1. Subterranean CO₂ ventilation and its role in the net ecosystem carbon balance of a karstic shrubland

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6 [1] Recent studies of carbonate ecosystems suggest a possible contribution of subterranean ventilation to the net ecosystem carbon balance. However, both the overall importance of such CO₂ exchange processes and their drivers remain unknown. Here we analyze several dry-season episodes of net CO₂ emissions to the atmosphere, along with soil and borehole CO₂ measurements. Results highlight important events where rapid decreases of underground CO₂ molar fractions, correlate well with sizeable CO₂ release to the atmosphere. Such events, with high friction velocities, are attributed to ventilation processes, and should be accounted for by predictive models of surface CO₂ exchange.


22 1. Introduction

23 [2] The FLUXNET community monitors ecosystem carbon exchanges, usually interpreting CO₂ fluxes as biological (photosynthetic or respiratory) [Falge et al., 2002; Reichstein et al., 2005], neglecting inorganic processes. However, recent studies over carbonate substrates reveal possible contributions by abiotic processes to the net ecosystem carbon balance (NECB) [Chapin et al., 2006], with relevant magnitudes at least on short time scales [Serrano-Ortiz et al., 2010; Were et al., 2010]. These processes can temporally dominate the NECB in areas with carbonate soils [Kowalski et al., 2008].

33 [3] Carbonates outcrop on ca. 12–18% of the water-free Earth [Ford and Williams, 1989] with an enormous capacity to store CO₂ below ground in macropores (caves) and fissures [Benavente et al., 2010; Ek and Gewelt, 1985]. Ventilation is a mass flow of air through a cavity, via the porous media in the case of closed caves, driven by an imbalance of forces (pressure gradients and gravity). Through the venting of these subterranean spaces, stored gaseous CO₂ can be lost to the atmosphere [Kowalczyk and Froelich, 2010; Weisbrod et al., 2009]. However, both the drivers of these ventilation processes and their relevance to regional CO₂ budgets remain unknown.

4 [4] Often ecologists estimate soil CO₂ effluxes neglecting advective transport of CO₂ through the vadose zone. Studies of surface exchange have usually been conducted either by manual [Janssens et al., 2001], or automatic soil respiration chambers [Drewitt et al., 2002]. Scientists often model underground, diffusive soil CO₂ fluxes based on single sampling [Davidson and Trumbore, 1995; Hirsch et al., 2002] or continuous monitoring of CO₂ profiles [Baldocchi et al., 2006; Plamann et al., 2008; Tang et al., 2003].

54 Such models based on diffusion processes neglect the effects of ventilation. However, Subke et al. [2003] revealed the importance of such effects at least on short-time scales.

5 [5] Here we analyze several episodes of subterranean CO₂ ventilation that occurred during a dry period in a carbonate ecosystem. We examine its determinants and implications for the NECB measured with an eddy covariance system.

2. Material and Methods

6 [6] The study site is El Llano de los Juanes, a shrubland plateau at 1600 m altitude in the Sierra de Gádor (Almería, Southeast Spain; 36°55′41.7″N; 2°45′1.7″W). It is characterized by a sub-humid climate with a mean annual temperature (T) of 12 °C and precipitation of ca. 465 mm. The soil, overlying Triassic carbonate rocks, varies from 0 to 150 cm in depth with a petrocalcic horizon and fractured rocks. More detailed site information is given by Serrano-Ortiz et al. [2009].

7 [7] Throughout the dry season of 2009 (9 June–9 September) two sensors (GMP-343, Vaisala, Inc., Finland) that measure CO₂ molar fraction (χc), were installed in the soil and in a borehole. The soil sensor was installed 25 cm deep, with a soil T probe (107, Campbell scientific, Logan, UT, USA; hereafter CSI) and water content reflectometer (CS616, CSI). The 7-m borehole (dia. 0.1 m), was sealed from the atmosphere with a metal tube cemented to the walls. Inside, sensors tracked χc (GMP-343) and T and relative humidity (HMP45, CSI). The CO₂ sensors were corrected for variations in T and pressure. A data-logger (CR23X, CSI) measured every 30 s and stored 5 min averages. Ecosystem-scale CO₂ fluxes were measured by eddy covariance atop a 2.5 m tower, Serrano-Ortiz et al. [2009] describe the instrumentation and quality control for eddy flux data.

3. Results

8 [8] Over the dry period, soil and borehole χc were inversely correlated. While the soil χc fell from its maximum near...
1500 ppm to about half (Figure 1a), the borehole $\chi_c$ doubled from ca. 8000 ppm and to 16000 ppm (Figure 1b). Apart from these long-term trends, during the first half of the summer, marked decreases occurred in both soil and borehole $\chi_c$ during three key events (Figure 1; grey bars). Such decreases correspond to higher CO$_2$ emissions to the atmosphere relative to the preceding and subsequent periods. Pressure and air temperature showed poor correlations with soil $\chi_c$, while radon and CO$_2$ fluctuations in the borehole are correlated in phase (see auxiliary material), suggesting that ventilation causes CO$_2$ losses. A cross-correlation analysis indicated that an increment in $u_*$ during daytime corresponds immediately to an increase in ecosystem CO$_2$ fluxes ($F_c$), whereas the decrease in soil $\chi_c$ is delayed by two hours, and the cave $\chi_c$ lags the soil by 53.5 hours.

