Improving the accuracy of the gradient method for determining soil carbon dioxide efflux

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Running title: Accurate long-term F_{soil} based on the GM

Key Points:

- Published diffusion models produced soil efflux underestimations from 55% to 361%
- Determining in situ diffusion estimates using conservative tracer injections did not produce favorable results
- Calibrating a gas transfer model using automated chambers produced accurate long-term soil effluxes

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Abstract

Soil CO_2 efflux (F_{soil}) represents a significant source of ecosystem CO_2 emissions that is rarely quantified with high-temporal resolution data in carbon flux studies. F_{soil} estimates can be obtained by the low-cost gradient method (GM), but the utility of the method is hindered by uncertainties in the application of published models for the diffusion coefficient. Therefore, to address and resolve these uncertainties, we compared F_{soil} measured by two soil CO_2 efflux chambers and F_{soil} estimated by 16 gas transport models using the GM across one year. We used 14 published empirical gas diffusion models and two *in situ* models: 1) a gas transfer model called "Chamber model" obtained using a calibration between the chamber and the gradient method and 2) a diffusion model called "SF_6 model" obtained through an inter-well conservative tracer experiment. Most of the published models using the GM underestimated cumulative annual F_{soil} by 55% to 361%, while the Chamber model closely approximated cumulative F_{soil} (0.6% error). Surprisingly, the SF_6 model combined with the GM underestimated F_{soil} by 32%. Differences between *in situ* models could stem from the Chamber model implicitly accounting for production of soil CO_2, while the conservative tracer model does not. Therefore, we recommend using the GM only after calibration with chamber measurements to generate reliable long-term ecosystem F_{soil} measurements. Accurate estimates of F_{soil} will improve our understanding of soil respiration's contribution to ecosystem fluxes.

1. Introduction

Soil CO_2 efflux (F_{soil}) represents a significant source of terrestrial CO_2 emissions [*Raich and Schlesinger*, 1992], and our ability to accurately represent F_{soil} and soil carbon stocks is key for accurately predicting carbon–climate feedbacks [*Todd-Brown et al.*, 2012]. Because of their large global magnitude, even small changes in soil CO_2 effluxes (F_{soil}) directly affect the atmospheric CO_2 content [*Raich and Schlesinger*, 1992], leaving F_{soil} as one of the most poorly constrained component of the terrestrial carbon cycle [*Bond-Lamberty and Thomson*, 2010]. Much of this uncertainty in this dominant flux stems from the fact that models of F_{soil} are not well estimated, as both positive and negative feedbacks between belowground carbon pools and effluxes, and temperature sensitivity in future climate scenarios largely ignored [*Davidson and Janssens*, 2006]. Most often, F_{soil} is measured using manual or automated soil chambers [*Pumpanen et al.*, 2004]. Manual chamber measurements have been frequently used due to their ease in deployment, but the sampling frequency is often low, normally weekly, monthly or seasonally and often only during the daytime in fair weather conditions [*Janssens et al.*, 2001a]. Automated chamber systems are more desirable as they allow for near-continuous (every 30 min or hourly) measurements of F_{soil} over longer periods of time [*Drewitt et al.*, 2002; *Hamerlynck et al.*, 2013; *Oishi et al.*, 2013], but deployment of these systems are limited due to their higher costs. Continuous estimation of F_{soil} can also be obtained by application of the gradient method (GM), where the soil CO_2 molar fraction is measured at different depths [*Tang et al.*, 2003; *Maier and Schack-Kirchner*, 2014; *Sanchez-Canete and Kowalski*, 2014]. This technique has been readily adopted due to the development of new low-cost and low-power CO_2 sensors. However, despite their widespread use, the utility of the GM is hindered by uncertainties associated with the application of *ex situ* published models of the soil diffusion coefficient (D_s, [*Werner et al.*, 2004; *Allaire et al.*, 2008]).

D_s is the only modeled parameter in the gradient method, yet its estimation is highly uncertain. Most researchers have applied a D_s model from the literature to estimate the F_{soil} [*Pumpanen et al.*, 2003; *Tang et al.*, 2003; *Davidson et al.*, 2006; *Rains et al.*, 2016], but a few have determined D_s for their soils of interest, either in the laboratory using field samples [*Jassal et al.*, 2005; *Maier et al.*, 2010; *Schack-Kirchner et al.*, 2011] or *in situ* [*Roland et al.*, 2015]. Recent studies demonstrate the enormous uncertainty in computed F_{soil} associated with different D_s models [*Pingintha et al.*, 2010; *Roland et al.*, 2015], suggesting that *in situ* estimation of D_s is necessary. *In situ* measurements of the soil diffusion coefficient can be determined through two different techniques [*Werner et al.*, 2004]. First, the most common technique, uses a tracer gas that is either a natural tracer such as radon [*Davidson and Trumbore*, 1995; *Uchida et al.*, 1997; *Ota and Yamazawa*, 2010] or a biologically inactive gas such as sulfur hexafluoride (SF_6) injected directly into the soil [*Ball et al.*, 1994; *Johnson et al.*, 1998; *Shcherbak and Robertson*, 2014]. The other, less common, technique uses the GM to determine the apparent diffusion coefficient (D_{app}), also called the gas transfer coefficient (k_s), *in situ*, by measuring the CO_2 molar fraction at two depths and F_{soil} from a chamber [*Roland et al.*, 2015]. This k_s is a more appropriate description of the parameter than a diffusion coefficient because k_s implicitly accounts for diffusive and non-diffusive transport as well as the production or consumption processes that can occur in the between-gradient soil layer.

The main goal of this paper was to obtain accurate long-term F_{soil} estimates based on the gradient method (GM). For that, we compare the two *in situ* methods for determining D_s and k_s and quantify the differences among the resultant D_s and k_s models based on porosity and soil water content with 14 D_s published models. Based on these models we obtained the F_{soil} by the GM, which we compared to F_{soil} measurements from two automated soil CO_2 chambers over a one-year period. We address the following questions: 1) Given the large interests in understanding soil CO_2 dynamics, but the significant uncertainties created by the range of methodologies, how can we best estimate cumulative F_{soil}? (i.e., what are the best practices for the accurate measurement of long-term soil efflux?) 2) Can we use limited chamber efflux measurements, such as when the field conditions are highly variable (e.g., after a precipitation pulse), in place of a complete year of chamber effluxes to obtain an accurate k_s model that accurately estimates F_{soil}? Finally, to respond to other studies that found poor agreements between sub-daily F_{soil} measurements using soil chambers and estimates using the GM [*Goffin et al.*, 2015; *Roland et al.*, 2015] and other studies that identified significant hysteretic behavior [Barron-Gafford et al., 2011; Hamerlynck et al., 2013; Zhang et al., 2015] we ask: 3) Can the GM method produce accurate sub-daily F_{soil} measurements?

2. Measurements and Analyses

2.1 Experimental site

This study was conducted at the Santa Rita Mesquite Savanna Ameriflux site (US-SRM), south of Tucson, AZ USA (31.821^o N, 110.866^o W), from November 1st 2014 to October 31th 2015. The climate is warm-winter Steppe [*Köppen*, 1918] with a mean annual precipitation of ca. 380 mm. About 50% of the annual precipitation occurs during the summer (July–September) with the driest months occurring between summer and winter [*Scott et al.*, 2009]. Mean annual temperature is 19ºC, with maximum in the summer of ~ 40ºC and minimum in winter ~5ºC. The vegetation is dominated by an overstory of 3-4m high *Prosopis velutina* (velvet mesquite) trees [*Wooton*, 1898], with a canopy cover about 35%, and an understory of perennial C_4 bunchgrasses and annual C_4 grasses, interspersed sub-shrubs and succulents. The soil texture is a loamy sand of >2 m depth. The soil layers from 0-10 cm, 10-20 cm, 20-50 cm and 50-80 cm contain approximately 0.73%, 0.46%, 0.26% and 0.27% soil organic carbon, 0%, 0%, 35% and 13% inorganic carbon and a root density of 0.0015 g cm^{-3}, 0.0014 g cm^{-3}, 0.0005 g cm^{-3}, 0.0001 g cm^{-3}, respectively. More details of the site can be found in Scott et al. [2009, 2015].

