Ph. D. DISSERTATION / TESIS DOCTORAL

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Promoters:

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Tesis Doctoral

Characterization of CO_2 exchanges in deep soils and caves and their role in the net ecosystem carbon balance

Trabajo de investigación presentado por **Enrique Pérez Sánchez-Cañete** para aspirar al grado de Doctor por la Universidad de Granada.

Esta Tesis Doctoral ha sido dirigida y supervisada por:

Dr. Francisco Domingo Poveda, Dr. Andrew S. Kowalski y

Dra. Penélope Serrano Ortíz

Mayo 2013

La Tesis doctoral que se expone en la siguiente memoria, titulada: “Characterization of CO_2 exchanges in deep soils and caves and their role in the net ecosystem carbon balance” ha sido realizada por Enrique Pérez Sánchez-Cañete para aspirar al grado de Doctor por la Universidad de Granada. Se ha realizado conjuntamente en el Departamento de Desertificación y Geoecología de la Estación Experimental de Zonas Áridas (CSIC) y el Departamento de Física Aplicada de la Universidad de Granada. La realización de esta Tesis ha sido financiada por una beca predoctoral de la Junta de Andalucía, enmarcada dentro del proyecto de Excelencia titulado “Balance de carbono en ecosistemas carbonatados: discriminación entre procesos bióticos y abióticos (GEOCARBO, RNM-3721) financiado por la Consejería de Innovación, Ciencia y Empresa de la Junta de Andalucía, incluyendo fondos European Regional Development Fund (ERDF) y European Social Fund (ESF) de la Unión Europea. El trabajo también ha sido financiado parcialmente por proyectos del Ministerio Español de Ciencia e Innovación, Carbored-II (CGL2010-22193-C04-02), SOILPROF (CGL2011-15276-E), CARBORAD (CGL2011-27493), por las acciones integradas (PRI-AIBDE-2011-0824 y HF2008-0057) y también por el Proyecto Europeo de Séptimo Programa Marco (GHG Europe; Call FP7-ENV-2009-1.1.3.1; Project Code 244122).

Como Directores de la Tesis confirmamos que el trabajo ha sido realizado por el doctorando bajo nuestra dirección respetándose los derechos de otros autores citados. Así mismo, el trabajo reúne todos los requisitos de contenido, teóricos y metodológicos para ser admitido a trámite, a su lectura y defensa pública, con el fin de obtener el referido Título de Doctor, y por lo tanto AUTORIZAMOS la presentación de la referida Tesis para su defensa.

Directores de la Tesis

Fdo.:F. Domingo Poveda Fdo.:A.S. Kowalski Fdo.: P. Serrano Ortíz

Aspirante a grado de Doctor:

Fdo.: Enrique Pérez Sánchez-Cañete

Granada, Mayo de 2013

Abstract

This Thesis arises to response to the anomalous CO_2 fluxes detected by the Eddy towers located on two carbonate and semiarid sites in the south-east of Spain. In the soil-atmosphere CO_2 exchanges in both *El Llano de los Juanes* in the *Sierra de Gádor* and also *Balsa Blanca* located in the Natural Park of *Cabo de Gata-Nijar* (Almeria province), significant CO_2 emissions to the atmosphere were detected. These emissions could only come from the soil and not from the vegetation, occurring as they did mainly during the summer, with senescent vegetation. For this reason, this Thesis focuses on monitoring and characterization of the soil, distinguishing which are the main factors implicated in CO_2 exchanges with the atmosphere.

For the characterization and monitoring of subterranean CO_2 soil CO_2 profiles were established in both experimental sites with sensors installed at three different depths (0.15, 0.5 and 1.5 m). Furthermore, in *El Llano de los Juanes* sensors were installed at 0.25 m depth and in a borehole of 7 m depth, which was sealed from the surface to simulate a karst cave.

With the first CO_2 data obtained from the borehole, we realized that the deep soil could store large amounts of CO_2, because in the first 7 meters we recorded values of up to 18000 ppm. Since we were interested in determining the factors involved in CO_2 ventilation from soils and particularly in karstic areas containing numerous cavities, we launched an examination of the literature regarding cave ventilation. This review triggered the first publication of this Thesis (Chapter 1), because we realized that to determine the buoyancy of air masses inside and outside the cave, and therefore its ventilation, scientists were treating both air masses as if they had equal composition. However, both our measurements in the borehole and many others scientists working in other places had found great concentrations

of CO_2 in soil air, demonstrating a clear difference between the compositions of soil and atmospheric air. These realizations led us to develop formulas to correctly determine the virtual temperature and hence buoyancy of the air masses considering the weight of CO_2 in the composition of both air masses.

In Chapter 2 of this thesis, we applied the formulas previously developed for 14 caves and holes around the world. We demonstrate the significant errors that occur when predicting cave ventilation if not taking into account the effect of CO_2 air composition. To clarify the calculation tasks, we provided an on-line tool to calculate the virtual temperature from input data comprised of CO_2, air temperature and relative humidity.

Having clarified the determination of ventilation between caves and atmosphere, it was necessary to characterize and monitor the main factors involved in soil ventilation and consequent CO_2 emissions to the atmosphere. From these measurements arose the publications corresponding to chapters 3 and 4 of this thesis.

In Chapter 3, is shown that in *El Llano de los Juanes* significant decreases occur in the CO_2 molar fraction of both soil (25 cm) and borehole (7 m) when the wind is strong, as represented a high friction velocity. These decreases in the CO_2 molar fraction involve CO_2 emissions to the atmosphere which are detected by the Eddy Covariance tower. Also, was observed that on days with light winds (calm), CO_2 accumulated in the soil, whereas during windy days large quantities of CO_2 were emitted to the atmosphere.

Chapter 4 presents observations from the vertical CO_2 profile located in *Balsa Blanca*, with significant variations in the underground CO_2 molar fraction in just a few hours. These variations can result in an increase or decrease of 400% compared with previous values. It is observed that changes in the molar fraction are due to changes in atmospheric pressure. There are two patterns in the subterranean CO_2 fluctuations, one daily with two cycles per day due to atmospheric tides and another cycle repeating every 3-4 days (atmospheric synoptic scale) due to transitions between low and high pressure systems. Also we observed that synoptic-scale pressure changes can affect the CO_2 fluxes detected by an eddy covariance tower. On days with rising pressure, the downward CO_2 flux is higher than on days with falling pressure because on these days CO_2 respired by plants tends accumulates in the soil.

Resumen

Esta tesis surge para dar respuesta a los flujos de CO_2 "anómalos" detectados por las torres de *Eddy Covariance* situadas en dos sitios carbonatados y semiáridos del Sureste español. En los intercambios de CO_2 suelo-atmósfera, tanto en el Llano de los Juanes en la Sierra de Gádor como en Balsa Blanca situada en el Parque Natural de Cabo de Gata-Níjar (provincia de Almería), se detectaron importantes emisiones de CO_2 a la atmósfera. Estas emisiones sólo podían provenir del suelo y no de la vegetación ya que ocurrían principalmente durante el verano, cuando la vegetación está senescente. Además, se observó que dichas emisiones "anómalas" llegaban a dominar los procesos de intercambio de CO_2 entre la atmósfera y la superficie contribuyendo notablemente en el balance anual de carbono de estos ecosistemas. Por este motivo, esta tesis se ha centrado en la monitorización y caracterización del CO_2 del suelo, estudiando los principales factores que intervienen en los intercambios de CO_2 con la atmósfera.

Para la caracterización y monitorización del CO_2 en el suelo se han instalado en los dos sitios experimentales dos perfiles de CO_2 con sensores a tres profundidades (0.15, 0.5 y 1.5 m). Además, en el Llano de los Juanes también se instaló un sensor a 0.25 m y se realizó una perforación de 7 m de profundidad que posteriormente fue sellada en superficie para simular una cavidad kárstica.

Con los primeros datos de fracción molar de CO_2 obtenidos en la perforación, nos dimos cuenta que el suelo en profundidad podía almacenar enormes cantidades de CO_2, ya que en los 7 primeros metros se llegaron a registrar valores de 18000 ppm. Dado que nos interesaba conocer los factores implicados en la ventilación del CO_2 del suelo y sus cavidades, el doctorando inició un trabajo de búsqueda bibliográfica sobre los aspectos relacionados

con la ventilación en cuevas. Esta revisión desencadenó la primera publicación de esta tesis (Capítulo 1) al comprobar que para determinar la flotabilidad de las masas de aire del interior y exterior de la cueva, y por tanto su ventilación, los artículos ya publicados consideraban ambas masas de aire con igual composición. Esta suposición era incorrecta en la gran mayoría de los casos donde las elevadas concentraciones de CO_2 en suelo marcaban una clara diferenciación en la composición del aire del suelo y la atmósfera. Todo esto nos llevó a proponer una nueva forma de calcular correctamente la flotabilidad de las masas de aire teniendo en cuenta el CO_2 en la composición de ambas masas de aire.

En el Capítulo 2 de esta tesis, se aplicaron las ecuaciones desarrolladas en el capítulo anterior en 14 cuevas y perforaciones de todo el mundo, demostrando los importantes errores que se cometen a la hora de interpretar la ventilación de las cuevas cuando no es tenido en cuenta el efecto del CO_2 en la composición del aire. Para facilitar las labores de cálculo, se ofrece gratuitamente y de forma “online” la metodología necesaria para su cálculo de una manera muy simple en la que sólo es necesario aportar los datos de CO_2, temperatura del aire y humedad relativa. Una vez conocida la forma de determinar la ventilación entre las cavidades y la atmósfera, se procedió a caracterizar y monitorizar los principales factores implicados en la ventilación del suelo y las emisiones a la atmósfera. Fruto de este estudio se publicaron una serie de artículos científicos que dan origen a los Capítulos 3 y 4 de esta tesis.

El Capítulo 3 se centra en el Llano de los Juanes y concluye que el viento es el principal factor responsable de las emisiones de CO_2 en épocas de sequía. En este ecosistema se midieron importantes descensos en la fracción molar tanto del suelo (0.25 m) como de la perforación (7 m) con fuertes vientos y por lo tanto alta velocidad de fricción (>0.3 m s^{-2}). Estos descensos en la fracción molar del CO_2 implican emisiones de CO_2 hacia la atmósfera que se ven reflejados en la torre *Eddy Covariance*. De este modo, en días ventosos el CO_2 almacenado en el suelo durante los días de calma es emitido a la atmósfera.

El Capítulo 4, centrado en Balsa Blanca, demuestra que en este ecosistema los cambios en la fracción molar de CO_2 se deben a cambios en la presión atmosférica. En el perfil vertical de CO_2 situado en Balsa Blanca, se registran importantes variaciones en la fracción molar de CO_2 en tan sólo unas horas. Estas variaciones pueden suponer un incremento o descenso de un 400% respecto a sus valores anteriores. En este sentido, de diferencian dos patrones en las fluctuaciones del CO_2 subterráneo, uno a escala diaria con dos ciclos por día debidos a las mareas atmosféricas y otro a escala sinóptica (3-4 días) debido a la transición entre bajas (borrasca) y altas presiones (anticiclón). También se ha observado como a escala sinóptica los cambios de presión pueden afectar a los flujos de CO_2 detectados por la torre *Eddy Covariance*. En días con incrementos en la presión atmosférica se produce mayor fijación de CO_2 que en días con menor presión en los que el CO_2 respirado por las plantas tiende a acumularse en el suelo.

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1. Background: The global carbon Cycle

The global carbon cycle in the atmosphere can be described simply as the sum of CO_2 inputs less outputs. Today's society and the way it interacts with the environment is causing a constant increase in the atmosphere CO_2 content, mainly due to the burning of fossil fuels and changes in land use. This increase in atmospheric CO_2 leads to increase of mean earth temperature, causing numerous feedbacks with the different ecosystems which deserve a better understanding through research.

1.1. Societal concern

During the last five decades a great number of scientists have worked to characterize accurately the role of the different terrestrial subsystems (biosphere, lithosphere, hydrosphere and atmosphere) in the global carbon cycle. The importance of characterizing the global carbon cycle and the factors involved is highlighted by the progressive increase in the atmospheric CO_2 molar fraction [*Keeling*, 1960]. Thus, in 1972 the Stockholm Conference was organized, being the first conference convened by the United Nations (UN) considering the need for a common outlook and principles to inspire and guide the peoples of the world in the preservation and enhancement of the human environment.

With growing concern over the increase in greenhouse gases (GHGs) and diverse environmental problem, the UN held a summit in Rio de Janeiro in 1992, known as the Earth Summit. At this summit an international environmental treaty was approved known as the United Nations Framework Convention on Climate Change (UNFCCC), with the objective of stabilizing greenhouse gas (GHG) concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system. Also, this stabilization was targeted for a timeframe that would allow ecosystems to adapt naturally to climate change, ensuring that food production not be threatened and allowing economic development to proceed in a sustainable way.

Later, after the signing of Kyoto Protocol in 1997, the need to reduce emissions of GHGs in net terms was affirmed, taking into account not only the total production of contaminating gases, but also the uptake capacity of such contaminants in each country. For this reason some countries chose to reduce their net emissions by increasing carbon sequestration by forests. In 2001 at the Seventh UN Conference on Climate Change held in Marrakech the legal aspects of the Kyoto Protocol were established and treated fundamental issues such as the development of methods to estimate, measure and monitor changes in carbon emitted or stored by the different sources and sinks.

For these reasons, it is essential to develop methodologies for the accounting of anthropogenic emissions by sources and/or anthropogenic removals by sinks. In this context, technological advancement has improved the quality of micro-meteorological information and thus understanding of CO_2 exchanges between the atmosphere and land surface. These advancements are generating much information on spatial scales from small (leaf, plant and soil) to large (ecosystem, regional and global).

1.2. Definition of the Global Carbon Cycle

The global carbon cycle depends on feedbacks among a number of source and sink processes occurring among different systems (reservoirs or pools): ocean, atmosphere, lithosphere and biosphere (Fig. 1). Between these reservoirs, carbon moves at various natural rates of exchange (fluxes). These exchange processes operate at different time scales: from seconds (photosynthesis) to millennia (formation of fossil fuels) modifying the C composition of reservoirs [*Boucot and Gray, 2001*]. While CO_2 represents only 0.039% of the atmosphere (molar fraction) and the atmosphere is a small carbon reservoir, CO_2 plays two vital roles for life on earth. 1) It is involved in the modification the energy balance of our planet because it is one of the principal gases involved in the greenhouse effect [*IPCC 2007*], absorbing infrared radiation from earth surface and reemitting part of that energy back towards the surface to increasing the average surface temperature. 2) Plants grow through photosynthesis, taking up CO_2, which is later emitted to atmosphere through respiration by plants, animals and microorganisms.

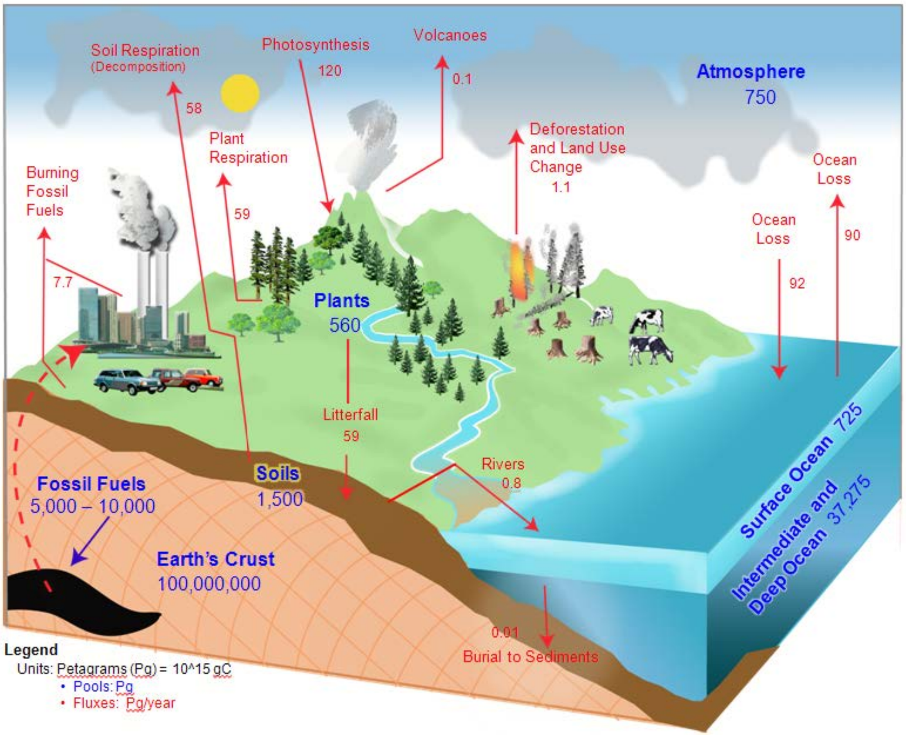

Figure 1. A simplified diagram of the global carbon cycle. Pools are shown in blue (Pg C) and fluxes in red (Pg C/year). (www.globe.gov/projects/carbon)

Nowadays the increasing CO_2 molar fraction of the atmosphere is causing an increase in the greenhouse effect and the consequent global warming. The growth rate of global average atmospheric CO_2 for 2000–2006 was 1.93 ppm y^{-1}, equivalent to an annual increase of 4.1 Pg C y^{-1} [*Canadell* *et al.*, 2007]. This occurs because there is an imbalance between sources (Fossil fuel and respiratory emissions) and sinks (photosynthesis).

At the ecosystem scale, the carbon balance can be reduced to interactions shown in Figure 2. Chapin et al. [2006] proposed the term net ecosystem carbon balance (NECB) to describe the net rate of C accumulation in ecosystems (positive sign) or loss (negative sign). The NECB characterizes the global ecosystem C balance from all sources and sinks physical, biological, and anthropogenic. Net fluxes of several forms of C contribute to NECB, as described in Figure 2 and the following equation:

$$NECB = -NEE + F_{CO} + F_{CH4} + F_{VOC} + F_{DIC} + F_{DOC} + F_{PC} \qquad \text{(Eq.1)}$$

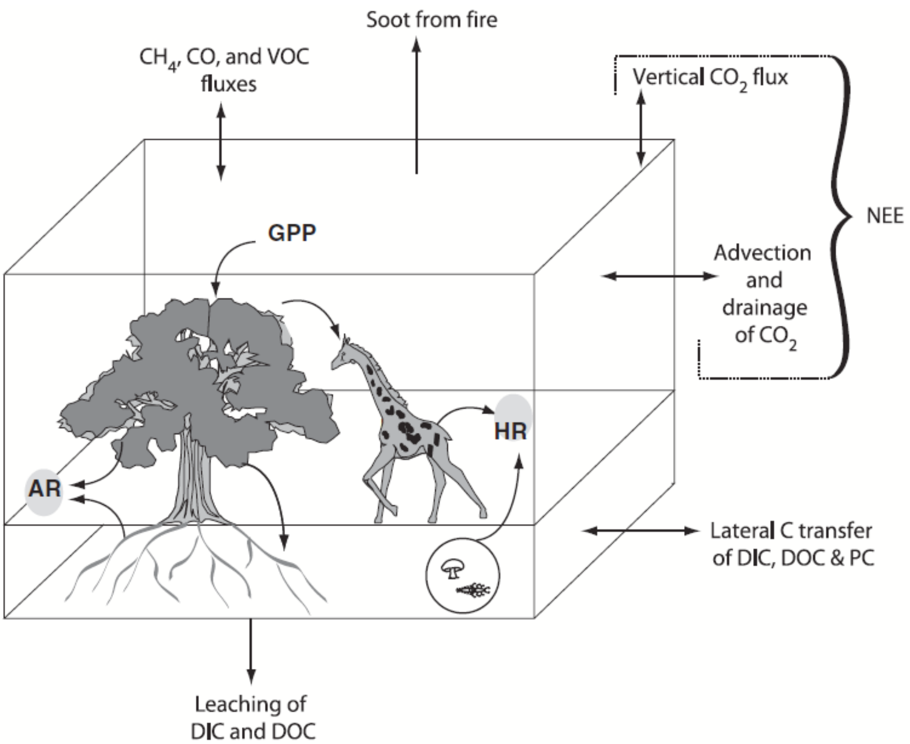

Figure 2. Relationship among the carbon (C) fluxes that determine net ecosystem carbon balance (NECB) (the net of all C imports to and exports from the ecosystem) and the fluxes (in bold) that determine net ecosystem production (NEP). The box represents the ecosystem. Fluxes contributing to NECB are emissions to or uptake from the atmosphere of carbon dioxide (CO_2) (net ecosystem exchange, or NEE), methane (CH_4), carbon monoxide (CO), and volatile organic C (VOC); lateral or leaching fluxes of dissolved organic and inorganic C (DOC and DIC, respectively); and lateral or vertical movement of particulate C (PC) (nongaseous,

nondissolved) by processes such as animal movement, soot emission during fires, water and wind deposition and erosion, and anthropogenic transport or harvest. Fluxes contributing to NEP are gross primary production (GPP), autotrophic respiration (AR), and heterotrophic respiration (HR), [*Chapin et al.*, 2006].

