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Reasons for large fluctuation of radon and CO_2 levels in a dead-end passage of a karst cave (Postojna Cave, Slovenia)

A. Gregorič[1,*], J. Vaupotič[1], and F. Gabrovšek[2]

[1]Jožef Stefan Institute, Ljubljana, Slovenia
[2]Research Centre of the Slovenian Academy of Sciences and Arts, Karst Research Institute, Postojna, Slovenia

[*]*Invited contribution by A. Gregorič, recipient of the EGU Outstanding Student Poster (OSP) Award 2011.*

Correspondence to: A. Gregorič (asta.gregoric@ijs.si)

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Abstract. Measurements of radon concentration were performed at three geomorphologically different locations in Postojna Cave, Slovenia. In the part of the cave open to visitors, annual average radon activity concentrations of $3255 \pm 1190\,\mathrm{Bq\,m^{-3}}$ and $2315 \pm 1019\,\mathrm{Bq\,m^{-3}}$ were found at the lowest point (LP) and in the Lepe jame (Beautiful Caves, BC), respectively. A much higher average of $25\,020 \pm 12\,653\,\mathrm{Bq\,m^{-3}}$ was characteristic of the dead-end passage Pisani rov (Gaily Coloured Corridor, GC), in which CO_2 concentration also reached very high values of 4689 ± 294 ppm in summer. Seasonal variations of radon and CO_2 levels in the cave are governed by convective airflow, controlled mainly by the temperature difference between the cave and the outside atmosphere. The following additional sources of radon and CO_2 were considered: (i) flux of geogas from the Earth's crust through fractured rocks (radon and CO_2 source), (ii) clay sediments inside the passage (radon source) and (iii) the soil layer above the cave (radon and CO_2 source).

1 Introduction

The karst cave environment is characterised by very high microenvironmental stability with essentially quasi-closed air masses (Badino, 2010), and may be considered stable in comparison to the outside atmosphere. Beyond this apparent stability, however, complex processes occur, which can today be brought to light thanks to advances in measurement techniques, data storage and data processing. All caves should be considered fragile systems, but show caves are particularly at risk because of anthropogenic impact. An understanding of cave microclimates is of great importance when studying the thermodynamics of karst processes, palaeoclimate proxies, hydrogeological aspects of speleothems, CO_2 build-up and cave ecosystems (Baldini et al., 2006; Faimon et al., 2011; Kowalczk and Froelich, 2010; Perrier and Richon, 2010; Spötl et al., 2005; Tremaine et al., 2011). The thermal and moisture characteristics of the cave air (Badino, 2010; De Freitas et al., 1982), as well as the concentration of gases (^{222}Rn, CO_2) and aerosols (Bezek et al., 2012) are mainly controlled by the degree of air exchange with the outside environment. Convective air circulation, driven by buoyancy forces created by the difference of air density between the external and internal air masses, is a major mechanism controlling air circulation in caves with more than one entrance at different elevations (Badino, 2010; Cigna, 1968; Hakl et al., 1996; Kowalczk and Froelich, 2010; Wigley, 1967). On the other hand so-called barometric circulation, driven by the internal–external pressure difference, can be very important for caves with large volumes connected by small passages, with one entrance or with extremely small entrances (Badino, 2010; Luetscher and Jeannin, 2004; Wigley, 1967). Therefore, in addition to outside atmosphere, cave geomorphology plays an important role in cave ventilation.

Radon (^{222}Rn, α-radioactive, half-life $t_{1/2} = 3.82$ days) has often been used as an excellent tracer for air circulation, since it is a noble gas and highly abundant in caves (Cigna, 2003; Cunningham and Larock, 1991; Hakl et al., 1996, 1997; Kies and Massen, 1997; Kowalczk and Froelich, 2010; Perrier et al., 2004; Przylibski, 1999). Its half-life, suitable for the timescales on which cave ventilation takes place, distinguishes ^{222}Rn from the other two radon isotopes (^{220}Rn and ^{219}Rn). An additional advantage is its radioactivity, which makes it relatively easy to monitor the activity concentration of radon with a very low detection limit. Variation of radon concentration in cave air arises from a balance of radon emission from cave surfaces and drip waters, its radioactive transformation, and exchange with the outside atmosphere (Wilkening and Watkins, 1976). Radon concentration in underground cave systems is also characterised by internal mixing of air masses (Perrier and Richon, 2010). In a study of 220 caves around the world, Hakl et al. (1997) reported an annual average radon concentration of 2800 Bq m^{-3}.

The most important parameter governing dissolution and precipitation processes in carbonate karst is CO_2 (Dreybrodt, 1999), so understanding CO_2 distribution and dynamics in caves is important for palaeoclimatic research. The dynamics of CO_2 in caves is governed by the distribution and intensity of its sources and (mainly) advective transport by air currents. The main sources of CO_2 in caves are diffusion from the epikarst, decomposition of organic matter and precipitation of calcite from supersaturated solutions. Many authors therefore include cave ventilation when modelling CO_2 variation over time in order to explain seasonality and trend (Baldini et al., 2008; Fernandez-Cortes et al., 2011; Milanolo and Gabrovšek, 2009; Tanahara et al., 1997). CO_2 was used in this study as an additional tool to characterise and explain the sources and reasons of high radon concentration and its variability in a dead-end passage in Postojna Cave. However, the exact interpretation of short-term fluctuation of the CO_2 level remains outside the scope of this study.

