Can flux tower research neglect geochemical CO_2 exchange?

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ARTICLE INFO

ABSTRACT

This study examines the hypothesis that surface-atmosphere exchange of CO_2 in terrestrial ecosystems always can be interpreted purely in terms of biological processes, neglecting geochemical cycling by karst systems that characterize 22 million km^2 in the world [Yuan Daoxian, G., 1997. The carbon cycle in karst, Zeitschrift für Geomorphologie 108 (Supplementbände), 91–102]. Eddy covariance data of net CO_2 fluxes are examined for two ecosystems over karstic substrates in contrasting climates in the North and South of Spain. A semi-arid matorral is found to behave similarly to previously studied ecosystems when well watered, but sizeable mid-day CO_2 emissions during extended drought and plant senescence are found to be incompatible with ecophysiological interpretations of the flux. For a temperate pasture overlying an accessible cave, afternoon CO_2 emissions in summer are likewise inexplicable in a biological context, but coincide with periods when ventilation is observed inside the subterranean cavity. These results suggest direct linkages at times in CO_2 exchanges among atmosphere, ecosystems, and carbonate substrates which represent more than a tenth of the Earth's land surface.

1. Introduction

In the last quarter century, the accurate characterization of the global carbon cycle has emerged as an outstanding scientific challenge. Since the revelation of rising atmospheric CO_2 concentrations (Keeling, 1960), concerns about terrestrial warming via the greenhouse effect have become global. The Kyoto Protocol, in addition to motivating emissions reductions, highlights the need to identify and quantify sinks (and sources) of atmospheric CO_2 to enable management for sink optimization. Lately, understanding has grown as research assesses exchange of CO_2 at a variety of spatial scales – from leaf to globe – between the atmosphere and Earth's surface, with micrometeorology providing valuable information at the ecosystem scale (Houghton, 2002).

Eddy covariance and other, indirect micrometeorological techniques quantify surface-atmosphere exchange of momentum and energy and mass (Dabberdt et al., 1993) such as CO_2. Direct flux measurement in near-surface turbulence generally requires fast-response (ca. 10 Hz) instruments and provides exchange information on timescales of hours or less. Despite the difficulties of keeping such instruments operating correctly, long-term integrations of CO_2 exchange have been demonstrated feasible (Wofsy et al., 1993) and since then the

use of ''flux towers'' has proliferated. Networks have been established on continental (Aubinet et al., 2000) and even global scales (Baldocchi et al., 2001), with hundreds of towers/nodes dedicated to the estimation of annual CO_2 exchange by the surface under the point of measurement. In these investigations – and indeed even at larger scales – the terrestrial CO_2 flux is generally interpreted in the context of an unstated hypothesis that biological processes alone determine surface exchange (Bala et al., 2005; Baldocchi, 2003; Houghton, 2002), with very few notable exceptions (Emmerich, 2003; Mielnick et al., 2005).

The mother material in karst systems, carbonate rocks are widespread globally and may play a direct role in the global carbon cycle. Carbonate rocks representing the world's largest carbon reservoir (Liu and Zhao, 2000) outcrop on ca. 12% of the water-free Earth surface (Ford and Williams, 1989). Along with biologically respired CO_2, karstic formations such as limestone and dolomite dissolve in groundwater to participate in chemical reactions. Carbonate rock dissolution represents a sink process with respect to CO_2 and solid stone, consuming both to produce bicarbonate and other aqueous phase ions. Rock weathering can enlarge fissures and form macropores (caves) capable of storing large quantities of carbon in both gaseous and aqueous phases. When geochemistry operates in reverse, carbonate precipitation represents a local source of both rock and CO_2, forming speleothems and tufa deposits. These geochemical processes are highly dependent on groundwater acidity (Cardell-Fernández et al., 2002) and may be important for inclusion in characterizations of the global carbon cycle (Cheng et al., 2005; Yuan Daoxian, 1997), with magnitudes representing a non-negligible fraction of the ''missing sink'' for atmospheric CO_2 (Gombert, 2002; Liu and Zhao, 2000).

Here we examine the hypothesis that such geological exchange processes can be neglected when interpreting surface-atmosphere exchange measured by micrometeorology. We present eddy covariance measurements above two distinct ecosystems growing on karstic formations in Spain, and attempt to model CO_2 exchange at half-hourly timescales in terms of widely-used empirical models for ecophysiological processes (photosynthesis and respiration). Particularities from each of the two field sites assist in the assessment: in one case data from an extended drought and in the other, where access to the underlying cave is possible, gas concentration measurements in this macropore. The objective here is not a quantitative characterization of carbon cycling at either site, but rather a qualitative examination of contributing processes.

2. Measurements and analyses

2.1. Field sites and instrumentation

All measurements were taken at each of two climatologically distinct sites on Spanish karstic formations, by two teams differing in equipment and initial objectives. Here we describe the relevant geological and biological aspects of the two study sites, as well as the measurement systems.

