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CONCENTRATIONS AND DYNAMICS OF CARBON DIOXIDE, RADIOACTIVITY AND RADON IN TWO CAVES OF ITALIAN CLASSICAL KARST (MUNICIPALITIES OF SAGRADO AND SAVOGNA D'ISONZO)

KONCENTRACIJA IN DINAMIKA OGLJIKOVEGA DIOKSIDA, RADIOAKTIVNOSTI IN RADONA V DVEH JAMAH ITALIJANSKEGA KLASIČNEGA KRASA (OBČINI ZAGRADEC (SAGRADO) IN SOVODNJE OB SOČI (SAVOGNA D'ISONZO)

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Abstract UDC 543.272.62+546.296:551.442(450)

Graziano Cancian, Damiano Cancian & Stefano Rejc: Concentrations and dynamics of carbon dioxide, radioactivity and radon in two caves of Italian Classical Karst (Municipalities of Sagrado and Savogna d'Isonzo)

A 13-month monitoring was carried out in two caves that open up in the north-western sector of the Classical Karst (Gorizia Karst): Antro Casali Neri and Grotta Due Piani. In both, ß + γ radioactivity, radon and CO_2 have a seasonal pattern, with maximums in summer and minimums in winter, even if their trends are somewhat different, due to the different morphological and thermal conditions. The increases begin when the outside temperature becomes higher than that of the caves and vice versa, decrease is recorded when outside temperature is below the cave temperature. The more modest daily variations of radon, on the other hand, are evident when its concentration is low. Sometimes they are related to meteorological variations or day/night rhythms, but, in other cases, they have no clearly identifiable causes. In Casali Neri cave the maximum radon activity was 50161 Bq/m^3, while the CO_2 concentration went off the instrument's scale (> 9999 ppm) only in the first days of August 2021. The highest radioactivity value was also recorded in this cave with 0.85 μSv/h (average of 8 minutes of recording), with peaks up to 1.05 μSv/h. In Due Piani cave, on the other hand, the radon activity was lower, with a maximum of 22138 Bq/m^3, however, the CO_2 values went off the scale from July to the first days of October 2021. In both cases, in the warm months, radon and CO_2 appear to come mainly from the fractured rock of epikarstic zone. Further accumulations can then form in points with poor ventilation. Furthermore, research has shown that high concentrations of these two gases are not only typical of large or deep caves, but also of modest and easily accessible caves.

Key words: Casali Neri cave, Due Piani cave, Italian Classical Karst, carbon dioxide, radioactivity, radon.

Izvleček UDK 543.272.62+546.296:551.442(450)

Graziano Cancian, Damiano Cancian & Stefano Rejc: Koncentracija in dinamika ogljikovega dioksida, radioaktivnosti in radona v dveh jamah italijanskega klasičnega krasa (občini Zagradec (Sagrado) in Sovodnje ob Soči (Savogna d'Isonzo)

Izvedeno je bilo 13-mesečno spremljanje v dveh jamah, ki se odpirata v severozahodnem delu klasičnega krasa (Goriški Kras), in sicer Casali Neri in Due Piani. V obeh so radioaktivnost žarkov ß + γ, radon in CO_2 sezonsko značilni, z najvišjimi vrednostmi poleti in najnižjimi vrednostmi pozimi, čeprav so njihovi trendi nekoliko drugačni zaradi različnih morfoloških in toplotnih razmer. Vrednosti se povečajo, kadar je zunanja temperatura višja od temperature v jamah, v obratnem primeru se vrednost znižajo. Ob tem so, kadar je njegova koncentracija nizka, opazna manjša dnevna nihanja vrednosti radona. Včasih so povezana z meteorološkimi spremembami ali izmenjavo dneva in noči, v drugih primerih pa nimajo jasno prepoznavnih vzrokov. V jami Casali Neri je bila največja aktivnost radona 50161 Bq/m^3, koncentracija CO_2 pa je z instrumentalne lestvice (> 9999 ppm) izginila šele v prvih dneh avgusta 2021. V tej jami je bila zaznana tudi največja vrednost radioaktivnosti, in sicer 0,85 μSv/h (povprečno 8 minut snemanja), najvišja vrednost je segala celo do 1,05 μSv/h. V jami Due Piani pa je bila aktivnost radona nižja, pri čemer je bila največja vrednost 22138 Bq/m3, vrednosti CO_2 pa so z lestvice izginile od julija do prvih dni oktobra 2021. V obeh primerih se zdi, da v toplih mesecih radon in CO_2 izhajata predvsem iz razpokane kamnine epikraškega območja. Nadaljnja kopičenja so možna na območjih, kjer je slaba prezračenost. Poleg tega so raziskave pokazale, da visoke koncentracije teh dveh plinov niso značilne le za velike ali globoke jame, temveč tudi za manjše in lahko dostopne jame.

Ključne besede: jama Casali Neri, jama Due Piani, italijanski klasični kras, ogljikov dioksid, radioaktivnost, radon.

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1. INTRODUCTION

Carbon dioxide, present in the air of caves, has been studied in various parts of the world and it has been found that its concentrations are very variable. For example, they are relatively low in the Nerja cave in Spain (525 ppm in autumn/winter and 750 ppm in spring/summer) (Linan et al., 2008) or medium in the Sainte Anne cave in Belgium (highs around 7500 ppm in August/September) (Ek & Gewelt, 1985). In the Classical Karst, however, Dambrosi (2015), in his degree thesis reports CO_2 percentages in the air equal to 3.05% in the Lipišca jama (Slovenia) and 3.33% in the Skilan Cave (Italy).

The origin of CO_2 in karst caves is still an open question, as long-term monitoring is scarce, when compared with the high number of caves and with the different geological, geographical and climatic situations. Often the origin of CO_2 in limestone caves has been considered biogenic, derived from plants with deep roots (Breecker et al., 2012), or originating from the soil and entering the underground cavities by degassing from dripping water (Baldini et al., 2006).

However, there are also reports of CO_2 of deep origin (Wood, 1985; Mattey et al., 2016; Bergel et al., 2017). For example, the presence, even abundant, of CO_2 in the karst subsoil was confirmed by drilling in an experimental site near the Nerja Cave, where increasing concentrations with depth and with average values of 40 000 ppm were detected (Vadillo et al., 2010). The much lower concentrations in cave, on the other hand, derive from the fact that it communicates both naturally and artificially with the outside atmosphere.

Ultimately, CO_2 in caves can have multiple origins. Kukuljan et al. (2021) indicate five possibilities: degassing of percolation waters, advection and diffusion from the soil and from the epikarstic zone, decomposition of organic substance introduced into the cave or deep vadose zone, anthropic or biogenic production, geogenic production.

Furthermore, some research has shown that CO_2 can act as a "carrier" of radon and carry it to surfaces (Etiope et al., 1995; Chyi et al., 2010; Castelluccio et al., 2012; etc.).

The presence of radon in the caves has long been known and many measurements have been made around the world. In Friuli Venezia Giulia it was mainly monitored in houses (Giovani et al., 2018; Fontani et al., 2019) but less in caves and mostly in the Classical Karst. In these environments, however, highly variable concentrations have been reported, from a few hundred to a few tens of thousands of Bq/m^3. Various information was given by Cucchi et al.,1996; Giovani et al., 2007, 2012, 2013; Del Maschio et al., 2011. Rather high values, up to 10 000 ± 3 Bq/m^3 were recorded in the Pearls cave and up to 13 400 ± 2 Bq/m^3 in the Skilan cave. (Commissone Grotte E. Boegan, 2009). In Divaska Jama (Slovenia), on the other hand, concentrations of 19 300 ± 2500 Bq/m^3 have been reported (Merlak, 2020), while in a passage of the Postojna Caves, not open to the public, an annual average of 25 020 ± 12 653 Bq/m^3 with maximum values that exceeded 40 000 Bq/m^3 (Gregorič et al., 2013).

