments of the study sites. The data analysis and graphic presentation was carried out by Lovel Kukuljan and Franci Gabrovšek. Vanessa E. Johnston and Matthew D. Covington proofread and corrected the manuscript. All authors have read and approved the final version of the manuscript.

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Electronic Supplementary Material

The online link to the electronic supplementary material of this article will be available after the final revision of the manuscript.

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Not applicable.

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Figures

Figure 1

Plan of (a) Postojna Cave (PC) and (b) Pisani Passage (PP) with the locations of the continuous monitoring and CO₂ spot measurements. Map source: cave register at the Karst Research Institute ZRC SAZU. The plan of the Pisani Passage is adapted from Gallino (1924). Labelling of the monitoring sites: (1) Old Cave (OC), (2) Brezimeni passage (BP), (3) Pisani passage entrance (PP_{ent}), (4) Ladder depression (LD), (5) Red Hall (RD), (6) Pisani passage end (PP_{end}), (7) Beautiful Caves (BC), (8) Tartarus. Labelling in the Pisani Passage: First depression (FD), SC Hall (SC), White Hall (WH). Red dashed lines in RD denote the CO₂ profiles shown in Fig. 9 (A–A') and Fig. S5 (B–B'). Postojna national meteorological

stations (old and new) are located in a suburban flat terrain 1.2 km and 2 km SSW from the main entrance (not shown) Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

Figure 2

Extended profile of Postojna Cave with typical ventilation regimes – winter (a) and summer (b). Legend: Yellow triangles – cave entrances; blue arrows – updraft; red arrows – downdraft; BP – Brezimeni Passage; PP – Pisani Passage. The horizontal scale is reduced by 50%. Besides the known entrances, many breathing holes, which are not explicitly shown, allow efficient ventilation throughout the year. The profile was drawn from the topographical data of PC available at the cave register of the Karst Research Institute ZRC SAZU, while the surface contour was acquired from the LiDAR data (ARSO 2020). c) Extended profile of the terminal part of Pisani Passage (Red Hall (RD) and White Hall (WH)) with continuous (green triangles) and spot (red x) CO₂ measuring points. The White Hall is highlighted with dashed contours for visual clarity. It extends in the same direction as Red Hall and connects to the Ladder depression (LD) via a small tube, representing another outflow point of Red and White Hall. The red gradient fill marks the locations with an increased CO₂ content in warm periods. The symbols for anemometers and temperature probes are analogous to Fig. 1. The complete profile of the PP is available in section S1 under supplementary materials

Figure 3

Time series of Postojna Cave climate data for the whole study period: (a) Time series of the external temperature and temperatures in Old Cave (OC) and Beautiful caves (BC) (point 1 and point 7 in Fig. 1), (b) Cave airflow velocity at OC (negative value for a downdraft or positive for an updraft), (c) $p\text{CO}_2$ at OC and BC. The value of 410 ppm is taken as the atmospheric $p\text{CO}_2$ value (NOAA/ESRL 2021).

Figure 4

Time series of the parameters of the Pisani Passage microclimate. (a) Difference between cave (T_3 in RD) and outside temperature (negative values typical in the summer season, positive values in winter); (b) airflow at PPent (negative = downdraft, positive = updraft); (c) pCO_2 in the RD at the floor and the ceiling stations (atmospheric $\text{pCO}_2 = 410$ ppm); (d) temperature dynamics in the RD at three different heights (T_1 is the highest, T_3 is the lowest)

Figure 5

Airflow dynamics in Postojna Cave compared to outside temperature and wind speed and direction (20-day window) in the cold (a) and warm period (b). Wind speed is oriented and colored depending on its direction, positive for all winds with direction 0–90° and 270–360° (winds 0–90° are colored red and marked NE), and negative for winds 90–270° (winds 135–225° are colored blue and marked S). Red arrow = NE wind forcing; Blue arrow = S wind forcing

Figure 6

Relation between the outside temperature T_{ext} (and $T_{cave}-T_{ext}$, top axis) and airflow velocity at PPent for the period 2018–2019. Blue and green point clouds present records when periods with wind gusts speed above 3 m/s and 1 m/s were excluded, respectively. The value of 8.8°C is taken as the cave temperature (avg. temp. in the Pisani Passage).

Figure 7

The longitudinal pCO₂ gradients across Pisani Passage, based on the mean pCO₂ values for a given measurement site. The pCO₂ values were categorized according to the ventilation regime prevailing in PC at the time of measurement – summer (red), winter (blue) or transitional (yellow). Legend: dashed lines – regression lines; red arrow – downdraft; blue arrow – updraft; vertical green lines – position and span of floor and ceiling CO₂ records; gray labels – high-CO₂ sites and PP_{end}. Only ventilated sites away from depressions are included in the linear regression calculation (i.e. sites with high-CO₂ content are excluded). pCO₂ values follow a typical linear relationship with the distance from the entrance up to a distance of about 400 m, then the summer and transitional lines show a negative trend

Figure 8

CO₂ and airflow dynamics in Red Hall in relation to the outside wind (colored in relation to the main direction as in Fig. 5). Vertical gray arrows mark the beginning of the characteristic pCO₂ change at floor and ceiling CO₂ stations. Although during some days $T_{cave} \gg T_{ext}$, the NE wind will force the airflow towards the downdraft and indirectly cause CO₂ accumulation at the floor of the Red Hall

Figure 9

Schematic representation of CO₂ stratification in the Red Hall as measured by profiling on 30 May 2018 (a). The exact position of the profile is marked in Fig. 1 (cross-section A–A'). Each grid intersection represents an average pCO₂ value for a certain horizontal (2–20; at 2 m intervals) and vertical position (levels A–J; at 1 m intervals). Note that the Tyrolean traverse used for instrument positioning is slightly tilted to the right. (b) All 10 vertical curves obtained from the profiling show a characteristic kink between 533 and 534 m above sea level

Figure 10

Vertical CO₂ profiling in the Red Hall in different ventilation regimes. The relative height scale starts at the lowest point of the RD and ends at the height of the ceiling CO₂ probe. Legend: blue curve – cold period, yellow curves – intermediate period, red curves – warm period; gray dashed lines – the levels and ranges of the fixed CO₂ probes

Figure 11

a) Vertical CO_2 profiles measured shortly before and after 20 minutes of intensive air mixing on 17 September 2019, when vertical $p\text{CO}_2$ gradients were reduced from ~ 620 ppm/m down to ~ 80 ppm/m, making the $p\text{CO}_2$ in the Red Hall practically uniform. b) The four CO_2 time series of the mixing experiment carried out on 17 September 2019 in the Red Hall. Note that the vertical axis is inverted. The apparent spikes in ceiling CO_2 prior to the mixing period (gray bar) occurred after our entry (gray dashed line) and the CO_2 profiling performed shortly before. Legend: Dark red – Red Hall floor CO_2 station; light red and light blue – CO_2 instruments; dark blue – ceiling CO_2 station. c) The absolute and relative vertical position of the CO_2 probes

Figure 12

Cross-section of the terminal part of Pisani Passage (Red Hall) with a schematic representation of many possible airflow pathways permeating the vadose zone and reaching the surface. a) Arrows show the direction and size (not to scale) of the airflow during the downdraft (red) and the updraft (blue). b) A simple conceptual view of the airflow into the RD during the downdraft and build-up of the CO₂ gradient. The size and transparency of the arrows indicate the flow rate and pCO₂ value of the incoming air, respectively. Large transparent red arrows = high flow rate, low pCO₂; small red arrows = low flow rate, high pCO₂

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Kukuljanetal2020Supplementarymaterialclean.docx](#)