Geologic carbon sources may confound ecosystem carbon balance estimates: Evidence from a semiarid steppe in the southeast of Spain

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[1] At a semiarid steppe site located in the SE of Spain, relatively large CO2 emissions were measured that could not be attributed to the ecosystem activity alone. Since the study site was located in a tectonically active area, it was hypothesized that a part of the measured CO2 was of geologic origin. This investigation included a survey of soil CO2 efflux, together with carbon isotope analyses of the CO2 in the soil atmosphere, soil CO2 efflux (i.e., Keeling plots), groundwater and local thermal springs. These measurements confirmed the hypothesis of degassing from geologic sources. In areas with local faults and ancient volcanic structures, soil CO2 efflux rates were significantly higher (i.e., up to 6.3 and 1.4 μmol CO2 m⁻² s⁻¹) than measurements in a comparable site that was some distance from fault sites (means of 1.0 and 0.43 μmol CO2 m⁻² s⁻¹ in March and June, respectively). The CO2 concentration in the soil atmosphere at the eddy covariance site reached 0.14% v/v at 0.70 m soil depth with a 13C-enriched isotopic composition (δ13C from −10.2‰ to −16.6‰), consistent with the isotopic composition of the soil CO2 efflux estimated by Keeling plots (i.e., −16.6‰). 13C-enriched CO2 also occurred in local aquifers, and there was evidence of degassing from deep crust and mantle at regional scale by the helium isotopic ratio in spring waters located about 30 km (R/Ra: 0.12) and 200 km (R/Ra: 0.95) NW of the eddy covariance site. This study highlights the importance of considering CO2 sources of geologic origin when assessing the net ecosystem carbon balance of sites that may possibly be affected by circulation of such CO2-rich fluids.


1. Introduction

[2] As a consequence of increasing concern about the impact of climate change on functioning of ecosystems, there has recently been considerable interest in understanding the variables that control carbon cycling, particularly in terrestrial ecosystems [Le Quéré et al., 2009]. As a result, substantial methodological advances have been made, increasing confidence in our estimates of the contributions of terrestrial ecosystems to the global carbon balance [Ciais et al., 2008; Le Quéré et al., 2009; Beer et al., 2010]. As a result, extensive data sets of fluxes of carbon dioxide (CO2) and methane (CH4) from a range of ecosystems are now available [e.g., Batjes and Bridges, 1994; Bonan, 1995; Law et al., 2002; U.S. Environmental Protection Agency (EPA), 2010, 2012].

[3] However, the majority of studies presuppose that virtually all the exchanges of CO2 and CH4 between terrestrial ecosystems and the atmosphere are the consequences of biologic processes resulting from photosynthesis, plant respiration, microbial activity and animal respiration. This approach may be inappropriate in situations where ecosystems may release gases of geologic origin, i.e., gases that have originated in the subsoil rocks and subterranean structures, ranging from the lithosphere to the Earth’s mantle [see review by Kerrick, 2001].

[4] It is well known that CO2 of geologic origin is released to the atmosphere not only by volcanoes, but also diffusely from the soil in geothermal areas or over tectonic faults, independently of the surface ecosystem. Geologic faults generally act as pathways for migration to the Earth’s surface of gas originating by deep (typically >1 km) thermo-metamorphism of carbonate rocks or mantle degassing
Table 1. Main Characteristics of the Balsablanca Eddy Covariance Site [After Rey et al., 2011]

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Longitude</td>
<td>2°15′58″W</td>
</tr>
<tr>
<td>Latitude</td>
<td>36°56′30″N</td>
</tr>
<tr>
<td>Altitude (m)</td>
<td>208</td>
</tr>
<tr>
<td>Orientation</td>
<td>NW</td>
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<tr>
<td>Slope (%)</td>
<td>2–6</td>
</tr>
<tr>
<td>Average annual temperature (°C)</td>
<td>18</td>
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<tr>
<td>Maximum summer temperature (°C)</td>
<td>34</td>
</tr>
<tr>
<td>Average annual rainfall (mm)</td>
<td>200</td>
</tr>
<tr>
<td>Mean annual atmospheric pressure (kPa)</td>
<td>99</td>
</tr>
<tr>
<td>Mean annual relative humidity (%)</td>
<td>69.3</td>
</tr>
<tr>
<td>Vegetation</td>
<td>Steppe alpha grass</td>
</tr>
<tr>
<td>Soil type*</td>
<td>Molllic Lithic Leptosol (Calcric)</td>
</tr>
<tr>
<td>Soil texture class</td>
<td>Sandy loam</td>
</tr>
<tr>
<td>Soil depth (cm)</td>
<td>0–30</td>
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<tr>
<td>Clay (%)</td>
<td>16.1</td>
</tr>
<tr>
<td>Silt (%)</td>
<td>22.8</td>
</tr>
<tr>
<td>Sand (%)</td>
<td>61.1</td>
</tr>
<tr>
<td>Bulk density (g cm⁻³)</td>
<td>1.25</td>
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<tr>
<td>Mean annual soil temperature (°C)</td>
<td>21.9</td>
</tr>
<tr>
<td>Mean annual soil water content (%)</td>
<td>13.8</td>
</tr>
</tbody>
</table>

*IUSS Working Group WRB [2006].

