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

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Abstract Soil CO2 efflux \( (F_{\text{soil}}) \) represents a significant source of ecosystem CO2 emissions that is rarely quantified with high-temporal-resolution data in carbon flux studies. \( F_{\text{soil}} \) 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 \( F_{\text{soil}} \) measured by 2 soil CO2 efflux chambers and \( F_{\text{soil}} \) estimated by 16 gas transport models using the GM across 1 year. We used 14 published empirical gas diffusion models and 2 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 “SF6 model” obtained through an interwell conservative tracer experiment. Most of the published models using the GM underestimated cumulative annual \( F_{\text{soil}} \) by 55% to 361%, while the Chamber model closely approximated cumulative \( F_{\text{soil}} \) (0.6% error). Surprisingly, the SF6 model combined with the GM underestimated \( F_{\text{soil}} \) by 32%. Differences between in situ models could stem from the Chamber model implicitly accounting for production of soil CO2, 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 \( F_{\text{soil}} \) measurements. Accurate estimates of \( F_{\text{soil}} \) will improve our understanding of soil respiration’s contribution to ecosystem fluxes.

1. Introduction

Soil CO2 efflux \( (F_{\text{soil}}) \) represents a significant source of terrestrial CO2 emissions [Raich and Schlesinger, 1992], and our ability to accurately represent \( F_{\text{soil}} \) and soil carbon stocks is key for accurately predicting carbon-climate feedback [Todd-Brown et al., 2012]. Because of their large global magnitude, even small changes in soil CO2 effluxes \( (F_{\text{soil}}) \) directly affect the atmospheric CO2 content [Raich and Schlesinger, 1992], leaving \( F_{\text{soil}} \) as one of the most poorly constrained components 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 \( F_{\text{soil}} \) are not well estimated, as both positive and negative feedback between belowground carbon pools and effuxes, and temperature sensitivity in future climate scenarios largely have been quantified [Davidson and Janssens, 2006]. Most often, \( F_{\text{soil}} \) 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 \( F_{\text{soil}} \) over longer periods of time [Drewitt et al., 2002; Hamerlynck et al., 2013; Oishi et al., 2013], but deployment of these systems is limited due to their higher costs. Continuous estimation of \( F_{\text{soil}} \) can also be obtained by application of the gradient method (GM), where the soil CO2 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 CO2 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 \( F_{\text{soil}} \) [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 $F_{\text{soil}}$ associated with different $D_i$ models [Pingintha et al., 2010; Roland et al., 2015], suggesting that in situ estimation of $D_i$ 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; Scherbak and Robertson, 2014]. The other, less common, technique uses the GM to determine the apparent diffusion coefficient ($D_{\text{app}}$), also called the gas transfer coefficient ($k_g$), in situ, by measuring the CO$_2$ molar fraction at two depths and $F_{\text{soil}}$ from a chamber [Roland et al., 2015]. This $k_g$ is a more appropriate description of the parameter than a diffusion coefficient because $k_g$ implicitly accounts for diffusive and nondiffusive 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 $F_{\text{soil}}$ estimates based on the gradient method (GM). For that, we compare the 2 in situ methods for determining $D_i$ and $k_g$ and quantify the differences among the resultant $D_i$ and $k_g$ models based on porosity and soil water content with 14 $D_i$ published models. Based on these models we obtained the $F_{\text{soil}}$ by the GM, which we compared to $F_{\text{soil}}$ measurements from two automated soil CO$_2$ chambers over a 1 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 $F_{\text{soil}}$? (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 $k_g$ model that accurately estimates $F_{\text{soil}}$? Finally, to respond to other studies that found poor agreements between subdaily $F_{\text{soil}}$ 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 subdaily $F_{\text{soil}}$ measurements?

2. Measurements and Analyses

2.1. Experimental Site

This study was conducted at the Santa Rita Mesquite Savanna AmeriFlux site, south of Tucson, AZ, USA (31.821°N, 110.866°W), from 1 November 2014 to 31 October 2015. The climate is warm-winter steppe [Köppen, 1918] with a mean annual precipitation of approximately 380 mm. About 50% of the annual precipitation occur during the summer (July–September) with the driest months occurring between summer and winter [Scott et al., 2009]. Mean annual temperature is 19°C, with maximum in the summer of ~40°C and minimum in winter ~5°C. The vegetation is dominated by an overstory of 3–4 m 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 subshrubs, 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 and 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$^{-3}$, and 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 multichamber monitoring system (LI-8100, LI-COR, 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 2 h. $F_{\text{soil}}$ 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 CO₂ sensor and thermistor were installed at 2 cm above the soil, in a radiation shield to avoid direct solar radiation, and measured the atmospheric CO₂ molar fraction and air temperature. Measurements were made every 30 s with all sensors and stored as 30 min averages by a data logger (CR1000, CSI). For this paper, 2 h averages of the above variables were used. Approximately every month the probe calibration was checked [Hamerlynck et al., 2013]. There were two significant gaps in the measurements (23 December to 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 Fₘᵦ, we report the mean and the range between both chambers.