1.3. CO_2 exchange measurements at ecosystem level

The study of CO_2 exchanges between the atmosphere and Earth's surface began in the 1980s with a few pilot studies, which were extended to regional networks in the 1990s. Today these studies have been extended to more than 500 locations where carbon exchange is measured in different ecosystems. To measure these exchange the eddy covariance technique (EC) is used. This technique is being applied in the main ecosystems: forests [*Carrara et al.*, 2004; *Valentini et al.*, 2000], crops [*Anthoni et al.*, 2004; *Aubinet et al.*, 2009], deserts [*Hasting et al.*, 2005; *Wohlfahrt et al.*, 2008] and shrublands [*Reverter et al.*, 2010; *Scott et al.*, 2012; *Serrano-Ortiz et al.*, 2009]. Furthermore this technique is used to evaluate the effects of disturbances like fire [*Amiro et al.*, 2003; *Serrano-Ortiz et al.*, 2011] or harvest [*Kowalski et al.*, 2003; *Kowalski et al.*, 2004].

The eddy covariance technique is used by the international network of flux towers "FLUXNET" (at present over 500 tower sites) to measure the exchanges of CO_2, water vapor, and energy between ecosystems and the atmosphere. FLUXNET is an integrated network of regional networks including Ameriflux from the Americas, AsiaFlux from Asia-Japan, OzNet from Oceania and Carboeurope from Europe, and each of these regional networks include networks of different countries. Concretely in Spain there is a systematic observation network of carbon and energy flows in terrestrial ecosystems called CARBORED-ES. The programs proposed by these networks interpret CO_2 fluxes as resulting directly from concurrent biological (photosynthetic or respiratory) activity [*Baldocchi*, 2003; *Falge et al.*, 2002; *Houghton*, 2002; *Reichstein et al.*, 2005].

1.4. Other processes involved in C sequestration and loss apart from concurrent biological activity

The non-biological processes that can contribute in the net ecosystem carbon balance (NEBC) are the following [*Serrano-Ortiz et al., 2012*]:

- Weathering processes, mainly by carbonates rocks. Weathering releases CO_2 during precipitation; however during dissolution atmospheric CO_2 is consumed [*Plummer et al.*, 1979].
- Biomineralization processes. Fungi, lichens and cyanobacteria can modify calcite dissolution or precipitation, taking up or emitting CO_2 [*Verrecchia et al*., 1990].
- Erosion processes. Transport of particles by air or water can decrease or increase the soil organic carbon in a soil [*Boix-Fayos et al.*, 2009; *Jacinthe and Lal*, 2001].
- Photodegradation processes. These occur mainly in dry ecosystems when the ultraviolet light provokes a direct breakdown of organic matter to CO_2 [*Brandt et al*., 2009].
- Ventilation processes. The wind penetrates into subsoil (cracks, pores and cavities) causing emission of previously stored CO_2. A large part of this thesis focuses on this topic, which is a novel line of research largely neglected by the FUXNET community.

The programs proposed by this network interpret CO_2 fluxes as resulting from concurrent biological (photosynthetic or respiratory) activity [*Baldocchi,* 2003*; Falge et al.,* 2002*; Houghton,* 2002*; Reichstein et al.,* 2005], neglecting CO_2 exchanges due to, as they shall be termed here, "alternative" processes. The emergence of studies focusing on alternative CO_2 exchanges dates from less than a decade. Emmerich [2003] attributed the CO_2

emitted after rain events following prolonged drought periods to carbonate dissolution in the soil. Mielnick et al. [2005] found large positive CO_2 effluxes in the summer that could be attributing to increased soil abiotic sources of CO_2. However, it was not until 2008 that the first clear evidence of alternative influences on net CO_2 exchange was detected by eddy covariance [*Kowalski et al.*, 2008].

Kowalski et al. [2008] found periods in which CO_2 exchanges could not be interpreted purely in terms of concurrent biological processes, but these should be explained by alternative processes. These alternative CO_2 contributions were detected in two carbonated experimental sites, one in the north of Spain (Altamira Cave) and the other in the South (Sierra de Gádor). At this last experimental site, Serrano-Ortiz et al. [2009] confirmed that during the whole study period from 2004 to 2007, episodes of alternative CO_2 fluxes were detected during dry season. These papers highlighted the important need to characterize the processes of subterranean ventilation and dissolution/precipitation of carbonates for the correct estimate of CO_2 fluxes exchanged by carbonated ecosystems.

1.5. Subterranean CO_2

Subterranean ventilation and CO_2 dissolution/precipitation processes have their greatest magnitudes in limestone and karst soils. Soils are a large pool of terrestrial carbon (*C*), estimated to contain 1576 Pg C [*Eswaran et al.*, 1993] which is nearly three times higher than the amount of *C* in aboveground biomass and double that of the atmosphere [*Schlesinger*, 1997]. A 10% decrease of total soil organic carbon would be equivalent to the emitted anthropogenic CO_2 over 30 years [*Kirschbaum*, 2000]. At present the outcropping of carbonate soils are extended on ca. 12-18% of the water-free Earth [*Ford and Williams*, 1989]. These present an enormous capacity to store large amounts of CO_2 in subsurface cracks, pores and cavities, reaching values that exceed 50000 ppm of CO_2 (5% of air volume) both in caves

[*Denis et al.*, 2005; *Howarth and Stone*, 1990] and in soil [*Crowther*, 1983; *Ek and Gewelt*, 1985]. Later, through the venting of these subterranean spaces the stored gaseous CO_2 can be exchanged with the atmosphere.

Knowing the distribution of large cavities and fractures that can emit CO_2 to the atmosphere is vital to the interpretation of ecosystem CO_2 fluxes [*Were et al.*, 2010]. Concretely, this study showed that two proximate EC towers with different footprints (or areas of surface influence) agreed for CO_2 measurements in periods when respiration and photosynthesis processes were dominant (biological periods), however during periods dominated by alternative processes ("abiotic periods") agreement was not good. They concluded that the disagreement between measurements was due to sub-surface heterogeneity within the footprint.

Therefore it is necessary to study the behavior of subterranean CO_2, mainly over carbonate soils, to understand when such alternative CO_2 exchanges are produced and so correctly interpret CO_2 fluxes at the ecosystem level for posterior modeling, helping to improve our overall understanding of the global carbon cycle.

1.6. Objectives and outline of the thesis

The main objective of this thesis is to improve the knowledge of subterranean CO_2 dynamics, distinguishing which are the drivers involved in its transport and exchange with the atmosphere.

In the different chapters of this thesis, we will try to achieve the main objective by meeting the specific objectives identified for each chapter:

- Study with precision the buoyancy of an underground air mass depending of the CO_2 content (Chapter 1).

- Examine the errors that can be committed in different caves around the world when neglecting CO_2 effects on air buoyancy and therefore its potential for ventilation (Chapter 2).

- Know the role of subterranean CO_2 ventilation in the net ecosystem carbon balance of a subalpine shrubland (Chapter 3).

- Identify the role of synoptic and shorter-period barometric changes (atmospheric tides) in subterranean CO_2 variations within a soil vertical profile of a low-altitude shrubland (Chapter 4).

Fundamentals

2.1. Measuring CO_2 in air

The results of this thesis are mainly generated by CO_2 measurements in air using different instruments and scenarios. In all cases, CO_2 was quantified through direct measurement of laser absorption by gaseous CO_2 in the air. Given a source with radiant power and a detector some distance away through the gas, in the absence of reflection, absorptance (α) by gas *i* is defined by the Beer–Bouguer- Lambert law as:

$$\alpha_i = 1 - \tau_i = 1 - \frac{I_i}{I_0} \qquad \text{(Eq. 2)}$$

where τ_i is transmittance through gas *i*, I_i is the intensity of the incident radiation in the absorption band with some concentration of gas *i* present, and I_0 is the intensity of the radiation in the absorption band with zero concentration of *i* present. Infrared gas analyzers (IRGAs) measure gases like CO_2 or H_2O [McDermitt et al., 1994] by determining the absorption by:

$$\alpha_i = 1 - \frac{A_i}{A_0} \qquad \text{(Eq. 3)}$$

where A_i is the power received from the source in an absorbing wavelength for gas *i*, and A_{io} is the power received from the source in a reference wavelength that does not absorb gas *i*. The number density (*n* in mmol/m^3) of gas *i* can be determined by:

$$n_i = P_{ei} f_i\left(\frac{\alpha_i S_i}{P_{ei}}\right) \qquad \text{(Eq. 4)}$$

Pressure is denoted as P_{ei} because it is the equivalent pressure for the gas i. Equivalent pressure is potentially different from total pressure P if there are gases present other than i that affect how gas i absorbs radiation. The calibration functions f_i and S_i are generated by measuring a range of known densities. Since gas standards are not available in "known densities", the n_i values are computed from a known molar fraction m_i (moles of gas per mole of air) using the ideal gas law:

$$n_i = m_i \frac{P}{RT} \qquad \text{(Eq. 5)}$$

For gas i the mass density (g/m^3) can be obtained by multiplying the number density by its molecular weight M_i:

$$n_{Mi} = M_i n_i \qquad \text{(Eq. 6)}$$

Finally the molar fraction for the gas i (χ_i, μmol/mol) can be obtained by:

$$\chi_i = \frac{n_{Mi} RT}{P} \qquad \text{(Eq. 7)}$$

where R is the universal gas constant and T the temperature.

2.2. Eddy covariance flux measurements

The eddy covariance technique is used for measure exchanges of heat, mass, and momentum between a flat, horizontally homogeneous surface and the overlying atmosphere. This technique is used by scientific community for the measurement of the turbulent exchanges of CO_2 and H_2O between an ecosystem and the atmosphere [*Baldocchi et al., 2001*]. Ecosystem exchanges, defined by much of something moves per unit time through a unit area, are truly flux densities by nonetheless commonly termed “fluxes”. The main equations involved in determining the CO_2 fluxes are described below.

In atmospheric turbulence, any variable ξ is typically broken into two parts in a process known as Reynolds decomposition:

$$\xi = \overline{\xi} + \xi' \qquad \text{(Eq. 8)}$$

representing the sum of a mean $\overline{\xi}$ and a fluctuation part ξ'. With the application of equation 8 and Reynolds’ rules, the turbulent flux can be written:

$$F = \overline{\rho_d}\,\overline{w's_c'} \qquad \text{(Eq. 9)}$$

where ρ_d is the dry air density, w the vertical wind and s_c the CO_2 mixing ratio.

Since the open path analyzers (Li-cor 7500) measure CO_2 density rather than mixing ratio, fluctuations in temperature and water vapor cause fluctuations in CO_2 and other trace gases that are not associated with the flux of the trace gas of interest. Therefore, systematic corrections are required to account for “density effects” (hereafter, WPL terms) [*Webb et al.*, 1980]. Thus, the turbulent CO_2 flux can be accurately determined by eddy covariance from gas density fluctuations according to

$$F_C = \overline{w'\rho_c'} + \underbrace{\mu\left(\frac{\overline{\rho_c}}{\overline{\rho_d}}\right)\overline{w'\rho_d'}}_{\substack{\text{Water flux term}\\ \text{(water dilution)}}} + \underbrace{(1+\mu\sigma)\left(\frac{\overline{\rho_c}}{\overline{T}}\right)\overline{w'T'}}_{\substack{\text{Heat flux term}\\ \text{(termal expansión)}}} \qquad \text{(Eq. 10)}$$

where F_C is the final corrected CO_2 flux, $w'\rho_c'$ is the covariance between vertical wind and CO_2 density, μ is the ratio of molar masses of dry air and water vapor (1.6077, m_d/m_v), ρ_c is CO_2 density, ρ_d is dry air density, σ is the ratio of density of water vapor and dry air (ρ_v / ρ_d), $\overline{T}$ is mean air temperature in K and $\overline{w'T'}$ is the covariance between vertical wind and temperature.

Another possible, related correction is due to sensor self-heating [*Burba et al.*, 2008]. Since the Li-Cor 7500 (open -path) IRGA actively heats to maintain an operating temperature, this correction would be higher in cold ecosystems [*Reverter et al.*, 2010] than in warm ecosystem [*Reverter et al.*, 2011]. At present, there is no consensus regarding how or whether to apply this correction, which would depend on wind speed, the inclination of the sensor and incident solar radiation. In any event, the self-heating correction is significant only when attempting long-term integrations, whereas its effect is minimal when the focus is on process studies, as is the case in this thesis.

More details of eddy covariance flux measurement can be found in specific books [*Aubinet et al.*, 2012] or relevant theses [*Reverter*, 2011; *Serrano-Ortiz*, 2008].

3. Experimental Field Sites

The studies presented in this thesis were conducted mainly in two ecosystems situated in southeast Spain, one at high elevation (El Llano de los Juanes, 1600 m) and the other close to sea level (Balsa Blanca, 200 m).

3.1 El Llano de los Juanes

Located in the *Sierra de Gádor, El llano de los Juanes* is a shrubland plateau at 1600 m above sea level (**N**36º55'41.7'', W2º45'1.7''). The climate is Sub-humid with mean annual precipitation of ca. 465 mm, falling mostly during autumn and winter, and with a very dry summer. Snow falls during winter, frequently persisting some weeks and covering the ground completely. The mean annual temperature is around 12ºC with maximum in summer (31ºC) and minimum in winter (-6ºC). The dominant ground cover is bare soil, gravel and rock (49.1%). The vegetation is diverse but sparse, with predominance of *Festuca scariosa* (18.8%), *Hormathophilla spinosa* (6.8%) and *Genista pumila* (5.5%). The parent soil material consists of Triassic carbonate rocks [*Vallejos et al.*, 1997]. The soil varies from 0 to 150 cm depth. The profile includes a petrocalcic horizon and fractured rocks. More detailed site information can be found in the work of Serrano-Ortiz et al. [2009].

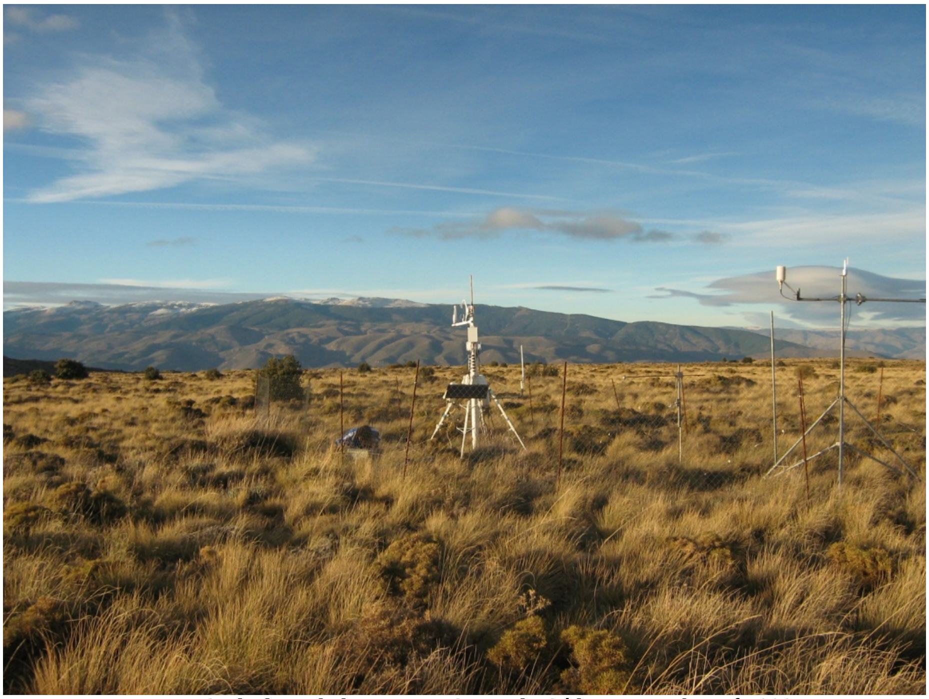

Figure 3.El Llano de los Juanes, Sierra de Gádor. December of 2009

An eddy covariance system was installed in May of 2004, mounted on a top of a 2.5 m micrometeorology tower. Densities of CO_2 and water vapour as well as barometric pressure were measured by an open-path infrared gas analyser (IRGA Li-Cor 7500, Lincoln, NE, USA), calibrated monthly. Wind speed and sonic temperature were measured by a three-axis sonic anemometer (CSAT-3, Campbell Scientific, Logan, UT, USA; hereafter CSI). The friction velocity (u_*) is defined as the turbulent velocity scale resulting from square root of the (density-normalized) momentum flux magnitude [*Stull*, 1988]. Temperature and relative humidity were measured by a thermohygrometer (HMP45C, CSI). At 1.5 m above ground level there were two quantum sensors (LI-190, Li-Cor) measuring incident and reflected photon fluxes, a net radiometer (NR-Lite, Kipp&Zonnen, Netherlands) and a tipping-bucket rain gauge (ARG100, CSI). Below ground there were two soil heat flux plates at 8 cm (HFP01, CSI), an averaging soil thermocouple probe (TCAV, CSI) and 3 water content reflectometers (CS616, CSI). A data-logger (CR3000, CSI) managed the measurements data at 10 Hz and recording at the same frequency only of the wind and IRGA data. The averages of the rest of the variables and turbulent fluxes were computed every half-hour.

Forty meters northwest of the tower several instrumentation were installed to measure different parameters associated with CO_2 production in subsoil. In June of 2009 two CO_2 molar fraction sensors (GMP-343, Vaisala, Inc., Finland; hereafter Vaisala) were installed in the soil and in a borehole penetrating a bedrock outcropping. The CO_2 soil sensor was installed horizontally at 25 cm depth, together with a soil temperature probe (107 temperature probe, CSI) and a water content reflectometer (CS616, CSI).

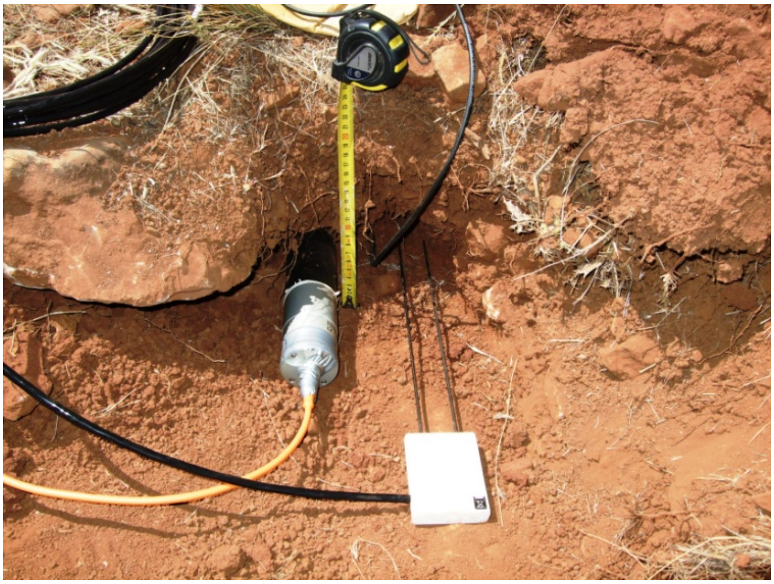

Figure 4. Installing CO_2 sensor, soil water content and temperature probe.

The borehole has 7-m depth and a diameter of 0.1 m; nearly solid rock cores were extracted with only a few small fractures indicated by clay infiltration. The upper 1 m is hermetically isolated from the atmosphere with a metal tube cemented to the walls of the borehole and a protective cap screwed onto the tube. In addition to CO_2, temperature and relative humidity (HMP45C, CSI), and radon content (Barasol MC BT45N, Bessines Sur Gartempe, France) were measured inside the borehole. Also, a barometer was installed at the soil level (PTB101B, Vaisala). Measurements were made every 30s and stored as 5min averages by a data-logger (CR23X, CSI).

Figure 5. Left, doing the borehole in Llano de los Juanes. Right, rock cores.

In February of 2010 the CO_2 molar fraction sensor buried in soil (25cm) was removed, and a new vertical profile was installed. A backhoe created a trench to facilitate differentiation in the profile between the different horizons. Accordingly, soil CO_2 sensors were inserted at 0.15, 0.5 and 1.5 meters. Together with each CO_2 sensor a soil temperature probe (107 temperature probe, CSI) and a water content reflectometer (CS616, CSI) were installed. Measurements were made every 30s and stored as 5 minutes averages by a data-logger.

