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Concentration and stable carbon isotopic composition of CO₂ in cave air of Postojnska jama, Slovenia

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Abstract: Partial pressure of CO₂ (pCO₂) and its isotopic composition ($\delta^{13}\text{C}_{\text{airCO}_2}$) were measured in Postojnska jama, Slovenia, at 10 locations inside the cave and outside the cave during a one-year period. At all interior locations the pCO₂ was higher and $\delta^{13}\text{C}_{\text{airCO}_2}$ lower than in the outside atmosphere. Strong seasonal fluctuations in both parameters were observed at locations deeper in the cave, which are isolated from the cave air circulation. By using a binary mixing model of two sources of CO₂, one of them being the atmospheric CO₂, we show that the excess of CO₂ in the cave air has a $\delta^{13}\text{C}$ value of -23.3 ± 0.7 ‰, in reasonable agreement with the previously measured soil-CO₂ $\delta^{13}\text{C}$ values. The stable isotope data suggest that soil CO₂ is brought to the cave by drip water.

Keywords: karst; cave; CO₂ concentration; ¹³C of cave-air CO₂; Postojnska jama

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INTRODUCTION

Speleothem formation in karst caves can be controlled by various parameters such as drip rate, drip water temperature, soil temperature and moisture, CO₂ partial pressure (pCO₂) in soil and in cave air, calcium and bicarbonate concentration in drip water (Baldini, 2010 and references therein). The spatial and temporal behaviour of many of these parameters is fairly well-constrained by numerous studies. During the last two decades several studies on pCO₂ in cave air showed the importance of seasonal variations of pCO₂ and the origin of CO₂ for speleothem formation (Bourges et al., 2006; Genty, 2008; Faimon et al., 2012). Intra- and inter-annual variability in stalagmite growth rate can be ascribed to rapid and seasonal shifts in cave air pCO₂ (Spötl et al., 2005; Baldini et al., 2008; Matthey et al., 2008; Genty, 2008). In addition, visitor activity (number of visitors, door opening and closing) can also influence cave CO₂ concentrations (Faimon et al., 2012; Šebela et al., 2013). Although cave air pCO₂ does not directly affect $\delta^{18}\text{O}$ of stalagmites, it may affect the seasonality of calcite deposition, and therefore the annual mean of $\delta^{18}\text{O}$ in stalagmites can be biased toward the $\delta^{18}\text{O}$ of the season with the fastest deposition and in such cases $\delta^{18}\text{O}$ of speleothems should not be used for paleotemperature studies (Baldini, 2010; Matthey et al., 2010).

Postojnska jama (jama means cave in Slovenian) (Fig. 1) is world's one of the largest and most famous karst cave. It has also been a site of extensive (scientific) investigations of cave environmental conditions and speleothem formation mechanisms (Urbanc et al., 1985, 1987; Gospodarič, 1988; Gams & Kogovšek, 1998; Genty et al., 1998; Vokal, 1999; Horvatinčić et al., 2003; Zupan Hajna et al., 2008; Šebela, 2010).

Studies of cave environmental conditions and their dependence on external temperature included studies of CO₂ concentration and cave air circulation (Gams, 1974a), radon concentration (Vaupotič & Kobač, 2004; Gregorič et al., 2011; Bezek et al., 2012), relation between number of tourists and the cave climate (Prelovšek et al., 2011; Šebela et al., 2013),

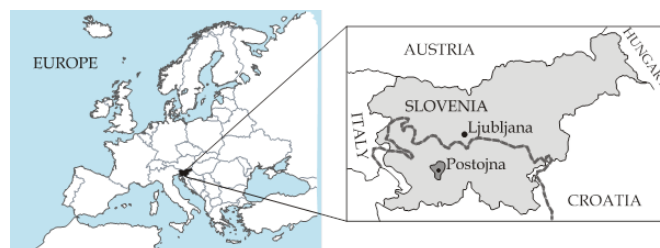


Fig. 1. Map showing the location of the study site. Postojnska Karst area is indicated by the dark gray area. Broken line on the right map represents the north-northwestern border of the Dinaric Karst area (after Gams, 1974b).

and microclimate characteristics (cave air pressure and temperature) (Šebela & Turk, 2011).

The first measurements of CO₂ concentration within the Postojna jama (Gams, 1974a) revealed seasonal fluctuations (lower concentration in winter and spring, higher in summer and autumn) and a spatial distribution along the passages, as well as different types of air circulation in the colder and in the warmer period of the year. No influence of the large number of visitors on the cave CO₂ concentration was observed. However, the origin of excess CO₂ concentration in the cave was not explained. CO₂ concentration (pCO₂) in the cave air has been recently monitored using a data logger at one location in the cave (Gabrovšek, unpublished).

The carbon isotopic composition (¹³C/¹²C and ¹⁴C) of the cave air CO₂ in Postojnska jama has not been studied systematically. The only available isotope data, δ¹³C and ¹⁴C activity (a¹⁴C), of CO₂ in the atmosphere outside and at a single location in the cave air showed that δ¹³C and a¹⁴C were lower inside the cave (-9.3 ± 0.2 ‰ and 102.6 ± 1.6 pMC¹, respectively) than outside (-8.0 ± 0.2 ‰ and 109.5 ± 1.1 pMC), and this difference was explained by contribution of soil CO₂ brought to the cave by drip water (Vokal, 1999; Horvatinčić et al., 1998). However, the CO₂ concentration was not measured so no further quantification was possible. The stable carbon isotopic composition of both soil CO₂ and soil organic matter (SOM) were measured at two locations above the Postojnska jama. The δ¹³C of SOM was -26.7 ‰ at both locations indicating the dominant vegetation of C3 type, while the δ¹³C values of CO₂ in the soil atmosphere were -21.7 ‰ and -20.0 ‰ (Vokal, 1999).

Measuring cave air composition, both pCO₂ and the carbon isotope composition δ¹³C, for at least one year could greatly assist geochemical and isotopic studies of speleothems (Baldini, 2010) and help identify the cave ventilation patterns. Therefore, as a part of the comprehensive monitoring of Postojnska jama (Mandić et al., 2012; Mandić, 2013), we measured concentration of CO₂ in cave air and its stable carbon composition (δ¹³C_{airCO₂}) during a one-year period at several sampling points inside the cave and in the outside atmosphere. The aim of this study was to determine spatial and temporal distribution of pCO₂ and δ¹³C_{airCO₂} of the cave air, and to determine how soil CO₂ and cave ventilation influence the cave air.