2.3. Interwell SF₆ Pulse Injection

Nine injection profiles were installed in the soil near the chambers and CO₂ profiles. Every SF₆ profile was composed of three stainless steel tubes (9.5 mm outside diameter (OD) and 8.1 mm inside diameter) 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 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 SF₆ in the injection well. At 3 min intervals, six 10 mL samples were extracted from both depths and analyzed within 24 h. We used a gas chromatograph (8610 SRI Instrument, USA) outfitted with a 1 mL injection loop (1.8 m × 3.175 mm Haysep D column) followed by a 30 cm × 3.175 mm Mol Sieve 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 28 July, and the other four campaigns were made after multiple rainy days (58 mm in 4 days; Figure 1) on 25, 27, and 29 September and 1 October.

2.4. Determination of Diffusion Coefficient (Dₛ), Transfer Coefficient (ks), and Fₚₘᵦ

Equations and soil information of published 14 Dₛ empirical models and 2 in situ models consisting of (1) a kₛ model, hereafter referred to as “Chamber model,” obtained using a calibration between the chamber and the gradient method (GM), and (2) a Dₛ model, hereafter referred to as “SF₆ model,” obtained through interwell pulse injection, are given in Table 1.

2.4.1. Fₚₘᵦ Determination Through the GM Using the Diffusion Coefficient (Dₛ)

The GM estimates soil CO₂ effluxes assuming that all the transport is due to diffusion processes through the equation [Kowalski and Argueso, 2011]

\[ F(x) = -\rho Dₛ \frac{\partial c}{\partial x} \]  

(1)

where \( F(x) \) is the \( Fₘᵦ\) at depth \( x \) (\( \mu mol CO₂ m⁻² s⁻¹ \)), \( Dₛ \) is the soil CO₂ diffusion coefficient (\( m² s⁻¹ \)), \( \rho \) is the mean air density (\( mol air⁻³ \)), \( c \) is the CO₂ molar fraction gradient (\( \mu mol CO₂ mol air⁻¹ \)), and \( \partial c / \partial x \) is the vertical gradient (m).

\( Dₛ \) was obtained by published 14 \( Dₛ \) empirical models, and in the in situ SF₆ model, \( \partial c / \partial x \) values were obtained as the difference between CO₂ molar fractions in the atmosphere and at 10 cm depth; \( \partial c / \partial x \) was 0.1 m, and \( \rho \) was obtained from the ideal gas law.

2.4.2. kₛ Determination Using a Soil CO₂ Chamber and CO₂ Sensors

Estimates of soil CO₂ effluxes through the GM are not only sensitive to diffusive transport but also to nondiffusive transport and production/consumption processes that can occur in the soil layer, through this equation:

\[ F(x) = -\rho kₛ \frac{\partial c}{\partial x} \]  

(2)

where \( kₛ \) is an empirical CO₂ transfer coefficient in \( m² s⁻¹ \) that includes diffusive and nondiffusive transport and production or consumption processes that can occur in the studied layer. The term \( kₛ \) is also known as an apparent diffusivity \( (Dₚₜₚ \text{ [Roland et al., 2015]}) \), and for this study was obtained by rearranging equation (2):

\[ kₛ = \frac{Fₚₘᵦ \partial c / \partial x}{\rho \partial c} \]  

(3)

where \( Fₚₘᵦ \) values were obtained from the chamber measurements, \( \partial c / \partial x \) values were obtained as the difference between CO₂ molar fractions in the atmosphere and at 10 cm depth; \( \partial c / \partial x \) was 0.1 m, and \( \rho \) was obtained from the ideal gas law.
2.4.3. Determination Through Interwell SF\textsubscript{6} Pulse Injection

\(D_s\) was calculated with the equation proposed by Werner et al. [2004] for the interwell method with an instantaneous point source:

\[
D_s = \frac{\theta_a^2}{\theta_a \text{max}} \left( \frac{D_a}{D_{SF_6}} \right)
\]

where \(\theta_a\) is the air-filled porosity \((\text{m}^3 \cdot \text{m}^{-3})\) obtained as the soil porosity \((\Phi)\) minus the volumetric soil water content. 