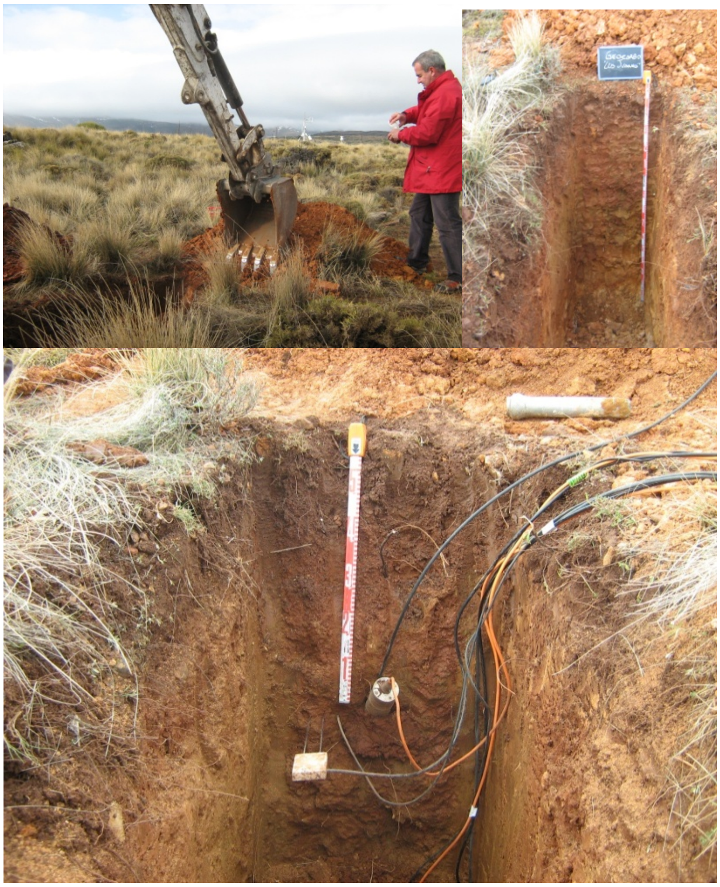

Figure 6. Pictures of vertical CO_2 profile installation.

3.2 Balsa Blanca

Balsa Blanca is located in the *Cabo de Gata-Nijar* Natural Park of southeast Spain (N36º56’26.0’’, W2º0.1’58.8’’). This is an alpha grass steppe at 200 m a.s.l situated on alluvial fans (glacis) of gentle slope (2%). The soil is classified as Calcaric Lithic Leptosol saturated in carbonates with 10cm depth on average, presenting petrocalcic horizons. The mean annual temperature is around 18ºC with maximum in summer (37ºC) and minimum in winter (1ºC). The climate is dry subtropical semiarid, with a mean annual precipitation of ca. 200 mm and an annual potential evapotranspiration around 1390 mm with an aridity index below 0.2, classifying this area as an arid zone [*Oyonarte et* *al.*, 2012]. The rainfall occurs mainly in sporadic events in autumn and spring, presenting a very dry summer. The vegetation is dominated by *Stipa tenacissima (Macrochloa tenacissima)* with 57% of vegetation cover; other species are *Chamaerops humilis, Rhamnus lycoides, and Pistacia lentiscus,* although the most abundant ground cover is bare soil, gravel and rock with a cover of 49.1%. More detailed site information can be found in the work of Rey et al. [2012].

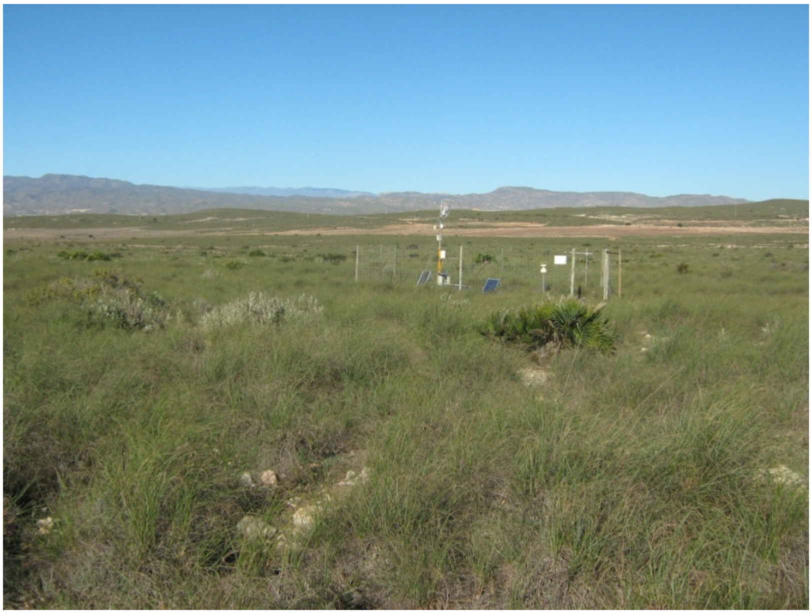

Figure 7. Balsa Blanca in December of 2009.

In May 2006, an Eddy Covariance system was mounted to the top of a tripod tower at 3.5 m above the ground. It was composed of two sensors used to measure in fast-response (10 Hz), an open-path infrared gas analyser (IRGA Li-Cor 7500, Lincoln, NE, USA) to measure densities of CO_2 and H_2O and a sonic anemometer (CSAT-3, CSI) to measure the wind speeds in three directions and sonic temperature. These measurements were stored at 10 Hz; also computed and stored were turbulent fluxes of CO_2, H_2O corrected for air density fluctuations [*Webb et al.*, 1980] every 30 minutes. On the same tower air temperature and relative humidity also were measured by a thermohygometer (HMP45C, CSI) at 3 m above ground level. A mast was installed at 8 m from the eddy tower to measure at 1.5 m above ground level incident and reflected photosynthetically active radiation (PAR, LI-190, Li-Cor), a net radiometer (NR-Lite, Kipp&Zonnen, Netherlands) and an tipping-bucket rain gauge (ARG100, CSI). Below ground, the soil heat flux was measured by four soil heat flux plates at 8 cm (HFP01SC, CSI), soil temperature was measured by two averaging soil thermocouple probes (TCAV, CSI) and soil moisture by two water content reflectometers (CS616, CSI). All data were measured at 10 Hz, averaged over 30 minutes, and recorded by a data-logger (CR3000, CSI).

Figure 8. Instalation of vertical Co2 profile in January of 2010

In February of 2010 a vertical soil CO_2 profile was installed at 15 meters to the east of the eddy tower. Three CO_2 molar fraction sensors (GMP-343, Vaisala) were buried at 0.15, 0.5 and 1.5 meters. Together with each CO_2 sensor a soil temperature probe (107 temperature probe, CSI) and a water content reflectometer (CS616, CSI) were installed. The profile was made by a backhoe, differentiating between the different horizons for subsequent burial of the sensors, each in its own soil horizon. Measurements were made every 30s and stored as 5 minutes averages by a data-logger.

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4. Results

4.1 Chapter 1

A New Definition of the Virtual Temperature, Valid for the Atmosphere and the CO_2-Rich Air of the Vadose Zone

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Abstract

In speleological environments, partial pressures of carbon dioxide (CO_2) are often large enough to affect overall air density. Excluding this gas when defining the gas constant for air, a new definition is proposed for the virtual temperature T_v that remains valid for the atmosphere in general but furthermore serves to examine the buoyancy of CO_2-rich air in caves and other subterranean airspaces.

4.1.1. Introduction

In recent years, boundary layer meteorology has broadened to explore surface–atmosphere interactions involving exchanges with caves and other airspaces of the vadose zone. The accumulation and subsequent ventilation of large [*Kowalski et al.*, 2008; *Milanolo and Gabrovsek*, 2009] quantities of carbon dioxide (CO_2) in such environments implies a potentially significant yet previously overlooked role for them in the global carbon cycle [*Serrano-Ortiz et al.*, 2009], whose characterization remains a Kyoto-motivated challenge. Gas exchange in the vadose zone can come about via convection [*Weisbrod et al.*, 2009], which is sometimes invoked to suggest a dependence of cave ventilation on the temperature difference with the external atmosphere [*Fernandez-Cortes et al.*, 2009; *Kowalczk and Froelich*, 2010; *Linan et al.*, 2008].

However, differences in air density at a given pressure level (altitude) are determined not only by temperature but also by air composition. In the troposphere, the only gas whose surface exchange and fluctuating partial pressure appreciably affect air density is water vapor, which varies from near 0% (volumetric) in cold environments to 4% in the tropics, and locally in the presence of evaporation. Thus, meteorologists employ a traditional definition of the virtual temperature (T_v) to account for air density variations associated with the molecular weight of water vapor [*Guldberg and Hohn* 1876; *Wallace and Hobbs* 2006]. By contrast, in speleological environments volumetric fractions of CO_2 have been often observed to exceed a few percent [*Ek and Gewelt*, 1985], a fact which highlights the need for an expanded definition of T_v for the purpose of studying air buoyancy in such spaces.

We propose a redefinition of T_v to accommodate such CO_2-rich air without compromising its validity for use in the atmosphere in general, including comparison with the traditional definition of T_v.

4.1.2. Analyses and approximations

In the following development, subscripts are used to identify individual gases including water vapor (v) and CO_2 (c), as well as gas mixtures defined by the mixture of nitrogen, oxygen, and argon (noa), ‘‘dry air’’ (d), and the overall mixture of moist air including CO_2 (mc).

The fundamental change proposed here is to substitute the mixture of nitrogen, oxygen, and argon for the traditional dry air, both in defining the nonvariable gas constant and also in the denominators defining the mixing ratios for water vapor (r_v) and carbon dioxide (r_c). Such a substitution modifies tropospheric values of r_v and r_c by less than 0.06% relative to the traditional definitions, according to the current mass fraction of CO_2 in such air.

The gas constant for the mixture mc shows variable behavior according to the mass M contributed by each constituent, weighting that constituent’s gas constant:

$$R_{mc} = \frac{M_{noa}R_{noa} + M_v R_v + M_c R_c}{M_{noa} + M_v + M_c} \qquad \text{(eq. 1)}$$

This is the constant that must be used when expressing the gas law $p = \rho R_{mc} T$ for the moist, CO_2-laden air of a subterranean airspace. Dividing both numerator and denominator of Eq. (1) by M_{noa} leaves

$$R_{mc} = \frac{R_{noa} + r_v R_v + r_c R_c}{1 + r_v + r_c} \qquad \text{(eq. 2)}$$

Generally this can be expressed

$$R_{mc} = R_{noa}\left[\frac{1+\sum_{i=1}^{N}(r_i/\varepsilon_i)}{1+\sum_{i=1}^{N} r_i}\right] \qquad \text{(eq. 3)}$$

which can be expanded to consider other gases for other applications. Equation (2) can be manipulated by multiplying both numerator and denominator by the factor (1 – r_v - r_c) to yield an expression that is complex but suitable for approximation:

$$R_{mc} = \frac{R_{noa} - r_v R_{noa} - r_c R_{noa} + r_v R_v - r_v^2 R_v - r_v r_c R_v + r_c R_c - r_v r_c R_c - r_c^2 R_c}{1 + r_v^2 - 2 r_v r_c - r_c^2} \qquad \text{(eq. 4)}$$

The denominator of Eq. (4) can be approximated as unity when recognizing that every second-order term is several orders of magnitude smaller. Similarly, second-order terms may be safely neglected in the numerator, simplifying to the following approximation:

$$R_{mc} = R_{noa} - r_v R_{noa} - r_c R_{noa} + r_v R_v + r_c R_c \qquad \text{(eq. 5)}$$

Substituting the gas constants for the noa mixture (287.0 J K^{-1} kg^{-1}; practically identical to that of dry air), water vapor (461.5 J K^{-1} kg^{-1}), and CO_2 (188.9 J K^{-1} kg^{-1}) into Eq. (5) allows an approximate definition of the (variable) gas constant for the moist, CO_2-laden mixture as

$$R_{mc} = R_{noa}\left(1 + 0.6079 r_v - 0.3419 r_c\right) \qquad \text{(eq. 6)}$$

Finally, in the context of the gas law, shifting the variability caused by constituent fluctuations from the gas constant to the virtual temperature results in the following new definition:

$$T_v = T\left(1 + 0.6079 r_v - 0.3419 r_c\right) \qquad \text{(eq. 7)}$$

This is the temperature that a mixture of nitrogen, oxygen, and argon would need in order to equal the density of the mixture of moist air including CO_2; it allows us to compare the densities of any (cave or atmospheric) air at equal pressures. Furthermore, this version of T_v can be used to compute the density of cave air from pressure using the gas law $p = \rho R_{noa} T_v$ (with R_{noa} = 287.0 J K^{-1} kg^{-1}) and compared with the traditional T_v for atmospheric air.

4.1.3. Implications and validity

The ramifications of the proposed change in definition depend directly on the CO_2 mixing ratio. In the troposphere, this is currently around 0.587 g kg^{-1}, equivalent to 387 ppm, or 0.0387% volumetric (fractional CO_2 content is expressed hereinafter in volumetric terms to correspond to the data typically reported in both speleological and atmospheric literature). For such low atmospheric CO_2 fractions the difference between the traditional definition of T_v and that defined in Eq. (7) is generally less than 0.1ºC. However, high levels of CO_2 in cave atmospheres can lead to situations where using the inappropriate definition of T_v (or simply the temperature) can lead to erroneous conclusions regarding buoyancy and the onset of convective processes.

A preliminary climatology of vadose-zone CO_2 volumetric fractions [*Ek and Gewelt*, 1985] indicated that while caves in subpolar and cold-temperate boreal zones rarely exceed double the atmospheric concentration (well below 0.1%), much larger values can be found in cool–temperate zones inside caves (approaching 1%), and particularly in fissures, sometimes exceeding 6% [*Denis et al.*, 2005]. More modest values have been reported in continental and subcontinental caves, but indications from warmer climates suggest that CO_2 volumetric fractions in excess of 5% can be reached, particularly in poorly ventilated fissures [*Benavente et al.*, 2010]. For such extreme cases the virtual temperature can differ from the air temperature by many degrees, and the former must be used to draw accurate conclusions about comparative density.

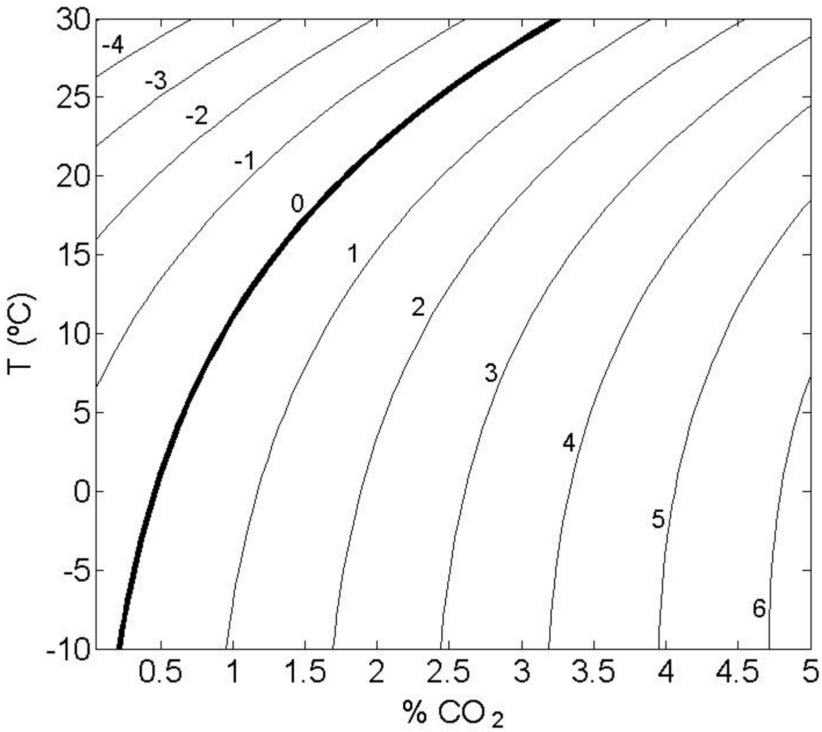

Figure 1. The virtual temperature depression (T-T_v) as a function of both the volumetric CO_2 concentration (1% is equivalent to 10000 ppm) and the temperature (T) for a subterranean environment with 100% relative humidity.

Figure 1 shows T_v, determined exactly from the gas law and Eq. (2), for a typical range of conditions in the terrestrial vadose zone, always assuming saturated humidity as is typical for cave atmospheres. The errors committed when approximating T_v using Eq. (7) have been evaluated explicitly for the range of gas concentrations typically found in terrestrial caves and found to be less than 0.1% (~0.3 K) over the full scale of Figure 1. At larger CO_2 fractions, however, the inadequacy of Eq. (5) increases rapidly, leading to errors exceeding 1 K not far above 6% CO_2, such that Eq. (2) must be used for the estimation of air density in fissures very rich in CO_2. To cite one example, for the Shaft of the Dead Man in the French Lascaux cave in late January 2001 with 6% CO_2 [*Denis et al.*, 2005], T_v is 6.9ºC lower than the cave air temperature (14ºC), explaining the stagnancy of this airspace exceeding the CO_2 limits for human safety [*Hoyos et al.*, 1998].

We propose defining T_v as in Eq. (7) for caves and other situations with volumetric CO_2 fractions ranging from a few tenths of a percent, up to 5%.

Acknowledgements

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Appendix

List of Symbols

Variables (units)

M_i	Mass of constituent *i* (kg)
p	Pressure (Pa)
ρ	Density (kg m^{-3})
R_i	Particular gas constant for constituent *I* (J K^{-1} kg^{-3})
r_i	Mixing ratio for constituent *i* (dimensionless)
T	Temperature (K)
T_v	Virtual temperature (K)
ε_i	Ratio of the molecular mass of constituent *i* to that of the gas mixture

Subscripts/gases

c	Carbon dioxide (CO_2)
d	Dry air
mc	Mixture of moist air including CO_2
noa	Mixture of nitrogen (N_2), oxygen (O_2), and argon (Ar)
v	Water vapor (H_2O)

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4.2 Chapter 2

Cave ventilation is influenced by variations in the CO_2-dependent virtual temperature

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Abstract

Dynamics and drivers of ventilation in caves are of growing interest for different fields of science. Accumulated CO_2 in caves can be exchanged with the atmosphere, modifying the internal CO_2 content, affecting stalagmite growth rates, deteriorating rupestrian paintings, or creating new minerals. Current estimates of cave ventilation neglect the role of high CO_2 concentrations in determining air density – approximated via the virtual temperature (T_v) –, affecting buoyancy and therefore the release or storage of $CO_{2.}$ Here we try to improve knowledge and understanding of cave ventilation through the use of T_v in CO_2-rich air to explain buoyancy for different values of temperature (T) and CO_2 content. Also, we show differences between T and T_v for 14 different experimental sites in the vadose zone, demonstrating the importance of using the correct definition of T_v to determine air buoyancy in caves. The calculation of T_v (including CO_2 effects) is currently available via internet using an excel template, requiring the input of CO_2 (%), air temperature (ºC) and relative humidity (%).

4.2.1. Introduction

There is currently growing interest in characterizing storage and ventilation of CO_2 in caves, both from external (atmospheric) and internal (speleological) perspectives. Measurements of rising atmospheric CO_2 by Keeling [1960] since the mid-20th century reveal that anthropogenic activities are causing CO_2 accumulation in the atmosphere and forcing global warming. Soils are a large pool of terrestrial carbon (C), estimated to contain 2344 Pg C in solid form in the top 3 m [*Jobbagy and Jackson*, 2000] – three times the aboveground biomass C reservoir and double that of the atmosphere [*Schlesinger*, 1997] – and also have an enormous capacity to store gaseous CO_2 in subsurface cracks, pores and cavities. The vadose zone is enriched in CO_2 and some caves often exceed 5% [volumetric CO_2 fraction of 50,000 ppm; [*Batiot-Guilhe et al.*, 2007; *Benavente et al.*, 2010; *Denis et al.*, 2005; *Ek and Gewelt*, 1985; *Howarth and Stone*, 1990] representing important air compositional differences with respect to the external atmosphere, currently near 395 ppm. Accumulated CO_2 in caves can be exchanged with the atmosphere [*Sanchez-Canete et al.*, 2011; *Serrano-Ortiz et al.*, 2010; *Weisbrod et al.*, 2009], modifying the internal CO_2 content and affecting stalagmite growth rates [*Baldini et al.*, 2008; *Banner et al.*, 2007], deteriorating rupestrian paintings [*Fernández et al.*, 1986] and creating new minerals [*Badino et al.*, 2011]. However due to the complexity and peculiarity of caves, as well as the variety of meteorological conditions that determine the degree and timing of ventilation [*Fairchild and Baker*, 2012], such exchanges are not well understood and their contributions to regional atmospheric CO_2 budgets remain unknown.

Estimation of cave ventilation can be realized by a number of means, the most common of which has traditionally neglected the role of high CO_2 concentrations and requires refinement. The drivers implicated in the cave ventilation can be classified as either dynamic or static [*Cigna*, 1968].