2.2 Soil CO_2 measurements from chambers and profiles

Two automated soil CO_2 efflux chambers with soil collars inserted 8 cm into the ground were installed under the canopy of two mesquite trees (located 5 m apart) and controlled by a multi-chamber monitoring system (LI-8100, LiCOR, Lincoln, NE, USA). This system was programmed to monitor chamber air temperature, relative humidity, CO_2 molar fraction, and atmospheric pressure every second during 90 s measurement intervals every two hours. F_{soil} was obtained using the LI-8100 software, and chamber runs where the model fit had a regression coefficient (R^2) less than 0.9 were rejected from analysis, representing <1% of the total data. Close to each chamber, two CO_2 sensors with a range of 0–5000 ppm, accuracy ±1.5 % of the range and ±2 % of the reading (GMM-222, Vaisala, Inc., Finland), two soil thermistors (107, Campbell Scientific, Logan, UT, USA; hereafter CSI), and two soil moisture probes installed horizontally (CS616, CSI) were installed at 10 cm depth. One final CO_2 sensor and thermistor were installed at 2 cm above the soil, in a radiation shield to avoid direct solar radiation, and measured the atmospheric CO_2 molar fraction and air temperature. Measurements were made every 30 s with all sensors and stored as 30 min averages by a datalogger (CR1000, CSI). For this paper, 2 hour averages of the above variables were used. Approximately every month the probes calibration was checked [*Hamerlynck et al.*, 2013]. There were two significant gaps in the measurements (23-December – 13-March, and 3-15 May) due to chamber malfunction or when the batteries were stolen. The two data gaps were simply excluded from our cumulative annual flux estimates. As an estimate of the uncertainty in the chamber F_{soil}, we report the mean and the range between both chambers.

2.3 Inter-well SF_6 pulse injection

Nine injection profiles were installed in the soil near the chambers and CO_2 profiles. Every SF_6 profile was composed of three stainless steel tubes (9.5 mm OD and ID 8.1 mm) filled with a threaded rod (7.9 mm OD) at 5, 10 and 20 cm depth. Perforations were made at the bottom of the steel tube, and the top was connected and sealed with a stopcock fitting. The 20 cm tube was used as the injection well, and the gas was sampled using the tubes at 5 and 10 cm. We injected 5 ml of air containing atmospheric air with 16 ppm of SF_6 in the injection well. At 3 min intervals, six 10 ml samples were extracted from both depths and analyzed within 24 hours. We used a gas chromatograph (8610 SRI instrument, USA) outfitted with a 1 ml injection loop (1.8 m x 3.175 mm Haysep D column) followed by a 30 cm x 3.175 mm Moleseive 5A column, and electron capture detector, similar to the protocol described by Johnson et al. [1998]. Five sampling campaigns were conducted to measure the diffusion rate at various soil water contents. The driest campaign was on July 28th, and the other four campaigns were made after multiple rainy days (58 mm in 4 days, Figure 1) on 25th, 27th and 29th of September and 1st October.

2.4 Determination of diffusion coefficient (D_s), transfer coefficient (k_s) and F_{soil}

Equations and soil information of published 14 D_s empirical models and two *in situ* models consisting of 1) a k_s model, hereafter referred to as "Chamber model", obtained using a calibration between the chamber and the gradient method (GM), and 2) a D_s model, hereafter referred to as "SF_6 model", obtained through inter-well pulse injection, are given in Table 1.

2.4.1 F_{soil} determination through the GM using the diffusion coefficient (D_s)

The GM estimates soil CO_2 effluxes assuming that all the transport is due to diffusion processes through the equation [*Kowalski and Argueso*, 2011]:

$$F_{(x)} = -\rho D_s \frac{\partial c}{\partial x} \qquad (1)$$

where $F(x)$ is the F_{soil} at depth x (μmol CO_2 m^{-2} s^{-1}), D_s is the soil CO_2 diffusion coefficient (m^2 s^{-1}), ρ is the mean air density (mol air m^{-3}), ∂c is the CO_2 molar fraction gradient (μmol CO_2 mol air^{-1}) and ∂x is the vertical gradient (m).

D_s was obtained by published 14 D_s empirical models, and in the *in situ* SF_6 model, ∂c values were obtained as the difference between CO_2 molar fractions in the atmosphere and at 10 cm depth; ∂x was 0.1m, and ρ was obtained from the ideal gas law.

2.4.2 k_s determination using a soil CO_2 chamber and CO_2 sensors

Estimates of soil CO_2 effluxes through the GM are not just sensitive to diffusive transport, but also due to non-diffusive transport and production /consumption processes that can occur in the soil layer, through this equation:

$$F_{(x)} = -\rho k_s \frac{\partial c}{\partial x} \qquad (2)$$

where k_s is an empirical CO_2 transfer coefficient in ($m^2\ s^{-1}$) that includes diffusive and non-diffusive transport and production or consumption processes that can occur in the studied layer. The term k_s is also known as an apparent diffusivity (D_{app}, [*Roland et al.*, 2015]), and for this study was obtained by rearranging Eq. 2:

$$k_s = -\frac{F_{soil}\,\partial x}{\rho\,\partial c} \qquad (3)$$

where F_{soil} values were obtained from the chamber measurements, ∂c values were obtained as the difference between CO_2 molar fractions in the atmosphere and at 10 cm depth, ∂x was 0.1m, and ρ was obtained from the ideal gas law.

2.4.3 D_s determination through inter-well SF_6 pulse injection

D_s was calculated with the equation proposed by Werner et al. [2004] for the inter-well method with an instantaneous point source:

$$\mathrm{D_s} = \left(\frac{\theta_a r^2}{6 f_a t_{max}}\right)\left(\frac{D_a}{D_{Sf6}}\right) \qquad (4)$$

where θ_a is the air-filled porosity (m^3 m^{-3}) obtained as the soil porosity (*Φ*) minus the volumetric soil water content (θ, cm^3 cm^{-3}), *r* is the distance from the point source (m), f_a the fraction of the injected mass of SF_6 conserved in the soil air (f_a=1), t_{max} is the time of the maximum SF_6 concentration (s), and D_a is the diffusion coefficient of CO_2 in free air (m^2 s^{-1}). *Φ* was calculated from soil bulk density (ρ_b) and particle density (ρ_d) data as $\Phi = 1-(\rho_b / \rho_d)$ resulting in 0.38 cm^3 cm^{-3} for our site. D_{Sf6} is the diffusion coefficient of the SF_6 in free air (m^2 s^{-1}), both calculated following Jones [1992]:

$$D_a = D_{a,0} \left(\frac{T}{T_0}\right)^{1.75} \left(\frac{P}{P_0}\right) \qquad (5)$$

$$D_{sf6} = D_{sf6,0} \left(\frac{T}{T_0}\right)^{1.75} \left(\frac{P}{P_0}\right) \qquad (6)$$

where $D_{a,0}$ is $1.47 \cdot 10^{-5}$ m^2 s^{-1}, $D_{Sf6,0}$ is $0.89 \cdot 10^{-5}$ m^2 s^{-1}, T_0 is 293.15 K, P_0 is 101325 Pa and *T* and *P* are temperature (K) and pressure (Pa) respectively. Through Eq. 4, the diffusion coefficient for the layer 10-20 cm and the layer 5-20 cm were obtained, D_{s10-20} and D_{s5-20} respectively. D_s from 0-10cm (D_{s0-10}) was calculated by:

$$D_{s0-10} = \left(\frac{D_{s5-20} - D_{s20-10}}{\partial_r}\right) \cdot \partial_x \qquad (7)$$

where ∂_r is the difference between the distances from the point source and the sampling tubes (m) and ∂_x is the soil layer thickness (m, 0.1 in our case).

