Deep CO₂ soil inhalation / exhalation induced by synoptic pressure changes and atmospheric tides in a carbonated semiarid steppe

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Abstract. Knowledge of all the mechanisms and processes involved in soil CO₂ emissions is essential to close the global carbon cycle. Apart from molecular diffusion, the main physical component of such CO₂ exchange is soil ventilation. Adective CO₂ transport, through soil or snow, has been correlated with the wind speed, friction velocity or pressure (p). Here we examine variations in subterranean CO₂ molar fractions (χc) over two years within a vertical profile (1.5 m) in a semiarid ecosystem, as influenced by short-timescale p changes.

Analyses to determine the factors involved in the variations in subterranean χc were differentiated between the growing period and the dry period. In both periods it was found that variations in deep χc (0.5–1.5 m) were due predominantly to static p variations and not to wind or biological influences. Within a few hours, the deep χc can vary by fourfold, showing a pattern with two cycles per day, due to p oscillations caused by atmospheric tides. By contrast, shallow χc (0.15 m) generally has one cycle per day as influenced by biological factors like soil water content and temperature in both periods, while the wind was an important factor in shallow χc variations only during the dry period. Evidence of emissions was registered in the atmospheric boundary layer by eddy covariance during synoptic pressure changes when subterranean CO₂ was released; days with rising barometric pressure – when air accumulated belowground, including soil-respired CO₂ – showed greater ecosystem uptake than days with falling pressure. Future assessments of the net ecosystem carbon balance should not rely exclusively on Fick’s law to calculate soil CO₂ effluxes from profile data.

1 Introduction

The characterization of the different mechanisms and processes involved in soil CO₂ emissions to the atmosphere is important for improving understanding of the global carbon cycle. Respiration is generally the only process considered by the FLUXNET community when modeling or interpreting soil–atmosphere CO₂ exchanges (Falge et al., 2002), presumably transported by molecular diffusion. Recently however, numerous studies of semiarid ecosystems have shown the importance in the net ecosystem carbon balance (NECB; Chapin et al., 2006) of other, abiotic components (Emmerich, 2003; Kowalski et al., 2008; Mielnick et al., 2005; Plestjak et al., 2012; Rey et al., 2012a; Serrano-Ortiz et al., 2010; Were et al., 2010).

Most researchers interpret soil CO₂ effluxes at the soil surface in terms of concurrent respiration, neglecting subterranean CO₂ storage. Ventilation (gas advection through porous media) can decouple the soil CO₂ source from emissions to the atmosphere with changes in pressure, wind or friction velocity. Scientists have confirmed subterranean advective transport in laboratories (Nachshon et al., 2012; Maier et al., 2012), soils (Clemets and Wilkening, 1974; Maier et al., 2010; Subke et al., 2003; Weisbrod et al., 2009), peatlands (Comas et al., 2005; Comas et al., 2007; Comas et al., 2011), and snow (Bowling and Massman, 2011; Fujiyoshi et al., 2010; Seok et al., 2009; Massman et al., 1997). Some have applied the gradient method – based on Fick’s law for molecular diffusion – to model exchange with the atmosphere during calm conditions, but highlight the importance of advective transport in exchanges at other times.
Advection of CO₂ through soil or snow has been correlated with changes in subterranean CO₂ molar fractions \( (\chi_c) \) in conjunction with variations in wind speed, friction velocity or barometric pressure \( (p) \). Advection has been detected using isotopic methods (Bowling and Massman, 2011), buried \( p \) sensors (Maier et al., 2010; Takle et al., 2004), \(^{222}\text{Rn} \) concentrations (Clemets and Wilkenning, 1974; Fujiyoshi et al., 2010), ground-penetrating radar (Comas et al., 2005) or variations in CO₂ and other gases (Seok et al., 2009; Hirsch et al., 2004; Reicosky et al., 2008). Even in volcanoes the atmospheric \( p \) has a strong influence on both CO₂ degassing (Rogie et al., 2001) and the CO₂ soil efflux (Granieri et al., 2003), as well as on their combination as measured by eddy covariance (Lewicki et al., 2008; Lewicki et al., 2007).