Dynamic drivers are defined by moving fluids such as water or wind [*Nachshon et al.*, 2012], while static drivers include variations of pressure, temperature or air composition (water vapor, CO_2, CH_4, etc.). Ventilation rates can be measured directly using anemometers, estimated indirectly through variations in Radon content [*Faimon et al.*, 2006; *Hakl et al.*, 1997], or other tracer gases [*de Freitas et al.*, 1982] or variations in air density. Most commonly, air density variations are approximated to evaluate buoyancy according to temperature differences between the internal (T_{int}) and exterior atmosphere (T_{ext}), neglecting air composition [*Baldini et al.*, 2008; *Faimon et al.*, 2012; *Fernandez-Cortes et al.*, 2006; *Linan et al.*, 2008; *Milanolo and Gabrovsek*, 2009]. Faimon et al. [2012] modelled the airflows into a cave, and found that the temperature explained more than 99% of variations in air density; therefore, temperature could be used as an alternative airflow predictor. However, de Freitas et al. [1982] concluded that reversal of airflow occurs when the densities in the cave and the exterior are equal, rather than when thermal conditions of the cave and external air are the same. For this reason, they suggest that the gradient in virtual temperature (T_v) between the cave and outside air would be the appropriate indicator. In this sense, Kowalczk & Froelich [2010], improved the determination of internal /external air densities by including the influence of water vapor, using the traditional definition of the virtual temperature. Nevertheless, in cases where CO_2 molar fractions of internal air exceed atmospheric values by an order of magnitude or more, it is necessary to take into account the heaviness of CO_2 when calculating the virtual temperature [*Kowalski and Sanchez-Canete*, 2010].

Whereas high CO_2 values registered in cave air have been attributed most often to the seepage of CO_2-enriched water from the root zone, the possibility of sinking flows of dense, CO_2-rich air should also be considered. Biological CO_2 is produced near the surface by respiration of plant roots and microorganisms [*Kuzyakov*, 2006]; in most caves, isotopic studies confirm a clear biological origin of cave CO_2 [*Bourges et al.*, 2001; *Bourges et al.*, 2012]. Soil CO_2 generally increases with depth, from near-atmospheric concentrations at a few centimeters to an order of magnitude more a few meters down [*Amundson and Davidson*, 1990; *Atkinson*, 1977]. High concentrations of CO_2 at depth have been explained in terms of shallow CO_2 dissolution, downward transport by seepage, and subsequent precipitation from water in deeper layers [*Spotl et al.*, 2005], whereas surface layers are depleted in CO_2 by exchange with the atmosphere. At depth and for caves in particular, another input of CO_2 could be due to the injection of dense, CO_2-rich air, flowing down through fissures due to differences in buoyancy, whose characterization is poorly known and requires information regarding T_v. This virtual temperature has been little applied to soils and caves, but could explain why CO_2 accumulates at depth yielding concentrations much higher than those in the atmosphere.

Here we show the error produced in determining the virtual temperature when not taking into account CO_2 effects, and demonstrate its repercussions for the determination of air buoyancy in caves. We try to improve knowledge and understanding of cave ventilation through the use of virtual temperature in CO_2-rich air. Accurate determinations of virtual temperature allow numerical evaluation of buoyancy, and thus can determine exactly when ventilation is possible, and therefore when a cave can release or store CO_2. Also we represent T_v - explaining the relative buoyancy relevant for cave ventilation - for different values of T and CO_2 content. Then, we show differences between T and T_v, - calculated both with and without accounting for CO_2 content - for 14 different experimental sites in the vadose zone, demonstrating the importance of using the correct definition of T_v to determine air buoyancy in caves.

4.2.2. Derivations and definitions

For purposes of characterizing air buoyancy, meteorologists define the virtual temperature (T_v) as the temperature that dry air must have to equal the density of moist air at the same pressure. The virtual temperature for the atmosphere is approximated as (see appendix A):

$$T_v = T(1 + 0.61r) \qquad \text{(eq. 1)}$$

where T and T_v are the absolute temperature (K) and virtual temperature (K) respectively and r is the mixing ratio (dimensionless), defined as the ratio of the mass of water vapor to that of dry air.

Thus variations in the virtual temperature serve as a proxy for those in air density (Stull, 1988), which can be obtained through the equation of state for moist air:

$$p = \rho R_d T_v \qquad \text{(eq. 2)}$$

where p, ρ and R_d are the pressure (Pa=J m^{-3}), air density (kg m^{-3}) and particular gas constant for dry air (286.97 J kg^{-1} K^{-1}) respectively. Equation (2) makes clear that, for a given altitude level (pressure), air density is related directly to T_v, which serves therefore as a surrogate variable for determining buoyancy.

Equation (2) is only valid for the free atmosphere, while for caves or soils it should not be used due to high concentrations of CO_2 in the air. This equation, normally used for assessing the buoyancy of an air mass by changes in its density, is valid in the atmosphere because the molar mass of dry air (m_d) is very constant, 0.02897 kg·mol^{-1}, since air composition is very constant once water vapor has been excluded. However the air composition in soils or caves differs from that of the atmosphere due to higher amounts of CO_2.

The correct equations to calculate the virtual temperature including CO_2 effects were developed by Kowalski & Sanchez-Cañete [2010]. Frequently caves exhibit values exceeding 0.4% in volumetric fraction of CO_2, ten times the atmospheric concentration [*Batiot-Guilhe et al.*, 2007; *Benavente et al.*, 2010; *Denis et al.*, 2005; *Howarth and Stone*, 1990]. This CO_2 increment with respect to atmospheric concentrations provokes changes in the composition of dry air and its molar mass (m_d) so that the definition of the virtual temperature in eq. (1) is inappropriate. An approximation to calculate the virtual temperature (T_v) including CO_2 effects is via the following equation (see appendix A):

$$T_v = T + \left(1 + 0.6079 r_v - 0.3419 r_c\right) \qquad \text{(eq. 3)}$$

where r_v and r_c are the water vapour and carbon dioxide mixing ratios respectively (dimensionless).

Therefore for determining air density in caves or soils including CO_2 effects, the virtual temperature can be used in the ideal gas law with the particular gas constant (R_{noa}, 287.0 J K^{-1} kg^{-1}) for the mixture of nitrogen (N_2), oxygen (O_2), and argon (Ar).

$$p = \rho \cdot R_{noa} \cdot T_v \qquad \text{(eq.4)}$$

This parameter can be computed exactly using an excel template found at http://fisicaaplicada.ugr.es/pages/tv/!/download, where it is only necessary to enter values of CO_2 (%), air temperature (ºC) and relative humidity (%).

4.2.3. Results and discussion

The difference between internal (cave) and external (atmosphere) virtual temperatures can be used to determine the potential for buoyancy flows. The virtual temperature is a variable used traditionally by meteorologists to determine air buoyancy. Knowing the internal and external virtual temperatures allows determination of air densities (using equation 4) and therefore calculation of the possibility of buoyancy flows. The following results are organized into two sections. First, general differences between T and T_v, including CO_2 effects and comparing the interior and exterior environments, are presented to highlight the importance of using the appropriate variable (T_v) to characterize air density. Then, differences are shown for the conditions of specific caves selected from the literature.

Quantifying T_v –T for caves in general

Differences between air temperature (T) and virtual temperature (T_v) (eq. 3) at different volumetric fractions of CO_2 are shown in Figure 1, assuming 100% relative humidity (RH) as is typical for internal conditions. To give an example, a cave with 3% CO_2, and 10ºC would have a T_v 3ºC lower than T (see dashed lines). Positive values (orange color) indicate that the virtual temperature is higher than the temperature due to the dominant influence of water vapor on compositionally determined air density (for low CO_2 concentrations). This is greater for higher temperatures since warm air can store more water vapor than cold air, decreasing the molar mass below that of dry air (28.96 g mol^{-1}) due to the increased importance of water vapor (18 g mol^{-1}), thus reducing the density.

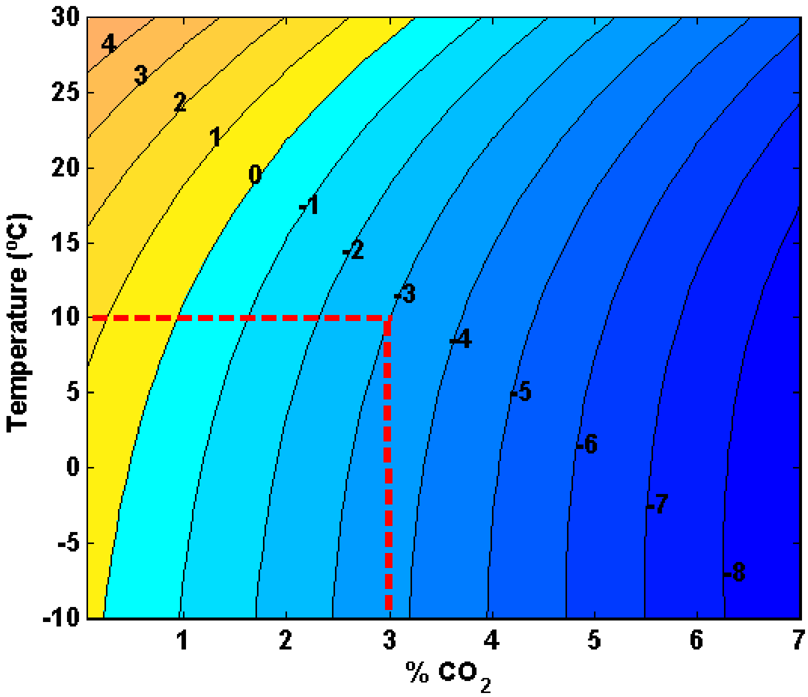

Figure 1. Isopleths of the difference between the virtual temperature and temperature (T_v - T), as a function of volumetric fraction CO_2 (1% = 10.000 ppm) and temperature, for 100% of *RH*.

Figure 2 shows that whenever the internal and external atmospheres have the same temperature and relative humidity, higher values of CO_2 inside the cave explain stagnation of the cave environment. For example, a cave with 3% CO_2 and exterior and interior temperature of 10ºC would have a virtual temperature 4.3ºC colder than that of the external air; consequently the internal air is denser than the exterior and therefore stagnant.

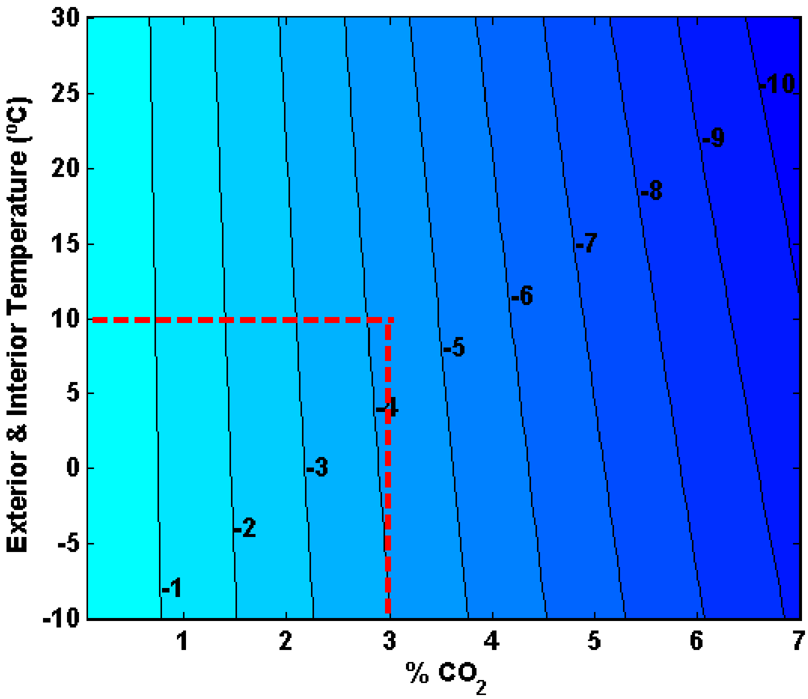

Figure 2. Isopleths of the difference between virtual temperatures of exterior and interior (Tv_{int} - Tv_{ext}) both with identical temperature and 100% of *RH*, as a function of temperature and volumetric fraction CO_2. The exterior is considered to contain 0.0395% CO_2.

Whereas differences between external and internal virtual temperatures are necessary for the correct interpretation of cave ventilation, the difference between external and internal temperatures is commonly used (Spötl et al., 2005; Fernàndez-Cortes et al., 2006, 2009; Baldini et al., 2008; Liñan et al., 2008; Milanolo & Gabrovšek, 2009; Faimon et al., 2012). Thus, with similar values of T_{ext} and T_{int}, the differences between virtual temperatures can be more than 10ºC (Fig. 2).

Fixing the internal CO_2 content (e.g., at 3% to continue with the example presented above), we can analyze differences between external and internal virtual temperatures (Fig. 3) at different temperatures. Negative values indicate that the interior air is denser than the exterior and therefore stagnant. For example, a cave with 3% CO_2, 100% RH and 10ºC presents neutral buoyancy when the external temperature is approximately 6ºC.

Consistent with the results of Figure 2, when both cave and external atmosphere are at 10ºC, T_v is lower than T by 4.3ºC. Higher values of the external temperature imply stagnant air inside the cave.

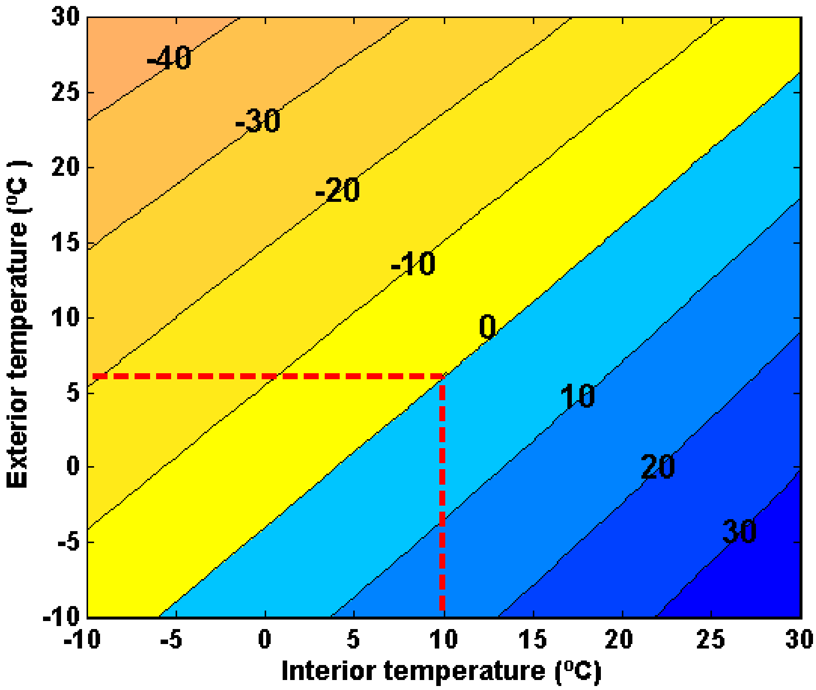

Figure 3. Isopleths of the difference between the virtual temperature of interior and exterior with 3% CO_2 ($Tv_{int} - Tv_{ext}$), each at 100% of RH, as a function of the internal and external temperatures.

Quantifying *T v –T* for specific caves

To determine when buoyancy flows are possible, scientists must compare the differences between external and internal virtual temperatures. Thus, if virtual temperatures are equal (independent of the amount of water vapor or CO_2) both air masses will be in equilibrium. On the other hand, if air mass A has a virtual temperature higher than air mass B, then air mass A will have the lower density. In this way, comparing the virtual temperatures of air masses specifies their relative densities (from eq. 4) and thus the tendency to float or sink.

Maximum CO_2 values and mean temperatures of 14 caves and boreholes of the world are shown in Table 1. These published data were taken as examples to calculate the differences between the virtual temperature and temperature. Although such differences also depend on the temperature, caves in excess of 1% CO_2 generally present negative differences between T_v and T, while lower values of CO_2 present positive differences (Fig. 4). However, for example, the subtropical Hollow Ridge cave (D) presents more positive values of T_v-T than does the temperate Císařská cave (C), despite similar volumetric fractions of CO_2 (0.42 and 0.4%, respectively). Such differences are due to differences in water vapor content, according to temperature (19.6 versus 9.6º C in Hollow Ridge and Císařská cave, respectively).

Country	**Cave/Soil**	**Name**	**% vol. CO_2 (Maximum)**	**Mean T(ºC)**	**ID**	**Source**
Italy	Cave	Grotta di Ernesto	0.170*	8*	A	(Frisia et al., 2011)
Bosnia and Herzegovina	Cave	Srednja Bijambarska Cave	0.220	6.2	B	(Milanolo & Gabrovsek, 2009)
Czech Republic	Cave	Císařská Cave	0.4	9.6*	C	(Faimon & Licbinska, 2010)
USA (Florida)	Cave	Hollow Ridge Cave	0.422	19.6	D	(Kowalczk & Froelich, 2010)
Spain	Cave	Cave Castanar de Ibor	0.44	17	E	(Fernandez-Cortes et al., 2009)
Ireland	Cave	Ballynamintra Cave	0.65	11.5	F	(Baldini et al., 2008)
Spain	Borehole	Sierra de Gádor	1.5	12	G	(Sanchez-Canete et al., 2011)
France	Cave	Aven d'Orgnac	3.5	13	H	(Bourges et al., 2001)
USA(Texas)	Cave	Natural Bridge Caverns	*4	20*	I	(Wong & Banner, 2010)
Spain	Cave	Cova de les Rodes	4.9	17.2 (other sources)	J	(Ginés et al., 1987)
Australia	Cave	Bayliss Cave	5.9	26	K	(Howarth & Stone, 1990)
France	Skinhole	Causse d'Aumelas	6	15.3 (other sources)	L	(Batiot-Guilhe et al., 2007)
Spain	Borehole	Cave of Nerja	6	21	M	(Benavente et al., 2010)
France	Cave	Cave of Lascaux	6	17.6 (other sources)	N	(Denis et al., 2005)

Table 1. Published carbon dioxide concentrations in cavity airspaces (*visual estimates).

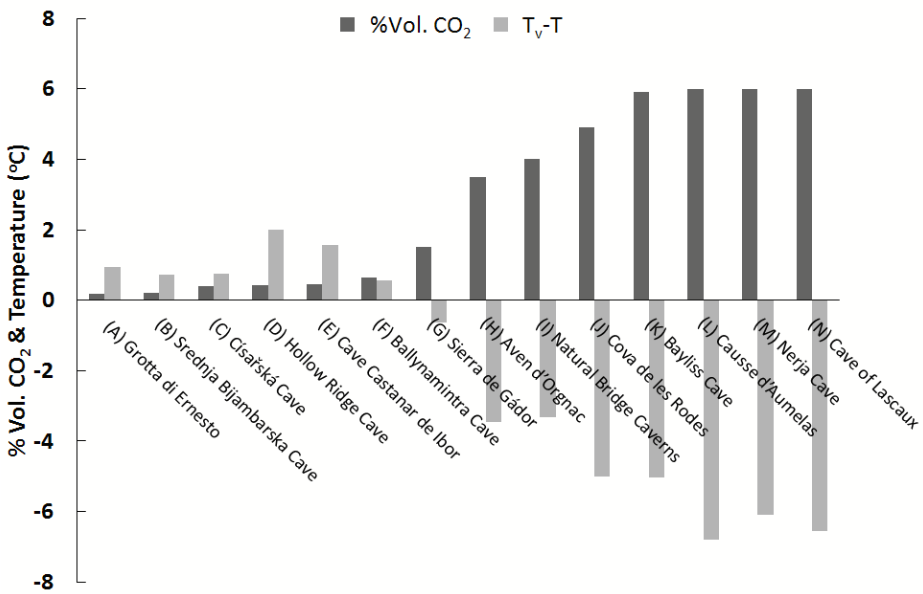

Figure 4. Volumetric fraction of CO_2 (%, dark gray) and differences between virtual temperature (T_v) and temperature (T), (ºC, light gray) in the different cavities.

Virtual temperature differences between the exterior and interior are compared to distinguish between periods of stagnant versus buoyant cave air for each experimental site, using their maximum values of CO_2 and the mean T (Fig. 5). Differences between the virtual temperatures (T_{v_ext}-T_{v_int}) increase with increasing CO_2 molar fraction and therefore higher CO_2 implies greater differences between internal and external densities, with the internal air denser than the external air and therefore causing stagnation (in the case of a cave lying below its entrance). For example, the Natural Bridge Caverns (I) with 4% CO_2 presents a difference of 6 ºC between the (mean annual) external and internal virtual temperatures. Therefore, the internal air is denser than that of the external atmosphere (on average), inducing its stagnation and explaining the storage of CO_2. In the Nerja cave borehole (M), with 6% and 0.0395% CO_2 for the internal and external atmosphere, respectively, the virtual temperature in the borehole is 8.9ºC lower than the outside (Fig. 5). This difference in T_v implies that the internal air is denser, inhibiting convective ventilation. Therefore, researchers who use differences between exterior/interior air temperatures to determine ventilation, may find differences between virtual temperatures close to 9 °C, when the exterior/interior air temperature is the same in both, and therefore over- or under-estimate the ventilation periods.