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

**Table 1.** Soil Diffusion Equations and the Porous Material That They Were Developed for

<table>
<thead>
<tr>
<th>Authors</th>
<th>Model</th>
<th>Porous Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Buckingham [1904]</td>
<td>(D_s = D_\Phi \theta_a^2)</td>
<td>Repacked soils</td>
</tr>
<tr>
<td>Penman [1940]</td>
<td>(D_s = D_\Phi 0.66 \theta_a^{1.8})</td>
<td>Different porous materials</td>
</tr>
<tr>
<td>Millington [1959]</td>
<td>(D_s = D_\Phi \beta S)</td>
<td>Comparison of publish results</td>
</tr>
<tr>
<td>Millington and Quirk [1961]</td>
<td>(D_s = D_\Phi \beta S)</td>
<td>Sand</td>
</tr>
<tr>
<td>Currie [1970]</td>
<td>(D_s = D_\Phi \beta S)</td>
<td>Undisturbed and repacked soils. Glys with clay content from 10.3 to 51.1%</td>
</tr>
<tr>
<td>Lai et al. [1976]</td>
<td>(D_s = D_\Phi \beta S)</td>
<td>Undisturbed and repacked soils. Glys with clay content from 10.3 to 51.1%</td>
</tr>
<tr>
<td>Sadeghi et al. [1989]</td>
<td>(D_s = D_\Phi \beta S)</td>
<td>Silty clay loam soils</td>
</tr>
<tr>
<td>Xu et al. [1992]</td>
<td>(D_s = D_\Phi \beta S)</td>
<td>Undisturbed and repacked soils. Glys with clay content from 10.3 to 51.1%</td>
</tr>
<tr>
<td>Moldrup et al. [1997]</td>
<td>(D_s = D_\Phi \beta S)</td>
<td>Silty clay loam soils</td>
</tr>
<tr>
<td>Moldrup et al. [1999]</td>
<td>(D_s = D_\Phi \beta S)</td>
<td>Undisturbed and repacked soils. Glys with clay content from 10.3 to 51.1%</td>
</tr>
<tr>
<td>Jabro et al. [2012]</td>
<td>(D_s = D_\Phi \beta S)</td>
<td>Sandy loam</td>
</tr>
<tr>
<td>Ghanbarian-Alavijeh and Hunt [2012]</td>
<td>(D_s = D_\Phi \beta S)</td>
<td>Repacked soils ranged from 6 to 54% clay sands</td>
</tr>
<tr>
<td>Sánchez-Cañete [2016] Chamber model</td>
<td>(k_i = D_\Phi 11.62 \theta_a^{0.035})</td>
<td>Loamy sand</td>
</tr>
</tbody>
</table>

\(D_s\) is the CO\textsubscript{2} diffusion coefficient, \(D_\Phi\) is the diffusion coefficient of the CO\textsubscript{2} in free air, \(k_i\) is the CO\textsubscript{2} transfer coefficient, \(\Phi\) is the soil porosity, \(\theta_a\) is the soil porosity \((\Phi - \text{soil water content})\), \(\beta = 2.9\) is for sandy and clayey soils, \(S = 0.948\) is the percent of mineral soil with particle size > 2 \(\mu\text{m}\), and \(\beta_2 = 0.1\Phi\) is the critical value for percolation in the porous medium.
content \( (\theta; \text{cm}^3 \text{cm}^{-3}) \), \( r \) is the distance from the point source \((m)\), \( f_a \) is the fraction of the injected mass of SF$_6$ conserved in the soil air \((f_a = 1)\), \( t_{\text{max}} \) is the time of the maximum SF$_6$ concentration \((s)\), and \( D_{a,i} \) is the diffusion coefficient of CO$_2$ in free air \((m^2 \text{s}^{-1})\). \( \Phi \) was calculated from soil bulk density \((\rho_b)\) and particle density \((\rho_d)\) data as \( \Phi = 1 - (\rho_d/\rho_b) \), resulting in 0.38 cm$^3$ cm$^{-3}$ for our site. \( D_{\text{SF6}} \) is the diffusion coefficient of the SF$_6$ in free air \((m^2 \text{s}^{-1})\), both calculated following Jones [1992]:

