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Interannual CO_2 exchange of a sparse Mediterranean shrubland on a carbonaceous substrate

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[1] This study presents the interannual CO_2 exchange of a semiarid shrubland overlying a carbonaceous substrate where abiotic processes may interact with biological processes in the ecosystem carbon cycle. Estimated by the eddy covariance technique and two different gap-filling models (RBF neural network and MDS "Marginal Distribution Sampling"), the mean annual net ecosystem exchange (NEE) of CO_2 varied from -63 to 29 g C m^{-2}, averaging -2 ± 23 g C m^{-2} from May 2004 to December 2007. In addition, CO_2 exchange was divided into periods likely dominated by clear signals of biological activity (high daytime uptake, low Bowen ratio) and periods of apparent plant senescence (dry conditions) to better understand the relative contributions of "biological versus abiotic processes" to the annual NEE and the interannual variability of these processes. During biological periods, CO_2 exchange appears to be related to changes in the ecosystem leaf area index, whereas abiotic fluxes are most closely related to evapotranspiration. The timing of rainfall events seems to be a main determinant of both activation and duration of biological processes. During apparent abiotic periods, CO_2 exchange is characterized by daytime emissions averaging 1.5 μmol m^{-2} s^{-1}, whereas biological periods are characterized by daytime CO_2 uptake with mean values of around 1.4 μmol m^{-2} s^{-1}. As a preliminary result, the abiotic period characterized from 19% of 2004 to 45% of 2007 with a mean duration of approximately 2 months. However, future research is needed in order to achieve a more reliable division between determinant processes involved in CO_2 exchange over carbonaceous substrates.

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1. Introduction

[2] The importance of characterizing the global carbon cycle is highlighted by the role of CO_2 as the principal greenhouse gas after water vapor [*Schimel*, 1995]. Anthropogenic CO_2 emissions and changes in land use have induced changes in the global carbon cycle and represent potential feedbacks to climate change [*Houghton*, 2002] due to the resulting increases in atmospheric CO_2 [*Keeling*, 1960]. Less than half of the anthropogenic CO_2 emissions have remained in the atmosphere and the rest have been absorbed by the ocean and land ecosystems [*Tans et al.*, 1990]. In the last two decades the global terrestrial carbon fluxes were approximately twice as variable as those with the ocean [*Bousquet et al.*, 2000], indicating that terrestrial ecosystems are the main driver of global interannual variability in atmospheric CO_2 [*Friend et al.*, 2007].

[3] Net CO_2 fluxes in different terrestrial ecosystems and their determinant processes are keys to characterizing the global carbon cycle and to assessing human impacts on ecosystems. The eddy covariance technique provides the only direct measurement of CO_2 exchange between the atmosphere and whole terrestrial ecosystems, and is therefore an indispensable tool for understanding and monitoring the global carbon cycle [*Matross et al.*, 2006]. This technique is one of the most important methods used worldwide and has a potential to quantify how whole ecosystems respond to a spectrum of climate regimes [*Baldocchi et al.*, 2001]. In this context, an international micrometeorological network (FLUXNET) was created that provides direct ecosystem measurements of carbon dioxide, water vapor and energy flux densities [*Baldocchi et al.*, 2001]. FLUXNET is one of the most important sources of information for the validation and improvement of models used to study regional and global carbon cycles [*Friend et al.*, 2007]. Thanks to the

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FLUXNET micrometeorological network, mainly forests and some agricultural ecosystems are well known in the context of their CO_2 sink or source behavior [*Bon-Lamberty et al.*, 2007; *Janssens et al.*, 2003; *Luyssaert et al.*, 2008; *Magnani et al.*, 2007; *Valentini et al.*, 2000].

[4] In these investigations, the net CO_2 flux has generally been interpreted as a biological flux (photosynthesis and respiration) neglecting carbonaceous rock dissolution or weathering processes. This net CO_2 flux is commonly termed net ecosystem exchange (NEE) and is often separated into in gross primary production (GPP) and total ecosystem respiration (TER) components using ecophysiological models [*Falge et al.*, 2001b]. In this context, the net flux of CO_2 associated with carbonate reactions is assumed negligible when compared to the gross biological flux, and therefore not taken into account in ecosystem-scale carbon cycle research. Little attention has yet been focused on carbon exchange by ecosystems with carbonaceous substrates [*Emmerich*, 2003; *Mielnick et al.*, 2005; *Stone*, 2008] where not only biological processes but also geochemical processes control this exchange. However, a recent publication [*Kowalski et al.*, 2008] demonstrates that abiotic exchange processes can at least temporarily, during drought periods, dominate the terrestrial carbon exchange with the atmosphere in areas with carbonaceous soils that occupy 12–17% of the Earth's land surface [*Ford and Williams*, 1989].

[5] Sparse shrubland ecosystems in Mediterranean climates represent an ecosystem type whose functional behavior, in terms of CO_2 exchange with the atmosphere, has not been studied extensively. These lands are composed by patches of vegetation and bare soil that interact with each other [*Domingo et al.*, 1999]. The Mediterranean climate is characterized by summer droughts and asynchronous annual patterns of sunlight and precipitation. Thus, such ecosystems are very sensitive to perturbations such as drought. In this context, a better understanding of the effect of drought over such ecosystems is essential in order to achieve reliable regional (and ultimately global) estimates of carbon cycling, as well as to predict the response of semiarid ecosystems to climate change.

[6] Here we present a study regarding the interannual carbon exchange of a sparse Mediterranean shrubland on a carbonaceous substrate (southeast Spain) subject hypothetically to both biological and abiotic processes driving surface CO_2 exchange. Nearly four years of eddy covariance data are presented, covering a range of meteorological conditions including extreme events. Since the complexity of these data prevent the application of commonly applied models for decomposing net carbon exchanges into underlying processes, we use two simple statistical approaches to fill data gaps and achieve long-term integration. We study the importance of the precipitation timing on the ecosystem functioning and the contribution of abiotic processes in the annual CO_2 exchange. Finally, we analyze the dependence of CO_2 exchange on meteorological variables during periods hypothetically dominated by biological and abiotic processes.

