

# 1 Subterranean CO<sub>2</sub> ventilation and its role in the net ecosystem 2 carbon balance of a karstic shrubland

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6 [1] Recent studies of carbonate ecosystems suggest a  
7 possible contribution of subterranean ventilation to the  
8 net ecosystem carbon balance. However, both the overall  
9 importance of such CO<sub>2</sub> exchange processes and their drivers  
10 remain unknown. Here we analyze several dry-season  
11 episodes of net CO<sub>2</sub> emissions to the atmosphere, along  
12 with soil and borehole CO<sub>2</sub> measurements. Results high-  
13 light important events where rapid decreases of underground  
14 CO<sub>2</sub> molar fractions, correlate well with sizeable CO<sub>2</sub> release  
15 to the atmosphere. Such events, with high friction veloc-  
16 ities, are attributed to ventilation processes, and should be  
17 accounted for by predictive models of surface CO<sub>2</sub> exchange.  
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## 22 1. Introduction

23 [2] The FLUXNET community monitors ecosystem car-  
24 bon exchanges, usually interpreting CO<sub>2</sub> fluxes as biological  
25 (photosynthetic or respiratory) [Falge *et al.*, 2002; Reichstein  
26 *et al.*, 2005], neglecting inorganic processes. However, recent  
27 studies over carbonate substrates reveal possible contribu-  
28 tions by abiotic processes to the net ecosystem carbon balance  
29 (NECB) [Chapin *et al.*, 2006], with relevant magnitudes  
30 at least on short time scales [Serrano-Ortiz *et al.*, 2010; Were  
31 *et al.*, 2010]. These processes can temporally dominate the  
32 NECB in areas with carbonate soils [Kowalski *et al.*, 2008].  
33 [3] Carbonates outcrop on ca. 12–18% of the water-free  
34 Earth [Ford and Williams, 1989] with an enormous capacity  
35 to store CO<sub>2</sub> below ground in macropores (caves) and fissures  
36 [Benavente *et al.*, 2010; Ek and Gewalt, 1985]. Ventilation is  
37 a mass flow of air through a cavity, via the porous media in  
38 the case of closed caves, driven by an imbalance of forces  
39 (pressure gradients and gravity). Through the venting of these  
40 subterranean spaces, stored gaseous CO<sub>2</sub> can be lost to the  
41 atmosphere [Kowalczyk and Froelich, 2010; Weisbrod *et al.*,

2009]. However, both the drivers of these ventilation pro- 42  
cesses and their relevance to regional CO<sub>2</sub> budgets remain 43  
unknown. 44

[4] Often ecologists estimate soil CO<sub>2</sub> effluxes neglecting 45  
advective transport of CO<sub>2</sub> through the vadose zone. Studies 46  
of surface exchange have usually been conducted either by 47  
manual [Janssens *et al.*, 2001], or automatic soil respira- 48  
tion chambers [Drewitt *et al.*, 2002]. Scientists often model 49  
underground, diffusive soil CO<sub>2</sub> fluxes based on single 50  
sampling [Davidson and Trumbore, 1995; Hirsch *et al.*, 51  
2002] or continuous monitoring of CO<sub>2</sub> profiles [Baldochi 52  
*et al.*, 2006; Pumpanen *et al.*, 2008; Tang *et al.*, 2003]. 53  
Such models based on diffusion processes neglect the effects 54  
of ventilation. However, Subke *et al.* [2003] revealed the 55  
importance of such effects at least on short-time scales. 56

[5] Here we analyze several episodes of subterranean CO<sub>2</sub> 57  
ventilation that occurred during a dry period in a carbonate 58  
ecosystem. We examine its determinants and implications for 59  
the NECB measured with an eddy covariance system. 60

## 2. Material and Methods 61

[6] The study site is *El Llano de los Juanes*, a shrubland 62  
plateau at 1600 m altitude in the *Sierra de Gádor* (Almería, 63  
Southeast Spain; 36°55'41.7"N; 2°45'1.7"W). It is charac- 64  
terized by a sub-humid climate with a mean annual temper- 65  
ature (*T*) of 12 °C and precipitation of ca. 465 mm. The soil, 66  
overlying Triassic carbonate rocks, varies from 0 to 150 cm 67  
depth with a petrocalcic horizon and fractured rocks. More 68  
detailed site information is given by Serrano-Ortiz *et al.* 69  
[2009]. 70