2.1.1. The Sierra de Gádor

A flux tower was installed in the spring of 2004 to assess the biological CO_2 source/sink of a *matorral* (scrub) ecosystem at *El Llano de los Juanes*, a 1600 m plateau in the *Sierra de Gádor* in the South-eastern Spanish province of Almería (36°55′41.7″N; 2°45′1.7″W). With its feet at the Mediterranean coast, the *Sierra de Gádor* consists of Triassic carbonate rocks – mainly dolomitic limestones (Vallejos et al., 1997). The measurement site is 18 km distant from the coast in a semi-arid climate with annual mean precipitation of 465 mm and mean annual temperature of 12 °C. Dominant ground cover types (as percent of total) are bare soil and rock (53.3%), *Festuca scariosa* (Lag.) Hackel (19%; this is the dominant non-woody plant), and a mix of woody plants including *Genista pumila* (Vierch) ssp pumila (11.5%) not exceeding 50 cm in height. The extent of homogeneous surface (i.e., ''fetch'') is several hundreds of meters from the tower in every direction. More details about vegetation and soil characteristics can be found in Serrano-Ortiz et al. (2007).

The measurement system centers on a datalogger (CR23X, Campbell Scientific, Logan, UT, USA; hereafter CSI) that records semi-processed data from ''fast'' turbulent sensors and ''slow'' instruments measuring atmospheric and soil states. The datalogger calculates and stores means, variances, and covariances every 15 min. Two ''fast'' instruments sample 10 Hz eddy fluctuations at 2.5 m above ground level (AGL). A three-axis sonic anemometer (CSAT-3, CSI) measures wind speed and temperature, and an open-path infrared gas analyser (Li-Cor 7500, Lincoln, NE, USA) measures CO_2 and H_2O densities. ''Slow'' instruments are queried by the datalogger once every 10 s. At 1.5 m AGL two quantum sensors (LI-190, Li-Cor) detect incident and reflected photon fluxes. In the soil, a water content reflectometer (CS615, CSI) measures volumetric soil water content at 15 cm depth and temperature is determined as the mean of four thermocouples (TCAV, CSI) at 1, 2, 4, and 8 cm.

An automated soil CO_2 flux system (LI-8100, Li-Cor) with 10-cm survey chamber made continuous measurement campaigns. The chamber was installed over a single PVC collar (10 cm inner diameter; 5.25 cm height) adjacent to the flux tower, and programmed to make a 2 min measurement every half-hour, allowing thorough aeration between measurements. Soil CO_2 effluxes were estimated using the initial slope of a fitted exponential curve (according to the instrument manual), adjusted for the total (chamber and collar) volume.

2.1.2. The Altamira cave

In the Northern Spanish province of Cantabria (43°22′40″N; 4°7′6″W), carbonate rock dissolution processes are studied in the Altamira cave with a goal of conserving its famous Palaeolithic artwork (http://museodealtamira.mcu.es/). The cave, one of many cavities in the upper vadose area of the karstic system, is situated at a depth of 3–22 m (averaging 8 m) below the surface, and is covered by a pasture. The rock consists of Cenomanian (Upper Cretaceous) carbonate rocks—mainly limestone, with very little porosity (<5%). Directly over the rock lies a porous (25–40%) artificial soil of little development (3–60 cm). The climate is more temperate than at the *Sierra de Gádor*, with annual precipitation of 1352 mm and a mean annual temperature of 14 °C.

Both internal and external environmental conditions are monitored. Inside the cave, a micro-environmental monitoring system records microclimatic data in the Polychromes Hall (Sánchez-Moral et al., 1999). A datalogger (dataTaker DT50, Grant Instruments Ltd., Cambridge, UK) accepts voltage and current inputs from a 16-channel multiplexer, and records 15 min means of measurements made every 10 s, including concentrations of CO_2 (Ventostat 8002, Telaire, Goleta, CA, USA) and ^{222}Rn (AB5 Continuous Passive Radon Detector, Pylon, Ottawa, Canada) in the air of the hall. Outside the cave, a weather station with autonomous datalogger (HOBO, Onset, Bourne, MA, USA) stores 15 min means of numerous variables of which only air temperature (S-TMB-M0XX 12-bit Smart Sensor, Onset) was applied to this study.

In spring 2004 an eddy covariance system was installed over the grassy lawn above the cave. The area of the homogeneous, flat lawn is ca. 4500 m^2; grass height was in the range of ca. 4–15 cm according to an unrecorded mowing scheme. A three-axis sonic anemometer (model 81000, R.M. Young, Traverse City, MI, USA) measures wind speed and temperature at 1.5 m (AGL). An open-path infrared gas analyzer (Li-Cor 7500) measures CO_2 and H_2O densities at the same height, and reports an analog voltage to the A/D converter on the anemometer. A microcomputer receives serial data via a serial communication port and stores them to disk. Micrometeorological calculations on these raw 20 Hz data are made using the University of Edinburgh EdiRe software package.