[e.g., Barnes et al., 1978; Grace and van Gardingen, 1997; Chiodini et al., 1999; Etope, 1999; Kerrick, 2001; Mörner and Etope, 2002]. This deep and widespread geologic CO₂ should not be confused with that produced locally by weathering (dissolution) of shallow calcareous rocks, which may be involved in the carbon balance of ecosystems located on karstic environments [e.g., Kowalski et al., 2008; Serrano-Ortiz et al., 2009]. Geologic CO₂ has been found to occur extensively in soils throughout wide areas characterized by grassland or woodland ecosystems in Europe and USA, even without evidence at the Earth surface of geothermal manifestations and far from volcanic systems [e.g., Gregory and Durrance, 1985; Hinkle, 1990; Chiodini et al., 1999; Etope, 1999; Klusman et al., 2000; Lewicki and Brantley, 2000; Klusman, 2005]. These “hidden” geologic sources may release several types of endogenous gases (e.g., CO₂, CH₄, N₂, He) to the atmosphere, some of which can contribute to the net ecosystem carbon exchange of terrestrial ecosystems.

While CO₂ is the most important carbon-bearing gas in geothermal-volcanic areas, geologic CH₄ emissions may be relevant in sedimentary basins with petroleum production [Etope and Klusman, 2010]. Indeed, geo-CH₄ sources are extremely important at global scale, representing the second largest natural CH₄ source (at least 60 Tg y⁻¹) [Etope, 2012] after wetlands, and about 10% of the total CH₄ emissions [Etope et al., 2008; EPA, 2010]. Earth’s degassing is considered to be a relatively minor CO₂ source globally (probably in the order of 600–1000 Tg CO₂ y⁻¹ i.e., ~2%–3% of the anthropogenic sources and 10% of the carbon source resulting from deforestation and land-use change, and about 18% of the current terrestrial sink [Mörner and Etope, 2002; Pan et al., 2011]). Both geo-CH₄ and geo-CO₂ may, however, affect surface ecosystem fluxes on wide areas and confound local scale carbon budgets attributed to biologic activity leading to inaccurate estimates. An example of such a phenomenon involving CH₄ may be represented by emission of geologic gas in agricultural rice paddies in Japan which can be confused with biologic gas emissions [Etope et al., 2011]. An example involving geo-CO₂ is presented in this paper.

A recent study carried out with the aim of quantifying the carbon, water and energy ecosystem fluxes using the eddy covariance technique in a natural grassland ecosystem in southeastern Spain reported relatively large CO₂ emissions over the dry period that could not be attributed to the vegetation activity alone [Rey et al., 2012]. Anomalous ecosystem CO₂ emissions and interannual patterns were observed at the Balsablanca eddy covariance site that suggested the presence of other nonbiologic carbon sources. As a consequence, we could not apply standard partitioning techniques to derive photosynthesis and respiration [Reichstein et al., 2005; Lasslop et al., 2010]. After examination of the study area, we concluded that the site of Balsablanca is located in a geothermal basin very close to a tectonic fault system of regional importance (the Carboneras Fault). This then led to the hypothesis of a geologic contribution to the CO₂ efflux from the soil [Rey et al., 2012].

Here, we verify this hypothesis through an investigation that includes a soil CO₂ efflux survey, carbon isotopic analyses of CO₂ in the soil atmosphere (at the eddy covariance site), aquifers and natural water springs located approximately 30 km southwest of Balsablanca (part of the same geologic system). Isotopic composition of helium (³He/⁴He), a tracer of deep-origin gas, was analyzed in a natural water spring and compared with literature data of other springs in the same geologic region (onshore Alboran Basin). In addition, Keeling plots, a widely used method to determine the carbon isotope composition of ecosystem respiration [Pataki et al., 2003], were used to assess the stable carbon isotopic ratio of soil CO₂ efflux. All data confirm the presence in the soil of CO₂ of geologic origin, which may confound assessments of the local ecosystem carbon balance that can be attributed to ecosystem activity.

2. Material and Methods

2.1. Site Description

The study site of Balsablanca is located in the Cabo de Gata Natural Park, in the province of Almería (Andalusia), in southeastern Spain (36°56′26.0″N, 2°01′58.8″W). The climate in this area is subtropical, dry, and semiarid with a mean annual precipitation of 250 mm and a mean annual temperature of approximately 18°C (Table 1). It is characterized by prolonged summer droughts (from May to September), and infrequent and random rainfall events when the vegetation is mostly inactive [Rey et al., 2011]. Annual potential evapotranspiration is approximately 1390 mm (nearby meteorological station of Nijar). Precipitation mostly occurs in spring and autumn with strong interannual variation and random events.