[7] Throughout the dry season of 2009 (9 June–9 71  
September) two sensors (GMP-343, Vaisala, Inc., Finland) 72  
that measure CO<sub>2</sub> molar fraction ( $\chi_c$ ), were installed in the 73  
soil and in a borehole. The soil sensor was installed 25 cm 74  
deep, with a soil *T* probe (107, Campbell scientific, Logan, 75  
UT, USA; hereafter CSI) and water content reflectometer 76  
(CS616, CSI). The 7-m borehole (dia. 0.1 m), was sealed 77  
from the atmosphere with a metal tube cemented to the walls. 78  
Inside, sensors tracked  $\chi_c$  (GMP-343) and *T* and relative 79  
humidity (HMP45, CSI). The CO<sub>2</sub> sensors were corrected for 80  
variations in *T* and pressure. A data-logger (CR23X, CSI) 81  
measured every 30 s and stored 5 min averages. Ecosystem- 82  
scale CO<sub>2</sub> fluxes were measured by eddy covariance atop a 83  
2.5 m tower; Serrano-Ortiz *et al.* [2009] describe the instru- 84  
mentation and quality control for eddy flux data. 85

## 3. Results 86

[8] Over the dry period, soil and borehole  $\chi_c$  were inversely 87  
correlated. While the soil  $\chi_c$  fell from its maximum near 88

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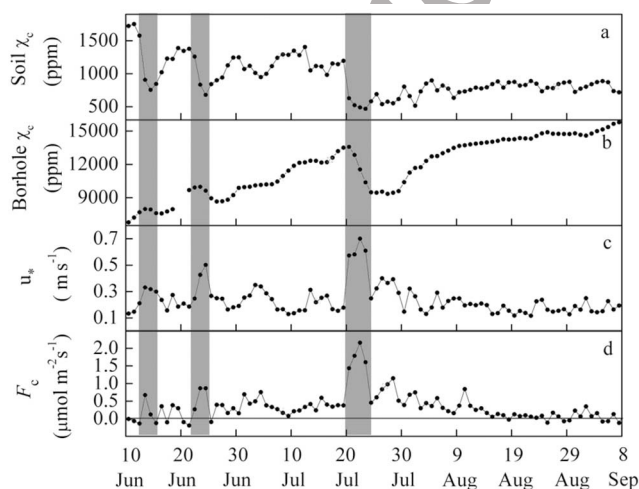
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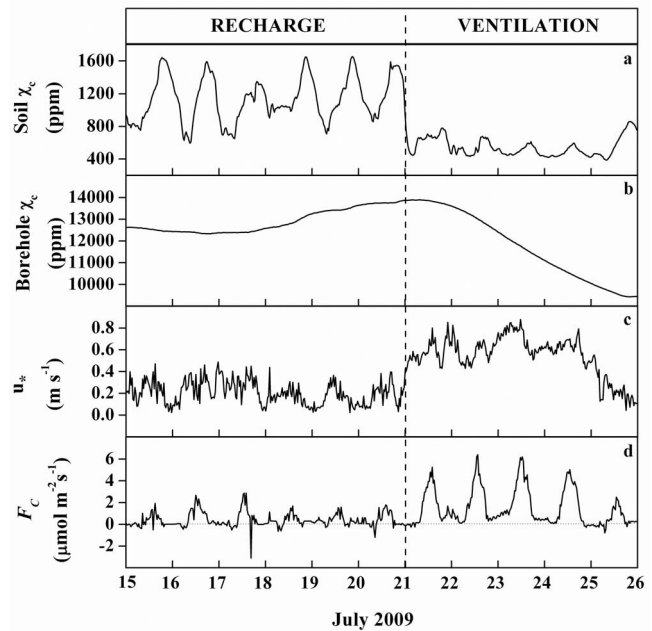
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89 1500 ppm to about half (Figure 1a), the borehole  $\chi_c$  doubled  
 90 from *ca.* 8000 ppm and to 16000 ppm (Figure 1b). Apart from  
 91 these long-term trends, during the first half of the summer,  
 92 marked decreases occurred in both soil and borehole  $\chi_c$   
 93 during three key events (Figure 1; grey bars). Such decreases  
 94 correspond to higher CO<sub>2</sub> emissions to the atmosphere rela-  
 95 tive to the preceding and subsequent periods. Pressure and air  
 96 temperature showed poor correlations with soil  $\chi_c$ , while  
 97 radon and CO<sub>2</sub> fluctuations in the borehole are correlated in  
 98 phase (see auxiliary material), suggesting that ventilation  
 99 causes CO<sub>2</sub> losses. A cross-correlation analysis indicated that  
 100 an increment in  $u_*$  during daytime corresponds immediately  
 101 to an increase in ecosystem CO<sub>2</sub> fluxes ( $F_c$ ), whereas the  
 102 decrease in soil  $\chi_c$  is delayed by two hours, and the cave  $\chi_c$   
 103 lags the soil by 53.5 hours.