2.4.4 Modeling D_s and k_s in function of soil air porosity

To obtain the diffusion and the gas transfer models, D_s and k_s were fit using a power function ($y = D_a\ ax^b$) of the soil air porosity (θ_a), where *y* is D_s or k_s, D_a is the diffusion coefficient of CO_2 in free air (m^2 s^{-1}), *x is* θ_a and *a* and *b* are the coefficients obtained by least squares regression. Two *in situ* models were obtained: 1) the Chamber model based on the k_s obtained during the whole period (Eq. 3), and 2) the SF_6 model based on the D_s obtained from the five campaigns (Eq. 4). Four additional k_s models were obtained using shorter, subsetted monitoring periods based on two rain pulses at the beginning and end of the summer rainy season (July 2nd-22nd and September 23rd –October 14th). Two of these four additional models were obtained using all the variables monitored continuously at the maximum frequency (every 2 hours, July Pulse and September Pulse) and the other two models only used one daily measurement at 10:00 am during these pulse periods (Daily July and Daily September). The time of 10:00 am is arbitrary, but chosen to simulate a field visit to take one measurement with a portable chamber. Also, a bootstrap analysis with 10,000 iterations was employed to take random samples at any hour with 5 different sampling frequencies of F_{soil} (1 sample every 2 months, and 1, 2, 3 or 4 samples per month) to simulate infrequent manual chamber measurements and determine the uncertainty in the resultant cumulative F_{soil} estimates due to the different sampling strategies.

3. Results

The F_{soil} and CO_2 molar fraction (χ_c) at 10 cm varied significantly at short temporal scales, driven mainly by rain pulses (Figure 1). During this period, the 10 cm soil temperature showed an annual pattern with a mean of 22.4^{o}C, a maximum in July (38.5^{o}C) and minimum in January (4.3^{o}C). Soil water content ranged between 0.15 m^3/m^3 after rains and 0.05 m^3 m^{-3} prior to summer monsoon (July). Over the yearlong period, the soil χ_c at 10 cm averaged 1342 ppm with a maximum in July (4725 ppm) and a minimum in January (603 ppm). Soil CO_2 effluxes measured with the chambers showed a similar pattern to the soil χ_c, with a mean value of 1.39 µmol m^2 s^{-1}, a maximum in July of 5.20 and a minimum in January 0.32 µmol m^2 s^{-1}.

At a given soil air porosity, we found large differences in the relative diffusion coefficient (D_s/D_a) and the relative gas transfer coefficient (k_s/D_a) for the 14 published D_s models and our two *in situ* models (Figure 2). The Chamber model yielded a higher k_s/D_a at a given soil air porosity than the D_s/D_a values in the SF_6 model, and, therefore, k_s was always higher than D_s. All published models, except that of Xu et al. [1992], underestimated the relative diffusion coefficient determined *in situ* at this site (SF_6 model). The equations and fitting parameters for these two *in situ* models can be found in Table 2 (Chamber model and SF_6 model).

After one year of near-continuous data, we found very large differences in the cumulative F_{soil} for the different diffusion and transfer models compared to the measured soil efflux (Figure 3a). The Chamber model showed the best agreement with the mean soil efflux (343 and 345 g C m^{-2} respectively, <0.6% error). The SF_6 model CO_2 flux summed to 260 g C m^{-2}, an underestimation of 32%. With the exception of Xu et al. [1992] (383 g C m^{-2}, 10% overestimation), all published models underestimated the CO_2 flux by 55% to 361% (222 g C m^{-2} to 75 g C m^{-2} respectively).

Four CO_2 transfer models (k_s) derived from short monitoring periods around two rain pulses at the beginning and end of the monsoon season (July 2nd and September 23rd; see arrows in Figure 1), used with the GM showed good cumulative soil efflux estimates, falling within the range of measured soil effluxes (Figure 3b). The cumulative F_{soil} obtained from the two k_s models obtained using all the variables monitored every 2 hours (July Pulse and September Pulse) underestimated the mean of the chamber efflux by 4.8% and 9.0% using the July and September pulses, respectively. The range of soil water content for the July pulse (0.06-0.1) represented 41.3% of the annual range, versus 57.8% (0.06-0.12) for the September pulse. The other two models based on one daily measurement during the pulse event resulted in a 1.6% overestimation during July and a 4.8% underestimation during

September (Figure 3b). The equations and fitting parameters for all *in situ* models can be found in Table 2. More statistical information comparing 2-week cumulative F_{soil} and the cumulative F_{soil} estimated by the others D_s and k_s models are shown as Supporting Information (Figure S1). We assumed a 10% uncertainty in the SF_6 injector-sampling distance, and this assumption resulted in a cumulative CO_2 efflux that falls within the range of measured soil effluxes (overlapping shadows areas, Figure 3b). Considering all k_s model estimates, only the SF_6 model and one D_s model (Xu et al. [1992]) produced estimates that were within the range of the chamber CO_2 efflux measurements.

An increase of the sampling frequency yielded a decrease of uncertainty in the estimates of cumulative F_{soil} due to a better calibration of the k_s model (Figure 4). Errors below ±5% were found in 82%, 77%, 76%, 65% and 56% of the k_s models obtained with a frequency of 4, 3, 2, 1 and 0.5 samples per month, respectively. The mean and standard deviation of the absolute difference between cumulative sums were 7.5 ± 5.4% for 1 sample every 2 months, 5.5 ± 4.1% for 1 sample per month, 4.2 ± 3.2% for 2 samples per month, 3.7 ± 2.7% for 3 samples per month and 3.3 ± 2.5% for 4 samples per month.

When the GM is applied, there is a lag between the daily maximum and minimum F_{soil} obtained by the automatic chamber and the GM using the Chamber model (Figure 5). A cross-correlation analysis determined a 2-hour lag based on surface temperature and 10 cm depth temperature, and this lag was applied to the F_{soil} estimated by the GM. This improved the comparison of the sub-daily measurements (Figure 5) with the coefficients of determination (R^2) for monthly averaged diurnal fluxes, where the R^2 between F_{soil} and the Chamber model were 0.47, 0.34 and 0.53 during June, July and August, respectively, and 0.68, 0.62 and 0.83 from F_{soil} and the Chamber model lagged 2 hours. During the whole study period the coefficient of determination between the raw diurnal F_{soil} and the Chamber model was 0.80 and with the lag applied it was 0.82.

The relatively low R^2 found between the soil air porosity and the gas transfer coefficient (k_s) indicated that variables other than soil water content were influencing k_s (Table 2). This may also indicate that non-diffusive transport mechanisms were involved. To study the wind effect on k_s, the whole data base was stratified, discerning between "windy days", days with daily mean of wind speed > 3.5 m s^{-1} and "calm days" with daily mean of wind speed < 1.6 m s^{-1}, equivalent to 90^{th} and 10^{th} percentile, respectively. During windy days, the fitting between soil air porosity and k_s was much poorer (standard error of the regression, S=0.089, Figure 6) than during calm days (S= 0.049). The k_s model obtained for windy days underestimated the cumulative F_{soil} by 2.3% during the whole year, however the k_s model obtained for calm days overestimated the cumulative F_{soil} by 6.7%.