SITE DESCRIPTION

Postojna karst area is located on NW part of the Dinaric Karst (Fig. 1). It is composed mostly of Cretaceous carbonate rocks, while Triassic and Jurassic dolomites appear on the northern and north-eastern side. On the western and south-western side this karst region is in contact with non-carbonate Eocene flysch rocks from where some rivers are flowing and sinking into the Postojna karst area in which more than 60 caves are known. The largest cave system is Postojnska jama, 20.5 km long, consisting of several caves separated by sumps among which Postojnska jama (10,399 m, Fig. 2) is the largest (Šebela, 1998).

The area is positioned between the sub-Mediterranean climate of the North Adriatic Sea

and the continental climate of central Slovenia. Annual precipitation in the period from 1971 to 2000 is 1587 mm and mean temperature is 8.7 °C (data from meteo.si). In the period 1982 – 2011, the mean temperature was higher (9.2 °C) and precipitation slightly lower (1528 mm) than in the previous period. The annual amount of precipitation has not significantly changed in this period, but deviations from the mean increased in the last decade, e.g., 2010 was the year with the highest (1940 mm), and 2011 with the lowest (1078 mm) amount of precipitation in the last 30-year period. Average temperature in the six-year period 2006 – 2011 at the meteorological station Postojna was 9.9 °C. The mean temperature showed an increase of about 0.05 °C/yr in 1982 – 2011. A similar increase was observed also for Zagreb, Croatia (0.06 °C/yr, 1983–2007, Barešić, 2009) and Nontron, France (0.09 °C/yr, 1984 – 2007, Genty, 2008).

Postojnska jama was formed by the sinking Pivka River. There are two main levels of cave passages (Fig. 3): the upper, which is mostly dry and the lower where the river flows. The entrance to the upper level of the cave is at an altitude of 529 m a.s.l., which is 18 m above the actual Pivka River sinkhole. The entrance leads to dry upper cave passages and larger halls which are also connected with the lower river passage. The surface above the cave is covered by numerous dolines and is about 50–100 m above the cave. This vertical development creates enough gradient for strong air circulation.

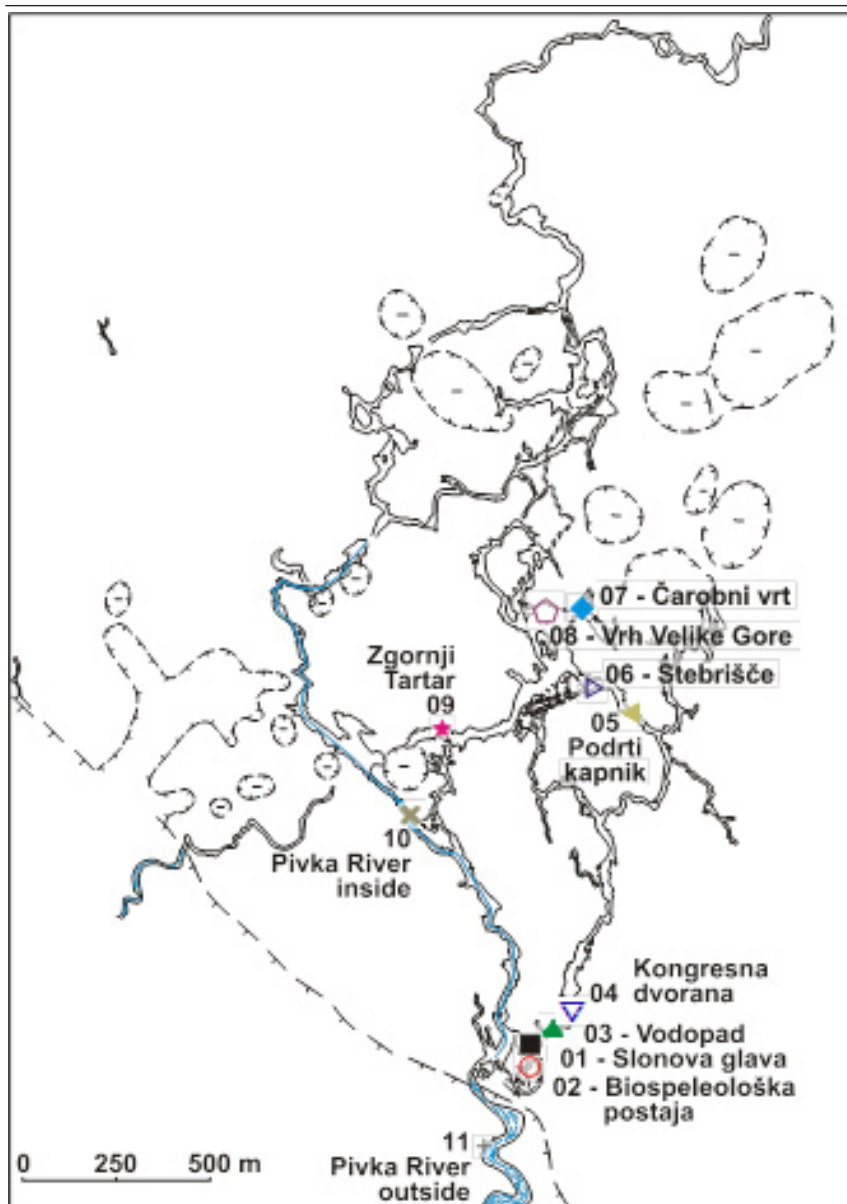
The relative humidity in the cave is high (>94%) and constant (Gams, 1974a; Vaupotič & Kobal, 2004; Bezek et al., 2012). Such a high relative humidity minimizes evaporation of cave drip water and the deposition of secondary calcite occurs by degassing of CO₂ from carbonate saturated drip waters (McDermott, 2004).