104 [9] These events occurred when the friction velocity ( $u_*$ )  
 105 exceeded 0.3 m s<sup>-1</sup> (Figure 1c), and are associated with  
 106 ventilation. The largest event occurred during a windy period  
 107 from July 21st–24th (daily mean  $u_* > 0.6$  m s<sup>-1</sup>), when  
 108 soil CO<sub>2</sub> more than halved from 1200 to 500 ppm and the  
 109 borehole lost *ca.* 4000 ppm. This underground CO<sub>2</sub> loss  
 110 corresponded to increased emissions to the atmosphere of  
 111 0.4–2  $\mu\text{mol m}^{-2} \text{s}^{-1}$  (Figure 1d). After the event, the borehole  
 112  $\chi_c$  recovered to exceed initial values (>14000 ppm) within a  
 113 couple of weeks. The 21–24 July ventilation event (3rd grey  
 114 bar, Figure 1) is detailed in Figure 2, showing 11 days of  
 115 half-hour values divided into periods of recharge and venti-  
 116 lation. During recharge, the borehole  $\chi_c$  increased slightly,  
 117 then fell quickly during ventilation, losing *ca.* 4000 ppm in  
 118 five days (Figure 2b). Soil CO<sub>2</sub> followed a daily cycle, with  
 119 late afternoon peaks and dawn minima (Figure 2a). During  
 120 recharge, diurnal ranges averaged *ca.* 800 ppm, versus just  
 121 200 ppm during ventilation. The mean soil  $\chi_c$  and  $u_*$  were  
 122 higher (Figure 2c) for the ventilated period. Finally,  $F_c$  was  
 123 near zero with little diurnal variation during recharge,  
 124 but daytime emissions exceeded 5  $\mu\text{mol m}^{-2} \text{s}^{-1}$  during the



**Figure 1.** Average daily values of (a) soil CO<sub>2</sub> molar fraction ( $\chi_c$ ) at 25 cm depth and (b) borehole  $\chi_c$  at 7 m depth, (c) friction velocity ( $u_*$ ; turbulent velocity scale) and (d) ecosystem CO<sub>2</sub> fluxes ( $F_c$ ; negative values represent uptake). Shaded columns delimit ventilation events.



**Figure 2.** Ventilation event detail, distinguishing between recharge and ventilation. Average half-hour values of (a) soil CO<sub>2</sub> molar fraction ( $\chi_c$ , 25 cm depth), (b) borehole  $\chi_c$  (7 m depth), (c) friction velocity ( $u_*$ ; turbulent velocity scale) and (d) CO<sub>2</sub> fluxes.

ventilated period. At night, CO<sub>2</sub> emissions were always close  
 to zero (Figure 2d).

## 4. Discussion

### 4.1. Evidence of Subterranean Ventilation

[10] This study shows clear empirical evidence of sub-  
 terranean 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<sub>2</sub> release on time scales from minutes to days. Particularly  
 high ecosystem emissions may occur with greater magnitudes  
 in karsts storing large amounts of CO<sub>2</sub>, 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.

