International Journal of Speleology	36 (1)	51-56	Bologna (Italy)	January 2007

Available online at www.ijs.speleo.it

International Journal of Speleology
Official Journal of Union Internationale de Spéléologie

Seasonal variations of CO_2 and ^{222}Rn in a mediterranean sinkhole - spring (Causse d'Aumelas, SE France)

Christelle Batiot-Guilhe[1], Jean-Luc Seidel[1], Hervé Jourde[1], Olivier Hébrard[1], Vincent Bailly-Comte[1]

Paper presented during the International Conference Aqua$_{in}$Med'06, Malaga (Spain) 24-28 April 2006.

Abstract:

Batiot-Guilhe C., Seidel J.L., Jourde H., Hébrard O., Bailly-Comte V. 2007. Seasonal variations of CO_2 and ^{222}Rn in a Mediterranean sinkhole - spring (Causse d'Aumelas, SE France).
International Journal of Speleology, 36 (1), 51-56. Bologna (Italy). ISSN 0392-6672.

Carbon dioxide and ^{222}Rn monitoring of the atmosphere of a Mediterranean sink hole - spring (SE France) during two hydrological cycles (from September 2004 to September 2006) showed seasonal variations with very high concentrations during summer (greater than 6% and 20 000 Bq/m^3, respectively). Gas dynamics in caves often show seasonal variations. Meteorological parameters (barometric pressure and temperature mainly), cave geometry and fracture networks control exchanges between the cavity and outside atmosphere. Carbon dioxide and ^{222}Rn may have different sources (atmosphere, soil, bedrock, deep gas diffusion, in situ oxidation of organic matter and, in some caves, the key role of swift underground streams). For a CO_2 origin, ^{13}C measurements on water and gas samples taken into the cavity suggest a superficial origin. Radon-222 appears to be locally produced and transported by biogenic CO_2. Further investigations will be carried out in order to study the relationship of gas-level variations with barometric pressure variations and piezometric level fluctuations within the aquifer.

Keywords: : CO_2, ^{222}Rn, Karst, Cave, ^{13}C, France, Languedoc-Roussillon

Received 7 July 2006; Revised 27 September 2006; Accepted 24 November 2006

INTRODUCTION

Carbon dioxide dynamics and transfer from soil to the deepest parts of an aquifer underlie the main karstification processes. Cavity ventilation plays an important role in speleothem formation and chemical equilibrium of water in the unsaturated zone of the aquifer.

Meteorological parameters (barometric pressure and temperature), cave geometry and fracture networks control exchanges between subterranean and outside atmosphere (De Freitas et al., 1982; De Freitas & Littlejohn, 1987; Smithson, 1991; Christoforou, 1996; Buecher, 1999; Fernandez-Cortes, 2005).

Gases currently studied in caves are CO_2 and ^{222}Rn. Their concentrations and variations can be explained by different parameters.

Carbon dioxide concentrations in cavities vary from 0.03 % to more than 6 % and may have different sources :

- atmosphere which is characterized by low values (0.03 %; Renault, 1968),
- soil, where biological activity produces one hundred times more CO_2 on average than in the atmosphere, and then is transported by water seeping through the soils and network of rock voids (Atkinson, 1977; White, 1988). In Mediterranean limestone soils, pCO_2 varies from 0.5 to 2% (Batiot, 2002),
- oxidation by bacteria of organic matter in carbonated rocks or cavity deposits,
- deep gas diffusion or transport (Wood & Petraitis, 1984; Wood, 1985).
- in some caves, draughts cause, for instance, by a swift underground stream (Ek & Gewelt, 1985).

High ^{222}Rn contents have been reported in caves and are primarily related to the uranium content of the bedrock or to ^{226}Ra, decay progeny of ^{238}U, readily transported from the source and precipitated as $RaCO_3$ on cave walls and deposits present in the cavity. Radon-222 is produced by the ^{238}U decay series and has a short half-life (3.82 days). Several studies carried out on 220 caves worldwide have shown concentrations ranging from 0.1 to 20 kBq/m^3 (Hakl et al., 1997a, b; Dueñas et al., 1999; Cigna, 2005).