In the north-western area of the Italian Classical Karts, a few years earlier, we had carried out a monitoring in the General Ricordi Cave, where very high concentrations of both CO_2 and radon were found (Cancian & Cancian, 2021). In particular, a radon peak of 66 840 Bq/m^3 was detected, the largest so far reported in the Italian Karst. An investigation with the Ludlums 700 gamma spectrometer allowed us, also, to identify these radionuclides: ^{40}K - ^{226}Ra - ^{214}Bi.

2. RESEARCH PLANNING AND INSTRUMENTS

The purposes of the new research was to verify whether high values of CO_2 and radon are found in other caves, as in the General Ricordi cave, in the same portion of Karst. We also wanted to verify if the various parameters have the same dynamics, bringing new data and new observations. In this regard, we considered two caves: "Antro Casali Neri" and "Grotta a Est di San Martino del Carso" known as "Grotta Due Piani". For simplicity, they will be referred to as ACN and DP in the following text.

In both, a thirteen-month monitoring was carried out, collecting the following data: temperatures, carbon dioxide concentrations, ß + γ radioactivity and radon activity. The research began in March 2021 and ended in March 2022.

Since, even in this new research, the measurements had to be carried out for a long time, in underground environments, the instruments had to be simple, easily transportable, not excessively expensive but reliable. A digital thermometer with probe, model Checktemp1

Figure 1: The instruments in the upper gallery of Due Piani cave.

(Hanna Instruments) was used for the temperatures, while the CO_2 concentrations were measured using the AZ7755 instrument (AZ Instrument Corp.). Radioactivity ß + γ was measured with a Geiger counter model BR9B (Brand Sanhe Ding Yi Technology) which provides both the immediate value, in µSv/h, and the average after seven minutes. Finally, the Radex MR107 (Quarta Rad) instrument was used for radon, which takes measurements at one-hour intervals and stores them. The internal battery lasts for approximately 140 hours.

To plan the research, it was necessary to take into account that the ACN is easily accessible to occasional visitors, while the DP is frequented by speleologists. In both caves, therefore, it was not possible to leave the instruments unattended, so the measurements were carried out at each inspection and transcribed on a notebook. One exception, however, was the detection of radon. In this case, in fact, the Radex MR107 starts making the first measurements after 4 hours, but they are reliable only after 8 or 9 hours from switching on. For this reason, every month, the instrument was left in the caves, normally for 5 or 6 consecutive days, in slightly hidden corners, near point 3 in DP (Figures 1 and 3) and near point 4 in ACN (Figures 3 and 4).

Full data collection occurred when the Radex MR107 instrument was left in the caves, usually within the first decade of the month. Other measurements of temperature, CO_2 and radioactivity ß + γ were also repeated when we were returned to collect it. In the following chapters, their average is considered.

Between the end of July and August, when the radioactivity values were high, it was decided to carry out a verification, certified by the Laboratory, using the passive sensors Fidotrack CR39 (Niton) which were left in the two caves for 27 and 28 days respectively.

3. CAVES AND GEOLOGICAL FRAMEWORK

The two caves open in the north-western sector of the Italian Classical Karst (Gorizia Karst) and develop within the Aurisina Limestones (upper Cenomanian - Turonian p.p. - lower Senonian) (Figure 2). They are located 450 m from each other. In this area the limestone formation is mainly represented by mudstones-packestones, often fossiliferous whit rudists, well stratified, with more common thicknesses ranging from a few decimetres to 1.5 meters.

In ACN, the situation is particularly interesting as it is a "doline-cave" morphological ensemble. It opens, in fact, with two entrances, at the bottom of an asymmetrical doline, about 13 meters deep. It is a well known cave, easy to access and often visited by tourists as it has

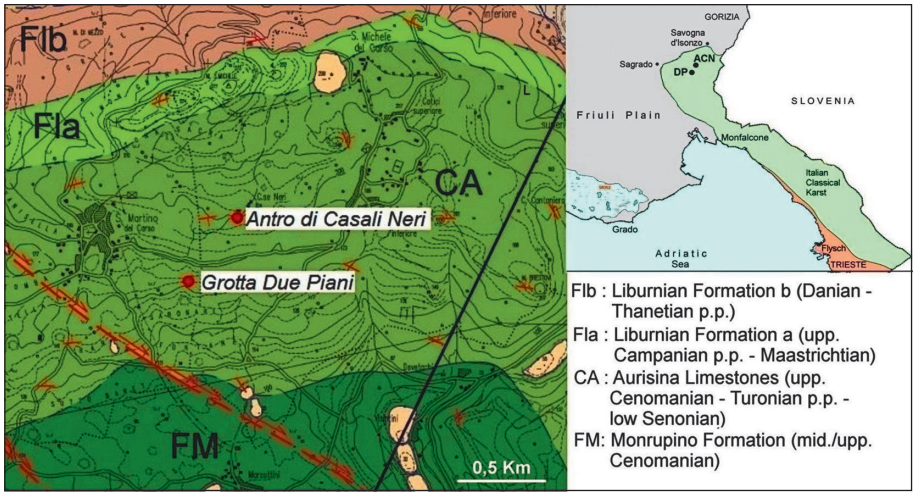

Figure 2: Geological map of the zone (from "Carta Geologica del Carso Classico" – Cucchi F. & Piano C. 2013).

an interest linked to the First World War. In practice it is a large cavern, with the floor completely cluttered with boulders of various sizes. Calcite speleothems are scarce. At the bottom of the cave there is a wall with a passage of 75x140 cm, which causes a narrowing of the section. The continuation, then, has more modest dimensions. The measurements were made in surface, in the bottom of the doline and in three points of the cave (Figure 3).In DP, instead, a well of 8.5 m leads to a gallery initially characterized by collapsed boulders and speleothems, then, continuing, the clayey deposits increase. Furthermore, in the first section, a 6 m well leads to the lower gallery, which has a different morphology. Here, in fact, the speleothems are scarce. Some mineralogical research, carried out in the past, has shown that the filling deposit is clayey/silty, for several meters, with some lenses of

