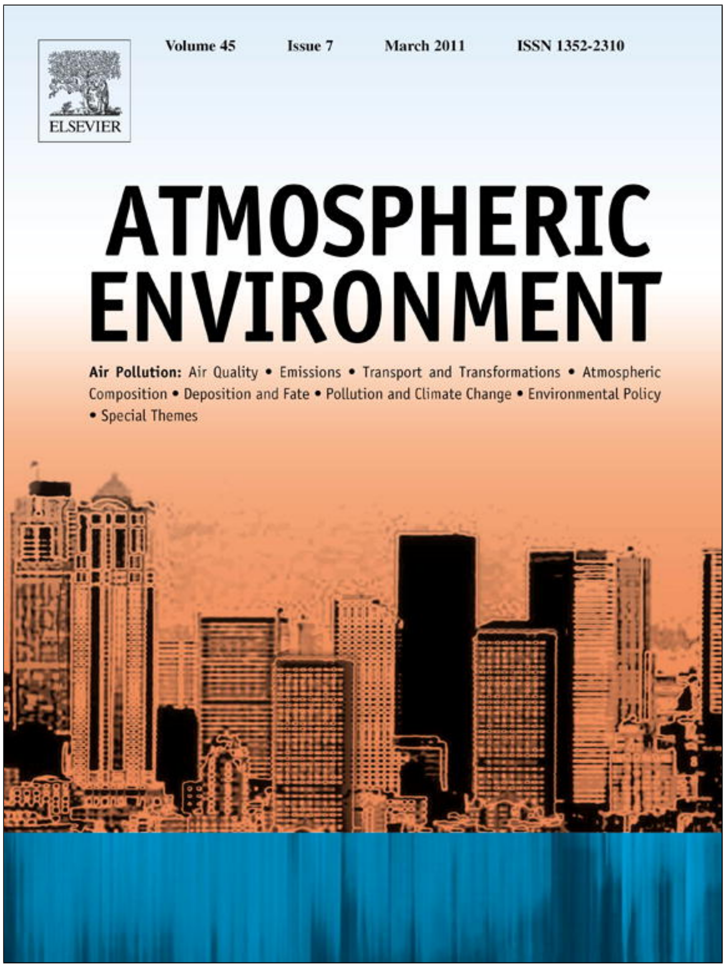
Volume 45
Issue 7
March 2011
ISSN 1352-2310
ELSEVIER
ATMOSPHERIC ENVIRONMENT
Air Pollution: Air Quality • Emissions • Transport and Transformations • Atmospheric Composition • Deposition and Fate • Pollution and Climate Change • Environmental Policy • Special Themes

Atmospheric Environment 45 (2011) 1418–1427

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Short-term CO_2(g) exchange between a shallow karstic cavity and the external atmosphere during summer: Role of the surface soil layer

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ARTICLE INFO

Article history:
Received 3 August 2010
Received in revised form
9 December 2010
Accepted 10 December 2010

Keywords:
Epikarst
Ventilation
Eddy covariance
Soil porosity
Evapotranspiration
Global carbon cycle

ABSTRACT

This study tests the hypothesis that the degree of moisture in the soil pore system determines gas exchange processes (ventilation/charge) between the outer atmosphere and the karst-epikarst during the warm, dry period (summer). These processes explain "anomalous" CO_2 fluxes measured over this and other ecosystems. Emission of CO_2 by ventilation of cavities requires an open double membrane system (host rock and soil) through which air movement can take place (H_2O_{vapour}, CO_2, ^{222}Rn, etc.). An experimental study on the behavior of the soil and host rock porous system under changing air humidity conditions, coupled with a broad analytical approach addressing CO_2 fluxes using the eddy-covariance technique and monitoring of the cave microclimate serves to define the suitable environmental conditions favoring air transfer between the cave atmosphere and exterior. This study shows the correlation between evapotranspiration, CO_2 emissions, and cave ventilation processes due to the daytime opening of the soil membrane. Thus, the role of the soil as a membrane/interface or transfer medium can be observed, and it is directly dependent on weather conditions (temperature, humidity, wind).

1. Introduction

In past decades, the need to characterize the global carbon cycle has led the scientific community to address new aspects of atmospheric CO_2 cycling, including the role of karstic systems. Gas phase CO_2 stocked in karstic systems may represent a substantial fraction of the unknown CO_2 atmospheric sink, but in terms of CO_2 exchange with the atmosphere, the process has not yet been sufficiently studied. Recently Serrano-Ortiz et al. (2010) estimated that the subterranean CO_2 pool could represent more than half of the annual atmospheric sink. Furthermore, CO_2 concentrations in karstic cavities show significant seasonal (Spötl et al., 2005; Fernandez-Cortes et al., 2006, among others) and even daily variations (Baldini et al., 2008; Kowalczk and Froelich, 2010). Large amounts of CO_2(g) are interchanged between the karstic systems and the atmosphere, and a single karstic cavity can act both as CO_2 sink or source (degasification/ventilation processes) at different times. Thus, the non-negligible potential contribution to the net carbon balance requires further research towards a better understanding and interpretation of CO_2 behavior in karstic environments, which must be quantified and distinguished from other (biological, geothermal, volcanic and tectonic) derived CO_2 sources.

An evaluation of CO_2 exchange between the atmosphere and the studied karstic cavities could provide qualitative-quantitative information about the contribution of karstic processes to the global carbon cycle. Exchange processes of CO_2 between the underground and exteriors environment depend on net CO_2 inflows and output, as a result of the (physical–chemical) matter and energy exchange processes between the underground and the surface environment. The CO_2 inputs that penetrate the cavity and become part of the karstic atmosphere do so either directly in gaseous form (Baldini et al., 2006) or through dissolved CO_2 in infiltration waters which generally achieve elevated CO_2 levels from the soil matter (Wood, 1985). This CO_2 derives mainly from soil bioproductivity: microbial respiration, root respiration and faunal respiration (Rastogi et al., 2002). Also, in some cases, there may be CO_2 contributions directly from decomposition of organic material in the cave interior, via microbial activity or through endogenous processes.

The cavities CO_2 outputs are mainly due to ventilation processes but the role of soil and host rock is not yet resolved. According to traditional models CO_2 outputs depend on cave morphology, the number and configuration of cave openings, and microclimatic

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doi:10.1016/j.atmosenv.2010.12.023

relationships with the exterior atmosphere (air temperature and barometric pressure). Rarely has the role of macro- and microfissural epikarstic network processes been contemplated in ventilation processes (Baldini et al., 2006; Bourges et al., 2006), and much less that of the soil. However, preliminary investigations have revealed a complex process of mass and energy transfer within a karstic subterranean environment, relative to the degree of water saturation in the double membrane system (host rock and soil) which envelops the cave atmosphere (Fernandez-Cortes et al., 2010). The eddy covariance technique provides a direct measurement of CO_2 surface-atmosphere exchange (Dabberdt et al., 1993), and therefore permits detection of the CO_2 flux upwelling from the subsoil (epikarst-karst). However, net CO_2 exchange is generally interpreted in terms of a classic model of ecosystem behavior based on purely eco-physiological processes (photosynthesis and respiration) (Baldocchi, 2003) neglecting other exchange processes. During the biological growth period, these classical models invoke for a predominance of the photosynthesis process during the day that result in a CO_2-sink behavior of the ecosystems (negative Fc). During the night, in absence of sunlight, the respiration is the only process and consequently, CO_2 is usually exhalated to the atmosphere (positive Fc). A previous study in the Altamira cave revealed the existence of large diurnal CO_2 emissions during the dry season that pointed out to the probable contribution of karstic CO_2 (Kowalski et al., 2008), but left unaddressed the nature of the environmental factor(s) determining the interconnection patterns between cavity and exterior.