SAMPLING AND MEASUREMENT

Nine locations (Figs. 2 and 3), at different distances from the entrance, were chosen as monitoring stations. Because of the importance of the Pivka River for the evolution of the Postojnska jama and its influence on environmental conditions two locations on the Pivka River were chosen for observation. One is outside of the cave near the sinkhole of the river (location 11). This represents the external atmospheric conditions. The other sampling site on the Pivka River is about 2.5 km downstream inside the cave (location 10). Field work was carried out in March, June, August, September and November 2010, and in February 2011.

Prior to each field trip 10 mL borosilicate vials were flushed with He gas 6.0 and capped by butyl rubber septa. At the test site the sample vial was opened for a couple of minutes and closed again. The concentration

¹ pMC – percent of modern carbon, unit for expressing the dimensionless quantity a¹⁴C, relative specific activity of ¹⁴C, by definition 100 pMC = 226 Bq/kg C (Mook & van der Plicht, 1999)



Location number and name	Symbol
01 - Slonova glava	■
02 - Biospeleološka postaja	○
03 - Vodopad	▲
04 - Kongresna dvorana	▼
05 - Podrti kapnik	◀
06 - Stebrišče	▷
07 - Čarobni vrt	◆
08 - Vrh Velike Gore	◊
09 - Zgornji Tartar	★
10 - Pivka River inside	×
11 - Pivka River outside	+

Fig. 2. Map of the Postojnska jama Cave with sampling locations.

of air CO₂ and air temperature were measured in situ by the hand-held detector Vaisala Carbocap GM 70 and a GMP 222 probe. At each location the drip rate, i.e., the number of drips per minute, was measured using a stopwatch, and the mean value of ten 1-minute measurements was recorded.

$\delta^{13}\text{C}$ analyses were carried out using an on-line continuous-flow system (Gasbench II) linked to a Thermo Fisher Scientific DELTA^{plus}XL isotope ratio mass spectrometer. The experimental design of the measurements was comparable to the experimental setup described by Spötl (2004). The samples, an in-house calcite standard and two international reference materials (NBS_19 and NBS_18) were simultaneously analyzed by using the phosphoric acid method. The measured values are reported according to the VPDB scale. For replicate measurements the overall analytical uncertainty (1σ) for $\delta^{13}\text{C}_{\text{airCO}_2}$ is 0.15 ‰.

RESULTS

Temperature

Cave-air temperature at all locations in the studied period March 2010 – February 2011 is shown in Fig. 4a,

while the mean values are presented in Table 1. The mean cave temperature reflects the average outside temperature of the last several years (9.9 °C) but shows much smaller variation at all sampling sites. In a poorly ventilated cave the cave-air temperature remains essentially constant throughout the year, typically with variations of ± 1 °C (McDermott, 2004). Most of our locations have similar variations of less than ± 1.6 °C. Somewhat larger variations are observed for sampling sites close to the entrance (e.g., location 01) where the exchange with the open atmosphere is expected, at location 10 where the Pivka River influences the cave temperature, and at the outside location 11. The mean temperature at this location is somewhat higher than the mean temperature in Postojna because our measurements were single-point measurements usually taken during the warmer part of the day.

Drip rate

Drip rate showed a large variability among different locations (Table 1), e.g., at location 02 the drip rate was constantly low and showed no dependence on the precipitation amount, while at locations 07 and 08 the drip rate was higher and showed large variability, being the highest about 2 months after major

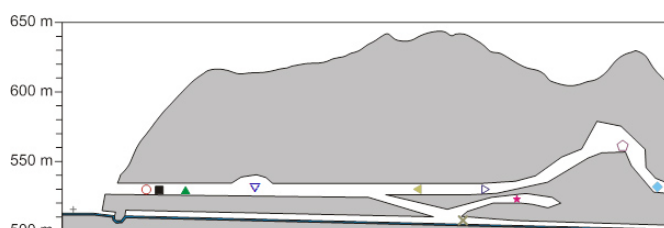


Fig. 3. Schematic plot of the longitudinal profile of the Postojnska jama Cave with altitudes of the sampling sites. Symbols are the same as in Fig. 2. Linear distances are not in scale.

Table 1. Mean air temperature (T_{air}), mean CO_2 concentration in air ($p\text{CO}_2$) and mean $\delta^{13}\text{C}$ isotope composition of the air ($\delta^{13}\text{C}_{\text{airCO}_2}$) at 11 sampling locations, and mean drip rate at nine sampling locations in the cave.

Location	T_{air} ($^{\circ}\text{C}$)	$p\text{CO}_2$ (ppmv)	$\delta^{13}\text{C}_{\text{airCO}_2}$ (‰ VPDB)	drip rate (min^{-1})
01 – Slonova glava	9.8 ± 2.2	782 ± 334	-13.1 ± 4.3	53 ± 53
02 – Biospeleoška postaja	9.9 ± 1.0	840 ± 335	-13.9 ± 4.5	14 ± 9
03 – Vodopad	9.7 ± 1.6	770 ± 320	-13.2 ± 4.6	60 ± 79
04 – Kongresna dvorana	10.3 ± 1.4	783 ± 300	-12.6 ± 4.5	50 ± 25
05 – Podrti kapnik	11.1 ± 0.4	1162 ± 463	-15.0 ± 3.7	56 ± 69
06 – Stebrišče	11.3 ± 1.2	1038 ± 399	-16.3 ± 3.7	108 ± 48
07 – Čarobni vrt	10.7 ± 0.8	1578 ± 885	-18.0 ± 2.1	144 ± 140
08 – Vrh Velike gore	11.6 ± 0.7	1187 ± 470	-17.5 ± 2.6	118 ± 173
09 – Zgornji Tartar	10.7 ± 0.9	937 ± 325	-16.1 ± 3.2	80 ± 103
10 – Pivka River inside	10.9 ± 4.1	995 ± 348	-14.6 ± 4.9	
11 – Pivka River outside	12.1 ± 9.8	398 ± 46	-7.8 ± 3.9	

precipitation events (Fig. 4b). However, according to the hydrology scheme of Smart and Friederich (1987) all drip sites belong to the seepage flow type.