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

\[
D_{\text{SF6}} = D_{\text{SF6,0}} \left( \frac{T}{T_0} \right)^{1.75} \left( \frac{P}{P_0} \right) \quad (6)
\]

where \( D_{a,0} \) is 1.47*10$^{-5}$ m$^2$ s$^{-1}$, \( D_{\text{SF6,0}} \) is 0.89*10$^{-5}$ m$^2$ s$^{-1}$, \( T_0 \) is 293.15 K, \( P_0 \) is 101,325 Pa, and \( T \) and \( P \) are the temperature \((K)\) and pressure \((Pa)\), respectively. Through equation (4), the diffusion coefficients for the layer 10–20 cm and the layer 5–20 cm were obtained, \( D_{10-20} \) and \( D_{15-20} \) respectively. \( D_5 \) from 0 to 10 cm \((D_{0-10})\) was calculated by

\[
D_{0-10} = \left( \frac{D_{15-20} - D_{20-10}}{\widehat{\rho}_i} \right) \widehat{\rho}_x \quad (7)
\]

where \( \widehat{\rho}_i \) is the difference between the distances from the point source and the sampling tubes \((m)\) and \( \widehat{\rho}_x \) is the soil layer thickness \((m; 0.1 \text{ in our case})\).

### 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 \((y = D_s ax^b)\) of the soil air porosity \((\theta)\), where \( y \) is the \( D_s \) or \( k_s \), \( D_s \) is the diffusion coefficient of CO$_2$ in free air \((m^2 \text{s}^{-1})\), \( x \) is \( \theta \), 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 (equation (3)) and (2) the SF$_6$ model based on the \( D_s \) obtained from the five campaigns (equation (4)). Four additional \( k_s \) models were obtained using shorter, subbed monitoring periods based on two rain pulses at the beginning and end of the summer rainy season (2–22 July and 23 September to 14 October). Two of these four additional models were obtained using all the variables monitored continuously at the maximum frequency (every 2 h, July pulse and September pulse), and the other two models only used one daily measurement at 10:00 A.M. during these pulse periods (daily July and daily September). The time of 10:00 A.M. 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 \( F_{\text{soil}} \) (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 \( F_{\text{soil}} \) estimates due to the different sampling strategies.

### 3. Results

The \( F_{\text{soil}} \) and CO$_2$ molar fraction \((\chi_c)\) 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°C, a maximum in July (38.5°C), and minimum in January (4.3°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 \( \chi_c \) 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 \( \chi_c \) 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 very 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 2 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 1 year of near-continuous data, we found very large differences in the cumulative \( F_{\text{soil}} \) 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 SF₆ model 
CO₂ 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 CO₂ flux by 55% to 361% 
(222 g C m⁻² to 75 g C m⁻², respectively).

Four CO₂ transfer models (kₛ) derived from short monitoring periods around two rain pulses at the beginning 
and end of the monsoon season (2 July and 23 September; 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 Fₙₙ obtained from the two kₛ models obtained using all the variables monitored every 2 h (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) repre-
sented 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 Fₙₙ and the 
cumulative Fₙₙ estimated by the other Dₛ and kₛ models are shown in the Figure S1 in the supporting infor-
mation. We assumed a 10% uncertainty in the SF₆ injector-sampling distance, and this assumption resulted in 
a cumulative CO₂ efflux that falls within the range of measured soil effluxes (overlapping shadow areas in 
Figure 3b). Considering all kₛ model estimates, only the SF₆ model and one 
Ds model [Xu et al., 1992] pro-
duced estimates that were within the range of the chamber CO₂ efflux measurements.