2.2. Analyses

All variables including turbulent fluxes are adapted to half-hour bases according to Reynolds' rules of averaging (Moncrieff et al., 1997). Covariances are converted to streamline coordinates via two rotations (McMillen, 1988). The CO_2 flux (F_c) is calculated including corrections for molar density variations within the open-path sensing volume (Webb et al., 1980), as a function of the (kinematic) fluxes of sensible and latent heat.

Two commonly employed empirical models are applied to describe ecophysiological processes as light-dependent photosynthesis and temperature-dependent respiration. Daytime F_c is assumed to depend mostly on light, with CO_2 release at low light levels and increasing uptake with increasing light, up to saturation. For the *Sierra de Gádor* site, the absorbed photon flux (F_p) is determined as the difference between incident and reflected photosynthetically active radiation. The hyperbolic "light-response" curve is then described as:

$$F_c = R_D - \frac{a_1 F_p}{a_2 + F_p} \tag{1}$$

where R_D is (assumed constant) daytime respiration and a_1 and a_2 are fitted parameters that, respectively, describe the maximum photosynthetic capacity and the light level at which half capacity is achieved. This hyperbolic model has been successfully employed to describe daytime F_c for a variety of ecosystem types, from forest to grassland to desert (Hastings et al., 2005; Hunt et al., 2002; Kowalski et al., 2004).

Respiration is often modeled in terms of an exponential temperature dependence, which can take various forms (Lloyd and Taylor, 1994). At the ecosystem scale corresponding to eddy fluxes, there is no standard for the choice of (air, soil, or leaf) temperature to be used and the temperature function giving the best fit appears to vary among sites (Berbigier et al., 2001; Janssens et al., 2003; Kowalski et al., 2003; Van Dijk and Dolman, 2004). Here, we employ the widely-used "Q_{10}" model (e.g., Curiel Yuste et al., 2003; van't Hoff, 1898) to fit non-photosynthetic carbon flux data (e.g., at night) empirically in the form:

$$F_c = R_R Q_{10}^{(T-T_R)/10} \tag{2}$$

describing a dependence on *available* temperature (T) data. At the *Sierra de Gádor* site, the soil temperature was used whereas air temperature was used at Altamira. This model defines respiration R_R at a reference temperature T_R, and a factor of Q_{10} change in respiration for any 10 °C change in T.

3. Results

3.1. The Sierra de Gádor matorral

Two years of CO_2 flux (F_c) data from *el Llano de los Juanes* reveal a complicated seasonal variability, as described in part by Serrano-Ortiz et al. (2007). Particularly germane to the hypothesis being tested here, however, is the drought period of late summer 2005. This is contrasted against the late spring of 2004 when abundant spring rains spurred lush development of the *matorral* ecosystem, particularly grasses which flourished to give the ecosystem nearly a grassland appearance at the time. Finally, corroboration of the eddy flux data was possible with the addition of soil chamber measurements in October 2006. The presentation of results from this site is chronological, beginning with the growing period, and initially employs the traditional assumption that CO_2 exchange can be explained entirely by biological processes.

After the profuse rains of May, with ample soil moisture the *matorral* ecosystem acted as a biological CO_2 sink during June 2004, as shown in Fig. 1. Daytime fluxes during this period of intense growth were negative (uptake) and far exceeded nighttime CO_2 releases associated with respiration. There was little evidence of water limitation; daytime CO_2 uptake was nearly symmetrical about mid-day and did not decrease in the afternoon as would be expected when stomatal controls activate to preserve water. Such conditions are nearly ideal for application of the ecophysiological models presented in Section 2.

Fig. 2 shows the hyperbolic light-response of F_c for a single day in June 2004, ranging from modest release in dim conditions to uptake at higher light levels. Consistent with the nighttime fluxes from Fig. 1, the model parameter R_D estimates daytime respiration at ca. 0.5 μmol m^{-2} s^{-1} (extrapolating the curve to zero light). The other model parameters suggest a maximum photosynthetic capacity (a_1) of 6.3 μmol m^{-2} s^{-1} and the light level of half-capacity (a_2) at F_p = 730 μmol m^{-2} s^{-1} as an indication of how rapidly
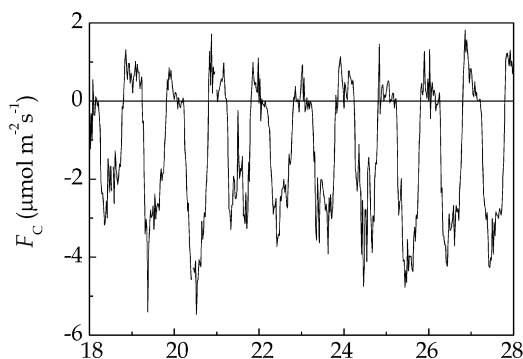
Fig. 1 – Time series of carbon dioxide fluxes (F_c) for the *Sierra de Gádor matorral*; the abscissa is labelled with the day of June 2004 at midnight GMT. Daytime carbon uptake (negative fluxes) of 3–4 μmol m^{-2} s^{-1} and lesser nighttime release are typical of CO_2 exchange for a growing ecosystem.
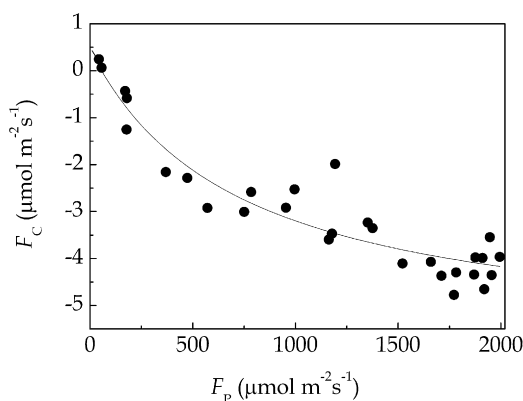

