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Cover photo : Keir Vaughan-Taylor on Lake 2, Koonalda Cave, Nullarbor Plain. (Photo by Kevin Moore)

Back Cover : The Khan and Beagum in Kubla Khan Cave Tasmania (Photo by Garry K. Smith)

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Preface

Welcome to the 17th International Congress of Speleology and we hope you enjoy the Congress and appreciate the papers presented here in the Proceedings. These Proceedings are issued by the 17th International Congress of Speleology (Speleo2107) on July 22-28, 2017 in Sydney, NSW, Australia.

The large number of papers and posters presented here represents a huge amount of work by the authors, the reviewers and the editorial team. There are about 250 oral paper presentations and 61 posters. This represents a huge number of received e-mails and a similar number of responses during the last 6 months, with a similar load of electronic files and over 800 printed pages of text. This is a large amount of interesting material concentrating on Cave and Karst matters.

The author's guidelines stipulated that the particular contributions should not exceed 6 pages of text and we were delighted to find that most authors prepared contributions close to this upper limit. This illustrates a clear willingness of the cavers and karst scientists to share their discoveries and research conclusions.

The presented contributions (abstracts/papers) stand for both oral and poster presentations as indicated in the headings. Contributions in each session are arranged alphabetically by the last name of the first author. All contributions were reviewed by invited reviewers. Assistance was given to improve the English expression for those whom English is not their primary language. This has improved the clarity and readability of the contributions. Unfortunately due matters out of our control this reviewing process took much longer than expected and the problems of lost emails and the vagaries of the internet added to the unfortunate delays.

Twenty two thematically different sessions three plenary lectures were scheduled to cover the whole range of subjects to be discussed within the wide scope of the 17th ICS. Low numbers of contributions for some sessions necessitated their grouping with others in the program but we have attempted to keep them separate here. The contributions are grouped into two separate volumes.

The volumes are published digitally and will be available on the Karst Information Portal. http://digital.lib.usf.edu/karst. There are very few copies printed in hard copy. This is partly due to issues of people travelling to Australia and needing to either carry bulky books or expensively post home. The printed copies are only in black and white whereas the digital are print quality full colour. In many cases it will be more cost effective for people to print from the data stick at home, and certainly much easier to transport.

We apologize for the all mistakes that might have crept into various submissions, from various versions of the manuscripts and other related files and emails which passed through our computers. We hope that everybody finds interesting reading here and we wish that the whole publication (Volumes 1 & 2) is a valuable record of the 17th meeting of enthusiasts addicted to the fascination of the underground world.

Finally we thank all the authors for their contributions and the reviewers for their work in improving the text. Thank you everyone for their patience.

Enjoy!

Kevin Moore and Susan White

Editors Speleo2017 Proceedings

Sourcing Carbon Dioxide Gas In Karst Systems

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Abstract

Recent studies have demonstrated that caves may act as significant reservoir of CO_2 gas on an annual scale and may be acting as sinks for atmospheric CH_4 on a daily scale, which provides evidence that the subterranean atmosphere of karst systems may play a key role in regulating greenhouse gases in the atmosphere. In this study, we have measured CO_2 variability and carbon isotope composition of subterranean air in karst environments. The cave sites cover a spectrum of local climates (oceanic and continental), bedrock lithology, cave microclimatic conditions, ventilation pattern, geomorphological and speleogenesis types (epigenic and hypogenic caves). The potential mechanisms involved on the CO_2 dynamic of either soil or geogenic-derived CO_2 in subterranean atmospheres are discussed. The atmospheric air that is inhaled into dynamically ventilated epigenic caves then return to the lower troposphere as CO_2-enriched air, during periods with higher ventilation. The first samples obtained in an active hypogenic cave (Vapor cave) exemplify the potential releasing of CO_2 along the faults and in the fractures occurring in the carbonate rocks and its significant influence on the conditions of the adjacent soil and local atmosphere at exterior.