These events occurred when the friction velocity ($u_*$) exceeded 0.3 m s$^{-1}$ (Figure 1c), and are associated with ventilation. The largest event occurred during a windy period from July 21st–24th (daily mean $u_*$ > 0.6 m s$^{-1}$), when soil CO$_2$ more than halved from 1200 to 500 ppm and the borehole lost ca. 4000 ppm. This underground CO$_2$ loss corresponded to increased emissions to the atmosphere of 0.4–2 $\mu$mol m$^{-2}$ s$^{-1}$ (Figure 1d). After the event, the borehole $\chi_c$ recovered to exceed initial values (>14000 ppm) within a couple of weeks. The 21–24 July ventilation event (3rd grey bar, Figure 1) is detailed in Figure 2, showing 11 days of half-hour values divided into periods of recharge and ventilation. During recharge, the borehole $\chi_c$ increased slightly, then fell quickly during ventilation, losing ca. 4000 ppm in five days (Figure 2b). Soil CO$_2$ followed a daily cycle, with late afternoon peaks and dawn minima (Figure 2a). During recharge, diurnal ranges averaged ca. 800 ppm, versus just 200 ppm during ventilation. The mean soil $\chi_c$ and $u_*$ were higher (Figure 2c) for the ventilated period. Finally, $F_c$ was near zero with little diurnal variation during recharge, but daytime emissions exceeded 5 $\mu$mol m$^{-2}$ s$^{-1}$ during the ventilated period. At night, CO$_2$ emissions were always close to zero (Figure 2d).

### 4. Discussion

#### 4.1. Evidence of Subterranean Ventilation

This study shows clear empirical evidence of subterranean ventilation and its implications in the NECB. Decreases in soil and borehole $\chi_c$ coincided with high $u_*$, corresponding to large $F_c$ (Figure 2). Ventilation induces soil CO$_2$ release on time scales from minutes to days. Particularly high ecosystem emissions may occur with greater magnitudes in karsts storing large amounts of CO$_2$, with the overlying soil acting as a semi-permeable membrane open to gas exchange on dry summer days [Cuezva et al., 2011]. Thus, ventilation processes can be more important in karstic ecosystems with arid soils and pronounced dry seasons.

In this study subsurface CO$_2$ followed a daily pattern. In soi pores, dusk/dawn had the maximum/minimum concentrations (Figure 2a). Borehole CO$_2$ values, integrating the whole column from 0 to 7 m, followed no daily trend as confirmed by autocorrelation analysis. Thus, a rise in $u_*$ corresponds to a direct decrease in soil $\chi_c$, while borehole $\chi_c$ falls several hours later.

#### 4.2. Main Drivers Controlling the Soil CO$_2$ Ventilation

Studies focused on soil CO$_2$ profiles have reported correlations between soil $\chi_c$ and wind speed [Jassal et al., 2005; Takle et al., 2004]. Lewicki et al. [2010] experimentally studied the correlation between temporal variations in soil CO$_2$ concentrations and several meteorological factors during a controlled shallow-subsurface CO$_2$ release.
experiment. Subke et al. [2003] suggested that the flux contributed by pressure pumping should be considerable for wind gusts following periods of relative calm, while its correlation should be smaller for similar wind conditions over previously flushed soil. We found a strong inverse correlation between soil $\chi$ and $u$. After de-trending the CO$_2$ series, $u$ explained 67% ($R^2$) of the variability during the studied period. Correlated radon and CO$_2$ fluctuations in the borehole also indicate that ventilation is the cause of CO$_2$ losses.

All this indicates that, for our study, the most appropriate variable determining soil CO$_2$ ventilation is $u$.

### 4.3. Outstanding Issues

Despite these clear relationships, uncertainties remain regarding the behavior of subterranean CO$_2$, and two particular questions arise. Firstly, where does the soil CO$_2$ go after reaching its daily maxima during recharge periods? For example, on the windy night of July 20th–21st, the soil lost ca. 1000 ppm but this CO$_2$ was not detected in eddy fluxes (Figure 2). Secondly, why are CO$_2$ emissions never detected by eddy covariance at night? One might attribute this to static stability, but high values of $u$ are evidence of dynamic instability [Stull, 1988] indicating that CO$_2$ exchange is not a limited by the turbulence. Rather, we posit that cold surface temperatures at night foment water vapor adsorption [Kosmas et al., 2001], humidify the surface, close the soil membrane to gas flow at night, and thus disable ventilation [Cuevas et al., 2011]. By contrast during ventilation the CO$_2$ that would otherwise have accumulated in the soil during daytime (see recharge period) is emitted directly to the atmosphere.

### 5. Conclusions

This study emphasizes the role of dry-season, subterranean transport processes in the net ecosystem carbon balance (NECB). Although several meteorological factors correlate with emitted CO$_2$, analyses suggest that ventilation is driven mainly by the friction velocity. Windy days are responsible for large emissions of CO$_2$ previously accumulated below ground, which are not accounted for in current models of surface CO$_2$ exchange. However, during calm days soil CO$_2$ accumulates, causing significant day-night contrast on centeration. The vast network of pores, cracks and cavities along with high molar fractions ($>15000$ ppm–$7$m) indicate that very large amounts of CO$_2$ can be stored inside karst systems. Further investigation is needed to explain the absence of CO$_2$ ventilation during windy nights, and characterize the CO$_2$ cycling of carbonate ecosystems.