4. Discussion

An accurate quantification of F_{soil} across ecosystem flux measurement sites would help to resolve the role that this component flux plays in the net ecosystem carbon balance and its dominant controls. Unfortunately, separate F_{soil} estimates are rarely available as automated chamber systems are typically expensive and difficult to maintain. The gradient method is attractive due to its simpler design and lower cost, but the accuracy of the method is questionable because of the use of off-the-shelf published models for the diffusion coefficient. Herein, we have addressed three questions whose answers lead to new best practices in the application of the GM technique.

4.1 Which method produces the best estimate of cumulative F_{soil}??

The most accurate long-term F_{soil} measurements were obtained by using an empirical soil CO_2 transfer coefficient *in situ* (Chamber model) applied to the GM, which produced only a 0.6% difference on cumulative F_{soil} measured by soil chambers. We found that published D_s models and the in situ D_s model that was obtained using the tracer injection technique did not result in very accurate cumulative F_{soil} estimates; rather, the Chamber k_s model showed the best agreement with the F_{soil}. At our experimental site, 93% (13 of 14) of published D_s models used with the GM method produced unsuitable F_{soil} estimates, as compared to our measurements with the automated chambers (Figure 3a). This result supports the need to determine D_s *in situ* at any experimental site, as suggested by Pingintha et al. [2010] and Roland et al. [2015]. The most common way to determine D_s is *ex situ*, either collecting undisturbed core samples in the field [*Moldrup et al.*, 1996] or collecting soil samples and repacking them [*Moldrup et al.*, 2000] to later test in laboratory. The main problem of *ex situ* determinations is that this methodology is very likely to disturb the soil structure during extraction and transport. Both *in situ* as *ex situ* published models yield large uncertainties when used in other soils, simply because these models were developed for specific soil conditions based mainly on soil porosity and water content (Table 1). Soil porosity can vary widely between soil layers especially in the upper horizon (in our case, the first few cm) due to the organic matter content, which changes bulk density and so affects porosity. The soil porosity has an important effect in the diffusion models (Figure 2); therefore, an accurate determination of this parameter in the studied layer is essential when *ex situ* diffusion models are used. In the same way, it is very complicated to obtain a water content estimation that is representative of the shallow soil layer, since sensors integrate a particular soil volume, are sensitive to differences in soil mineralogy [*Vaz et al.*, 2013], and can be influenced by the soil-atmosphere interface when installed at shallow depths. The soil volume measurements vary depending on the probe installation position either in horizontal, vertical or at angle, with the angle position being the most adequate to determine the soil water content in the layer of interest.

All of these uncertainties in the determination of the soil porosity, insertion strategy and probe calibration could have contributed to the error magnitude of the 14 published empirical diffusion models. These uncertainties will be propagated to whatever D_s model chosen in future studies because these models are empirical in nature, and thus they would not be expected to hold under all conditions. At this site and with this experimental design, we found a large underestimation when using 13 published empirical diffusion models. However, the magnitude of error in F_{soil} in the published models would be expected to decrease if CO_2 is measured at shallower depths because there would be less soil CO_2 production between the CO_2 measurement and the soil surface.

Differences in cumulative F_{soil} estimates between D_s models and k_s models (Figure 3), also could be due to the k_s models implicitly accounting for the diffusive and non-diffusive transport and production processes of CO_2 in the soil between sampling depths, whereas D_s models are subject to diffusion alone. When comparing both *in situ* gas transport models, the Chamber model implicitly accounted for the diffusive and non-diffusive transport and production processes of CO_2 in the soil between sampling depths, but the SF_6 model used a conservative tracer subject to diffusion alone. The classic gas diffusion models are based on a conservative tracer, assuming that all molecules are conserved in the soil air, neglecting production or consumption processes. Although there are differences in solubility in water between SF_6 and CO_2 (CO_2 *ca.* 30 times higher than SF_6 [*Wilhelm et al.*, 1977]), this contribution is usually neglected because diffusion of these gases in water is about 10000 times lower than in the air [Allaire et al., 2008].

Different models using conserved gases determine the diffusion coefficient for any gas of interest by using the ratio between the molecular diffusion coefficient (D_m) for the gas of interest and D_m for the conserved gas used [*Werner et al.*, 2004; *Allaire et al.*, 2008]. Therefore, the gas of interest also is treated as a conservative gas, which is not valid for soil gases like CO_2, CH_4, NO_x, N_2O, H_2S and SO_2 that may be both produced or consumed as they move through the soil matrix. We would expect CO_2 production in the 0-10 cm layer, and for this reason the SF_6 model likely underestimated CO_2 effluxes (Figure 3). Differences between SF_6 and Chamber models could also be due to two more reasons. First, we estimated D_s for the 10-20 cm and 5-20 cm depths and then extrapolated D_s to the 0-10 cm layer. If D_s decreases with depth, this would result an underestimate of D_s from 0-10 cm. Second, the SF_6 method was only carried out five times, and this may have contributed to a regression that was not statistically significant (P=0.264, Table 2). While this may not necessarily create a bias, it limits our confidence in the relationship between water content and diffusion. Finally, the CO_2 production of this layer plays an important role in the k_s models based on rain pulses. As expected, the July pulse (early monsoon) obtained higher values of cumulative annual F_{soil} than the September pulse (later monsoon) because soil effluxes for a given pulse size tend to be larger at the onset of rains versus later in a rainy season [*Franzluebbers et al.*, 2002; *Sponseller*, 2007; *Vargas et al.*, 2012].

4.2 Can we use a limited set of soil CO_2 effluxes over a rain pulse to produce an accurate cumulative efflux estimate?

Gas transfer models based on continuous soil efflux measurements, or more simply by a once-a-day measurement that follows a soil water dry-down event (i.e., to simulate sampling with a portable chamber), produce better estimates of F_{soil} than any published empirical diffusion model (Figure 3b). Comparing a limited set of measurements, we found that gas transfer models derived from the daily measurement at 10:00 am resulted in even a slightly better estimation of cumulative F_{soil} than models using continuous measurements, but, more importantly, all pulse models were better than the SF_6 model and the published empirical diffusion models (Figure 3b). The slightly better estimation of cumulative F_{soil} in the models derived from one daily measure than the models using continuous measurements over the same pulses is simply a coincidence due to chosen 10:00 am sampling time. Alternative models derived from a once daily measurement at a specific hour do not always result in a better estimation of cumulative F_{soil} than models using continuous measurement, but all of them fall within the cumulative efflux measurement range (Table S1). The best cumulative F_{soil} estimations were derived from once daily samplings, resulting in a 0.8% overestimation (sampling at 04:00 am during the July pulse) and a 1.2% underestimation (06:00 am, September pulse); the worst F_{soil} estimations resulted in a 17.3% underestimation (16:00 pm, July) and a 15.4% underestimation (18:00 pm, September). Windy days underestimated F_{soil} (Figure 6). For this reason, we believe the improved F_{soil} estimations using pre-dawn sampling time (04:00-06:00) may be due to increased wind in the late afternoon (16:00-18:00). The efflux measurement range found between the chambers highlights probable measurement uncertainty due to the instrumentation as well as the likely heterogeneity in the soil CO_2 effluxes (Figure 3), due to micrometeorological conditions, such as differences in shading, as well as differences in soil properties and root density.

