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Chamber Systems Measurements of Soil CO_2 effluxes: Application and Methodology

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Presentation of the Investigation Group

During six months I worked at the University of Grenada in the South of Spain (Andalusia). My research group is *GFAT* (*Grupo Física de la Atmósfera*), one of eight groups researching within the Applied Physics department. The research group occupies space concurrently in two buildings in the city of Granada: the Faculty of Science (where I was stationed) and the *CEAMA* (*Centro Andaluz de Medio Ambiente*); group members move freely between the two buildings, which are nonetheless separated by more than 1km. The research group is divided into two work groups, one focused on climatology and my own group doing atmospheric research.

The atmospheric group is further divided in two parts: those studying radiation, clouds and aerosols, and finally my group working on micrometeorology and gas exchange. This group is formed of the *Contract Professor* Andrew S. Kowalski, the *post-doctoral researcher* Penélope Ortiz-Serrano (my supervisors), the doctoral student Borja Mari Ruiz Reverter, and the technician Enrique Pérez Sánchez-Cañete.

This group is involved in projects assessing the carbon cycle and carbon balance. They are working on Mediterranean ecosystems at the regional and national scales. Currently, three projects finance the study of CO_2 fluxes. The BACAEMA, INIA, and CARBORED-ES projects highlight the importance of CO_2 exchange in semi-arid ecosystems. Thanks to their financing, eddy-covariance towers have been installed numerous shrubland ecosystems in order to study soil–vegetation-atmosphere exchanges. These tower systems record microclimatic data and measure turbulent fluxes of water vapor and carbon dioxide to understand how the atmosphere exchanges such greenhouse gases with terrestrial surface, as a function of environmental variables.

The first, *Balance de Carbono y de Agua en Ecosistemas de Matorral Mediterráneo en Andalucía: efecto del cambio climático (BACAEMA)* is a regional project aiming at investigating how Mediterranean ecosystems function in terms of carbon exchange and what their role is in the global carbon balance. This project has installed three permanent eddy covariance towers to study CO_2 fluxes in shrubland ecosystems across an altitudinal gradient in eastern Andalusia: Laguna Seca (2200m); Sierra de Gádor (1600m), and Cabo de Gata (50m), and further employs a mobile tower to examine differences between ecosystems as a function of perturbations including fire and desertification. The project is coordinated by the group from GFAT, but also includes researchers from the *Estación Experimental de Zonas*

Áridas; Consejo Superior de Investigación Científica (EEZA, CSIC), the University of Almería, and the Sierra Nevada National Park.

The second research project is funded by the *INIA (Instituto Nacional de Investigacion y Tecnologia Agraria y Alimentaria)*, a national project with economic and social implications, is focused specifically on burned Mediterranean ecosystems, to understand which post-fire forestry management practices would be more appropriated in order to maximize ecosystem carbon sequestration, in accordance with Kyoto objectives. The project is managed by GFAT, and integrates researchers from the Applied Physics and Ecology departments of the University of Granada. In this project, a permanent tower has been installed in a burned forest with no post-fire treatment applied (dead trees left standing), with fluxes to be compared to those from a mobile tower employed in different treatments (cutting but leaving burned trunks and branches in situ; also the traditional treatment where burned timber is extracted and residues mulched into the soil).

Ultimately, these projects are complementary and are focused on carbon exchange issues and soil-atmosphere exchanges. Moreover, they will permit to study and compare CO_2 fluxes of mature/undisturbed shrublands with those recovering from disturbance such as fire.

Finally, the group participates in the national research project CARBORED-ES, with coordination in the CEAM (*Fundación Centro de Estudios Ambientales del Mediterráneo*; Valencia). The CARBORED-ES project represents a network of flux-tower measurements in Spain, coordinating methodologies to provide a centralized database on carbon and water exchange in Spanish ecosystems.

Thus, during my *stage* I worked with researchers from numerous groups at several different institutes in Andalusia, in the context of different projects, made measurements at a variety of sites within Andalucía, and even presented an informal seminar on soil CO2 chamber measurements at the EEZA in Almería.

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TABLE CONTENT

SUMMARY

Soil respiration is a major component of CO_2 emissions and the global carbon balance. In the context of global change it of interest to know how Mediterranean ecosystems would respond to predicted climate change including enhanced summer droughts, particularly in terms of diurnal and seasonal tendencies in soil CO_2 effluxes. This study focuses on patterns in soil evaporation in a series of Mediterranean ecosystems, examining water treatment effects and the comparison of two chamber measurement systems, one of which requires correction for its lack of information regarding chamber humidity.

Important differences were found in soil CO_2 effluxes between measured by two devices (PP-Systems versus LI-8100). The dilution effect by water soil evaporation explained underestimation one of the two instruments (PP-Systems) in which the humidity of the chamber was not estimated. Characterizing the soil evaporation within a soil chamber thanks to raw data from the other system (LI-8100) enabled correction of the soil CO_2 flux estimates from the PP-Systems chamber, and furthermore to establish minimum values (including reductions due to chamber effects) of soil evaporation in a Mediterranean ecosystem.

For the summer season measured, soil humidity was clearly the main factor determining the soil respiration. By contrast, for the diurnal soil respiration measurements made in autumn (following rains), soil temperature was found to be a determinant. Evaporation within a chamber does not seem to be affected by short-term changes in chamber ambient conditions (chamber shading). Finally, the correction of CO_2 soil effluxes in a chamber system by the dilution effect is far from negligible.

Key-words: soil respiration, Mediterranean ecosystems, climate change, soil evaporation, soil CO_2 chamber systems, soil CO_2 flux corrections.

GLOSSARY

Symbols

$\beta = \frac{H}{LE}$: Bowen ratio where H and LE are the sensible and latent heat fluxes (W m^{-2})

$E = \frac{\partial \chi_v}{\partial t} * \rho_d * h$ **:** Evaporation or water vapor flux (µmol m^{-2} s^{-1})

$\frac{\partial \boldsymbol{\chi}}{\partial \boldsymbol{t}}$ **:** CO_2 molar fraction variation in the total air

$\boldsymbol{W_0}$ ***:*** initial water vapor mole fraction (mmol H_20 mol^{-1} air)

$\boldsymbol{\rho}$***:*** density (Kg m^{-3})

$\boldsymbol{\chi_d}$***:*** molar fraction (mol mol^{-1})

$\partial \boldsymbol{C}'/\partial \boldsymbol{t}$ ***:*** initial rate of change in water-corrected CO_2 mole fraction (µmol s^{-1}).

$\chi_d * E$ ***:*** PP system CO_2 flux correction (µmol m^{-2} s^{-1})

$\boldsymbol{\rho_d}$***:*** dry air density ($\boldsymbol{\rho_d}$ =P/(R_{d*}T)) (kg m^{-3})

$\boldsymbol{P_0}$***:*** pressure (kPa)

Abbreviation and definitions

A: soil surface area (m^2)

Abiotic : said about physical factors in the environment (temperature, water content, O_2)

Biotic: said about a biological factor (root, microbial…)

Closed: relative to the CO_2 concentration calculation in the chamber. The increase of CO_2 within the chamber during the time measurement is calculated.

dC: CO_2 concentration variation (mol)

Dynamic: in relation with the air flow into the chamber: here the air flow exists

dt: time variation of measurement (s)

E: Evaporation or water vapour flux (µmol m^{-2} s^{-1})

Eddy-Covariance: principle to quantify vertical turbulent flux (mass or energy) thanks to measurement of scalars.

Fc: CO_2 flux (µmol m^{-2} s^{-1})

H : Sensible heat (W m^{-2})

h: height (m)

IRGA: InfraRed Gas Analizer

LE : Latent heat (W m^{-2})

Lv: Number of latent heat vaporization (kJ kg^{-1})

n: number of molecules (mol)

n_a: molecules of the dry air (mol)

n_v: molecules of the water vapour (mol)

Open : relative to the CO_2 concentration within the chamber. In this system the concentration is calculated as the difference of CO_2 concentration between the inlet and the outlet of the chamber.

P: pressure (Pa)

PAR: Photosynthetical Active Radiation

R: soil respiration

Radiative forcing : "measure of how the energy balance of the Earth atmosphere system is influenced when factors that affect climate are altered" (W.m^{-2}) (definition of IPCC, 2007)

R_d: air dry constant of gas (mol J^{-1} K^{-1})

S: soil surface area (cm^2)

Static: relative to the air flow within the chamber. This system does not have air flow.

T: soil temperature (°c)

T_0: Initial air temperature (°c)

V: the volume (m^3)

I. INTRODUCTION

Since the industrial revolution, atmospheric CO_2 has risen from 280 to 379 ppm in 2005 (Forster *et al.*, 2007; Van der Werf *et al.*, 2004) leading to rising temperatures (Schwartz, 2007). These could provoke changes in CO_2 exchanges including soil respiration (Soe & Buchman, 2005), and cause feedback leading to amplification and greater problems. Emissions of CO_2 by fossil fuel combustion continue to increase, but atmospheric accumulation is less than global balance models predict, leading to a search for CO_2 sink mechanisms. The Kyoto protocol (1997), in which the CO_2 is the first gas listed (Shine & Sturges, 2007), aims to reduce emissions of greenhouse gases, identify sinks of CO_2 and try to maintain or even create them. Indeed, the goal is to reduce the major greenhouse gases and thus global warming. Many fluxes of CO_2 exist and another means to control them is thus via knowledge of CO_2 sinks and sources (Johnson & Curtis, 2001; Raich *et al.*, 2002).