The site is equipped with meteorological and eddy covariance towers designed to measure the exchange of carbon, water, and energy between the ecosystem and the atmosphere (part of the CARBOEUROPE and FLUXNET networks of flux sites since May 2006). The ecosystem is a natural grassland characterized by open vegetation-free areas (65% ground coverage), dominated by Stipa tenacissima. The dominant soils are classified as Lithic leptosols (calcric) [IUSS Working Group WRB, 2006], and are thin, of variable depth (on average 10 cm), alkaline (pH > 8), saturated...
in carbonates with a moderate stone content and with frequent rock outcrops (additional details of the site are given by Rey et al. 2011, 2012).

[10] Geologically, the site of Balsablanca is in the Betic Cordilleras, at the western margin of the Cabo de Gata volcanic complex of Miocene age (last volcanic episode is about 7.5 Ma old), formed as a consequence of extensional processes related to the development of the Alboran Basin after the Alpine collision between the African and Eurasian plates [Sanz de Galdeano, 1990; Martín et al., 2009]. The Balsablanca site is located exactly over the Carboneras Fault System (CFS; Figure 1), one of the three main regional tectonic faults of southeast Spain (the other two are the Palomares, and Guadalentín sinistral strike-slip faults) producing a shear zone with crustal thinning ("rifting") and regional seismicity [Sanz de Galdeano et al., 1995]. The area represents a rift basin related to the formation of other European similar rifts, like the Rhine basin in Germany and the Rhone and Algero-Provençal basins in France [Sanz de Galdeano, 1990]. The CFS produced a large-scale deformation zone with relevant fracturation of the Miocene sedimentary and volcanic rocks. The adjacent ancient volcano hosted hydrothermal systems with several fluid emission points, including fumaroles (Cinto, Los Tolles), today extinct, located at about 13 km southwest of Balsablanca. The contemporary geothermal condition of the Cabo de Gata area is evidenced by the relatively high heat flow, 84 mW m^{-2} (against an average of 65 mW m^{-2} for the Iberian mainland) measured in a well about 20 km southwest of Balsablanca [Fernández et al., 1998].

[11] The stratigraphic rock sequence in the Balsablanca area is formed by outcrops of old Quaternary alluvial fans, calcareous conglomerates and sands (Pliocene), marine carbonates (Messinian and Tortonian) and volcanic rocks (Tortonian) at about 80–100 m below the ground, overlying the Betic carbonatic Mesozoic basement [Martín et al., 2009].

2.2. Soil CO2 Efflux Survey

[12] We postulated that soil CO2 efflux rates were likely to be higher or anomalous in areas associated with geologic gas exhalation. We therefore tested whether we could detect higher soil CO2 efflux rates associated with proximity to the fault and an ancient volcano area and compared those rates with rates measured in a reference "background" location far from the volcano fault system, but with similar vegetation (alpha grass) and soil substrate (calcaric Lithic leptosol), as shown in Figure 1.

[13] Because soil chamber methods provide a flux measurement at small spatial scale, numerous measurements were made to characterize both spatial trends and variability of fluxes at both sites. The so-called reference background site, is an area supposedly not affected by any geothermal activity in the ground, where we would expect the measured soil CO2 efflux rates to be solely the result of biologic activity or soil respiration. A total of 200 soil CO2 efflux measurements were made by static closed-chamber methods on two occasions: in March (when the vegetation is still active) and in June 2011 (the vegetation is mostly dormant and soil respiration is strongly limited by water shortage [Rey et al., 2011]). The measurements were made in five
different locations along the Carboneras fault, at the top of an ancient volcano (the Majada Redonda volcanic caldera), at the eddy covariance tower site of Balsablanca, and at the reference background site. Four sites along the Carboneras fault (Faults 1–4) refer to alpha grass ecosystems located exactly in correspondence with the main Carboneras fault line, based on published geologic maps, satellite images and field recognition of morphological tectonic scarps and outcrops. The “Near Fault” site (close to Fernán Pérez village) is along a minor morphological scarp of probable tectonic origin, 500 m south of the main fault line (in correspondence with Fault 2 site).

