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Subterranean CO_2 ventilation and its role in the net ecosystem carbon balance of a karstic shrubland

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[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 CO_2 exchange processes and their drivers remain unknown. Here we analyze several dry-season episodes of net CO_2 emissions to the atmosphere, along with soil and borehole CO_2 measurements. Results highlight important events where rapid decreases of underground CO_2 molar fractions correlate well with sizeable CO_2 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 CO_2 exchange.

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1. Introduction

[2] The FLUXNET community monitors ecosystem carbon exchanges, usually interpreting CO_2 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].

[3] Carbonates outcrop on ca. 12–18% of the water-free Earth [*Ford and Williams*, 1989] with an enormous capacity to store CO_2 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 CO_2 can be lost to the atmosphere [*Kowalczk and Froelich*, 2010; *Weisbrod et al.*, 2009]. However, both the drivers of these ventilation processes and their relevance to regional CO_2 budgets remain unknown.

[4] Often ecologists estimate soil CO_2 effluxes neglecting advective transport of CO_2 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 CO_2 fluxes based on single sampling [*Davidson and Trumbore*, 1995; *Hirsch et al.*, 2002] or continuous monitoring of CO_2 profiles [*Baldocchi et al.*, 2006; *Pumpanen et al.*, 2008; *Tang et al.*, 2003]. 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] Here we analyze several episodes of subterranean CO_2 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] 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 depth with a petrocalcic horizon and fractured rocks. More detailed site information is given by *Serrano-Ortiz et al.* [2009].

[7] Throughout the dry season of 2009 (9 June–9 September) two sensors (GMP-343, Vaisala, Inc., Finland) that measure CO_2 molar fraction (χ_c), 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 χ_c (GMP-343) and T and relative humidity (HMP45, CSI). The CO_2 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 CO_2 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] Over the dry period, soil and borehole χ_c were inversely correlated. While the soil χ_c fell from its maximum near

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1500 ppm to about half (Figure 1a), the borehole χ_c doubled from *ca.* 8000 ppm 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 χ_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 χ_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 χ_c is delayed by two hours, and the cave χ_c lags the soil by 53.5 hours.

[9] 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 μmol m^{-2} s^{-1} (Figure 1d). After the event, the borehole χ_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 χ_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 χ_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 μmol m^{-2} s^{-1} during the ventilated period. At night, CO_2 emissions were always close to zero (Figure 2d).

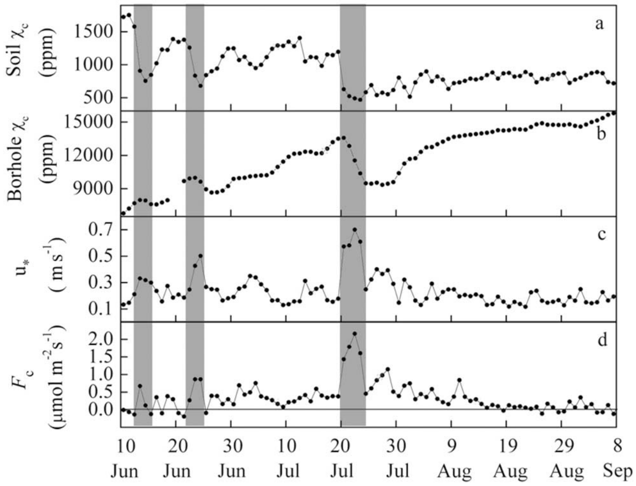

Figure 1. Average daily values of (a) soil CO_2 molar fraction (χ_c) at 25 cm depth and (b) borehole χ_c at 7 m depth, (c) friction velocity (u_*; turbulent velocity scale) and (d) ecosystem CO_2 fluxes (F_C; negative values represent uptake). Shaded columns delimit ventilation events.