Here we present a study regarding the role of karstic hypogeal environment CO_2 exchange processes that could be involved in the global carbon cycle on short time scales. This study takes place in the Altamira Cave (Cantabria Province, Spain), a shallow (vadose) karstic cavity characterized by remarkable stable environmental conditions (Quindos et al., 1987; Sanchez-Moral et al., 1999; Cuezva et al., 2009) in an area of temperate-humid oceanic climate. The main objective of this study is to shed some light on the nature of the environmental factor(s) allowing interconnection processes between cavity and exterior. Special attention is given to the assessment of gas variations and short-term transfer processes between soil-epikarst and external atmosphere, taking into account water condensation onto the cavity host rock and in the overlying soil. Variations of CO_2 and radon contents in cave air are presented as key parameters to assess the outgassing and isolation processes of a subterranean atmosphere. A closer (shorter timescales) examination is made of the warm, dry period at the end of the summer, when the cave is most coupled to the external atmosphere.

2. Site, materials and methodology

2.1. Field site description

The Altamira cave is world-famous (World Heritage Site, UNESCO) for possessing a remarkable collection of Palaeolithic rock paintings and engravings. Is located in northern Spain, Cantabria province (43°22′40″N; 4°7′6″W), 4 km south of the Bay of Biscay (Fig. 1A). In this geographic area the climate is humid and moderately oceanic. The cave, one of many cavities in the upper vadose area of the karstic system, is located under a hill 161 m.a.s.l. Altamira is situated at a depth of 3–22 m (averaging 8 m) below the surface. The cavity has a sole entrance, situated on a topographical high (152 m.a.s.l.), shut from the outside by a solid door which prevents the free circulation of air and isolates it thermally from the outside. The main cave chamber where the microenvironmental study was performed (The Polychromes Hall) is situated 60 meters from the entrance at a lower topographic level (146.5 m.a.s.l.) (Fig. 1B and C). The rock layer over the chamber averages 7.5 to 8 m thickness. Some exokarstic features (dolines) can be described in the vicinities of the cave.

The host rock of the Altamira Cave is a thin to medium, parallel bedded, Cenomanian (Upper Cretaceous) limestone succession of 13.5 to 15 m thickness, mainly biomicrite and biosparite limestones (99% calcite – LMC-, <0.5%mol $MgCO_3$, 1% quartz), except for a thin interbedded dolomitic level (99% dolomite, 1% quartz).

Overlying the cave is a heterogeneous artificial soil with little development (30–70 cm). Poorly differentiated as a result of its anthropogenic origin (a surface horizon "A" and directly beneath it a subsurface petrocalcic horizon), it is a silicate-based soil with a quartz-rich upper level (above 10 cm with 70–80%) and progressively more clay towards the bottom (lower levels with 50–70% quartz, 15–25% illite, 5–10% of montmorillonite and 0–5% calcite). There is a developed plant cover (mainly pasture) and high organic carbon (10–15%) derived from it.

2.2. Instrumentation

Both internal and external environmental conditions were specifically observed during the summer of 2005. Inside the cave, a micro-environmental monitoring system recorded microclimatic data in the Polychromes, Grave and Well Halls (Fig. 1). A datalogger (dataTaker DT50, Grant Instruments Ltd., Cambridge, UK) was fed voltage and current inputs from a 16-channel multiplexer, and recorded fifteen-minute means of air temperature and relative humidity measurements made every ten seconds (HygroClip S3, which combines a Pt100 1/10 DIN temperature sensor and a humidity sensor, Rotronic), atmospheric pressure (Vaisala BARO-CAP silicon capacitive), and concentrations of CO_2 (Ventostat 8002, Telaire, Goleta, CA, USA) and ^{222}Rn (AB5 Continuous Passive Radon Detector, Pylon, Ottawa, Canada). Outside the cave, a weather station with autonomous datalogger (HOBO, Onset, Bourne, MA, USA) stores fifteen-minute means of air temperature (S-TMB-M0XX 12-bit Smart Sensor, Onset) and total shortwave radiation (PYR-PA Pyranometer precision sensor, Apogee Instruments Inc.).

An open-path eddy covariance system was installed over the grassy lawn above the cave to measure CO_2 fluxes and evapotranspiration. Wind speed and sonic temperature were measured by a three-axis sonic anemometer (model 81000, R. M. Young, Traverse City, MI, USA) at 1.5 m (AGL). Densities of CO_2 and H_2O were measured at the same height by an open-path infrared gas analyzer (Li-Cor 7500, Lincoln, NE, USA) calibrated periodically using an N_2 standard for zero and (variable but known) 500 μmol (CO_2) mol^{-1} gas standards for span. A microcomputer receives serial data via a serial communication port and stores them to disk. Means, variances, and covariances of 20 Hz data were calculated every 30 min using the University of Edinburgh EdiRe Software package according to Reynolds's rules of averaging (Moncrieff et al., 1997). The software includes corrections for density perturbations (Webb et al., 1980) and two coordinate rotations (McMillen, 1988). The area of the homogeneous, flat lawn is ca. 4500 m^2. The height of the grass is in the range of ca 4–15 cm according to an unrecorded mowing scheme.

2.3. Experimental procedures

Several analytical and experimental procedures have been conducted to assess gas variations and transfer processes between the epikarst and external atmosphere, taking into account water condensation onto the cavity host rock and in the overlying soil. To that aim, the host rock and soil pore structure, and the soil water retention and soil water vapor transfer at different relative air humidities were calculated. Five fresh/unweathered rock samples representative of each of the stratigraphic levels were collected inside the cave. In addition to the petrophysical analysis, mineralogical and geochemical characterizations of each sample were