CO_2 concentration

Seasonal variations of CO_2 concentration ($p\text{CO}_2$) are shown in Fig. 5. The mean $p\text{CO}_2$ at sampling site 11, (398 ± 46) ppmv (Table 1), corresponds to the open atmosphere. This value can be compared to the mean yearly atmospheric CO_2 concentrations at the global reference site on Mauna Loa (Hawaii) in 2010 and 2011 (389.8 ppmv and 391.6 ppmv, respectively, average 390.7 ppmv) (<http://www.esrl.noaa.gov/gmd/ccgg/trends>). The $p\text{CO}_2$ in cave air is always higher than the outside atmospheric $p\text{CO}_2$. The lowest mean CO_2 concentration in the cave is observed at sampling locations 01 – 04 that are close to the entrance (770 to 840 ppmv), while locations 05 – 08 deeper in the cave show mean values >1000 ppmv and larger seasonal variations (Table 1). Locations 09 and 10 can be considered as a separate group with similar mean $p\text{CO}_2$ as well as similar seasonal variations, which are determined by the possible air circulation between these two locations (Fig. 3). The highest mean $p\text{CO}_2$ (1578 ppmv) and also the highest individual value (2940 ppm in September 2010) was measured at location 07, which is the most isolated location (Fig. 3) closed for visitors. Maximum values at other locations were measured in August or September 2010 and the lowest in February 2011 or March 2010. The lowest winter $p\text{CO}_2$ values were close to the atmospheric $p\text{CO}_2$ at locations 01 – 04, while at locations 05 – 08 even the lowest winter values were higher than atmospheric $p\text{CO}_2$. No correlation was observed between individual data of the drip rate and the $p\text{CO}_2$ at any location ($R^2 < 0.5$, $p > 0.15$). Seasonal variations of $p\text{CO}_2$ have the same pattern at all locations irrespective of the response of the drip rate on major precipitation event.

$p\text{CO}_2$ was continuously measured in the period from July 2010 to July 2011 at location 03 (Gabrovšek, unpublished). The mean value of 600 ± 210 ppmv is in good agreement with our average value at the same location (770 ± 320 ppmv), considering the partial overlap of the monitoring periods and the fact that our data present only periodic data in comparison to the continuous monitoring of Gabrovšek. Seasonal variations also corroborate our measurement, whereby $p\text{CO}_2$ values lower than the mean were measured in the colder period of the year (November 2010 – April 2011), and the highest $p\text{CO}_2$ was measured in September (1300 ppmv).

Carbon isotope ($\delta^{13}\text{C}$) composition of cave air

Seasonal variations of $\delta^{13}\text{C}_{\text{airCO}_2}$ in cave air are shown in Fig. 6. $\delta^{13}\text{C}_{\text{airCO}_2}$ of the outside air (location 11) with the mean value $-7.8 \pm 3.9 \text{‰ VPDB}$ is in agreement with global $\delta^{13}\text{C}$ values of atmospheric CO_2 (Verburg, 2007). Mean values of $\delta^{13}\text{C}_{\text{airCO}_2}$ in cave-air CO_2 are lower than in the outside atmosphere. At locations 01 – 04 mean $\delta^{13}\text{C}_{\text{airCO}_2}$ varies from -12.6 to -13.9‰ , while at other locations it has more negative values, the lowest being -18.0‰ at location 07 – “Čarobni vrt” where the highest mean $p\text{CO}_2$ was measured (Fig. 6, Table 1).

All locations inside Postojnska jama show similar seasonal variations, i.e., the lowest $\delta^{13}\text{C}_{\text{airCO}_2}$ values were measured in September 2010 and the highest in February 2011 (Fig. 6). A good correlation between individual $p\text{CO}_2$ and $\delta^{13}\text{C}_{\text{airCO}_2}$ data was observed at each location ($R^2 > 0.7$, $p < 0.1$): the higher the $p\text{CO}_2$, the lower the $\delta^{13}\text{C}_{\text{airCO}_2}$. No correlation was observed between the individual drip rate and $\delta^{13}\text{C}_{\text{airCO}_2}$ data. Exceptionally low $\delta^{13}\text{C}$ was measured in September 2010 at the outside location 11 (-15.5‰), and this was probably caused by strong ventilation from the cave. The general cave air circulation in Postojnska jama is from the interior towards the exit in the warmer part of the year (May – October). When the cave temperature is higher than the outside temperature (November – April), cave air is released from the cave into the open atmosphere due to air draught caused by the “chimney effect” (Bezek et al., 2012; Šebela et al., 2013). The two main types of air circulation in Postojnska jama are schematically summarized in Fig. 7.

DISCUSSION

Fig. 8 presents mean values of both $p\text{CO}_2$ and $\delta^{13}\text{C}_{\text{airCO}_2}$ at each location as functions of the distance from the main entrance and the grouping of locations is obvious. Locations 01 – 04, which are relatively close to the entrance, have lower $p\text{CO}_2$ and higher $\delta^{13}\text{C}_{\text{airCO}_2}$ than locations 05 – 08 deeper in the cave. Locations 09 and 10 have similar both $p\text{CO}_2$ and $\delta^{13}\text{C}_{\text{airCO}_2}$ values, in between the two main groups of locations, and can be treated as the separate group.

Comparison of data presented in Figs. 5, 6 and 8 shows that the carbon isotopic composition of cave-air CO_2 varies inversely with $p\text{CO}_2$. The relation