2. Site, Material, and Methods

2.1. Site Description

[7] Measurements of CO_2, water vapor and energy exchange were made from May 2004 to December 2007 in "El Llano de los Juanes," a Mediterranean shrubland plateau at 1600 m altitude and 25 km from the coast, located in the Sierra de Gádor (Almería, southeast Spain; 36°55′41.7″N; 2°45′1.7″W). "El Llano de los Juanes" is characterized by a subhumid montane Mediterranean climate with a mean annual temperature of 12°C and mean annual precipitation of *ca*. 475 mm, falling mostly during autumn and winter, and by a very dry summer. Predominant winds come from the north-northeast during the day (45% of the total daytime wind) and from the south at night (52%). The dominant ground cover is bare soil, gravel and rock (49.1%). The vegetation is diverse but sparse, with predominance (% ground cover) of three perennial species, *Festuca scariosa* (Lag.) *Hackel* (18.8%), *Hormathophilla spinosa* (L.) *Küpfer* (6.8%) and *Genista pumila* (Vierh) *ssp. pumila* (5.5%). Other species present include *Thymus serpilloides, Phlomis lychnitis, Ramnus murtifolis* and *Quercus sp.* More detailed site information can be found in the work of *Serrano-Ortiz et al.* [2007].

[8] The parent soil material of the Sierra de Gádor consists of Triassic carbonate rocks [*Vallejos et al.*, 1997]; in "El Llano de los Juanes" these carbonate rocks are mainly dark limestones, with 98 ± 2% calcite (X-ray diffraction analysis). Soils are classified as Lithic Haploxeroll (Soil Survey Staff 1999) with silt loam texture (15 ± 1% clay, 37 ± 5% loam and 48 ± 5% silt) and neutral pH (7.5 ± 0.1); the apparent density is 1.05 ± 0.01 g cm^{-3} and C/N is 15 ± 5 (50 ± 10 g kg^{-1} of carbon and 3.2 ± 0.4 g kg^{-1} of nitrogen); the bicarbonate content at the surface is 2.1 ± 1.8% [*Oyonarte*, 1992]. There are two horizons: surface "A" (0–10 cm) and subsurface "B" (variable, from 10 to 30 or even 150 cm) including a petrocalcic horizon.

2.2. Meteorological and Eddy Covariance Measurements

[9] Environmental and soil measurements including wind speed, air temperature and humidity, soil water content, soil temperature, net radiation, soil heat flux, rainfall and fluxes of incident and reflected photons in photosynthetic wavelengths were measured as described in Table 1. Fluxes of CO_2 and H_2O were determined with an eddy covariance system installed atop a 2.5 m tower (Table 1). The one-sided leaf area index (LAI) was estimated periodically for the five most abundant species from reflectance measurements with an Agricultural Digital Camera (ADC, Dycam, Woodland Hills, CA, USA). In our study LAI values were calculated from an NDVI-LAI relationship obtained by correlating NDVI values from the ADC camera with LAI values from destructive sampling. Ecosystem LAI was estimated using individual values measured per species together with information regarding percentage of cover.

[10] Densities of CO_2 and H_2O were measured by an open-path infrared gas analyzer, calibrated monthly using an N_2 standard for zero and (variable but known) ~500 μmol (CO_2) mol^{-1} gas standards for span. A data logger (CR23X, CSI) managed the measurements and recorded the data. Means, variances, and covariances of 10 Hz data were calculated and stored every 15 min. Environmental and soil measurements made every 10 s were stored as 15 min averages. Eddy flux corrections for density perturbations [*Webb et al.*, 1980] and two coordinate rotations [*McMillen*, 1988] were carried out in postprocessing, as was the

Table 1. List of Variables Measured in "El Llano de los Juanes"[a]

Measurements	Sensor	Height
	Open Path Eddy System (10 Hz)	
CO_2 and H_2O vapor densities	open-path infrared gas analyzer (Li-Cor 7500, Lincoln, NE, USA	2.5 m
H_2O vapor density fluctuations	Krypton Hygrometer (KH-20, Campbell Scientific, Logan, UT, USA	2.5 m
Wind speed (3-D) and sonic temperature	three-axis sonic anemometer (CSAT-3, Campbell Scientific, Logan, UT, USA)	2.5 m
	Environmental and Soil Measurements (0.1 Hz)	
Air temperature	thermohygrometer (HMP35-C, Campbell Scientific, Logan, UT, USA)	1.5 m
Relative humidity	thermohygrometer (HMP35-C, Campbell Scientific, Logan, UT, USA)	
Photon flux density (up and down)	PAR sensors (Li-190, Li-Cor, Lincoln, NE, USA)	1.5 m
Net radiation	net radiometer (NR Lite, Kipp & Zonen, Delft, Netherlands)	1.5 m
Soil water content	Water Content Reflectometer (CS615, Campbell Scientific, Logan, UT, USA)	−15 cm
Soil temperature	TCAV (Campbell Scientific, Logan, UT, USA)	(−1, −3, −5, −7) cm
Soil heat flux	2 heat flux plates (HFP01, Hukseflux, Delf, Netherlands)	−8 cm
Rain	tipping bucket (0.2 mm) rain gauge (model 785 M, Davis Instruments Corp., Hayward, CA, USA)	

[a]Southeastern Spain, Almería.

conversion to half-hour means following Reynolds' rules [*Moncrieff et al.*, 1997].

2.3. Analysis Methods

2.3.1. Flux Data Processing and Quality Control

[11] When applying the density corrections, to avoid CO_2 density (ρ_c) underestimations due to open path IRGA lens contamination and resulting errors in density corrections, optical windows of the open path IRGA were cleaned periodically and mean gas densities were corrected according to errors estimated by comparison with the thermohygrometer [*Serrano-Ortiz et al.*, 2008].

[12] Quality control of the half-hourly flux data was applied in a three-step procedure: First, we detect periods when the eddy covariance system does not work properly due to environmental conditions or instrument malfunction; data from the open-path IRGA are rejected if <75% of 18000 possible data sets during each averaging period are available. Second, we detect periods when the IRGA does not work properly due to dew or dirty rain events. Half-hour periods marked by changes in the diagnostic parameter for window purity (AGC) are considered unreliable in terms of fluctuations in CO_2 density (fluxes rejected); by contrast, when AGC is constant but above the baseline for window purity, CO_2 fluctuations are accepted whereas the mean CO_2 density is not [*Serrano-Ortiz et al.*, 2008]. Finally, averaging periods with low turbulence (friction velocity, $u^* < 0.2 \text{ m s}^{-1}$) are rejected [*Gu et al.*, 2005]. The contribution of storage to net CO_2 exchange, very small for low measurement heights and aerodynamically simple surfaces [*Suyker and Verma*, 2001], is neglected [*Kowalski et al.*, 2003; *Santos et al.*, 2004].