Fig. 2 – Carbon dioxide fluxes (F_c) for the *matorral* in the *Sierra de Gádor* vs. the absorbed photon flux (F_p) on 26 June 2004. The hyperbolic model fit to the data explains 90% of the variability in the data ($R^2 = 0.90$) according to Eq. (1) with parameters $R_D = 0.5 \pm 0.4$ μmol m^{-2} s^{-1}, $a_1 = 6.3 \pm 0.5$ μmol m^{-2} s^{-1}, and $a_2 = 730 \pm 280$ μmol m^{-2} s^{-1}.

Fig. 3 – Nighttime carbon dioxide fluxes (F_c) for the *matorral* in the *Sierra de Gádor* vs. soil temperature (T_s) for 18–27 June 2004 (the same period presented in Fig. 1). Only data with sufficient turbulence ($u^* > 0.2$ m s^{-1}) are included. The exponential model described by Eq. (2) is presented, fitting the data using a reference temperature (T_R) of 22 °C. The model with parameters $R_R = 0.77 \pm 0.04$ μmol m^{-2} s^{-1} and $Q_{10} = 3.2 \pm 0.6$ explains about half the variability in the data ($R^2 = 0.48$).

light-saturation is approached. Most importantly, the variance described by the model is robust ($R^2 = 0.90$), particularly for such inherently "noisy" (turbulent) fluxes. Thus, biological models appear to be sufficient to describe this well-watered period of growth, at least during daytime when turbulence never lacks.

For the nighttime case, it was necessary to reject flux data during non-turbulent periods, and a threshold in the friction velocity was applied removing all data with $u^* < 0.2$ m s^{-1}. The temperature dependence of F_c for nocturnal periods that passed this filter is presented in Fig. 3. Estimates of nighttime respiration are somewhat higher than those for the daytime case described above, and the temperature dependence ($Q_{10} = 3.0 \pm 0.6$) is within the range of biological expectations (Davidson and Janssens, 2006). The variance explained by the model, while not impressive, is nonetheless typical and due to the inherent difficu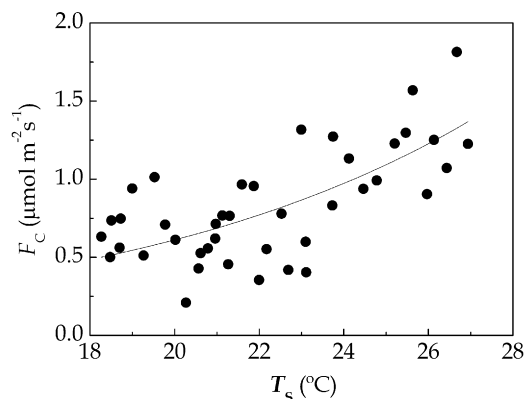lty in applying eddy covariance to the nighttime case. Thus the empirical models of ecophysiological processes describe the data well for this period of high growth.

We now turn our attention to the drought period of late summer 2005 and carbon exchange that is not readily explained by ecophysiological models. Virtually no rain fell in the *Sierra de Gádor* from April through July 2005, and this hot and sunny spell appears to have conditioned the CO_2 fluxes strongly for an extended period. Fig. 4A presents 10 days of F_c in August; these CO_2 fluxes are in stark contrast to the data from the previous figures but are quite representative of the drought period from July through October. For much of these months, we note daytime carbon release (not uptake) with a fairly symmetric appearance and a peak near midday; night-time fluxes are near zero. Simply from the sign of these exchanges, it is clear that the hyperbolic photosynthesis model represented by Eq. (1) cannot fit the data. If a biological explanation is to be found, then it can only be that respiration is the dominant biological process for these daytime data.