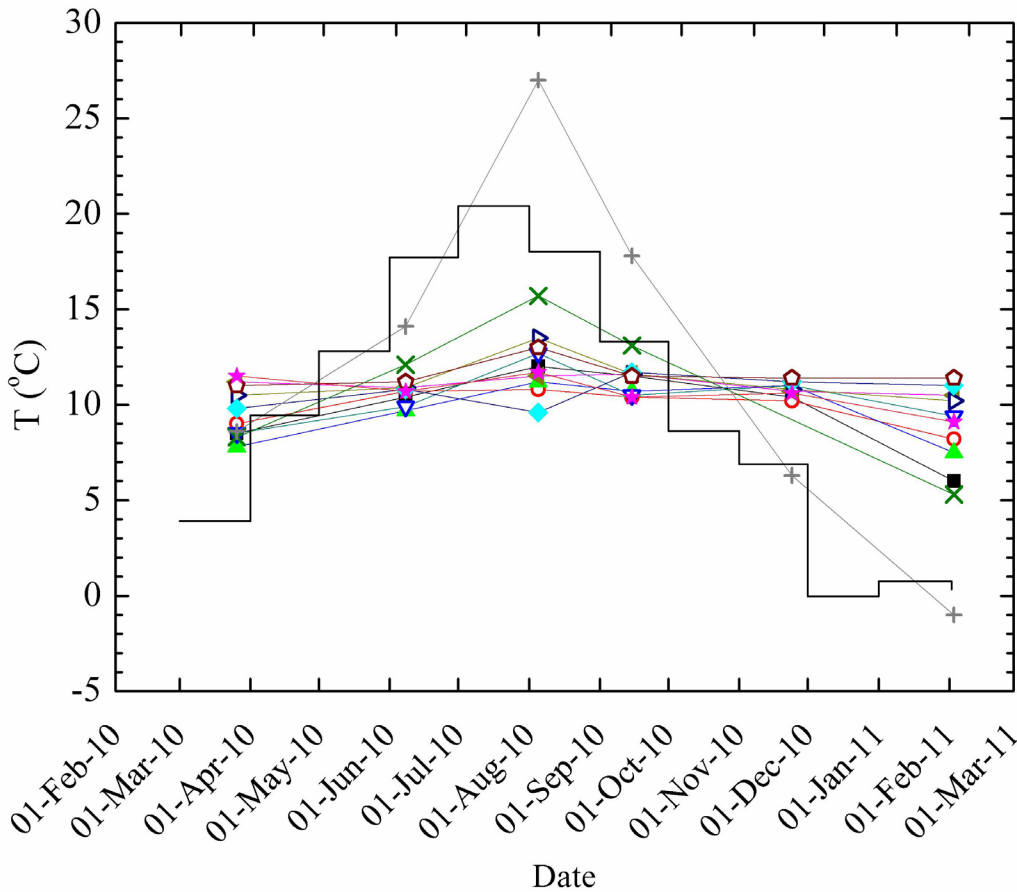
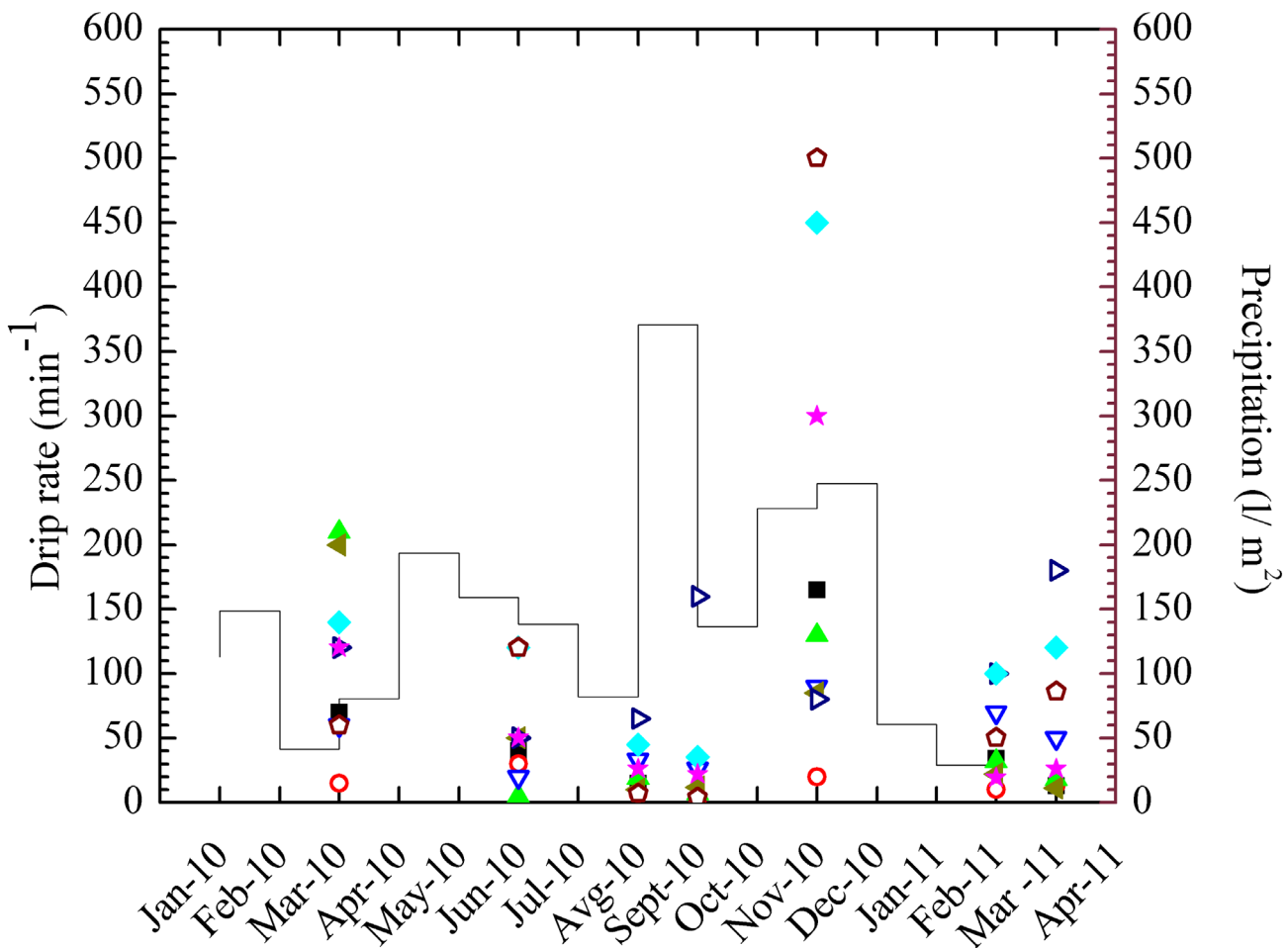


Fig. 4. a) Measured cave-air temperature at different locations (symbols) and mean monthly temperature (step line) at the meteorological station Postojna (-). b) Drip rate (symbols) and monthly precipitation (solid line) at meteorological station Postojna.