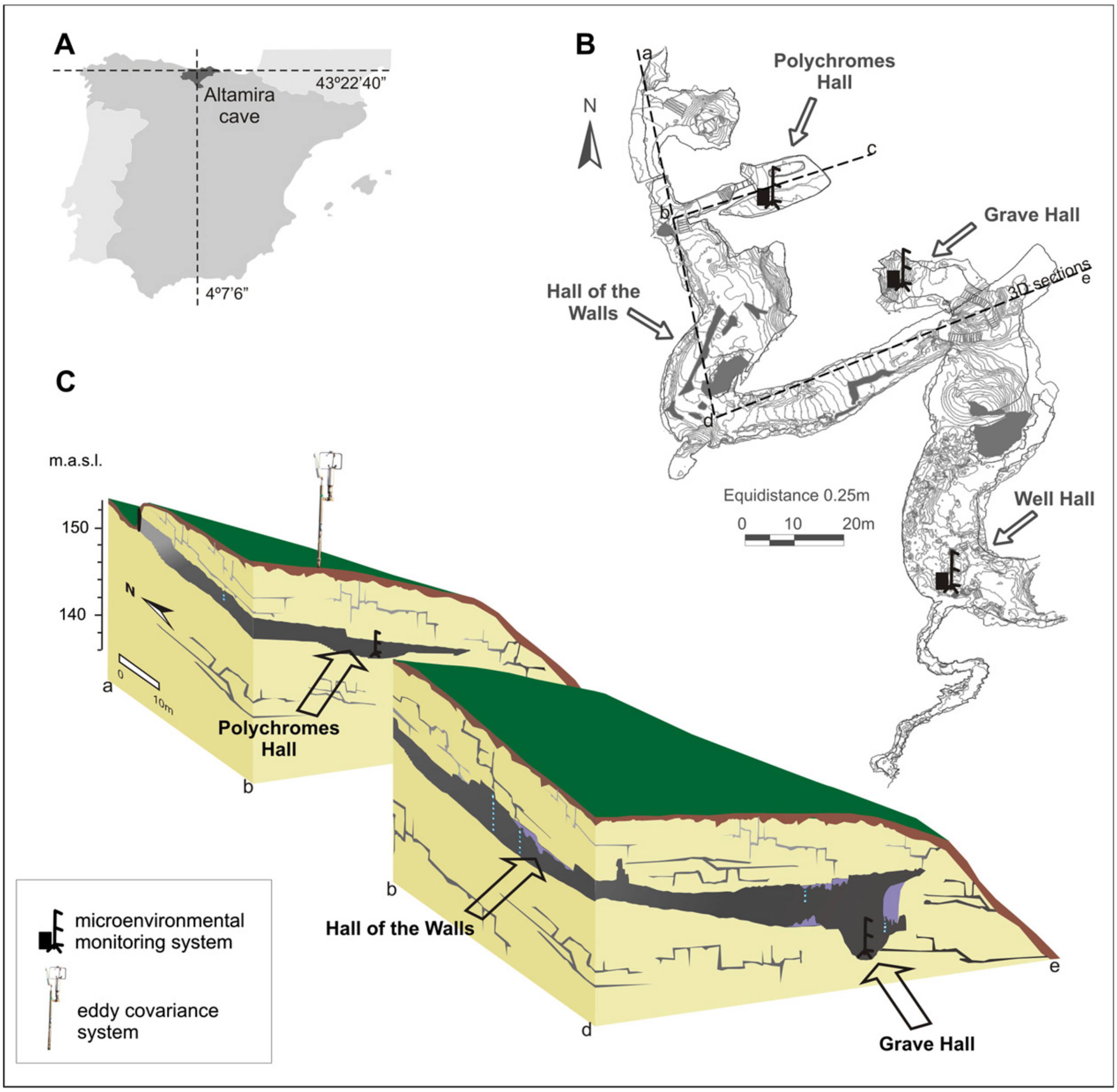

Fig. 1. (A) Geographic location of the Altamira Cave (Cantabria province, Spain). (B) Plan view and soil topography of the cave. Location of the microenvironmental monitoring systems inside the cavity. (C) 3D idealized model of the cave area, as indicated in section B. Location of the microenvironmental and eddy covariance monitoring systems.

performed. Three points were selected for soil sampling, two in the soil zone immediately over the Polychrome Hall and one over the Hall of the Walls. At each point, three different samples were taken at 10–15 cm intervals along a vertical profile, depending on total profile depth. Each sample had approximate dimensions of $25 \times 25 \times 25$ cm^3 and was packed to conserve its structure and thermohygrometric conditions.

2.3.1. *Porous media characterization*

The host rock and soil media were described in terms of pore size distribution, pore volume and specific surface area (SSA) using mercury intrusion porosimetry (MIP; Autopore Micrometics IV 9500), helium pycnometry (AccuPyc 1330 Helium pycnometer) and nitrogen absorption (Autosorb-6B Quantachrome apparatus). Total porosity of soil samples was calculated from the relationship between bulk and true density, which was obtained from helium picknometry. The nitrogen absorption technique was used to complete the micro–mesopore analysis (0.0009–0.015 μm pore radius). Determination of the SSA was realized through the BET method and the pore size distribution was obtained using the non-local density functional theory for N_2 at 77 K on silica. A detailed description of these analytical techniques and procedures has been provided by Benavente et al. (2009).

2.3.2. *Water retention (adsorption–desorption curve)*

The maximum moisture contents of the soil at different relative humidities, for long exposure time (weeks-months) and constant temperature (isothermal equilibrium conditions) were achieved by calculating the *adsorption curve*. Samples were previously dried in an oven at 105 °C for 48 h (m_0) and placed in desiccators and subsequently in atmospheres of different relative humidities (33–100%) maintained by saturated salt solutions (Wexler, 1994; Benavente et al., 2009). The temperature was held constant at 20 ± 1 °C, the average outside temperature during the summer study period. Samples were weighed at regular intervals. The time to reach the equilibrium depends on relative humidity: approximately a week for low relative humidity and 6–8 weeks for high relative humidity. The adsorption curve was plotted using the mass of adsorbed water per unit of dried sample (m/m_0) against relative humidity.

2.3.3. Water vapor transfer

The *water vapor transfer*, or variation of water content per sample area with time, was quantified by means of the diffusion coefficient D ($g\,m^{-2}\,h$). This is defined as a steady-state flux in the pore water per unit of porous surface medium, normalized by the concentration gradient. The methodology used to calculate the diffusion coefficients was adapted from Rose (1963) and Beck et al. (2003). Measurements of water vapor transfer were carried out using a set-up of two cells containing different saturated salt solutions, creating a vapor pressure gradient (suction difference) between the two sides of the soil. The water diffused from the more concentrated zone (lower cell) to the less concentrated one (upper cell) condenses in the salt solution saturated in the upper cell. The humidity range during the simulation experiment was determined by minimum (∼ 30%) and maximum (∼ 100%) monthly average exterior values. The experimental procedure started with the lower value of surface moisture (33%) and increased as water flowed steadily to each external relative humidity (43, 53, 62, 69, 75, 85, 93 and 100%) while the higher relative humidity (inside the container) is 100% (saturation). All tests were carried out at 20 °C. The upper container of each cell was weighed every 48 h over 42 weeks.