Table 2. Equations for the Derived CO₂ Transfer Modelsa

<table>
<thead>
<tr>
<th>Model</th>
<th>Equations</th>
<th>R²</th>
<th>RMSE</th>
<th>Samples</th>
<th>F Value</th>
<th>p Value</th>
<th>p Values Coeff. 1–2</th>
<th>Range θₐ</th>
<th>RMSE Validation Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chamber model</td>
<td>kₛ = Dₛ1.162θₐ0.05</td>
<td>0.24</td>
<td>0.08</td>
<td>4,380</td>
<td>28,790</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.23–0.33</td>
<td>-</td>
</tr>
<tr>
<td>SF₆ model</td>
<td>kₛ = Dₛ4.97θₐ0.56</td>
<td>0.85</td>
<td>0.02</td>
<td>5</td>
<td>451</td>
<td>&lt;0.01</td>
<td>0.026, 0.026</td>
<td>0.26–0.32</td>
<td>-</td>
</tr>
<tr>
<td>July pulse</td>
<td>kₛ = Dₛ8.71θₐ0.84</td>
<td>0.23</td>
<td>0.05</td>
<td>240</td>
<td>877</td>
<td>&lt;0.01</td>
<td>0.016, &lt;0.01</td>
<td>0.28–0.32</td>
<td>0.08</td>
</tr>
<tr>
<td>Daily July</td>
<td>kₛ = Dₛ5.45θₐ0.49</td>
<td>0.41</td>
<td>0.03</td>
<td>20</td>
<td>3,724</td>
<td>&lt;0.01</td>
<td>0.236, &lt;0.01</td>
<td>0.28–0.32</td>
<td>0.08</td>
</tr>
<tr>
<td>September pulse</td>
<td>kₛ = Dₛ4.14θₐ0.24</td>
<td>0.51</td>
<td>0.03</td>
<td>264</td>
<td>926</td>
<td>&lt;0.01</td>
<td>&lt;0.01, &lt;0.01</td>
<td>0.26–0.32</td>
<td>0.09</td>
</tr>
<tr>
<td>Daily September</td>
<td>kₛ = Dₛ4.73θₐ0.32</td>
<td>0.56</td>
<td>0.03</td>
<td>22</td>
<td>10,743</td>
<td>&lt;0.01</td>
<td>0.110, &lt;0.01</td>
<td>0.26–0.32</td>
<td>0.08</td>
</tr>
</tbody>
</table>

                      a Soil air porosity (θₐ = soil porosity – soil water content). Dₛ is the diffusion coefficient of the CO₂ in free air. kₛ is the soil CO₂ transfer coefficient. The coefficient of determination (R²), root-mean-square error (RMSE), number of samples, F statistic, p values, range of soil air porosity, and RMSE validated with the whole data-
base are also given.
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 $\pm 5\%$ 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 $7.5 \pm 5.4\%$ for one sample every 2 months, $5.5 \pm 4.1\%$ for one sample per month, $4.2 \pm 3.2\%$ for two samples per month, $3.7 \pm 2.7\%$ for three samples per month, and $3.3 \pm 2.5\%$ for four samples per month.

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 $\pm 10\%$ 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.

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 $\pm 5\%$ 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 $7.5 \pm 5.4\%$ for one sample every 2 months, $5.5 \pm 4.1\%$ for one sample per month, $4.2 \pm 3.2\%$ for two samples per month, $3.7 \pm 2.7\%$ for three samples per month, and $3.3 \pm 2.5\%$ for four samples per month.

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). The vertical dashed lines show the errors obtained with some previous models: Chamber model 0.6%, daily July 1.6%, and daily September 4.8%. Model error(%) = $\frac{|F_{soil,meas} - F_{soil,model}|}{F_{soil,meas}} \times 100$. 

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When the GM is applied, there is a lag between the daily maximum and minimum $F_{\text{soil}}$ obtained by the automatic chamber and the GM using the Chamber model (Figure 5). A cross-correlation analysis determined a 2 h lag based on surface temperature and 10 cm depth temperature, and this lag was applied to the $F_{\text{soil}}$ estimated by the GM. This improved the comparison of the subdaily measurements (Figure 5) with the coefficients of determination ($R^2$) for monthly averaged diurnal fluxes, where the $R^2$ between $F_{\text{soil}}$ 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 $F_{\text{soil}}$ and the Chamber model lagged 2 h. During the whole study period the coefficient of determination between the raw diurnal $F_{\text{soil}}$ 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 nondiffusive transport mechanisms were involved. To study the wind effect on $k_s$, the whole database was stratified, discerning between "windy days," days with daily mean of wind speed $>3.5 \text{ m s}^{-1}$, and "calm days" with daily mean of wind speed $<1.6 \text{ m s}^{-1}$, equivalent to 90th and 10th percentile, respectively. During windy days, the fitting between soil air porosity and $k_s$ was much poorer (standard error of the regression, $S = 0.049$; Figure 6) than during calm days ($S = 0.089$). The $k_s$ model obtained for windy days underestimated the cumulative $F_{\text{soil}}$ by 2.3% during the whole year; however, the $k_s$ model obtained for calm days overestimated the cumulative $F_{\text{soil}}$ by 6.7%.

**Figure 5.** Monthly average diurnal of soil CO2 efflux ($F_{\text{soil}}$) obtained with the automatic chamber (green), the Chamber model (blue), and the Chamber model lagged 2 h (black dashed line) during the months of June, July, and August.