[1] Laboratoire HydroSciences Montpellier, Université Montpellier II, Maison des Sciences de l'Eau, Place Eugène Bataillon, CC MSE, F-34095 MONTPELLIER Cedex 5, France
seidel@msem.univ-montp2.fr

Gas dynamics in caves often show seasonal variations as a function of the temperature difference between the cave and outside atmosphere (James, 1977; Jovanovic, 1996; Hakl et al., 1996; Przylibski, 1999; Bourges et al., 2001, 2006; Cigna, 2005; Fernandez-Cortes, 2005). In summer, the outside temperature is higher than the inside temperature and precludes large-scale convections. The cavity atmosphere tends to reach equilibrium with CO_2 concentrations present in the microfractures network. Confined conditions are predominant and CO_2 concentrations increase in the cavity. In winter, the external temperature is lower than within the cavity, outside air enters by large openings and is released through large fractures. Cave ventilation is more efficient and dilution induces low CO_2 and ^{222}Rn levels. Moreover, barometric pressure variations can play an important role for "vertical caves" whereas the temperature is the main parameter regulating gas levels for "horizontal caves" (Hakl et al., 1996). Causse d'Aumelas caves are "horizontal" caves which present two types of thermo-convective circulation in function of the thermal regime outside during winter and summer time.

The Languedoc-Roussillon area (SE France) is characterized by a complex geological and tectonic history. The karstic formations essentially consist of Jurassic and Cretaceous deposits. Triassic evaporite formations often underlay these formations. Numerous springs containing CO_2 were identified in the area and are always associated to regional fractures (Grillot et al., 1983; Arthaud et al., 1994). Some cavities exhibit high CO_2 levels (oral communication from speleologists and punctual measurements). Since September 2004, hydrochemical and hydrodynamic monitoring has been carried out over the Causse d'Aumelas, an experimental site located 20 km near Montpellier (Jourde et al., 2006). This karst aquifer is crossed by the intermittent Coulazou River. Water sampling and measurements of different parameters (temperature, pH, electrical conductivity, major ions concentration, Total Organic Carbon) have been conducted at several sites of this hydrosystem (springs, boreholes, cavities, river) in order to characterize the karst behaviour and the connections between the Coulazou River and the aquifer, especially during flood events.

Very high CO_2 levels were registered in Les Grands Combes cavity, an estavelle (functioning either as sink-hole or spring), located within the bed of the Coulazou River. To better identify the gases origin, regular measurements of CO_2 and ^{222}Rn levels as well as punctual analyses of ^{13}C on gas and water within the cavity were carried out.

STUDY AREA AND METHODS

The Causse d'Aumelas karst aquifer (about 200 km^2) is composed of 2000 m thick Jurassic deposits. This unit belongs to the Aumelas-Thau karstic system, which is an unconfined aquifer in its northern part (Causse d'Aumelas) and becomes confined in its southern part, under the Miocene Montbazin-Gigean basin which is composed of clay and sandstones deposits (Fig. 1). Climate is typically Mediterranean with flood periods occurring in the spring and autumn, and a dry season in summer.

During low flow periods, the intermittent Coulazou River sinks when it traverses the karstic aquifer. More than 15 estavelles, alternately functioning as sink-holes or springs, have been observed in the Coulazou River bed.

During this study, very high CO_2 levels (up to 6 %) were periodically registered (overall during low flow periods) in Les Grandes Combes estavelle (see Fig. 1 and Fig. 2). The cavity is more confined and deeper than the Puits de l'Aven estavelle (Fig.1), located just in the river bed, 1500 m from Les Grandes Combes estavelle. To understand the origin of the high CO_2 levels, observed in Les Grandes Combes, CO_2 and ^{222}Rn measurements were carried out monthly or bimonth in the two estavelles, except during flood events when their discharge is active. Carbon dioxide measurements were conducted using an Infra-Red landfill gas analyser (Model GA 94A; Geotechnical Instruments), with an accuracy of 0.1%. Radon-222 concentrations were measured using an ALPHAGARD® device (Genitron Instruments GmbH) with 10% accuracy.