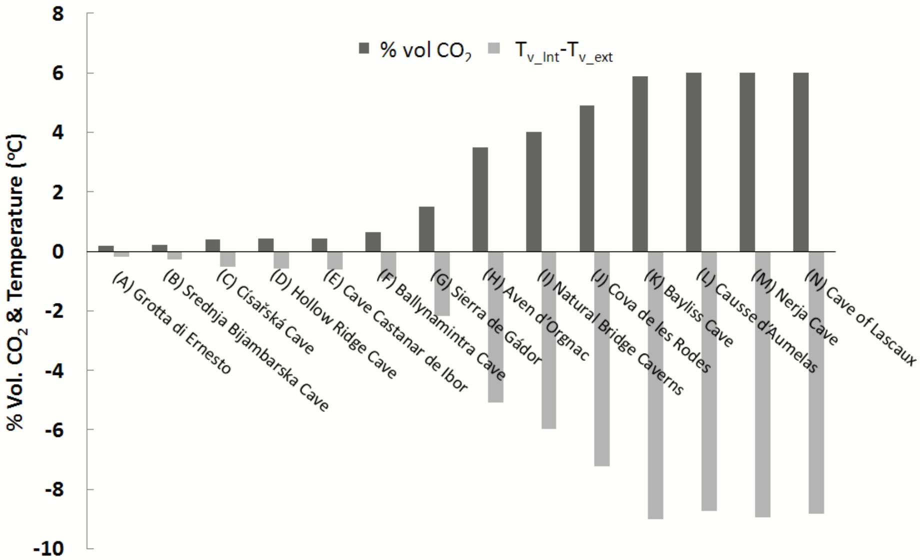

Figure 5. Volumetric fraction of CO_2 (%, dark gray) and differences between the virtual temperature of interior and an exterior (T_{v_int} -T_{v_ext} in ºC, light gray) in the different cavities. Both internal and external air are assumed to have the same temperature, which is the annual mean for the cave.

Differences between virtual temperatures in two air masses indicate density differences between both, and thus the potential for ventilation due to buoyancy. However, two possible issues must be considered that hamper or facilitate ventilation of the cave. The first includes atmospheric conditions such as the wind [*Kowalczk and Froelich*, 2010] and pressure changes [*Baldini et al.*, 2006; *Denis et al.*, 2005] inside and outside of the cave. The relevancy of buoyancy-induced cave ventilation is greatest on days with atmospheric stability, where there are little pressure changes and low winds. During these days static processes [*Cigna*, 1968] are dominant. The second issue is the number of entrances to the cave and their different altitudes and orientations (up or down). In caves with a single entrance the air will flow inward along the floor or roof, and return outward along the roof or floor, according to the sign of the density difference. However if the cave has many entrances at different levels, it may be necessary to monitor more than one entrance [*Cigna*, 1968]. Due to the strong spatial variability of the temperature, simply knowing T_v at a single point inside (and outside) the cave may not necessarily be sufficient for determining the potential for ventilation.

4.2.4. Conclusions

We used the information of several caves together with gas law to demonstrate that the difference between external and internal virtual temperatures including CO_2 effects determines the buoyancy and should be used for the correct interpretation of cave ventilation. Often scientists estimate ventilation neglecting CO_2 effects, but this can cause errors close to 9 °C in the difference between external and internal virtual temperatures when the air temperature is the same in both. Thus, the common use of the difference between external and internal temperatures could over- or under-estimate the existence of ventilation processes, depending on CO_2 content and relative humidity.

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Appendix A

The starting point for deriving the virtual temperature is the ideal gas law:

$$pV = nR^*T \qquad \text{(eq. A1)}$$

where *p, V, n,* R^* and *T* are the pressure (Pa), volume (m^3), number of moles (moles), universal gas constant (8.314 m^3 Pa K^{-1} mol^{-1}) and absolute temperature (K) of the gas, respectively. Since the number of moles (*n*) is equal to the mass (*m,* in kg) divided by the molar mass (*M,* in kg mol^{-1}), equation 1 can be written as:

$$pV = \frac{m}{M} R^*T \qquad \text{(eq. A2)}$$

By substituting the density, $\rho = m/V$ this can be rewritten in the form:

$$p = \rho \frac{R^*}{M} T \qquad \text{(eq. A3)}$$

When defining the particular gas constant (*R*) as $R = R^*/M$, the equation of state for the atmosphere can be written in the form convenient for meteorologists as:

$$p = \rho RT \qquad \text{(eq. A4)}$$

where *p, ρ, R* and *T* are the pressure (Pa=J m^{-3}), density (kg m^{-3}), particular gas constant (J kg^{-1} K^{-1}) and absolute temperature (K) of the gas, respectively.

The individual gas laws for any gas (suffix "i"), including the mixture defined as dry air (suffix "d"), water vapor (suffix "v") and another mixture defined as moist air (suffix "m") are described in the following equations

$$p_i = \rho_i R_i T \quad \text{(eq.A5.a)}$$

$$p_d = \rho_d R_d T \quad \text{(eq.A5.b)}$$

$$p_v = \rho_v R_v T \quad \text{(eq.A5.c)}$$

$$p = \rho_m R_m T \quad \text{(eq.A5.d)}$$

Dry air

The equation of state for dry air is shown in equation (A5.b), where water vapor is excluded from the air mass. Here, R_d is the gas constant for dry air, which can be determined by using the principle of mass conservation

$$\rho = \sum \rho_i \quad \text{(eq.A6)}$$

and Dalton's law of partial pressures:

$$p = \sum p_i \quad \text{(eq.A7)}$$

By combination of equations A5.a, A6 and A7 we obtain

$$p = T \sum \rho_i R_i \quad \text{(eq.A8),}$$

which compared with equation A5.b yields

$$R_d = \frac{\sum \rho_i R_i}{\sum \rho_i} \quad \text{(eq.A9)}$$

Replacing the density ($\rho = m/V$) in equation A9

$$R_d = \frac{\sum \frac{m_i}{V} R_i}{\sum \frac{m_i}{V}} \qquad \text{(eq.A10)}$$

and eliminating volume, which is identical for both the mixture and any individual component, it is found that:

$$R_d = \frac{\sum m_i R_i}{\sum m_i} \qquad \text{(eq.A11)}$$

showing that the effective particular gas constant for a mixture (such as dry air) can be calculated by the (mass) weighted combination of the particular constants for the individual components. To determine R_d it is necessary to know the composition of the dry atmosphere, by mass (Table A1).

Gas	Individual gas constant Ri (J kg-1 K-1)	% Mass
N_2	296.7	75.52
O_2	259.8	23.15
Ar	208.1	1.28
CO_2	188.9	0.05

Table A1. Components of dry air with their particular gas constants and fractional contribution by mass (NOAA et al., 1976).

Substituting into equation A11:

$$R_d = \frac{75.52 \cdot 296.7 + 23.15 \cdot 259.8 + 1.28 \cdot 208.1 + 0.05 \cdot 188.9}{100} = 286.97 \cong 287\, JKg^{-1}K^{-1}$$

Moist air

The equation of state for moist air is given in equation A5.d. The moist air density can be written using equation A6:

$$\rho_m = \frac{m_v + m_d}{V} = \rho_v + \rho_d \qquad \text{(eq.A12)}$$

where ρ_v and ρ_d are the densities of water vapor and dry air respectively. Using equations A11 and A12, and the principle that the effective particular gas constant for the mixture (now moist air) is the (mass) weighted combination of the particular constants for the individual components, yields the gas constant of moist air (R_m),

$$R_m = \left(\frac{m_v R_v + m_d R_d}{m_v + m_d} \right) \qquad \text{(eq.A13)}$$

Multiplying by $\left(\frac{1/m_d}{1/m_d} \right)$ produces

$$R_m = \left(\frac{\frac{m_v}{m_d} R_v + \frac{m_d}{m_d} R_d}{\frac{m_v}{m_d} + \frac{m_d}{m_d}} \right) \qquad \text{(eq.A14)}$$

Considering that the mixing ratio (r) is defined as the ratio of the mass of water vapor (m_v) to that of dry air (m_d) $r \equiv m_v / m_d$, and substituting this into equation A14 gives

$$R_m = \left(\frac{rR_v + R_d}{r + 1} \right) \qquad \text{(eq.A15)}$$

To simplify, equation A15 is multiplied by $\left(\frac{1-r}{1-r}\right)$ to give:

$$R_m = \frac{rR_v - r^2 + R_d - rR_d}{r - r^2 + 1 - r} \qquad \text{(eq.A16)}$$

The denominator of equation A16 can be approximated as unity when recognizing that every second-order term is several orders of magnitude smaller. The numerator can be similarly simplified, leading to the following approximation:

$$R_m = R_d + rR_v - rR_d \qquad \text{(eq.A17).}$$

To simplify, the second term is multiplied by $\left(R_d / R_d \right)$

$$R_m = R_d + r\frac{R_v}{R_d}R_d - rR_d \qquad \text{(eq.A18)}$$

Substituting the gas constants of dry air (R_d=287 J kg^{-1} K^{-1}) and water vapor (R_v=461.51 J kg-1 K-1), equation A18 can be written and organized as:

$$R_m = R_d + rR_d 1.61 - rR_d \qquad \text{(eq.A19)}$$

$$R_m = R_d(1 + 1.61r - r) \qquad \text{(eq.A20)}$$

$$R_m = R_d(1 + r(1.61 - 1)) \qquad \text{(eq.A21)}$$

$$R_m = R_d(1 + 0.61r) \qquad \text{(eq.A22)}$$

Substituting into equation A5.d we can write the equation of state for moist air

$$p = \rho_m R_d \left(1 + 0.61r\right)T \qquad \text{(eq.A23)}$$

Rather than associating the varying water vapor effect (1+0.61r) with the gas constant (and thus producing a variable constant), meteorologists traditionally associate this term with the temperature. Thus, through equation A23, the virtual temperature for the atmosphere is defined as:

$$T_v = T(1 + 0.61r) \qquad \text{(eq.A24)}$$

CO_2 rich-air

Equations to calculate the virtual temperature including CO_2 effects were developed by Kowalski & Sanchez-Cañete (2010). An approximation to calculate the virtual temperature (T_v) including CO_2 effects is via the following equation:

$$T_v = T(1 + 0.6079r_v - 0.3419r_c) \qquad \text{(eq.A25)}$$

where T_v is the virtual temperature (K), and r_v and r_c are the water vapour and carbon dioxide mixing ratios respectively (dimensionless).

The errors when using equation A25 as an approximation to T_v (including CO_2 effects) were evaluated explicitly for the range of gas concentrations typically found in terrestrial caves and found to be less than 0.1% (0.3 K) for volumetric CO_2 fractions of up to 5%.

For a calculation without error, the virtual temperature should be defined using the particular gas constant for the mixture of moist air including high concentrations of CO_2, denoted as R_{mc} and defined as:

$$R_{mc} = \frac{R_{noa} + r_c R_c + r_v R_v}{1 + r_c + r_v} \qquad \text{(eq. A26)}$$

where R_{noa} is the particular gas constant for the mixture of nitrogen (N_2), oxygen (O_2), and argon (Ar) (287.0 J K^{-1} kg^{-3}), R_c is the particular gas constant for CO_2 (188.9 J K^{-1} kg^{-3}), R_v is the particular gas constant for water vapor (461.5 J K^{-1} kg^{-3}), r_v is the water vapor mixing ratio (dimensionless), and r_c is the carbon dioxide mixing ratio (dimensionless).

The exact expression for T_v is then.

$$T_v = T\left(\frac{\dfrac{R_{noa} + r_c R_c + r_v R_v}{1 + r_c + r_v}}{R_{noa}} \right) \qquad \text{(eq. A27)}$$

which is programmed in an Excel file freely available at http://fisicaaplicada.ugr.es/pages/tv/!/download

Therefore for determining air density in caves or soils including CO_2 effects, the virtual temperature can be used in the ideal gas law with the particular gas constant for the mixture of nitrogen (N_2), oxygen (O_2), and argon (Ar)

$$p = \rho \cdot R_{noa} \cdot T_v \qquad \text{(eq.A28).}$$

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4.3 Chapter 3

Subterranean CO_2 ventilation and its role in the net ecosystem carbon balance of a karstic shrubland

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Abstract

Recent studies of carbonate ecosystems suggest a possible contribution of subterranean ventilation to the net ecosystem carbon balance. However, both the overall importance of such CO_2 exchange processes and their drivers remain unknown. Here we analyze several dry-season episodes of net CO_2 emissions to the atmosphere, along with soil and borehole CO_2 measurements. Results highlight important events where rapid decreases of underground CO_2 molar fractions correlate well with sizeable CO_2 release to the atmosphere. Such events, with high friction velocities, are attributed to ventilation processes, and should be accounted for by predictive models of surface CO_2 exchange.

4.3.1. Introduction

The FLUXNET community monitors ecosystem carbon exchanges, usually interpreting CO_2 fluxes as biological (photosynthetic or respiratory) [*Falge et al.*, 2002; *Reichstein et al.*, 2005], neglecting inorganic processes. However, recent studies over carbonate substrates reveal possible contributions by abiotic processes to the net ecosystem carbon balance (NECB;[*Chapin et al.*, 2006]), with relevant magnitudes at least on short time scales [*Serrano-Ortiz et al.*, 2010; *Were et al.*, 2010]. These processes can temporally dominate the NECB in areas with carbonate soils [*Kowalski et al.*, 2008].

Carbonates outcrop on ca. 12-18% of the water-free Earth [*Ford and Williams*, 1989] with an enormous capacity to store CO_2 below ground in macropores (caves) and fissures [*Benavente et al.*, 2010; *Ek and Gewelt*, 1985]. Ventilation is a mass flow of air through a cavity, via the porous media in the case of closed caves, driven by an imbalance of forces (pressure gradients and gravity). Through the venting of these subterranean spaces, stored gaseous CO_2 can be lost to the atmosphere [*Kowalczk and Froelich*, 2010; *Weisbrod et al.*, 2009]. However, both the drivers of these ventilation processes and their relevance to regional CO_2 budgets remain unknown.

Often ecologists estimate soil CO_2 effluxes neglecting advective transport of CO_2 through the vadose zone. Studies of surface exchange have usually been conducted either by manual [*Janssens et al.*, 2001], or automatic soil respiration chambers [*Drewitt et al.*, 2002]. Scientists often model underground, diffusive soil CO_2 fluxes based on single sampling [*Davidson and Trumbore*, 1995; *Hirsch et al.*, 2002] or continuous monitoring of CO_2 profiles [*Baldocchi et al.*, 2006; *Pumpanen et al.*, 2008; *Tang et al.*, 2003]. Such models based on diffusion processes neglect the effects of ventilation. However, Subke et al. [2003] revealed the importance of such effects at least on short-time scales.

Here we analyze several episodes of subterranean CO_2 ventilation that occurred during a dry period in a carbonate ecosystem. We examine its determinants and implications for the NECB measured with an eddy covariance system.

4.3.2. Material and Methods

The study site is *El Llano de los Juanes*, a shrubland plateau at 1600 m altitude in the *Sierra de Gádor* (Almería, Southeast Spain; 36º55'41.7''N; 2º45'1.7''W). It is characterized by a sub-humid climate with a mean annual temperature (*T*) of 12 ºC and precipitation of ca. 465 mm. The soil, overlying Triassic carbonate rocks, varies from 0 to 150 cm depth with a petrocalcic horizon and fractured rocks. More detailed site information is given by Serrano-Ortiz et al.[2009].

Throughout the dry season of 2009 (9 June - 9 September) two sensors (GMP-343, Vaisala, Inc., Finland) that measure CO_2 molar fraction (χ_c), were installed in the soil and in a borehole. The soil sensor was installed 25 cm deep, with a soil *T* probe (107, Campbell scientific, Logan, UT, USA; hereafter CSI) and water content reflectometer (CS616, CSI). The 7-m borehole (dia. 0.1 m) was sealed from the atmosphere with a metal tube cemented to the walls. Inside, sensors tracked χ_c (GMP-343), radon (Barasol MC BT45N, Bessines Sur Gartempe, France) and *T* and relative humidity (HMP45, CSI). The CO_2 sensors were corrected for variations in *T* and pressure. A data-logger (CR23X, CSI) measured every 30 s and stored 5 min averages. Ecosystem-scale CO_2 fluxes were measured by eddy covariance atop a 2.5 m tower; Serrano-Ortiz et al., [2009] describe the instrumentation and quality control for eddy flux data.

4.3.3. Results

Over the dry period, soil and borehole χ_c were inversely correlated. While the soil χ_c fell from its maximum near 1500 ppm to about half (Fig. 1a), the borehole χ_c doubled from *ca.* 8000 ppm and to 16000 ppm (Fig. 1b). Apart from these long-term trends, during the first half of the summer, marked decreases occurred in both soil and borehole χ_c during three key events (Fig. 1; grey bars). Such decreases correspond to higher CO_2 emissions to the atmosphere relative to the preceding and subsequent periods. Pressure and air temperature showed poor correlations with soil χ_c, while radon and CO_2 fluctuations in the borehole are correlated in phase (data not shown), suggesting that ventilation causes CO_2 losses. A cross-correlation analysis indicated that an increment in u_* during daytime corresponds immediately to an increase in ecosystem CO_2 fluxes *(F_c)*, whereas the decrease in soil χ_c is delayed by two hours, and the cave χ_c lags the soil by 53.5 hours.

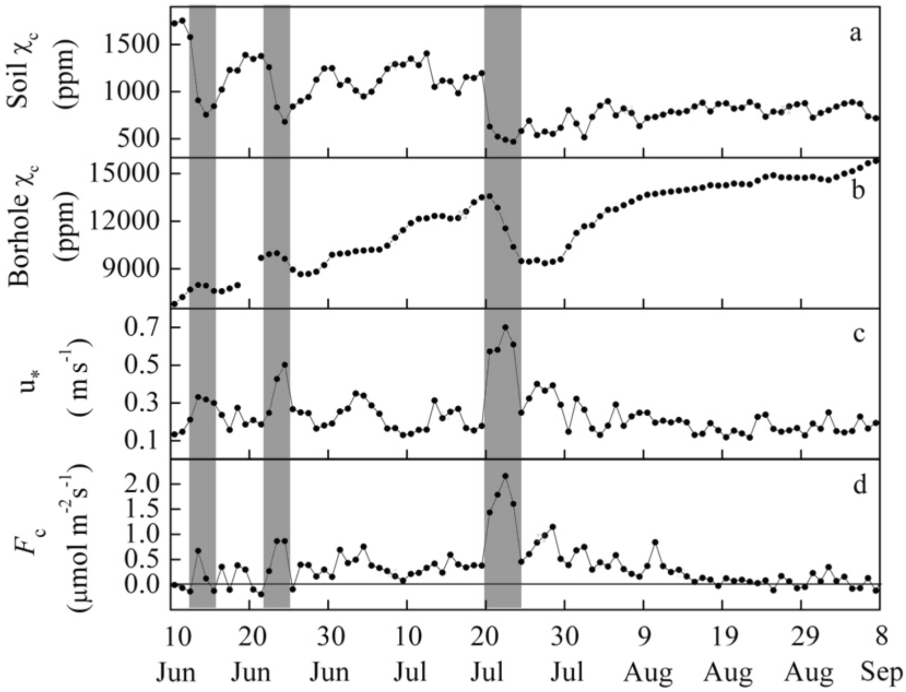
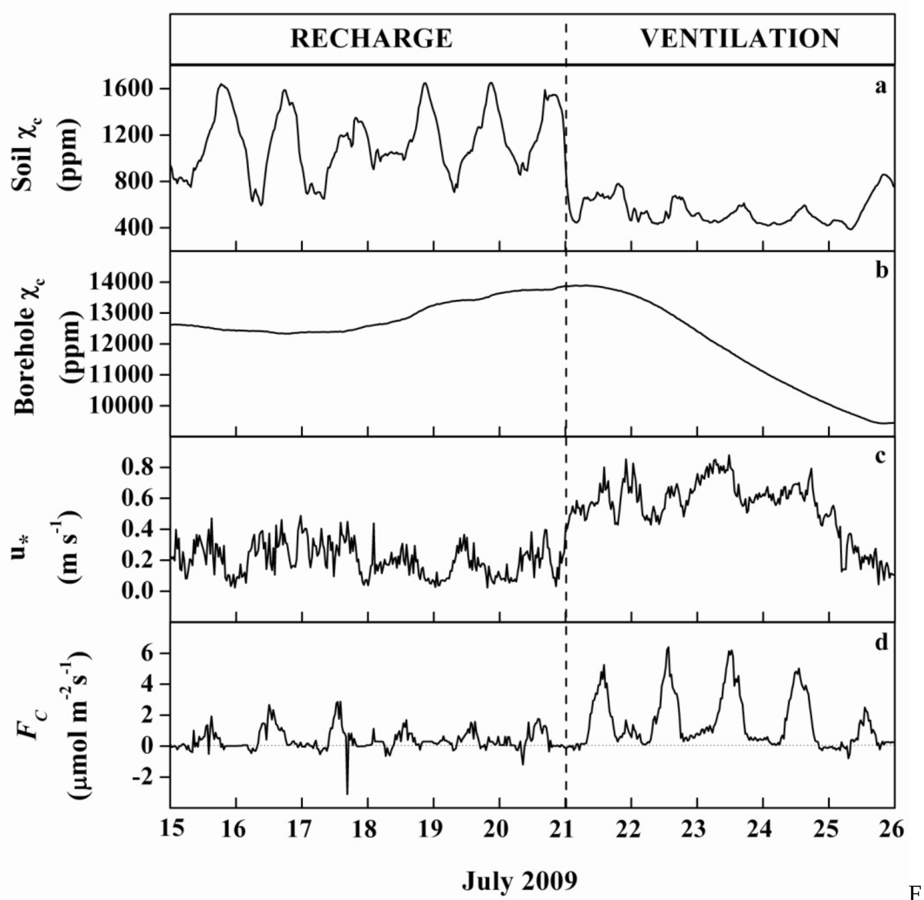


Figure 1. Average daily values of (a) soil CO_2 molar fraction (χ_c) at 25 cm depth and (b)

borehole χ_c at 7 m depth, (c) friction velocity (u_*; turbulent velocity scale) and (d) ecosystem CO_2 fluxes (F_C; negative values represent uptake). Shaded columns delimit ventilation events.