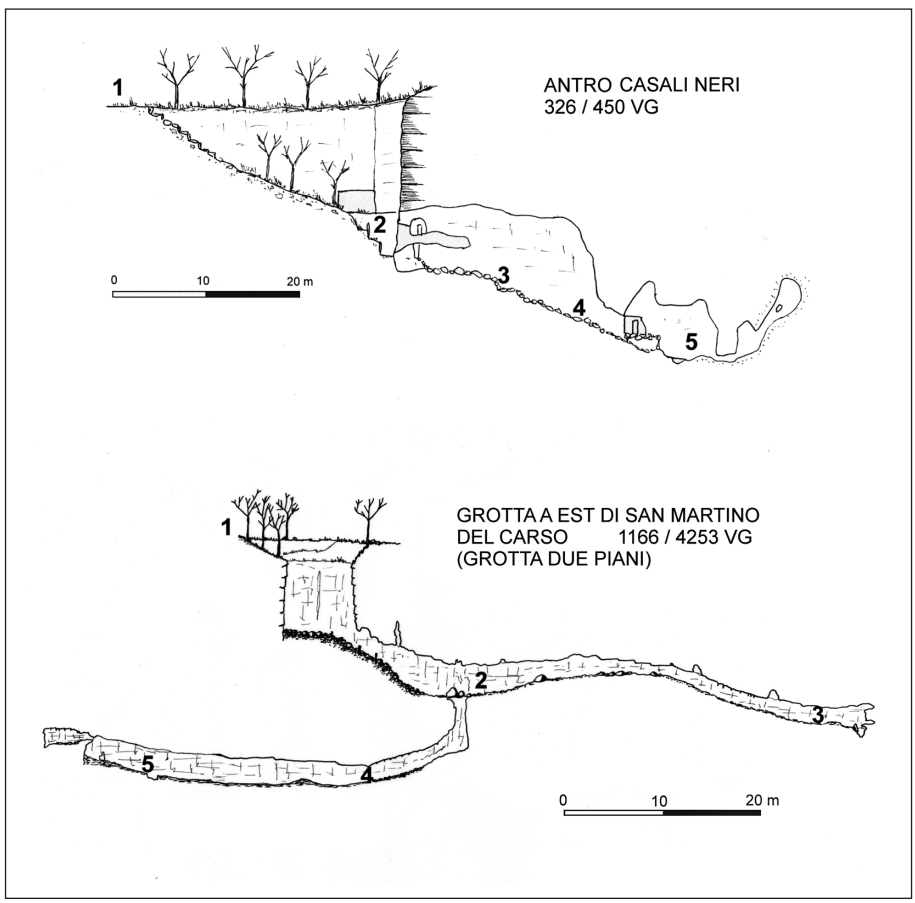

Figure 3: Caves and points where the measurements were carried out.

Table 1: Cadastral data of the two caves.

Name	Antro Casali Neri	Grotta a Est di San Martino del Carso
Other name	Pecina	Grotta Due Piani (Two floors cave)
Cadaster number	326/450 VG	1166/4253 VG
Municipality	Savogna d'Isonzo	Sagrado
Altitude entrance	191 m	162 m
Depth	14.4 m (+ ~ 13 m of doline)	27.2 m
Development	55 m	113.6 m

guano, phosphate minerals and gypsum (Cancian, 1985; Cancian & Princivalle, 1997). The measurements were made in surface, in two points of the upper gallery and in two of the lower one (Figure 3).

Figure 4: Control of the instruments in point 4 of the Casali Neri cave. Note the floor cluttered with collapsed boulders.

4. RESULTS

4.1 TEMPERATURES

In the Doberdò plateau, that is located immediately south of the area in question, the warm season lasts from the first days of June to the first ten days of September, with a maximum daily temperature often above 25° C. The hottest month is July. The cold season, on

Table 2: Statistical data regarding temperatures, measured outside and inside the two caves. In Casali Neri cave they were generally measured between 10 and 11 a.m. while in the Due Piani between 06 and 07 p.m. The minimum and maximum values refer to the entire monitoring period (March 2021-March 2022). The 12-month average refers to the period March 2021 - February 2022.

measuring points	**Temperatures Casali Neri cave**		
	average 12 months (° C)	**minimum (° C)**	**maximum (° C)**
1 surface	16.0	4.4 (Dec. 2021)	34.7 (Aug. 2021)
2 bottom doline	12.6	3.9 (Dec. 2021)	22.1 (Aug. 2021)
3 cavern (top)	9.5	5.4 (Mar. 2022)	11.8 (Sep. 2021)
4 cavern (bottom)	8.9	5.6 (Mar. 2022)	11.1 (Aug. Sep. 2021)
5 bottom cave	9.4	6.9 (Mar. 2022)	10.9 (Oct. 2021)
measuring points	**Temperatures Due Piani cave**		
	average 12 months (° C)	**minimum (° C)**	**maximum (° C)**
1 surface	13.7	1.8 (Jan. 2022)	31.8 (Jul. 2021)
2 upper gallery	8.7	7.6 (Feb. 2022)	12.3 (Oct. 2021)
3 upper gallery	12.6	12.2 (Apr. 2021)	13.0 (Nov. 2021)
4 lower gallery	11.9	11.0 (Feb. 2021)	12.4 (Oct. 2021)
5 lower gallery	12.6	12.4 (Apr. 2021)	12.8 (Aug. Nov. 2021)

the other hand, runs from the end of November to the first days of March, with maximum daily temperature often below 13° C. In winter, moreover, the minimum night temperatures below zero are frequent. The coldest month is January.

The thermal characteristics of the two caves are different. In the ACN, the morphological ensemble "doline-cave" forms a sort of trap for cold air, moreover the internal temperatures are affected quite sensitively by external weather variations. For this reason, in point 4, near which the radon monitoring was carried out, the maximum temperature was 11.1° C in August and September 2021, while the minimum dropped to 5.6° C in March 2022. It should be noted, however, that the first part of this month was characterized by temperatures below the seasonal averages and cold wind.

The situation is different in the DP. Here the temperatures are more constant and slightly higher, especially towards the bottom of the two galleries, where they are between 12.2° C and 13.0° C.

It is useful to add that in both caves, the humidity is close to 100% and that, during the monitoring period, with some exceptions, the dripping was scarce and sometimes almost absent. Finally, the atmospheric pressure was measured several times on the surface, in the bottom of the ACN cave and in the lower gallery of DP. Inside the caves it was generally higher, with average differences of + 2.80 and + 2.22 hPa.

4.2 CARBON DIOXIDE - CO_2

During this research, elevated CO_2 concentrations were recorded in both caves. The curves that show the annual trend in the diagrams have the typical seasonal "bell trend" (Figure 5 and 6). The first rises occur between late April and May, while the first decreases occur in October and can be quite rapid. For example, at point 4 of the ACN, on 4 October 2021 the CO_2 concentration was 5819 ppm but, only five days later, it had dropped to 549 ppm. In DP, on the other hand, the highest concentrations did not occur in the lower gallery, but in the upper one, where, from July to early October 2021, the values continuously went off the instrument's scale (> 9999 ppm). In ACN, however, the value went off-scale only in the first days of August 2021.

Finally, it was interesting to observe that, in the warm months, the CO_2 was a bit high (1400 - 1900 ppm) even at the bottom of the doline, therefore outside.

Table 3: Statistical data regarding CO_2 concentrations in the air outside and inside the two caves. The minimum and maximum values refer to the entire monitoring period (March 2021-March 2022). The 12-month average refers to the period March 2021- February 2022. The annual average in point 3 of DP was only estimated as in some cases the value went out of the instrument scale (>9999).

measuring points	CO_2 Casali Neri cave		
	average 12 months (ppm)	minimum (ppm)	maximum (ppm)
1 surface	430	396 (Dec. 2021)	465 (Aug. Oct. 2021)
2 bottom doline	759	383 (Dec. 2021)	1920 (Aug. 2021)
3 cavern (top)	1983	401 (Dec. 2021)	8290 (Aug. 2021)
4 cavern (bottom)	2750	389 (Dec. 2021)	9990 (Aug. 2021)
5 bottom cave	3032	405 (Mar. 2022)	> 9999 (Aug. 2021)

measuring points	CO_2 Due Piani cave		
	average 12 months (ppm)	minimum (ppm)	maximum (ppm)
1 surface	418	383 (Aug. 2021)	441 (Sep. 2021)
2 upper gallery	2226	414 (Jan. 2022)	7649 (Aug 2021)
3 upper gallery	> 8500	442 (Apr. 2021)	> 9999 (Jul.Sep. 2021)
4 lower gallery	2191	427 (Apr. 2021)	7567 (Aug. 2021)
5 lower gallery	2150	415 (Apr. 2021)	7509 (Aug. 2021)