Besides molecular diffusion, the main physical process affecting soil-atmosphere CO₂ exchange is ventilation driven by pressure pumping. Pressure pumping is caused by atmospheric processes including short-period turbulence, longer-period barometric changes and quasi-static pressure fields induced by wind (Massman et al., 1997). Subterranean convection, with CO₂-rich air subsiding due to its enhanced density (Kowalski and Sanchez Canete, 2010), may also play a role. Most studies attribute gas advection to two atmospheric mechanisms: quasi-static pressure fields and short-period atmospheric turbulence (Huwald et al., 2012), neglecting longer-period barometric changes.

At a nearby experimental site, it was found that wind provoked deep CO₂ emissions to the atmosphere (Sanchez Canete et al., 2011). Also, at this experimental site, the wind was found to be the main driver of large CO₂ emissions to the atmosphere (Rey et al., 2012a), suggesting a possible geothermal origin (Rey et al., 2012b). Given these precedents, our objective was to determine the main drivers involved in subterranean CO₂ ventilation and thereby improve knowledge of this little-studied process. Hypothesizing that these CO₂ emissions to the atmosphere could be the result of CO₂ transported from depth towards the surface, we installed a vertical soil profile to monitor subterranean CO₂ variations at depth (0.15, 0.5 and 1.5 m) during two years in this semiarid ecosystem.

2 Material and methods

2.1 Study site

The study was conducted in Balsa Blanca within the Cabo de Gata-Nijar Natural Park of southeast Spain (36°56′26.00″ N, 2° 0.15′58.8″ W). This is an alpha grass steppe situated on an alluvial fan (glacis) at 200 m a.s.l. The soil is classified as Calcaric Lithic Leptosol (WRB, 2006) saturated in carbonates (0.15 m) over petrocalcic horizons overlying marine carbonate sediments with the presence of fissures and fractures not visible above ground, and volcanic rocks. The texture is sandy loam with sand (61.1%), silt (22.8%) and clay (16.1%) with a bulk density of 1.25 (g cm⁻³). The climate is dry subtropical semiarid, with a mean annual temperature \( (T) \) of 18°C and precipitation of ca. 200 mm. The ground water level of the main aquifer of Balsa Blanca is situated at a depth of 140 m. The most abundant ground cover is bare soil, gravel and rock (49.1%), and vegetation is dominated by Macrochloa tenacissima (57% of cover) with other species present, including Chamaerops humilis, Rhamnus lycoides, and Pistacia lentiscus; the vegetation is most active during winter (January–April). More detailed site information is given by Rey et al. (2012a).

2.2 Field measurements

A vertical soil profile was installed in January 2010 to measure CO₂ molar fractions, temperature, and humidity at three depths that we characterized as “shallow” (0.15 m; A horizon), and “deep” (0.5 and 1.5 m; caliche horizon). Here, “deep” is used merely to distinguish between measured horizons, recognizing that all sensors are quite close to the surface. Sensors oriented horizontally in the profile included CO₂ molar fraction \( (\chi_c) \) probes (GMP-343, Vaisala, Inc., Finland) with soil adapters and hydrophobic filters, thermistors (107 temperature sensor, Campbell Scientific, Logan, UT, USA; hereafter CSI) and water content reflectometers (CS616, CSI) to measure the soil water content (SWC, m³ m⁻³). The GMP343 sensors were configured at 25°C and 1013 hPa and corrected in post-processing for variations in \( T \) and pressure. Measurements were made every 30 s and stored as 5 min averages by a data-logger (CR23X, CSI).