[11] In this study subsurface CO<sub>2</sub> followed a daily pattern.  
 In soil pores, dusk/dawn had the maximum/minimum con-  
 centrations (Figure 2a). Borehole CO<sub>2</sub> 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<sub>2</sub> Ventilation

[12] Studies focused on soil CO<sub>2</sub> profiles have reported  
 correlations between soil  $\chi_c$  and wind speed [Jassal *et al.*,  
 2005; Takle *et al.*, 2004]. Lewicki *et al.* [2010] experimen-  
 tally studied the correlation between temporal variations  
 in soil CO<sub>2</sub> concentrations and several meteorological fac-  
 tors during a controlled shallow-subsurface CO<sub>2</sub> release

154 experiment. Subke *et al.* [2003] suggested that the flux con-  
 155 tributed by pressure pumping should be considerable for  
 156 wind gusts following periods of relative calm, while its cor-  
 157 relation should be smaller for similar wind conditions over  
 158 previously flushed soil. We found a strong inverse correlation  
 159 between soil  $\chi_c$  and  $u_*$ . After de-trending the CO<sub>2</sub> series,  $u_*$   
 160 explained 67% (R<sup>2</sup>) of the variability during the studied  
 161 period. Correlated radon and CO<sub>2</sub> fluctuations in the bore-  
 162 hole also indicate that ventilation is the cause of CO<sub>2</sub> losses.  
 163 All this indicates that, for our study, the most appropriate  
 164 variable determining soil CO<sub>2</sub> ventilation is  $u_*$ .

### 165 4.3. Outstanding Issues

166 [13] Despite these clear relationships, uncertainties remain  
 167 regarding the behavior of subterranean CO<sub>2</sub>, and two par-  
 168 ticular questions arise. Firstly, where does the soil CO<sub>2</sub> go  
 169 after reaching its daily maxima during recharge periods? For  
 170 example, on the windy night of July 20th–21st, the soil lost  
 171 ca. 1000 ppm but this CO<sub>2</sub> was not detected in eddy fluxes  
 172 (Figure 2). Secondly, why are CO<sub>2</sub> emissions never detected  
 173 by eddy covariance at nights? One might attribute this to  
 174 static stability, but high values of  $u_*$  are evidence of dynamic  
 175 instability [Stull, 1988] indicating that CO<sub>2</sub> exchange is not a  
 176 limited by the turbulence. Rather, we posit that cold surface  
 177 temperatures at night foment water vapor adsorption [Kosmas  
 178 *et al.*, 2001], humidify the surface, close the soil membrane  
 179 to gas flow at night, and thus disable ventilation [Cuezva  
 180 *et al.*, 2011]. By contrast during ventilation the CO<sub>2</sub> that  
 181 would otherwise have accumulated in the soil during daytime  
 182 (see recharge period) is emitted directly to the atmosphere.

### 183 5. Conclusions

184 [14] This study emphasizes the role of dry-season, sub-  
 185 terranean ventilation processes in the net ecosystem carbon  
 186 balance (NECB). Although several meteorological factors  
 187 correlate with emitted CO<sub>2</sub>, analyses suggest that ventila-  
 188 tion is driven mainly by the friction velocity. Windy days are  
 189 responsible for large emissions of CO<sub>2</sub> previously accumu-  
 190 lated below ground, which are not accounted for in current  
 191 models of surface CO<sub>2</sub> exchange. However during calm days  
 192 soil CO<sub>2</sub> accumulates, causing significant day-night con-  
 193 centration differences. The vast network of pores, cracks and  
 194 cavities along with high molar fractions (>15000 ppm–7 m)  
 195 indicate that very large amounts of CO<sub>2</sub> can be stored inside  
 196 karst systems. Further investigation is needed to explain the  
 197 absence of CO<sub>2</sub> ventilation during windy nights, and charac-  
 198 terize the CO<sub>2</sub> cycling of carbonate ecosystems.

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