The biosphere carbon (C) budget is an imbalance between photosynthesis and respiration and Valentini *et al.*, (2000) showed that respiration was the main determinant of C balance in temperate forests. Furthermore, deforestation, changes in soil use, land transformations and disturbances all lead to modifications of the C balance because an important part of the resulting CO_2 fluxes goes to the atmosphere (Abril *et al.*, 2005; Foley *et al.*, 2005; Vitousek *et al.*, 1997), contributing to radiative forcing. (Raich & Schlesinger) showed soil C emissions were the second main flux (1992). Moreover, the soil is considered as either the first. (IGBP, 1998) or the second (Peng & Thomas, 2006) main pool of terrestrial C after forest (Pregtizer *et al.*, 2006).

Soil research history is almost 200 years-old and the first goal was to understand soil metabolism, fertility and activities (Luo & Zhou, 2006). Soil respiration measured at the soil surface, Rs, is defined as the sum of the root and microbial decomposition of soil organic matter respectively R_b (below ground, root respiration) and R_m (microbial respiration) (Jassens *et al.*, 2003; Subke *et al.*, 2006). Many studies deal with soil respiration determinants and now we know that abiotic and biotic factors are closely implicated. Among abiotic components, temperature and soil moisture are decisive in soil efflux (Davidson *et al.*, 1998; Granier *et al.*, 2007; Jassens *et al.*, 2003; Lloyd & Taylor, 1994) because they condition biotic factors such as root growth and microbial life. Moreover, many others like microclimate or soil composition may play non-negligible roles in soil respiration.
So it is important to understand which mechanisms and factors predominate to allow/improve soil C sequestration. Moreover, it is still poorly understood how the soil reacts to changes in ambient climatic conditions and thus to climatic change (Gardenas, 2000).

Depending upon how it is measured (see section II.B.a), accumulated CO_2 within a soil chamber can be diluted by water vapor added to the chamber by soil evaporation, causing underestimation of the soil CO_2 efflux. Water vapor exchange by evaporation is the dominant gas exchange between the atmosphere and Earth's surface, exceeding other gas exchanges by orders of magnitude. Although generally smaller than transpiration, soil evaporation is a non-negligible fraction of total evaporation (Yepez *et al.*, 2005). However, soil evaporation is not usually measured directly, but rather estimated via indirect means such as the difference between total evapotranspiration (via eddy covariance; (Kurpius *et al.*, 2003) and sap-flow transpiration, or estimated via modeling (Poyatos *et al.*, 2007) or lysimetry (Kinama *et al.*, 2005) or via isotopic labeling (Yepez *et al.*, 2005). However, some IRGA/chamber systems can directly measure soil evaporation within the (modified) chamber environment, and here we will examine this process. Soil evaporation remains a subject about which little is known, however, and few publications report on this major ecosystem component in the water balance.

The primary purpose of this work was to learn about soil CO_2 efflux measurement systems applying meteorology to ecology, and generally to understand the impact of climatic variability on semi-arid ecosystems. The specific objectives were first to calculate the systematic error made with one measurement system, and to study soil CO_2 effluxes in the Sierra Nevada. To do that, treatments simulating three different climatic scenarios are used in an experimental site. This experiment is part of a doctoral thesis study involved in the DINAMED project *(Dinámica del Bosque Mediterráneo en un escenario de cambio global)* and dealing with the forest regeneration under different climatic scenarios following an experimental approach. We will focus on the fourth experiment dealing with CO_2 fluxes from soil to atmosphere, studying soil respiration. Several questions may be asked: (i) What are soil respiration patterns in relation to temperature and moisture? (ii) What is the magnitude of soil evaporation in a soil CO_2 chamber? (iii) What is the correction to the soil CO_2 efflux for a chamber system not taking into account this soil evaporation?

II. METHODOLOGY AND MATERIAL

A. Ecology

a.Study site and vegetation

The study was conducted in southeastern Spain, in Sierra Nevada National Park in Andalusia. The field site is the Cortijuela Botanical Garden, a fenced area of 12 ha at 1600m a.s.l . Forests, shrublands and grassy clearings are present in this valley.

The site is formed by three vegetation strata. The overstory is dominated by Scots pine, *Pinus sylvestris* ssp. *nevadensis*, an endemic local subspecies. Several other tree species are present including oaks (*Quercus ilex, Q. Pyrenaica*), European Black pine (*P.nigra*), and other genus such as *Sorbus aria*, *Taxus baccata* and endemic Granada Maple (*Acer granatense*). Shrublands are mainly composed of *rosaceaes* (*Crataegus granatensis, Prunus ramburii, Prunus prostrata, Rosa* spp.) and *Berberis hispanica.* The clearing area is defined by the absence of woody canopy (trees or shrubs) and the herbaceous cover.

b. Disposition and treatments

Three plots were chosen in terms of vegetation composition. Patches of forest, shrubland and clearings define the system of the study. These different cover types constitute the spatial scale (ecosystem). The temporal scale is represented by simulation of mild or dry summers as predicted under a global change scenario thanks to the manipulation of water rates reaching the soil.

1. Spatial scale

The three distinct ecosystems types of vegetation covers are shown in the Fig. 1. Different types of cover implicate different microclimates (soil water content, soil temperature, light…) within each ecosystem. The three ecosystems studied are forest mainly composed of pines and some deciduous species, shrubland, and clearings.

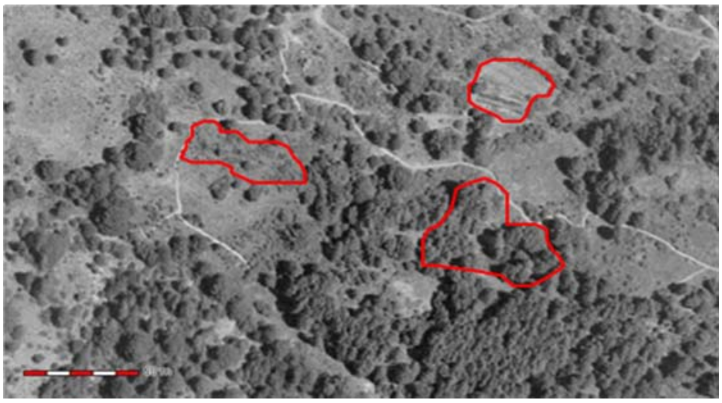

Fig. 1 Aerial map of the three experimental sites (left to right and upwards: shrubland, clearing area and forest ecosystems)

2. Temporal scale

The rate of water reaching the soil surface is manipulated in order to simulate different climatic scenarios, taking effect during late spring and summer. Three levels of water supply are applied.

The first treatment, *exclusion,* simulates an increase in summer drought (climate change scenario): to do so, the rainout shelter (Fig. 2) described by (Yahdjian & Sala, 2002) was used. It occupies an area of 4m² and the mean height is 1m. Without UV filter and wall, this system maintains conditions as natural as possible, only removing 33% of rain water. This treatment simulates dryer and longer summers, as predicted by the principal climatic models.

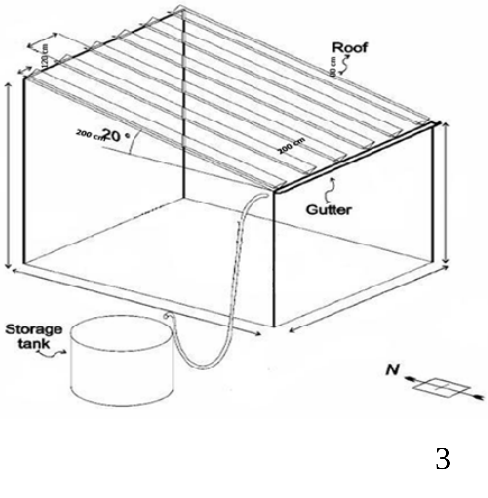

Fig. 2 Rainout shelter diagram.

In the second treatment, *current natural conditions*, no water is added or removed.

The last treatment, *irrigation*, simulates a sporadic wet summer, which occurs naturally in Mediterranean mountains every 40 to 60 years. The irrigation amount is about 15mm per week, simulating summer storms and adding a total of 180mm over three months. Irrigation began on the 12th of June and was applied on 4, 10, 17 and 25 July; 1,8, 13, 22, 29 August; and 5, 10 and 15 September of 2007.

Other abiotic variables are measured as air and soil temperature, soil humidity and photosynthetically active radiation (PAR) using HOBO total microclimatic stations installed only in half of the treatment replications. Natural precipitation is measured by a pluviometer, checked and manually emptied daily.

For each ecosystem 6 station plots were sampled (replicates) in three subplots of 0.04 ha separated by 50 cm. A subplot (water treatment replicate) corresponds to the water treatment in which three collars were placed in the soil at three corners of a square. Six replicates of each treatment were made. Thus, total sampling includes18 collars by water treatment, 54 collars by ecosystem and 162 collars in total (Fig. 3).

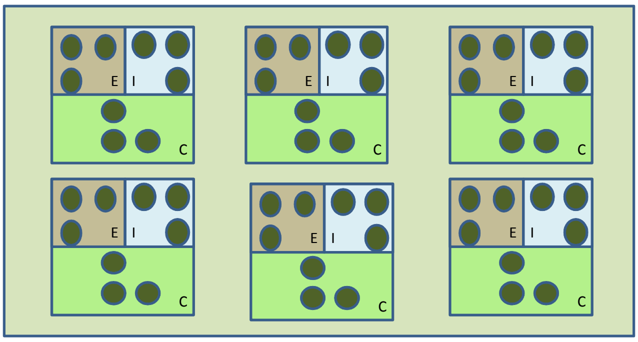

Fig. 3 Experimental design. (C : Current natural conditions; E: water Exclusion; I : Irrigated)

c. Measurements and statistical analysis.

One temporal and seven spatial field campaigns of soil CO_2 flux measurements were made from July to October 2007. During the winter 2007/2008 snow cover prohibited site access and measurement, but in any event this study focuses on summer climate change scenarios.