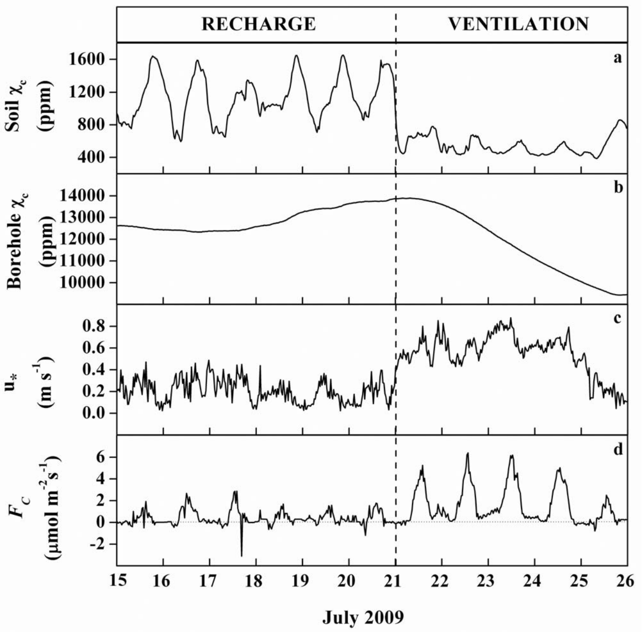

Figure 2. Ventilation event detail, distinguishing between recharge and ventilation. Average half-hour values of (a) soil CO_2 molar fraction (χ_c, 25 cm depth), (b) borehole χ_c (7 m depth), (c) friction velocity (u_*; turbulent velocity scale) and (d) CO_2 fluxes.

4. Discussion

4.1. Evidence of Subterranean Ventilation

[10] This study shows clear empirical evidence of subterranean ventilation and its implications in the NECB. Decreases in soil and borehole χ_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.

[11] In this study subsurface CO_2 followed a daily pattern. In soil 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 χ_c, while borehole χ_c falls many hours later.

4.2. Main Drivers Controlling the Soil CO_2 Ventilation

[12] Studies focused on soil CO_2 profiles have reported correlations between soil χ_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 χ_c 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

[13] 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 [*Cuezva 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

[14] This study emphasizes the role of dry-season, subterranean ventilation 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 concentration differences. 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.

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References

Baldocchi, D., J. Tang, and L. Xu (2006), How switches and lags in biophysical regulators affect spatial-temporal variation of soil respiration in an oak-grass savanna, *J. Geophys. Res.*, *111*, G02008, doi:10.1029/2005JG000063.

Benavente, J., I. Vadillo, F. Carrasco, A. Soler, C. Linan, and F. Moral (2010), Air carbon dioxide contents in the vadose zone of a Mediterranean karst, *Vadose Zone J.*, *9*(1), 126–136, doi:10.2136/vzj2009.0027.

Chapin, F. S., et al. (2006), Reconciling carbon-cycle concepts, terminology, and methods, *Ecosystems*, *9*(7), 1041–1050, doi:10.1007/s10021-005-0105-7.

Cuezva, S., A. Fernandez-Cortes, D. Benavente, P. Serrano-Ortiz, A. S. Kowalski, and S. Sanchez-Moral (2011), Short-term CO_2(g) exchange between a shallow karstic cavity and the external atmosphere during summer: Role of the surface soil layer, *Atmos. Environ.*, *45*(7), 1418–1427, doi:10.1016/j.atmosenv.2010.12.023.

Davidson, E. A., and S. E. Trumbore (1995), Gas diffusivity and production of CO_2 in deep soils of the eastern Amazon, *Tellus, Ser. B*, *47*(5), 550–565, doi:10.1034/j.1600-0889.47.issue5.3.x.

Drewitt, G. B., T. A. Black, Z. Nesic, E. R. Humphreys, E. M. Jork, R. Swanson, G. J. Ethier, T. Griffis, and K. Morgenstern (2002), Measuring forest floor CO_2 fluxes in a Douglas-fir forest, *Agric. For. Meteorol.*, *110*(4), 299–317, doi:10.1016/S0168-1923(01)00294-5.

Ek, C., and M. Gewelt (1985), Carbon dioxide in cave atmospheres. New results in Belgium and comparison with some other countries, *Earth Surf. Processes Landforms*, *10*(2), 173–187, doi:10.1002/esp.3290100209.

Falge, E., et al. (2002), Seasonality of ecosystem respiration and gross primary production as derived from FLUXNET measurements, *Agric. For. Meteorol.*, *113*(1–4), 53–74, doi:10.1016/S0168-1923(02)00102-8.

Ford, D. C., and P. W. Williams (1989), *Karst Geomorphology and Hydrology*, 601 pp., Unwin Hyman, London.

Hirsch, A. I., S. E. Trumbore, and M. L. Goulden (2002), Direct measurement of the deep soil respiration accompanying seasonal thawing of a boreal forest soil, *J. Geophys. Res.*, *107*(D23), 8221, doi:10.1029/2001JD000921.

Janssens, I. A., A. S. Kowalski, and R. Ceulemans (2001), Forest floor CO_2 fluxes estimated by eddy covariance and chamber-based model, *Agric. For. Meteorol.*, *106*(1), 61–69, doi:10.1016/S0168-1923(00)00177-5.

Jassal, R., A. Black, M. Novak, K. Morgenstern, Z. Nesic, and D. Gaumont-Guay (2005), Relationship between soil CO_2 concentrations and forest-floor CO_2 effluxes, *Agric. For. Meteorol.*, *130*(3–4), 176–192, doi:10.1016/j.agrformet.2005.03.005.