Ecosystem-scale CO₂ fluxes were measured by eddy covariance atop a 3.5 m tower. An open-path infrared gas analyzer (LI-Cor 7500, Lincoln, NE, USA) – calibrated monthly – measured barometric pressure \( (p) \) and densities of CO₂ and water vapor. A three-axis sonic anemometer (CSAT-3, CSI) measured wind speed and sonic temperature. At 1.5 m above ground level, two quantum sensors (LI-190, LI-Cor) measured incident and reflected photon fluxes. A data-logger (CR3000, CSI) managed the measurements and recorded data at 10 Hz (quantum sensors, storing only half-hour means). Turbulent fluxes were computed every half-hour according to Reynolds rules of averaging, corrected for dry air molar density variations (Webb et al., 1980) and coordinate rotation (Kowalski et al., 1997). The friction velocity \( (u_*) \) is determined as the turbulent velocity scale resulting from square root of the kinematic momentum flux (Stull, 1988). Quality control of the eddy flux data was performed according to Serrano-Ortiz et al. (2009).

2.3 Statistical analyses

To study the effect of longer-period barometric changes (atmospheric tides and synoptic events) and the friction velocity versus subterranean CO₂ variations, these variables were
Table 1. Mean ± standard error of soil CO$_2$ molar fractions ($\chi_c$), soil temperatures ($T$), soil water contents (SWC), friction velocity ($u_s$), barometric pressure and air temperature during growing (March / April) and dry (July / August) periods of 2010 and 2011.

<table>
<thead>
<tr>
<th>Depth</th>
<th>$\chi_c$</th>
<th>Soil T</th>
<th>SWC</th>
<th>Pressure</th>
<th>Air T</th>
<th>$u_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>March–April</td>
<td>0.15 m</td>
<td>514.8 ± 3.3</td>
<td>15.6 ± 0.1</td>
<td>11.1 ± 0.1</td>
<td>987.7 ± 0.1</td>
<td>14.3 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>0.5 m</td>
<td>943.3 ± 7.1</td>
<td>15.7 ± 0.0</td>
<td>11.6 ± 0.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.5 m</td>
<td>813.2 ± 7.4</td>
<td>15.5 ± 0.0</td>
<td>15.3 ± 0.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>July–August</td>
<td>0.15 m</td>
<td>473 ± 4.0</td>
<td>30.8 ± 0.0</td>
<td>1.4 ± 0.0</td>
<td>986.3 ± 0.1</td>
<td>25 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>0.5 m</td>
<td>1114.9 ± 11.2</td>
<td>29.4 ± 0.0</td>
<td>7.2 ± 0.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.5 m</td>
<td>1142 ± 12.6</td>
<td>26.1 ± 0.0</td>
<td>13.7 ± 0.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

normalized. This is because different variables are not strictly comparable due to extreme seasonal variations in both means and variances. Additionally, high-pass filtering was applied using two cut-off values to examine both diurnal and synoptic relationships. The normalized data (standardized anomalies; Wilks, 2006) for any meteorological variable are then given by

$$N_i = (X - \bar{X}_i) / \sigma_i,$$ (1)

where $N_i$ is the normalized value, $X$ the measurement, $\bar{X}_i$ the running mean for a window of width $i$ (0.5 or 3 days, diurnal and synoptic timescale, respectively) centered on the time of measurement, and $\sigma_i$ the standard deviation over the same window. Correlations ($R^2$) were then examined for both $N_{0.5}$ and $N_3$ and for two different vegetative periods: the growing period, where the vegetation is most active (March–April), and the dry period, where the vegetation is mostly dormant (July–August). Daytime half-hour data were fitted using an empirical hyperbolic light-response model (Falge et al., 2001) to describe the dependence of CO$_2$ ecosystem exchange [$F_C$, µmol m$^{-2}$ s$^{-1}$] on the incident photon flux [$F_P$, µmol m$^{-2}$ s$^{-1}$]:

$$F_C = -\frac{a\beta F_P}{\alpha F_P + \beta} + \gamma,$$ (2)

where $a$ (µmol C J$^{-1}$) is the canopy light utilization efficiency and represents the initial slope of the light-response curve, $\beta$ (µmol C m$^{-2}$ s$^{-1}$) is the maximum CO$_2$ uptake rate of the canopy at light saturation and $\gamma$ (µmol C m$^{-2}$ s$^{-1}$) is the ecosystem respiration during the day. All parameters are positive as defined.