Yet the observed temperature variability is insufficient to explain the large CO_2 flux variations via exponential respiration modeling. To demonstrate this clearly, air temperature (data concurrent with F_c in Fig. 4A) is presented in Fig. 4B; note that soil temperature variations are smaller still. Throughout the afternoon of 10 August for example, CO_2 emissions consistently are four times as large as those on the following day. To explain such a change in respiration with an exponential temperature response, assuming a typical Q_{10} value in the range of 2–3 (Davidson et al., 2006), would require temperature differences between the 2 days well over 10 °C. On the contrary, afternoon temperatures only differed by a few degrees between the 2 days. Likewise, with a diurnal air temperature range of ca. 8 °C, exponential modeling fails entirely to explain the near zero values of nocturnal fluxes; this is particularly the case on windy nights (such as that of
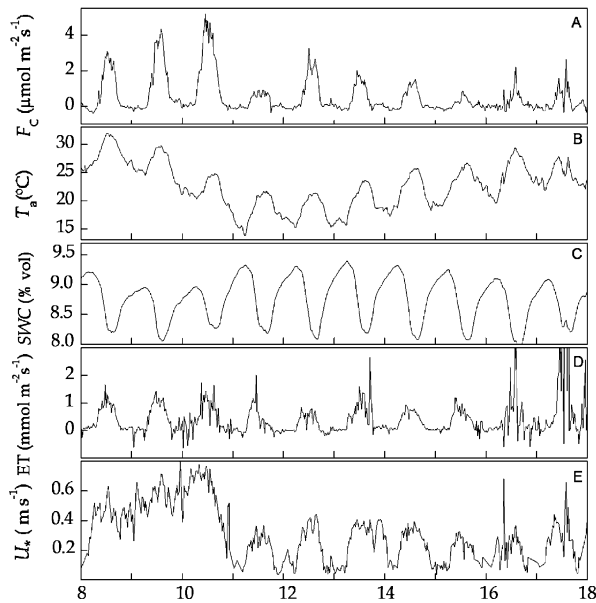
Fig. 4 – Time series of measurements for the *Sierra de Gádor matorral*; the abscissa is labelled with the day of August 2005 at midnight GMT and is the same for all five panels. The ordinates for the five panels are as follows: (A) Carbon dioxide fluxes (F_c) during these drought conditions show daytime carbon release (positive fluxes) peaking at noon with 1–3 μmol m^{-2} s^{-1} and nighttime fluxes near zero or slightly negative. (B) Air temperature (T_a) decreases during the first 3 days and then shows a slow steady climb during 1 week. (C) The volumetric soil water content (SWC) displays diurnal oscillations, with late-afternoon nadir and pre-dawn maximum. (D) Evapotranspiration (ET) takes place mainly during the daytime and is quite noisy. (E) The friction velocity (u^*) shows 3 days of high winds, followed by a week with the typical pattern including suppressed turbulence on stable nights.

Fig. 5 – Time series of CO$_2$ flux measurements (panel A) and the friction velocity (u^*, panel B) for the *Sierra de Gádor matorral*. The abscissa is labelled with the day of October 2006 at midnight GMT and is the same for both panels. Panel A presents turbulent CO$_2$ fluxes (eddy covariance; left ordinate, thin line) and soil CO$_2$ effluxes (chamber measurements; right ordinate, thick line).

10–11 August) when eddy covariance yields reliable estimates of surface exchange. Nor does soil water content (Fig. 4C) allow flux interpretation in terms of drought-limited respiration, since the days of largest CO$_2$ emissions were very dry. Rather than being governed by biological determinants (water, light, temperature) F_c appears to follow other patterns during the drought season, as will now be shown.

Evapotranspiration (ET) and the friction velocity (u^*) each appear to covary with the CO$_2$ fluxes, albeit on different time scales as is seen in Fig. 4D and E. Among numerous correlated variables (e.g., solar radiation, F_p), ET is presented because it is the only one directly related to the CO$_2$ flux via an identifiable process (see discussion). On any given day, both the CO$_2$ and water vapor fluxes follow similar, symmetrical patterns. Fluxes are typically near zero at night and reflect the diurnal course of local solar radiation. In terms of day-to-day variability however, there is a wind-related disconnect between fluxes of the two gases for the drought period. The CO$_2$ flux is much higher on days with high turbulence levels (u^*), while water vapor shows no such dependence.
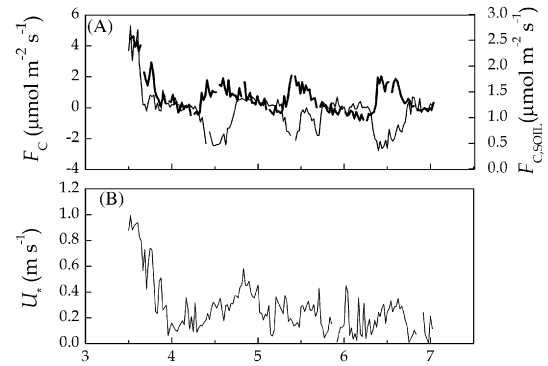
The observed daytime CO$_2$ emission and wind dependence, no eddy covariance artifact, is corroborated by independent chamber measurements. Fig. 5 compares half a week of continuous flux data (panel A), both micrometeorological and via soil chamber measurements for the only campaign which exhibited high winds (u^*, panel B). These data are from the 2006 dry season, when ecophysiological processes continued, and daytime net CO$_2$ emissions were detected only on very windy days. While the dissimilar magnitudes are to be expected for a single soil collar versus footprint-integrated eddy fluxes (hence the dual ordinates), the similar tendencies in relation to winds are striking. For both fluxes, large emissions are observed only on the windy afternoon of 3 October. For low- and moderate-wind conditions on subsequent days, the fluxes revert to apparent ecophysiological behaviour. Before attempting to interpret the flux data, we will now present relevant data from the other field site.