[13] For this site with several hundred meters of homogeneous surface upwind of the tower in every direction, flux data were subjected to two standard validity criteria. First, a footprint model verified that fluxes originate from well within the fetch, even during periods of atmospheric stability. The Flux-Source Area model [*Schmid*, 1994] estimated the maximum source location (X_m) as 27 m and the maximum source location far end (e) as 114 m of 90% contributing area ellipse, during moderate turbulence ($0.2 \text{ m s}^{-1} < u^* < 0.4 \text{ m s}^{-1}$) for downward sensible heat fluxes ($H < 0$). Second, the energy balance closure (ratio the sum of sensible and latent turbulent flux, H + LE, to the sum of net radiation and soil heat flux, R_n + G) was 72% (R^2 = 0.89; n = 31211). This value, providing additional information regarding turbulent flux quality [*Moncrieff et al.*, 1997], is in the range reported by most FLUXNET sites [*Wilson et al.*, 2002].

2.3.2. Data Coverage and Gap Filling for Long-Term Integration of Fluxes

[14] Over nearly 4 years, measurement failures amounted to 30.5% of the total period while low wind turbulence conditions rejected 27.1% of the data, resulting in 57.6% of data missing and requiring gap filling in order to estimate the annual CO_2 exchange. Considering that the overall uncertainty of annual CO_2 exchange is dominated by the contribution of the gap-filling model [*Dragoni et al.*, 2007], two different techniques were applied: a neural network [*Cazorla et al.*, 2008; *Ooba et al.*, 2006; *Papale and Valentini*, 2003] and "Marginal Distribution Sampling" (MDS) [*Reichstein et al.*, 2005]. Notice that due to the complexity of these data, commonly applied models for gap filling that decompose net carbon exchanges into photosynthesis and respiration [*Falge et al.*, 2002] cannot be used [*Kowalski et al.*, 2008; *Serrano-Ortiz et al.*, 2007].

[15] The neural network applied is a Radial Basis Function (RBF) network [*Haykin*, 1994] and is especially suitable for function approximation. The inputs to the radial basis networks are the variables of the function, and the output is the function approximation. The topology of the RBF network consists of a two-layer feed forward neural network characterized by two sets, input and output, separated by a hidden layer of processing units. Each layer implements a radial basis function. Determining the RBF weights is termed network training. A training set of input-output pairs is used to optimize the network parameters that fit the network outputs to the given inputs. The fit is evaluated by means of a cost function, in this case the mean square error. After training, the RBF network can be used with data whose underlying statistics are similar to those of the training set [*Cazorla et al.*, 2008].

[16] The complete data set was divided randomly to form two independent subsets. One subset (2/3 of the complete data set, 11719 samples) was used as a training data set for the gap-filling model. The other subset (1/3; 5860 samples) was used for validation. Input variables were selected using a principal component analysis (PCA). After multiple

Table 2. Statistical Comparison Between RBF Network and MDS Methods[a]

Method	Artificial Gap	Slope	R^2	ε (μmol m^{-2} s^{-1})	RMSE (μmol m^{-2} s^{-1})
RBF network	Jun 2006	0.89	0.71	−0.04	1.07
	Sep 2004	0.83	0.56	−0.12	2.77
MDS method	Jun 2006	0.90	0.52	0.10	2.58
	Sep 2004	0.92	0.29	−0.08	1.82

[a]Where "slope" refers to the linear regression between observed CO_2 exchange and estimated CO_2 exchange, R^2 is the coefficient of the determination, ε is the residual error, and RMSE is root mean square error.

attempts, the most confident RBF network ($R^2 = 0.50$) was obtained with the following inputs: Fuzzy transformation of the month, day and time of day [*Papale and Valentini*, 2003], air and soil temperature (T_a and T_s, respectively), wind direction (WD), wind speed (WS), net radiation (R_n), photon flux density (PPFD), relative humidity (HR), friction velocity (u*), soil water content (SWC) and vapor pressure deficit (VPD). Input variables were scaled between 0 and 1.

[17] Missing values for environmental and soil inputs to the RBF network procedure were filled using redundant measurements. Where these lacked, gaps of less than two hours were filled using linear interpolation between adjacent values. Missing observations exceeding two hours were filled using the mean for that (half-hour) time period based on seven adjacent days using a "gliding" window [*Falge et al.*, 2001b]. Exceptionally, missing values from an extensive period lacking power (battery theft, winter access; 5 November 2006 to 15 February 2007) were not filled.

[18] The "Marginal Distribution Sampling" (MDS) [*Reichstein et al.*, 2005] is based on methods similar to those determined for original continental flux-tower networks [*Falge et al.*, 2001a, 2001b]. The MDS technique replaces missing values using a time window of several adjacent days. The length of the time window depends on environmental conditions and meteorological data availability (for more information, see *Reichstein et al.* [2005, Appendix A]).

[19] Although three and a half years of CO_2 exchanges were compared using both gap-filling models (RBF network and MDS method), it was convenient to select one method for analyses of interannual variability. To select the most appropriate gap filling method, we evaluated both by creating artificial gaps in the database and comparing measured half-hourly CO_2 fluxes with values estimated with the RBF network and MDS methods. For 1 month during the growing and drought season (June 2004 and September 2006, respectively) 75% of measured data were selected randomly to create artificial gaps. We used the slope of the linear regression, the coefficient of determination (R^2), the residual error (ε) and the root mean square error (RMSE) to evaluate both models (Table 2). Although the slope of the linear regression between observed and estimated CO_2 exchange was larger using MDS method, the RBF model was superior in terms of variance explained and residual errors. The RMSEs favored the RBF network in June 2006 but conversely the MDS method in September 2004.