For future studies working with the gradient method, we recommend taking at least one F_{soil} manual chamber measurement per month over the largest range of soil water content possible. Seasonality is captured in the CO_2 gradient through time; combined with measures of F_{soil} by the manual chamber that can capture a range of environmental conditions, revised F_{soil} estimates by the GM will be significantly improved. Given similar conditions to our study, this would allow the building of a k_s model that would yield yearly F_{soil} estimates within 5.5% of the mean between the absolute difference between F_{soil} estimated and F_{soil} obtained from chamber measurements. However, as the bootstrap analysis showed, an increase in the sampling frequency would yield better calibrated k_s models, and therefore better F_{soil} estimates (Figure 4).

4.3 Can the GM method produce accurate sub-daily F_{soil} measurements?

We have shown that accurate F_{soil} estimations can be obtained by the GM at daily to seasonal scales, but it is necessary to correct for an apparent lag associated with the measurement depth to improve the agreement at sub-daily scales. A schematic drawing of the diurnal patterns of temperature, soil CO_2 molar fraction and F_{soil} measured by the chamber and F_{soil} obtained by the gradient method at different depths are shown in Figure S2. This decoupling between the F_{soil} measured by the chamber and the F_{soil} estimated by the GM at different depths occurs because the time to reach the maximum CO_2 molar fraction is delayed at deeper depths, just like soil temperature. Previous studies have identified significant hysteretic behaviour [*Barron-Gafford et al.*, 2011; *Hamerlynck et al.*, 2013; *Zhang et al.*, 2015] associated with lags between CO_2 production and soil temperature [Vargas et al., 2010], and we have attempted to systematically correct for these by following a technique widely used in eddy-covariance studies to determine the lag between variables [*Finkelstein and Sims*, 2001; *Langford et al.*, 2015]. Just as the GM is based on the difference between the mole fraction at one depth and the atmosphere, the deeper the sensor, the greater the delay with respect to F_{soil} at the surface. To correct for this lag, we used a cross-correlation analysis to determine the lag between surface temperature and the temperature at the depth of interest, and we applied it to the delay the F_{soil} series. At our experimental site, the cross-correlation analysis resulted on a 2-hour lag and after applying it, on the series of F_{soil} obtained by the GM using the Chamber model, produced sub-daily estimates in phase with the soil effluxes (Figure 5).

In contrast, Roland et al. [2015] found that none of their F_{soil} models were able to suitably predict the F_{soil} variations at the sub-daily time scale. They suggest that this was likely due to the lack of large diurnal soil CO_2 variations which might have been due to more wind-driven advective transport [*Hirsch et al.*, 2004; *Maier et al.*, 2010; *Sánchez-Cañete et al.*, 2011]. Our results showed that during calm days the explained variance between soil air porosity and k_s was greatly improved with respect to windy days (S=0.049 and S=0.089, respectively, Figure 6). This suggests that non-diffusive transport induced by the wind contributed to a high source of noise in our data, justifying the low R^2 found with our Chamber model (Table 2). On the other hand, Goffin et al [2015] did not find evidence that turbulence-induced transport could explain the poor agreement in sub-daily F_{soil} and recommended that the focus should be placed on other factors affecting the CO_2 production. However, the failure in their simulated sub-daily F_{soil} could be due to the application of a diffusion coefficient in the GM rather than an *in situ* determined transfer coefficient that implicitly can account for the CO_2 production in the soil layer.

The application of GM considering diffusion processes exclusively and neglecting non-diffusive ones leads to several sources of error that may contribute to differences on F_{soil} with respect to chamber measurements. Research on non-diffusive transport has found that the main drivers are wind, fluctuations in atmospheric pressure, soil-atmosphere thermal gradient or air density associated with its composition. Numerous authors have found that advective transport driven by the wind, can provoke changes in the soil CO_2 molar fraction [*Drewitt et al.,* 2005; *Seok et al.,* 2009; *Bowling and Massman,* 2011; *Goffin et al.,* 2014], soil CO_2 effluxes [*Subke et al.*, 2003; *Risk et al.*, 2013; *Roland et al.*, 2015] or in the atmosphere [*Kowalski et al.*, 2008; *Sánchez-Cañete et al.*, 2011; Nachshon et al., 2012; *Rey et al.*, 2012]. Non-diffusive transport has been associated both with small changes in pressure induced by the wind, commonly called pressure pumping [*Massman et al.,* 1997; *Takle et al.,* 2004; *Maier et al.,* 2010], or from synoptic atmospheric pressure changes [*Rogie et al.,* 2001; *Fujiyoshi et al.,* 2010; *Comas et al.,* 2011; *Sánchez-Cañete et al.,* 2013b]. The soil-atmosphere thermal gradient also can generate convective transport provoking the exchange of the air between soil and atmosphere, both in fractures [*Weisbrod et al.,* 2009; *Moore et al.,* 2011] and in caves [*Serrano-Ortiz et al.,* 2010]. Finally, other non-diffusive transport processes are due to the effects on soil air buoyancy that result from the added density in the soil pore space air associated with CO_2 enrichment in the root zone [*Kowalski and Sanchez-*

Canete, 2010; *Sánchez-Cañete et al.*, 2013a]. All of these non-diffusive transport mechanisms can generate important errors in the gradient method depending on their magnitudes.

4.4 Importance of accurate long-term soil efflux measurements in ecosystem studies.

Although F_{soil} represents a significant source of terrestrial CO_2 emissions [*Raich and Schlesinger*, 1992], continuous measurements of this important land-atmosphere exchange are only sparsely available despite a call from national ecosystem fluxes networks [*McFarlane et al*, 2014]. At the ecosystem scale, the measurement of net ecosystem CO_2 exchange (*NEE*) can be partitioned into ecosystem respiration (R_{eco}) and gross ecosystem production (*GEP*) by temperature sensitive model-based estimates using the nighttime *NEE* data [*Falge et al.*, 2001; *Stoy et al.*, 2006; *Mahecha et al.*, 2010]. Despite advances on the net ecosystem CO_2 exchange (NEE) partitioning [*Desai et al.*, 2008], there are large uncertainties of *NEE* mainly associated to low-turbulence conditions at night, and these uncertainties are transferred to the partitioning of NEE into ecosystem respiration (R_{eco}) and gross ecosystem production (*GEP*) [*Barr et al.*, 2013]. Furthermore, R_{eco} consists of a belowground component, F_{soil}, and an aboveground component attributed to plant respiration. F_{soil} is commonly measured manually, yielding a low sampling frequency, which translates into annual estimates that are highly uncertain (>99% of half hour periods throughout a year for biweekly sampling) [*Gomez-Casanovas et al.*, 2013]. Therefore, comparative studies between F_{soil} at high resolution (spatially and temporally) and ecosystem fluxes are very useful to a better understanding about carbon cycle processes [*van Gorsel et al.*, 2008] and may influence on how we parameterize and construct models [*Vargas et al., 2011]*.

Although F_{soil} is generally the largest flux contributing to R_{eco}, few studies have compared both fluxes. Reported estimates of the relative contribution of F_{soil} to R_{eco} range between 48%-71% found by Lavigne et al. [1997] at six coniferous boreal sites, 92% reported by Longdoz et al. [2000] in a mixed forest, 69% obtained by Janssens et al. [2001b] from 18 forest ecosystems and 81% measured by Knohl et al. [2008] in an old beech forest. Only Longdoz et. [2000] used continuous F_{soil} measures during the whole year, the other authors obtained annual F_{soil} from extrapolation of low-frequency measures using manual chambers. Clearly the F_{soil} contribution is strongly dependent on the ecosystem and we need to produce accurate long-term estimates of F_{soil} across changing environmental conditions to improve our understanding of its contribution to R_{eco}.