[14] All measurements were done on similar alpha grass ecosystems but on bare soil patches between plants (at least 50 cm from a plant), and on the same vegetation type as at the Balsablanca site (*Stipa tenacissima*). In March, a 10 dm³ closed chamber was connected to West Systems flux meter with Licor CO₂ analyzer (West Systems, Pontedera, Italy) [*Etiöpe et al., 2011*] and in June a 3.5 dm³ closed chamber connected to a soil respiration system EGM-4 (PP Systems, Hitchin, UK) was used. We intended to use the same instrument in both occasions but it was not possible because of a malfunction problem with the EGM-4 instrument at the first sampling period. However, both sets of equipment were calibrated against each other for consistency and soil CO₂ efflux rates corrected accordingly using a regression between both estimates (*n* = 10, *R²* = 0.90). All measurements were made between 10.00 h and 14.00 h during several days to avoid diurnal fluctuations and to obtain a range of environmental conditions: growing season in March soon after a rainy period (soil volumetric water content above 5% and air temperature below 20°C) and thus with the vegetation still active) and a dry period in June (soil volumetric water content below 5% and air temperature above 20°C, with the vegetation mostly dormant, as shown by Rey et al. [2011]). The exact location of each measurement point was recorded with a GPS. Soil temperature at 3.5 cm depth was measured with a digital thermometer and soil volumetric water content with a portable theta probe (ML2x, Devices Ltd., Cambridge, UK) at the time of each soil CO₂ efflux measurement. To test whether soil CO₂ efflux rates measured in both periods differed between sites, a single analysis of variance at a probability of 5% was done (PROC ANOVA) using SAS statistical software 9.2. (SAS Software, SAS Institute, Cary, N.C., USA).

### 2.3. Keeling Plots

[15] In order to determine the carbon isotopic composition of soil CO₂ efflux we used the Keeling plot approach as described by *Pataki et al., 2003*. This approach uses a two-component mixing model that consists of the carbon isotope ratio of CO₂ (*δ¹³C*) released and that in the background atmosphere. The intercept of a linear regression of *δ¹³C* of atmospheric CO₂ versus 1/[CO₂] (where [CO₂] is the mole fraction of CO₂) provides an estimate of the *δ¹³C* of the soil CO₂ efflux (CR).

[16] For this purpose, we designed 15 clear opaque chambers with soil collars made of PVC (20 cm in diameter and 10 cm high). The soil collars were inserted 3 cm into the ground one day before each measurement campaign. The chambers were designed with a sealed T-connector at the top to allow air sampling during each measurement campaign.

The lids were placed at time 0 and a first sample of air from a chamber was taken with a 50 cm³ Luer LOK syringe with an insulin needle; the sample was injected under slight pressure into a 20 cm³ vial previously left under vacuum. Five samples from each chamber were taken every 15 min, so that all five samples per chamber were taken in 75 min. Chamber dimensions and measuring time interval were estimated based on previous soil CO₂ efflux rates at the site to ensure a large enough CO₂ gradient (75 ppmv, as advised by *Pataki et al., 2003*) and linearity between [CO₂] and *δ¹³C* [*Takahashi and Liang, 2007*]. The glass vials were sealed with rubber stop-corks and a hot glue gun until analyses. Septum-capped vials have been tested and proven to be suitable for air transport [*Glatzel and Well, 2008*]. The vials, including vials with standards, were taken to the laboratory in the Centro Nazionale delle Ricerche at Porano (Italy) and analyzed for CO₂ concentration and *δ¹³C* with a Gas Chromatography-Isotopic Ratio Mass Spectrometry (ISOPRIME mod. JB287, GV Instruments, Manchester, UK) connected to a multifold Gissson 222XL auto-sampler. We determined the evolution rate and isotopic composition ([*δ¹³C*‰]: *δ¹³C* = 1,000 [([Rsample — Rstandard]/Rstandard)] ‰, where: *R* = *¹³C/¹²C*) of the CO₂ from the soil sample. The CO₂ evolution rate and *δ¹³C* of the evolved CO₂ were calculated from the change over time in CO₂ concentration and *δ¹³C* of the CO₂ in the sampled vials.

[17] Samples were taken on the 3–4 June 2011. We placed the soil chambers in the most representative soil covers at the site [*Rey et al., 2011*] laid out in five plots each one with three soil cover types: under plant, biologic soil crust and bare soil. Soil temperature and soil volumetric water content measured at 3.5 cm was recorded at the time of each measurement adjacent to each chamber as described above. To ensure further that vial usage, overpressurization and storage did not influence the results; we carefully evaluated each step (including transport from the site in Spain to the lab in Italy) by comparing all measurements with a standard of known concentration and carbon isotopic composition in the mass spectrometer (standard deviation less than 0.02‰), since there were no statistically significant differences between the regression lines of individual replicates (*P* < 0.05). By fitting all measured points for each soil cover type to a single regression line in order to calculate the intercept for each soil cover—i.e., the *¹³C* of the CO₂ released under each soil cover type—and compared the regression lines for any significant differences among the slopes and intercepts (general linear models (GLM) in SAS statistical software).