3.2. The Altamira cave

Over the course of a year, CO$_2$ in the Altamira cave undergoes an order-of-magnitude variation that appears to depend on ventilation. Molar concentrations of CO$_2$ (Fig. 6A) are relatively steady in summer, maintaining near-atmospheric values not far above ca. 500 ppm. Winter concentrations are much higher and also more erratic than in summer, sometimes exceeding 5000 ppm. Because neither emission nor decay of ^{222}Rn depends on conditions within the cave, the amount of this otherwise inert gas (Fig. 6B) serves as a proxy for the degree of communication between the cave and the external atmosphere (Fernández et al., 1986). High ^{222}Rn concentrations correspond to isolation, while lower values result from enhanced exchange of air with the outside. Thus, the similar patterns in Fig. 6A and B indicate 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. For both gases, the effects of some below-ground source (yet to be named in the case of CO$_2$) combine with variable ventilation to produce
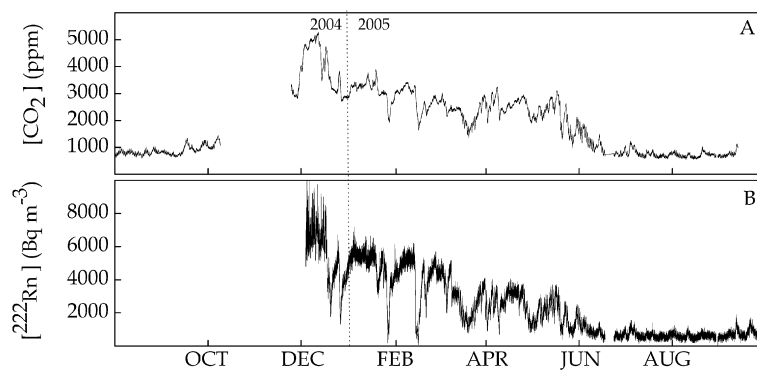
Fig. 6 – Time series of gas concentrations inside the Polychrome hall of the Altamira cave; the abscissa is labelled with months from summer 2004 through summer 2005, and is the same for both panels. The ordinates are (A) Carbon dioxide concentrations and (B) ^{222}Rn concentrations. Both gases exhibit high, erratic winter concentrations and low, steady summer concentrations.

the observed seasonal cycle. As before, examination of shorter timescales is focused on the hot and dry period at the end of summer, when the cave is most coupled to the external atmosphere.

Ventilation affects gas concentrations in the Altamira cave on shorter timescales as well, and follows a diurnal cycle related in some way to external solar forcing. During the first week of August 2005, CO_2 inside the cave (Fig. 7A) exhibits a decreasing trend dominated by sinusoidal, diurnal fluctuations with a magnitude of ca. 100 ppm and maximum concentrations near mid-day. The ^{222}Rn measurements, despite considerable noise, show similar diurnal variations that are clearly in phase with CO_2 (Fig. 7B). Thus ventilation is greatest during the afternoon when gas concentrations fall from their mid-day peak, but is reduced or absent at night allowing build-up of gas concentrations in the cave. The typical 150 ppm decrease (over 12 h), when scaled by air density and a 3 m vertical dimension for Altamira, suggests a ventilation flux of order 0.4 μmol m^{-2} s^{-1}. As we will now see, this is not inconsistent with the magnitude of variations in F_c measured above the cave.

Although complicated by the influence of biological processes, the turbulent CO_2 fluxes (F_c) above the Altamira cave support the notion of cave degasification during summer afternoons. The lawn over the cave retained a green color suggesting sustained photosynthetic capacity throughout the summer of 2005. Despite the inherent noisiness of turbulent flux data, F_c shows a consistent daily trend (Fig. 7C). Modest CO_2 uptake-probably associated with grass photosynthesis-occurs in the morning (generally less than 1 μmol m^{-2} s^{-1}) until around mid-day when cave ventilation becomes prominent and larger emission fluxes are measured throughout the afternoon (ca. 2–3 μmol m^{-2} s^{-1}). Nighttime fluxes are generally small and positive, probably due exclusively to respiration since they correspond to the time when these atmospheric fluxes are decoupled from the cave (as ^{222}Rn accumulates inside).