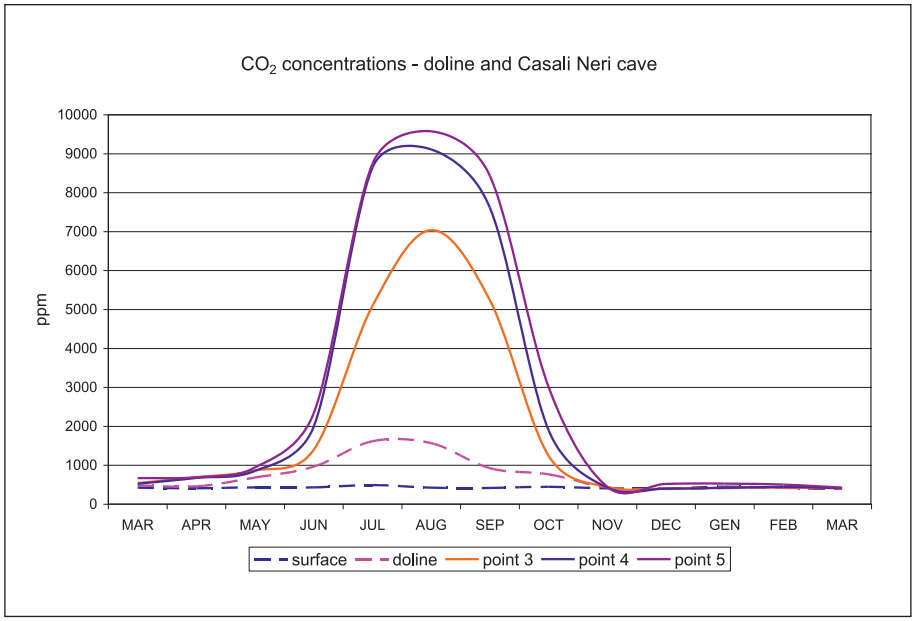

Figure 5: Trend of carbon dioxide concentrations in doline and in Casali Neri cave (March 2021 – March 2022).

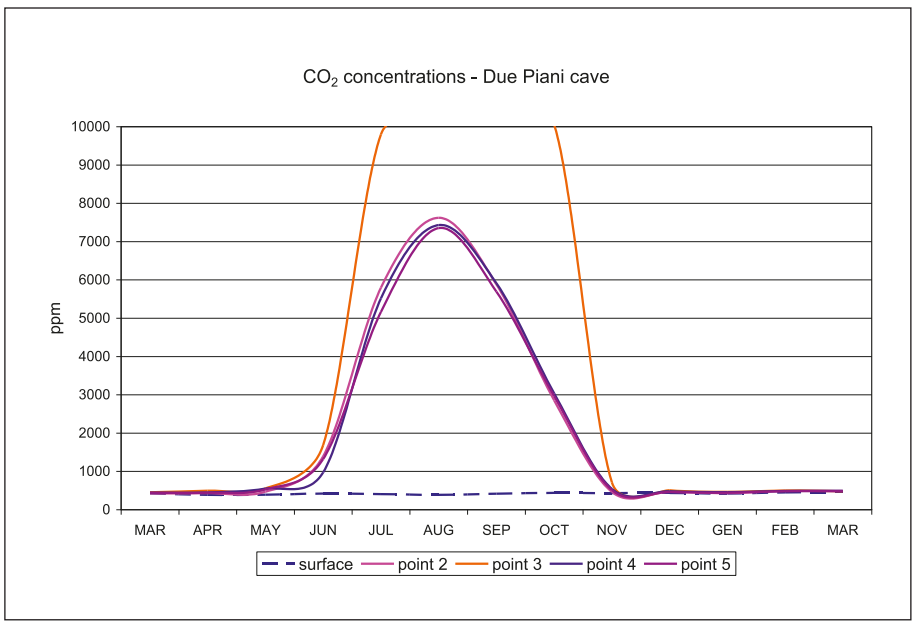

Figure 6: Trend of carbon dioxide concentrations in Due Piani cave (March 2021- March 2022).

4.3 β + γ RADIOACTIVITY

Radioactivity was measured by Geiger counter sensitive to β and γ radiation. Also in this case, the maximum values occurred in the warm months and the minimum in the cold ones. In all probability, these radiations are largely due to the decay products of radon, as we had seen in the General Ricordi cave. A gamma spectrometer, in fact, had demonstrated the presence of ^{40}K - ^{226}Ra - ^{214}Bi (Cancian & Cancian, 2021). The first is ubiquitous, while the last two are part of the decay chain of ^{238}U, within which there is ^{222}Rn isotope:

^{238}U →(α) ^{234}Th →(ß) ^{234}Pa →(ß) ^{234}U →(α) ^{230}Th →(α) ^{226}Ra →(α) ^{222}Rn→(α) ^{218}Po →(α) ^{214}Pb →(ß) ^{214}Bi →(α e ß) ^{214}Po →(α) ^{210}Pb →(ß) ^{210}Bi →(ß) ^{210}Po →(α) ^{206}Pb (stable).

The radioactivity was greater in ACN, where the highest values were not observed in the deepest section of the cave, but at the end of the cavern (point 4). Here, on 7 August 2021, the maximum of 0.85 μSv/h (average of 8 minutes of recording) was reached, with peaks up to 1.05 μSv/h.

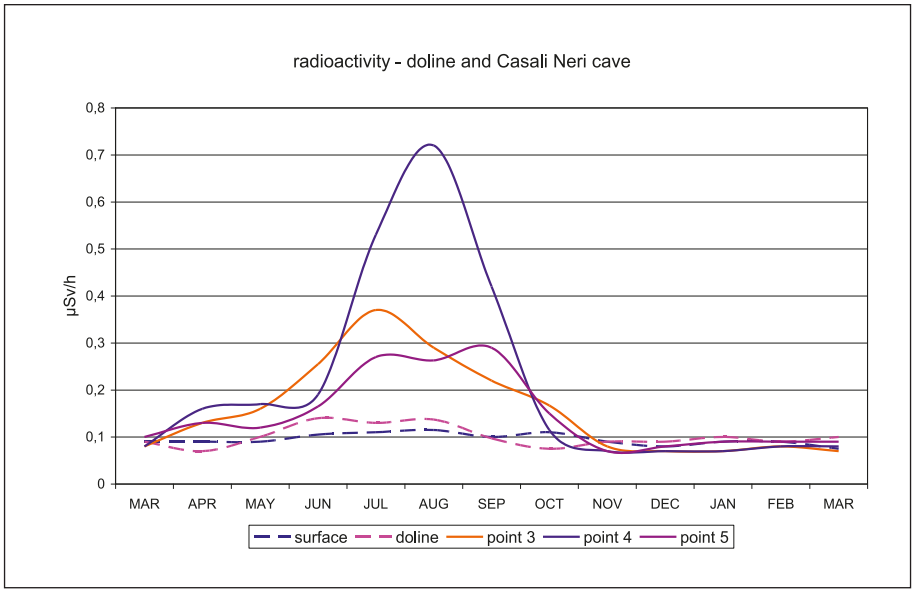

Figure 7: Trend of ß + γ radioactivity in doline and in Casali Neri cave (March 2021 – March 2022).