The complexity and size of Postojna Cave, with its numerous known and unknown entrances at different levels and a long and highly ramified cave system, makes this cave a fascinating study site for a variety of physical and environmental studies (Bezek et al., 2012; Gosar et al., 2009; Gregorič et al., 2011; Kobal et al., 1988; Mulec et al., 2012; Šebela et al., 2010; Šebela and Turk, 2011; Vaupotič, 2008). In general the ventilation of Postojna Cave is characterised by convective airflow, controlled mainly by the temperature difference between the cave and the outside atmosphere, as discussed by Gregorič et al. (2011) for one measurement location in the Velika Gora (Great Mountain) chamber of Postojna Cave. Different ventilation regimes in the cold and warm periods of the year are responsible for the observed seasonal pattern of radon concentration with low winter and high summer levels, as already reported for this (Gregorič et al., 2011; Kobal et al., 1988; Vaupotič, 2008) and several other caves (Gillmore et al., 2002; Kowalczk and Froelich, 2010; Nagy et al., 2012; Perrier and Richon, 2010; Przylibski, 1999; Tanahara et al., 1997; Wilkening and Watkins, 1976).

In one passage of Postojna Cave, known as the Pisani rov, very high radon levels have been observed (annual mean 25 020 ± 12 653 Bq m^{-3}) which are comparable to the highest radon levels of 32 246 Bq m^{-3} (annual mean) measured in Castañar de Ibor karst cave in Spain (Lario et al., 2006), although the rest of the cave is characterised by radon levels similar to world average values (Hakl et al., 1997). This paper presents the results of 18 months (March 2011–September 2012) of continuous measurements of radon concentration in three passages in Postojna Cave, including Pisani rov, in which CO_2 concentration was additionally measured in two periods: 1 March–9 May and 28 June–1 September 2012. The aim of this study is to reveal the geophysical processes and geomorphological characteristics of cave passages that are responsible for very significant differences in the amplitude of fluctuations of radon and CO_2 levels.

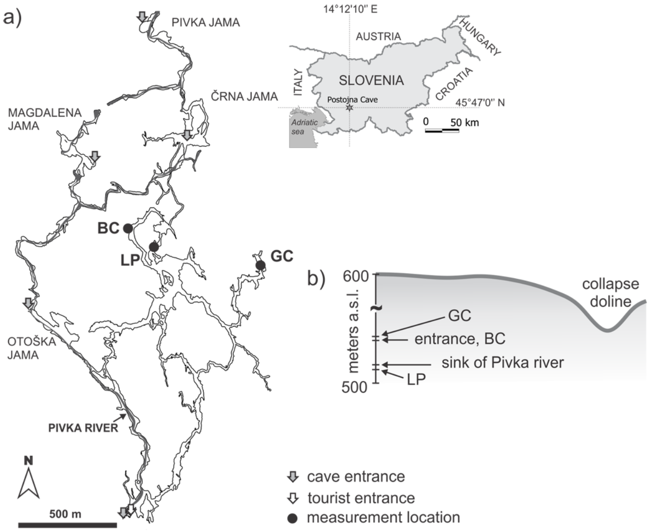

Fig. 1. Postojna Cave System. **(a)** ground plan of the Postojna Cave System with marked monitoring sites: Lepe jame (BC), the lowest point (LP) and the Pisani rov (GC); **(b)** the level of measurement locations.

2 Site and methodology

2.1 Site description

The Postojna Cave System (Fig. 1a), with its 20 570 m of known passages, is the second longest of 10 000 registered karst caves in Slovenia and one of the most visited show caves in Europe. The passages were formed at two main levels. The river Pivka sinks at the lower entrance to the cave at 511 m above sea level (m a.s.l.) (Fig. 1b) and the active river passages are mostly smaller than the higher ones. The river bed is composed mostly of gravels derived from the Eocene flysch. The entrance to the main, currently dry, passage is situated at 526.5 m a.s.l. and is 10 m high and 6 m wide. This entrance is also used as a tourist entrance. The cave passages have developed in an approximately 800 m thick layer of Upper Cretaceous bedded limestone situated

Table 1. Geomorphological characteristics of cave passages with measurement locations.

Cave passage	Abbrev.	Level/m a.s.l.	Tourist route	Geomorphological characteristics and sediments
Lepe jame (Beautiful Caves)	BC	526	15 m away	– narrow solutional fissure, created along a fault plane – loam in the fissure
Lowest point	LP	508	yes	– wide passage – thin layer of loam
Pisani rov (Gaily Coloured Corridor)	GC	529	no	– 920 m long dead-end passage – grey loam originating from weathered flysch rocks along the whole passage – 145 cm thick profile at the end of the passage: fine-grained sediments (yellowish brown silts to clays with dark stains in the upper part showing cubic to columnar disintegration with Fe stains on the fractures) covering the collapse boulders and massive flowstone

between two important Dinaric faults (Šebela et al., 2010). The cave passages are mostly horizontal. The system has six known entrances; however, unknown connections to the surface along corrosionally widened fissures undoubtedly exist. There is no forced ventilation in the cave, and air is only exchanged via natural air flow through the numerous cracks, passages and breathing holes (Gams, 1974) connecting the cave with the outside atmosphere. In the interior part the temperature is relatively stable at around 10 °C. Measurements were performed at three locations (Fig. 1a). Geomorphological characteristics of the passages are summarised in Table 1. The first location is inside a narrow solutional fissure, created along a fault plane in the Lepe jame (Beautiful Caves, BC), 526 m a.s.l. and about 15 m off the guided tourist route. The second location is situated at the lowest point (LP) of the tourist route, at 508 m a.s.l., where the passage widens significantly. The distance between the two locations is about 250 m. The third measurement location lies at the end (529 m a.s.l.) of the 920 m long Pisani rov (Gaily Coloured Corridor, GC), which deviates from the main passage to the north. This passage is not a part of the tourist route. It terminates below the slopes of a collapse doline where the bottom is filled by sediments at 535 m a.s.l. (Fig. 1b) (Šebela and Čar, 2000). Along the whole passage grey loam originating from weathered flysch rocks can be found. The roughly 145 cm thick profile of fluvial sediments situated at the end of GC consists of fine-grained sediments (yellowish brown silts to clays with dark stains in the upper part showing cubic to columnar disintegration with Fe stains on the fractures) covering the collapse boulders and massive flowstone (Zupan Hajna et al., 2008). The deepening of the collapse doline interrupted the continuation of GC towards the north (Šebela and Čar, 2000). The smallest thickness of the cave ceiling is about 30 m. Between BC and Črna jama (Black Cave) (Fig. 1a), an artificial tunnel is closed by doors that are opened only during occasional tourist visits. The ventilation from Črna jama does not have a significant impact on our monitoring locations.