Calculations and graphics were done with Microsoft Excel, and the statistical analysis of variance (ANOVA) was done with the Statview software, which also generated tables and bars graphs.

B. Physics

***a.* Soil CO_2 flux measurements**

1. Overview of measurement methods

There exist several means to measure CO_2 fluxes, and they are summarized here in an order that naturally leads to the technique employed here. The least common is the method using CO_2 concentration and soil gas diffusivity (Kabwe *et al.*, 2002; Rayment & Jarvis, 1997) using soil samples, measurements of CO_2 concentration, and gas diffusion at several depths. The flux is then calculated via Fick's law. But it remains very difficult to characterize accurately the diffusivity parameters (Hutchinson & Livingston, 2002) because of their high spatial variation.

The Eddy-Covariance technique is used more and more, not only to study the CO_2 surface-atmosphere exchange but also to measure soil effluxes. This method permits measurement of net turbulent fluxes. During day time a net flux comprised of photosynthetic and respiratory components is measured. At night only respiration contributes to the net flux, but any above-ground, includes the effects of respiring vegetation below the measurement system. As a final limitation, due to the lack of turbulence during stable atmospheric conditions (positive temperature gradient, frequent at night), respiration cannot always be measured. The main advantage of eddy covariance the lack of ecosystem perturbation (Janssens *et al.*, 2000). However, instruments required are quite expensive.

2. Chamber systems

The most common methods used to measure soil fluxes are chamber systems (Le Dantec *et al.*, 1999; Livingston & Hutchinson, 1995; Pumpanen *et al.*, 2004; Widen & Lindroth, 2003), divided into two main types. Static chambers - based on enrichment or CO_2 absorption by Soda lime (alkali traps) - agree well with the dynamic systems (Rochette *et al.*, 1997) after some corrections (Janssens *et al.*, 2000), but are less used because they are less sensitive, with long measurement times required and biases generated by the lack of air motion inside the chamber. Moreover, (Campos, 2006) showed that this method underestimates large fluxes and overestimates small fluxes. Closed Dynamic Chambers (non-steady-state through flow) are more popular due to short measurement times and small size. Moreover, in a field comparison study Freijer & Bouten found them to be more accurate (1991). The method excludes exchange with ambient air; fans mix system air in order to homogenize pressure, CO_2 gradients and temperature.

Principle used

The two closed dynamic chamber systems used measure the increase of CO_2 in a chamber closed to the atmosphere but exposed to soil exchange, during a precise time. In each case, a non-dispersive, InfraRed Gas Analyzer (IRGA) is used to measure soil respiration. Both systems include barometers, and IRGAs, and the LI-8100 has a soil temperature probe (soil temperatures are measured separately with the PP-Systems). Brief descriptions follow of the two commercial systems used in this study.

3. Instruments

PP-systems (PP-Systems, Hitchin, UK)

This is a manual system composed of an EGM-4 IRGA system linked to a cylindrical soil respiration chamber SRC-1 (diameter 10 cm; height 15 cm). This system makes "Auto-zero" mainly in order to adapt to environmental conditions and afford a stability of the CO_2 signal.

LI-8100

This is an automated system (Li-Cor Lincoln, NE) made of a hydraulic 10 cm survey soil chamber (15,2×15,2×25,4 cm) controlled by an electronic system, and an IRGA measuring H_20 and CO_2 densities. An auxiliary sensor interface allows the additional temperature or moisture sensors. The operator selects the desired number and time of measurements with a field computer. The chamber is placed on a collar, closes and measures during the selected time, and then opens again. This system is programmable to enable measurements at determined intervals over long periods.

A fundamental difference between the two systems is that the Li-8100 IRGA measures (absolute) humidity. Instrument software uses measured CO_2 density, along with the dry air and the water vapor flux, to compute the CO_2 flux as according to the change in the molar fraction with respect to dry air (χ_d). By contrast, the PP-Systems has only an *optional* humidity sensor for integration within the chamber, and when not excluded, changes in the molar fraction (χ) measured by the system are susceptible to the influences of evaporation within the chamber.

b. Fundamental principles for detecting gas exchanges

1. IRGA functioning

As stated above, CO_2 accumulation in a chamber is quantified by IRGAs which measure absorption and thus estimate the number of CO_2 molecules. At a precise wavelength (λ), an IRGA system measures the number of CO_2 molecules in a volume defined by the laser beam. Using the Beer-Lambert Law, the quantity of CO_2 absorption is proportional to the density and path length.

$$A_\lambda = \varepsilon_\lambda * \ell * C \qquad (1)$$

Where A_λ is the absorptance, ε_λ is the molar extinction coefficient (L.mol^{-1}.cm^{-1}), ℓ the path length (cm), C the molar density (mol L^{-1}).

2. Scales of CO_2 effluxes

The amount of CO_2 in a soil chamber can change via several processes including photosynthesis and respiration rates but also changes in air volume and evaporation effects. Therefore, it is important to identify the processes that can cause changes in the CO_2 quantity we are measuring. Soil respiration adds CO_2 molecules to a chamber volume, and can change many scalar indices of CO_2 amount; however, many CO_2 scalars are affected by (not conserved during) other atmospheric processes, as summarized in table 1.

We can assume that there are n molecules in moist air, defined as the sum of dry air molecules (n_a) and water vapor (n_v) in molar units as:

$$n_t = n_a + n_v \qquad (2)$$

Diffusion of heat and water have strong effects on the density of any constituent such as CO_2 (Webb *et al.*, 1980). Indeed, there is an issue first with temperature which has the effect to decrease gas density in one hand as explained by the gas law, and secondly (and most relevant here) with water vapor, which can decrease some measures of CO_2 because it decreases "dry air" gas density.

Too frequently, CO_2 in the atmosphere or in the soil chamber measurement is expressed as a density (ρ) or a molar fraction (χ). But, as (Baldocchi *et al.*, 1988; Kowalski & Serrano-Ortiz, 2007) point out in eddy-covariance, these variables can be biased because of temperature effects (expansion or compression) or water diffusion. These processes affect air volume and thus change the CO_2 values measured in chambers independent of CO_2 sources or sinks. These authors suggest using the mixing ratio *c* defined as the mass ratio of CO_2 to dry air (all air constituents excluding water vapor) and which can be written as ρ_c/ρ_a which is not susceptible to water or temperature in order to obtain true CO_2 fluxes values. Table 1 shows the advantages and drawbacks of each variable, and specifically that the mixing ratio changes only due to true CO_2 respiration fluxes.

Table 1 Scalar variables and their comparison concerning temperature and water effect on them.(after Kowalski & Serrano-Ortiz, 2007)

Variable	**CO_2 density** ρ_d	**Molar Fraction** χ	**Molar fraction in the dry air** χ_d	**Mixing ratio c**
Definition	CO_2 mass per unit of volume	CO_2 to total molecules	CO_2 to "dry air "molecules	CO_2 to "dry air" mass
Unit	$Kg.m^{-3}$	$Mol.mol^{-1}$	$Mol.mol^{-1}$	$Kg.kg^{-1}$
Temperature effect (heat conduction)	Non conservative	Conservative	Conservative	Conservative
Water effect (evaporation, diffusion)	Non conservative	Non conservative	Conservative	Conservative

In the case of the IRGA systems used in this study, both systematically remove temperature effects (by examining changes in molar fractions), but we are specifically interested in correcting fluxes for the diluting effects of evaporation where the PP-Systems has been applied without an (optional) humidity sensor integrated.

c. Equations for determining soil CO_2 fluxes with chamber measurements.

$$\frac{\partial \chi_d}{\partial t} \longrightarrow F_c$$

Soil CO_2 fluxes F_c into a chamber lead directly to proportional increases in the CO_2 molar fraction with respect to the dry air (or in the mixing ratio) over time, and specifically are proportional to $\frac{\partial \chi_d}{\delta t}$. This relation gives the CO_2 flux (Appendix I). As mentioned above, measuring devices should determine the flux as a function of this variable, but it is not the case for one of the system used.

1. PP-systems (EGM-4/SRC-1)

Following the chamber manual, the equation used to calculate the soil respiration (R) is:

$$R = \frac{d\rho_c}{dt} * \frac{44{,}01 * V}{(0.75 + 0.00025\mathrm{P}) * 22.41 * \mathrm{A}} = \frac{\partial \chi}{\partial t} \tag{3}$$

With $d\rho_c$ the increment in CO_2 density measured directly by the IRGA during the interval dt (s), V the chamber volume in m^3, P the pressure (mb), A the soil surface area (m^2), and $\frac{\partial \chi}{\partial t}$ the change in CO_2 molar fraction in the total air as a function of time (µmol mol^{-1} s^{-1}). The value 44,01 is the CO_2 mass in kg and 22,41 is the volume in m^3 , each for 1000 moles of CO_2. From equation (3), it is clear that the PP-systems uses the wrong scalar (χinstead of χ_d), and therefore leaves the estimate of the CO_2 flux susceptible to the influence of evaporation inside the chamber. So, we propose to relate the CO_2 flux to the change in the CO_2 mixing ratio with respect to dry air as explained below.