3 Results

3.1 Seasonal and interannual patterns

Clear annual patterns are evident in the average daily values of soil temperature ($T$), water content (SWC), and CO$_2$ molar fraction ($\chi_c$) at 0.15 m (“shallow”) as well as at 0.5 m and 1.5 m depths (“deep”; Fig. 1). Shallow-soil $T$ has its maximum (ca. 34°C) in summer (June, July and August) and minimum (5°C) in winter (December, January and February); the SWC shows inverse correlation with $T$, with basal values near 5% in summer but often more than 20% in winter.

Soil CO$_2$ molar fractions ($\chi_c$) generally increase with depth, with a constant baseline for each horizon over the years, but also with periodic surges to more than double the mean value within a few days. The two deep sensors behave similarly (Fig. 1a), with the blue line (1.5 m depth) overlapping the red line (0.5 m depth) so nearly that the 0.5 m data are practically obscured. They show clear annual patterns with maxima in summer and minima in winter, similar means over the two years ($\chi_c \sim 1032$ ppm at 0.5 m, and 994 ppm at 1.5 m) and rapid variability. By contrast, the shallow sensor (Fig. 1d) has about half the mean ($\chi_c \sim 529$ ppm CO$_2$) and notably less variability - in both frequency and magnitude. Also in contrast to the deep case, shallow-soil $\chi_c$ is highest in winter and lowest in summer. Differences between the deep and shallow probes are less pronounced in winter. Pressure ($p$) varies from 967–1007 hPa (Fig. 1e), with increased variability in winter due to the passage of synoptic systems, and suppressed variability in summer under the Mediterranean high. To clarify the relation between $\chi_c$ and $p$, we focus on two different periods of 2011 (Fig. 1. Red rectangles): the growing period from March to May and the dry period from July to September.

3.2 Synoptic patterns

Table 1 shows the mean and standard error of environmental variables associated with varying soil CO$_2$ molar fractions ($\chi_c$) during both periods. For the growing period (from March to May) deep-soil CO$_2$ molar fractions ($\chi_c$) are nearly double ($\chi_c \sim 943$ ppm at 0.5 m, and 813 ppm at 1.5 m) the shallow $\chi_c$ (∼515 ppm at 0.15 m). At all depths the soil temperature has a similar mean (15.6°C, 15.7°C and 15.5°C at 0.15 m, 0.5 m and 1.5 m, respectively) as can be appreciated in Fig. 1a, and the soil water content increases with depth with values of 11.1%, 11.6%, and 15.3%. During the dry period (from July to September) the deep-soil CO$_2$ molar fractions ($\chi_c$) are more than double ($\chi_c \sim 1115$ ppm at 0.5 m, and 1142 ppm at 1.5 m) that of the shallow layer (∼473 ppm).
Fig. 1. Average daily values at soil depths of 0.15 m (black), 0.5 m (red) and 1.5 m (blue) for (A) temperature, (B) volumetric soil water content, (C) deep-soil CO$_2$ molar fraction ($\chi_c$) and (D) shallow-soil CO$_2$ molar fraction ($\chi_c$), as well as (E) the atmospheric pressure (orange) over two years. The red rectangle delimits the period amplified in Fig. 2.

at 0.15 m). The soil temperature decreases with depth, showing values of 30.8 °C, 29.4 °C and 26.1 °C at 0.15 m, 0.5 m and 1.5 m, respectively, and for the same depths the soil water content increased from 1.4 % to 7.2 % and 13.7 %, respectively.