2.4. Statistical analyses

We combined the technique of entropy of curves (Denis and Cremoux, 2002) with a nonparametric Kendall's test to ascertain temporal trends and correlation of environmental data (Helsel and Hirsch, 2002), in order to analyze the correlation between the carbon dioxide fluxes and several climatic factors (wind velocity, total radiation, air pressure, evapotranspiration and relative humidity) registered at the external atmosphere. The entropy of curves technique allows delimiting stationary segments (with constant entropy) or segments where data transformation produces stationary series. Variations in the entropy value of CO_2 fluxes indicate changes in the degree of influence of a certain environmental parameter or a prevailing biological process on surface exchange (light-dependent photosynthesis versus temperature-dependent respiration). A nonparametric test such as Kendall's test has been used for ascertaining data stationarity for each time-segment (Helsel et al., 2006). Once the stationarity requirements are achieved for both CO_2 fluxes and climatic parameters, it is possible to analyze the cause-effect relationship between them computing the Kendall's tau non-parametric correlation coefficient and its test of significance for any set of paired observations (Helsel and Hirsch, 2002). This test determines whether the entropy change in the CO_2 flux is caused by the prevailing influence of a certain climatic factor.

3. Results

All results are reported in Coordinated Universal Time (UTC).

3.1. Characterization of the host rock and overlying soil

The host rock present low values of interparticle porosity (∼3%). Depending on the size and number of bioclasts the pore size distribution ranges between 0.1–10 μm. The rock has a very broad range of secondary porosity (fractures, fissures, and solution channels) usually above 100 μm opening and often exceeding 500 μm (0.5 mm). These values indicate that the analyzed rock samples are moderate to low permeable to liquids. However secondary porosity strongly increases their fluid permeability because allows the preferential movement of water.

The soil is a complex porous media and presents high values of connected porosity (∼50%) that decrease with depth. The pore size distribution is polymodal, ranging from 0.001 to 1000 μm. The pore size distribution is variable and depends on compaction, grain size and mineral composition. The quartz-rich upper level presents an interparticle porosity with large pores (1–100 μm) and progressively the pore radius decreases towards the clay-rich bottom, where pores in the interval 0.001–0.1 μm become important. The variation of porosity and pore size is reflected in the mean soil surface area (SSA) of the analyzed samples, which is around 7.42 $m^2\,g^{-1}$ near the surface but higher at depth (SSA = 12.3 $m^2\,g^{-1}$). This is very significant when considering the connection patterns between the inner and outer atmosphere, as the porous system determines the movement of fluids (liquid water and gases) through the soil.

The water retention (adsorption) curves quantify the amount of adsorbed soil water at different values of relative humidity in the atmosphere (Fig. 2). In porous materials, such as the studied host rock and overlying soil, water condenses at relative humidities below saturation (100% relative to a planar water surface). Thus, in the studied soils, the amount of water adsorbed increases slightly

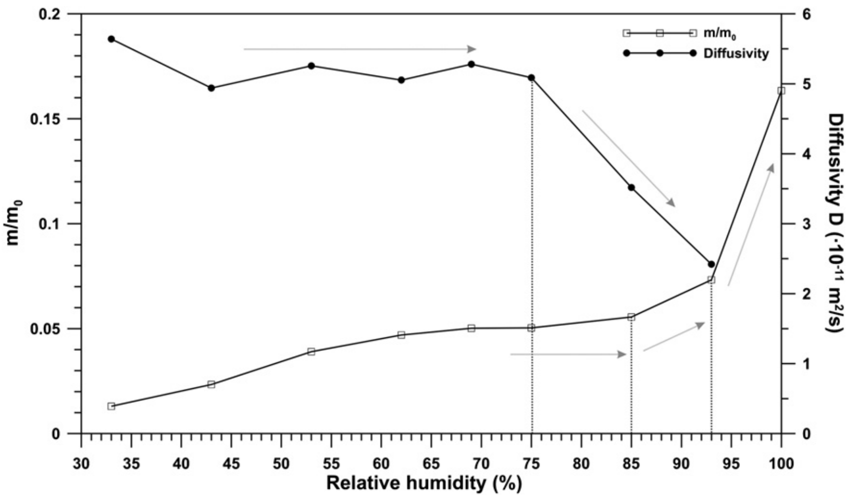

Fig. 2. Experimental results from soil samples from Altamira cave. Water absorption (m/m_0) and vapor diffusivity coefficient (D) curves over a range of relative humidity for isothermal conditions (T = 20 °C). Each point represents the average of all soil samples in the profile.

and gradually between 33 and 75% RH (water vapor from the atmosphere starts to form a layer, and with rising RH a multilayer is produced). For RH values between 75–85%, the water layers merge into the small pores due to capillary condensation, which is effective for pore radii close to *ca.*10^{-7} m (0.1 μm). When the RH exceeds 85%, capillary condensation becomes important and a significant increase in soil water content is produced. Capillary condensation continues until pores with radius ~1 μm are filled. These ranges can be considered an approximation, since all the models are constructed by assuming cylindrical pore geometry, and therefore they are in poor agreement with the real pore structure.

Water vapor transfer at different RH in isothermal conditions ($T = 20$ °C) is quantified by the diffusivity coefficient, D. Fig. 2 shows the close relationship between water adsorption and D curves. The diffusivity coefficient curve shows that water vapor flow occurs mainly in the interval between 30–75%. For values under 75%, water is adsorbed in the smaller, less-connected pores, and at the surface for larger pores (creating a single-multilayer), but never completely closing the pore. In this situation, the soil acts as permeable membrane to H_2O_{vap} movement.

For RH values ≥ 75% D decreases dramatically, reaching values below 2×10^{-11} m^2 s^{-1} at 100% RH. At this point, water vapor starts to condense in the capillary pores, which are filled by liquid water. When the RH exceeds 85%, the content of condensed water in pores rises and obstructs the direct passage of vapor. This reduces available porosity and thereby vapor diffusion through the soil, which becomes less permeable to gases as the RH approaches saturation.

3.2. Pattern of trace gases (CO_2 and ^{222}Rn) and turbulent CO_2 flux (Fc) during a representative dry and warm period in summer

Despite the prevailing high thermo-hygrometric stability in Altamira cave (about 1.5 °C annual thermal amplitude and indoor relative humidity values near saturation; Cuezva et al., 2009), a stair-step pattern with strong seasonal shifts over the course of the year is distinguishable in terms of tracer gas levels (CO_2 and ^{222}Rn; Sanchez-Moral et al., 1999; Kowalski et al., 2008; Fig. 3A). Altamira cave shows an outgassing stage during summer season and a gas recharge phase during wet and rainy periods. In summer, CO_2 concentrations are relatively steady near 500 ppm. Winter concentrations are much higher and more erratic, sometimes exceeding 5000 ppm, with weekly-monthly isolated degassing events. The two trace gases (CO_2 and ^{222}Rn) show significant similarities in their seasonal evolution, with the lowest values during summer and peaks in winter and early spring. This indicates that the annual-scale variations in CO_2 are due in large part to variable ventilation of the cave, which is most efficient in summer.