Keywords: carbon dioxide, methane, caves, carbon isotopes, karst, subsoil.

1. Introduction

The increasing concentration of greenhouse gases (GHGs) in the atmosphere and its relationship to the Earth's climate are deserving a special scientific attention focused on the identification and characterization of all possible sources, reservoirs and sinks of GHGs, in order to calculate more accurately the carbon greenhouse gases budget, mainly CO_2 and CH_4 (Ciais *et al.* 2013 and references therein). The subterranean atmospheres are key locations to be considered regarding the balance of atmospheric carbon. Karst settings are reported to cover between 12 and 25% of the land surface of the Earth mainly linked to outcrops of carbonates (Ford and Williams 2007). These areas are potentially capable of harboring underground air masses (e.g. caves) that are periodically renewed by interaction with the atmospheric boundary layer and directly influence their physicochemical properties.

Some previous tracing studies employing carbon isotopes (Frisia *et al.*, 2011; Garcia-Anton *et al.*, 2014 and 2017; among others) or an analytical approach addressing CO_2 fluxes (Cuezva *et al.*, 2011; Corinne *et al.*, 2013), have demonstrated that the deep soil air CO_2 is the main source of this gas in cave air in near-surface cavities (generally formed under an epigenic context). CO_2 air in some deeper caves results from the interaction of cave ventilation with a reservoir of CO_2-enriched ground air formed by the decay of organic matter washed down into the deeper unsaturated zone (Mattey *et al.* 2016) and held within the smaller voids and fissures of the bedrock-surrounding cave.

Caves formed by specific hydrogeochemical mechanisms of hypogene speleogenesis and their interaction, e.g. hydrothermal, sulfuric acid, mixing corrosion, dissolution of evaporites, dissolution in mixed sulfate-carbonate sequences (Klimchouck *et al.*, 2014; Chavez and Reehling, 2016) can harbour subterranean atmospheres with a distinctive gas composition with presence of abiotic CO_2 gas (formed by chemical reactions which do not directly involve organic matter), which are frequently mixtures of multiple sources. This composition results from the current activity or residual signs of some processes as degassing from CO_2-rich groundwater or deep-sourced (geothermal) CO_2.

The pathways and mechanisms that control the fluxes of CO_2 among atmosphere, soil and subsurface reservoirs in karst terrains have not been characterised to date from an overall view, i.e. including at the same time diverse geological, tectonic and hydrogeological environments in the data analysis process. Here, we put forward some general insights concerning the GHGs behaviour in the upper vadose zone of karst terrains, based on climatic and gas composition monitoring combined with geochemical tracing using the stable carbon isotopic signature ($\delta^{13}C$) of CO_2. This study contributes with new data and findings to define and characterize the biotic and abiotic processes that regulate the CO_2 dynamic in near-surface epigenetic and hypogenic caves and assess their interaction with the external atmosphere.

2. Sites, materials and methodology

Fieldwork based on tracking gases has been deployed in sites were authors maintain a comprehensive cave monitoring and sampling networks in place for air analysis of soil and subsurface. Here it is only presented four of the most outstanding cave sites that summarize a wide range of processes that regulate the consumption and storage of CO_2 and CH_4. Ojo Guareña cave (northern Spain) is a highly ventilated cave with large daily and climate-driven oscillations of CO_2 levels (680–1900 ppm/day) (Fernandez-Cortes *et al.*, 2015). Castañar cave (central Spain) is a low-energy and quite isolated cave with very high thermal stability and poorly ventilated at daily scale (Fernandez-Cortes *et al.*, 2011). Pech Merle cave (southern France) is an example of cave atmosphere enriched in soil-derived CO_2 (1.4–2.8%) and depleted in O_2 (<19.5%), with clear evidences of stability of its underground microclimate since last two decades (Bourges *et al.*, 2014). Vapor cave (southeastern Spain) represents a particular case of chasm developed in a karstic area of active faulting with evidence of geogenic sources for CO_2 and CH_4, hydro-thermalism (38–43 °C), hypoxic conditions (O_2 ranging 17–18%), related to upwelling flow in or from the zone of fluid-geodynamic influence (Perez-Lopez *et al.*, 2016).