By following the temporal variation of CO_2 and ^{222}Rn in the caves, we have tried to better constrain the CO_2 origin as either superficial (biogenic) or deep (magmatic).

RESULTS AND DISCUSSION

Figure 3 shows the temporal variations for CO_2 and ^{222}Rn levels measured over more than one hydrological cycle in Les Grandes Combes estavelle, from September 2004 to September 2006. Gas monitoring only started at the end of the low flow period in 2004 because no symptoms (breathing difficulties, headaches, etc.) were noted during water sampling within the estavelle before this period. Carbon dioxide levels were estimated afterwards by comparing the symptoms and the concentration measured in 2005 and 2006 for the same period. Carbon dioxide and ^{222}Rn show similar seasonal variations :

(1) during fall and winter, CO_2 and ^{222}Rn levels exhibit the lower concentrations. CO_2 values are lower than the detection limit (<0.1 %), whereas ^{222}Rn levels corresponded to natural background activity (< 250 Bq/m^3);

(2) in spring and summer, CO_2 and ^{222}Rn levels increase step by step to a maximum value at the end of the dry season, with concentration higher than 6% and 20 000 Bq/m^3, respectively;

(3) at the beginning of the autumn, CO_2 and ^{222}Rn levels decrease very quickly. Measurements are difficult during this period, because the cavity is often flooded by river infiltration or karst discharge.

The seasonal variations of CO_2 and ^{222}Rn are linked with seasonal variations of the outside temperature which is in agreement with the literature (James,