5. Conclusions

An accurate depiction of CO_2 production and diffusion processes in soil is a key uncertainty in obtaining accurate measurements of F_{soil}. In this study, we found that the application of 13 out of 14 published diffusion models to the GM grossly underestimated (55%-361%) cumulative soil effluxes. An *in situ* diffusion model obtained by SF_6 injection also did not generate accurate estimations in cumulative F_{soil}, underestimating by 32%. Instead, we found great improvements by using the GM and chamber measurements to determine an empirical soil CO_2 transfer coefficient *in situ* (Chamber model), which produced nearly identical (0.6% difference) cumulative soil effluxes over 243 days. The difference between both *in situ* models could be a result of the Chamber model implicitly accounting for diffusive and non-diffusive transport, as well as including production of CO_2 in the soil layer, while the SF_6 model only accounts for diffusion processes.

Therefore, we recommend not using methodologies based on conservative tracers to build diffusion models that later will be applied in the GM. Rather, a long period of side-by-side measurements is the most appropriate way to build an *in situ* gas transfer model that is statistically more robust (more points to fit) and require less extrapolation outside of the soil water range. However, we found that a limited sampling of F_{soil} (e.g., using a portable chamber) can result in an adequate gas transfer model that generates accurate F_{soil} estimates.

Therefore, we recommend that future F_{soil} studies use a combination of the GM and targeted manual or automatic F_{soil} chamber measurements to build the gas transfer model *in situ* and produce accurate long-term estimates of F_{soil}.

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Figure captions

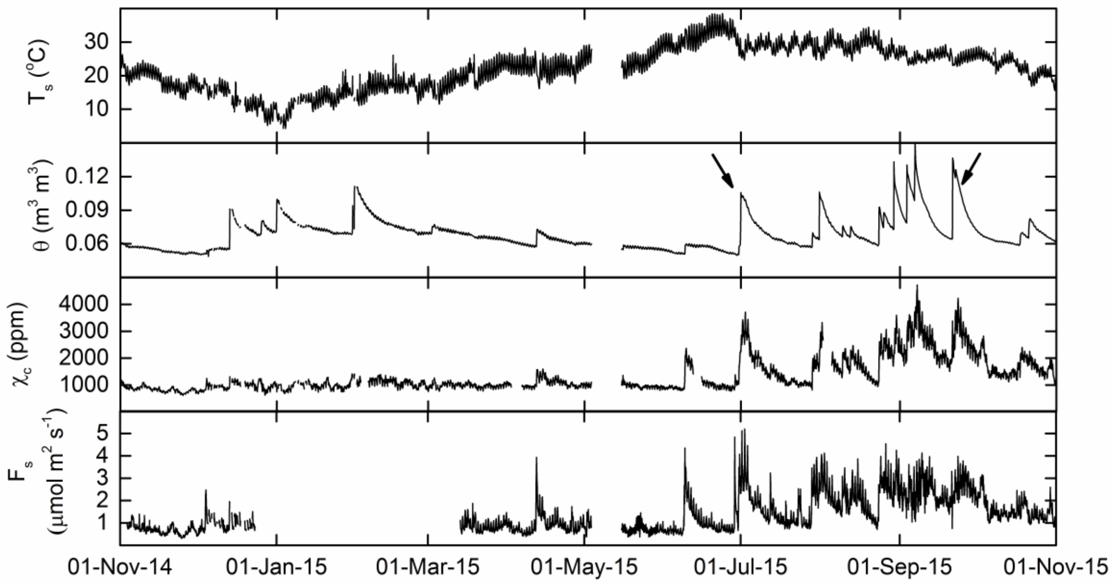

Figure 1. Average of soil temperature (T_s, n=4), volumetric water content (θ, n=2), CO_2 molar fraction (χ_c, n=4) all of them at 10 cm depth and average of soil CO_2 efflux (F_{soil}, n=2) measured from chambers. The black arrows indicate the two rain pulses over which subsetted data were used for separate GM calibration.

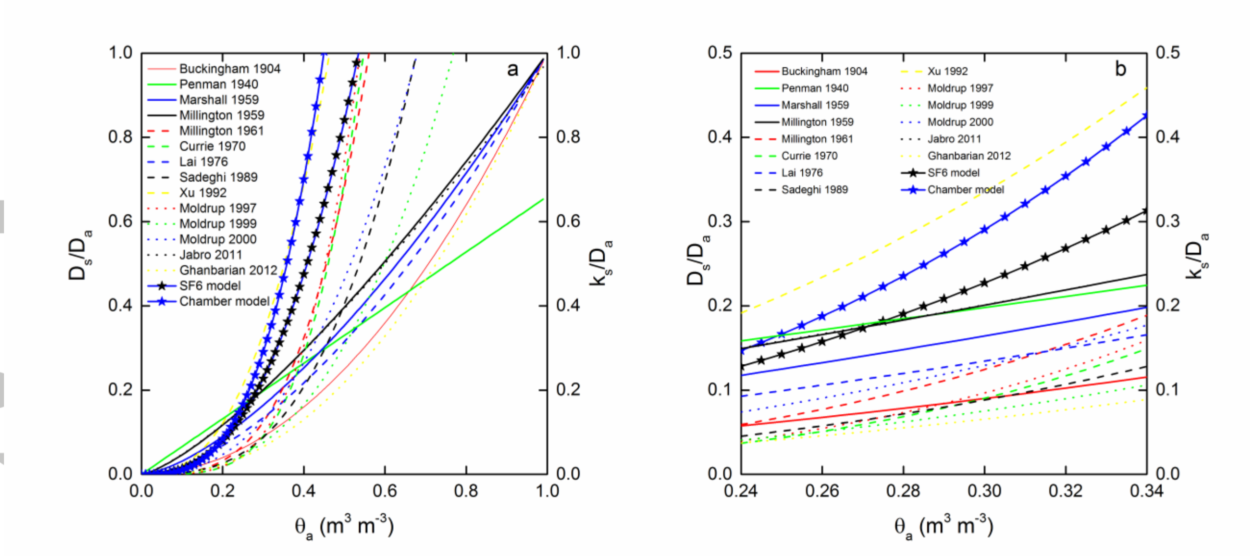

Figure 2. Relative CO_2 diffusion coefficient (D_s/D_a) for 14 published empirical models and the SF_6 model (black stars) and the relative CO_2 transfer coefficient (k_s/D_a) obtained by the Chamber model (blue stars), including the whole possible range of soil air porosity (θ_a), (panel a), and for the range of soil air porosity found in this study (panel b).