Spot air sampling was conducted in a predefined network of points spatially distributed inside each cave and exterior atmosphere. Soil air collection was also conducted at sites located vertically above each cave at a depth of 50 cm, near the bedrock–soil interface. Air samples were collected into 1 L Tedlar bags with lock valves and using a micro-diaphragm gas pump. Samples were obtained on a bi-monthly basis in Ojo Guareña and Castañar cave during more than annual cycle. Pech Merle and Vapor cave were sampled under, at least, two different meteorological seasons.

Bag samples were analyzed using a CRDS analyzer model G2201-i (Picarro Inc., Santa Clara, CA, USA) belonging to the National Museum of Natural Sciences (Spanish Research Council). The device was calibrated before each analysis session using synthetic gases with known concentrations. Further details about the methodological procedures can be found in Fernandez-Cortes *et al.* (2015). CO_2 mole fractions of samples were also measured independently in the greenhouse gas laboratory at Royal Holloway University of London with a Picarro G1301 CRDS analyzer, calibrated against the NOAA reference gases. The carbon isotopic ratio ($\delta^{13}C$-CO_2) of bag samples was measured in the RHUL lab in triplicate to high precision (±0.05‰) by continuous flow gas chromatography isotope ratio mass spectrometry (CF GC-IRMS) (Fisher *et al.* 2006).

3. Results and Discussion

Figure 1 summarizes some prevailing processes once the dataset of gas concentrations (CO_2) and its carbon isotopic ratio were analyzed for the studied caves. The extrapolation down to the X-axis of the keeling functions (colored lines of Figure 1) gives the $\delta^{13}C$ for the CO2 sources at each cave site (-26.16‰ at Ojo Guareña, -26.19‰ at Castañar, -23.08‰ at Pech Merle). These $\delta^{13}C$-CO_2 data confirm that CO_2 in shallow caves (Castañar and Ojo Guareña) results from from mixing atmospheric air and CO_2 produced by microbial respiration in soils containing organic material from C3 vegetation (around -27‰ according to Amundson *et al.*, 1998, in contrast to the observed $\delta^{13}C$ values for C4 vegetation; approximately -14%, O'Leary, 1988).

The $\delta^{13}C$ of the CO_2 source in Pech Merle is heavier than other caves despite of the woodland vegetation with a C3 pathway is predominant on the surface. This suggests that ground air is influenced by the decay of organic material washed down into the deep soil and unsaturated zone and it could be another important CO_2 source of this cave.The organic matter from soil can transported by infiltration of water through fractures and voids in the vadose zone immediate below the deepest layers of soil. The microbial decomposition of this organic matter leached from the soil produces air enriched in CO_2 and, undoubtedly, with a different isotopic composition from the CO_2 generated directly by modern-day soil. This CO_2 with a heavier $\delta^{13}C$ can then enter the cave through diffusion via cracks and fissures in the bedrock. Mattey *et al.* (2016) have also described this additional CO_2 source in Gibraltar caves and it seems to be also responsible for the high accumulation of this gas in Pech Merle, which is favoured by the prevailing low air renewal of this cave site. The high CO_2 concentration in Pech Merle (ranging 1.5–2.7%) determines the tendency to hypoxic conditions of the cave atmosphere due to a mole-to-mole replacement of O_2 by CO_2 in air (O_2 levels ranging 17.9–19.5%)".