3. Results

3.1. Meteorological Conditions

[20] Figure 1 shows the annual and seasonal variability in environmental conditions. Air temperature (T_a) and incident flux of photosynthetically active photons ($PPFD_d$) followed sinusoidal patterns during the study period. The annual daily T_a averages were 11.3, 12.9 and 11.6°C in 2005, 2006 and 2007, respectively (Figure 1a). Maximum values of $PPFD_d$ were observed in early summer reaching average daily values exceeding 700 μmol m^{-2} s^{-1}; minimum values of $PPFD_d$ were measured during January (<30 μmol m^{-2} s^{-1}) (Figure 1b). Over the study period rainfall and $PPFD_d$ were strongly asynchronous. Rain fell mostly in autumn and winter, when $PPFD_d$ reached its minimum value. The annual rainfalls were 373, 168, 411 and 251 mm in 2004, 2005, 2006 and 2007, respectively (Figure 1c). According to the deficiency in rain events and the soil water content (SWC) baseline (<15% volumetric) we observed seasonal water deficits consistently during summer and early autumn (Figure 1c).

[21] The observation period was influenced by some extreme meteorological events. An intense rain period preceded installation of the EC system in spring 2004, when less than 2 months produced 373 mm of precipitation, more than the annual sum of 2005 or 2007. In addition, it is important to remark the extreme cold in winter 2005 (minimum daily T_a of −8.9°C followed by a warm February) and the extreme drought in summer 2005 (maximum period without rain lasted 50 days (10 April to 30 May) and 5 months with SWC < 15%). These meteorological extreme events can cause plant injuries [*Jones*, 2000; *Pockman and Sperry*, 1997; *Resco et al.*, 2009] from which some exposed species of the studied ecosystem may never recover. Finally it is relevant that snowfall was prominent in winter 2004/05 with more than 20 days of snow cover. These events could lead to lasting influences on carbon exchange.

3.2. Carbon Exchange

3.2.1. Carbon Exchange Behavior

[22] Figure 2 shows daily ecosystem carbon loss during the study period using the RBF network and MDS methods for gap filling. "El Llano de los Juanes" acts as a carbon sink during spring (negative values) and as a carbon source during summer (positive values), with very similar patterns for the two methods during the whole study period. However, some differences are evident. In May 2004 the ecosystem captured carbon according to MDS method, (approximately 1.5 g C m^{-2} d^{-1}) while using RBF network the ecosystem appears to have been carbon neutral. In addition, in February 2005, the RBF network indicates a peak in carbon uptake (1.7 g C m^{-2}) that does not appear in the MDS results; this corresponds to a winter period with high mean daily values of T_a and SWC (10°C and 30%, respectively; Figure 1). In addition, notice that during June 2007 ecosystem carbon sequestration estimated by the RBF network is far more variable than that resulting from the

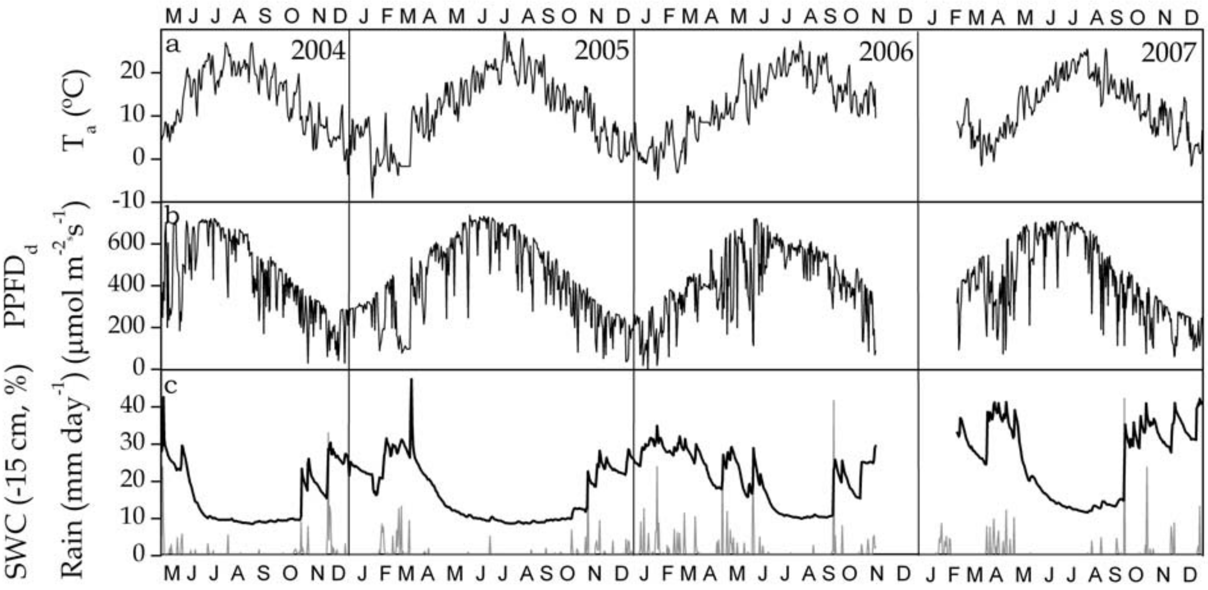

Figure 1. Average daily environmental conditions in the montane shrubland "El Llano de los Juanes" from May 2004 to December 2007. (a) Air temperature, T_a. (b) The incident flux of photosynthetically active photons, $PPFD_d$. (c) Volumetric soil water content, SWC (black line) and total rainfall (mm d^{-1}) (gray line).

MDS method, due to smoothing that is inherent to the MDS technique. Finally however, the mean annual carbon exchange during the whole period was -3 ± 16 and 0 ± 30 g C yr^{-1} using the RBF network and MDS method, respectively. Given this generally good agreement between the two independent gap-filling methods, both the interannual variability of net carbon exchange and its dependence on biological and geological forcing will be presented using only results from the RBF network.

[23] As mentioned in the introduction, a recent publication [*Kowalski et al.*, 2008] demonstrates the existence of abiotic carbon exchange processes that can temporarily dominate the local carbon cycle. For this reason, it is interesting to divide carbon exchange into periods which we posit as dominated by abiotic processes (henceforth, abiotic periods) versus those dominated by photosynthesis and respiration (from now on, biological periods). For this purpose, abiotic periods were defined during drought seasons (SWC < 15%) when the mean, daytime Bowen ratio (H/LE) exceeded 4, signaling senescence of many plants and marked decreases in photosynthesis and respiration. Furthermore, biological periods were defined when the daily Bowen ratio (H/LE) was less than 4 and the daytime average of T_a was higher than 4°C [*Serrano-Ortiz et al.*, 2007]. Days falling into neither category were characterized as indeterminate.