4.   Discussion

Micrometeorological measurements quantify boundary-layer fluxes representing net exchange with the surface, but cannot
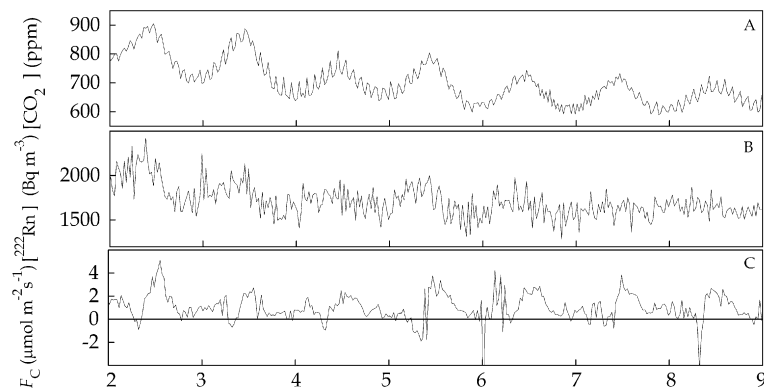

Fig. 7 – Time series of measurements for the Altamira cave; the abscissa is labelled with the day of August 2005 at midnight GMT and is the same for all three panels. The ordinates for the three panels are (A) Carbon dioxide concentrations in the Polychrome hall of the cave interior, (B) ^{222}Rn concentrations also in the Polychrome hall, and (C) Carbon dioxide fluxes (F_c) over the lawn above the cave. The largest fluxes are upward in the afternoon during cave ventilation as indicated by the falling gas concentrations (particularly ^{222}Rn).

directly identify the underlying processes responsible for the flux. In the case of CO_2 exchange, the net flux has generally been interpreted as ''net ecosystem exchange'' (NEE), a biological flux defined as the sum of photosynthetic and respiratory components. In addition to biological processes, karst processes add the complexity of below-ground storage (and ventilation), but also the possibility of an abiotic CO_2 source. Results presented here from two sites where ecosystems live on karstic substrates strongly suggest the need, when interpreting turbulent fluxes in such cases, to characterize the influence of these abiotic processes.

Independent data from both sites point to the presence of a below-ground CO_2 source that is not concurrent respiration. For the eddy flux data of *Gádor*, the failure of the Q_{10} respiration model and especially the correlations with evapotranspiration and the friction velocity are strong clues that afternoon CO_2 release during the drought season is not a direct result of respiration. Results from these direct F_c measurements – CO_2 emission during extended soil drying and plant senescence over a carbonate substrate, and even dramatic windspeed dependence – are consistent with determinations from an inferential technique at another site with carbonaceous soils in Arizona (Emmerich, 2003). The author of this previous study also sought inorganic explanations for such emissions, but did not interpret the data in the context of macropore ventilation. In *Gádor* at least, the presence of numerous dolines (sinkholes) in the immediate vicinity of the tower (Li et al., 2007) strongly suggests the presence of subterranean cavities, but for information from inside the caves we must look further north.

At Altamira, both above- and below-ground data corroborate the hypothesis of an underground, abiotic CO_2 source. Similar to *Gádor*, attempts to fit an exponential soil respiration model to emissions yielded biological absurdities, with Q_{10} often an order of magnitude larger than what is typical for enzyme kinetics (data not shown). On a daily timescale, afternoon emissions appear to correspond clearly to ventilation episodes detected inside the cave. On an annual scale, cave CO_2 fluctuations with high concentrations from November until degasification in May/June have been measured during other years (Fernández et al., 1986; Lario et al., 2005; Sánchez-Moral et al., 1999) and in other caves (Hoyos et al., 1998). Whatever the timescale, however, oscillations in both CO_2 and especially ^{222}Rn inside the cave represent an imbalance between local source processes acting to raise gas concentrations but competing with degasification by ventilation.

The source of CO_2 inside the cave is almost certainly not due to local respiration. Bacterial colonies have minimal extent (and biomass), existing only on thin ceiling layers very near cave entrances, and so the metabolic activity of heterotrophic organisms cannot likely explain the source. Furthermore, recent studies demonstrate that the heterotrophic bacteria in Altamira and other oligotrophic subterranean environments are preferably consumers (not producers) of CO_2, explaining the neoformation of metastable minerals (Sanchez-Moral et al., 2003). If respiration from the soil is somehow responsible for CO_2 increases deep in the cavity, the meters-thick layer of rock separating the cave from the overlying, respiring soil implies a prolonged diffusion process before respired CO_2 can reach the cave. For karst systems, any examination of CO_2 thus stored underground must consider the geochemical processes of carbonate rock dissolution directly responsible for the formation of such cavities.

Carbon dioxide dissolves in water and dissociates to yield bicarbonate and a proton; in the presence of carbonate rocks, the proton further dissolves stone to produce more bicarbonate (Emmerich, 2003). The chemical reactions are frequently written as though the carbonate rock were pure limestone, as follows (Kaufman and Dreybrodt, 2007):

$$CO_2 + H_2O \Leftrightarrow HCO_3^- + H^+ \tag{3}$$

$$CaCO_3 + H^+ \Leftrightarrow Ca^{2+} + HCO_3^- \tag{4}$$

For dolomitic rocks (chiefly dolomite $CaMg[CO_3]_2$), dissolution reactions are analogous but with double molar requirements for consumption of CO_2 and water, while precipitation prefers the formation of calcium carbonate rather than more dolomite. Such aqueous phase chemistry is of constant significance at karstic sites, since even when very dry the soil maintains a significant volume of water (in excess of 5%). From the point of view of atmospheric CO_2, aqueous bicarbonate thus represents a source or sink, depending on the disequilibrium tendency.