### 2.4. Sampling and Analyses of Soil-Air and Gas Dissolved in Aquifers and Springs

[18] Seven soil-gas samples (0.70 m deep) were collected at two points (P1 and P2) at the Balsablanca site by inserting into the soil a metallic probe (3 cm in diameter and 100 cm long), that was sealed at the top and left to equilibrate with the soil atmosphere for a day. A syringe and silicon tube equipped with a T-valve, were used to reduce atmospheric air contamination during sampling. The first sample at P1 was stored in a 150 cm³ glass tube equipped with two stop-cocks, for molecular compositional analyses. The other six samples (three in P1 and three in P2) were stored in 12 cm³ evacuated vials for CO₂ and *δ¹³C* analyses.
The samples were then purified following standard procedures [see Sano and Wakita, 1988]. The isotopic analyses of the purified helium fraction were performed by a static vacuum mass spectrometer (GVI5400TFT) that allows for simultaneous detection of $^3$He and $^4$He-ion beams, thereby keeping the $^3$He/$^4$He error of measurement to very low values. Typical uncertainties in the range of low-$^3$He samples are within 5%. Helium isotopic ratio is expressed in the R/Ra notation, which is the $^3$He/$^4$He ratio between sample and atmospheric air (=1.4 $10^{-6}$); the ratio has been corrected for atmospheric contamination (based on the $^3$He/$^4$He ratio) [Hilton, 1996].

3. Results and Discussion

3.1. Soil CO$_2$ Efflux

[22] Environmental conditions differed between the two periods, with optimal conditions for plant and soil activity in March, whereas conditions were most likely minimal during the dry period in June [Rey et al., 2011]. Soil CO$_2$ efflux rates were always higher in March than in June, including measurements on bare soil (where biologic activity is minimal compared to the autotrophic and autotrophic respiration in patches beneath plants with high fine root density and soil organic matter content). However, the tendency for higher soil CO$_2$ efflux rates on sites associated with proximity to the fault and ancient volcano was found in both measurement periods. Rates of soil CO$_2$ efflux measured at all the fault sites and at the volcanic caldera were systematically higher than the rates measured at the reference site, with rates ranging from 6.3 to 2.2 $\mu$mol CO$_2$ m$^{-2}$ s$^{-1}$ and from 1.4 to 0.77 $\mu$mol CO$_2$ m$^{-2}$ s$^{-1}$ in March (when fault sites were significantly different from the reference site, $P < 0.05$) and June (when fault sites were significantly different from the reference site, $P < 0.001$), respectively (Figure 2). In June, the highest mean soil CO$_2$ efflux was recorded at the ancient caldera. At the reference site, soil CO$_2$ efflux rates ranged from 1.0 to 0.4 $\mu$mol CO$_2$ m$^{-2}$ s$^{-1}$ in March and June, respectively. At the Balsablanca site, soil CO$_2$ efflux rates were intermediate with an average value of 3.0 and 0.9 $\mu$mol CO$_2$ m$^{-2}$ s$^{-1}$ in March and June, respectively. The measured soil CO$_2$ efflux rates at Balsablanca are consistent with those measured previously on bare soil at the site [Rey et al., 2011] but higher than expected based on rates typically occurring on bare soils under similar environmental conditions in semiarid grasslands [e.g., Conant et al., 2000; Maestre and Cortina, 2006; Carbone et al., 2008]. In particular, soil CO$_2$ efflux rates measured along the fault are higher than soil respiration rates reported in semiarid grasslands, although still low compared to the mean biologic CO$_2$ efflux from soils, which ranges from 0.2 to 21 g C m$^{-2}$ d$^{-1}$ [e.g., Raich and Tufekcioglu, 2000; Bond-Lamberty and Thomson, 2010]. Since wind is the main driver of the short-term net ecosystem carbon balance (NECB) at the eddy covariance site of Balsablanca where CO$_2$ effluxes of up to 15 $\mu$mol CO$_2$ m$^{-2}$ s$^{-1}$ were measured over the dry period in concurrence with strong winds [Rey et al., 2012], it is likely that closed static chambers may preclude some of the CO$_2$ from deep origins to be released, so that soil CO$_2$ efflux rates were underestimated. However, we were primarily concerned with the relative comparison between sites and would, therefore, still expect the observed differences.
The geologic CO₂ component coming from deeper layers would be the most underestimated component when using closed chamber methods. Since all measurements were made on bare soil far from any plant and under very dry conditions, particularly over the dry season, we would expect minimal biologic contribution to the measured soil CO₂ effluxes. Indeed, we observed relatively low rates at the reference steppe site compared to other ecosystems [Bond-Lamberty and Thomson, 2010]. Instead, soil CO₂ efflux measured within fault areas were larger than expected based on previous long-term soil CO₂ efflux records measured under similar environmental conditions at the Balsablanca site [Rey et al., 2011] and those measured in other ecosystems in the area located far from the fault and ancient volcanic caldera [Oyonarte et al., 2012]. Although the absolute values may be low compared to other ecosystems, and even more compared to other active geothermal areas where large soil CO₂ emissions have been reported [e.g., Werner and Brantley, 2003; Chiodini et al., 2008], the relative contribution to carbon emissions in this ecosystem may be considerable as indicated by the relatively large CO₂ emissions measured during dry periods by eddy covariance at the Balsablanca site [Rey et al., 2012]. Indeed, in a follow-up study in which we have partitioned net ecosystem carbon balance into biologic and geologic components, it has been estimated that approximately half of the CO₂ emitted comes from geologic sources (A. Rey et al., Partitioning estimates of net ecosystem carbon balance into biologic and geological sources in a semiarid steppe ecosystem in the southeast of Spain, manuscript in preparation, 2012).