[24] Table 3 shows daily averages of some meteorological and phenological variables related to the behavior of CO_2

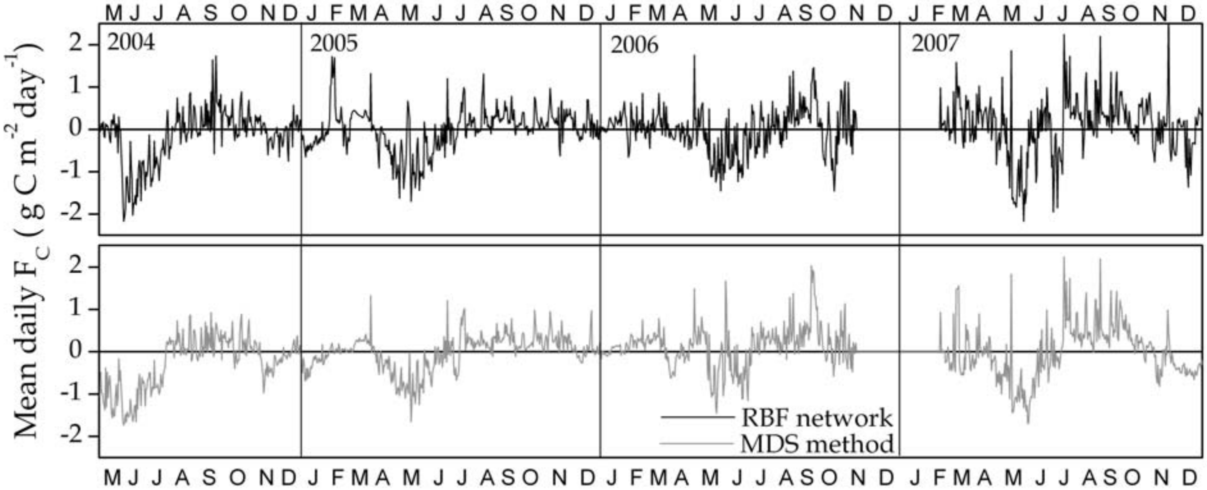

Figure 2. Daily carbon loss by "El Llano de los Juanes" from May 2004 to December 2007, using two gap-filling models: neural network (RBF network) (black line) and Marginal Distribution Samples (MDS) method (gray line).

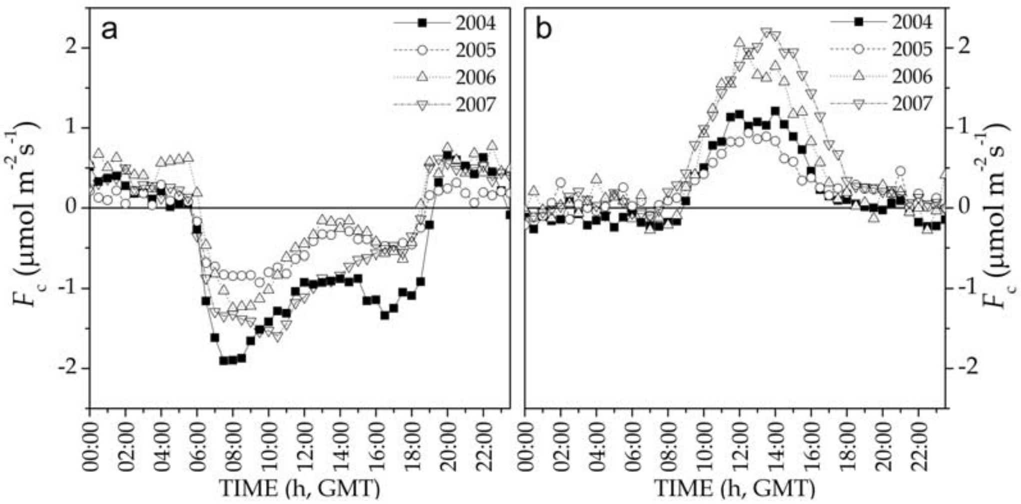

Figure 3. Diurnal trends in net ecosystem exchange of carbon (F_c, μmol m^{-2} s^{-1}) during periods (from 2004 to 2007) hypothesized to be dominated by (a) biological processes or by (b) abiotic processes.

fluxes (F_c) during biological and abiotic periods from 2004 to 2007. Table 3 also shows the total NEE, duration and daily mean carbon flux for these periods. In addition, Figure 3 shows the mean diurnal trends in measured F_c (μmol m^{-2} s^{-1}) during biological (Figure 3a) and abiotic periods (Figure 3b). Figure 3a shows daytime uptake from early morning (0600 GMT) to evenings (1900 GMT) reaching maximum sequestration at 0800 GMT with decreased photosynthetic uptake around noon (1200 GMT). The highest values of CO_2 uptake where detected in 2004 with a peak of -2 μmol m^{-2} s^{-1} in the morning and another peak of -1.5 μmol m^{-2} s^{-1} in the early evening; mean daily PPFD$_d$ and T_a are also higher than other years (530 ± 170 μmol m^{-2} s^{-1} and 16 ± 7°C, respectively), and ecosystem LAI is 1.13 m^2 m^{-2} (Table 3). In 2005, with an ecosystem LAI decrease of 19% (0.92 m^2 m^{-2}) compared to 2004, the magnitude of the CO_2 uptake peak decreased more than 40% (and similarly in 2006). In 2007, although ecosystem LAI was somewhat higher than in 2004 (1.18 m^2 m^{-2}) peak values of CO_2 uptake decreased more than 25%; compared to 2004, mean daily PPFD$_d$ and T_a were 25% and 60% lower, respectively (390 ± 180 μmol m^{-2}s^{-1} and 10 ± 5°C).

[25] During nighttime, the lowest values of CO_2 release were observed in 2005 (less than 0.3 μmol m^{-2} s^{-1}) and similar values were detected for other years but with an increase in CO_2 release in 2006 (more than 0.5 μmol m^{-2} s^{-1}; Figure 3a). In this context, we observed that the net ecosystem CO_2 exchange for the whole biological period in 2004 (measured and filled data) was nearly 3 times higher than for 2007 with duration of 160 and 197 days, respectively. Similar values of NEE were detected during biological periods in 2005 and 2006 (42 g m^{-2} and 31 g m^{-2}, respectively) with 20 more days of duration for the biological period in 2006. Mean daily carbon uptake decreased from 0.36 g m^{-2} d^{-1} in 2004 to 0.11 g m^{-2} d^{-1} in 2007.