Although the data presented above are from a summer period, we begin our examination of geochemical CO_2 cycling in a karst system during the rainy season. Rainwater enters the soil, where both high concentrations of CO_2 produced by respiration and reduced bicarbonate concentrations (due to dilution) push Eqs. (3) and (4) to the right; the result is production of soluble, inorganic carbon (CO_2, HCO_3^-, and CO_3^{2-}). This dissolved inorganic carbon percolates into the karst system along with the drainage water, and enters cavities like the Altamira cave where local concentrations determine whether the reverse processes precipitate carbonate stone and enrich the cave air CO_2 concentration. Poor ventilation (or none) keeps gas concentrations high all winter. These wet season processes describe a sustained belowground sink for gaseous CO_2 whose magnitude may be important for the interpretation of net flux measurements in turbulence above the moist karst system.

During summer afternoons, ventilation extracts CO_2 from subterranean cavities and produces sizeable upward fluxes in the atmospheric boundary layer. Once the macropore CO_2 falls below the equilibrium concentration relative to the other reactants in Eqs. (3) and (4), geochemical conversion of aqueous bicarbonate represents a below-ground CO_2 source. Evapotranspiration (loss of soil water and increased bicarbonate concentrations) can likewise pull Eqs. (3) and (4) to the left and cause the karst system to act as a considerable CO_2 source (up to $4 \, \mu mol \, m^{-2} \, s^{-1}$), perhaps explaining in part the correlation between CO_2 fluxes and evapotranspiration (ET) at the *Sierra de Gádor* site (Fig. 4). Since these geochemical equations are tied to both the carbon and water cycles, it is improbable that they would remain in equilibrium for very long, and the effects of these geochemical equations are likely important at any time of year.

Yet the data from June 2004 at the *Sierra de Gádor* site did exhibit typical biological behavior, and might suggest that

geochemical processes can be neglected at times even in the presence of a karst system. Results for this period may be considered typical of ecosystem fluxes during the growing season (cf. Cook et al., 2004). It may be that ventilation was not a complicating factor during this period following above-normal rainfall. However, we cannot discount the possibility that, with the soil well watered, the existence of a below-ground carbonate dissolution sink induced undetected biases in the partitioning of the net CO_2 flux into photosynthesis and respiration (as in Figs. 2 and 3). In contrast to the dry season, where geological CO_2 emissions are related to evapotranspiration and therefore follow a clear diurnal cycle, geological CO_2 consumption during the wet season probably is not characterized by pronounced diurnal variation and is therefore easily overlooked by the ecophysiological models. A correct partitioning of net turbulent fluxes into ecophysiological and geochemical components will likely require isotopic analyses to discern among processes with different fractionation signatures, but is beyond the scope of this study.

What can we infer from the observed behavior of cave ventilation and the differing wind dependence of gas fluxes? In physical terms, CO_2 emission by ventilation of deep cavities with aqueous bicarbonate reservoirs requires open soil pore spaces, through which air movement is facilitated by higher winds. By contrast, evaporation is predominantly from the near-surface soil (maximum thermal forcing) such that communication between water vapor source and atmosphere requires neither winds nor open pores. The disparate flux magnitudes for water vapor (mmol) and CO_2 (μmol) preclude any interpretation via reaction stoichiometry, so their diurnal similarity could be due to dry soil evaporation *enabling* – not driving – karst ventilation and CO_2 exchange by opening pore space for gas flow. The lack of nocturnal ventilation may be related to soil re-humidification, a poorly understood phenomenon evident in Fig. 4, observed elsewhere during Mediterranean summers (e.g., Kosmas et al., 1998, 2001), and arguably capable of closing pores to air flow. In any event, a clear understanding of karst cavity ventilation will require further investigation.

In the context of the qualitative objectives set forth, it appears that geochemical cycling requires more attention in flux tower investigations over carbonaceous soils, and perhaps even at a global scale. Each year about 200 Mt C, originating from carbonate rock weathering, flows from the continents into the ocean (Ludwig et al., 1998). Our data show that the reverse process, the precipitation of $CaCO_3$ and associated release of CO_2 back into the atmosphere, becomes dominant during the dry season. Whether or not the global annual total masks substantial seasonal variation in the geological CO_2 fluxes remains to be tested. In any case, our results represent strong evidence against the validity of the prevailing hypothesis that geochemical CO_2 cycling can be neglected in ecosystem-scale flux tower research on carbonaceous soil.

5. Conclusions

Interpretations of CO_2 exchange over carbonaceous substrates cannot universally ignore the possibility of geochemical source/sink processes, particularly during dry seasons when they can dominate the flux. A combination of micrometeorological and subterranean data at two sites – one semi-arid and another temperate maritime – has given strong indications that karst geochemical processes play important roles in the local carbon cycle on timescales associated with turbulent exchange. Unresolved issues for future investigation include:

- the partitioning of net carbon fluxes into biological and geochemical components;
- the nature of the mechanism(s) that control ventilation in karst macropores;
- the net effect of karst geochemistry in the global carbon balance.

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