The grey-shaded area in Figure 1 show the air-mixing model in shallow epigenic caves (e.g. Ojo Guareña and Castañar) between background atmosphere and a theoretical composition of pure CO_2 produced by microbial respiration in soil. The black-solid straight lines of the mixing area are labeled as % of pure additional CO_2 from soil remaining in the cave air and soil air. As the distance of the cave air samples from the y-intercept of the Keeling models increases, there is greater ventilation and greater influence of the external atmosphere. Conversely, when CO_2 concentration is high and $\delta^{13}C[CO_2]$ tends toward the y-intercept, the gas enters by diffusion and has a mainly edaphic origin. Cave air in highly ventilated sited as Ojo Guareña is well mixed with background atmosphere and the remaining soil-derived CO_2 is usually below 5% with a marked seasonal variation, except for air samples collect during summer months (from July to early September) when this percentage is above 10%. By contrast, air of poor-ventilated cave as Castañar the remaining soil-derived CO_2 is usually above 10%.

The black-solid curved arrows in Figure 1 show the kinetic fractionation trajectory of soil CO_2 due to its upwards diffusion to open atmosphere, modelled by a Rayleigh-type distillation process with a fractionation coefficient of 4.4‰ (based on the theoretical mass-dependent fractionation between $^{12}CO_2$ and $^{13}CO_2$ during diffusion, according to Camarda *et al.*, 2007). The Rayleigh equation is an exponential relation that describes the partitioning of isotopes between two reservoirs as one-reservoir decreases in size, in this case the CO_2 content in soil air. Each curve arrow starts from a soil air with a different percentage of remaining pure CO_2 produced by respiration in soil, i.e.; theoretical source of CO_2 (2% CO_2 and -27‰ $\delta^{13}CO_2$), 20% remaining and 50% remaining, from the lower to upper arrow respectively. As an example, the upper curve arrow is labelled with the fraction of CO_2 remaining after Rayleigh fractionation associate to the diffusion process. Some cave air samples from Ojo Guareña and Castañar fit well to these diffusion curves, i.e. CO_2 of cave air tends to be heavier while its concentration almost no change, which could indicate a slight diffusion of this gas from the monitored areas of this cave to deepest or nearby locations of the vadose zone.

A distinctive case is represented by the air samples from Vapor cave, where the high concentration of CO_2 and its heavier $\delta^{13}C$-CO2 (5.97‰ on average) result from a deep source of CO_2 in cave-air. The hypogene speleogenesis and the current

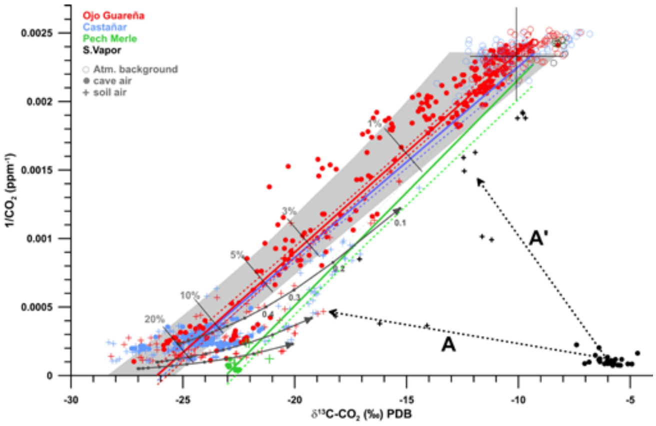

Figure 1. Keeling plot of 1/CO_2 versus δ^{13}C-CO_2 considering three air reservoirs: (1) background atmosphere, (2) cave air and (3) soil air (see legend). The average composition of the background atmosphere for the 4 fieldwork sites is indicated by the crosshair. The colored continous lines indicate the keeling functions the three-component mixture (atm, cave and soil) and almost it does not differ from the two-component functions (atm-soil and atm-cave); R^2=0.95 (Ojo Guareña), R^2=0.94 (Castañar), R^2=0.99 (Pech Merle). Dotted lines show the 95% confidence intervals for each Keeling function. See text for further data interpretation and discussion.