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

The soil CO$_2$ molar fraction ($\chi_c$) shows strong inverse correlation with atmospheric pressure ($p$) on synoptic scales throughout the whole study period, as exemplified for four selected months (Fig. 2). Increments in $\chi_c$ correspond to decreases in $p$ and vice versa both in the growing period (Fig. 2a) and in the dry period (Fig. 2b). The changes in the magnitude of $p$ are higher in the growing period than in the dry period; however the variability in $\chi_c$ is lower in the growing period. Approximately every 3 days important changes occur in deep $\chi_c$, with nearly identical values and trends at 0.5 and 1.5 m. Shallow $\chi_c$ has a similar trend, in that the highest peaks occur on the same days; however not all deep $\chi_c$ peaks correspond to maxima near the surface (e.g. 22 July and 31 July). Such inverse correlation between $\chi_c$
Fig. 2. Average daily values at 0.15 m (black), 0.5 m (red) and 1.5 m (blue) depth of soil CO\(_2\) molar fraction (\(\chi_c\)) and atmospheric pressure (orange) during two months for the growing period (panel A, March–April) and dry period (panel B, July–August). The red rectangle delimits the period amplified in Fig. 3.

Fig. 3. Average half-hour values at 0.15 m, 0.5 m and 1.5 m depth of soil CO\(_2\) molar fraction (\(\chi_c\)) and atmospheric pressure for a period of 14 days during the growing period (panel A, April) and dry period (panel B, August).

and \(p\) extends to shorter timescales during the two vegetative periods, which will now be seen in higher resolution data corresponding to the red rectangles in Fig. 2.

### 3.3 Daily patterns

The deep-soil CO\(_2\) molar fraction (\(\chi_c\)) can jump to more than triple its mean value within a few hours, and shows inverse correlation with pressure (\(p\)) even at hourly timescales. Half-hour resolution data show that both \(p\) and deep \(\chi_c\) (0.5 and 1.5 m) display two cycles per day, both during the growing season (Fig. 3a) and in the dry season (Fig. 3b). Excepting synoptic pressure changes such as the events on 14 April and 8 August, pressure typically has semi-diurnal changes with an amplitude of ca. 3 hPa. Deep \(\chi_c\) shows a similar pattern with clear periodicity and two cycles per day, but some days have an amplitude up to 2000 ppm in a few hours (14 August) during this period of modest deep \(\chi_c\) variability (cf. Figs. 1 and 2). However, shallow \(\chi_c\) shows no such clear cyclic behavior.

Environmental factors that correlate with \(\chi_c\) are summarized in Table 2 for the growing and dry periods, respectively. During the growing period, the shallow \(\chi_c\) (0.15 m) shows correlation with \(T\) at 1.5 m and SWC at 0.5 m (\(R^2\) of 0.25 and 0.37, respectively). Whereas for deep \(\chi_c\) (0.5 m and 1.5 m) the main factor implicated are \(P\) and SWC at 0.5 m (\(R^2\) of 0.39 and 0.50, respectively). During the dry period, shallow \(\chi_c\) variations show maximum correlation with \(u_s\), \(\chi_c\) and SWC at 0.15 m (\(R^2\) of 0.29, 0.28 and 0.23, respectively). For deep \(\chi_c\) the maximum correlations are found only with \(p\) (\(R^2\) of 0.46).

Subterranean \(\chi_c\) variations and correlation with atmospheric tides (0.5 days), synoptic events (3 days) and \(u_s\) are shown in the Table 3. During the growing period, \(u_s\) does not show correlation with \(\chi_c\) variations at any depth, however deep \(\chi_c\) variations show correlation with \(p\) on synoptic timescales increasing with depth (\(R^2\) of 0.35 and 0.43 at 0.5 m and 1.5 m, respectively) and on daily timescales only at 1.5 m (\(R^2\) of 0.23). During the dry period, shallow \(\chi_c\) variations show high correlation with \(u_s\) whereas deep \(\chi_c\) variations show high correlations with pressure both on synoptic
timescale ($R^2$ of 0.49 and 0.50 at 0.5 m and 1.5 m, respectively) and on daily timescales ($R^2$ of 0.4 and 0.45 at 0.5 m and 1.5 m, respectively).