[26] Figure 3b shows mean measured F_c during hypothesized abiotic periods from 2004 to 2007. We observe daytime carbon release with a fairly symmetric appearance and a peak just after midday (1300 GMT); nighttime

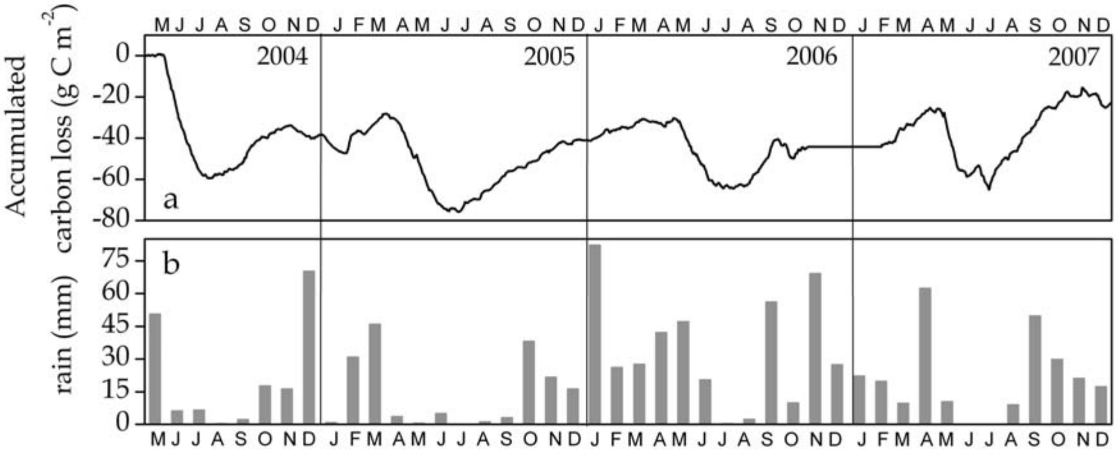

Figure 4. (a) Accumulated carbon loss and (b) monthly precipitation in "El Llano de los Juanes" from May 2004 to December 2007.

Table 3. Daily Mean Values of Meteorological Variables, Integrated Sums of Net Ecosystem Exchange of Carbon, Period Duration, and Daily Mean Carbon Flux for Periods Hypothesized to be Dominated by Biological and Abiotic Processes[a]

Period of Biological Dominance	PPFDd (μmol m^{-2} s^{-1})	ET (mg m^{-2} s^{-1})	T_a (°C)	NEE (g m^{-2})	Duration (days)	F_C (g m^{-2} d^{-1})	LAI (m^2 m^{-2})
2004	530 ± 170	14 ± 9	16 ± 7	−57 ± 23	160	−0.36 ± 0.14	1.13
2005	480 ± 190	9 ± 5	13 ± 7	−42 ± 22	195	−0.22 ± 0.11	0.92
2006	440 ± 50	11 ± 7	14 ± 6	−31 ± 12	214	−0.14 ± 0.05	-
2007	390 ± 180	8 ± 5	10 ± 5	−21 ± 8	197	−0.11 ± 0.04	1.18
Period of Abiotic Dominance	**PPFDd (μmol m^{-2} s^{-1})**	**ET (mg m^{-2} s^{-1})**	**T_a (°C)**	**NEE (g m^{-2})**	**Duration (days)**	**F_C (g m^{-2} d^{-1})**	**u* (m s^{-1})**
2004	420 ± 120	4.3 ± 2.5	17 ± 4	14 ± 7	62	0.2 ± 0.1	0.3 ± 0.2
2005	460 ± 130	4.6 ± 2.7	17 ± 4	22 ± 10	98	0.2 ± 0.1	0.2 ± 0.1
2006	500 ± 70	5.3 ± 2.2	20 ± 3	13 ± 4	30	0.4 ± 0.1	0.2 ± 0.1
2007	530 ± 150	5.8 ± 2.7	20 ± 4	34 ± 10	67	0.5 ± 0.1	0.3 ± 0.1

[a] Meteorological variables include incident flux of photosynthetically active photons, evapotranspiration, and air temperature. The ecosystem leaf area index in May and the friction velocity are shown for the biological and abiotic periods, respectively.

fluxes are near zero. In 2004 and 2005, with mean daily $PPFD_d$ lower than 500 μmol m^{-2} s^{-1}, mean daily ET of c.a. 4.4 ± 2.6 mg m^{-2} s^{-1} and mean daily T_a of 17 ± 4°C, mean CO_2 release never reached 1.2 μmol m^{-2} s^{-1}. In 2006 and 2007, compared to 2004 and 2005, we observe a 40% increase in mean CO_2 release; in addition mean daily $PPFD_d$ and ET increased 20% and mean daily T_a increased by 3°C compared to 2004 and 2005. In this context although the abiotic period lasts 31 days longer in 2005 than in 2007, the NEE during abiotic periods is 50% higher in 2007 (34 g C m^{-2}) than in 2005 (Table 3). In 2004, NEE during the abiotic period was 14 g C m^{-2} during approximately 2 months, while in 2006 the NEE was nearly the same as in 2004 with only 1 month duration. In this context, the mean daily carbon flux is 0.2 g m^{-2} d^{-1} for 2004 and 2005, twice that in 2006, and larger still in 2007 (0.4 and 0.5 g m^{-2} d^{-1}, respectively).

[27] Finally, during periods of indeterminate dominance the mean diurnal trends in measured F_c have no clear daily pattern (data not show); from 2004 to 2006 we observed low emissions during the whole day (normally less than 0.5 μmol m^{-2} s^{-1} and near zero in 2005) and slight uptake (less than 0.4 μmol m^{-2} s^{-1}) during daytime in 2007. The duration of these indeterminate periods is usually less than 2 months per year with mean daily carbon fluxes less than 0.2 g m^{-2} d^{-1}.