Kosmas, C., M. Marathianou, S. Gerontidis, V. Detsis, M. Tsara, and J. Poesen (2001), Parameters affecting water vapor adsorption by the soil under semi-arid climatic conditions, *Agric. Water Manage.*, *48*(1), 61–78, doi:10.1016/S0378-3774(00)00113-X.

Kowalczk, A. J., and P. N. Froelich (2010), Cave air ventilation and CO_2 outgassing by Rn^{222} modeling: How fast do caves breathe?, *Earth Planet. Sci. Lett.*, *289*(1–2), 209–219, doi:10.1016/j.epsl.2009.11.010.

Kowalski, A. S., P. Serrano-Ortiz, I. A. Janssens, S. Sanchez-Moraic, S. Cuezva, F. Domingo, A. Were, and L. Alados-Arboledas (2008), Can flux tower research neglect geochemical CO_2 exchange?, *Agric. For. Meteorol.*, *148*(6–7), 1045–1054, doi:10.1016/j.agrformet.2008.02.004.

Lewicki, J. L., G. E. Hilley, L. Dobeck, and L. Spangler (2010), Dynamics of CO_2 fluxes and concentrations during a shallow subsurface CO_2 release, *Environ. Earth Sci.*, *60*(2), 285–297, doi:10.1007/s12665-009-0396-7.

Pumpanen, J., H. Ilvesniemi, L. Kulmala, E. Siivola, H. Laakso, P. Kolari, C. Helenelund, M. Laakso, M. Uusimaa, and P. Hari (2008), Respiration in boreal forest soil as determined from carbon dioxide concentration profile, *Soil Sci. Soc. Am. J.*, *72*(5), 1187–1196, doi:10.2136/sssaj2007.0199.

Reichstein, M., et al. (2005), On the separation of net ecosystem exchange into assimilation and ecosystem respiration: Review and improved algorithm, *Global Change Biol.*, *11*(9), 1424–1439, doi:10.1111/j.1365-2486.2005.001002.x.

Serrano-Ortiz, P., F. Domingo, A. Cazorla, A. Were, S. Cuezva, L. Villagarcía, L. Alados-Arboledas, and A. S. Kowalski (2009), Interannual CO_2 exchange of a sparse Mediterranean shrubland on a carbonaceous substrate, *J. Geophys. Res.*, *114*, G04015, doi:10.1029/2009JG000983.

Serrano-Ortiz, P., M. Roland, S. Sanchez-Moral, I. A. Janssens, F. Domingo, Y. Godderis, and A. S. Kowalski (2010), Hidden, abiotic CO_2 flows and gaseous reservoirs in the terrestrial carbon cycle: Review and perspectives, *Agric. For. Meteorol.*, *150*(3), 321–329, doi:10.1016/j.agrformet.2010.01.002.

Stull, R. B. (1988), *An Introduction to Boundary Layer Meteorology*, 667 pp., Kluwer Acad., Dordrecht, Netherlands.

Subke, J. A., M. Reichstein, and J. D. Tenhunen (2003), Explaining temporal variation in soil CO_2 efflux in a mature spruce forest in southern Germany, *Soil Biol. Biochem.*, *35*(11), 1467–1483, doi:10.1016/S0038-0717(03)00241-4.

Takle, E. S., W. J. Massman, J. R. Brandle, R. A. Schmidt, X. H. Zhou, I. V. Litvina, R. Garcia, G. Doyle, and C. W. Rice (2004), Influence of high-frequency ambient pressure pumping on carbon dioxide efflux from soil, *Agric. For. Meteorol.*, *124*(3–4), 193–206, doi:10.1016/j.agrformet.2004.01.014.

Tang, J. W., D. D. Baldocchi, Y. Qi, and L. K. Xu (2003), Assessing soil CO_2 efflux using continuous measurements of CO_2 profiles in soils with small solid-state sensors, *Agric. For. Meteorol.*, *118*(3–4), 207–220, doi:10.1016/S0168-1923(03)00112-6.

Weisbrod, N., M. I. Dragila, U. Nachshon, and M. Pillersdorf (2009), Falling through the cracks: The role of fractures in Earth-atmosphere gas exchange, *Geophys. Res. Lett.*, *36*, L02401, doi:10.1029/2008GL036096.

Were, A., P. Serrano-Ortiz, C. M. de Jong, L. Villagarcia, F. Domingo, and A. S. Kowalski (2010), Ventilation of subterranean CO_2 and eddy covariance incongruities over carbonate ecosystems, *Biogeosciences*, *7*(3), 859–867, doi:10.5194/bg-7-859-2010.

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