gas exchange processes are controlled by the upwelling air flow from the zone of fluid-geodynamic influence associated to an active fault with frequent microseisms (Perez-Lopez *et al.*, 2015). The $\delta^{13}CO_2$ values in air are also consonant with those measured in the CO_2-rich thermal waters of the aquifer spatially associated to the active fault (between -8.1 and -3.8‰, according to Ceron *et al.*, 1998). Therefore, degassing from CO_2-rich groundwater and deep-sourced geothermal CO_2 are the prevailing process responsible of the high abundance of CO_2 and its heavier carbon isotopic composition, which is clearly distinguishable from the epigenetic caves where the isotopically light endmember CO_2 is soil-derived. The upwelling flow of geogenic gases in this cave has a clear influence on the δ^{13}C-CO_2 of the soil air above the cave and, to a lesser extent, on the local atmosphere. This effect is noticeable in both the soil air well-mixed with open atmosphere and the soil air mixture with a higher percentage of remaining pure CO_2 produced by respiration in soil (arrows A' and A in Figure 1, respectively). The soil air in Vapor cave sometimes have lower CO_2 values than the other caves, despite the input of geothermal CO_2. There is an intense upward flux of CO_2 from soil to atmosphere, likely higher than other sites with deeper and wetter soils. Consequently, the soil CO_2 at Vapor cave results from a mixing between atmosphere and the composition of geogenic CO_2 coming from the subterranean atmosphere.

Pending to a full comparative analysis of $\delta^{13}CO_2$ and other isotopes (D/H for CH_4 and $^3He/^4He$) of air samples from Vapor cave, the obtained results ($\delta^{13}CO_2$ ranging from -4.5 to 7.5‰) indicate that the likely source is a mantle-rooted CO_2, i.e. a mantle-derived CO_2 flux. Similar carbon isotopic ratios have been described for soil air samples from hydrothermal areas within wider volcanic regions (Wen *et al.*, 2016) and magma-derived CO_2 emissions (Zhang *et al.*, 2016). Other previous studies in hydrothermal sites have describe some wider ranges carbon isotope composition of CO_2, e.g. from -2.4 to -7.8‰ in submarine hydrothermal vents (Botz *et al.*, 1999) or -1.0 to -9.1‰ in hot springs (Yokoyama *et al.*, 1999). Taking these $\delta^{13}CO_2$ values as references, the higher $\delta^{13}CO_2$ may indicate the addition of CO_2 directly from volcanic sources (Mazot *et al.*, 2014) or from underlying sedimentary rocks containing more marine carbonate minerals, i.e. CO_2 is produced mainly by thermal decarbonation (Cinti *et al.*, 2014). On the contrary, the lighter $\delta^{13}CO_2$ suggest a likely contamination by crustal organic sediments (Zhang *et al.*, 2014).

4. Conclusions

In an attempt to understand the GHGs dynamics in karst systems, we have carried out a pooled analysis of data of abundance and carbon isotopic composition of CO_2 in air from different cave sites with distinctive and opposite environmental conditions. The CO_2 dynamic within the upper vadose zone of karst (accumulation, mixing with background atmosphere or mobilization by diffusion) changes seasonally depending on the air-exchange rate with the external atmosphere, which involves substantial variations on the gas abundances and their carbon isotopic signal. In general, results provide evidence that atmospheric air that is inhaled into dynamically ventilated epigenic caves (at daily or seasonally scale) can then return to the lower troposphere as CO_2-enriched air. CO_2 depletion by mixing cave air with background atmosphere prevails during periods and subterranean sites with higher ventilation. On the contrary, when air renewal is hindered the CO_2 of cave air can be mobilized by diffusion to nearby air voids of the vadose zone. In contrast, the first samples obtained in an active hypogenic cave (Vapor cave) exemplify the potential releasing of CO_2 along the faults and in the fractures occurring in the carbonate rocks, which can be an important source in the seismically active areas. The role of subterranean air of karst as sink or source of CO_2 can vary seasonally and it may have a significant influence on the conditions of the adjacent soil and local atmosphere at exterior.

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