Correction for the humidity. Underestimations made with the PP-systems because the water flux is lacking can be corrected thanks to the insertion of the error $\chi_d * E$ (Appendix I) to the time rate of change of the molar fraction, as follows:

$$F_c \cong \rho_d * h * \left(\frac{\partial \chi}{\partial t} + \chi_d * E \right) \tag{4}$$

Where Fc is the CO_2 flux, ρ_d the dry air density (ρ_d =P/R_dT; P the chamber pressure, R_d the dry Air gas constant and T the soil temperature), h the collar height (m) and E the water evaporation defined as $E = \frac{\partial \chi_v}{\partial t} * \rho_d * h$ (µmol m^{-2} s^{-1}), thus in terms of $\frac{\partial \chi_v}{\partial t}$ the time rate of change of the water vapor molar fraction (mol $mol^{-1}s^{-1}$)

2. LI-8100

This system uses the CO_2 molar fraction in the dry air χd , called Cdry in the LI-8100 manual, to calculate the CO_2 flux, so the dilution correction (water correction) is not necessary:

$$F_c = \frac{10VP_0\left(1-\frac{W_0}{1000}\right)*\partial\chi_d'}{RS\left(T_0+273.15\right)*\partial t} \quad (5)$$

Where F_c is the soil CO_2 efflux rate (µmol m^{-2} s^{-1}), V the volume (cm^3); P_0 the pressure (kPa); W_0 the initial water vapor mole fraction (mmol mol^{-1}); S the soil surface area (cm^2), T_0 the initial air temperature (°c), and $\partial\chi_d'/\partial t$ the initial rate of change in water-corrected CO_2 mole fraction (µmol s^{-1}).

3. *Volume correction for both devices.*

To calculate the flux from the collar, it is necessary to correct the volume value because the volume of the collar is added at the chamber volume.

So the total volume (m^3) of both measurement systems is :

$$V_{total} = V_{chamber} + V_{collar} \quad (6)$$

With the total volume, V_{total} the sum of the chamber volume, $V_{chamber}$ and the collar volume V_{collar}.

d.Estimation of evaporation in collars and PP-systems fluxes correction

As a first step towards correcting PP-systems fluxes determined without humidity information, we aimed to bound the correction (i.e., determine the maximum) in relation to evaporation inside the chamber. To know how PP-systems and LI-8100 are correlated, we have calculated the carbon flux error of PP-systems due to the evaporation. As this chamber system did not measure water evaporation, we estimated the evaporation thanks to the measure of "mean H_20" given by the LI-8100 supposing that the systems are quite similar. To do that we had to determine the evaporation

$$E \cong \frac{\partial H_2O}{\partial t} * \rho_d * h \quad (7)$$

Where E (evaporation) is the water vapor flux in kg.$m^{-2}s^{-1}$, and $\frac{\partial H_2O}{\partial t}$ the change in H_2O (mmol s^{-1}) during the measurement interval, measured directly by the LI-8100. Then we had to calculate the latent heat to do the correlation between the error $\chi_d * E$ and the LE the latent heat (W m^{-2}).

$$LE = Lv * E \quad (8)$$

Where Lv is the latent heat of vaporization in kJ/kg a term dependent of the temperature as $Lv = 2501{,}2 - 2{,}4346T$ in kJ.kg^{-1}, with T the temperature in K (P., 2008)

RESULTS

These results present an analysis of CO_2 effluxes measured with two soil respiration chamber systems from July to October of 2007. First, summer soil respiration tendencies of the Cortijuela sites as a function of different climate scenarios, and then, the relation between abiotic factors as soil temperature and humidity and soil respiration CO_2 effluxes are presented.

Different chamber systems were by ecosystem: the LI-8100 in the clearing, the PP-systems in the shrubland, and both devices in the Forest. Although the two chamber systems showed reasonably good agreement, the systematically lower fluxes measured by the PP-systems may be explained in part because this instrument did not take into account the (dilution) effect of evaporation. Therefore, we characterized soil evaporation into a chamber system via direct measurements of the H_2O molar fraction by the LI-8100. Thus, in the second part of the results only data measured in the clearing ecosystem are used to extract evaporation data from the LI-8100 chamber.

In the last subsection, we examine the effects of correcting the PP-systems soil CO_2 fluxes for evaporation effects for the lone comparison campaign between these two instruments prior to the installation of a humidity sensor in the PP-systems chamber during the winter of 2008.

A.Characterizations of the Cortijuela CO_2 soil effluxes

The year 2007 had a fairly typical Mediterranean summer, with no precipitation recorded from June-August. However, significant thunderstorm activity took place in September, with 40.0 mm of rainfall on 11-13 September, and an additional 88.6mm on 21-22 September.

The soil responds differently during summer versus autumn because of differences in temperature and soil water content, on both diurnal and monthly scales. We study here the impact of abiotic variables as soil temperature and water content on soil respiration

a.Seasonal variation in soil CO_2 effluxes.

1. Ecosystems and treatments differences

Bar graphs of ecosystem's soil respiration in relation to campaign date are represented below. Effects of the water treatments can be studied in relation to the season.

Clearing plots (Fig 4.) show variability during the summer with an augmentation of the flux during the month of July and a decrease until the autumn. We can see that soil respiration was highest in the irrigated plot (versus other treatments) throughout the summer, while the rain exclusion treatment showed the lowest respiration. This tendency reversed in autumn following intense thunderstorms in Sierra Nevada around 20 September. After these rain events, both the current natural conditions and exclusion plots showed peaks in respiration, while the irrigated treatment showed the least respiration and was quite low compared to its summer values.

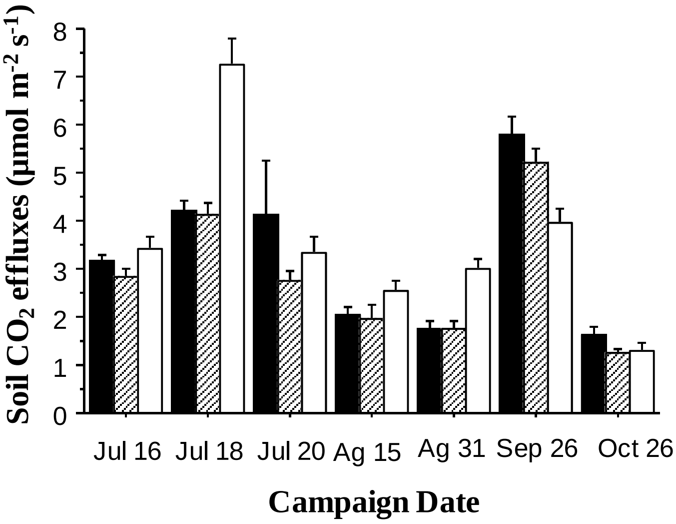

Fig. 4 Evolution of the soil CO_2 effluxes during summer 2007: effects of water treatment in the Cortijuela clearing: (black bars : current natural conditions; grey bars : exclusion, white bars : irrigation treatments)

The shrubland ecosystem (Fig. 5) shows a similar pattern decreasing respiration through summer, highest values in the irrigated plot, and a peak following September rains with the highest flux and a response to irrigation a little bit more important.

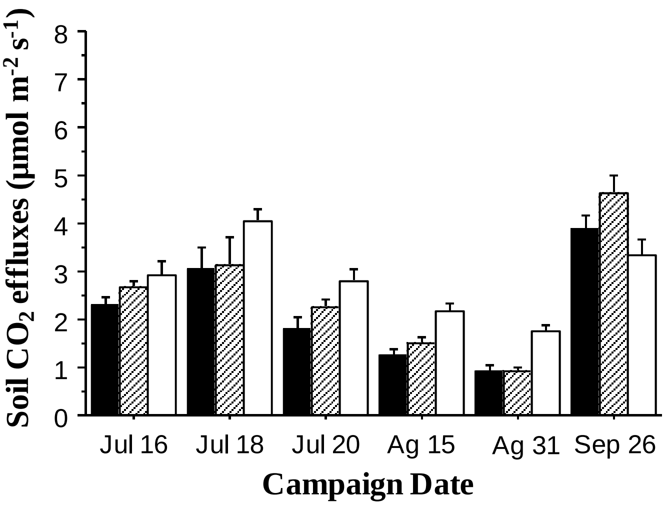

Fig. 5 Evolution of the soil CO_2 effluxes during summer 2007 in the Cortijuela Shrubland and water treatment (black bars: current natural conditions; grey bars : exclusion, white bars : irrigation treatments)

The forest shows a greater response to irrigation, which persisted after autumn rains, and less variability than the other ecosystems for the season (Fig. 6). We can see the same rise as the other ecosystems on 26 September 2007 with a mean flux double that from the previous month. The current natural conditions and exclusion plots are quite similar compared to the irrigation treatment.

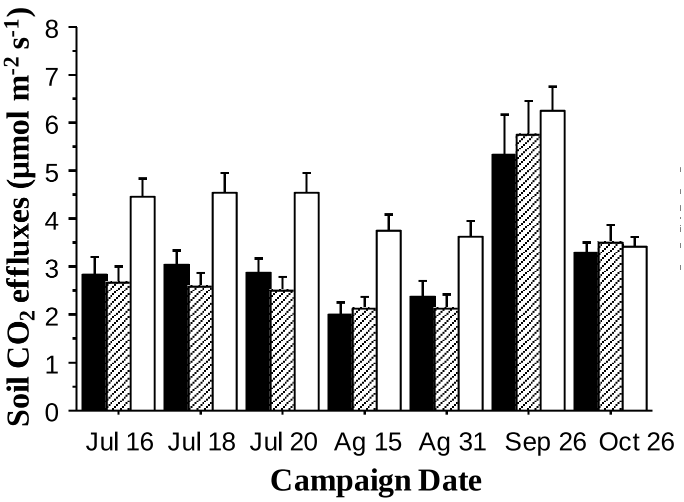

Fig. 6 Evolution of soil CO_2 effluxes in summer 2007 at the Cortijuela Forest and water treatment (black bars : current natural conditions; grey bars : exclusion, , white bars : irrigation treatments)

Analysis of variance shows that CO_2 soil effluxes are significantly different ($p<0,001$) between ecosystems and treatments (Appendix II, Fig 1). A Bonferroni/Dun test yields significant differences between irrigation and current natural conditions treatment and irrigation and exclusion ($p<0,001$) but no difference between current natural conditions and exclusion ($p=0,5530$) (Appendix II, Fig. 2)

2.Relation between soil CO_2 effluxes, humidity and temperature.