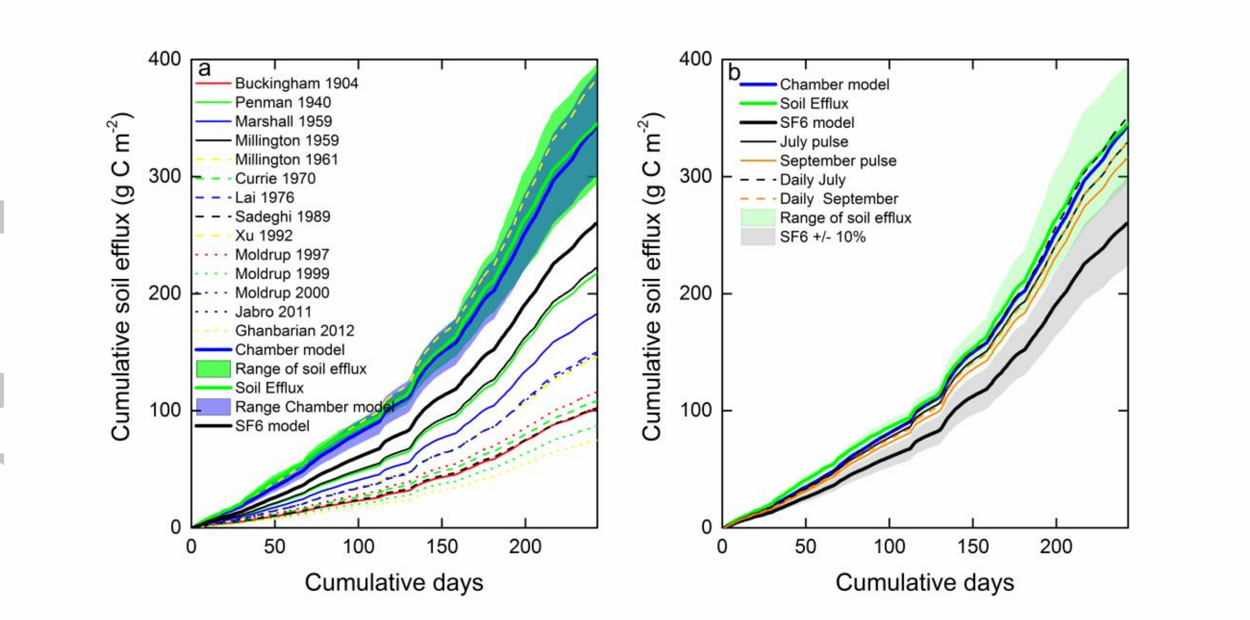

Figure 3. Over the whole period of available data: (a) Cumulative F_{soil} for 14 published empirical models, SF_6 model, Chamber model and its range at 95% confidence interval and mean soil efflux from the chamber and its range. (b) Cumulative F_{soil} for the soil efflux chamber and its range, SF_6 model ± 10% of error in the injector-sampling distance, Chamber model (obtained using the whole monitoring period) and four models based on two rain pulses (July and September) with continuous monitoring of the F_{soil} or with only one daily measurement per day during the rain pulse considered.

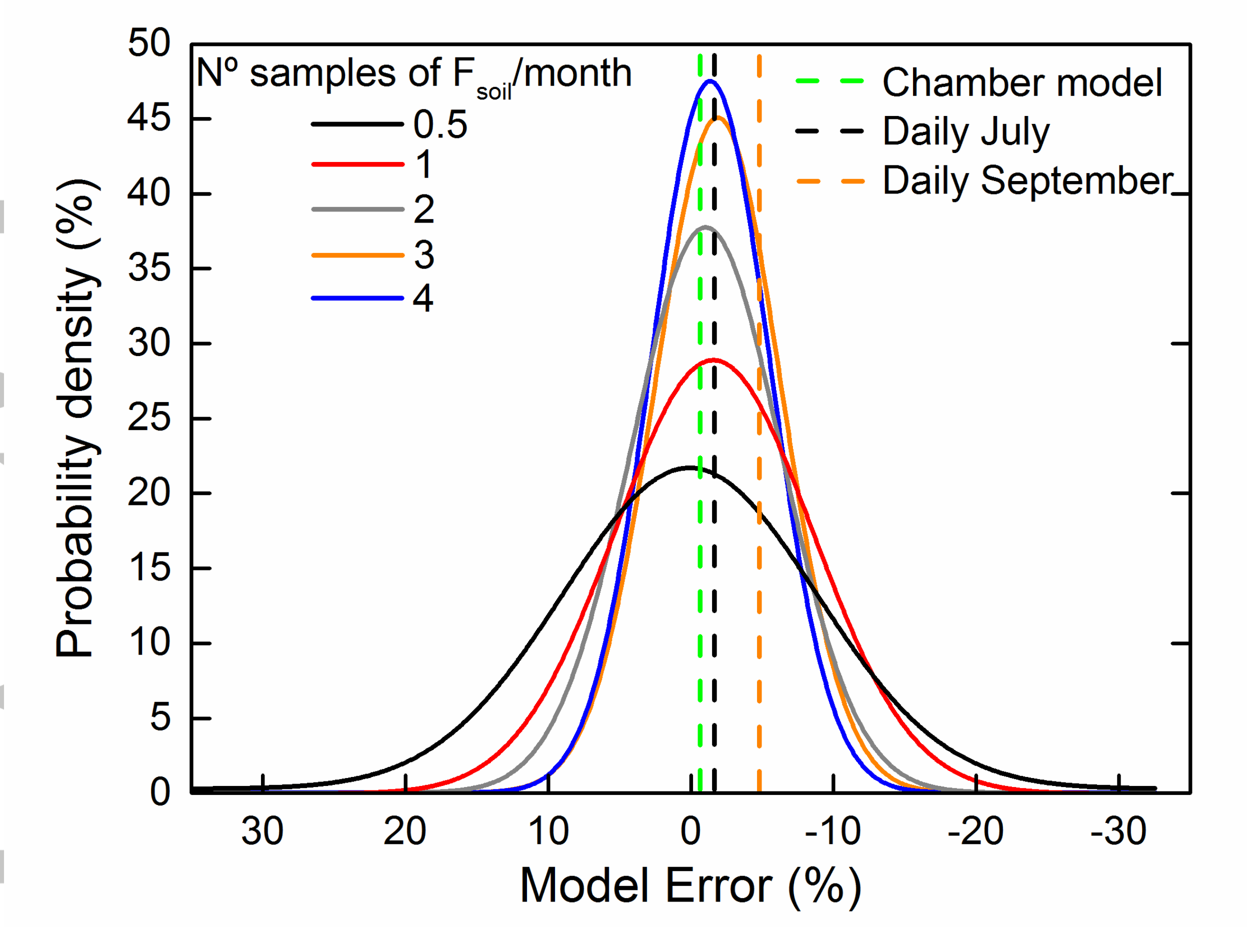

Figure 4. Probability density function of error between the cumulative F_{soil} measured by chambers and estimated from 10,000 CO_2 transfer coefficient (k_s) models at 5 different sampling frequencies (continuous lines). Vertical dashed lines shown errors obtained with some previous models: Chamber model 0.6%, Daily July 1.6% and Daily September 4.8%.

$$\text{Model error}(\%) = \frac{\left|\Sigma F_{soil}^{meas} - \Sigma F_{soil}^{model}\right|}{\Sigma F_{soil}^{meas}} x100.$$

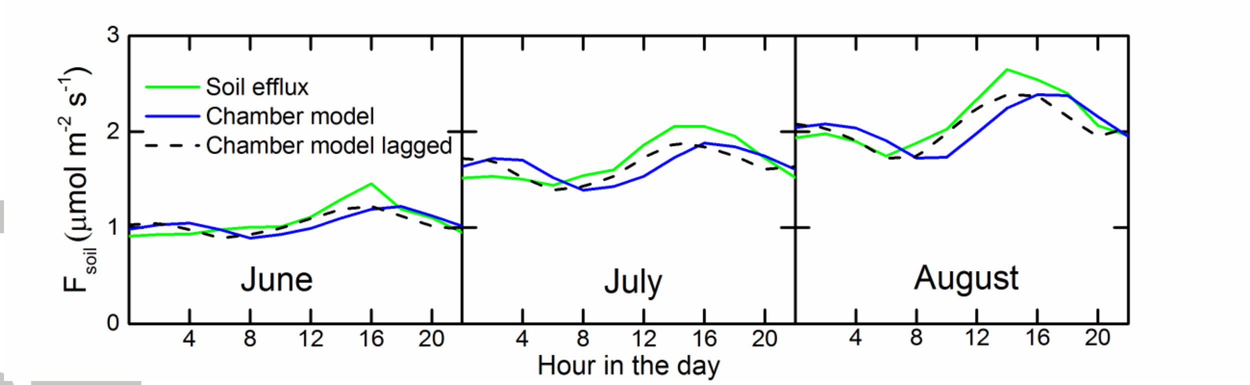

Figure 5. Monthly average diurnal of soil CO_2 efflux (F_{soil}) obtained with the automatic chamber (green), the Chamber model (blue) and the Chamber model lagged 2 hours (black dashed line) during the months of June, July and August.