2.2 Instrumentation

At all three measurement locations, radon activity concentration (C_{Rn}) was measured continuously once an hour from March 2011 to September 2012.

Radon measurements at BC were performed using a Radim 5 monitor (SMM Company, Czech Republic), which is mainly designed for radon measurements in indoor air. It determines radon concentration by measuring gross alpha activity of the radon decay products ^{218}Po and ^{214}Po, collected electrostatically on the surface of a semiconductor detector. The lower limit of detection is about 50 Bq m^{-3} and the sampling frequency is twice an hour. Hourly averages are calculated for further data evaluation in order to correspond to measurements performed using other types of measuring devices.

At the LP and GC locations, Barasol probes (MC-450, ALGADE, France) were used for radon measurements. The probe is primarily designed for radon measurements in soil gas, and it therefore has a higher lower limit of detection (about 500 Bq m^{-3}) than the Radim 5 monitor. It gives radon concentration based on alpha spectrometry of radon decay products in the energy range of 1.5 MeV to 6 MeV using an implanted silicon detector. The detector sensitivity is 50 Bq m^{-3} per 1 imp h^{-1} with a sampling frequency of once an hour. It also records temperature and relative atmospheric pressure.

In both instruments data are stored in the internal memory and are transferred to a personal computer. The instruments are checked regularly, using a portable AlphaGuard radon monitor (Saphymo, Germany) as a reference instrument, and were calibrated in the Radon Chamber at the Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland (Kozak et al., 2009).

Continuous measurements of CO_2 concentrations were performed in two periods, spring and summer 2012, at the GC location. CO_2 is measured along with the other microclimatic parameters within broader monitoring of cave micrometeorology. A Vaisala Carbocap CO_2 module GMM 221 with a measurement of interval 0–7000 ppm and an accuracy range of 1.5 % is used for the task. It is connected to a data logger with a sampling interval of 10 min. Probe operation is based on measurements of infrared absorption by CO_2.

Atmospheric parameters (temperature, barometric pressure and relative humidity) were measured continuously by a DL-180THP data logger (Voltcraft, Germany) in front of the tourist entrance. Daily height of rainfall was additionally provided by the Postojna weather station of the Slovenian Environment Agency (Ministry of Agriculture and Environment of the Republic of Slovenia).

3 Results

On a long timescale, radon concentration in the Postojna Cave exhibits annual cycles with high summer and low winter values (Gregorič et al., 2011), reflecting the ventilation pattern. However, amplitudes of fluctuation of radon levels differ from point to point. Annual mean radon concentration recorded at LP is $3255 \pm 1190\,\mathrm{Bq\,m^{-3}}$ and at BC, $2315 \pm 1019\,\mathrm{Bq\,m^{-3}}$, which is in the same range as values recorded at the Great Mountain location (Gregorič et al., 2011). On the other hand, radon concentration at GC is up to ten times higher than in other cave passages (Fig. 2) with the annual mean of $25\,020 \pm 12\,653\,\mathrm{Bq\,m^{-3}}$ (Table 2).

At LP radon concentration follows significant annual cycles, with average values of $1742 \pm 666\,\mathrm{Bq\,m^{-3}}$ in winter months (period D, Table 2) and constantly high summer concentrations of $4130 \pm 370\,\mathrm{Bq\,m^{-3}}$ (average of summer 2011 (B) and 2012 (F), Table 2). The biggest variations between minimum and maximum values are, as expected, characteristic of transitional periods in spring and autumn.

Situated in a side branch of the main passage, characterised by cracked and faulted rocks and possibly connected to an unknown passage, the BC location exhibits a far more variable radon concentration pattern, not only on an annual scale but also from year to year. Changes of behaviour of radon concentration were, for example, observed after floods in 2010 (Gregorič and Vaupotič, 2011). Concentration during the period discussed in this paper shows a different seasonal pattern from the LP location, with the highest values in spring and autumn, reaching up to about $5500\,\mathrm{Bq\,m^{-3}}$ (Fig. 3), whereas the concentration in summer usually remains below $4000\,\mathrm{Bq\,m^{-3}}$. Minimum radon levels are still found in the cold period of year (period D, Table 2). The radon concentration at BC exhibits high variation throughout the whole measurement period. Short periodic cycles (24 h) can be observed at BC in the transitional periods, spring and autumn, as a result of the changing ventilation regime during cold nights, when outside temperature drops below cave temperature (10 °C), and warm sunny days with outside temperature above cave temperature.

The GC location is, in contrast to LP and BC, characterised by much higher radon levels in summer, reaching up to $44\,500\,\mathrm{Bq\,m^{-3}}$, with a mean summer value of $35\,857 \pm 3259\,\mathrm{Bq\,m^{-3}}$ in 2011 and $33\,038 \pm 3015\,\mathrm{Bq\,m^{-3}}$ in 2012 (Table 1). During the cold part of the year, however, radon concentration in the periods of active ventilation drops below $500\,\mathrm{Bq\,m^{-3}}$ – the lowest of all three measurement locations (Fig. 3). The mean value in winter is $8684 \pm 7648\,\mathrm{Bq\,m^{-3}}$.