Humidity

The results concerning soil respiration as a function of the humidity are presented below. For each ecosystem type, soil CO_2 effluxes are represented for the three water treatments. Figure 8 shows a relation between the soil respiration and soil moisture, with increasing soil CO_2 effluxes as a function of soil humidity. As expected, soil moisture is highest in the irrigation treatment, while the exclusion and current natural conditions are quite similar.

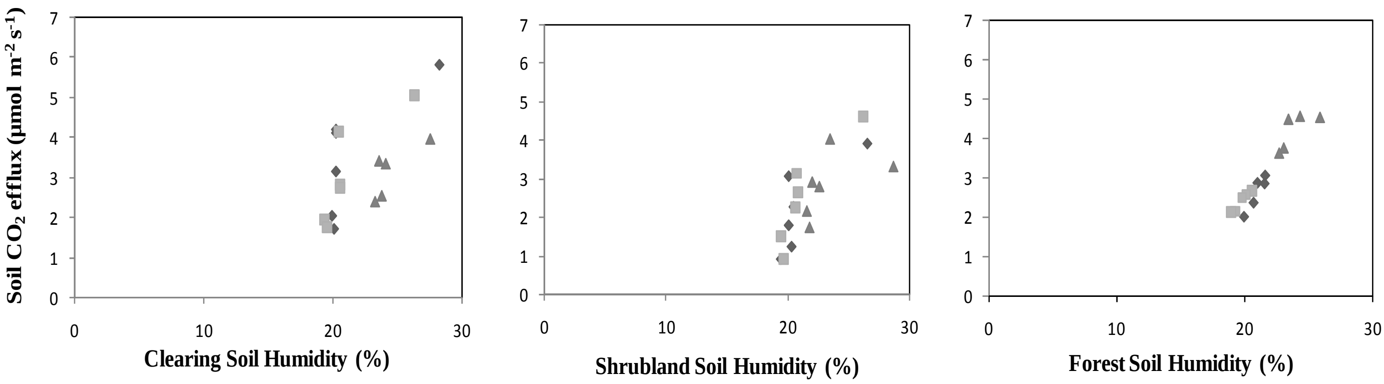

Fig. 7 Soil respiration in the each ecosystem for all water treatments (grey squares: exclusion; dark diamonds: current natural conditions and grey triangles: irrigation)

The clearest pattern here is that the forest shows the most obvious (and nearly linear) relation between soil respiration and soil humidity, while differences among treatments are more pronounced than in the other ecosystems. Indeed, the exclusion treatment shows lower fluxes and lower humidity; for current natural condition humidity is only slightly higher, while the irrigation treatment shows higher humidity and respiration values. The forest effluxes are otherwise intermediate (not extreme), between lowest respiration values in the shrubland and the highest in the clearing.

We can see here that the exclusion treatment shows the lowest moisture values as expected.

Temperature

The relation between the soil CO_2 effluxes and temperature was examined but showed no correlation, in contrast to the case for humidity (Appendix II, Fig 3).

b.Diurnal variation in soil CO_2 effluxes.

Figure 8 shows daily temporal trends in soil CO_2 effluxes measured during the first two weeks of autumn for each ecosystem type and treatment. Each point represents a 90s respiration measurement every half-hour with the LI-8100 operating in automatic mode over a single collar.

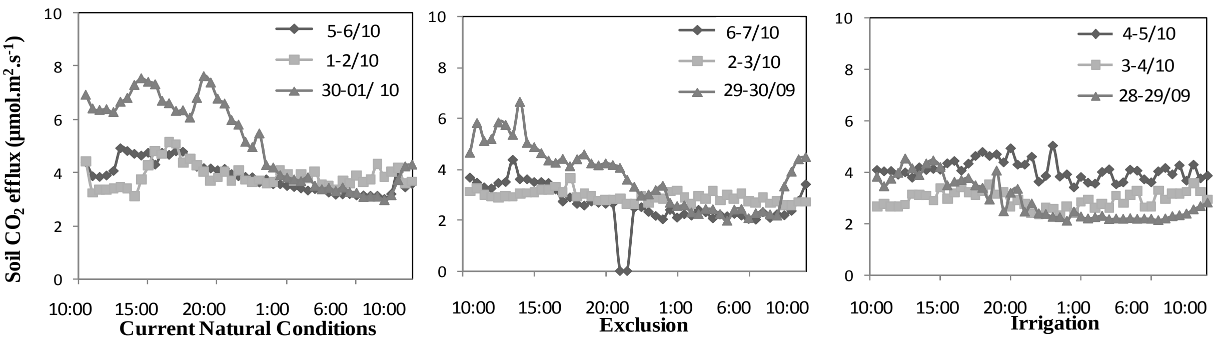

Fig. 8 Diurnal pattern of soil respiration in each ecosystem (triangle: clearing area, grey square Shrubland and dark diamond: forest)

We can see the variation of the flux during the day. In each ecosystem and treatment there is an increase in the soil efflux in morning and a decrease during afternoon and night, with less diurnal variability apparent in the irrigation plot. Soil CO_2 effluxes in irrigation and exclusion treatments are generally lower than in the current natural conditions treatment.

The current natural conditions treatment shows more variation during daytime, and the clearing ecosystem seems to respond more than the other ecosystems to changes in ambient conditions. Indeed, the midday flux is twice the nighttime flux. The shrubland and forest ecosystems have similar soil effluxes after 16:00. Moreover, it seems that for these days, soil respiration in the forest is quite similar at the shrubland respiration in the morning and that the tendency changes at night to be almost the same as the clearing soil respiration.

The exclusion treatment shows the same pattern as the current natural conditions treatment. The only difference is that fluxes are lower and the clearing ecosystem show less differences with the other ecosystem types. The two points with zero flux represent a measurement error.

For irrigation treatments, the pattern for ecosystem type is reversed, with forests respiring more than clearing. The flux is less variable and lower in the irrigation treatment for these autumn days following rains. Forest soil respiration is higher in the irrigation treatment contrary to clearings ecosystem where there is only half in this climate scenario versus current natural conditions.

B.Characterizations of the Clearing Cortijuela site soil evaporation effluxes within a chamber system

a.Diurnal range of Latent Heat as a function of water treatment.

Soil evaporation follows similar patterns in all treatments, rising in the morning (15 to 70W m^{-2}) and peaking in the afternoon. It then decreases after 16:00 to reach values near zero at 20:00. At night it can have negative values (not shown) but generally is near zero until 8:00 when it increases again.

The current natural conditions treatment shows higher evaporation than the two other treatments and during the night fluxes are higher than those from the exclusion or supplying treatment.

The exclusion treatment evaporation is almost the half of the current natural conditions treatment evaporation, and night fluxes are the lowest. The greatest variability is found in irrigation.

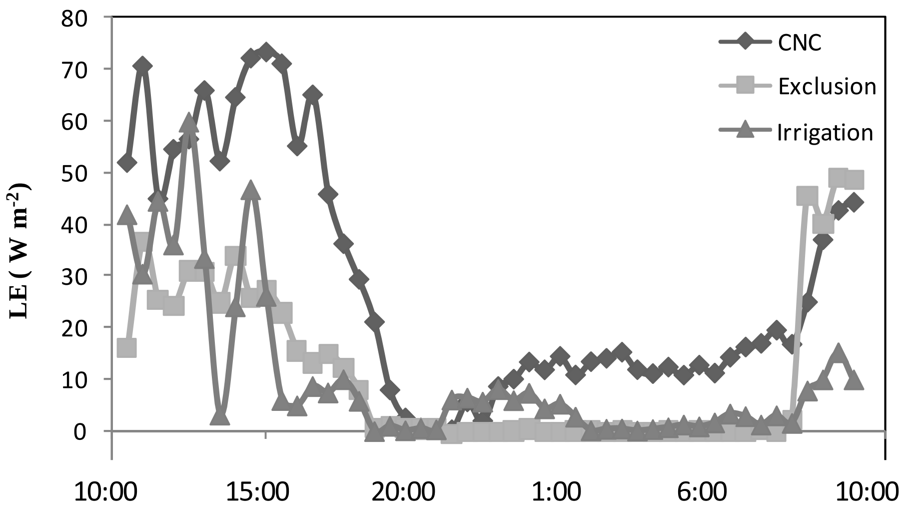

Fig. 9 Diurnal soil evaporation in each water treatment from 10:00 to 10:00 am solar time (CNC: Current natural conditions: 30-1Oct; Exclusion: 29-30Sep; Irrigation: 28-29Sep)

b.Range of the soil evaporation within a soil chamber.