Location	Symbol
01 – Slonova glava	■
02 – Biospeleološka postaja	○
03 – Vodopad	▲
04 – Kongresna dvorana	▽
05 – Podrti kapnik	▶
06 – Stebrišče	▷
07 – Čarobni vrt	◆
08 – Vrh Velike gore	◊
09 – Zgornji Tartar	★
10 – Pivka River inside	×
11 – Pivka River outside	+



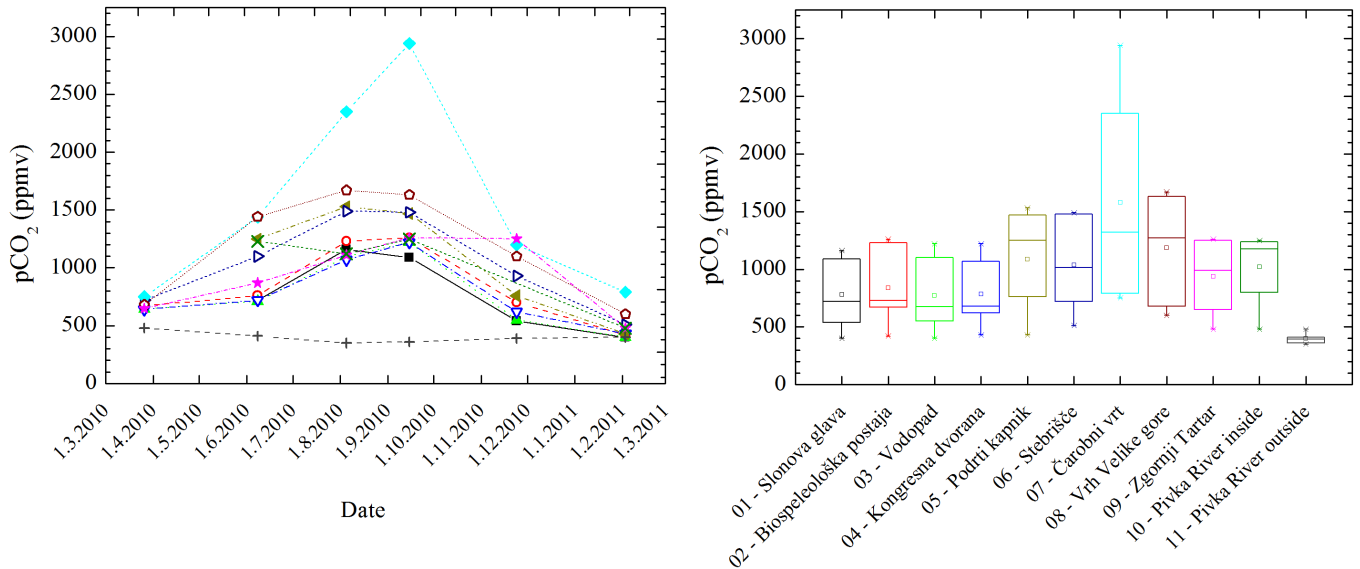


Fig. 5. CO₂ concentration (pCO₂) in cave air, a) seasonal variations, b) box-plot analysis. Symbols defined in Figs. 2 and 4.

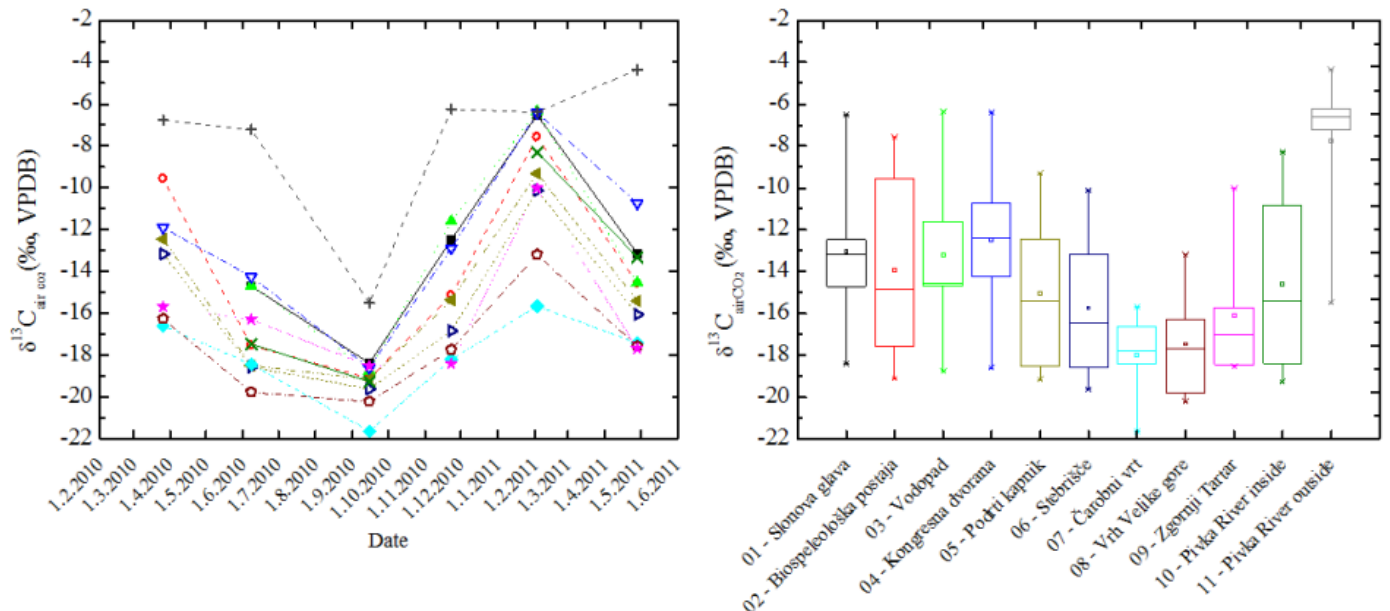


Fig. 6. δ¹³C_{airCO₂} of atmospheric and cave-air CO₂. a) seasonal variations, b) box-plot analysis. Symbols defined in Figs. 2 and 4.

between pCO₂ and δ¹³C_{airCO₂} is shown as Keeling plot in Fig. 9. A good correlation between 1/pCO₂ and its δ¹³C_{airCO₂} value has been obtained:

$$\delta^{13}\text{C}_{\text{airCO}_2} = (6.2 \pm 0.4) 1000/\text{pCO}_2 + (-23.3 \pm 0.7), N = 49, R^2 = 0.79 \quad (1)$$

The δ¹³C value of -23.3 ‰ (intercept in eq. 1) is close to the previously determined carbon isotopic composition of soil CO₂ (-21.7 and -20.5 ‰, Vokal, 1999) in the area.