CO_2 levels at the GC location show similar seasonal characteristics in spring and summer as radon levels, with mean values of 1522 ± 614 ppm and 4689 ± 294 ppm, respectively. Higher fluctuation of CO_2 levels is observed in spring, which represents a transitional period in terms of the ventilation regime. During this period high correlation ($R^2 = 0.91$) is observed between CO_2 and ^{222}Rn concentrations, pointing to a common driving force (i.e. cave ventilation) (Fig. 4). In summer, CO_2 levels remain high, consistent with decreased ventilation. However, different behaviour of these two gases is observed, reflecting in a weaker correlation ($R^2 = 0.69$) than in spring.

3.1 Spatial differences in radon levels

Linear correlation of radon levels between the GC and LP locations, with coefficient of determination (R^2) 0.85, can be observed throughout the annual cycle, as seen in Fig. 5a and b. From Fig. 5a, where the point colour represents daily mean outside temperature, it can be noted that the lowest radon levels are usually observed at outside temperatures between 0 and 10 °C, while the highest radon levels are typical for days with daily mean outside temperatures around 15 °C. On extremely cold winter days, when T_{out} remains below 0 °C for several days, slightly higher radon levels are observed at both locations (GC and LP). Conversely, during extremely warm summer days ($T_{\mathrm{out}} >$ 23 °C), radon levels slightly below maximum are observed. Atmospheric pressure (Fig. 5b), on the other hand, does not show a significant role in controlling radon levels in the cave. Therefore, although the amplitude of fluctuation of radon concentration at GC is some orders of magnitude higher than at LP, it is obvious that both locations are subject to a similar ventilation pattern.

In contrast to GC and LP, the measurement location at BC shows slightly different behaviour, with radon levels being roughly in the same range as at the LP location. A moderate correlation ($R^2 = 0.46$) is observed between radon concentrations at BC and GC in winter months, when fresh outside

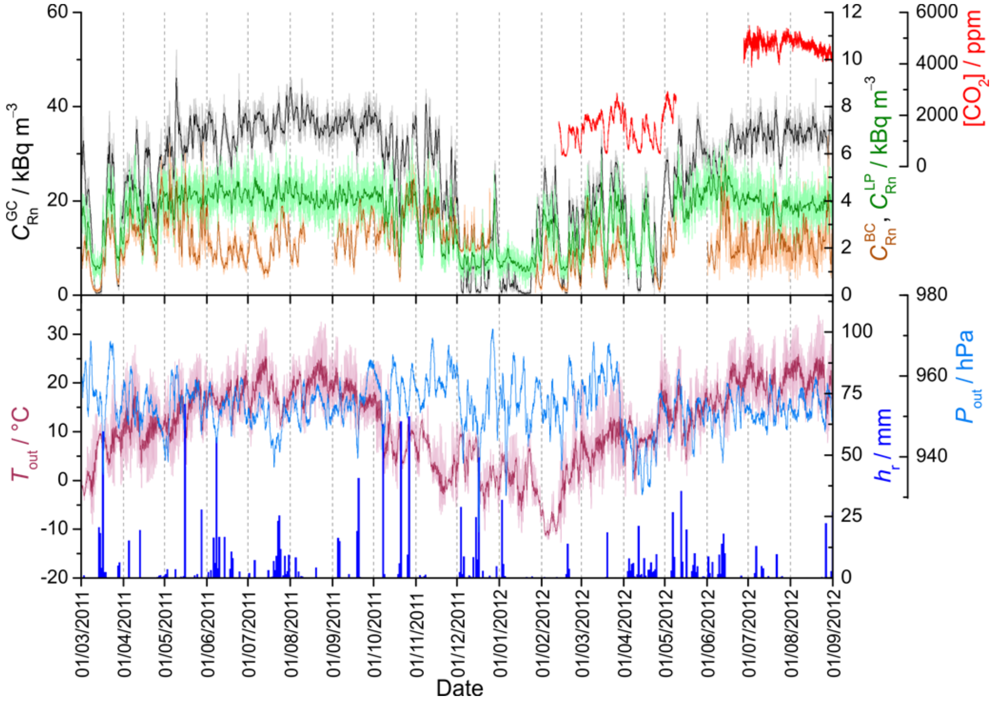

Fig. 2. Time series of radon concentration at three measurement locations (Pisani rov – $C_{\mathrm{Rn}}^{\mathrm{GC}}$, Lepe jame – $C_{\mathrm{Rn}}^{\mathrm{BC}}$ and the lowest point – $C_{\mathrm{Rn}}^{\mathrm{LP}}$) and CO$_2$ concentration recorded at the GC location. Time series of main atmospheric parameters controlling radon concentration in the cave: outside air temperature (T_{out}), air pressure (P_{out}) and daily height of rainfall (h_{r}). Radon concentration and atmospheric parameters are expressed in hourly values, 24-h weighted average smoothing is applied to radon concentration and temperature; rainfall is expressed as absolute daily values.

air enters the cave through the large tourist entrance, and warmer cave air rises through narrow vertical cracks and channels and exits into the outside atmosphere. Radon concentration at BC ($C_{\mathrm{Rn}}^{\mathrm{BC}}$) is higher than at LP ($C_{\mathrm{Rn}}^{\mathrm{LP}}$) in autumn and lower in spring (Fig. 3). The negative correlation ($R^2 = 0.26$) observed when daily mean T_{out} exceeds 20 °C (Fig. 5c) indicates that other parameters take control of ventilation at BC and the air connection between LP and BC is cut off.