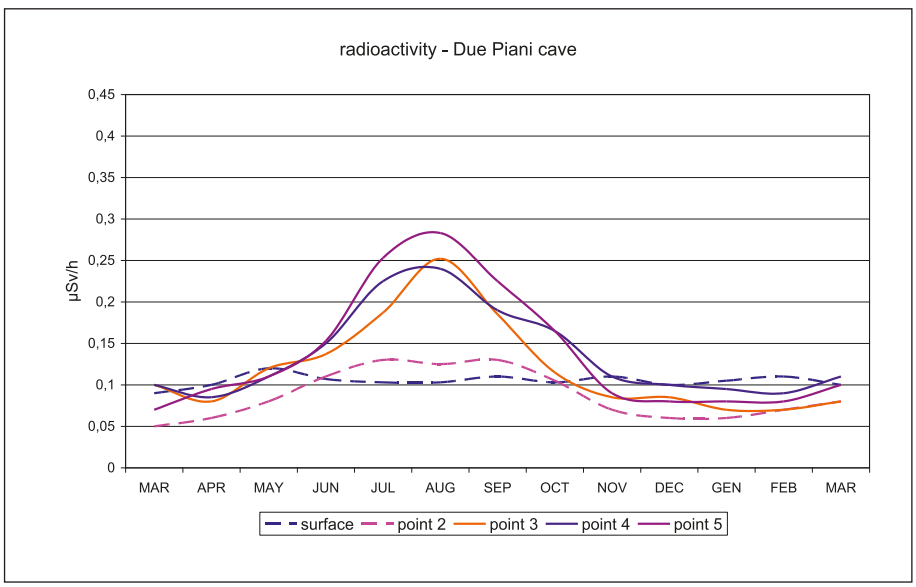

Figure 8: Trend of ß + γ radioactivity in Due Piani cave (March 2021 – March 2022).

Table 4: Statistical data regarding γ + ß radioactivity outside and inside the two caves. The minimum and maximum values refer to the entire monitoring period (March 2021-March 2022). The 12-month average refers to the period March 2021 - February 2022.

measuring points	β +γ radioactivity - Casali Neri cave		
	average 12 months (µSv/h)	minimum (µSv/h)	maximum (µSv/h)
1 surface	0.097	0.08 (Dec. 2021)	0.13 (Aug. 2021)
2 bottom doline	0.101	0.07 (Apr. Dec. 2021)	0.15 (Aug. 2021)
3 cavern (top)	0.164	0.05 (Dec. 2021)	0.37 (Jul. 2021)
4 cavern (bottom)	0.223	0.07 (Nov. Dec. 2021)	0.85 (Aug. 2021)
5 bottom cave	0.151	0.07 (Nov. 2021)	0.30 (Aug. 2021)

measuring points	β + γ radioactivity - Due Piani cave		
	average 12 months (μSv/h)	minimun (μSv/h)	maximum (μSv/h)
1 surface	0.106	0.08 (Dec. 2021)	0.12 (Jun. Sep. 2021)
2 upper gallery	0.087	0.05 (Mar. 2021)	0.14 (Jul. Oct. 2021)
3 upper gallery	0.124	0.07 (Jan. 2022)	0.26 (Aug. 2021)
4 lower gallery	0.138	0.08 (Jan. Feb. 2022)	0.25 (Jul. Aug. 2021)
5 lower gallery	0.140	0.07 (Mar. Dec. 2021)	0.31 (Aug. 2021)

4.4 RADON

During this research some rather high values were found. The maximum was recorded in September 2021 in ACN: 50 161 Bq/m^3.

The monitoring was carried out once a month, except in October 2021, when two were carried out. In that period, in fact, there was an abrupt change in weather conditions, with rapid lowering of temperatures and therefore we wanted to see if this had influenced the concentrations of radon. Indeed, its concentration dropped from 34 724 to 1748 Bq/m^3 in ACN and from 10 804 to 833 Bq/m^3 in DP.

The annual radon trend, as shown in Figure 9, cannot be exactly overlapped in the two caves. The maxi-

Table 5: Activity of radon in the bottom of the great cavern in Casali Neri cave and in the upper gallery of Due Piani cave.

days of monitoring	Radon - Casali Neri cave		
	average (Bq/m^3)	minimum (Bq/m^3)	maximum (Bq/m^3)
03 - 07 Apr. 2021	1313	96	4212
10 -15 May. 2021	10 683	7576	13 402
03 – 07 Jun. 2021	10 728	7111	15 179
08 – 13 Jul. 2021	28 043	24 041	33 094
03 – 07 Aug. 2021	30 670	26 612	36 595
06 – 11 Sep. 2021	44 065	39 193	**50 161**
04 – 09 Oct. 2021 17 – 28 Oct. 2021	34 724 1748	5497 582	49 778 4793
05 – 10 Nov. 2021	579	164	2817
04 – 08 Dec. 2021	162	150	187
04 – 08 Jan. 2022	680	91	3063
06 – 12 Feb. 2022	827	347	3446
06 – 12 Mar. 2022	600	211	2429

days of monitoring	Radon - Due Piani cave – upper gallery		
	average (Bq/m^3)	minimum (Bq/m^3)	maximum (Bq/m^3)
04 – 07 Apr. 2021	558	318	1031
28 Apr. – 03 May. 2021	2504	722	3706
05 – 10 Jun. 2021	5986	4145	7373
02 – 08 Jul. 2021	18 873	11 728	**22 138**
18 – 20 Aug. 2021	14 041	10 372	15 128
12 – 15 Sep. 2021	11 254	10 009	13 161
04 – 08 Oct. 2021 12 – 16 Oct. 2021	10 804 833	7984 478	14 345 2445
05 – 10 Nov. 2021	1567	617	3725
19 – 22 Dec 2021	258	178	299
04 – 09 Jan. 2022	361	207	787
09 – 13 Feb. 2022	389	142	568
08 – 12 Mar. 2022	338	180	552

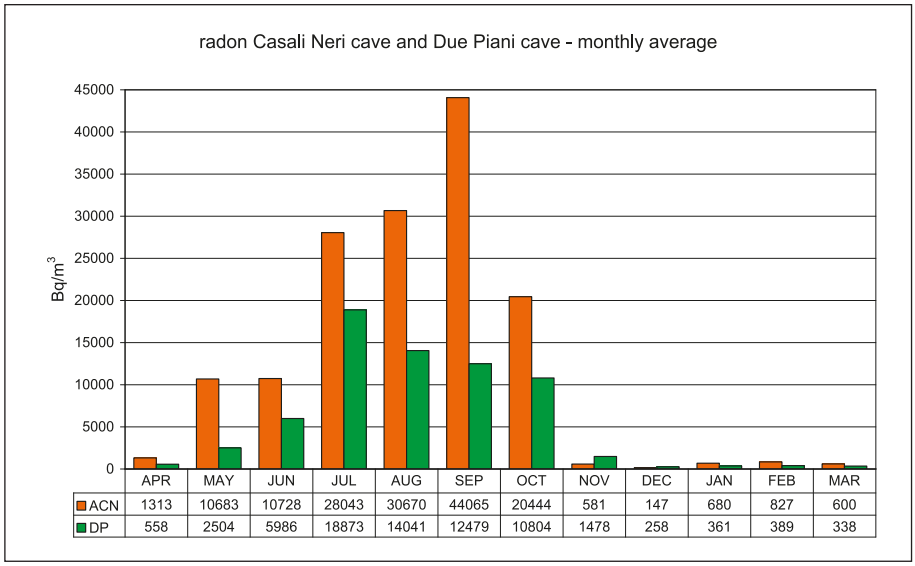

Figure 9: Average concentrations of radon in the two caves, from April 2021 to March 2022.

mum values, in fact, were reached in July in DP and in September in ACN. The monthly declines were also slow in DP and faster in ACN. Most likely this depends on the different geometry of the two caves and the different ventilation conditions. The argument, however, requires further measurements and observations.

Some monitoring was also carried out in the lower gallery of DP, always using the Radex instrument, obtaining these results:

Table 6: Radon activity in the lower gallery of Due Piani cave.

days of monitoring	average (Bq/m³)	minimum (Bq/m³)	maximum (Bq/m³)
28 Apr. – 3 May 2021	2691	1182	4431
10 - 15 Jun. 2021	7088	5771	8670
12 - 17 Sep. 2021	12 479	10 776	13 785
19 - 22 Dec. 2021	726	547	850

For further integration of the research, measurements were also carried out using the Fidotrack CR39 passive detectors. Since they had to remain in position for 27 days, in ACN, which is also accessible to occasional visitors, the detectors were hidden in two cavities of the cavern, where only one arm could be inserted, the first towards the entrance and the other towards the lower part. Remember that these sensors only give the average value with respect to the time in which they were positioned. For this reason it is not possible to make a direct comparison with the data obtained in the same month with the Radex tool. The values obtained, however, are of the same order of magnitude.