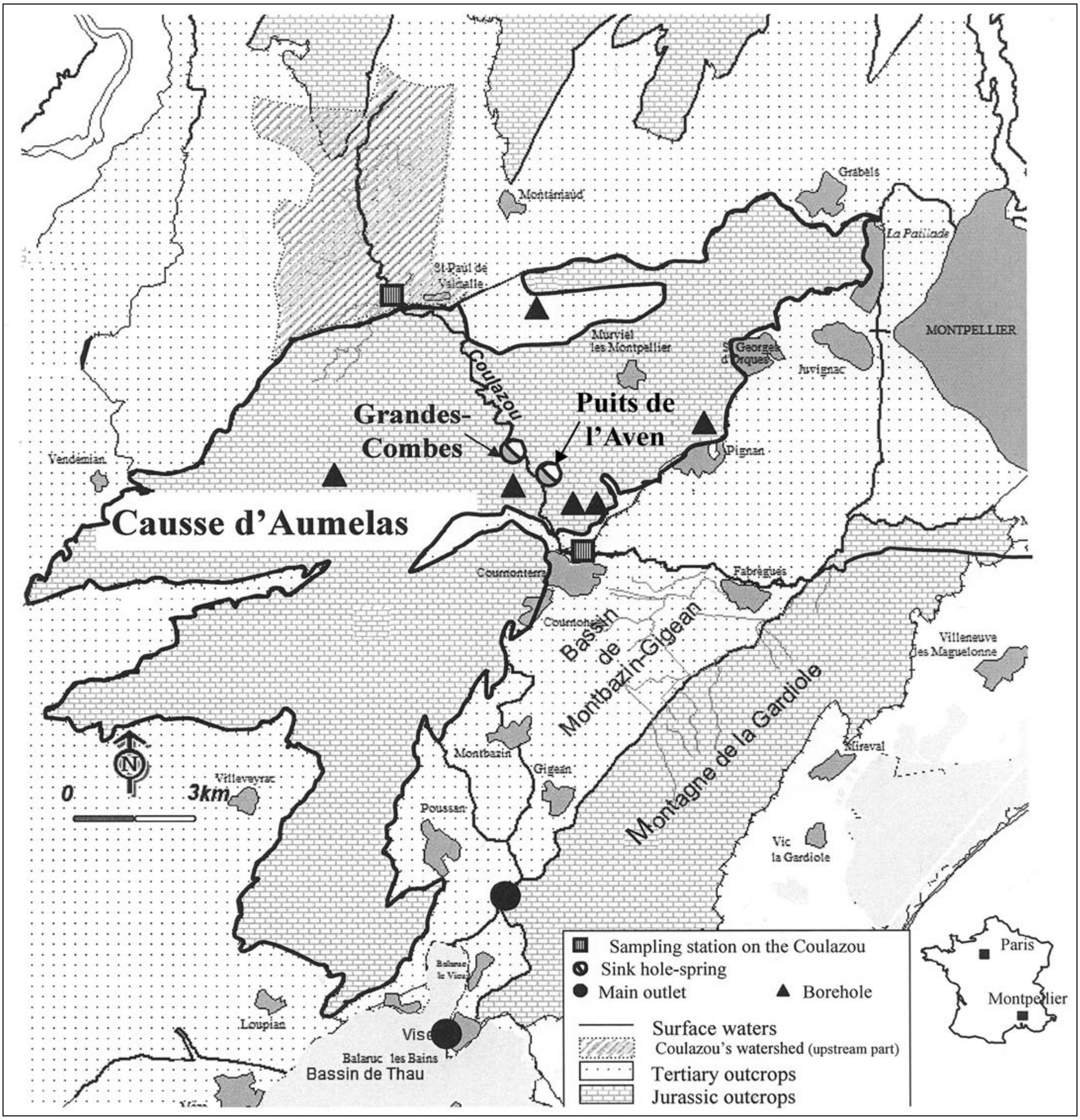

Fig. 1. Study area and location of the estavelles Les Grandes-Combes and Puits de l'Aven.

1977; Jovanovic, 1996; Hakl et al., 1996; Hakl et al., 1997b; Przylibski, 1999; Bourges et al., 2001, 2006; Fernandez-Cortes et al., 2006). The difference in temperature between the cavity and the outside atmosphere in winter is responsible for the efficient ventilation and thus gas dilution. In summer, outside temperature is higher than cave temperature and the cavity atmosphere tends to reach equilibrium with the gases present in the microfractures network, so that allows concentrations to increase. Maximum values of CO_2 and ^{222}Rn are very high, compared to the literature data, and representative of this cavity only. The geometry of the estavelle is very peculiar when compared to the Puits de l'Aven, located 1500 m downstream. In this second one, gas levels only reflect

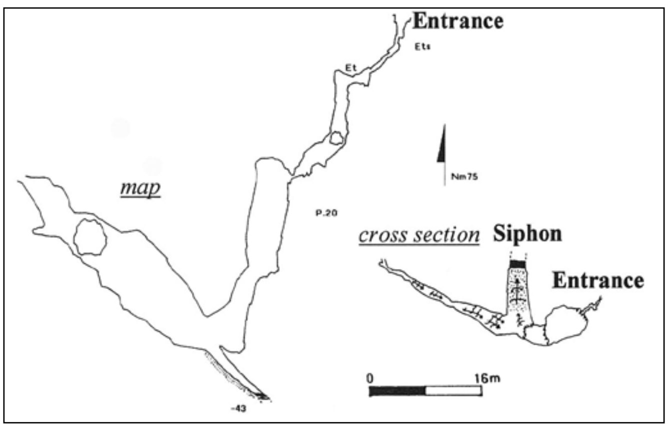

Fig. 2. Cross section and map of Les Grandes-Combes estavelle (from Vasseur, 1998).