During summer (from June to October, both in 2004 and 2005) variations in CO_2 and ^{222}Rn concentrations in short periodic cycles (daily) have been observed. They follow a sinusoidal pattern and present oscillation that around 200 ppm and 300–600 Bq/m^3 respectively (inside Polychromes Hall). Fig. 3B shows in detail of representative daily variations in the concentration of CO_2 (and ^{222}Rn) in the cave air and the turbulent CO_2 (Fc) and water vapour (ET) fluxes, together with other variables related to external meteorological conditions, throughout two days during August 2005 (half-hour data) preceded by no rain episodes during the previous days. The Fc has been seen to show a daytime "anomaly" with respect to the classic model of ecosystem behavior based on purely eco-physiological processes (photosynthesis, respiration), as described by Kowalski et al. (2008). Night emissions (CO_2 release from the soil to the external atmosphere) are registered, normally less than 4 μmol m^{-2} s^{-1}. At dawn, between 6:15 and 6:45 (irradiance > 100–120 W m^{-2}) a small amount of CO_2 consumption is recorded (Fc negative generally less than 1 μmol m^{-2} s^{-1}) probably due to grass photosynthesis. However this only occurs for a couple of hours. Beginning around 8:30 "anomalous" positive Fc flows are detected. This situation continues into the afternoon (ca 2–3 mol m^{-2} s^{-1}). During this "anomalous" daytime episode, the cave is degassing (CO_2 and ^{222}Rn decrease) and relative humidity remains below 70%. Finally, at dusk (irradiance <10–11 W m^{-2}) between 19:15 and 19:45, a small flux positive Fc is detected due probably to respiration.

3.3. Statistical analyses

A statistical analysis combining the entropy curves technique with a nonparametric Kendall's test has been developed in order to corroborate the laboratory experiment. Analysis from the technique of entropy of curves allows setting the time-boundaries of the functional relationship at daily scales between the carbon dioxide fluxes and several climatic factors (wind speed, solar radiation, air pressure, evapotranspiration and relative humidity) registered at the external atmosphere. The experimental functions $L(t)$ were calculated for the Fc signal and for each external climatic parameter. $L(t)$ function is the cumulative sum of absolute amplitude differences of signal for each time lag increment, therefore it has the same units as the corresponding variable.

Fig. 4 shows the seven different statistically homogeneous and stationary segments, or potentially so after detrending, for the Fc time series. The stationary segments and corresponding entropy, $H(t)$, have been calculated directly from the slope on a time scale of the experimental linear function $L(t)$. Entropy is constant for each stationary and linear segment. The borders of each stationary region have been established considering the coincident limits of the linear $L(t)$ functions for Fc and each climatic factor.

Table 1 gives the results of the entropy analysis performed on the seven selected major stationary segments for the 38-h study period (1–3 August 2005). The entropy H(t) of Fc ranges from 29 to 70. Entropy results suggest that the functional relationship between Fc and each climatic factor could be different according to the stationary segment. For instance, the maximum entropy value for Fc is registered during morning (from 8:15 to 13:45; segment F) matching up with the maximum entropy of evapotranspiration signal.

The data sets for each segment were then examined for stationarity using Kendall's test (KT, Table 1). Linear trends were evaluated using ordinary least squares and, in each case, subtracted from raw data producing residual signals that were found to be stationary.

Once the stationarity requirements were achieved, a correlation analyses were performed between Fc and each weather factor, again using a nonparametric Kendall test (Fc = f[parameter], Table 1). The Tau coefficient measures the strength of the monotonic relationship between each climatic factor and Fc. The coefficient of determination (R^2) indicates the fraction (ranging from 0 to 1) of variance in the dependent variable explained by variability in the independent variable. For periods that failed the previous stationarity test (segments with a temporal trend), correlation analyses were performed using residual datasets in order to identify reliable relationships (without trends) between parameters. In such cases the Tau coefficient and coefficient of determination (R^2) correspond to relationships, after trend removal, between variations in Fc and those in each weather factor.

The p-value of Table 1 is the probability of obtaining the computed Kendall's test statistic, or one even less likely, when the non-correlation hypothesis is true. Therefore, correlation between variables is accepted if the 2-side quartile (p-value) is lower than 5% significance (statistical tradition uses a default of 5%, 0.05, for α-value), corresponding to 95% confidence.

On the whole, the selected stationary segments exhibit both low R^2 and Tau correlation coefficients and, in any case, this correlation is