3.2 Influence of outside atmospheric parameters in governing radon levels in the cave

Correlation between radon levels at each location with outside atmospheric parameters – outside temperature (T_{out}), pressure (P_{out}) and accumulated rainfall in the last 7 days ($h_{\mathrm{r}\text{-}7}$) (Table 2) – reveals that T_{out} has the highest influence on radon levels. The response of fluctuation of radon concentration on T_{out} is comparable at the GC and LP locations in all periods except the summer months (periods B and F), when radon concentration at BC and LP decreases with increasing T_{out}.

Correlation between P_{out} and P_{cave} (pressure in the cave) was discussed by Šebela and Turk (2011) in the study of climate characteristics of Postojna Cave, where simultaneous pressure variations at the surface and at three locations in the underground was shown. Therefore, air pressure may in this case have an influence on radon concentration only by the effect of "barometric pumping" of radon from the pore space (Perrier and Richon, 2010). However, no significant influence of P_{out} can be observed, possibly due to the obscured effect of pressure changes by airflows driven by temperature gradients.

The most sensitive measurement location for rainfall with respect to radon concentration seems to be BC, where significant changes of radon levels after heavy flooding in 2010 (Gregorič and Vaupotič, 2011) provide further evidence for high sensitivity to precipitation. Rainfall acts in two ways at this location; firstly, by reducing the air connection between the outside atmosphere and the cave atmosphere due to saturation of soil pores on the surface (thus causing an increase of radon concentration) and, secondly, by reducing radon exhalation from rock surface and cracks (decrease of radon concentration shown about a week after heavy rainfall) (Gregorič and Vaupotič, 2011). On the other hand, no significant correlation with rainfall was observed for the GC location.

3.3 Estimation of radon source

The ventilation characteristics of a cave can be reflected in the fluctuation of radon concentration provided the turnover time is shorter than about five mean lives of ^{222}Rn

Table 2. Basic statistics (min – minimum, max – maximum, AM – arithmetic mean and SD – standard deviation) of radon concentration (C_{Rn}) at locations LP, BC and GC in 6 periods (A to F) and correlation coefficient R between C_{Rn} and outside air temperature (T_{out}), C_{Rn} and atmospheric pressure (P_{out}), and C_{Rn} and cumulative height of rainfall in the last 7 days ($h_{\mathrm{r\text{-}7}}$) for each location and time period.

		period	C_{Rn} / Bq m^{-3}						
			min	max	AM	SD	$R(C_{\mathrm{Rn}}, T_{\mathrm{out}})$	$R(C_{\mathrm{Rn}}, P_{\mathrm{out}})$	$R(C_{\mathrm{Rn}}, h_{\mathrm{r\text{-}7}})$
LP		Mar 2011–12 Mar 2012	1019	5030	3255	1190			
	A	Mar–May 2011	1138	4636	3370	993	0.51	0.05	0.19
	B	Jun–Aug 2011	3662	5030	4244	302	−0.30	−0.01	0.36
	C	Sep–Nov 2011	1608	4826	3653	850	0.60	−0.15	0.30
	D	Dec 2011–Feb 2012	1019	4019	1742	666	−0.55	0.18	−0.16
	E	Mar–May 2012	1275	4729	3164	980	0.57	0.31	0.26
	F	Jun–Aug 2012	2874	5389	4022	440	−0.40	−0.17	0.52
BC		Mar 2011–Mar 2012	185	4909	2315	1019			
	A	Mar–May 2011	185	4909	2430	1154	0.30	−0.06	0.09
	B	Jun–Aug 2011	937	3636	2039	654	−0.52	−0.18	0.23
	C	Sep–Nov 2011	937	4865	2925	804	−0.24	0.19	0.43
	D	Dec 2011–Feb 2012	209	3825	1543	828	0.30	−0.06	0.47
	E	Mar–May 2012	260	4059	1853	852	−0.14	−0.01	−0.27
	F	Jun–Aug 2012	1093	4428	2282	710	−0.41	−0.04	0.40
GC		Mar 2011–Mar 2012	344	44 578	25 020	12 653			
	A	Mar–May 2011	486	44 578	24 514	10 307	0.47	0.15	0.08
	B	Jun–Aug 2011	25 861	43 872	35 857	3259	0.10	0.12	−0.21
	C	Sep–Nov 2011	10 571	40 123	30 910	6884	0.64	−0.10	0.10
	D	Dec 2011–Feb 2012	344	26 666	8684	7648	−0.51	0.28	−0.31
	E	Mar–May 2012	1095	36 939	20 147	8821	0.39	0.33	0.11
	F	Jun–Aug 2012	24 373	38 776	33 038	3015	0.53	0.29	−0.27

(approximately four weeks) (Kowalczk and Froelich, 2010). Cave ventilation represents the proportion of cave air exchanged per time unit. If the cave atmosphere is just pulled back and forth due to an alternating ventilation regime during transitional periods in spring and autumn, there is no air exchange in the deeper parts of the cave. This period can be called a stagnant ventilation period and could be the reason for higher radon levels at BC in spring and autumn. By contrast, ventilation is considered active when the cave remains in one ventilation regime for long enough in comparison to the time that air is retained in the cave (i.e. residence time) (Faimon et al., 2011).

According to Wilkening and Watkins (1976) and Perrier et al. (2004), the temporal evolution of radon concentration at a given location in the cave can be described as

$$\frac{dC_{\mathrm{Rn}}^{\mathrm{cave}}}{\mathrm{d}t} = \frac{S}{V}\Phi - \lambda C_{\mathrm{Rn}}^{\mathrm{cave}} - v\left(C_{\mathrm{Rn}}^{\mathrm{cave}} - C_{\mathrm{Rn}}^{\mathrm{out}}\right), \tag{1}$$

where S (m^2) and V (m^3) are, respectively, the total surface area and volume of the cave; Φ (Bq m^{-2} h^{-1}) represents the radon exhalation rate from the rock surface; λ (h^{-1}) is the radioactive decay constant of ^{222}Rn; v (h^{-1}) is the cave ventilation rate; and $C_{\mathrm{Rn}}^{\mathrm{out}}$ (Bq m^{-3}) is the radon concentration in the outside air. Note that the radon concentration in the outside air is on the order of tens of Bq m^{-3} and thus negligible in comparison to the radon concentration in the cave air.