These events occurred when the friction velocity (u_*) exceeded 0.3 m s^{-1} (Fig. 1c), and are associated with ventilation. The largest event occurred during a windy period from July 21st-24th (daily mean u_*>0.6 m s^{-1}), when soil CO_2 more than halved from 1200 to 500 ppm and the borehole lost *ca.* 4000 ppm. This underground CO_2 loss corresponded to increased emissions to the atmosphere of 0.4 - 2 μmol m^{-2} s^{-1} (Fig. 1d). After the event, the borehole χ_c recovered to exceed initial values (>14000 ppm) within a couple of weeks. The 21-24 July ventilation event (3rd grey bar, Fig. 1) is detailed in Figure 2, showing 11 days of half-hour values divided into periods of recharge and ventilation. During recharge, the borehole χ_c increased slightly, then fell quickly during ventilation, losing *ca.* 4000 ppm in five days (Fig. 2b). Soil CO_2 followed a daily cycle, with late afternoon peaks and dawn minima (Fig. 2a). During recharge, diurnal ranges averaged *ca.* 800 ppm, versus just 200 ppm during ventilation. The mean soil χ_c and u_* were higher (Fig. 2c) for the ventilated period. Finally, F_c was near zero with little diurnal variation during recharge, but daytime emissions exceeded 5 μmol m^{-2} s^{-1} during the ventilated period. At night, CO_2 emissions were always close to zero (Fig. 2d).



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igure 2. Ventilation event detail, distinguishing between recharge and ventilation. Average half-hour values of (a) soil CO_2 molar fraction (χ_c, 25 cm depth), (b) borehole χ_c (7 m depth), (c) friction velocity (u_*; turbulent velocity scale) and (d) CO_2 fluxes.

4.3.4. Discussion

4.3.4.1 Evidence of subterranean ventilation

This study shows clear empirical evidence of subterranean ventilation and its implications in the NECB. Decreases in soil and borehole χ_c coincided with high u_*, corresponding to large F_c (Fig.2). Ventilation induces soil CO_2 release on time scales from minutes to days. Particularly high ecosystem emissions may occur with greater magnitudes in karsts storing large amounts of CO_2, with the overlying soil acting as a semi-permeable membrane open to gas exchange on dry summer days [*Cuezva et al.*, 2011]. Thus, ventilation processes can be more important in karstic ecosystems with arid soils and pronounced dry seasons.

In this study subsurface CO_2 followed a daily pattern. In soil pores, dusk/dawn had the maximum/minimum concentrations (Fig. 2a). Borehole CO_2 values, integrating the whole column from 0 to 7 m, followed no daily trend as confirmed by autocorrelation analysis. Thus, a rise in u_* corresponds to a direct decrease in soil χ_c, while borehole χ_c falls several hours later.

4.3.4.2 Main drivers controlling the soil CO_2 ventilation

Studies focused on soil CO_2 profiles have reported correlations between soil χ_c and wind speed [*Jassal et al.*, 2005; *Takle et al.*, 2004]. Lewicki et al [2010] experimentally studied the correlation between temporal variations in soil CO_2 concentrations and several meteorological factors during a controlled shallow-subsurface CO_2 release experiment. Subke et al. [2003] suggested that the flux contributed by pressure pumping should be considerable for wind gusts following periods of relative calm, while its correlation should be smaller for similar wind conditions over previously flushed soil. We found a strong inverse correlation between soil χ_c and u_*. After de-trending the CO_2 series, u_* explained 67% (R^2) of the variability during the studied period. Correlated radon and CO_2 fluctuations in the borehole also indicate that ventilation is the cause of CO_2 losses (Fig. 3). All this indicates that, for our study, the most appropriate variable determining soil CO_2 ventilation is u_*.

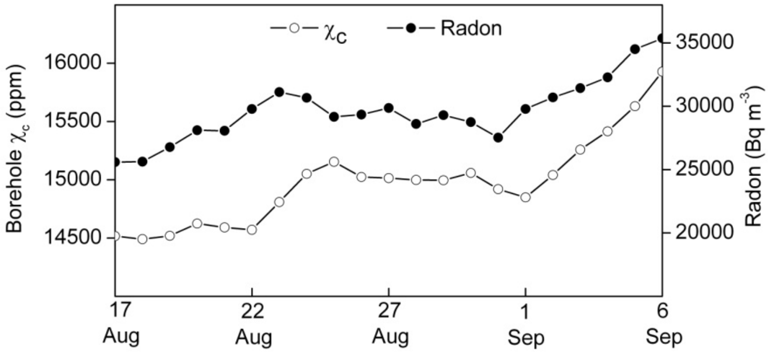

Figure 3. 3 weeks of Radon and CO_2 data during the dry season.

4.3.4.3 Outstanding issues

Despite these clear relationships, uncertainties remain regarding the behavior of subterranean CO_2, and two particular questions arise. Firstly, where does the soil CO_2 go after reaching its daily maxima during recharge periods? For example, on the windy night of July 20th-21st, the soil lost *ca*. 1000 ppm but this CO_2 was not detected in eddy fluxes (Fig. 2). Secondly, why are CO_2 emissions never detected by eddy covariance at nights? One might attribute this to static stability, but high values of u_* are evidence of dynamic instability [*Stull*, 1988] indicating that CO_2 exchange is not a limited by the turbulence. Rather, we posit that cold surface temperatures at night foment water vapor adsorption [*Kosmas et al.*, 2001], humidify the surface, close the soil membrane to gas flow at night, and thus disable ventilation [*Cuezva et al.*, 2011]. By contrast during ventilation the CO_2 that would otherwise have accumulated in the soil during daytime (see recharge period) is emitted directly to the atmosphere.

4.3.5. Conclusions

This study emphasizes the role of dry-season, subterranean ventilation processes in the net ecosystem carbon balance (NECB). Although several meteorological factors correlate with emitted CO_2, analyses suggest that ventilation is driven mainly by the friction velocity. Windy days are responsible for large emissions of CO_2 previously accumulated below ground, which are not accounted for in current models of surface CO_2 exchange. However during calm days soil CO_2 accumulates, causing significant day-night concentration differences. The vast network of pores, cracks and cavities along with high molar fractions (>15000ppm-7m) indicate that very large amounts of CO_2 can be stored inside karst systems. Further investigation is needed to explain the absence of CO_2 ventilation during windy nights, and characterize the CO_2 cycling of carbonate ecosystems.

Acknowledgements

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4.4 Chapter 4

Deep CO_2 soil inhalation/exhalation induced by synoptic pressure changes and atmospheric tides in a carbonated semiarid steppe

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Abstract

Knowledge of all the mechanisms and processes involved in soil CO_2 emissions is essential to close the global carbon cycle. Apart from molecular diffusion, the main physical component of such CO_2 exchange is soil ventilation. Advective CO_2 transport, through soil or snow, has been correlated with the wind speed, friction velocity or pressure (p). Here we examine variations in subterranean CO_2 molar fractions (χ_c) over two years within a vertical profile (1.5 m) in a semiarid ecosystem, as influenced by short-timescale p changes.

Analyses to determine the factors involved in the variations in subterranean χ_c were differentiated between the growing period and the dry period. In both periods it was found that variations in deep χ_c (0.5 -1.5 m) were due predominantly to static p variations and not to wind or biological influences. Within a few hours, the deep χ_c can vary by fourfold showing a pattern with two cycles per day, due to p oscillations caused by atmospheric tides. By contrast, shallow χ_c (0.15 m) generally has one cycle per day as influenced by biological factors like soil water content and temperature in both periods, while the wind was an important factor in shallow χ_c variations only during the dry period. Evidence of emissions was registered in the atmospheric boundary layer by eddy covariance during synoptic pressure changes when subterranean CO_2 was released; days with rising barometric pressure – when air accumulated belowground, including soil-respired CO_2 – showed greater ecosystem uptake than days with falling pressure. Future assessments of the net ecosystem carbon balance should not rely exclusively on Fick's law to calculate soil CO_2 effluxes from profile data.

4.4.1. Introduction

The characterization of the different mechanisms and processes involved in soil CO_2 emissions to the atmosphere is important for improving understanding of the global carbon cycle. Respiration is generally the only process considered by the FLUXNET community when modeling or interpreting soil-atmosphere CO_2 exchanges [*Falge et al.*, 2002], presumably transported by molecular diffusion. Recently however, numerous studies of semiarid ecosystems have shown the importance in the net ecosystem carbon balance (NECB; [*Chapin et al.*, 2006]) of other, abiotic components [*Emmerich*, 2003; *Kowalski et al.*, 2008; *Mielnick et al.*, 2005; *Plestenjak et al.*, 2012; *Rey et al.*, 2012b; *Serrano-Ortiz et al.*, 2010; *Were et al.*, 2010].

Most researchers interpret soil CO_2 effluxes at the soil surface in terms of concurrent respiration, neglecting subterranean CO_2 storage. Ventilation can decouple the soil CO_2 source from emissions to the atmosphere with changes in pressure, wind or friction velocity. Scientists have confirmed subterranean advective transport in laboratories [*Martin Maier et al.*, 2012; *Nachshon et al.*, 2012], soils [*M. Maier et al.*, 2010; *Subke et al.*, 2003], peatlands [*Comas et al.*, 2005; *Comas et al.*, 2007; *Comas et al.*, 2011], and snow [*Bowling and Massman*, 2011; *Fujiyoshi et al.*, 2010; *Massman et al.*, 1997; *Seok et al.*, 2009]. Some have applied the gradient method - based on Fick's law for molecular diffusion - to model exchange with the atmosphere during calm conditions, but highlight the importance of advective transport in exchanges at other times.

Advective transport of CO_2 through soil or snow has been correlated with changes in subterranean CO_2 molar fractions (χ_c) in conjunction with variations in wind speed, friction velocity or pressure (p). Advection has been detected using isotopic methods [*Bowling and Massman*, 2011], buried p sensors [*M. Maier et al.*, 2010; *Takle et al.*, 2004], ^{222}Rn concentrations

[*Fujiyoshi et al.*, 2010], ground penetrating radar [*Comas et al.*, 2005] or variations in CO_2 and other gases [*Hirsch et al.*, 2004; *Reicosky et al.*, 2008; *Seok et al.*, 2009]. Even in volcanoes the atmospheric p has a strong influence on both CO_2 degassing [*Rogie et al.*, 2001] and the CO_2 soil efflux [*Granieri et al.*, 2003], as well as on their combination as measured by eddy covariance [*Lewicki et al.*, 2008; *Lewicki et al.*, 2007].

Besides molecular diffusion, the main physical process affecting soil-atmosphere CO_2 exchange is ventilation (gas advection through porous media) driven by pressure pumping. Pressure pumping is caused by atmospheric processes including short-period turbulence, longer-period barometric changes and quasi-static pressure fields induced by wind [*Massman et al.*, 1997]. Subterranean convection, with CO_2–rich air subsiding due to its enhanced density [*Kowalski and Sanchez-Canete*, 2010], may also play a role. Most studies attribute gas advection to two atmospheric mechanisms: quasi-static pressure fields and short-period atmospheric turbulence [*Huwald et al.*, 2012], neglecting longer-period barometric changes.

This study shows subterranean CO_2 variations that are driven by longer-period barometric changes (atmospheric tides and synoptic events). We examine variations over two years within a vertical profile (1.5 m depth) in a semiarid ecosystem, highlighting the influence of changes in static pressure p on χ_c at depth (0.5 and 1.5 m). Increases in deep χ_c are not due to biological factors, with important increments registered, increasing to four times previous values approximately every 3 days over two years. The main factors implicated in subterranean χ_c changes vary according to depth as well as the (daily-synoptic-seasonal) timescale examined.

4.4.2. Material and Methods

Study site

The study was conducted in Balsa Blanca within the Cabo de Gata-Níjar Natural Park of southeast Spain (N36º56’26.0’’, W2º0.1’58.8’’). This is an alpha grass steppe situated on an alluvial fan (glacis) at 200 m a.s.l. The soil is classified as Calcaric Lithic Leptosol saturated in carbonates (0.15 m) over petrocalcic horizons overlying marine carbonate sediments and volcanic rocks. The climate is dry subtropical semiarid, with a mean annual temperature (T) of 18 ºC and precipitation of *ca. 200* mm. The most abundant ground cover is bare soil, gravel and rock (49.1%), and vegetation is dominated by *Macrochloa tenacissima* (57% of cover) with other species present including *Chamaerops humilis*, *Rhamnus lycoides*, and *Pistacia lentiscus*; the vegetation is most active during winter (January-April). More detailed site information is given by Rey et al. [2012b].

Field measurements

A vertical soil profile was installed in January 2010 to measure CO_2 molar fractions, temperature, and humidity at three depths characterized as “shallow” (0.15 m; A horizon), and “deep” (0.5 and 1.5 m; caliche horizon). Sensors oriented horizontally in the profile included CO_2 molar fraction (χ_c) probes (GMP-343, Vaisala, Inc., Finland) with soil adapters and hydrophobic filters, thermistors (107 temperature sensor, Campbell scientific, Logan, UT, USA; hereafter CSI) and water content reflectometers (CS616, CSI). The GMP343 sensors were configured at 25ºC and 1013 hPa and corrected in post processing for variations in T and pressure. Measurements were made every 30 s and stored as 5-min averages by a data-logger (CR23X, CSI).

Ecosystem-scale CO_2 fluxes were measured by eddy covariance atop a 3.5 m tower. An open-path infrared gas analyser (Li-Cor 7500, Lincoln, NE, USA) - calibrated monthly - measured barometric pressure (*p*) and densities of CO_2 and water vapor. A three axis sonic anemometer (CSAT-3, CSI) measured wind speed and sonic temperature. At 1.5 m above ground level two quantum sensors (LI-190, Li-Cor) measured incident and reflected photon fluxes. A data-logger (CR3000, CSI) managed the measurements and recorded data at 10 Hz (quantum sensors, storing only half-hour means). Turbulent fluxes were computed every half-hour according to Reynolds rules of averaging, corrected for dry air molar density variations [*Webb et al.*, 1980] and coordinate rotation [*Kowalski et al.*, 1997]. The friction velocity (u_*) is determined as the turbulent velocity scale resulting from square root of the kinematic momentum flux [*Stull*, 1988]. Quality control of the eddy flux data was performed according to Serrano-Ortiz et al. [2009].

Statiscal analyses

All variables were normalized prior to statistical analysis. This is because different variables are not strictly comparable due to extreme seasonal variations in both means and variances, particularly for sensors buried at different depths. Additionally, high-pass filtering was applied using two cut-off values to examine both diurnal and synoptic relationships. The normalized data (standardized anomalies; [*Wilks*, 2006]) for any meteorological variable are then given by:

$$N_i = \left(X - \overline{X_i}\right)/\sigma_i \qquad \text{(eq. 1)}$$

where N_i is the normalized value, X the measurement, $\overline{X_i}$ the running mean for a window of width i (0.5 or 3 days, diurnal and synoptic time scale respectively) centered on the time of measurement, and σ_i the standard deviation over the same window. Correlations (R^2) were then examined for both $N_{0.5}$ and N_3 and for two different vegetative periods: the growing period, where the vegetation is most active (March-April), and the dry period, where the vegetation is mostly dormant (July-August).

Daytime half-hour data were fitted using an empirical hyperbolic light–response model [*Falge et al.*, 2001] to describe the dependence of CO_2 ecosystem exchange [F_C, μmol m^{-2} s^{-1}] on the incident photon flux [F_P, μmol m^{-2} s^{-1}]:

$$F_C = -\frac{\alpha\beta F_P}{\alpha F_P + \beta} + \gamma \qquad \text{(eq. 2)}$$

where α (μmol C J^{-1}) is the canopy light utilization efficiency and represents the initial slope of the light–response curve, β (μmol C m^{-2} s^{-1}) is the maximum CO_2 uptake rate of the canopy at light saturation and γ (μmol C m^{-2} s^{-1}) is the ecosystem respiration during the day. All parameters are positive as defined.

4.4.3. Results

Seasonal and interannual patterns

Clear annual patterns are evident in the average daily values of soil temperature (*T*), water content (*SWC*), and CO_2 molar fraction (χ_c) at 0.15 m ("shallow") as well as at 0.5 m and 1.5 m depths ("deep"; Fig. 1). The soil *T* has its maximum (*ca*. 34 ºC) in summer (June, July and August) and minimum (5 ºC) in winter (December, January and February); the *SWC* shows inverse correlation with *T*, with basal values near 5% in summer but often more than 20% in winter.

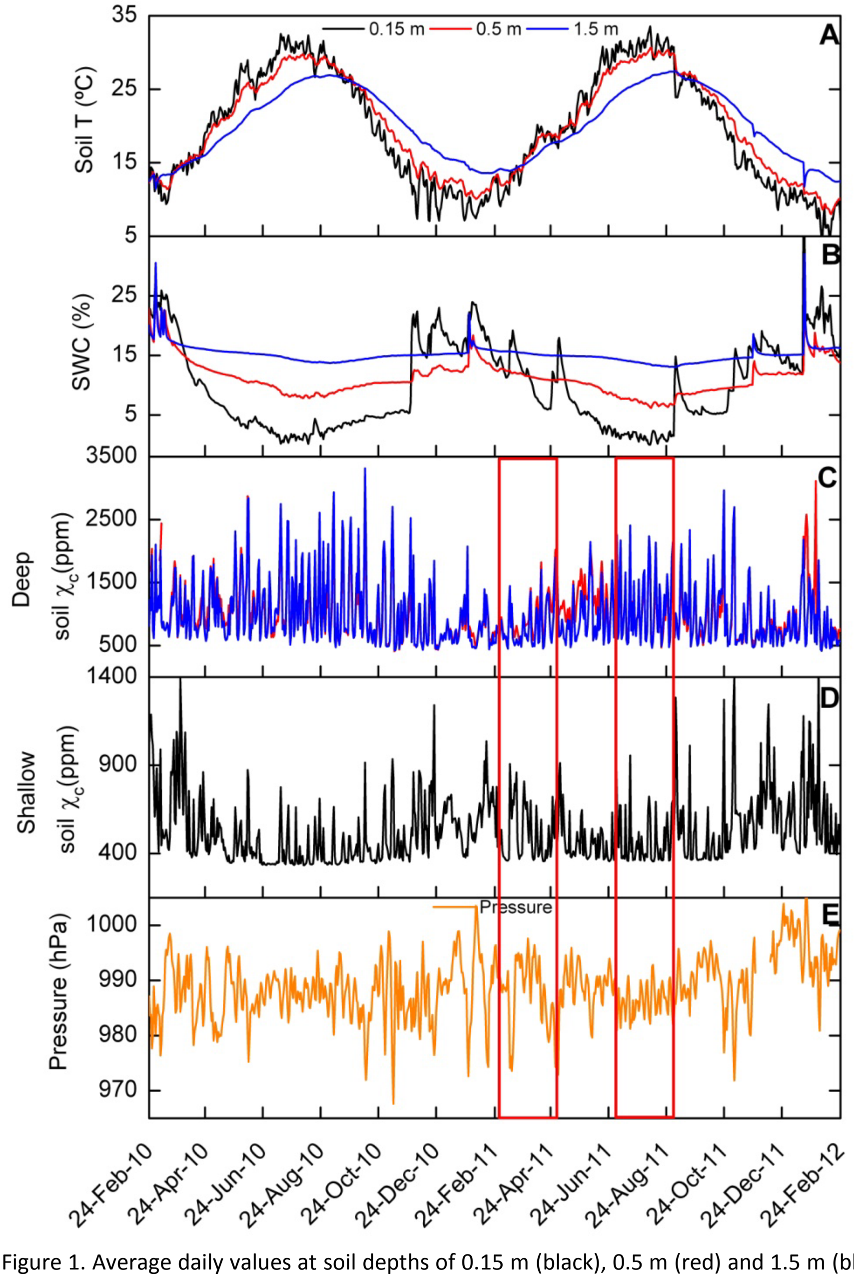

Figure 1. Average daily values at soil depths of 0.15 m (black), 0.5 m (red) and 1.5 m (blue) for (A) temperature, (B) volumetric soil water content, (C) deep soil CO2 molar fraction (χ_c) and (D) shallow soil CO2 molar fraction (χ_c), as well as (E) the atmospheric pressure (orange) over two years. The red rectangle delimits the period amplified in Figure 2.