3.4 Coupling deep-soil CO$_2$ variations with the atmosphere

Ecosystem-scale CO$_2$ exchanges ($F_C$) are shown during the growing period (6–17 April 2011) together with the soil CO$_2$ molar fraction ($\chi_c$) at different depths in Fig. 4. Positive fluxes indicate emissions to the atmosphere and negative fluxes indicate uptake, so that during this period the ecosystem acts as a carbon sink. Over the week presented, the daily minima in $F_C$ (corresponding to maximum uptake), coincide with the variations in $\chi_c$. Days with high soil $\chi_c$ (9, 10, 13 and 14 of April) correspond to lower CO$_2$ uptake during daytime (Fig. 4).

The week presented was sunny with typical variation in the air temperature and no rain (data not shown), so the $F_C$ variations cannot be attributed to changing physiological drivers. Figure 5 shows the ecosystem light response using the hyperbolic model described in the Eq. (2), distinguishing between days with decreasing versus increasing atmospheric pressures (Figs. 3a and 4). Table 4 shows parameters obtained from ecosystem light response curves; for both days with decreasing and increasing $p$, the canopy light utilization efficiency ($\alpha$) and the ecosystem respiration ($\gamma$) are similar, however the maximum CO$_2$ uptake rate of the canopy at light saturation ($\beta$) increased by 43% during days with increasing pressure.

### Table 2. Correlation coefficients ($R^2$) during both the growing period and the dry period between soil CO$_2$ molar fractions ($\chi_c$) at three depths (0.15, 0.5 and 1.5 m), versus environmental parameters: friction velocity ($u_*$), pressure ($p$) and soil temperatures ($T$) and soil water contents ($SWC$) at the same three depths. Highlighted values denote the highest magnitudes for each depth.

<table>
<thead>
<tr>
<th>Depth Window (Days)</th>
<th>Growing period</th>
<th>Dry period</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15 m</td>
<td>0.08 0.17 0.01</td>
<td>0.23 0.06 0.06</td>
</tr>
<tr>
<td>0.5 m</td>
<td>0 0.13 0.39</td>
<td>0.18 0.46 0.43</td>
</tr>
<tr>
<td>1.5 m</td>
<td>0.08 0.26 0.05</td>
<td>0.28 0.11 0.12</td>
</tr>
<tr>
<td>0.15 m</td>
<td>0.17 0.27 0.2</td>
<td>0.02 0.02 0</td>
</tr>
<tr>
<td>0.5 m</td>
<td>0.37 0.50 0.27</td>
<td>0.01 0.02 0</td>
</tr>
<tr>
<td>1.5 m</td>
<td>0.25 0.28 0.1</td>
<td>0.01 0.03 0</td>
</tr>
<tr>
<td>SWC 0.1 m</td>
<td>0.08 0.26 0.05</td>
<td>0.28 0.11 0.12</td>
</tr>
<tr>
<td>SWC 0.5 m</td>
<td>0.08 0.26 0.05</td>
<td>0.28 0.11 0.12</td>
</tr>
<tr>
<td>SWC 1.5 m</td>
<td>0.08 0.26 0.05</td>
<td>0.28 0.11 0.12</td>
</tr>
</tbody>
</table>

### Table 3. Correlation coefficients ($R^2$) with normalized variables during both the growing period and the dry period (Fig. 2) between soil CO$_2$ molar fractions ($\chi_c$) at three depths (0.15, 0.5 and 1.5 m), on timescales of 0.5 days and 3 days, versus pressure ($p$) and the friction velocity ($u_*$).

<table>
<thead>
<tr>
<th>Depth</th>
<th>Window (Days)</th>
<th>Growing period</th>
<th>Dry period</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15 m</td>
<td>0.5</td>
<td>0.01 0.13 0.53</td>
<td>0.53 0</td>
</tr>
<tr>
<td>0.5 m</td>
<td>0.5</td>
<td>0.01 0.13 0.53</td>
<td>0.53 0</td>
</tr>
<tr>
<td>1.5 m</td>
<td>0.5</td>
<td>0.01 0.13 0.53</td>
<td>0.53 0</td>
</tr>
</tbody>
</table>