As the total area and volume of the cave are very hard to determine without exact measurements, we considered the radon source for different locations separately:

$$\Phi_{\mathrm{ch}} = \frac{S_{\mathrm{ch}}}{V_{\mathrm{ch}}}\Phi, \tag{2}$$

where Φ_{ch} (Bq m^{-3} h^{-1}) is the radon source in a specific chamber, either GC or LP; S_{ch} (m^2) and V_{ch} (m^3) are, respectively, the surface area and volume of the chamber; and Φ (Bq m^{-2} h^{-1}) represents the radon exhalation rate from the rock surface.

The radon source can be estimated for the summer period at the GC and LP locations when radon concentration remains constantly high – around 40 kBq m^{-3} at GC and 4 kBq m^{-3} at LP location. If we consider the summer period as a stagnant ventilation period and a constant radon concentration, Eq. (1) can be transformed to

$$\Phi_{\mathrm{ch}} = \lambda C_{\mathrm{Rn-max}}^{\mathrm{ch}}, \tag{3}$$

where $C_{\mathrm{Rn-max}}^{\mathrm{ch}}$ (Bq m^{-3}) represents the highest radon concentration in a specific chamber. This means that in order to maintain 40 kBq m^{-3} (4 kBq m^{-3}) during stable conditions in summer at the GC (LP) location, the radon source should not be less than about 300 Bq m^{-3} h^{-1} (30 Bq m^{-3} h^{-1}).

Winter ventilation should be similar at the BC and LP locations, while during other periods of year the BC location

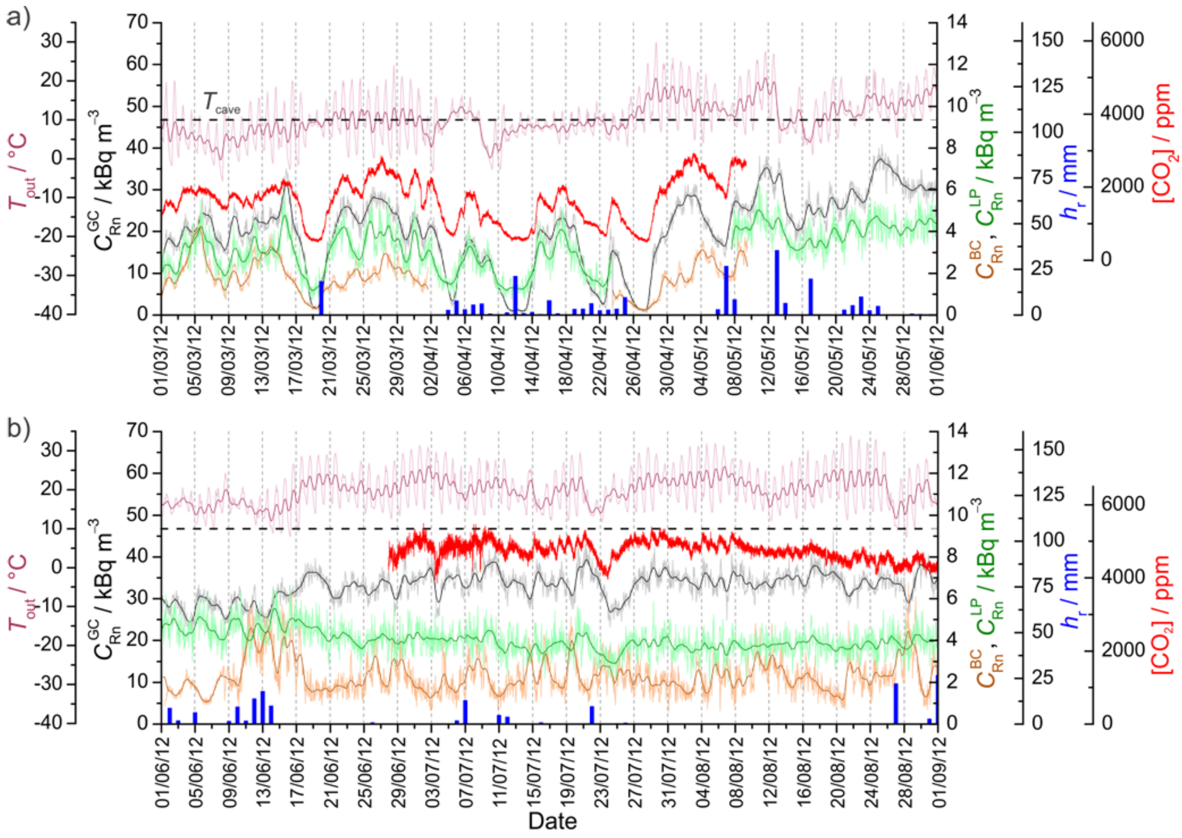

Fig. 3. Time series of radon concentration at three measurement locations (Pisani rov – C_{Rn}^{GC}, Lepe jame – C_{Rn}^{BC} and the lowest point – C_{Rn}^{LP}), CO_2 concentration at the GC location and atmospheric parameters: outside air temperature (T_{out}) and daily height of rainfall (h_r) in two periods: spring **(a)** and summer **(b)** 2012. Radon concentration and atmospheric parameters are expressed in hourly values; 24-h weighted average smoothing is applied to radon concentration and air temperature; rainfall is expressed as absolute daily values. CO_2 concentration is measured at 10-min intervals.