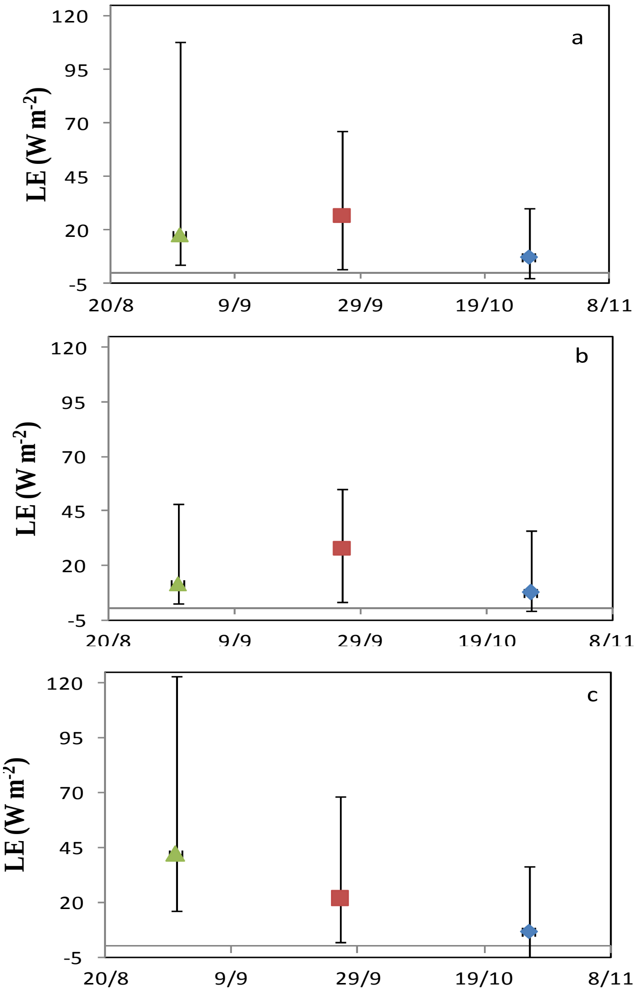

Figure 10 shows significant soil evaporation within the chamber. The range of soil evaporation was very high during the first campaign, with LE near 100W m^{-2}. Further these values relate directly to the error in the soil CO_2 for the second chamber system lacking a humidity sensor. Depending on the soil water content, it is clear that the exclusion treatment (b) shows lower soil evaporation than the current natural conditions or irrigation.

Fig. 10 Mean, maximum and minimum soil evaporation fluxes measured with the LI-8100 for three campaigns of soil effluxes measurements at the clearing ecosystem (a. Current natural conditions; b. Exclusion; c. Irrigation treatments)

C.Correction of the PP-systems Soil effluxes

a.Magnitude of the water vapor correction

Figure 11 shows that the correction of CO_2 effluxes can be important, increasing with evaporation. The correction can surpass 0.7µmol m^{-2} s^{-1} which is far from negligible, often representing more than 10% of the CO_2 flux.

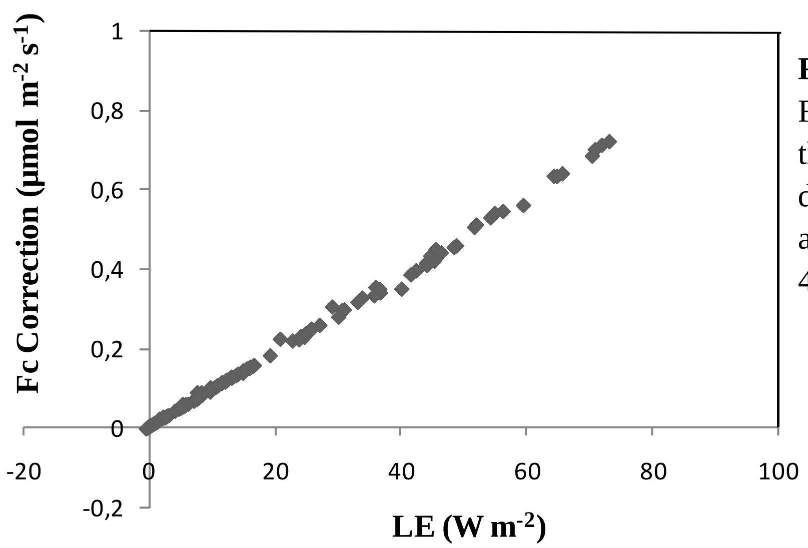

Fig. 11 Relationship between the Fc correction and evaporation in the LI-8100 chamber system during the temporal campaign for all water treatments (144 points, 48 per treatment).

b.Comparison both with and without the correction.

1. Magnitude of the correction as a function of the water treatments.

In this comparison campaign we can see that the correction is quite large in a single instance, but most measurement fall within a range of 0 - 25 W m^{-2} for the latent heat flux.

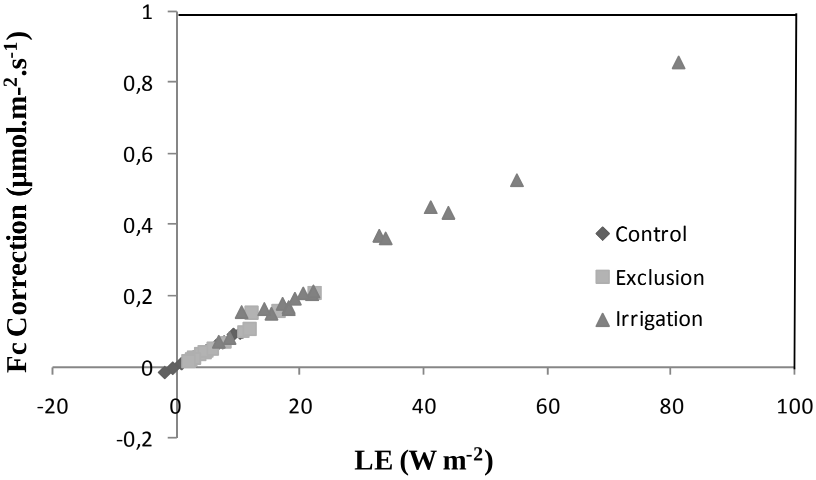

Fig. 12 Relationship between the Fc correction and the evaporation into the LI-8100 chamber system 26 of July 2007 on the morning within all ecosystems and treatments (18 points for each treatment).

During this campaign on the day following an irrigation application, we can see clearly that the irrigation treatment shows more evaporation than the other treatments as expected, and that there is little difference between the current natural conditions and the exclusion treatments.

2. Effect of the water vapor correction on PP-systems soil CO_2 effluxes.

The following graph shows the correlation of LI-8100 and PP-systems fluxes both with and without the correction applied, for the lone comparison campaign on the 26th July of 2007 after an irrigation day. We see that the PP-systems measures lower fluxes than the LI-8100. Moreover it seems that small fluxes are overestimated by the LI-8100 or underestimated by the PP-systems.

We can see that the correction improves the comparison: the regression parameters at left refer to non-corrected PP-systems data, while those at right include the correction. Both the slope and the correlation coefficient show that the corrected PP-systems fluxes more closely approximate the LI-8100 fluxes. More than 78 % the variation is explained by the regression.

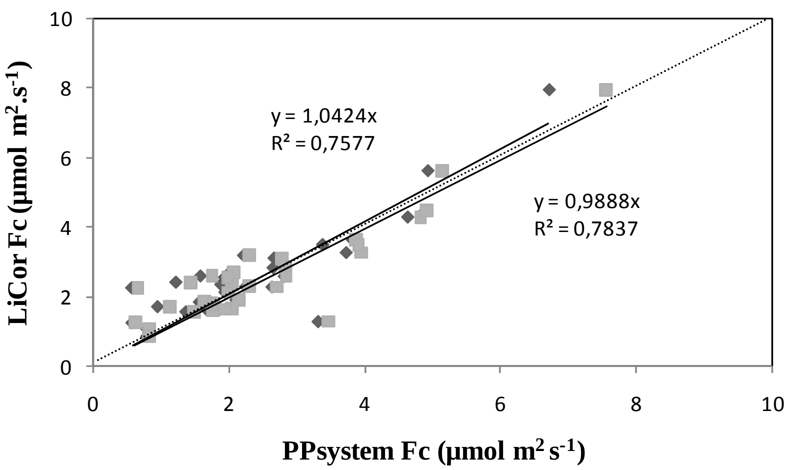

Fig. 13 Comparison of the LI-8100 and PP-systems CO_2 fluxes without and with the water correction (dark diamonds: correlation without correction; grey squares: correlation with the correction)

DISCUSSION

A.Characterizations of the Cortijuela CO_2 soil effluxes

a. Seasonal variation in soil CO_2 effluxes.

At this site, soil respiration seems to be water limited. During the dry summer of 2007, for all ecosystems the larger respiration of the irrigation plots, compared with exclusion and natural conditions, demonstrates this clearly. Furthermore, bursts in soil respiration are observed following rain events, even for the irrigated plots. The lowest fluxes were associated with the driest soils (particularly in exclusion and current natural condition) likely because the vegetation and soil components were water limited, with soil (root and microbial) activities possibly even suspended during drought events. Water pulses in the soil enable root and microbe activity, leading to soil respiration peaks(Schwinning & Sala, 2004; Xu *et al.*, 2004).

Rains enabled soil respiration, particularly for the two dryer treatments, and this further confirms the fact that soil water availability is a very important soil respiration determinant here.

The forest ecosystem was unique in showing enhanced responses to irrigation after rains in every treatment (including irrigation).

It may be that high summer variability in soil CO_2 effluxes in the clearing are due to extreme soil evaporation (lack of vegetation to provide a protected microclimate), however no data are available to examine this hypothesis because different systems (LI-8100 versus PP-systems) were used in different ecosystems, preventing such a comparison.

b.Relation between soil CO_2 effluxes, humidity and temperature.

We can see that soil humidity is a very important factor in Mediterranean ecosystems. This tendency is most clear in the forest, consistent with the above discussion.

The temperature did not show any clear effect on soil respiration on seasonal timescales. We can explain this because these Mediterranean ecosystems are strongly limited by water soil content, particularly for such summer conditions, as previously seen. However, weak temperature dependence can be seen on diurnal scales following autumn rains, as shown next.

Indeed, the diurnal variation shows that at sunrise, CO_2 fluxes show a continual rise until sunset. This is explained largely by soil temperature trends (Appendix II, Fig. 4), but there are insufficient data for significant linear regression to approximate temperature dependence (Q_{10}).