3.2.2. Integration to Annual and Longer Timescales

[28] Figure 4 shows accumulated carbon loss by the ecosystem, using the RBF network method to fill gaps (Figure 4a), and monthly precipitation (Figure 4b). Following the heavy rains at the beginning of May 2004, the ecosystem acted as a carbon sink absorbing 59 g C m^{-2} until the beginning of August 2004. Then, during the drought period of 2004 with daily average T_a higher than 15°C and few rain events with magnitudes less than 5 mm d^{-1}, the ecosystem lost 26 g C m^{-2}. After a rainy period in winter 2005, the growing season started in April, with daily average T_a above 10°C, the ecosystem acted as a carbon sink until the end of June 2005 absorbing 47 g m^{-2}. Then, from July 2005 to April 2006 the ecosystem acted as a carbon source losing 43 g C m^{-2}. After this long period of carbon loss, the ecosystem became again a carbon sink absorbing 32 g m^{-2} during the growing period in 2006. Then, from August 2006 to April 2007 the ecosystem acted usually as a carbon source, losing 42 g m^{-2}. After that, the growing period started in 2007, with daily $PPFD_d$ higher than 500 μmol m^{-2} and daily average T_a between 10°C and 20°C, from May to July 2007 the ecosystem absorbed 39 g C m^{-2}. Finally, the ecosystem reverted to a source losing 49 g C m^{-2} during summer and beginning of autumn 2007. During autumn and winter, although rain events are prominent, carbon fluxes represented either a small source or a small sink.

4. Discussion

[29] This study presents a first approximation of the interannual CO_2 exchange over a carbonaceous substrate were abiotic processes may interact with biological processes in the ecosystem behavior related with the carbon cycle. Due to the complexity of these data, commonly applied models for decomposing net carbon exchanges into biological processes of photosynthesis and respiration [*Falge et al.*, 2002] cannot be used to fill data gaps and achieve long-term integration [*Kowalski et al.*, 2008; *Serrano-Ortiz et al.*, 2007]. In this context, two independent statistical techniques were applied to fill gaps: a Radial Basis Function (RBF) network [*Cazorla et al.*, 2008] and the MDS technique [*Reichstein et al.*, 2005]. The use of these two methods resulted in similar mean annual carbon exchange (−3 ± 16 and 0 ± 30 g C yr^{-1}, respectively). However, some discrepancies have been detected using both methods where anomalies in meteorological conditions were observed: an extremely rainy period in the beginning of May 2004, and the warm February of 2005. This disagreement is due to the inability of the MDS technique to respond to anomalies in meteorological conditions. The MDS technique replaces missing values using a time window of several days while the RBF network uses meteorological variables as inputs of the function.

[30] In addition, this study represents a step toward the partitioning of interannual ecosystem CO_2 exchange over a carbonaceous substrate into abiotic and biological influences on the carbon cycle. This preliminary division was made as a first step to determine their contributions in the annual NEE and the interannual variability of these processes related to interannual differences in meteorological and phenological variables (Figure 3 and Table 3).

[31] During biological periods (H/LE < 4 and daytime $T_a > 4°C$) interannual variability in mean diurnal trends of measured F_c appeared to be related mainly to ecosystem LAI and secondarily to $PPFD_d$ and T_a. The highest values of mean CO_2 uptake were in 2004 when the ecosystem LAI was 1.13 m^2 m^{-2}. In 2007, although similar values of ecosystem LAI were measured, daily means of $PPFD_d$ and T_a decreased by 20% and 60%, respectively, and mean CO_2 uptake fell by more than 20%. Similar mean values of nighttime release were detected in 2004 and 2007. In 2005, mean daytime CO_2 uptake decreased by more than 50% with an ecosystem LAI decrease of 19% compared to 2004; this may have been due to plant injuries [*Pockman and Sperry*, 1997] caused by the extreme cold in winter of 2005.

[32] We observed no correlation between the length and total net uptake of biological periods possibly because of offsetting increases in ecosystem respiration [*Dunn et al.*, 2007]. In 2006, compared to 2005, the total net uptake of the biological period was reduced by 30% due to an increase in CO_2 release observed during nighttime (respiration increased by 40% due to a 3°C increase in mean nighttime soil temperature). However, 2007 presents a special case where, although mean diurnal trends in measured CO_2 uptake were more than 15% higher than 2005 and 2006, the total net uptake was reduced by more than 50%. This is likely due to the high proportion (>80%) of filled nighttime data, especially in March and June. The RBF network yielded nighttime values of CO_2 release exceeding 2 μmol m^{-2} s^{-1} and these decreased the total net uptake in 2007.

[33] During abiotic periods (H/LE > 4 and SWC < 15%), we observed an interannual variability in mean diurnal trends in measured F_c that appeared to be related mainly to ET. In 2006 and 2007, the mean diurnal CO_2 release was 50% larger compared to 2004 and 2005, while mean daily ET and T_a were respectively 20% and 15% higher. A combination of chemical equilibrium and transport processes must be considered to understand the behavior of subterranean CO_2 in aqueous and gaseous phases.

[34] How ET may affect CO_2 release can be summarized in several physiochemical steps. First, it opens pore space to mass airflow (an indirect, physical effect) which flushes CO_2-rich air out of the subterranean system. This lowering of the CO_2 partial pressure in the karst system perturbs the Henry's law equilibrium

$$CO_{2(aq)} + H_2O_{(l)} \rightarrow CO_{2(g)} + H_2O_{(l)}, \quad (1)$$

pulling CO_2 out of solution. Secondarily, ET enriches aqueous concentrations by removing pure water, also pushing equation (1) to the right. The continuity of this process during the dry season is assured by constant replenishment of dissolved CO_2 in the soil water by conversion of carbonic acid via ionic recombination

$$HCO^-_{3\,(aq)} + H^+_{(aq)} \rightarrow H_2CO_{3(aq)} \rightarrow CO_{2(aq)} + H_2O_{(l)}, \quad (2)$$

[35] Although the forward procession of the above equations (to the right) consumes protons, the essential role of karst geochemistry is to resupply protons and so buffer the system against basification

$$Ca^{2+}_{(aq)} + HCO_{3^-\,(aq)} \rightarrow CaCO_3 + H^+_{(aq)}. \quad (3)$$

[36] As a consequence of this buffering, which enables the production of gaseous CO_2 via equations (1) and (2) [*Emmerich*, 2003], carbonates are precipitated [*Langmuir*, 1997]. Note that the forward procession of equations (2) and (3) is not limited by the consumption of HCO_3^-, which is massively abundant in the karst system (and dominates CO_3^{2-} at the relevant pH); thus the fundamental role of equation (3) is to buffer the system.