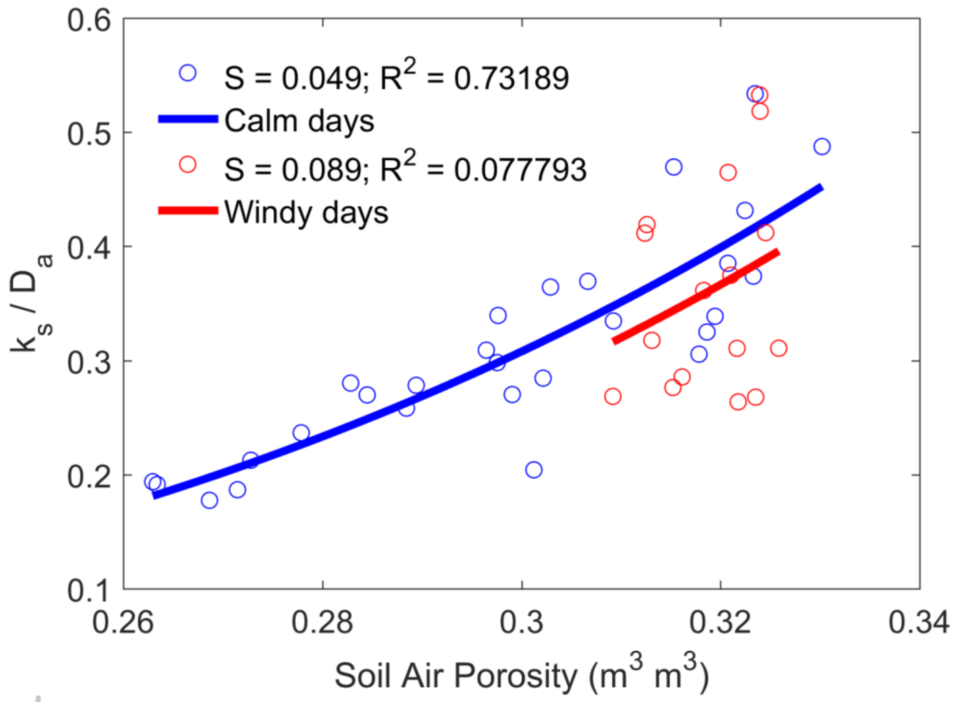

Figure 6. Relative CO_2 transfer coefficient (k_s/D_a) versus soil air porosity for calm days (blue dots, N=28) and windy days (red dots, N=16). The standard error of the regression (S) and coefficient of determination (R^2) is given from the fitting at a power function ($y= D_a ax^b$).

Table 1

Authors	Model	Porous material
Buckingham – 1904	$D_s = D_a \theta_a^2$	Repacked soils
Penman – 1940	$D_s = D_a 0.66 \theta_a$	Different porous materials
Marshall – 1959	$D_s = D_a \theta_a^{3/2}$	Different porous materials Equation derivate from Marshall 1957
Millington – 1959	$D_s = D_a \theta_a^{4/3}$	Comparison of publish results
Millington – 1961	$D_s = D_a \frac{\theta_a^{10/3}}{\Phi^2}$	Different porous materials
Curiee1970	$D_s = D_a \left(\frac{\theta_a}{\Phi}\right)^4 \Phi^{3/2}$	Sand
Lai – 1976	$D_s = D_a \theta_a^{5/3}$	Undisturbed and repacked soils. Sandy loam
Sadeghi – 1989	$D_s = D_a 0.18 \left(\frac{\theta_a}{\Phi}\right)^{2.98}$	Soils with clay content from 10.3 to 51.1%
Xu – 1992	$D_s = D_a \frac{\theta_a^{2.51}}{\Phi^2}$	Silty clay loam soils
Moldrup – 1997	$D_s = D_a 0.66 \theta_a \left(\frac{\theta_a}{\Phi}\right)^{\frac{12-m}{3}}$	Undisturbed and repacked soils. m=3 for undisturbed
Moldrup – [1999]	$D_s = D_a \Phi^2 \left(\frac{\theta_a}{\Phi}\right)^{\beta S}$	Undisturbed soils
Moldrup – 2000	$D_s e D_a \frac{\theta_a}{\Phi}^{2.5}$	Repacked soils ranged from 6–54% clay
Jabro – 2012	$D_s = D_a 0.98 \theta_a^{1.315}$	Sandy loam
Ghanbarian – 2012	$D_s = D_a \left(\frac{\theta_a - \varepsilon_t}{1 - \varepsilon_t}\right)$	Different porous materials
Sánchez-Cañete – 2016 Chamber model	$k_s = D_a 11.62 \theta_a^{3.05}$	Loamy sand
Sánchez-Cañete – 2016 SF_6 model	$k_s = D_a 4.97 \theta_a^{2.56}$	Loamy sand

Table 1. Soil diffusion equations and the porous material that they were developed for. D_s is the CO_2 diffusion coefficient, D_a is the diffusion coefficient of the CO_2 in free air, k_s is the CO_2 transfer coefficient, Φ is soil porosity, θ_a is soil air porosity (= Φ - soil water content). β=2.9 for sandy and clayey soils and S=0.948, is the % of mineral soil with particle size >2 μm. ε_t=0.1Φ, is the critical value for percolation in the porous medium.

Table 2

Model	Equations	R^2	RMSE	Samples	F value	p-value F	p-values Coeff.1-2	Range θ_a	RMSE Validation data
Chamber model	$k_s = D_a 11.62\theta_a^{3.05}$	0.24	0.08	4380	28790	<0.01	<0.01, <0.01	0.23-0.33	-
SF_6 model	$k_s = D_a 4.97\theta_a^{2.56}$	0.85	0.02	5	451	<0.01	0.264, 0.026	0.26-0.32	-
July Pulse	$k_s = D_a 8.71\theta_a^{2.84}$	0.23	0.05	240	877	<0.01	0.016, <0.01	0.28-0.32	0.08
Daily July	$k_s = D_a 5.45\theta_a^{2.39}$	0.41	0.03	20	3724	<0.01	0.236, <0.01	0.28-0.32	0.08
September Pulse	$k_s = D_a 4.14\theta_a^{2.24}$	0.51	0.03	264	926	<0.01	<0.01, <0.01	0.26-0.32	0.09
Daily September	$k_s = D_a 4.73\theta_a^{2.32}$	0.56	0.03	22	10743	<0.01	0.110, <0.01	0.26-0.32	0.08

Table 2. Equations for the derived CO_2 transfer models. Soil air porosity (θ_a= soil porosity - soil water content). D_a is the diffusion coefficient of the CO_2 in free air. k_s is the soil CO_2 transfer coefficient. The coefficient of determination (R^2), root-mean-square error (RMSE), number of samples, F statistic, p-values, range of soil air porosity and RMSE validated with the whole database are also given.