Even though the days of measurement were different, and some differences are likely due to variation in ambient conditions, we can see that the irrigation treatment (although applied weeks previously) shows lower diurnal variability. The reduced water limitations make the system more stable with respect to soil respiration.

B.Characterizations of the Clearing Cortijuela site soil evaporation effluxes within a chamber.

a.Diurnal range of Latent Heat as a function of water treatment.

Soil evaporation in the chamber environment increases around sunrise, stays high throughout the day, and decreases with sunset, in direct correlation with solar forcing. The largest fluxes were observed in the current natural conditions treatment. The peak magnitudes are consistently near 50 W m^{-2} for these days in early autumn. Large values of ecosystem evapotranspiration for well-watered vegetation can approach 300 W m^{-2} (mid summer, in very humid ecosystems) (Arya, 1988). Considering that the chamber environment during the day is likely cooler than ambient (sheltered from the sun), this demonstrates that soil evaporation can be a non-negligible fraction of total evapotranspiration.

At night, soil evaporation dropped below 10 W m^{-2} and was usually very near zero. This is clearly due to the lack of solar forcing, and likely associated with calm nights under the Mediterranean high. The anomalous soil evaporation of the current condition treatment might be explained by a windy night (no data available).

b.Range of the soil evaporation within a soil chamber.

Soil evaporation measured at the clearing site varied widely as a function of date or treatments. There is a great variability in the evaporation and we can see that in our case, the stronger the solar forcing, the higher the range of soil evaporation, as seen particularly for the late August campaign of where the soil evaporation reaches the highest values. However, in late September following rains, larger values of soil evaporation are measured thanks to enhanced soil water availability (lower Bowen ratio).

Excluding the irrigation treatment we see that the highest mean values of soil evaporation in early autumn following rain events. In these conditions, which also correspond to the largest CO_2 fluxes measured, evaporation during the soil CO_2 efflux measurement campaigns is consistently of order 30 W m^{-2}; as will be seen immediately, such evaporation corresponds to a non-negligible correction to the soil CO_2 fluxes measured by the PP-Systems with no humidity sensor installed.

C.Correction of the PP-systems Soil effluxes

a.Magnitude of the water vapor correction

The near-perfect linear relationship in Figure 12 is a result of the corrections equations derived in the Appendix, with small deviations from linearity due to variations of the ambient CO_2 dry air molar fraction (χ_d) within the chamber. This value of χ_d varied between 400 and 600 ppm, as a function of micrometeorological variations during the measurement campaigns (data not shown). The typical value of the correction is 0.20µmol m^{-2} s-^{1}, which is far from negligible.

b.Comparison with and without the correction.

1.Magnitude of the correction and differences between water treatments.

The highest evaporation was obtained in the irrigation treatment for the warmest month July, corresponding to a correction of 0.8 µmol m^{-2} s^{-1} for the soil CO_2 efflux measured by the PP-systems with no humidity sensor. However, the other treatments had consistently lower evaporation and hence corrections to the PP-systems soil CO_2 efflux. Soil evaporation is higher in a soil full of water and when natural conditions are warm and solar forcing strong.

2.Effect of the water vapor correction on PP-systems soil CO_2 effluxes.

Let us recall that soil CO_2 effluxes determined by a chamber system neglecting to account for dilution by evaporation (such as the PP-systems) will be underestimated. The comparison between fluxes taken with the two instruments is clearly improved by the dilution corrections. More comparison campaigns are needed to determine a more precise relation, to verify the corrections, and to determine their magnitudes over a larger range of environmental conditions.

Moreover, these results conflict with literature data showing that the PP-systems measures higher fluxes than the LI-8100 (Janssens *et al.*, 2000; Le Dantec *et al.*, 1999)

CONCLUSIONS

The Cortijuela soil CO_2 effluxes are dependent on the ecosystem type and treatment applied. The effect of soil humidity on soil respiration is dominant. The forest is the ecosystem whose respiration responds most to the irrigation treatment.

During the summer months if no rain falls the soil respiration is lower. The current natural conditions trends are quite similar to the exclusion treatment during the summer 2007 because there was no rain. In terms of future predictions, it seems that if the climate change scenario is dryer, actual soil CO_2 respiration will not change, whereas an increase in sporadic wet summers may enhance CO_2 effluxes from soil.

The humidity seems to be the predominant factor in the Cortijuela site, as in Mediterranean ecosystems in general.

Soil CO_2 efflux measurements with soil chamber systems can be biased by soil evaporation.

We intended to quantify soil evaporation thanks to one of our chamber systems (LI-8100) in a grassland (clearing ecosystem), and found that the diurnal evaporation trend *within* soil chambers followed the *external* solar forcing. Less surprisingly, wetter soils (following autumn rains) were found to exhibit more evaporation.

The evaporation correction to the soil CO_2 flux is generally below 0.25 µmol m^{-2} s^{-1} but can range up to 1 µmol m^{-2} s^{-1} in some cases. Thus it can represent between 5 and 25% of the soil CO_2 fluxes for a system which does not take into account the chamber humidity.

Our goals were to characterize the tendencies of the Cortijuela site soil CO_2 effluxes and test the instrumentation used. To validate soil evaporation tendencies and errors made with our instrument more comparison field campaigns are necessary, and ideally multiple instruments would be required to enable simultaneous measurements. The study should be repeated using the PP-systems with the humidity sensor (now installed) and see the effects on the instrument inter-comparison.

The CO_2 flux correction derived here are likely be most important in semi-arid ecosystem immediately following rain events (when evaporation is likely maximum). Thus, the errors in CO_2 fluxes made without accounting for chamber humidity are likely a worst case scenario.

Modeling of soil evaporation may benefit from the results presented here, which demonstrate that the LI-8100 chamber system is capable of detecting soil evaporation on short time scales, where local surfaces fluxes do not adjust immediately to dramatic changing environmental conditions.

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APPENDIX I

CORRECTIONS FOR A CO_2 FLUXES DERIVED FROM A MANUAL, NON STEADY-STATE TROUGH FLOW CHAMBER FOR THE EFFECTS OF WATER VAPOR DILUTION

Context

Scalars

As (Webb *et al.*, 1980) and later (Kowalski & Serrano-Ortiz, 2007) highlight in their papers on micrometeorological methods exchanges studies, the expressing of concentration or flux in terms of CO_2) (number or mass of molecules in density (an air volume) is not appropriate because it is a term which can change because of temperature, pressure and/or humidity variations.

The mixing ratio (*c*), defined as the mass of molecules normalized by the mass of dry air is the appropriate scalar because it is conserved through processes of heating and humidification. Thus, changes in this scalar within a hermetic soil CO_2 chamber come about only due to CO_2 exchange with the soil (respiration). No water processes can bias the measurements. Another scalar, the molar fraction (χ) which represents the ratio of CO_2 to total molecules is only conserved during pressure and temperature changes, but decreases with evaporation. However the dry air molar fraction (χ_d , directly proportional to the mixing ratio) can be used.

Instruments and issues

Certain field Instruments, specifically Soil chamber systems, have some weaknesses to detect the processes they are intended to characterize. More than disturbances and environmental variables variations (Janssens *et al.*, 2000) the main issue with some of these systems is precisely the scalar quantity estimated. We examine two systems of soil CO_2 fluxes measurement: the LI-8100 (Li-Cor Lincoln, NE) and the PPsystem EGM-4 (PP-Systems, Hitchin, UK) & SRC-1 (PP-Systems, Hitchin, UK). The first allows estimation of the molar fraction in the dry air (χ_d) but the second, in certain commercial versions, only allows determination of the molar fraction to total molecules (χ). When used without a humidity sensor, this system measures CO_2 amounts with reference to total air. Consequently, CO_2 accumulation can be underestimated because of dilution due to water vapor diffusion (Kowalski & Serrano, 2007).

The errors are due to the water vapor flux from soil evaporation. Evaporation (E) is defined as the water vaporization t the surface, separating water from the surface and releasing it to the gas phase (Elias Castilo & Castellvi Senti, 1996)

Indeed, in the CO_2 concentration measured by the PPsystem can decrease as CO_2 and other dry air components are diluted by soil evaporation. Thus, underestimation of the soil CO_2 flux can occur with the PPsystem chamber when water vapor fluctuations are not quantified.

Purpose

Here the goal is to examine the definitions of scalar quantities such as the mixing ratio and molar fraction, and demonstrate that the former best quantifies CO_2 accumulation relevant to the determination of a soil respiration flux.

Definitions, Simplifications, and Approximations

Molar Fraction

To start, in the equation (1) we define the molar fraction of CO_2 in the ambient air (χ) as the ratio between the CO_2 molar density (n_c) and the total (or moist) air density (n) defined as the sum of two air molar densities n_d and n_v ; where (c), (d) and (v) denote respectively CO_2, dry and water vapor.

$$\chi = \frac{n_c}{n_d + n_v} \tag{1}$$

In order to obtain a form more suitable and easier to separate CO_2 and H_2O dry air molar fractions we multiply equation (1) by $\frac{n_d - n_v}{n_d - n_v}$ to obtain

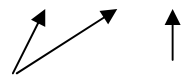
$$\chi = \frac{n_c}{n_d + n_v} * \frac{n_d - n_v}{n_d - n_v} \tag{2}$$

which can be simplified as

$$\chi = \frac{n_c * n_d - n_c * n_v}{n_d{}^2 \text{-} n_v{}^2} \tag{3}$$

Recognizing that the number of molecules in the dry air (n_d) is many times greater than the H_2O molecular number ($n_d \succ\succ n_v$), we can approximate very accurately the difference of their squares by neglecting the effects water vapor density in the denominator ($n_d{}^2 \succ\succ\succ n_v{}^2$)of equation (3), and so simplify the result

$$\chi \cong \frac{n_c}{n_d} - \frac{n_c}{n_d} * \frac{n_v}{n_d} \tag{4}$$



χ_d χ_v

using the definitions of the dry air CO_2 and H_2O molar fractions respectively $\chi_d = \frac{n_c}{n_d}$ and $\chi_v = \frac{n_v}{n_d}$.