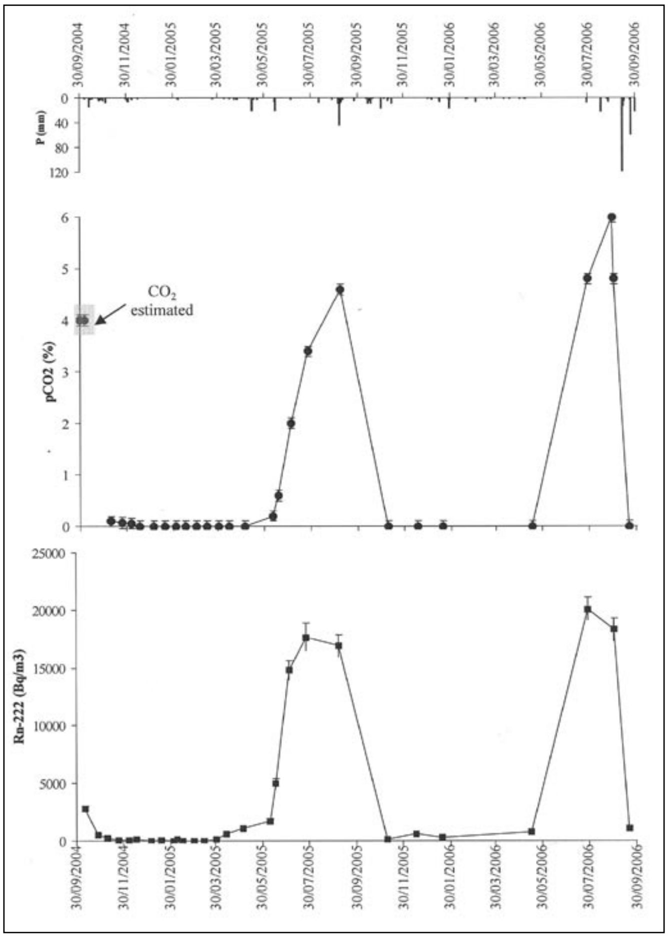

Fig. 3. CO_2 and ^{222}Rn temporal variations measured in the Les Grandes Combes estavelle. Rainfall at la Tour.

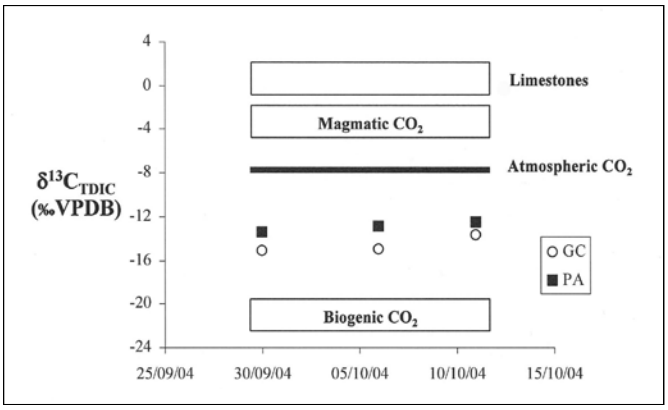

Fig. 4. Ranges for $\delta^{13}C_{TDIC}$ values, in ‰VPDB (Clark and Fritz, 1997) and for karst waters sampled in the two estavelles (GC = Les Grandes Combes and PA = Puits de l'Aven).

atmospheric variations because the entrance is well-developed when compared to Les Grandes Combes whose entrance is very narrow (0.5 × 0.5 m).

Different origins were considered for these two gases. The study area is located in a zone characterized by a complex geological structure and tectonic evolution. Deep CO_2 possibly associated with thermal waters frequently occurs in the Languedoc-Roussillon area (Grillot et al., 1983; Arthaud et al., 1994). The karst system of Causse d'Aumelas is located near the graben of Montbazin-Gigean and close to the hydrothermal system of Balaruc where deep fluids circulations have been identified (Bonnet & Paloc, 1969). Regional fracturing plays a major role in the transfer and dynamics of thermal fluids and magmatic CO_2.

Carbon dioxide and ^{222}Rn variations are very well correlated, suggesting a common mechanism of transfer. Moreover, ^{222}Rn is produced by the decay series of ^{238}U contained in bedrock or by ^{226}Ra, decay progeny of ^{238}U, readily transported from the source and precipitated as $RaCO_3$ on cave walls and deposits. But it can also originate from the deeper parts of the aquifer and may be related to a magmatic contribution. Radon-222 is always transported by other fluids (gas or water), but its short half-life (3.82 days) precludes a very deep origin because it must be transported so quickly to the surface which induces very high fluxes of magmatic CO_2.