### 3.2. δ¹³C of Soil CO₂ Efflux

Based on the mixing model approach described in the Material and Methods section [Pataki et al., 2003], we calculated an averaged δ¹³CR (of the three soil covers at the eddy covariance site) to be −18.3‰ (±0.51). Within each soil type, variability was low and replicated measurements of δ¹³CR-soil were statistically indistinguishable so all replicates were used to fit a single regression line for each soil cover (Figure 3). In contrast, the δ¹³CR-soil of CO₂ efflux from soils differed among soil cover types as expected (P < 0.001). In June 2011, the δ¹³CR-soil was −19.4 (±0.39), −18.9 (±0.76) and −16.6 (±0.40)% for soil CO₂ efflux measured under plant, biologic soil crust and bare soil, respectively (Figure 3). The intercept was significantly different among soil covers (P < 0.001). This pattern of δ¹³CR-soil increasing with plant proximity is reasonable given that the contribution of depleted carbon from organic sources is expected to increase with proximity to plants (most roots and soil organic matter are found below plants) [see Rey et al., 2011]. However, all values confirmed the presence of a nonbiologic component of CO₂ in the respired CO₂. The δ¹³C value of present atmospheric CO₂ is close to −8‰ [Bowling et al., 2008]. The δ¹³C composition of CO₂ respired from plant roots is isotopically depleted relative to the atmosphere as a result of isotopic fractionation during photosynthesis and will have an isotopic composition between −24 to −38‰ in C₃ plants [Pataki et al., 2003]. When most of the CO₂ released comes from biologic sources, one would expect the carbon isotopic signal of the respired soil CO₂ to be close to that of the plant material [Hungate...
**Table 2.** CO₂ Concentration and δ¹³C Values (CO₂ or TDIC) in Soil-Air (0.7 m Deep) at the Balsablanca Eddy Covariance Tower Site, in the Local Aquifer of Fernán Pérez and in the Closest Thermal Springs (Including a Water Sample With Helium Concentration and Isotopic Ratio)

<table>
<thead>
<tr>
<th>Site</th>
<th>Type</th>
<th>CO₂ (ppmv)</th>
<th>δ¹³C_CCO₂ (‰, VPDB)</th>
<th>δ¹³C_TDIC (‰, VPDB)</th>
<th>TDIC (mM)</th>
<th>He (ppmv)</th>
<th>R/Ra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Balsablanca P1 (n = 1)</td>
<td>Soil-air</td>
<td>1400</td>
<td>–10.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Balsablanca P1 (n = 3)</td>
<td>Soil-air</td>
<td>555–588</td>
<td>–16.6 ± 0.19</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Balsablanca P2 (n = 3)</td>
<td>Soil-air</td>
<td>436–521</td>
<td>–14.5 ± 0.01</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Fernán Pérez (n = 3)</td>
<td>Aquifer</td>
<td></td>
<td>–14.1 ± 0.29°</td>
<td>–6.1 ± 0.3</td>
<td>1.80 ± 0.36</td>
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<td>Alhama de Almeria spring</td>
<td>Spring</td>
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<td>Sierra Alhamilla spring</td>
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<td>19595</td>
<td>–16.4</td>
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<td></td>
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<td></td>
</tr>
</tbody>
</table>

1VPDB: Vienna Pee Dee Belemnite standard.
2Recalculated values based on the procedure by Mook et al. [1974].

*et al., 1997; Werner and Gessler, 2011]. Foliar δ¹³C values of Stipa tenacissima measured in the same area are on average –24‰ [Maestre and Cortina, 2006; Armas et al., 2009]. Instead, when other carbon sources are present, the isotopic signal of the CO₂ released should be ¹³C enriched. Note that as a result of fractionation during diffusion (ca. –4.4‰) [Amundson et al., 1998], the soil respired CO₂ is depleted in ¹³C relative to the soil CO₂ (Table 2). This is not apparent under steady state conditions, in which case soil derived CO₂ becomes enriched by +4.4‰ and the δ¹³C of soil-respired CO₂ approaches that of the source organic material [Dör and Münich, 1987; Cerling et al., 1991].

In most cases, respiration processes predominantly operate in the soil zone. Therefore, the isotopic composition of CO₂ beneath the soil should be less affected by isotopic composition of the soil gases. In particular, numerous studies have reported CO₂ carbon isotopic (i.e., δ¹³C-CO₂) compositions down vertical soil gas profiles, demonstrating that CO₂ undergoes significant isotopic fractionation during its diffusive pathway through the soil atmosphere both in volcanic-hydrothermal degassing areas [Camard et al., 2007], where a deep CO₂ source is present, and in vegetated areas [Amundson et al., 1998; Cerling et al., 1991], where the soil CO₂ flux is the result of biogenic sources alone. The δ¹³C values of this CO₂ will be similar to that of the organic source mass and may not vary significantly from values of the soil-respired CO₂.