Finally, this leaves the CO_2 molar fraction

$$\chi \cong \chi_d * (1 - \chi_v) \cong \chi_d - \chi_d * \chi_v \tag{5}$$

defined in terms of the dry air molar fractions CO_2 and H_2O.

Flux

In soil CO_2 flux chamber systems, the methodology is to detect the time rate of change in the CO_2 concentration and relate it to biological exchange at the surface. The time (t) derivative of equation (5) is

$$\frac{\partial \chi}{\partial t} \cong \frac{\partial \chi_d}{\partial t} - \left[\chi_v * \left(\frac{\partial \chi_d}{\partial t} \right) + \chi_d * \left(\frac{\partial \chi_v}{\partial t} \right) \right] \tag{6}$$

This can be simplified to show that changes in the CO_2 molar fraction (determined by the PPsystems) can come about due to changes in two terms that are each determined by the LI-8100, one representing the concentration with respect to dry air and the other changes in the water vapor concentration

$$\frac{\partial \chi}{\partial t} \cong (1 - \chi_v) * \frac{\partial \chi_d}{\partial t} - \chi_d * \frac{\partial \chi_v}{\partial t} \tag{7}$$

Moreover, we can admit that the term $1 - \chi_v$ is negligible because χ_v is very small compared with 1.

Thus, the equation (7) can be written as

$$\frac{\partial \chi}{\partial t} \cong \frac{\partial \chi_d}{\partial t} - \chi_d * \frac{\partial \chi_v}{\partial t} \tag{8}$$

PPsystem (Wrong value) Respiration → $\frac{\partial \chi}{\partial t}$

LI-8100 (True value) Respiration → $\frac{\partial \chi_d}{\partial t}$

Evaporation → $\frac{\partial \chi_v}{\partial t}$

This equation clearly shows how surface exchange of any one gas can directly affect the molar fractions of all gases. Specifically, evaporation increases the water vapor molar fraction, and so causes the CO_2 molar fraction to decrease. The LI-8100 properly determines χ_d, or more specifically $\frac{\partial \chi_d}{\partial t}$ for the determination of a CO_2 efflux. For the PPSystems, however, the increase in the CO_2 molar fraction must be incremented by the correction $\chi_d * \frac{\partial \chi_v}{\partial t}$. Thus, the true soil respiration flux should be related to the source for CO_2 molecules (S_c):

$$S_c \cong \frac{\partial \chi}{\partial t} + \chi_d * \frac{\partial \chi_v}{\partial t} \tag{9}$$

In a similar manner, the water vapor flux E is expressed

$$S_v = \frac{\partial \chi_v}{\partial t} \tag{10}$$

In summary, fluxes of CO_2 (Fc) and H_2O (E)can be determined according to increments in the scalar quantities

LiCor $\frac{\partial \chi_d}{\partial t} \longrightarrow F_c$

$\frac{\partial \chi_v}{\partial t} \longrightarrow E$

To calculate the flux in appropriate units, the concentration change must be multiplied by the dry air density and the chamber height

$$E = S_v * \rho_d * h \quad (11a)$$

$$S_v = \frac{E}{\rho_d * h} \quad (11b)$$

Correction

These equations for the H_2O and CO_2 fluxes can be summarized

H_2O
$$\frac{E}{\rho_d * h} = \frac{\partial \chi_v}{\partial t} \quad (12a)$$

CO_2
$$\frac{F_c}{\rho_d * h} = \frac{\partial \chi_d}{\partial t} \quad (12)$$

Thus, evaporation can be written multiplying equation (12a) by χ_d

$$\chi_d * \frac{\partial \chi_v}{\partial t} = \chi_d * \frac{E}{\rho_d * h} \quad (13)$$

Combining the equations (13), (12) and (8) we obtain

$$F_c \cong \rho_d * h * \frac{\partial \chi}{\partial t} + \chi_d * E \quad (14)$$

defining the correction $\chi_d * E$ to eliminate underestimation of the CO_2 flux by the PPsystems chamber lacking a humidity sensor.

PPsystem Fc correction(µmol/m²/s) = χ_d* E

Scalar Quantities

χ : molar fraction (mol/mol) without dimensions (ratio between two numbers of molecules), but often expressed in units of ppm

χ_d : CO_2 molar fraction with respect to dry air molar (e.g., 380 ppm or $3{,}7.10^{-4}$)

ρ_d : dry air density (µmol/m^3)

E : Evaporation (µmol/m²/s)

n : number of molecules (mol or µmol)

h : height (meter)

t : time (second)

APPENDIX II

ANOVA Table for LI-8100 soil fluxes

	DF	Sum of Squares	Mean Square	F-Value	P-Value	Lambda	Power
Treatment	2	139.885	69.942	20.288	<.0001	40.577	1.000
Landscape	2	183.598	91.799	26.629	<.0001	53.257	1.000
Treatment,Landscape	4	48.106	12.027	3.489	.0077	13.954	.871
Residual	1053	3630.106	3.447				

Fig.1 Analyse of variance for all CO2 effluxes during the seven campaigns

Bonferroni/Dunn for Li-8100 CO_2 fluxes
Effect: Treatment
Significance Level: 5 %

	Mean Diff.	Crit. Diff.	P-Value	
CNC, Exclusion	.083	.335	.5530	
CNC, Irrigation	-.739	.334	<.0001	S
Exclusion, Irrigation	-.822	.335	<.0001	S

Fig. 2 Post-Hoc test, Bonferroni/Dunn test for treatment and ecosystems effect with a level significance of 5%

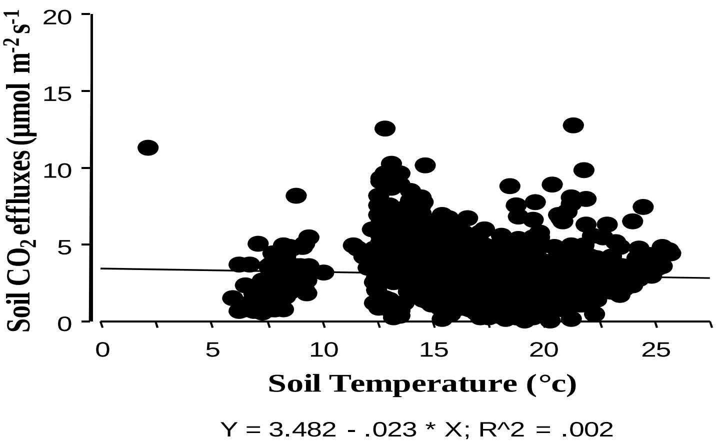


Fig. 3 Regression plot of the soil CO_2 effluxes in all ecosystems all for treatments during the seven seasonal campaigns.

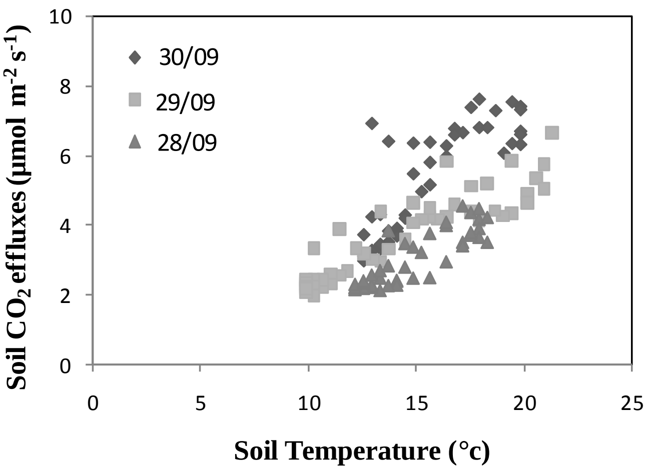


Fig. 4 Soil CO_2 effluxes as a function of the temperature in the clearing eco-system: for the temporal campaign (triangle: clearing area, grey square Shrubland and dark diamond: forest)

SUMMARY

Soil respiration is a major component of CO_2 emissions and the global carbon balance. In the context of global change it of interest to know how Mediterranean ecosystems would respond to predicted climate change including enhanced summer droughts, particularly in terms of diurnal and seasonal tendencies in soil CO_2 effluxes. This study focuses on patterns in soil evaporation in a series of Mediterranean ecosystems, examining water treatment effects and the comparison of two chamber measurement systems, one of which requires correction for its lack of information regarding chamber humidity.

Important differences were found in soil CO_2 effluxes between measured by two devices (PP-Systems versus LI-8100). The dilution effect by water soil evaporation explained underestimation one of the two instruments (PP-Systems) in which the humidity of the chamber was not estimated. Characterizing the soil evaporation within a soil chamber thanks to raw data from the other system (LI-8100) enabled correction of the soil CO_2 flux estimates from the PP-Systems chamber, and furthermore to establish minimum values (including reductions due to chamber effects) of soil evaporation in a Mediterranean ecosystem.

For the summer season measured, soil humidity was clearly the main factor determining the soil respiration. By contrast, for the diurnal soil respiration measurements made in autumn (following rains), soil temperature was found to be a determinant. Evaporation within a chamber does not seem to be affected by short-term changes in chamber ambient conditions (chamber shading). Finally, the correction of CO_2 soil effluxes in a chamber system by the dilution effect is far from negligible.

Key-words: soil respiration, Mediterranean ecosystems, climate change, soil evaporation, soil CO_2 chamber systems, soil CO_2 flux corrections.