[37] On daily timescales, CO_2 release is more closely related to $u*$ ($R^2 = 0.4$, data not shown), as ventilation of subterranean pore space removes gaseous CO_2 from the karst and provokes sizable upward turbulent fluxes [*Kowalski et al.*, 2008]. Although apparently related to ET and winds, the determinants of such ventilation processes are still poorly understood. At least, as was the case for the biological period, the contribution of abiotic processes in the annual NEE seems to be independent of the length of the abiotic period. In 2007 and 2004 the duration of abiotic period was similar and the contribution of abiotic processes in the annual net ecosystem was 19% and 68%, respectively. In 2006 and 2005 the lengths of the abiotic periods were 1 and 3 months, respectively, and their contributions to annual NEE were 23% and 19%, respectively.

[38] These preliminary divisions of CO_2 exchange during biological and abiotic periods guarantee neither the lack of abiotic processes during biological periods, nor vice versa. For example, during the biological period, soil respiration increases the partial pressure of soil CO_2, which dissolves into water and drips into the karst system. The increase in soil P_{CO2} drives the dissolution of carbonate rock resulting in a sink of CO_2 and the increase in Ca^{2+} and HCO_3^- of karst water (see equations (2) and (3)) [*Liu and Zhao*, 2000]. In addition, during the abiotic period, we consider that most plants are senescent and autotrophic respiration is negligible, furthermore neglecting heterotrophic respiration [*Eliasson et al.*, 2005]. Furthermore approximately 2 months per year define days with indeterminate dominance of processes, which are not included in the analyses. Thus, new methodologies are needed to separate net CO_2 fluxes into abiotic and biological components.

[39] Given the existence of biological models [*Krinner et al.*, 2005] capable of simulating photosynthesis, photosynthate partitioning, autotrophic respiration and heterotrophic respiration, as well as geochemical models for rock weathering processes [*Goddéris et al.*, 2006], a coupled biogeochemical modeling exercise would likely be informative in terms of achieving a more credible flux partitioning. Alternatively, or additionally, stable carbon isotopes could be used to discern among different processes involved in the net ecosystem exchange via isotopic analyses [*Flanagan et al.*, 2005; *Yakir and Sternberg*, 2000]. Finally, leaf-level flux measurements can be used to estimate the contribution of photosynthesis and plant respiration processes in the carbon ecosystem exchange and determine the length of senescence periods.

Table 4. Mean Annual Air Temperature, Total Annual Rainfall, and Mean Annual Net Ecosystem Exchange of CO_2 Over Carbonaceous Ecosystems

Carbonaceous Ecosystems	Location	Year(s)	T (°C)	Rain (mm)	NEE (g C m^{-2})
Shrubland (this study)	Sierra de Gádor (southeast of Spain)	2004–2007	12	277	−2(±23)
Desert shrub [*Hastings et al.*, 2005]	Baja California (Mexico)	2002–2003	24	158	−45
Semiarid shrubland [*Emmerich*, 2003]	southeastern Arizona (USA)	1997–2000	17	356	144
Semiarid grassland [*Emmerich*, 2003]	southeastern Arizona (USA)	1997–2000	17	356	126
Desert grassland [*Mielnick et al.*, 2005]	Las Cruces (New Mexico)	1996–2001	-	272	145
Mojave Desert [*Wohlfahrt et al.*, 2008]	northwest of Las Vegas (USA)	2005–2006	16	103	−106

[40] In Mediterranean and carbonaceous ecosystems, total rainfall and its distribution over the seasons are important climatic variables that can affect carbon exchange. Similar to other ecosystems with sparse vegetation and noncarbonaceous bare soil, rainfall events occurring during active growth phases (spring) may be proportionally more important than the total amount of rainfall, or than rainfall during nongrowth periods (winter) [*Hunt et al.*, 2004; *Huxman et al.*, 2004]. In these ecosystems, net carbon uptake after spring rains is associated with photosynthesis activation. However, in carbonaceous ecosystems not only photosynthesis but also $CaCO_3$ dissolution (consuming CO_2, see equations (2) and (3)) can contribute to the net ecosystem CO_2 sink [*Emmerich*, 2003; *Gombert*, 2002]. In addition, during drought periods we observed CO_2 emissions that seem to be more related to precipitation of $CaCO_3$ (and associated release of CO_2, see equations (2) and (3)) because CO_2 from microbial activity and plant growth would be minimal [*Emmerich*, 2003]. However, we do not discount the possible existence of rain pulse events [*Noy-Meir*, 1973; *Schwinning and Sala*, 2004] during drought season that, together with high temperature, can activate respiration processes.

[41] Finally, after nearly four years of continuous eddy flux measurements, a mean annual net carbon exchange can be estimated. The shrubland on a carbonaceous substrate located in Sierra de Gádor (southeast of Spain) presents an annual carbon exchange that varied from -63 to 29 g C m^{-2}, averaging -2 ± 23 g C m^{-2} a^{-1} (near neutral carbon sink) over the period from May 2004 to December 2007. With small magnitudes compared to the annual net carbon exchange of forest ecosystems types [*Kowalski et al.*, 2004; *Valentini et al.*, 2000], these results are consistent with similar studies over carbonaceous ecosystems (Table 4). All such studies remark on the importance of precipitation timing and the contribution of inorganic component of net CO_2 exchange.

5. Conclusions

[42] The complexity of processes determining ecosystem CO_2 exchange over carbonaceous substrates requires future research in order to separate and characterize the underlying processes. These processes are mainly photosynthesis, respiration, ventilation of subterranean macropores, carbonate rock dissolution and carbonate precipitation. Photosynthesis and carbonaceous rock dissolution are CO_2 uptake processes while respiration, macropore ventilation and carbonate precipitation cause CO_2 release. In this context, although biological processes (photosynthesis and respiration) and their partitioning are well known for some ecosystems, their interactions with geochemical processes are still unknown. Taking into account that these processes act together in most periods, the eddy covariance technique and meteorological measurements cannot be applied alone to characterize the ecosystem CO_2 exchange over carbonaceous ecosystem. In this context future investigations could combine: (1) biogeochemical modeling via, for example, the coupling of existing models for biological and geochemical processes, to separate net CO_2 fluxes into geochemical and biological components; (2) stable carbon isotopic analyses to discern among different processes involved in the net ecosystem exchange; and (3) portable Photosynthesis Systems to measure leaf gas exchange and estimate photosynthesis rates during periods of supposed senescence.

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