The diagrams relating to two significant moments of radon activity are shown below: in the phase of increase (Figure 10) and in reaching the maximum values (Figure 11).

Table 7: Results of radon activity through the CR39 detectors.

Casali Neri cave		
position of CR39 detectors	**days of monitoring**	**activity**
beginning of cavern, east wall	from 8 July to 3 August 2021	28 769 Bq/m³ (± 9%)
bottom of cavern, east wall	from 8 July to 3 August 2021	30 765 Bq/m³ (± 9%)
Due Piani cave		
bottom of upper gallery	from 8 July to 4 August 2021	14 915 Bq/m³ (± 10%
bottom of lower gallery	from 8 July to 4 August 2021	10 321 Bq/m³ (± 10%)

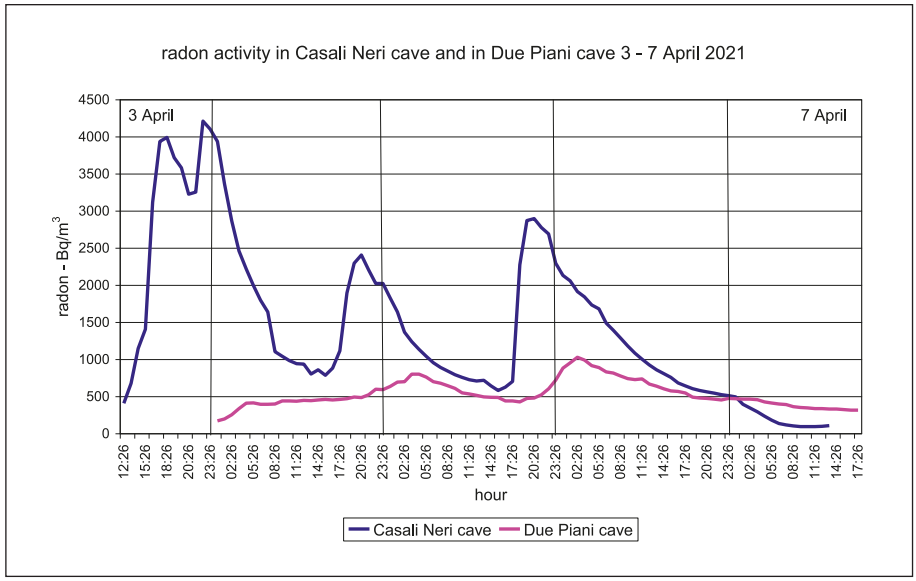

Figure 10: Radon monitoring from 3-4 to 7 April 2021 in the two caves. The maximum values occurred at night at the minimums in the afternoons.

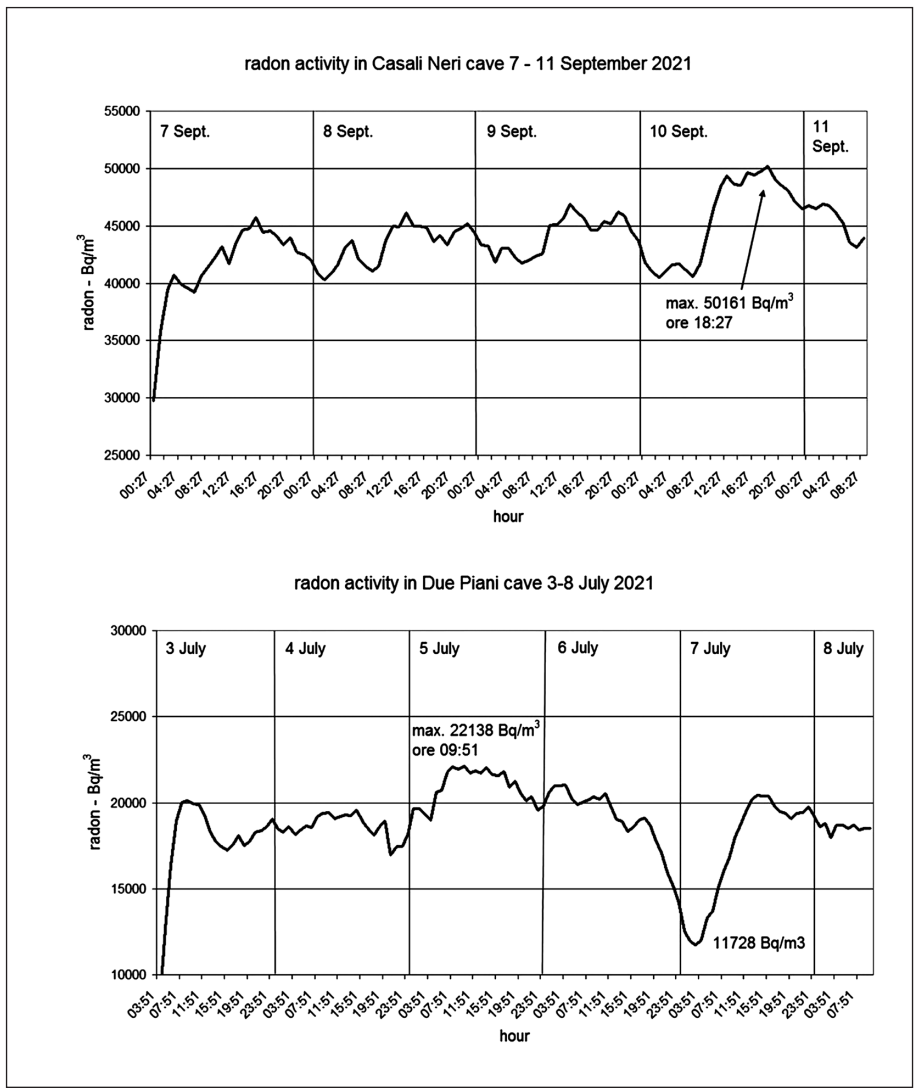

Figure 11: The maximum activity in ACN was recorded in September (50 161 Bq/m³), while in DP it was recorded in July (22 138 Bq/m³). In this case, the highs and lows are clearly not affected by the day/night rhythm. Furthermore, the decrease up to 11 728 Bq/m³ in DP is not related to particular weather events, in fact it occurred on a normal hot summer day, without significant changes in atmospheric pressure.

5. PARAMETERS ANALYSIS

5.1 CORRELATIONS BETWEEN ß + γ RADIOACTIVITY AND RADON ACTIVITY

The verification of this correlation is important for practical purposes, because the speleologist or the tourist can have a first indication about the possible presence of high radon values by simply carrying out a quick measurement with a pocket Geiger counter. In this regard, it should be noted that cheap instruments do not record α radiations, such as those emitted during the decay from ^{226}Ra to ^{222}Rn, however the radon that accumulates in the caves is usually accompanied by other radionuclides, as highlighted in chapter 4.2 and which also emit ß and γ radiation.

In our case, in both caves an "extremely significant" linear correlation was found between ß + γ radioactivity and radon activity (Figure 12).

5.2 CORRELATIONS BETWEEN TEMPERATURE GRADIENTS, CO_2 AND β + γ RADIOACTIVITY

We then wanted to see if there are correlations between the other parameters, measured in the points where the instruments for radon monitoring had been placed. As for the temperature, the parameter used was ΔT, which is the difference between the external temperature and that of the point considered inside the cave, at the time of the measurements.