Soil CO_2 molar fractions (χ_c) generally increase with depth, with a constant baseline for each horizon over the years, but also with periodic surges to more than double the mean value within a few days. The two deep sensors behave similarly (Fig. 1C), with the blue line (1.5 m depth) overlapping the red line (0.5 m depth) so nearly that the 0.5 m data are practically obscured. They show clear annual patterns with maxima in summer and minima in winter, similar means over the two years (χ_c ~1032 ppm at 0.5 m, and 994 ppm at 1.5 m) and rapid variability. By contrast, the shallow sensor (Fig. 1D) has about half the mean (χ_c ~ 529 ppm CO_2) and notably less variability - in both frequency and magnitude. Also in contrast to the deep case, shallow soil χ_c is highest in winter and lowest in summer. Differences between the deep and shallow probes are less pronounced in winter. Pressure (p) varies from 967-1007 hPa (Fig. 1E), with increased variability in winter due to the passage of synoptic systems, and suppressed variability in summer under the Mediterranean high. To clarify the relation between χ_c and p, we focus on two different periods of 2011 (Fig. 1. Red rectangles): the growing period from March to May and the dry period from July to September.

Synoptic patterns

Table 1 shows the mean and standard error of environmental variables associated with varying soil CO_2 molar fractions (χ_c) during both periods. For the growing period (from March to May) deep soil CO_2 molar fractions (χ_c) are nearly double (χ_c ~943 ppm at 0.5 m, and 813 ppm at 1.5 m) the shallow χ_c (~515 ppm at 0.15 m). At all depths the soil temperature has a similar mean (15.6 ºC, 15.7 ºC and 15.5 ºC at 0.15 m, 0.5 m and 1.5 m respectively) as can be appreciated in Figure 1A, and the soil water content increases with depth with values of 11.1 %, 11.6 %, and 15.3 %. During the dry period (from July to September) the deep soil CO_2 molar fractions (χ_c) are more than double (χ_c

~1115 ppm at 0.5 m, and 1142 ppm at 1.5 m) that of the shallow layer (~473 ppm at 0.15 m). The soil temperature decreases with depth, showing values of 30.8 ºC, 29.4 ºC and 26.1 ºC at 0.15 m, 0.5m and 1.5 m respectively, and for the same depths the soil water content increased from 1.4 % to 7.2 % and 13.7 % respectively.

Comparing the growing period *versus* dry period, it is observed that the shallow sensor detects more χ_c during the growing period, whereas deep χ_c is higher during the dry period (Table 1). As is commonly found in semiarid sites, soil temperatures are higher in the dry period than in the growing period, as opposed to what occurs with the soil water content. The mean pressure (p) and friction velocity (u_*) are similar for both periods, while air temperature is 10ºC higher during the dry period.

	Depth	χ_c	Soil T	SWC	Pressure	Air T	u_*
March-April	0.15 m	514.8 ± 3.3	15.6 ± 0.1	11.1 ± 0.1	987.7 ± 0.1	14.3 ± 0.1	0.4 ± 0.0
	0.5 m	943.3 ± 7.1	15.7 ± 0.0	11.6 ± 0.0			
	1.5 m	813.2 ± 7.4	15.5 ± 0.0	15.3 ± 0.0			
July-August	0.15 m	473 ± 4.0	30.8 ± 0.0	1.4 ± 0.0	986.3 ± 0.1	25 ± 0.1	0.4 ± 0.0
	0.5 m	1114.9 ± 11.2	29.4 ± 0.0	7.2 ± 0.0			
	1.5 m	1142 ±12.6	26.1 ± 0.0	13.7 ± 0.0			

Table 1. Mean ± standard error of soil CO_2 molar fractions (χ_c, ppm), soil temperatures (T, ºC), soil water contents (SWC, $m^3\ m^{-3}$), friction velocity (u_*, $m\ s^{-1}$), barometric pressure (hPa) and air temperature (ºC) during growing (March/April) and dry (July/August) periods of 2010 and 2011.

The soil CO_2 molar fraction (χ_c) shows strong inverse correlation with atmospheric pressure (p) on synoptic scales throughout the whole study period, as exemplified for four selected months (Fig. 2). Increments in χ_c correspond to decreases in p and *vice versa* both in the growing period (Fig. 2A) and in the dry period (Fig. 2B). The changes in the magnitude of p are higher in the growing period than in the dry period; however the variability in χ_c is lower in the growing period. Approximately every 3 days important changes occur in deep χ_c, with nearly identical values and trends at 0.5 and 1.5 m. Shallow χ_c has a similar trend, in that the highest peaks occur on the same days; however not all deep χ_c peaks correspond to maxima near the surface (e.g. 22 July and 31 July). Such inverse correlation between χ_c and p extends to shorter time scales during the two vegetative periods, which will now be seen in higher resolution data corresponding to the red rectangles in Figure 2.

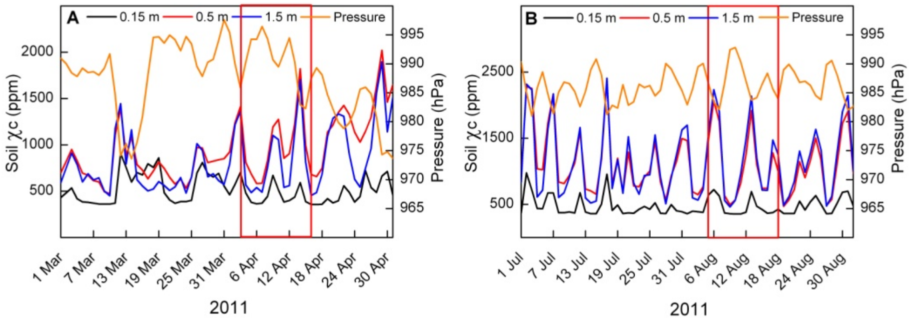

Figure 2. Average daily values at 0.15 m (black), 0.5 m (red) and 1.5 m (blue) depth of soil CO_2 molar fraction (χ_c) and atmospheric pressure (orange) during two months for the growing period (panel A, March-April) and dry period (panel B, July-August). The red rectangle delimits the period amplified in Figure 3.

Daily patterns

The deep soil CO_2 molar fraction (χ_c) can jump to more than triple its mean value within a few hours, and shows inverse correlation with pressure (p) even at hourly time scales. Half-hour resolution data show that both p and deep χ_c (0.5 and 1.5 m) display two cycles per day, both during the growing season (Fig. 3A) and in the dry season (Fig. 3B). Excepting synoptic pressure changes such as the events on 8&14 April and 6&12 August, pressure typically has diurnal changes with an amplitude of ca.3 hPa and a 12-hour period. Deep χ_c shows a similar pattern with clear periodicity and two cycles per day, but some days have an amplitude up to 2000 ppm in few hours (14 August) during this period of modest deep χ_c variability (*cf*. Figs. 1 and 2). However shallow χ_c shows no such clear cyclic behavior.

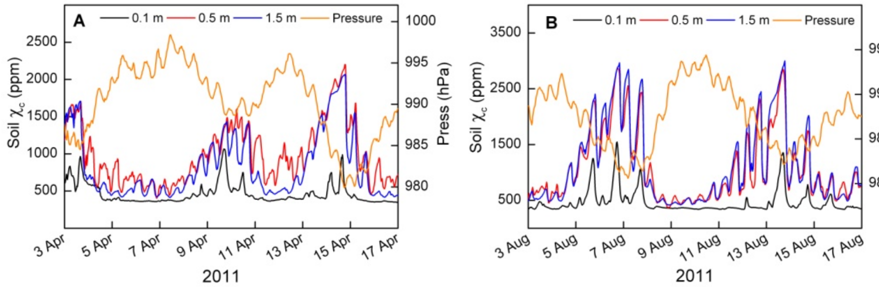

Figure 3. Average half-hour values at 0.15 m, 0.5 m and 1.5 m depth of soil CO_2 molar fraction (χ_c) and atmospheric pressure for a period of 14 days during the growing period (panel A, April) and dry period (panel B, August).

Environmental factors that correlate with χ_c are summarized in Tables 2 and 3 for the growing and dry periods, respectively. During the growing period the main factors implicated in the soil χ_c variations are the soil *T* and *SWC* (Table 2), whereas in the dry period they are u_* and *p* together with *SWC* (Table 3). In the growing period (Table 2), the shallow χ_c variations on daily timescales (0.5 days) show high correlation with *T* and *SWC* at 0.15 m (R^2 0.66 and 0.58, respectively). On daily timescales the main factors implicated in the deep χ_c variations are *T* and *SWC* at 1.5 m, however on synoptic timescale (3 days) pressure is the main determinant (R^2 0.35 and 0.43 at 0.5 m and 1.5 m respectively). During the dry period (Table 3), shallow χ_c variations show maximum correlation on daily timescales with u_* ($R^2 = 0.53$). For deep χ_c variations, the maximum correlations are found with *p* at daily timescales, and with both *p* and *SWC* at synoptic scales.

	Shallow		Deep			
	0.15 m		0.5 m		1.5 m	
	0.5 days	3 days	0.5 days	3 days	0.5 days	3 days
u*	0.00	0.01	0.01	0.00	0.05	0.00
T 0.1	**0.66**	**0.21**	0.21	0.10	0.23	**0.12**
SWC 0.1	**0.58**	**0.16**	0.23	0.11	0.24	0.05
T 0.5	0.04	0.03	0.12	0.03	0.12	0.01
SWC 0.5	0.05	0.05	0.12	0.03	0.15	0.03
T 1.5	0.30	**0.16**	**0.39**	**0.12**	**0.38**	0.10
SWC 1.5	0.37	**0.16**	**0.40**	**0.12**	**0.39**	0.10
Pressure	0.00	-0.13	-0.06	**-0.35**	-0.23	**-0.43**

Table 2. Correlation coefficients (R2) during the growing period (Fig. 2A) between soil CO2 molar fractions (*χc*) at three depths (0.15, 0.5 and 1.5 m), on timescales of 0.5 days and 3 days, versus environmental parameters: pressure, friction velocity (u*), soil temperatures (*T*) and soil water contents (*SWC*) at the same three depths. Negative values denote inverse correlation. Highlighted values denote the two highest magnitudes for each depth and time scale.

	Shallow		Deep			
	0.15 m		0.5 m		1.5 m	
	0.5 days	3 days	0.5 days	3 days	0.5 days	3 days
u*	**0.53**	0.24	0.04	0.05	0.08	0.06
T 0.1	**0.46**	**0.32**	0.05	0.10	0.12	0.10
SWC 0.1	**-0.46**	**-0.33**	-0.07	-0.11	-0.14	-0.12
T 0.5	-0.38	-0.03	-0.06	0.01	-0.12	0.00
SWC 0.5	0.39	0.03	0.07	0.00	0.13	0.00
T 1.5	-0.09	-0.14	-0.14	-0.25	-0.17	-0.24
SWC 1.5	0.06	0.26	**0.28**	**0.61**	**0.30**	**0.62**
Pressure	0.00	-0.14	**-0.40**	**-0.49**	**-0.45**	**-0.50**

Table 3. Correlation coefficients (R^2) during the dry period (Fig. 2B) between soil CO_2 molar fractions (χ_c) at three depths (0.15, 0.5 and 1.5 m), on timescales of 0.5 days and 3 days, versus environmental parameters: pressure, friction velocity (u_*), soil temperatures (*T*) and soil water contents (*SWC*) at the same three depths. Negative values denote inverse correlation. Highlighted values denote the two highest magnitudes for each depth and time scale.

Coupling deep soil CO_2 variations with the atmosphere

Ecosystem-scale CO_2 exchanges (F_C) are shown during the growing period (6-17 April 2011) together with the soil CO_2 molar fraction (χ_c) at different depths in Figure 4. Positive fluxes indicate emissions to the atmosphere and negative fluxes indicate uptake, so that during this period the ecosystem acts as a carbon sink. Over the week presented, the daily minima in F_C (corresponding to maximum uptake), coincide with the variations in χ_c. Days with high soil χ_c (9, 10, 13 and 14 of April) correspond to lower CO_2 uptake during daytime (Fig. 4).

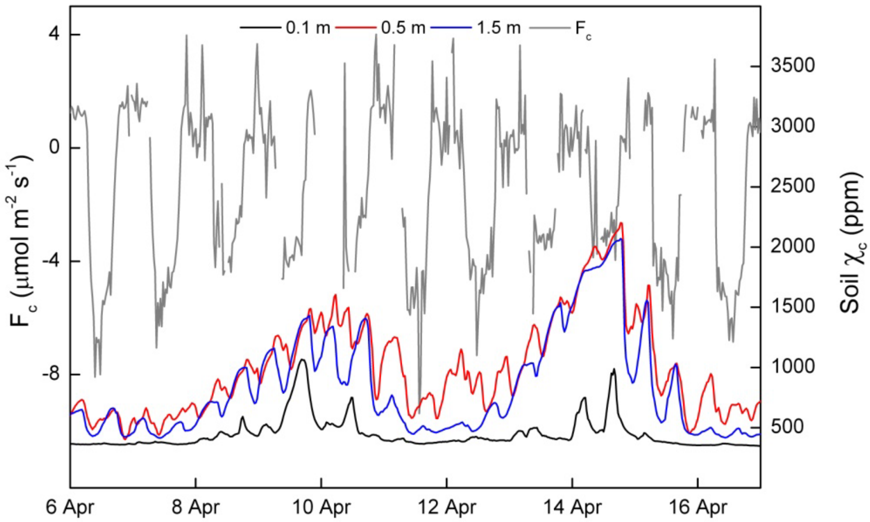

Figure 4. Average half-hour values at 0.15 m (black), 0.5 m (red) and 1.5 m (blue) depth of soil CO_2 molar fraction (χ_c) and ecosystem-scale CO_2 fluxes (gray) measured by eddy covariance (F_C; negative values represent uptake).

The week presented was sunny with typical variation in the air temperature and no rain (data not shown), so the *Fc* variations cannot be attributed to changing physiological drivers. Figure 5 shows the ecosystem light response using the hyperbolic model described in the equation (2), distinguishing between days with decreasing versus increasing atmospheric pressures (Figs. 3A and 4). Table 4 shows parameters obtained from ecosystem light response curves; for both days with decreasing and increasing *p*, the canopy light utilization efficiency (α) and the ecosystem respiration (γ) are similar, however the maximum CO_2 uptake rate of the canopy at light saturation (*β)* increased by 43% during days with increasing pressure.

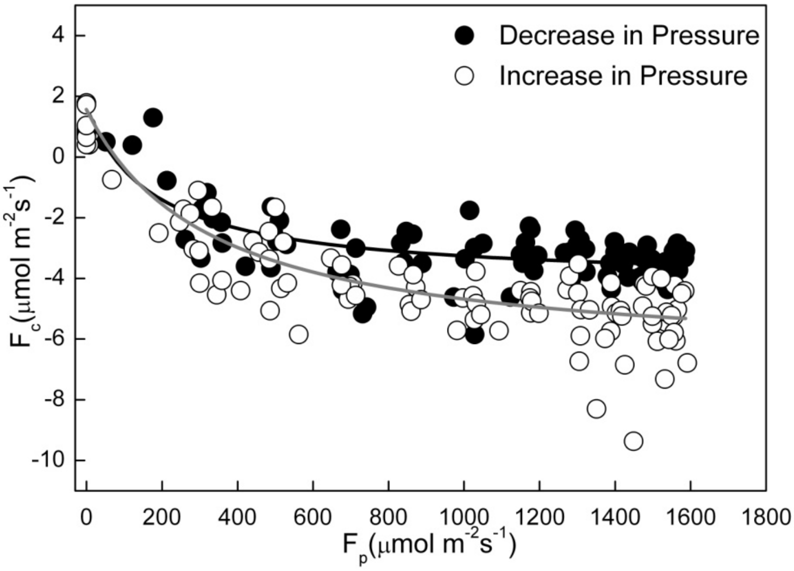

Figure 5. Ecosystem light response curves. Daytime ecosystem CO_2 flux (F_C, μmol m^{-2} s^{-1}) versus the flux of photosynthetically active photons (F_P; μmol m^{-2} s^{-1}) for days from Figures 3A and 4 falling into two categories: days with decreasing atmospheric pressure and increasing deep soil CO_2 (black circles; 9,10,13,14 April) and *vice versa* (white circles; 11, 12, 15, 16 April). No changes in daily patterns of physiological drivers (temperature, relative humidity, net radiation or soil water content) were observed over the selected days.

Days	α	β	γ
Decreasing pressure	-0.032 ±0.007	-5.8±0.3	1.6±0.2
Increasing pressure	-0.025±0.006	-8.3±0.5	1.6±0.3

Table 4. Parameters obtained from ecosystem light response curves shown in Figure 5. Where α (μmol C J^{-1}) is the canopy light utilization efficiency and represents the initial slope of the light–response curve, β (μmol C m^{-2} s^{-1}) is the maximum CO_2 uptake rate of the canopy at light saturation and γ (μmol C m^{-2} s^{-1}) is the ecosystem respiration during the day.

4.4.4. Discussion

Variations in these deep soil CO_2 molar fractions (χ_c) are due, not to biology, but rather to physical factors, most notably changes in pressure (p). These variations can be divided into two scales: the seasonal scale (Fig. 1), where deep χ_c correlates with soil temperature (T) and is inversely correlated to soil water content (*SWC*); and shorter – synoptic and hourly – scales (Figs. 2 and 3), where deep χ_c is clearly inversely correlated with *p* and can increment by a factor of four in a few hours. This behavior of deep χ_c is in contrast with that of shallow χ_c, which on seasonal scales (Fig.1) is better described in terms of commonly reported semiarid conditions where soil respiration is clearly restricted by drought [*Barron-Gafford et al.*, 2011; *Maranon-Jimenez et al.*, 2011; *Oyonarte et al.*, 2012; *Rey et al.*, 2011], showing an inverse correlation with *T* and correlation with *SWC*. Shallow χ_c shows maxima in winter and minima in summer coinciding with vegetation activity during winter [*Rey et al.*, 2012b]. The similar behavior of the two deep sensors suggests that the deep pore spaces are highly interconnected, at least within the same caliche horizon.

Such large variations in deep χ_c have no direct biological explanation, but suggest an underlying CO_2 reservoir in communication with the surface depending on factors such as *p*, u_* or *SWC*. The origin of the CO_2 reservoir could be either geothermal (i.e., magmatic or metamorphic; [*Rey et al.*, 2012a]) or biological in origin. Geothermal sources may exist at depth below Balsa Blanca because the site is located over a large active tectonic fault system. Biological origins would be due to CO_2 storage in deep layers resulting from plant activity. The CO_2 respired in the root zone increases air density [*Kowalski and Sanchez-Canete*, 2010; *Sanchez-Canete et al.*, 2013], and so enables gravitational percolation through the pore space toward deeper layers where it can be stored.

Although in this study *p* is the main factor implicated in deep χ_c variations, Figure 1 shows that χ_c variability is greater in summer when *p* variations are reduced. This highlights the important role of *SWC* in CO_2 exchange: despite greater synoptic pressure variability, winter has lower χ_c variations because soil pores are filled with water, limiting gas flows. In summer, by contrast, ventilation is facilitated by dry soil conditions with gas-filled pore space [*Cuezva et al.*, 2011; *M. Maier et al.*, 2010]. This explains why the growing period shows a positive correlation between shallow χ_c and *SWC* at 0.15 m (Table 2) and a negative correlation during the dry season (Table 3), since during the dry season there is less water in the shallow soil layer allowing the flow of CO_2-rich air from the deep soil to near surface layers.

At synoptic scales, passing frontal systems cause increases/decreases in *p* leading to fourfold decreases/increases in deep χ_c (Fig. 2). Such variability can only be explained by CO_2 transported from depth towards the surface. A simple model to explain the role of pressure (*p*) in subterranean CO_2 transport is shown in Figure 6. When *p* increases, the soil air is compressed and atmospheric air penetrates into the soil decreasing the deep χ_c. Similarly, when *p* decreases, the soil air expands increasing the deep χ_c since deeper soil air distends toward the surface.