### 3.3. CO₂ in Soil-Air at Balsablanca

[26] The concentration of CO₂ detected at a depth of 0.70 m in the soil at Balsablanca ranged from 436 to 1400 ppmv (Table 2). The 1400 ppmv CO₂ sample had 77.8% N₂, 19.1% O₂, 2 ppmv CH₄ and 5 ppmv He. δ¹³C_CCO₂ ranged from –10.2‰ (in the 1400 ppmv sample) to –16.1‰ (555 ppmv), with an average value of –14‰. This is approximately 6‰ lower than atmospheric CO₂ and 10 to 24% higher than typical biologic CO₂ released in soil respiration [Petaki et al., 2003]. The δ¹³C signature of CO₂ derived from geothermal sources (e.g., magmatic or metamorphic sources) typically ranges from –2‰ to –6‰ [Faure, 1986] and will mix with CO₂ derived from C₃ plants. The 1400 ppmv concentration is considerable given that the sample was taken from a depth with no mineral soil [Rey et al., 2011]. This value is, however, rather low for areas with deep CO₂ degassing [e.g., Etope, 1999; Etope et al., 1999; Williams-Jones et al., 2000]. However, taken together with the δ¹³C of soil air, which was similar to that of soil water and the thermal spring nearby, this value further suggests that some CO₂ occurring in the soil is inorganic, derived from deep carbon sources. These may include CO₂ produced by thermo-metamorphism of carbonate rocks and mantle material (typically producing δ¹³C of about 0‰ and –6.5‰ respectively [Sano and Marty, 1995]. Values of δ¹³C similar to those of Balsablanca are known to occur in soils affected by deep-origin CO₂ degassing in several countries, e.g., in central Italy [Klusman et al., 2000]. In particular, values in the range of –17‰ to –5‰ have been considered to represent mixing between biologic CO₂ (<–17‰) and hydrothermal CO₂ (–5‰) [Chiodini et al., 2008]. The measured Balsablanca values of δ¹³C_CCO₂ are in agreement with values that have been derived from Keeling plots, as reported in Section 3.2.

### 3.4. CO₂ Dissolved in Groundwater and Helium at Sierra Alhamilla

[27] The average δ¹³C_TDIC value of three water samples of the local aquifer was –6.1‰. This is similar to the values of between –8.1‰ and –3.8‰, reported for groundwater located in the Guadalentín Fault System (GFS), which is a rift basin similar to the study area, about 35 km north of Balsablanca [Cerón et al., 2000] (Figure 1). It is known that in aquifers affected by even low CO₂ degassing, CO₂ should be dominantly present in the aqueous phase as dissolved inorganic carbon (TDIC, i.e., CO₂(aq), H₂CO₃, HCO₃⁻, and CO₃²⁻). With the increasing degassing of CO₂, DIC also increases.

[28] The values of δ¹³C-CO₂ (–14.1‰) recalculated on the basis of equilibrium constants of the dissolved carbon species (with isotope enrichment factors for the CO₂ gas–HCO₃⁻ and the CO₂ gas–CO₂ aq. systems [Mook et al., 1974]) are similar to those measured in the soil-air at Balsablanca and lie within the range of those measured in the thermal springs. The two thermal springs located about 30 and 40 km west of Balsablanca in fact showed δ¹³C_CCO₂ values of –12.1‰ and –16.4‰, with concentrations of CO₂ in the extracted gas-phase of up to 25000 ppmv. The δ¹³C_CCO₂ values are consistent with those of the soil and the aquifers, and this suggests that mixing between the biologic, meteorologic and geologic carbon pools is a widespread and general process in the area.

[29] The helium isotopic ratio (R/Ra) measured in the gas extracted from the Sierra Alhamilla spring was 0.12. This is associated to a ³He/²⁰Ne ratio of about 8, which is about 28 times higher than the atmospheric ratio, and thus indicates negligible atmospheric contamination.

[30] The R/Ra versus δ¹³C_CCO₂ plot (Figure 4a), traditionally used to estimate crustal versus mantle components of CO₂.
Sano and Marty, 1995], showed that the Sierra Alhamilla spring is close to the mixing line between sedimentary and mantle end-members. The stable carbon isotopic composition of CO₂ exhaled from the soil derived by the Keeling plots is within the range of the values measured in the soil-air. However, all the values are higher than the range expected for biologic soil respiration (BSR). The helium isotopic ratio then suggests a deep gas source, with a dominant crustal component and minor (about 1%) mantle signal (Figure 4b). A similar R/Ra value, 0.1, has been reported for CO₂-rich waters at Lanjarón (Granada), about 100 km southwest of Balsablanca (Figure 1) [Pérez et al., 1996]. Higher values, 0.95, were found at Cofrentes [Pérez et al., 1996], which is 200 km northeast of Balsablanca. This last value suggests that about 10% of helium has a mantle origin. The increase of the mantle signal from south to north, passing through the Balsablanca area, reflects a younger and more active (seismic) tectonic activity toward the northern sector of the southeast Spain rift [Pérez et al., 1996]. It is known, then, that CO₂ degassing may increase or decrease in relation to seismicity [e.g., Bräuer et al., 2003], and consequently the geo-CO₂ component in the Balsablanca soil may change over time, thus reflecting the tectonic activity of CFS.