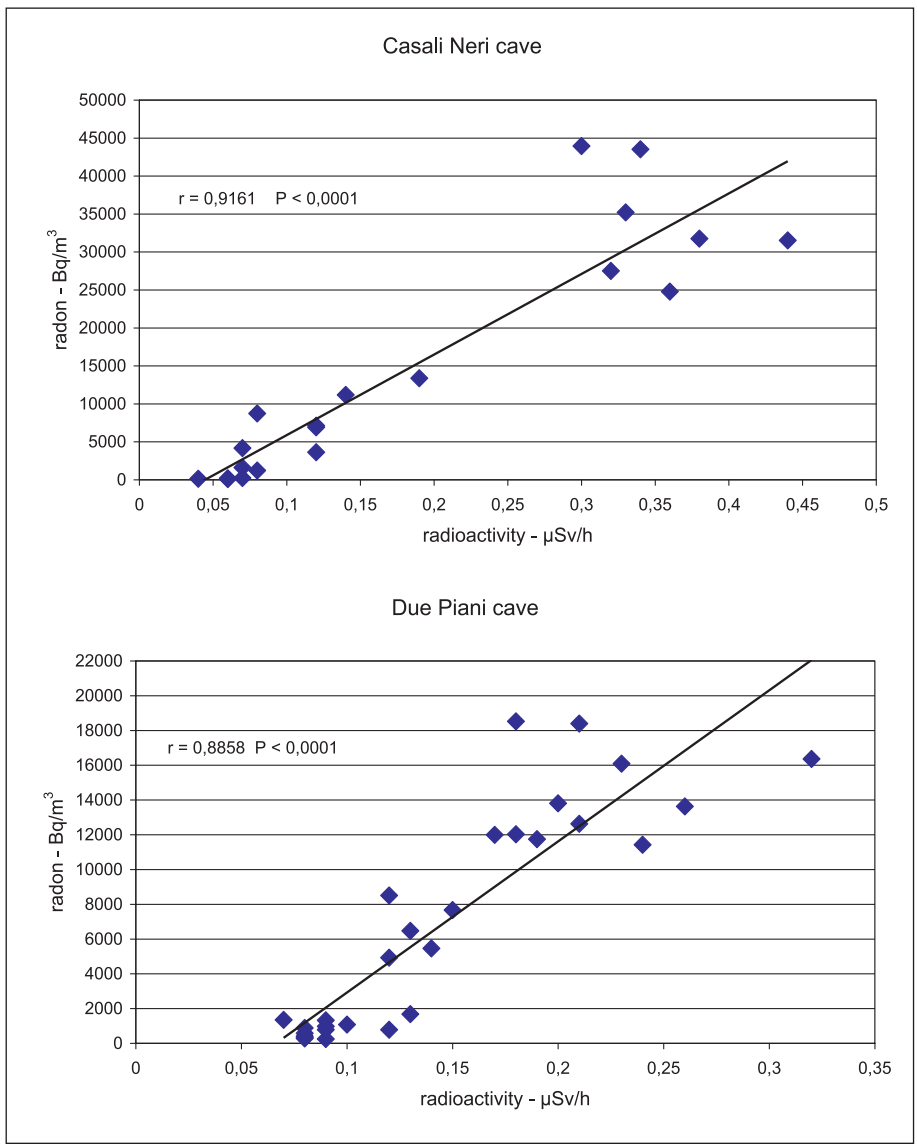

Figure 12: Correlation between radon activity (Bq/m³) and ß + γ radioactivity (µSv/h) in Casali Neri cave and in Due Piani cave. P value < 0.0001, r = 0.9161 and 0.8858 (Pearson).

Table 7: Linear correlation indices r (Pearson) and P values between ΔT, CO_2 and β +γ radioactivity. The measurements were carried out, throughout the monitoring period, at point 4 in the Casali Neri cave and at point 3 in the Due Piani cave. For the Due Piani cave, obviously, the CO_2 measurements that went outside the instrument scale (> 9999 ppm) were not considered.

	Casali Neri cave – point 4	
	r	P value
ΔT - CO_2	0.8383	< 0.0001
ΔT - β +γ radioactivity	0.8619	< 0.0001
CO_2 - β +γ radioactivity	0.9316	< 0.0001

	Due Piani cave – point 3	
	r	P value
ΔT - CO_2	0.7254	= 0.0001
ΔT - β +γ radioactivity	0.7946	< 0.0001
CO_2 - β +γ radioactivity	0.7895	= 0.0001

In both caves the reciprocal linear correlations between ß + γ radioactivity, CO_2 and ΔT were found to be "extremely significant" with a "P value" less than or equal to 0.0001. These data, therefore, confirm that the three parameters interact with each other. In particular, the increases in CO_2 and β + γ radioactivity are positively correlated to the ΔT parameter. The increases, therefore, occur when the outside temperatures are higher than those of the caves.

6. CONCLUSIONS

High concentrations of CO_2 and radon were already known in large or deep caves of the Italian Classical Karst, but, in this case, it has been shown that the same phenomena also occur in modest and easily accessible caves. In the ACN, for example, radon reached a peak of 50 161 Bq/m^3, while in the DP the CO_2 values went off the instrument scale (> 9999 ppm) from July to October 2021.

The two gases have the typical seasonal pattern, but it is not exactly the same in the two caves, most likely due to the geomorphologic, thermal and ventilation differences. The main mechanism influencing their dynamics is the thermal gradient ΔT. The greatest increases of both gases occur, in fact, when the external temperatures are higher than those of the caves, throughout the day or at least for a significant part of it. Furthermore, in the warm months, they appear to come mainly from the fractured rock.

As for the contribution of CO_2 from the outside air, through ventilation and accumulation in the deepest parts of the caves, it is instead a phenomenon that certainly occurs, but does not seem to be the main one. In this regard, it should be noted that, in winter, when cold air enters the ACN easily, pockets of CO_2 are formed only in the deepest part, where there is little air exchange, but with values between only 480 and 560 ppm. The contribution by degassing of the dripping water also appears scarce, in fact, precisely in the summer months, when the dripping was scarce - or even absent in various sections of the cave - the highest concentrations of CO_2 were recorded. In December, however, when the dripping was present, the CO_2 concentration had even lowered compared to the previous months.

Finally, it is interesting to add that in ACN the highest values of β + γ radioactivity did not occur exactly on the bottom, but in the terminal section of the large cave (point 4). In DP, on the other hand, two measurements, carried out simultaneously, using the CR39 detectors, showed that radon did not have higher concentrations in the lower gallery but in the upper one. This indicates that radon - and the radionuclides that accompany it - does not necessarily come out of the deepest parts of the caves, but where the rock has a network of fractures more suitable for the exit of this gas.

REFERENCES

Baldini J.U.L., Baldini L.M., McDermott., Clipson N., 2006. Carbon dioxide sources, sinks, and spatial variability in shallow temperate zone caves: evidence from Ballynamintra cave, Ireland. Journal of Cave and Karst Studies, april 2006, pp. 4-11.

Bergel S.J., Carlson P.E., Larson T.E., Wood T.C., Johnson K.R., Banner J.L., Brecker D.E., 2017. Constraining the subsoil carbon source to cave-air CO_2 and speleothem calcite in central Texas. Geochim. et Cosmochim. Acta, 217 (2017): 112.127. https://doi.org/10.1016/j.gca.2017.08.017

Breecker D.O., Payne A.E., Quade J., Banner L.J., Bali.

E.C., Meyer K.W., Cowan B.D., 2012. The sources and sinks of CO_2 in caves under mixed woodland and grassland vegetation. Geochimica et Cosmochimica Acta, v. 96, 1 nov. 2012, pp. 230-246. https://doi.org/10.1016/j.gca.2012.08.023

Cancian G., 1985. I fosfati della Grotta ad Est di San Martino del Carso (Gorizia): brushite, idrossiapatite, francoanellite, taranakite. Atti 3° Conv. Triv. di Speleologia (Vicenza 1984), Safigraf, Vicenza.