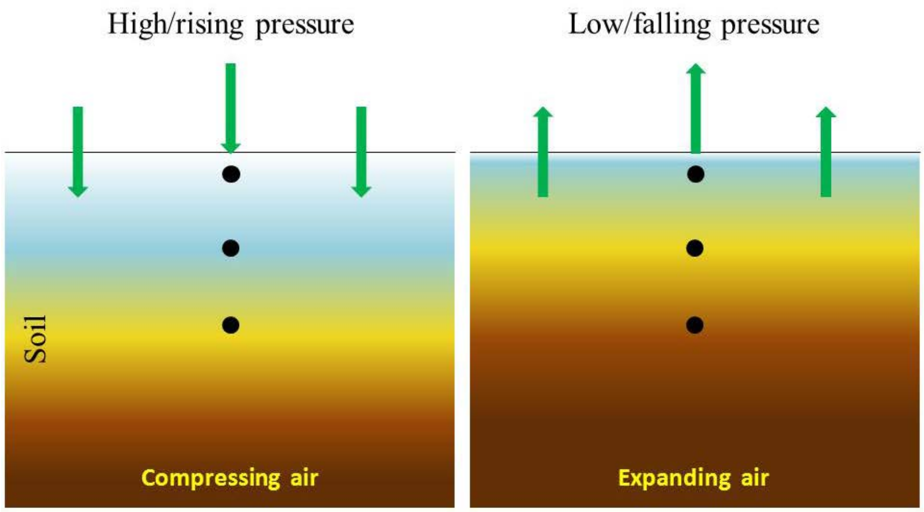

Figure 6. Schematic of CO_2 transport in soil air layers (a) compressing under high/rising synoptic pressure, and (b) expanding under low/falling pressure. High CO_2 molar fractions are denoted in brown and low values in blue.

Hourly time scales (Fig. 3) show clear inverse correlation between the deep χ_c and *p*, where even small daily p oscillations (3 hPa) due to twice daily atmospheric tides (Lindzen, 1979) generate large variations in χ_c at depth (2000 ppm; e.g., falling χ_c on 12 August, Fig. 3B). Deep soil χ_c (0.5 and 1.5 m) shows two cycles per day, in rhythm with *p*, whereas shallow χ_c has just one. This is consistent with correlations with the friction velocity and biological drivers (*T*, *SWC*), but not with p (Table 3). Shallow χ_c is more affected by friction velocity because it is in the upper part of the soil, and thus more easily ventilated decreasing χ_c [Hirsch et al., 2004; Sanchez-Canete et al., 2011]. Similarly, Rey et al. (2012a) concluded that the wind was the main driver of the net ecosystem carbon balance at this experimental site.

The effects of emissions from deep CO_2 soil were registered in the atmosphere driven by synoptic pressure changes. The light-response curves demonstrated that on both consecutive and non-consecutive days and near-constant environmental conditions (temperature, relative humidity, net radiation and soil water content), the maximum downward CO_2 flux toward the canopy at light saturation increased by 43% during days with increasing synoptic pressure, versus those with falling pressure. This is in accordance with the explanatory diagram of Figure 6. With rising pressure, part of the CO_2 respired by plants tends to accumulate in the soil, registering more negative eddy fluxes and therefore obtaining a high value of β, which might be interpreted erroneously as the maximum CO_2 uptake rate of the canopy at light saturation (as in Eq. 2). However, with falling pressure, both CO_2 stored in the soil and that respired by plants is emitted to the atmosphere, making eddy fluxes less negative and lowering the value of β. The results presented in this paper invite research on other semiarid ecosystems regarding the influence of synoptic pressure changes on variations in deep soil CO_2 molar fractions and its role on the net ecosystem carbon balance.

4.4.5. Conclusions

This study reveals that during both growing periods and dry periods, variations in the deep soil CO_2 molar fraction (χ_c) are due predominantly to atmospheric pressure (p) variations and not directly to biological influences. In a few hours, the deep χ_c can increase or decrease fourfold, highlighting the need for continuous (versus sporadic) monitoring of soil CO_2 effluxes. Deep χ_c has a pattern with two cycles per day, due to p oscillations caused by atmospheric tides. Nonetheless shallow χ_c has a pattern with one cycle per day, due to it is dependence mainly on the friction velocity during the dry period and on biological factors during both dry and growing periods, showing maxima for this semi-arid ecosystem when soil water content is not limiting, with temperature dependence as well. The effects of emissions from deep soil CO_2 were registered in the atmosphere driven by synoptic pressure changes: on days with rising pressure the downward CO_2 flux is higher than days with falling pressure because on these days CO_2 respired by plants accumulates in the soil. Future studies focused on determining the net ecosystem carbon balance should not rely exclusively on Fick's law to calculate soil CO_2 effluxes from profile data.

Acknowledgements

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5. General discussion and conclusions

5.1 General discussion

State of the art Subterranean CO_2

The study of CO_2 underground in both soils and caves has been undertaken since the late 20th century [*Crowther*, 1983; *Ek and Gewelt*, 1985; *Kiefer and Amey*, 1992]. Such studies have focused mainly on measurements in the first few centimeters of soil, through air sampling and subsequent laboratory analysis. From the last decade of 20th century until the present, underground CO_2 studies have mainly focused on surface-atmosphere CO_2 exchanges, through the use of surface chambers and disregarding what happens at depth.

In the first decade of the 21st century new studies have arisen focused on measurements of subterranean CO_2. Hirsch et al. [2002] is one of the first authors that monitored CO_2 behavior with an automated soil gas sampling system in a vertical profile (0-50cm), followed by others scientists [*DeSutter et al.*, 2006; *Hirsch et al.*, 2004; *Jassal et al.*, 2005; *Novak*, 2007; *Pumpanen et al.*, 2008; *Risk et al.*, 2008; *Takahashi et al.*, 2004; *Tang et al.*, 2003]. Many of these authors estimated CO_2 fluxes emitted by applying Fick's Law, also termed the gradient method. However, our studies show that Fick's law is not applicable in semi-arid lands when the wind is high [*Sanchez-Canete et al.*, 2011] or when pressure changes [*Sanchez-Canete et al.*, 2013b].

In addition, studies of CO_2 in caves have focused mainly on identifying the factors involved in cave ventilation. Until the publication of the article by Kowalski & Sánchez-Cañete, [2010] and subsequently Sánchez-Cañete et al. [2013a], cave ventilation was determined as a function of differences between outside and inside temperatures. However these articles represent a landmark because they show the importance of CO_2 in determining the cave ventilation.

Now it is necessary to change the point of view regarding CO_2 exchange studies from an inappropriately conceived static system in which all CO_2 respired is directly emitted by molecular processes to the atmosphere, to a dynamic system with gas transport by three different processes: convection, advection and molecular diffusion. It has been observed than soils can exchange/store large CO_2 amounts as a function of numerous natural processes. Large amounts of CO_2 are stored in the soil with possibility to be exchanged with the atmosphere [*Benavente et al.*, 2010; *Ek and Gewelt*, 1985] through processes of convection, advection or molecular diffusion. **Convective processes** are mainly relevant in caves, where the values of relative humidity, temperature and CO_2 molar fraction determine the buoyancy of the external-internal air masses, and therefore determine when ventilation can occur [*Kowalski and Sanchez-Canete*, 2010; *Sanchez-Canete et al.*, 2013a]. These convective processes also are important in large fractures when temperature differences between surface and depth can generate air convection, transporting CO_2 from deep layers to the atmosphere. **Advective processes** occur both in caves and in soils and the CO_2 exchanges are mainly due to three factors:

1) the wind, which can penetrate into the soil permitting forcing gas exchange [*Bowling and Massman*, 2011; *Maier et al.*, 2012; *Sanchez-Canete et al.*, 2011];
2) changes in atmospheric pressure, which compress and expand the soil air allowing its exchange [*Comas et al.*, 2011; *Sanchez-Canete et al.*, 2013b], and
3) changes in the water table; variations in the aquifer volumes can provoke emission or storage of CO_2 within the soil pore space as demonstrated with variations due to ocean tides [*Jiao and Li*, 2004; *Werner et al.*, 2013].

Processes due to molecular diffusion are being widely applied in the determination of soil-atmosphere gas exchanges [*Barron-Gafford et al.*, 2011; *Bowling et al.*, 2011; *Davidson and Trumbore*, 1995; *Pingintha et al.*, 2010; *Pumpanen et al.*, 2008]. However Fick's Law should only be applied in the absence of advective or convective processes.

Recent relevant publications

During the years of writing this dissertation, and since publication of the first articles, numerous papers have emerged to improve knowledge of CO_2 exchanges between the atmosphere and the subsurface (caves and soils). Articles focused on Cave-Atmosphere exchanges have focused mainly on determining ventilation as a function of temperature differences, disregarding the effects of air composition on buoyancy. Following publication of the specious Badino [2009] article entitled "The legend of carbon dioxide heaviness", and having reviewed literature that highlights high concentrations of CO_2 in soil air, Kowalski & Sánchez-Cañete in [2010] developed some formulas to correctly determine the buoyancy of a CO_2–rich air mass. Still, some speleologists continued to use temperature differences to incorrectly determine ventilation [e.g., *Boch et al.*, 2011; *J. Faimon and Licbinska*, 2010; *J. Faimon et al.*, 2012; *Gregoric et al.*, 2011; *Kowalczk and Froelich*, 2010]. This motivated the publication of Sanchez-Cañete et al. [2013a], who provided a more practical overview, showing in different caves of the world the substantial errors that can occur when the role of carbon dioxide is ignored. Although some authors are already using the new equations to correctly interpret ventilation in caves [*Bourges et al.*, 2012; *Jiří Faimon and Lang*, 2013; *Fairchild and Baker*, 2012; *Nachshon et al.*, 2012], studies still may be found that do not take into account the CO_2 effect [*Gregoric et al.*, 2013].

Regarding the research line of soil-atmosphere CO_2 exchanges, numerous contributions to the literature have appeared over the past four years. Deserving of special attention are publications determining CO_2 exchange with the atmosphere through the use of subterranean profiles, using the gradient method [*Liang et al.*, 2010; *Pingintha et al.*, 2010; *Sullivan et al.*, 2010]. Although in less in number, other studies have also appeared showing that the gradient method, based on the Fick's Law, is not always applicable because the transport of gases from the ground to the atmosphere is affected by other factors such the wind [*Bowling and Massman*, 2011; *Nachshon et al.*, 2012; *Sanchez-Canete et al.*, 2011], soil thermal gradients [*Ganot et al.*, 2012; *Moore et al.*, 2011; *Weisbrod et al.*, 2009], or changes in pressure [*Lampkin*, 2010; *Rinaldi et al.*, 2012; *Sanchez-Canete et al.*, 2013b]. Despite these and other publications, knowledge of subterranean CO_2 dynamics is still a novel research area in which there remain many gaps of understanding to enable correct modeling [*Perez-Priego et al.*, 2013; *Roland et al.*, 2013].

Perspectives on future research

The study of subterranean CO_2 is a field which can still be explored from many points of view. I hope to continue along this same line of research because it offers many opportunities for advancing the state of science. Here I outline some lines of inquiry that could generate knowledge and clarify uncertainties.

a) Additional subterranean CO_2 profiles, such as those measured in the Sierra de Gádor and in Balsa Blanca, could be installed in other semiarid ecosystems around the world to check whether the results from these sites can be extrapolated elsewhere. For this reason, in my last research visit (2011) to the Southwest Watershed Research Center

(Arizona, EE UU), we installed several profiles whose data I intend to analyze during the summer of 2013.

b) Monitor CO_2 in different boreholes of the world, to characterize the mean CO_2 molar fraction in the different ecosystems, lithologies and depths, and so estimate at the planetary scale: how much CO_2 is stored in the vadose zone? And furthermore, what factors are implicated in its exchange with the atmosphere?

c) Monitor CO_2 and heat fluxes between the atmosphere and boreholes, fractures or caves. We have recently initiated such an effort at the Nerja Cave (Málaga, Spain).

d) Investigate gas emissions produced - mainly in karst areas - due to increments in the water table and consequent displacement of the air to the atmosphere.

5.2 Conclusions

This thesis contributes to increase scientific knowledge on CO_2 exchanges between the atmosphere and deep soil, distinguishing the drivers involved in its transport. The main conclusions of the thesis are the following:

From a methodological point of view, never before has a study has taken into account the role of underground CO_2 in modifying air density, despite numerous studies of the buoyancy of cave air. Due to results developed in this thesis, it is now possible to determine when ventilation may occur due to differences between the buoyancy of air masses. It has been shown that in cases where CO_2 molar fractions of internal air exceed atmospheric values by an order of magnitude or more, it is necessary to take into account the heaviness of CO_2 when calculating the virtual temperature and thereby buoyancy. If CO_2 is not taken into account when external and internal air masses have the same temperature, it can cause errors close to 9ºC in the virtual temperatures. Therefore, for the correct interpretation of cave-atmosphere exchanges it is necessary to use the formulas developed in this thesis.

Similarly, the results of this thesis have shown the important effect that wind (through friction velocity) and atmospheric pressure changes can have on CO_2 emissions to the atmosphere from soil. In *El Llano de los Juanes* subterranean ventilation, detected both in soil (25 cm) and in the borehole (7 m) during periods of plant senescence (drought), is mainly driven by high values of the friction velocity. During calm days soil CO_2 accumulates in the soil, whereas during windy days large quantities of CO_2 are emitted to the atmosphere. By contrary, in *Balsa Blanca*, variations in soil CO_2 molar fractions (χ_c) depend on different factors depending on the depth. Shallow χ_c (15 cm) has a pattern with one cycle per day, due to the friction velocity during the dry period and *T* or *SWC* during the growing period. However variations in deep χ_c (0.5-1.5 m) were mostly due to atmospheric pressure changes during both periods and not due to biological factors related with soil respiration (which depend on *SWC* or soil temperature). At depth, χ_c exhibited two cycles per day caused by pressure changes due to atmospheric tides, and also responded to synoptic pressure changes. On days with rising pressure, the downward CO_2 flux is higher than on days with falling pressure because on these days CO_2 respired by plants accumulates in the soil. Emissions of CO_2 from the deep soil were registered in the atmosphere driven by synoptic pressure changes.

Finally, the results obtained from both ecosystems demonstrate the value of continuous (versus sporadic) monitoring of soil CO_2 effluxes, because sporadic measurements can over/underestimate soil CO_2 emissions, depending on whether they coincide with windy or calm days, and also with rising or falling atmospheric pressure. What is more, CO_2 accumulated in the soil can be quickly emitted to the atmosphere via ventilation and therefore such processes should be included in current models of surface CO_2

exchanges. Future studies focused on determining the net ecosystem carbon balance should not rely exclusively on Fick's law to calculate soil CO_2 effluxes from profile data.

5.3 Conclusiones

Esta tesis contribuye a incrementar el conocimiento científico de los intercambios de CO_2 entre la atmósfera y el subsuelo, poniendo el énfasis en los diferentes factores implicados en su transporte. Las principales conclusiones que esta tesis aporta a la ciencia son las siguientes.

Desde un punto de vista metodológico, nunca antes un estudio ha tenido en cuenta el papel del CO_2 subterráneo en la modificación de la densidad del aire, a pesar de los numerosos estudios sobre la flotabilidad del aire en cavidades subterráneas. Con el trabajo desarrollado en esta tesis, ahora es posible determinar con precisión cuándo puede ocurrir la ventilación debido a diferencias entre la flotabilidad de las masas de aire exterior e interior de una cavidad. Se ha demostrado que en los casos en que la fracción molar del CO_2 del aire de la cueva excede un orden de magnitud o más de los valores exteriores, es necesario tener en cuenta el efecto del CO_2 para la determinación de su temperatura virtual y con ello su flotabilidad. Si no se tiene en cuenta el efecto del CO_2, cuando la diferencia temperatura del aire en el exterior y en el interior es la misma, se pueden cometer errores cercanos a 9ºC en las temperaturas virtuales. Por lo tanto, es necesario la aplicación de la metodología desarrollada en esta tesis para la correcta interpretación de los intercambios cueva-atmósfera.

Igualmente, fruto de esta tesis, es la demostración del importante efecto que el viento (a través de la velocidad de fricción) y los cambios en la presión atmosférica pueden tener en las emisiones de CO_2 a la atmósfera procedentes del suelo. En el Llano de los Juanes, se encontró que la ventilación subterránea, detectada tanto en el suelo (0.25 m) como en una perforación (7 m) en periodos de senescencia (sequía), es producida fundamentalmente por la velocidad de fricción. Se observó que durante días sin viento el CO_2 se acumula en el suelo, mientras que en días ventosos las grandes cantidades de CO_2 previamente acumuladas son emitidas a la atmósfera. Por el contrario, en Balsa Blanca, las variaciones en la fracción molar de CO_2 del suelo dependen de distintos factores en función de la profundidad. Las medidas de CO_2 en el horizonte más superficial (0.15 m) mostraron un sólo ciclo diario como consecuencia de variaciones en la velocidad de fricción durante el periodo sequía y variaciones en la temperatura del suelo y/o el contenido de agua durante la época de crecimiento biológico. Por el contrario, en profundidad (0.5-1.5 m), tanto en el periodos de sequía como en periodos de crecimiento, las variaciones en la fracción molar de CO_2 responden a variaciones en la presión atmosférica y no a factores abióticos directamente relacionados con la respiración (temperatura o el contenido de agua en el suelo). Así, en la fracción molar de CO_2 profundo se observaron dos ciclos diarios causados por las oscilaciones de presión debidas a las mareas atmosféricas. Los cambios en la fracción molar profunda debidos a cambios sinópticos en la presión dieron lugar a emisiones de CO_2 que fueron registradas con la torre *Eddy Covariance*.

Finalmente, los resultados obtenidos en ambos ecosistemas demuestran la enorme importancia de las medidas en continuo del contenido de CO_2 en el suelo frente a medidas puntuales. El principal motivo radica en que estas medidas puntuales pueden llegar a sobrestimar o subestimar las emisiones de CO_2 procedentes del suelo, en función de las condiciones ambientales en las que se realicen las campañas (días con más o menos viento o con alta o baja presión atmosférica). Igualmente, se ha observado en ambos ecosistemas que el CO_2 acumulado en el suelo puede ser rápidamente emitido a la atmósfera por procesos de ventilación y por tanto estos procesos deberían incluirse en los modelos de intercambio de CO_2 entre el suelo y la superficie. En este sentido, futuros estudios centrados en la determinación del balance neto de carbono no deberían basarse exclusivamente en la ley de Fick para calcular las emisiones de CO_2 procedentes de los datos de un perfil.

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List of abbreviations

AR	Autotrophic respiration
C	Carbon
DIC	Dissolved inorganic carbon
DOC	Dissolved organic carbon
EC	Eddy covariance
GHG	Greenhouse gas
GHGs	Greenhouse gases
GPP	Gross primary production
HR	Heterotrophic respiration
IRGA	Infrared gas analyzer
NECB	Net ecosystem carbon balance
NEE	Net ecosystem exchange
NEP	Net ecosystem production
PAR	Photosynthetically active radiation
RH	Relative humidity
SWC	Soil water content
UN	United Nations
UNFCCC	United Nations Framework Convention on Climate Change
VOC	Volatile organic carbon

List of symbols

α	Canopy light utilization efficiency
A_i	Power received from the source in an absorbing wavelength for gas *i*
α_i	Absorptance by gas i
A_{io}	Power received from the source in a reference wavelength that does not absorb gas *i*
β	Maximum CO_2 uptake rate of the canopy at light saturation
χ_c	CO_2 molar fraction
ε_i	Ratio of the molecular mass of constituent *i* to that of the gas mixture
F	Turbulent flux
F_C	CO_2 flux
$\mathrm{F_P}$	Incident photon flux
γ	Ecosystem respiration during the day
I_0	Intensity of radiation in the absorption band with zero concentration of *i* present
I_i	Intensity of incident radiation in the absorption band with some concentration of gas *i* present
m	Molar mass
M_i	Mass of constituent *i*
n_i	Number density
P	Pressure
R	Universal gas constant
ρ	Density
R_d	Particular gas constant for dry air
r_i	Mixing ratio for constituent *i*
σ	Ratio of density of water vapor and dry air
s_c	CO_2 mixing ratio
T	Temperature
τ	Transmittance
T_{ext}	Internal temperature
T_{int}	Exterior temperature
T_v	Virtual temperature
u_*	Friction velocity
w	Vertical wind

Subscripts

c	Carbon dioxide (CO_2)
d	Dry air
noa	Mixture of nitrogen (N_2), oxygen (O_2), and argon (Ar)
mc	Mixture of moist air including CO_2
v	Water vapor

Curriculum Vitae of Enrique Pérez Sánchez-Cañete

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