To determine the origin of CO_2, we use ^{13}C isotope whose values are characteristic of the different sources of carbon within a system. We sampled water in the two estavelles and analysed ^{13}C on the Total Dissolved Inorganic Carbon (TDIC) fraction, as well as samples of gas (CO_2) in the estavelle of Les Grandes Combes during low flow periods when gas levels were the highest. Results are presented in Table 1 and Figure 4. The ranges of ^{13}C values for the different possible sources of carbon are also reported (values are defined versus the international reference material, VPDB, which is a fossil Belemnitella americana from the Cretaceous Pee Dee formation in South Carolina; Craig, 1957). For Clark and Fritz (1997), TDIC in water may originate from the dissolution of :

- carbonate rocks (end-member the most enriched: 0 ± 2 ‰ VPDB),
- atmospheric CO_2(−8 ‰ VPDB)
- biogenic CO_2 (very negative for plants with a C_3 cycle, from −21 to −31 ‰ VPDB),
- magmatic CO_2 (−4 to −8‰ VPDB)

All the $\delta^{13}C_{TDIC}$ values range from −12.60 to −15.11 ± 0.2 δ‰ VPDB and reflect the typical evolution of waters only influenced by two ^{13}C end-members: biogenic CO_2 and carbonated rocks (Arthaud et al., 1994; Emblanch et al., 2003; Batiot et al., 2003).

Puits de l'Aven $\delta^{13}C_{TDIC}$ values are always enriched compared to Les Grandes Combes values. If CO_2 in Les Grandes Combes had a magmatic origin, the ^{13}C values for water should be more enriched whereas, on the contrary, they are more negative. To discriminate the CO_2 origin in Les Grandes Combes estavelle, two samples of gas were analysed in July 2005 when CO_2 levels were maximum. The mean VPDB value of −24.2 ‰ VPDB (Table 1) is typical of a biogenic CO_2 origin and exclude a deep magmatic contribution.

To confirm the superficial origin of the two gases, in particular for ^{222}Rn, the ^{238}U content of limestones and clay deposits in the estavelle must be known. Uranium-238 contents in rock samples have not yet been determined, but generally limestones contain about 1.3–2.5 ppm of ^{238}U (Hakl et al., 1997a, b). Moreover, a previous study has been carried out on the Lamalou karst system (near Montpellier) developed

	Water	Gas
Samples	$^{13}C_{TDIC ‰ VPDB}$	$^{13}C_{CO2 ‰ VPDB}$
GC 30-9-04	-15.11	
PA 30-9-04	-13.42	
GC 06-10-04	-14.97	
PA 06-10-04	-12.89	
GC 11-10-04	-13.74	
PA 11-10-04	-12.60	
GC 05-07-05		-24.20

Table 1. Isotopic composition for ^{13}C contents (‰ VPDB) for water and gas sampled in Les Grandes Combes (GC) and Puits de l'Aven (PA) cavities.

in cretaceous sedimentary rocks, with lithology characteristics close to these of the Jurassic deposits forming the Causse d'Aumelas. The data showed that ^{238}U content is low (Valanginian limestones: 1.36 ppm; Berriasian marls: 1.38 ppm; clay deposits within cavity: 3.53 ppm according to Pane-Escribe (1995), but could explain the high ^{222}Rn levels in the estavelles. Carbonate soil and clay deposits in Les Grandes-Combes cave have also been sampled and a ^{222}Rn activity lower than 300 Bq/kg has been measured. Even if a bedrock contribution cannot be totally excluded, all these data indicate a superficial origin of ^{222}Rn which is locally produced within the fracture network of the aquifer and transported into the cave atmosphere with biogenic CO_2 during summer time by a simple air flow as gas carrier.