Cancian G., Princivalle F., 1997. Mineralogia e stratigrafia del deposito di riempimento della Grotta "Due Piani" (Carso Goriziano). Studi Trentini di Sc. Naturali, acta geologica, v. 71, 1994, pp. 79-90, Trento.

Cancian G., Cancian D., 2021. Diossido di carbonio, radioattività e radon nella Caverna Generale Ricordi (Carso Classico, comune di Doberdò del Lago). Atti Mus. Civ. St. Nat. Trieste, v. 62, 2021, pp. 5-32, ISSN: 0335-1576.

Carulli G.B., 2006. Carta geologica del Friuli Venezia Giulia. Regione Fr. Ven. Giulia, Direz. Centr. Amb. e Lav. Pubbl., Servizio Geologico.

Castelluccio M., Giannella G., Lucchetti C., Moroni M., Tuccimei P., 2012. La classificazione della pericolosità radon nella pianificazione territoriale finalizzata alla gestione del rischio. Italian Journal of Engineering Geology and Environment, 2:2012, Sapienza Univ. Editr. https://DOI: 10.4408/IJEGE.2012-02.O-XX

Chyi L.L., Quick T.J., Yang T.F., Chen C.H., 2010. The experimental investigation of soil gas radon migration mechanism and its implication in earthquake forecast. Geofluids (2010) 10: 556-563. DOI:10.1111/j.1468-8123.2010.00308.x

Commissione Grotte E. Boegan, 2009. Radon e grotte turistiche. Available from: https://www.boegan.it/2009/10/radon-e-grotte-turistiche/

Cucchi F., Giacomich R., Coslovich C., Giacomich P., Vascotti M., 1996. Il radon nei calcari e nelle cavità del Carso Triestino. Stato delle conoscenze. Boll. Soc. Adriatica di Scienze, vol. LXXVII (1996), pp. 31-47

Cucchi F., Piano C., a cura di. 2013. Carta geologica del Carso Classico (tratta dalla Carta di sintesi geologica alla scala 1:10.000 – Progetto GEO-CGT) e Brevi Note Illustrative della Carta Geologica del Carso Classico Italiano, con Fanucci F., Pugliese N., Tunis G., Zini L. Ed. Direzione centrale ambiente energia e politiche per la montagna, Servizio Geologico, Regione Autonoma Friuli Venezia Giulia, Trieste. http:// www.regione.fvg.it/rafvg/cms/RAFVG/ambiente-territorio/tutela-ambiente-gestione-risorse-naturali/FOGLIA201/ FOGLIA9/

Dambrosi S., 2015. Indagine sulla presenza di diossido di carbonio in alcune cavità naturali del Carso Classico. Degree Thesis, academic year 2014-2015, Univ. di Trieste, Dip. di Matem. e Geoscienze.

Del Maschio F., Giovani C., Garavaglia M., Piccini L., 2011. Anomalie di Radon in Grotta Gigante (Radon in Giant Cave, Trieste, Italy). Conference AIRP, Convegno Nazionale di Radioprotezione (National Radioprotection Conference). Conference paper. Reggio Calabria, Italy, ott. 2011.

Ek C., Gewelt M., 1985. Carbon dioxide in cave atmospheres. New results in Belgium and comparison whit some other countries. Earth Surface Processes and landforms, 10: 173-187. https://doi.org/10.1002/esp.3290100209.

Etiope G., Lombardi S., 1995. Evidence for radon transport by carrier gas through faulted clays in Italy. Journal of Radioanalytical and Nuclear Chemistry. Articles 193, 291.300.

Fontani S., Innocenzi V., Menna G., Salvi F., Torri G., Zennaro S., Zeppa P., 2019. La sorveglianza della radioattività ambientale in Italia. Isp. Naz. per la sicur. nucl. e la radioprot., pp. 119.

Giovani C., Candolini G., Di Marco P., Feliciosi D., Garavaglia M., Lizzi S., Piccini L., Pividore S., Zoccolan R., 2018. "Progetto radon misure per 1000 famiglie" Uno studio di citizen science in Friuli Venezia Giulia. Atti XXXVII Congresso Naz. AIRP di radioprotezione. Bergamo 17-18-19 ott. 2028, pp. 9-18.

Giovani C., Cucchi F., Nadalut B., 2007. La distribuzione della concentrazione di radon indoor in Friuli Venezia Giulia: aspetti geologici. Airp, Convegno Nazionale di Radioprotezione: Sicurezza e qualità in radioprotezione. Vasto Marina, 1-3 ottobre 2007. ISBN 88-88648-06-2.

Giovani C., Garavaglia M., Pividore S., Cucchi F., Zini L., 2012 – Uso dei sistemi informativi territoriali per lo studio della distribuzione della concentrazione di radon e dei parametri ad essa correlati in Friuli Venezia Giulia. In: Atti del V Convegno Nazionale "Il controllo degli agenti fisici: ambiente, salute e qualità della vita", Novara 6-7-8 giugno 2012, ISBN 978-88-7479-118-7.

Giovani C., Garavaglia M., Pividore S., Cucchi F., Zini L., 2013. Sistemi informativi territoriali: studio dei parametri correlati alla distribuzione di radon indoor in Friuli Venezia Giulia. In: Bollettino Associazione Italiana di Radioprotezione, agosto 2013, pp. 29-36.

Gregorič A., Vaupotič J., Gabrovšek F., 2013. Reasons for large fluctuation of radon and CO_2 levels in a dead-end passage of a karst cave (Postojna Cave, Slovenia). Natural Hazards an Earth. https://doi.org/10.5194/nhess-13-287-2013, 2013.

Kukuljan L., Gabrovšek F., Covington M. D., Johnston V. E., 2021. CO_2 dynamics and heterogeneity in a cave atmosphere: role of ventilation patterns and airflow pathways. Theoretical and applied climatology (2021), 146, pp. 91-109. *DOI:* 10.1007/s00704-021-03722-w

Linan C., Vadillo I., Carrasco F., 2008. Carbon dioxide concentration in air within the Nerja Cave (Malaga, Andalusia (Spain). International Journal of Speleology (ediz. ital.), 37(2): 99-106, July 2008. DOI:10.5038/1827-806X.37.2.2

Mattey D.P., Atkinson T.C., Barker J.A., Fisher R., Latin J.P., Durrel R., Ainsworth M., 2016. Carbon dioxide, ground air and carbon cycling in Gibraltar karst. Geochim. et Cosmochim. Acta, 184: 88-113. DOI 10.1016/j.gca.2016.01.041.

Merlak E., 2020. Radon e speleonauti. Sopra e Sotto il Carso. Rivista on-line, a. IX, n. 7, luglio 2020, pag. 20-25, www.seppenhofer.it

Vadillo I., Benavente J., Carrasco F., Soler A., Liñan., 2010. Isotopic (13C) Signature of CO_2 Sources in the Vadose Zone of a Mediterranean Karst (Nerja Cave Site, Southern Spain). In: Andreo B., Carrasco F., Durán J., LaMoreaux J. (eds) Advances in Research in Karst Media. Environmental Earth Sciences, Springer. DOI:10.1007/978-3-642-12486-0_71

Wood W.W., 1985. Origin of caves and other solution openings in the unsaturated (vadose) zone of carbonate rocks: A model for CO_2 generation. Geology (1985), 13 (11), pp. 822-824. DOI:10.1130/0091-7613(1985)13<822:OOCAOS>2.0.CO