$\chi_c$ correlates with soil temperature ($T$) and is inversely correlated to soil water content ($SWC$); and shorter – synoptic and hourly – scales (Figs. 2 and 3), where deep $\chi_c$ is clearly inversely correlated with $p$ and can increment by a factor of four in a few hours. This behavior of deep $\chi_c$ is in contrast with that of shallow $\chi_c$, which on seasonal scales (Fig. 1) is better described in terms of commonly reported semiarid conditions where soil respiration is clearly restricted by drought (Barron-Gafford et al., 2011; Maranon-Jimenez et al., 2011; Oyonarte et al., 2012; Rey et al., 2011), showing an inverse correlation with $T$ and correlation with SWC. Shallow $\chi_c$ shows maxima in winter and minima in summer coinciding with the vegetation’s active period (Rey et al., 2012a) and favored by higher soil water contents limiting soil gas diffusivity. The similar behavior of the two deep sensors suggests that the deep pore spaces are highly interconnected, at least within the same caliche horizon.
Such large variations in deep $\chi_c$ have no direct biological explanation, but suggest an underlying CO$_2$ reservoir in communication with the surface, depending on factors such as $p$, $u_e$ or SWC. The origin of the CO$_2$ reservoir could be either geothermal (i.e., magmatic or metamorphic; Rey et al., 2012b) or biological in origin. Geothermal sources may exist at a depth below Balsa Blanca because the site is located over a large active tectonic fault system. Biological origins would be due to CO$_2$ storage in deep layers resulting from plant activity and microbes, whose metabolic activities might well be affected by the large variations in $\chi_c$ (a secondary effect, at most). The CO$_2$ respired in the root zone increases air density (Sanchez-Canete et al., 2013; Kowalski and Sanchez-Canete, 2010), and so enables gravitational percolation through the pore space toward deeper layers where it can be stored.

Although in this study, $p$ is the main factor implicated in deep $\chi_c$ variations, Fig. 1 shows that $\chi_c$ variability is greater in summer when $p$ variations are reduced. This highlights the important role of SWC in CO$_2$ exchange: despite greater synoptic pressure variability, winter has lower $\chi_c$ variations because soil pores are filled with water, limiting gas flows. In summer, by contrast, ventilation is facilitated by dry soil conditions with gas-filled pore space (Cuezva et al., 2011; Maier et al., 2010). This would allow superficial CO$_2$ values to increase during the dry season because soil pore space opens to the flow of CO$_2$-rich air from the deep soil to near-surface layers.

At synoptic scales, passing frontal systems cause increases / decreases in $p$ leading to fourfold decreases / increases in deep $\chi_c$ (Fig. 2). Such variability can only be explained by CO$_2$ transported from depth towards the surface. A simple model to explain the role of pressure ($p$) in subterranean CO$_2$ transport is shown in Fig. 6. When $p$ increases, the soil air is compressed and atmospheric air penetrates into the soil decreasing the deep $\chi_c$. Similarly, when $p$ decreases, the soil air expands increasing the deep $\chi_c$ since deeper soil air distends toward the surface.

Hourly timescales (Fig. 3) show clear inverse correlation between the deep $\chi_c$ and $p$, where even small daily $p$ oscillations (3 hPa) due to twice daily atmospheric tides (Lindzen, 1979) generate large variations in $\chi_c$ at depth (2000 ppm; e.g., falling $\chi_c$ on 12 August, Fig. 3b). Deep-soil $\chi_c$ (0.5 and 1.5 m) shows two cycles per day, in rhythm with $p$, whereas shallow $\chi_c$ has just one. Shallow $\chi_c$ is more affected by friction velocity (Table 3) because it is in the upper part of the soil, and thus more easily ventilated decreasing $\chi_c$ (Hirsch et al., 2004; Sanchez-Canete et al., 2011). Similarly, Rey et al. (2012a) concluded that the wind was the main driver of the net ecosystem carbon balance at this experimental site. At a nearby ecosystem with carbonate soils, such subterranean ventilation represented up to 62% of the annual emissions during dry periods (Perez-Priego et al., 2013).