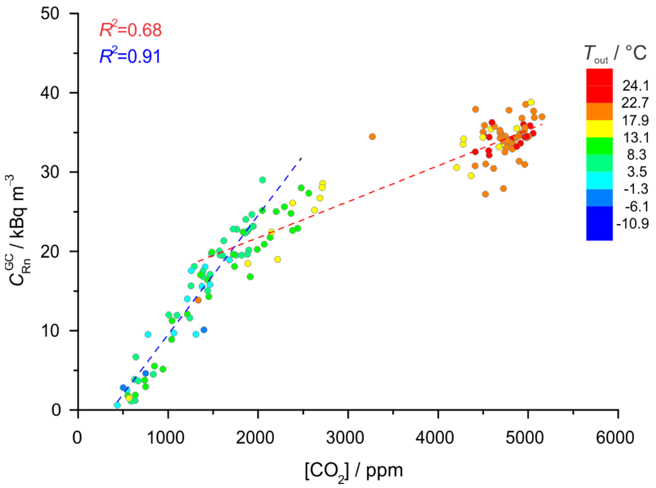

Fig. 4. Correlation between daily mean values of radon concentration (C_{Rn}^{GC}) and CO_2 concentration at GC location depending on outside air temperature (colour scale).

is subject to mixing of different air currents, carrying cave air from different passages with various radon levels. On the other hand, occasional strong winter ventilation is expected at the GC location, in order to decrease radon concentration to lower levels than at other two locations (Fig. 3a).

4 Discussion

Based on the morphology of the cave and several openings at different altitudes, we can characterise the Postojna Cave as a dynamic cave which is ventilated throughout the year. Different parts of the cave, however, exhibit different ventilation patterns based on local geomorphology. As also reported in the study of radon concentration in the Great Mountain chamber in this cave (Gregorič et al., 2011) and for several other caves (De Freitas, 2010; Spötl et al., 2005; Wilkening and Watkins, 1976), two main ventilation regimes can be distinguished in the main passage of the Postojna Cave. The measurement locations considered in this study, i.e. LP, BC and GC, have unique characteristics. Comparing the LP and BC locations, situated in the central part of the cave in galleries extending from the main passage, LP lies at 508 m a.s.l., while BC, located at 526 m a.s.l., has a specific geomorphology and microlocation – a narrow corrosionally widened fissure, located 15 m from the central part of the passage, characterised by numerous, more or less pronounced fault planes. Significant differences can therefore be found in their ventilation pattern and radon fluctuation, while the annual mean radon concentration is roughly the same for both locations. GC, on the other hand, is situated in a dead-end passage off the main passage and is therefore characterised by a higher stability of the cave atmosphere. The entrance is located below the ceiling of the main passage, and the measurement location is situated at 529 m a.s.l.

During the winter period, the difference in density between the cold outside air and warm cave air triggers a rise of warmer cave air, which exhales to the outside atmosphere through vertical cracks and fissures, thus giving space to cold, denser outside air, which enters the cave through lower entrances. This so called "chimney effect" predominates throughout the winter and can be observed through the entire cave system. On the basis of relatively good correlation between radon concentration at all three locations (Fig. 5) in winter, as well as the good correspondence between CO$_2$ and radon at the GC location (Fig. 4), it may be assumed that a current of fresh outside air comes in from the tourist entrance and river entrance, is lifted upwards, and leaves the cave through vertical cracks and openings. The artificial tunnel that connects Lepe jame with Črna jama is closed off by a door, thus preventing the airflow in direction from Črna jama. Therefore, both ^{222}Rn and CO$_2$ concentrations at GC tend to decrease toward their atmospheric levels (≈10–30 Bq m^{-3} for ^{222}Rn and ≈380 ppm for CO$_2$) during periods with an active chimney effect, whereas radon levels at LP, located lower than the tourist entrance, still remain higher than at GC. Owing to the remote location of BC, a slower increase of $C_{\mathrm{Rn}}^{\mathrm{BC}}$ in comparison to $C_{\mathrm{Rn}}^{\mathrm{LP}}$ is observed in spring, and a slower decrease in autumn (Fig. 3). The chimney effect is most pronounced at GC when T_{out} is lower than the cave temperature ($<$ 10 °C), but remains above 0 °C. Below that temperature, the snow layer and water freezing in the upper few centimetres of the soil layer above the cave prevent the exhalation of cave air and provoke cave air isolation. Consequently, an increase of radon concentration (and CO$_2$) is observed first at GC (Fig. 5a and c) and then, at lower temperatures, also at BC and LP.

Ventilation decreases in summer and is more pronounced at the beginning of the main passage, where fresh, warmer outside air enters the cave below the ceiling and cold cave air is swept out of the cave near the bottom. When the temperature difference of outside and cave air reaches the critical point, around 10 °C (at mean daily $T_{\mathrm{out}} > 20$ °C), warm air enters the cave system through known and unknown entrances, fissures and cracks at higher elevations and leaves the cave through lower entrances. There is frequent strong ventilation from the BC location toward the main passage in summer (Šebela and Turk, 2011). Behind the BC location, fresh air could enter through subvertical corrosionally widened fissures, possibly through some undiscovered cave chambers. On the other hand, summer ventilation has only a small effect on the LP location, and is almost undetectable at the GC location.