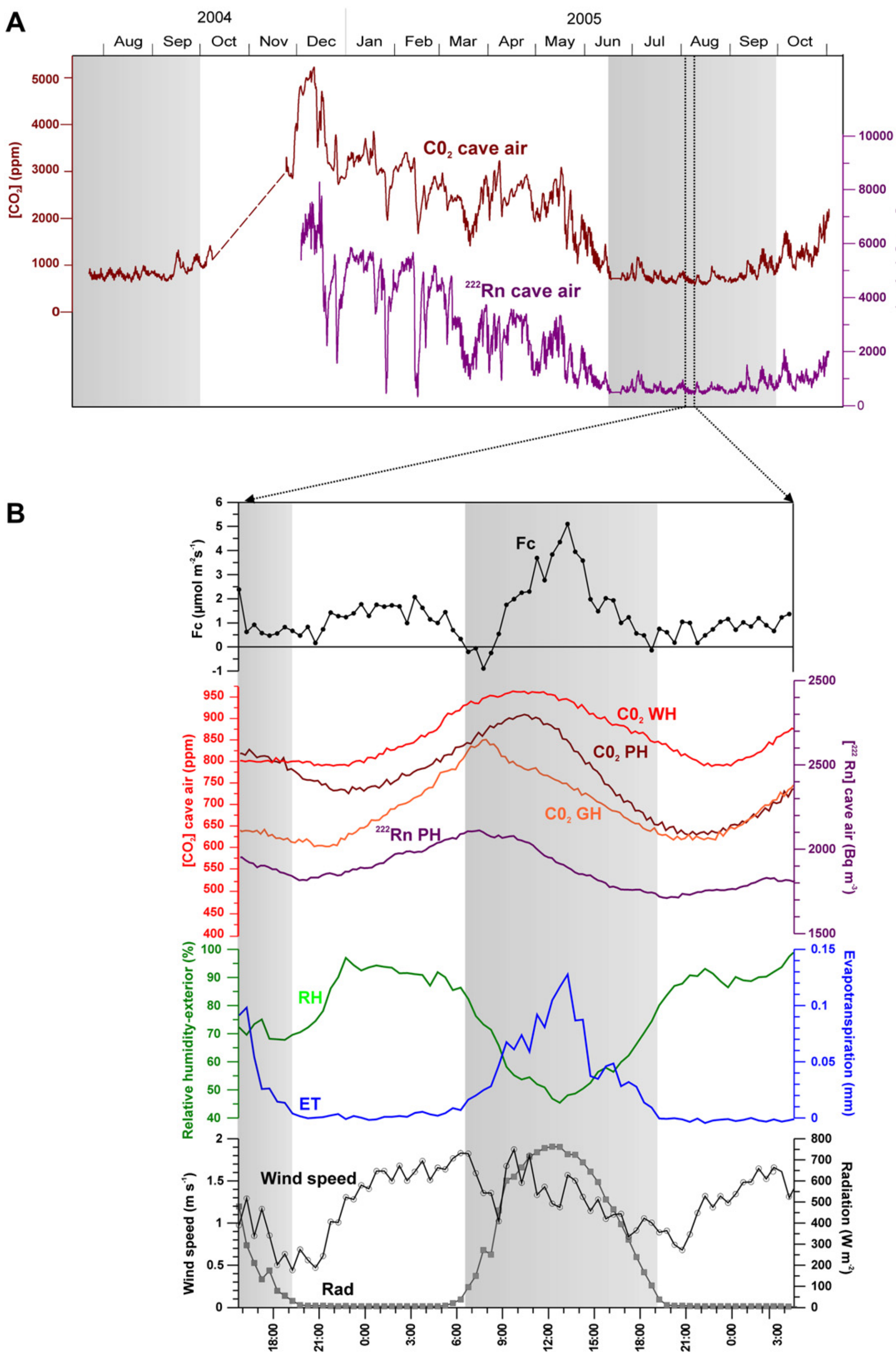

Fig. 3. (A) Annual period (August 2004–October 2005) of trace gases (^{222}Rn and CO_2) levels in cave air; (B) Half-hourly series of turbulent CO_2 fluxes (Fc), trace gases (^{222}Rn and CO_2) levels in the Polychromes (PH), Grave (GH) and Well (WH) Halls air and weather parameters: relative humidity (RH), evapotranspiration (ET), wind speed and solar radiation (Rad) during a detailed monitoring period in summer 2005 (1 to 3 August). The shaded area represents the daylight period.

not statistically significant at 95%. Time segment *F*, corresponding to morning (8:15 to 13:45) represents an exception with positive values of Fc. This segment shows strong negative correlation between Fc and air humidity (Table 1). Nevertheless, the most remarkable correlation is found between evapotranspiration and Fc for this time segment *F*, reaching high Tau and R^2 coefficients, statistically significant with 95% confidence. For instance, the R^2 between both variables for time segment *F* is 0.82. Then, surface evapotranspiration also exerts an

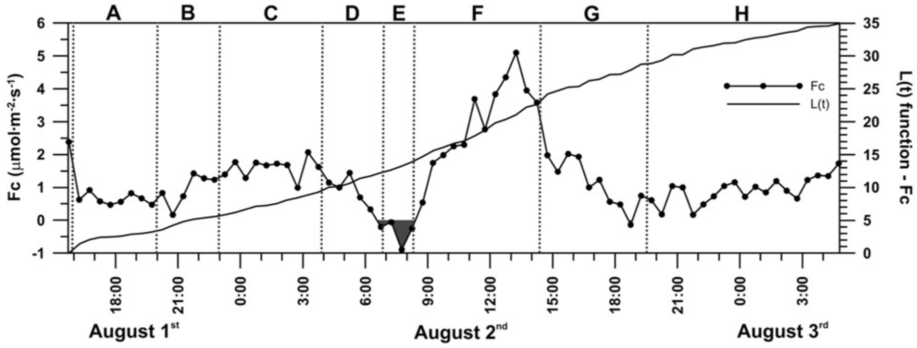

Fig. 4. CO_2 flux (Fc), $L(t)$ function and stationary clusters of constant entropy during the monitoring period in summer 2005.

indirect control on levels of CO_2 and ^{222}Rn of cave air, since the continuous upward trend of the turbulent CO_2 flux (Fc > 0) from 8:15 h to 13:45 provokes a decrease of both trace gases with a delay of roughly 1.5 h. This delay provokes that correlation between variations of surface evapotranspiration and cave gas content changes is characterized by low correlation, statistically significant with only 90% confidence.

4. Discussion

This study demonstrates that the soil overlying the Altamira cave acts as a permeable/impermeable membrane, open to gas exchange during dry summer days with low atmospheric relative humidity, but closed at night and during winter due to the presence of liquid water in the soil pores. These conclusions, which proceed directly from a laboratory study, are corroborated by the behavior of cavity gas concentrations and external Fc measurements. The experimental studies are focused on H_2O_v transfer through the porous soil media. Results can be used to predict the behavior of CO_2 and ^{222}Rn flows through the host-rock and soil, and consequently to understand gas exchange processes between cavity and external atmosphere.

During the cold, rainy season the system of macro and micro epikarstic fissures is almost permanently saturated with water making the host rock membrane impermeable. In contrast, during the warm, dry season the macro and micro epikarstic porous system is not water saturated and therefore acts as a connecting pathway between the outside and underground environments. Free movement of H_2O_v, CO_2 and ^{222}Rn gases is possible through these channels, except following rainfall events of sufficient intensity or duration to saturate either porous system. Therefore, during the dry summer period, the host rock acts as a permeable membrane or interface for gas transfer. Similar behavior has been observed in other porous materials (Rose, 1963; Beck et al., 2003; Benavente et al., 2009) due to the clogging of pores (closed) by water condensation with increasing RH. These results indicate that the Altamira soil has the ability to act as a membrane or barrier to gas movement and therefore to limit gas exchange between the cavity and outside. This mechanism is highly dependent on water, not only in the sealing of the pores through saturation, but also through adsorption and condensation in the porous system.

Gas transport through the overlying soil is determined by the pore size distribution, inter-particle porosity, and water content. Results show that the studied soil porosity is determined by water condensation in non-saturated environments (HR < 100%) and also that water vapor diffusivity varies with soil water content at different air RH. Thus, for values under 75%, the amount of adsorbed water is small and mainly found in the thinnest, least connected pores, and at the surface of larger pores, but never completely closing the pore. In this case the soil acts as a permeable membrane. For RH values over 85%, there is greater condensation in the soil, closing most capillary porosity and, therefore, hindering H_2O_v movement. The loss of porosity (air-filled) gradually becomes greater with the increase in RH. The pore system is then finally closed stopping cavity ventilation and preventing communication between the cave and exterior. The soil acts in this case as an impermeable membrane to gaseous exchange.

These laboratory results are confirmed by the cavity gas concentrations and external Fc behavior. In summer, during night hours there is a progressive increase (up to 200 ppm) in the amount of CO_2 inside the cave; during daytime, CO_2 is progressively reduced by a similar magnitude. The parallelism between the CO_2 and ^{222}Rn fluctuations in the cavities indicates the existence of a daily scale cyclic alternation phenomenon that either insulates or ventilates the cavities. This corresponds to daily degasification (CO_2 emission) from the cavity and recharge processes (system shutdown). Moreover, statistical analysis of the environmental parameters outside the cave has shown a clear daily and cyclical relationship between the CO_2 (and ^{222}Rn) concentration inside and the "anomalous" Fc

Table 1
Summary of entropy values $H(t)$ for each parameter (Fc: CO_2 flux, RH: Relative humidity, ET: Evapotranspiration, WS: Wind speed, and Pr: Air pressure), results of the Kendall's test (KT) for ascertaining the stationarity conditions (P: Passed; F: Failed) and correlation analysis between the CO_2 flux and weather factors for each stationary segment, based on a nonparametric Kendall's tau test (Helsel and Hirsch, 2002). Values marked with grey show the time segment with a statistically noteworthy correlation between parameters.