Based on the observed correlation between pCO₂ and δ¹³C_{airCO₂} (Fig. 8) we propose a simple mixing model of CO₂ with two sources contributing to the cave air CO₂. We assume the atmospheric CO₂ with δ¹³C = -7.8 ‰ and a concentration of 398 ppmv as one source, as determined here for location 11 (Table 1). The other source is ¹³C-depleted CO₂, and we assume it is the CO₂ generated by the decay of soil organic matter and root respiration.

Mathematically, the mixing model can be described as

$$p_{\text{atm}} \times \delta^{13}\text{C}_{\text{atm}} + (p_{\text{meas}} - p_{\text{atm}}) \times \delta^{13}\text{C}_x = p_{\text{meas}} \times \delta^{13}\text{C}_{\text{airCO}_2} \quad (2)$$

where p_{atm} and δ¹³C_{atm} are the concentration and stable isotope composition of atmospheric CO₂, respectively, (location 11, Table 1), and p_{meas} and δ¹³C_{airCO₂} are the corresponding measured values for each location 01 to 09, respectively. δ¹³C_x is the carbon isotopic composition of the unknown end member, source of additional CO₂ inside the cave, which in our model contributes to the difference between the atmospheric pCO₂ and the measured pCO₂. Equation (2) has been applied to all individual measurements and the obtained δ¹³C_x values range mostly between -22 and -26 ‰ (Fig. 10), in reasonable agreement with the δ¹³C of soil CO₂ (Vokal, 1999) and the intercept of the Keeling plot (eq. 1). Therefore we conclude that the soil CO₂ brought to the cave by drip water contributes to the CO₂ concentration in the cave. To corroborate such a conclusion the relations between mean values of drip rate and pCO₂ as well as between drip rate and δ¹³C_{airCO₂} are shown in Fig. 11: the higher the mean drip rate, the higher the mean pCO₂ (R² = 0.6, p = 0.01) and the lower the mean δ¹³C_{airCO₂} (R² = 0.7, p = 0.003). It should be noted here that although there were not observed

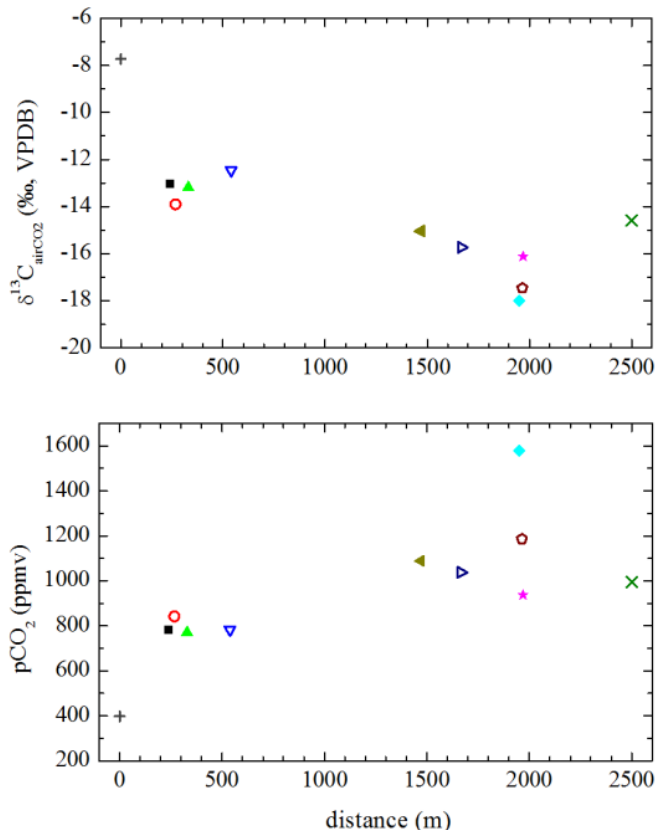


Fig. 7. pCO₂ and δ¹³C_{airCO₂} as function of the distance from the cave entrance.

correlations between individual instantaneous values of the drip rate and pCO₂ as well as between the drip rate and the δ¹³C_{airCO₂} at any of the studied locations, the statistically significant correlations have been obtained for the corresponding mean values (Fig. 11).

Up to 500,000 visitors yearly visit Postojnska jama per year (Šebela et al., 2013). Human breath contains about 40 000 ppmv CO₂ (Faimon et al., 2012), considerably higher than the atmospheric pCO₂ (380 – 400 ppmv) and the cave air pCO₂ (up to 3000 ppm, Fig. 5). δ¹³C of exhaled anthropogenic CO₂ reflects the δ¹³C of the source organic matter used as food and cannot be distinguished from the δ¹³C of soil

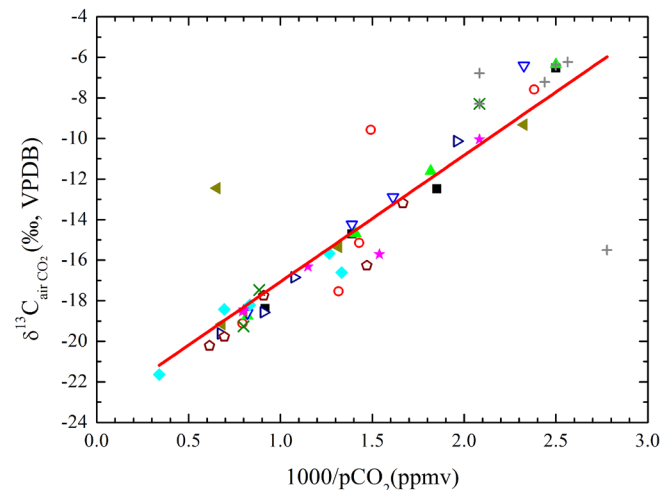


Fig. 9. Plot of δ¹³C_{airCO₂} vs. pCO₂ (“Keeling plot”).