### Table 4. Parameters obtained from ecosystem light response curves shown in Fig. 5. Where $\alpha$ (µmol CO$_2$ m$^{-2}$ s$^{-1}$) is the canopy light utilization efficiency and represents the initial slope of the light-response curve, $\beta$ (µmol CO$_2$ m$^{-2}$ s$^{-1}$) is the maximum CO$_2$ uptake rate of the canopy at light saturation and $\gamma$ (µmol CO$_2$ m$^{-2}$ s$^{-1}$) is the ecosystem respiration during the day.

<table>
<thead>
<tr>
<th>Days</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decreasing pressure</td>
<td>$-0.032 \pm 0.007$</td>
<td>$-5.8 \pm 0.3$</td>
<td>$1.6 \pm 0.2$</td>
</tr>
<tr>
<td>Increasing pressure</td>
<td>$-0.025 \pm 0.006$</td>
<td>$-8.3 \pm 0.5$</td>
<td>$1.6 \pm 0.3$</td>
</tr>
</tbody>
</table>

![Fig. 5. Ecosystem light response curves. Daytime ecosystem CO$_2$ flux ($F_c$; µmol m$^{-2}$ s$^{-1}$) versus the flux of photosynthetically active radiation (PAR; µmol m$^{-2}$ s$^{-1}$) for days from Figs. 3a and 4 falling into two categories: days with decreasing atmospheric pressure and increasing deep-soil CO$_2$ (black circles; 9, 10, 13, 14 April) and vice versa (white circles; 11, 12, 15, 16 April). No changes in daily patterns of physiological drivers (temperature, relative humidity, net radiation or soil water content) were observed over the selected days.](image-url)
The effects of emissions from deep CO$_2$ soil were registered in the atmosphere, driven by synoptic pressure changes. The light response curves demonstrated that on both consecutive and non-consecutive days and near-constant environmental conditions (temperature, relative humidity, net radiation and soil water content), the maximum downward CO$_2$ flux toward the canopy at light saturation increased by 43% during days with increasing synoptic pressure, versus those with falling pressure. This is in accordance with the explanatory diagram of Fig. 6. With rising pressure, part of the CO$_2$ respired by plants tends to accumulate in the soil, registering more negative eddy fluxes and therefore obtaining a high value of $\beta$, which might be interpreted erroneously as the maximum CO$_2$ uptake rate of the canopy at light saturation (as in Eq. 2). However, with falling pressure, both CO$_2$ stored in the soil and that respired by plants is emitted to the atmosphere, making eddy fluxes less negative and lowering the value of $\beta$. The results presented in this paper come from a vertical CO$_2$ profile of three depths without horizontal replication but with a long and continuous data series. For this reason, the results invite further research at this and other semiarid ecosystems regarding the influence of synoptic pressure changes on variations in deep-soil CO$_2$ molar fractions at different locations, and their role on the net ecosystem carbon balance.

5 Conclusions

This study reveals that during both growing periods and dry periods, variations in the deep-soil CO$_2$ molar fraction ($\chi_c$) are due predominantly to atmospheric pressure ($p$) variations and not directly to biological influences. In a few hours, the deep $\chi_c$ can increase or decrease fourfold, highlighting the need for continuous (versus sporadic) monitoring of soil CO$_2$ effluxes. Deep $\chi_c$ has a pattern with two cycles per day, due to $p$ oscillations caused by atmospheric tides. Nonetheless shallow $\chi_c$ has a pattern with one cycle per day, due to its dependence mainly on the friction velocity during the dry period and on biological factors during both dry and growing periods, showing maxima for this semiarid ecosystem when soil water content is not limiting, with temperature dependence as well. The effects of emissions from deep-soil CO$_2$ were registered in the atmosphere driven by synoptic pressure changes: on days with rising pressure the downward CO$_2$ flux is higher than days with falling pressure because on these days CO$_2$ respired by plants accumulates in the soil. Future studies focused on determining the net ecosystem carbon balance should not rely exclusively on Fick’s law to calculate soil CO$_2$ effluxes from profile data.

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References