4. Conclusions and Recommendations for Future Work

[31] The hypothesis proposed initially by Rey et al. [2012], regarding the occurrence of endogenous CO₂ released from beneath the steppe ecosystem under study, is supported here by a combination of soil CO₂ efflux measurements and carbon isotopic analyses of soil air and groundwater.

[32] In correspondence with local faults and ancient volcanic structures, soil CO₂ efflux rates were higher than those measured far from fault sites regardless of the measuring period (Figure 5); the soil CO₂ efflux at the eddy covariance site, accidentally positioned over a large fault system, reached concentrations of 0.14% v/v at 0.70 m depth with a 13C-enriched isotopic composition (δ13C from −10.2‰ to −16.6‰), consistent with the values derived from Keeling plots (i.e., −16.6‰ in bare soil). 13C-enriched carbon also occurred in local aquifers, and signals of degassing from deep crust and even mantle were detected at regional scale by the helium isotopic ratio in thermal spring waters. The geologic origin of CO₂ is probably not related to weathering processes acting on relatively shallow calcareous rocks or subterranean cavity ventilation (as hypothesized by Kowalski et al. [2008] and Serrano-Ortiz et al. [2009] for some karstic areas), but is most likely related to deeper, regional geothermal fluid circulation systems connected to the ancient volcanism of Cabo de Gata. As also suggested by the relatively high geothermal heat flow and the helium isotopic composition in springs, the relevant CO₂ production mechanism may be similar to that of typical geothermal CO₂-degassing areas, widespread on all continents (i.e., thermo-metamorphism of deep carbonate rocks and degassing from the mantle) [e.g., Mörner and Etiope, 2002; Chiodini et al., 2008].

[33] 1) In an earlier study of the steppe ecosystem [Rey et al., 2012], it was estimated that the NECB ranged from

![Figure 4](image-url) **Figure 4.** He isotopic ratio R/Ra versus δ13C CO₂ (A) and versus 4He/20Ne (B). SA: Sierra Alhamilla spring; AA: Alhama de Almería spring; BS: Balsablanca soil. CO₂ isotope zonation modified after Etiope et al. [2011]. AO, aerobic hydrocarbon oxidation; KD, kerogen decarboxylation; AC, alteration of marine carbonates; BSM, biodegradation and secondary methanogenesis; BSR, biologic soil respiration; ASW, air-saturated water. Cofrentes and Lanjarón springs data are from Pérez et al. [1996]. Vertical arrow indicates the δ13C CO₂ value derived by the Keeling plot of Figure 3.

![Figure 5](image-url) **Figure 5.** Schematic model of geo-CO₂/soil-CO₂ mixing in relation to geologic factors of the Cabo de Gata area.
65.7 to 143.6 g C m⁻² y⁻¹, suggesting that the steppe ecosystem could be an appreciably large carbon source to the atmosphere. The present investigation has shown that even in areas where emissions of geologic CO₂ are not immediately evident, the contribution of "hidden" endogenous sources of CO₂ may be of major importance to the ecosystem carbon budget.

[34] 2) Given the low content of soil organic matter and small standing biomass at the site, an initial interpretation was that the ecosystem under study was highly unsustainable. The present investigation has clarified that a significant part of the carbon released did not result from ecosystem activity but was derived from geologic sources.

[35] 3) When ecosystems are on geologically active or geochemical areas, additional sources of carbon do contribute negatively to the net ecosystem carbon balance and must be taken into account when estimating the net ecosystem carbon exchange with the atmosphere.

[36] 4) By not taking into account geologic CO₂ sources, considerable errors in the estimates of the NECB attributed to vegetation activity may result. A further study aimed at separating the geologic from the biologic components of the CO₂ released, has estimated an average contribution of geologic CO₂ to the NECB of 55% (Rey et al., manuscript in preparation, 2012).

[37] 5) At local ecosystem scale, an appropriate initial geologic site inspection is recommended in relation to carbon budget objectives. On national, continental and global scales, carbon emission data sets from geographic areas potentially affected by geologic gas releases should be the object of further examination.

[38] 6) Thus the FLUXNET community should be aware of geologic CO₂ and CH₄ carbon sources when planning field measurements and should take these into account when estimating the net ecosystem carbon balance of vegetation, particularly in tectonically active areas, but more widely when modeling regional, continental and global carbon budgets.

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