CONCLUSION

Gas monitoring carried out within a Mediterranean estavelle (SE France) suggests seasonal variations of CO_2 and ^{222}Rn levels, the highest gas contents being registered during summer time, greater than 6% and 20 000 Bq/m^3 respectively. Different origins have been considered for these geogases (biogenic, bedrock or magmatic). The determination of ^{13}C in water and gas samples from the cavity confirms the superficial source of CO_2. Because of the short half-life of ^{222}Rn and its relatively high activity (< 300 Bq/kg) in the carbonate soil and clay deposits, a deep origin can be excluded for this gas. Radon-222 is only produced in the microfracture network and transported by biogenic CO_2 from the deeper parts of the aquifer towards the surface. The seasonal increase of gas levels during spring, with a maximum at the end of summer is commonly described in the literature and can be explained by the poor ventilation of the cavity during this period. During summer time, outside temperature is higher than air cave temperature and the atmosphere of the cavity tends to reach equilibrium with the gases released by the microfractures network. Further investigations will be carried out in order to determine how gas level variations can be related to barometric pressure variations and piezometric levels fluctuations within the aquifer.

ACKNOWLEDGEMENTS

We thank Yves Travi and Christophe Emblanch from the Hydrogeology Laboratory of Avignon (France) as well as the technical staff of this laboratory for their collaboration for ^{13}C analyses. We also want to thank R. Bourier who gave us helpful information concerning the site. Reviews by A. Cigna, M.S. Field and an anonymous reviewer greatly improved the manuscript.

REFERENCES

Arthaud F., Dazy J. & Grillot J.C., 1994 - *Distribution of deep carbon dioxide in relation to the structure and tectonic evolution of south-east France*. Geodin. Acta, **7(2)**: 86-102.

Atkinson T.C., 1977 - *Carbon dioxide in the atmosphere of the unsaturated zone: an important control of groundwater hardness in limestone*. J. Hydrol., **35**: 111–123.

Batiot C., 2002 - *Etude expérimentale du cycle du carbone en régions karstiques. Apport du carbone organique et du carbone minéral à la connaissance hydrogéologique des systèmes. Site expérimental de Vaucluse, Jura, Larzac, Région Nord-Montpelliéraine, Nerja (Espagne)*. PhD Thesis, Univ. d'Avignon, 247 p.

Batiot C., Emblanch C. & Blavoux B., 2003 - *P_{CO2} – ^{13}C : an interesting tool to characterize types of karstic aquifers*. In: International Symposium on Isotope Hydrology and Integrated Water Resources Management, Vienna, Austria, 19-23 May 2003, International Atomic Energy Agency.

Bonnet A. & Paloc, H., 1969 - *Les eaux des calcaires jurassiques du bassin de Montbazin-Gigean et de ses bordures*. Bull. BRGM, **2(3)**:1-12.

Buecher R.H., 1999 - *Microclimate study of Kartchner caverns, Arizona*. J. Cave and Karst St., **61**: 108–120.

Bourges F., Genthon P., Mangin A. & D'Hulst D., 2006 - *Microclimates of l'Aven d'Orgnac and other French limestones caves (Chauvet, Esparros, Marsoulas)*. Int. J. Climatol., **26** :1651-1670.

Bourges F., Mangin A. & D'Hulst D., 2001 - *Le gaz carbonique dans la dynamique de l'atmosphère des cavités karstiques : l'exemple de l'Aven d'Orgnac (Ardèche)*. C. R. Acad. Sci. Paris, Earth and Planetary Sciences, **333**: 685-692.

Christoforou C.S., Salmon L.G. & Cass G.R., 1996 - *Air exchange within the buddhist cave temples at Yungang, China*. Atmos. Environ., **30 (23)**: 3995–4006.

Cigna A.A., 2005 - *Radon in caves*. Int. J. Speleol., **34(1-2)**: 1-18.

Clark I. & Fritz P., 1997 - *Tracing the carbon cycle*. In: *Environmental Isotopes in Hydrogeology*, Lewis Publishers, New York, 328 p.

Craig H., 1957 – *Isotopic standards for carbon and oxygen and correction factors for mass spectrometric analysis of carbon dioxide*. Geochim. Cosmochim. Acta, **12**: 133-149.

De Freitas C.R. & Littlejohn R.N., 1987 - *Cave climate: assessment of heat and moisture exchange*. J. Climatol., **7**: 553–569.

De Freitas C.R., Littlejohn R.N., Clarkson T.S. & Kristament I.S., 1982 - *Cave climate: assessment of airflow and ventilation*. J. Climatol., **2**: 383–397.