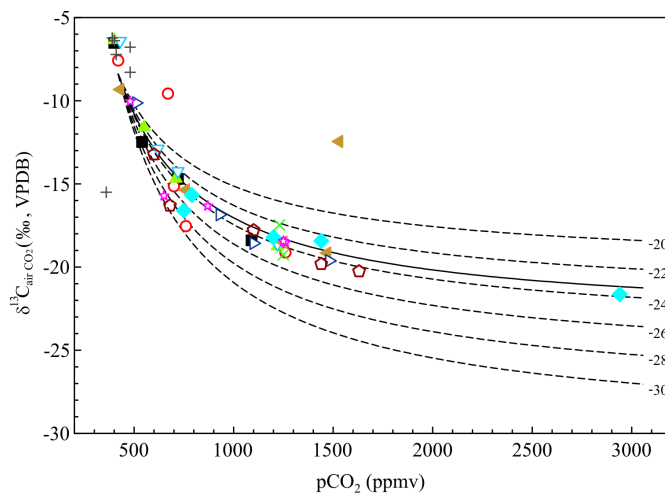


Fig. 10. Relation between δ¹³C_{airCO₂} and pCO₂ of individual measurements at all sampling locations. Broken lines represent the modelled (eq. 2) δ¹³C_{airCO₂} values for different δ¹³C of soil CO₂. Solid line is obtained by using δ¹³C obtained from the Keeling plot and eq. (1), Fig. 9.

CO₂ providing that C3 plants prevail in the region and that the human diet is based on C3 plants (Epstein & Zeiri, 1988). Human breath can thus significantly alter cave CO₂ concentrations while its influence on δ¹³C_{airCO₂} cannot be simply determined. A recent study of pCO₂ in Postojnska jama during and immediately after a large number (2000 – 4000) of visitor per day over the course of several holiday periods showed that during the visit pCO₂ significantly increases, e.g., the observed increase in pCO₂ was between 450 and 1750 ppmv, but it returned to background levels within 1 – 10 days (Šebela et al., 2013). Our measurements were performed on days when only few visitors were present in the cave, and the highest pCO₂ and lowest δ¹³C_{airCO₂} were observed at locations closed for tourists, so we believe that we measured the background pCO₂ levels in the cave, i.e. that the excess pCO₂ (above the atmospheric level) was brought to the cave by drip water.

CONCLUSION

The monitoring of pCO₂ in cave air and its δ¹³C value at several locations in Postojnska jama revealed their seasonal and spatial variations. The seasonal variations in both pCO₂ and δ¹³C_{airCO₂} are

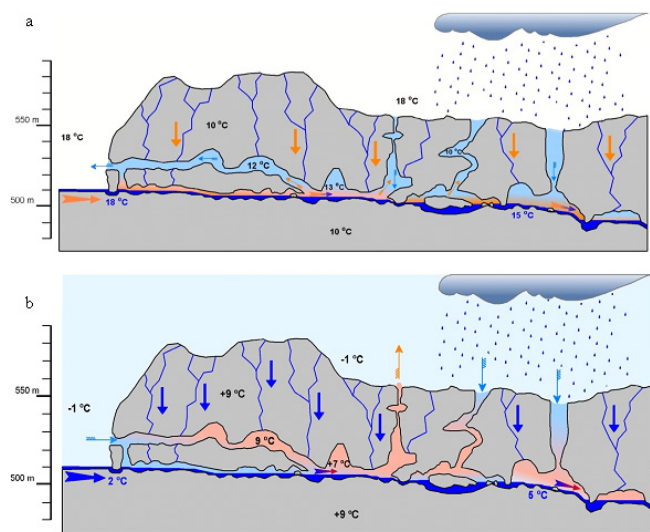


Fig. 8. Schematic summary of the two main types of air circulation in Postojnska jama Cave: a) summer regime, May – October, b) winter regime, November – April.

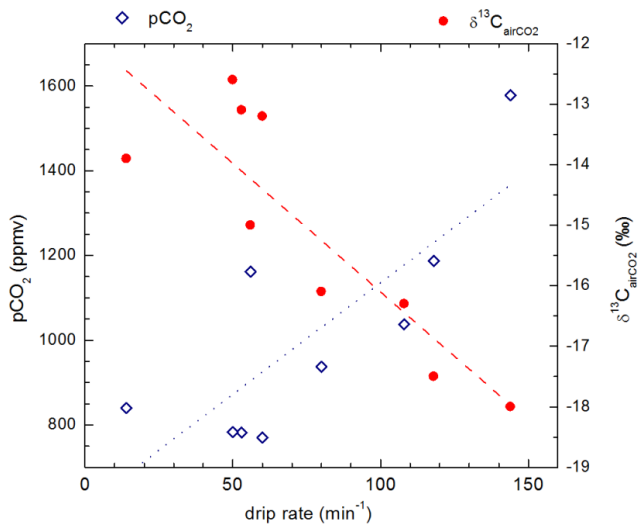


Fig. 11. Dependence of mean values of $p\text{CO}_2$ (\diamond) and $\delta^{13}\text{C}_{\text{airCO}_2}$ (\bullet) on mean drip rate at various locations in Postojnska jama Cave. Dashed and dotted lines represent respective linear regression lines.

more pronounced in deeper and closed parts of the cave, while some locations close to the entrance are prone to ventilation. Ventilation is observed in both directions, from the open atmosphere to the cave in winter and vice-versa in summer. Production of CO_2 in the soil zone and its transport by percolating water into the cave is the main source of CO_2 in the cave atmosphere. The excess of CO_2 in the cave air has a $\delta^{13}\text{C}$ value of -23.3 ± 0.7 ‰. Postojnska jama can be described as well-ventilated cave with relatively low maximum and mean $p\text{CO}_2$ values, although not all locations show the same degree of ventilation.

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