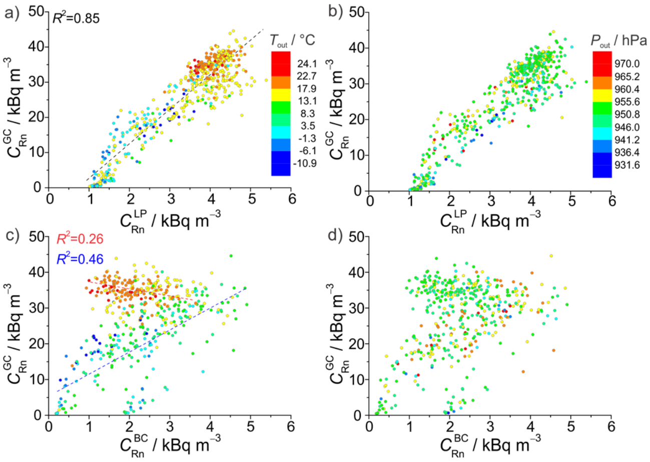

Fig. 5. Correlation between radon concentration at GC ($C_{\mathrm{Rn}}^{\mathrm{GC}}$) and LP ($C_{\mathrm{Rn}}^{\mathrm{LP}}$) depending on: **(a)** outside air temperature (colour scale) and **(b)** atmospheric pressure (colour scale) and correlation between radon concentration at GC and BC ($C_{\mathrm{Rn}}^{\mathrm{BC}}$) depending on: **(c)** outside air temperature (colour scale, R^2 for summer and winter period) and **(d)** atmospheric pressure (colour scale). Daily mean values are used.

The results show that the intense winter ventilation regime takes control over the behaviour of gases in the cave, resulting in a high correlation between different locations as well as a good correspondence in the fluctuation of different gases (e.g. CO$_2$ and ^{222}Rn). On the other hand, together with diminishing effect of ventilation in summer, the response of gases to other processes becomes apparent (e.g. changes of radon exhalation from the rock surface and from deeper parts of the Earth's crust, and changes of the flux of CO$_2$ from the epikarst).

The question of high differences in the spatial distribution of gases cannot, however, be explained simply by the ventilation characteristics of the cave, although it is obvious that the atmosphere in the Pisani rov is more stable than in the main cave passages. Stable conditions are reflected additionally in cave air temperature, with the highest daily amplitude of 0.2 °C at the LP location and only 0.03 °C at the GC location. A rapid increase in both radon and CO$_2$ concentrations during decreased ventilation points to strong radon and CO$_2$ sources, which could be the sum of different contributions: (i) flux of gases from the ground in faulted rocks, (ii) cave loam sediments as a radon source and (iii) deep soil layer in the collapse doline – on the surface where the Pisani rov terminates – as a source of radon and CO$_2$. The process (i), known as advection of geogas (Etiope and Martinelli, 2002), is a common source of both radon and CO$_2$

and can act as a major radon source in fractured rocks. CO_2 (together with other gases) works as a carrier gas for radon (Kristiansson and Malmqvist, 1982). While numerous fault zones are found along the Pisani rov (Šebela, 1992), this process may have a substantial role in controlling the concentration of radon and CO_2 in this passage. The second source of radon (ii) are rock surfaces and cave sediments, from where radon diffuses to the cave air. While limestone has basically the same characteristics in all cave passages, a large amount of cave sediments at the GC location makes this part different compared to other cave passages. Clays, especially when radium is absorbed to clay minerals and ferrous oxides, may have a high emanation capacity (Miklyaev and Petrova, 2011), which determines the amount of free radon in the geologic medium. Considering the stable atmospheric conditions in the cave throughout the year, the radon emanation from clays should be constant. Process (iii) could be expressed when outside air temperature is higher than cave temperature and the chimney effect stops. Airflow in summer is decreased as the fresh outside air moves downwards through narrow fissures, soil and rock matrices. Vertical connection of the cave and outside air in summer, responsible for decreasing radon concentration at BC (and partially LP), is influenced at the GC location by the deeper soil layer in the bottom of the collapse doline. The soil in such areas on carbonate rocks (e.g. dolines, sinkholes) could become enriched with natural radionuclides (also ^{226}Ra as a radon source) due to their migration by water, as presented in the study of natural radionuclides in Slovenian soils (Gregorič et al., 2012). The soil layer on the surface can therefore have high radon potential. Furthermore, the soil layer can be also an efficient CO_2 source due to biological activity, with CO_2 entering the cave environment by degassing from percolating water and gravity seepage through rock fractures in the thin cave ceiling. The above mechanisms, with the emphasis on process (iii), are the main reason for significant difference of gas concentrations between the Pisani rov and the main cave passages during the summer ventilation regime. On the other hand, the difference in the behaviour of radon and CO_2 in summer, observed by decreased correlation between them, can be explained by processes (ii) and (iii).

5 Conclusions

Investigations of radon and CO_2 levels carried out at three geomorphologically different locations in the Postojna Cave uncovered significant differences in the spatial distribution of radon concentration, and a high amplitude of fluctuation of radon and CO_2 concentrations in the Pisani rov, a dead-end passage in the cave. Concentrations of radon measured in this passage are, according to the published data, one of the highest concentrations measured in limestone caves. This research enables better understanding not only of the ventilation characteristics of Postojna Cave, but also of radon and CO_2 sources and mechanisms leading to very high concentrations of both gases. Significant differences in radon concentration between the main passages of the cave (up to $5400\,\mathrm{Bq\,m^{-3}}$) and the Pisani rov (up to $44\,600\,\mathrm{Bq\,m^{-3}}$), as well as high CO_2 concentration at the GC location, lead to the conclusion that ventilation itself could not be the only reason for the extremely high variability in the spatial distribution of radon and CO_2 in Postojna Cave. Taking into account the geomorphological characteristics of cave passages, a substantial contribution to radon and CO_2 concentration may be represented by the deeper soil layer above this passage, formed at the bottom of the collapse doline – this effect being additionally emphasised by the thin cave ceiling. Additional radon sources with very low variability may be the clay sediments which are present along the whole of the Pisani rov.

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