Segment	Entropy and stationarity analyses										Correlation analysis: Fc = f[parameter]											
	H[Fc]	KT	H[RH]	KT	H[ET]	KT	H[WS]	KT	H[Pr]	KT	Fc = f [RH]			Fc = f [ET]			Fc = f [WS]			Fc = f [Pr]		
											Tau	*p*-value	R^2	Tau	*p*-value	R^2	Tau	*p*-value	R^2	Tau	*p*-value	R^2
A	29	P	228	P	1.28	F	28	F	7.27	F	0.17	0.61	0.09	0.17	0.61	0.02	−0.28	0.36	0.17	0.06	0.92	0.10
B	42	P	490	F	0.15	P	19	P	5.88	P	0.20	0.72	0.14	0.20	0.72	0.20	0.6	0.14	0.70	0.20	0.70	0.22
C	35	P	76	F	0.12	F	12	F	8.69	P	−0.02	1	0	0.02	1	0.10	0.29	0.29	0.25	−0.20	0.37	0.08
D	44	P	293	P	0.25	P	8	P	6.88	P	0.40	0.48	0.35	−0.20	0.82	0.41	−0.8	0.08	0.65	−0.40	0.22	0.58
E	55	P	344	P	0.39	P	16	P	8.96	P	0.33	0.75	0.15	−0.33	0.75	0.16	0.67	0.33	0.31	0	0.73	0
F	70	F	211	F	1.70	F	25	P	4.73	P	−0.46	0.05	0.50	0.79	4.10^{-4}	0.82	0.09	0.73	0.02	0.12	0.63	0.08
G	46	F	309	F	0.81	F	11	F	8.26	F	−0.07	0.86	0	0.20	0.48	0.15	−0.29	0.29	0.22	0.11	0.59	0.02
H	31	F	178	F	0.16	P	13	F	8.56	P	−0.01	1	0	−0.02	0.94	0.01	−0.30	0.08	0.18	0.18	0.26	0.07

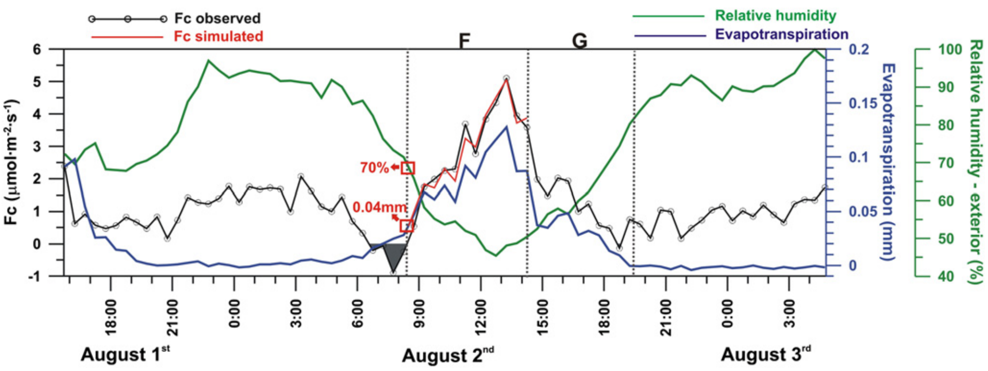

Fig. 5. Half-hourly series of CO_2 fluxes (Fc) in relation to exterior humidity parameters (relative humidity and evapotranspiration). The CO_2 flux has been simulated in stationary segment F, where correlation coefficient with evapotranspiration was statistically significant with 95% confidence.

(daily maxima) with daily variations in the external hygrometric air conditions. The statistical analysis has shown that surface evapotranspiration (ET) exerts a remarkable control on Fc during the stationary time-segment F (Fig. 5). The monitored and simulated series Fc shows a high degree of correlation with evapotranspiration for this time segment, validating the optimum results obtained from segmentation and the correlation between both parameters. In addition, evapotranspiration is found to be the main factor responsible for the positive anomaly in CO_2 fluxes usually detected during the summer season. During the early morning Fc becomes positive once the relative humidity decreases below *ca*. 70%, and evapotranspiration is above 0.04 mm per half-hour. These dry environmental conditions provoke intense soil evaporation process, favoring CO_2 exchange with the atmosphere ($F_C > 0$).

At midday relative humidity and evapotranspiration reach their extremes (minimum and maximum, respectively) and subsequently, during time segment G, humidity conditions at the surface undergo a continuous recovery (Fig. 5). During this daylight period (segment G) a correlation still remains between ET and Fc, however, the constant CO_2 capture by a photosynthesis process disguises the control of the CO_2 flux signal exerted by evapotranspiration (low correlation coefficient and not statistically significant).

By extrapolating test results to the actual site, gas behavior in the soil can be interpreted. The soil, directly connected to the outer atmosphere, is affected by the thermo-hygrometric daily oscillations recorded in Altamira, especially in the upper profile. As observed in the laboratory experiment the gradual increase of RH at night (Fig. 5) induces adsorption and condensation of atmospheric water vapor in the porous system until transfer of gases ceases and the gas becomes trapped in cavities (isolated from the outside by a impermeable membrane). Thus, we observe that during the night there is a progressive increase of CO_2 and ^{222}Rn, when the RH outside stands at about 85–90% and the ET value is negligible. On the other hand, beginning at dawn there is an increase in evapotranspiration, and a progressive soil drying allowing gas transfer between the cave and exterior. The CO_2 outflow is detected for values of ET = 0.04 mm and RH = 70% outside (above the cave) as indicated previously (Fig. 5) while decreases in CO_2 and radon concentrations are measured in the cave with some delay in regard to the outside (Fig. 3).

An approach for the CO_2 output mechanisms that reduce its concentration (and ^{222}Rn) in the cave entails a certain complexity and involves new studies. During daytime, internal and external atmosphere are interconnected. Classical models remark that soil CO_2 outgassing is driving by gas diffusion favored by turbulence. In addition, advective processes (Venturi Effect at the soil surface) can be more efficient in the gas exchange. Pressure pumping driven by wind speed and subsequent soil efflux of CO_2 and ventilation has been already described in the literature (Takle et al., 2004). By inflow of CO_2-poor air, and outflow of CO_2-rich air, ventilation reduces the belowground CO_2 concentrations in soil pores and cave. Small cracks and fractures in deep areas of the cavity close to the adjacent sinkhole may be acting at times as channels of direct communication with the outside. They would allow the entry of air and ventilation in response to the advective pumping on the floor. During nighttime, cave's CO_2 recharge process occurs. In special, during hot-dry season, CO_2 recharge through infiltration waters is not significant in Altamira cave due to the fact that infiltration rate is minimal and the active drip points are scarce. However, the organic CO_2 production in the soil (soil bioproductivity) is enhanced, at which point a CO_2(g) flux could take place from the internal edaphic zone to the karstic macropores. This favours the CO_2 recharge of the macropores' atmosphere and, consequently the karst acts as CO_2(g) reservoir.