Dueñas C., Fernandez M.C., Cañete S., Carretero J., Liger E., 1999 – *222Rn concentrations, natural flow rate and the radiation exposure level in the Nerja Cave.* Atmos. Environ., **33**: 501-510.

Ek C. & Gewelt M., 1985 - *Carbon dioxide in cave atmospheres. New results in Belgium and comparison with some other countries.* Earth Surf. Proc. Land., **10**: 173–187.

Emblanch C., Zuppi G.M., Mudry J., Blavoux B. & Batiot C., 2003 - *^{13}C of TDIC to quantify the role of the Unsaturated Zone : the example of the Vaucluse karst systems (Southeastern France).* J. Hydrol., **279 (1-4)**: 262-274.

Fernandez-Cortes A., 2005 - *Caracterizacion microclimatica de cavidades y analisis de la influencia antropica de su uso turıstico.* Ph.D, University of Almerıa, Servicio de Publicaciones de la Universidad de Almerıa, Almerıa, Spain, 424p.

Grillot J.C., Bousquet J.C., Philip H. & Dazy J., 1983 – *Hydrothermalisme carbo-gazeux, radioactivité et sismotectonique: exemple du Languedoc-Roussillon.* Hydrogéologie, Géologie de l'ingénieur, **4**: 313-320.

Hakl J., Csige I., Hunyadi I., Varhegyi A., & Geczy G., 1996 - *Radon transport in fractured porous media – Experimental study in caves.* Environ. Int., **22 (1)**: 433-437.

Hakl J., Hunyadi I., & Varhegyi A., 1997a- *Radon monitoring in caves.* In: Durrani, S.A., and Ilic R.(Eds.) - *Radon measurements by etched track detectors. Applications in radiation protection, earth sciences and the environment*, World Scientific: 261-283.

Hakl J., Hunyadi I., Csige I., Geczy G., Lénart, L. & Varhegyi A., 1997b- *Radon transport phenomena studied in karst caves – International experiences on radon levels and exposures.* Radiat. Meas., **28 (1-6)**: 675-684.

James J.M., 1977 - *Carbon dioxide in the cave atmosphere.* Trans. British Cave Research Assoc., **4 (4)**: 417-429.

Jourde H., Roesch A., Guinot V., Bailly-Comte V., 2006 - *Dynamics and contribution of karst groundwater to surface flow during mediterranean flood.* Environ. Geol., in press.

Jovanovic P., 1996 - *Radon measurements in karst caves in Slovenia.* Environ. Int., **22 (1)** : 429-432.

Pane-Escribe M.B., 1995 - *Utilisation des éléments traces comme traceurs des circulations souterraines en milieu karstique (Site du Lamalou, Hérault).* PhD, Univ. Montpellier II, 296 p.

Przylibski T.A., 1999 - *Radon concentration changes in the air of two caves in Poland.* J. Environ. Radioact., **45**: 81-94.

Renault P., 1968 - *Sur la distinction de plusieurs régions karstiques en raison de la teneur en anhydride carbonique des atmosphères de grottes.* C. R. Acad. Sci. Paris, **267**: 2288–2290.

Smithson PA., 1991 - *Inter-relationships between cave and outside air temperatures.* Theor. Appl. Climatol., **44**: 65–73.

Vasseur F., 1998 - *Sur les palmes d'Henri Lombard* - Inventaire spéléologique des siphons héraultais et des secteurs limitrophes, Tome 2, Association Celadon – Fédération Française de Spéléologie, Montpellier, 284 p.

White W.B., 1988 - *Geomorphology and Hydrology of Karst Terrains.* Nueva York: Oxford University Press.

Wood W.W., 1985 - *Origin of caves and other solution openings in the unsaturated (vadose) zone of carbonate rocks: a model for CO2 generation.* Geology, **13**: 822–824.

Wood W.W. & Petraitis M.J., 1984 - *Origin and distribution of carbon dioxide in the unsaturated zone of the southern High Plains.* Water Resour. Res., **20**: 1193–1208.