5. Conclusions

An experimental behavioral study of the overlying soil pore system under changing air humidity conditions, coupled with a multivariate statistical analyses (entropy of curves technique; nonparametric Kendall's test) allows defining the suitable environmental conditions that favor daytime gas exchange between the cave atmosphere and exterior during the warm, dry season (end of the summer). The soil has the ability to act as a membrane or barrier limiting gas exchange depending directly on weather conditions. Adsorption and condensation processes that partially or completely fill the porous system with water can at times determine the intensity of the processes involved in gas-phase connections: ventilation in the karst-epikarst and CO_2 inflow or outflow. The interaction pattern of the soil porous system with daily hygrometric fluctuations determines the daily cyclic operation of the membrane: (1) evapotranspiration acts as a determining factor, opening the soil membrane to gas flow during daytime, and (2) RH increases with decreases in temperature and ET to close the soil membrane to gas flow at night.

Thus, during a daily cycle two stages of gas transfer between the cavity and the outer atmosphere through the overlying soil and karst-epikarst environments can be observed during summer (Fig. 6):

(A) Day time processes (partial or totally permeable membrane to gas):

During daytime the soil loses water via evapotranspiration and pore space opens to gas exchange. Both the macro and micro fractures-fissures of the epikarst and the soil porous system become pathways to gas exchange between the underground and

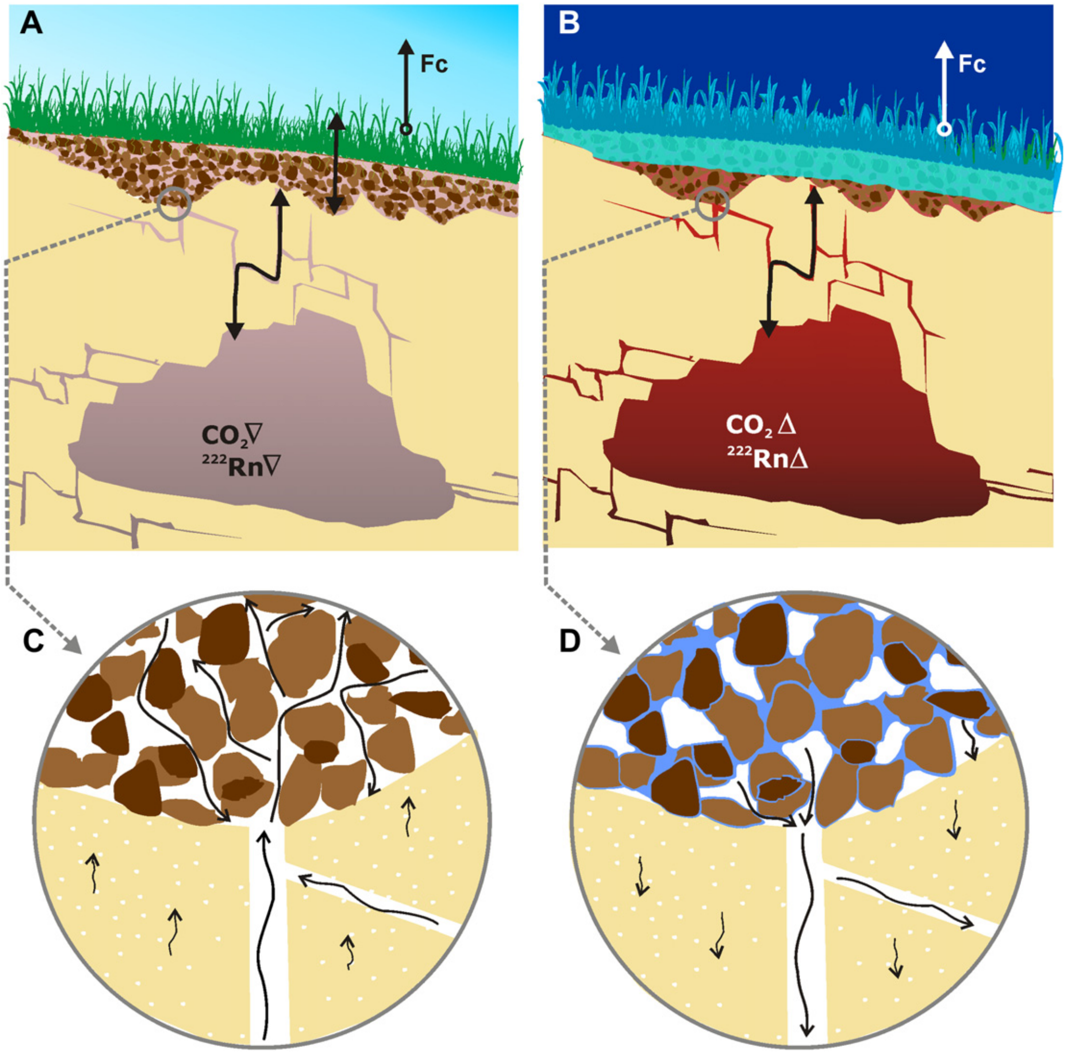

Fig. 6. Model of the soil's role in daily gas exchange processes between the karstic macropore and external atmosphere (warm, dry period). (A) Schematic depicting daytime processes, (B) nighttime processes. (C and D) In detail, the soil pore system's role during day and night time respectively. Arrows indicate gas flow; Δ indicates increases in gas concentrations; ∇ indicates decreases in gas concentrations.

the exterior environments. Throughout the day, internal and external atmospheres are interconnected and flows of $CO_{2(g)}$ (and $^{222}Rn_{(g)}$) take place, which is reflected in the $CO_2(g)$ emissions outside (positive Fc). The karst acts as $CO_2(g)$ emitter.

(B) Night time (soil membrane impermeable to gas):

The topsoil experiences adsorption and water vapor condensation (re-humidification), which fill and close the pore space. Once saturated with water, it can be virtually impermeable to gas movement (CO_2 and ^{222}Rn). The edaphic interior zone, as well as the karstic media (karst-epikarst) become isolated from the exterior and in turn produce the "stagnation" of the internal atmosphere. The karst acts as $CO_2(g)$ reservoir.

Daily episodes of ventilation through the overlying soil and karst-epikarst environments (micro, meso and macroporosity) represent net $CO_2(g)$ emissions to the exterior. Future research to determine the underground micro-environmental dynamics should consider the role of this double membrane, especially in regard to the pore system (micro and meso-porosity). Also, the non-negligible role of cavities as temporal reservoirs of CO_2 and emitters/sources at different time scales (daily, yearly), manifest the importance of this study achieve a complete understanding of the different media and amounts that intervene in the global carbon cycle.

Acknowledgments

This research was supported by the Spanish Ministry of Science's projects CGL2006-11561/BTE and CGL2010-17108/BTE. Fernandez-Cortes benefits from the JAE-Doc Program (CSIC) and Cuezva from a Spanish Ministry *Juan de la Cierva* fellowship. The Altamira Cave Research Centre and Museum staff are acknowledged for their constant and invaluable collaboration. We sincerely thank to the anonymous reviewers for their valuable comments and suggestions for improving the manuscript.

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