**Figure 6.** Relative CO2 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 ($R^2$) are given from the fitting at a power function ($y = D_a \alpha x^\beta$).
4. Discussion

An accurate quantification of $F_{\text{soil}}$ 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 $F_{\text{soil}}$ 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 $F_{\text{soil}}$?

The most accurate long-term $F_{\text{soil}}$ 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 $F_{\text{soil}}$ measured by soil chambers. We found that published $D_k$ models and the in situ $D_k$ model that was obtained using the tracer injection technique did not result in very accurate cumulative $F_{\text{soil}}$ estimates; rather, the Chamber $k_f$ model showed the best agreement with the $F_{\text{soil}}$. At our experimental site, 93% (13 of 14) of published $D_k$ models used with the GM method produced unsuitable $F_{\text{soil}}$ estimates, as compared to our measurements with the automated chambers (Figure 3a). This result supports the need to determine $D_k$ in situ at any experimental site, as suggested by Pingintha et al. [2010] and Roland et al. [2015]. The most common way to determine $D_k$ 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 and 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 centimeters) 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 that 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 $D_k$ 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 $F_{\text{soil}}$ 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 $F_{\text{soil}}$ estimates between $D_k$ models and $k_f$ models (Figure 3) also could be due to the $k_f$ models implicitly accounting for the diffusive and nondiffusive transport and production processes of CO$_2$ in the soil between sampling depths, whereas $D_k$ models are subject to diffusion alone. When comparing both in situ gas transport models, the Chamber model implicitly accounted for the diffusive and nondiffusive 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$_2$ approximately 30 times higher than SF$_6$ [Wilhelm et al., 1977]), this contribution is usually neglected because diffusion of these gases in water is about 10,000 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 \(D_{soil}\) 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 \(\text{CO}_2\), \(\text{CH}_4\), \(\text{NO}_x\), \(\text{N}_2\text{O}\), \(\text{H}_2\text{S}\), and \(\text{SO}_2\) that may be both produced or consumed as they move through the soil matrix. We would expect \(\text{CO}_2\) production in the 0–10 cm layer, and for this reason, the SF6 model likely underestimated \(\text{CO}_2\) effluxes (Figure 3). Differences between SF6 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 to an underestimate of \(D_s\) from 0 to 10 cm. Second, the SF6 method was only carried out 5 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 \(\text{CO}_2\) production of this layer plays an important role in the

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 \(\text{CO}_2\) 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 A.M. 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 SF6 model and the published empirical diffusion models (Figure 3b). The slightly better estimation of cumulative \(F_{soil}\) in the models derived from one daily measurement than the models using continuous measurements over the same pulses is simply a coincidence due to chosen 10:00 A.M. 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 in the supporting information). The best cumulative \(F_{soil}\) estimations were derived from once daily samplings, resulting in a 0.8% overestimation (sampling at 04:00 A.M. during the July pulse) and a 1.2% underestimation (06:00 A.M., September pulse); the worst \(F_{soil}\) estimations resulted in a 17.3% underestimation (16:00 P.M., July) and a 15.4% underestimation (18:00 P.M., September). Windy days underestimated \(F_{soil}\) (Figure 6). For this reason, we believe that the improved \(F_{soil}\) estimations using predawn 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 \(\text{CO}_2\) 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 \(\text{CO}_2\) 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 Subdaily \(F_{soil}\) 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 subdaily scales. A schematic drawing of the diurnal patterns of temperature, soil \(\text{CO}_2\) 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 behavior [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 is, the greater the delay with respect to $F_{\text{soil}}$ at the surface is. 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 delay the $F_{\text{soil}}$ series. At our experimental site, the cross-correlation analysis resulted on a 2 h lag and after applying it, on the series of $F_{\text{soil}}$ obtained by the GM using the Chamber model, produced subdaily estimates in phase with the soil effluxes (Figure 5).

In contrast, Roland et al. [2015] found that none of their $F_{\text{soil}}$ models were able to suitably predict the $F_{\text{soil}}$ variations at the subdaily 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; Sanchez-Canete 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 nondiffusive 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 subdaily $F_{\text{soil}}$ and recommended that the focus should be placed on other factors affecting the CO$_2$ production. However, the failure in their simulated subdaily $F_{\text{soil}}$ 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 nondiffusive ones leads to several sources of error that may contribute to differences on $F_{\text{soil}}$ with respect to chamber measurements. Research on nondiffusive 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; Sanchez-Canete et al., 2011; Nachshon et al., 2012; Rey et al., 2012]. Nondiffusive 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; Sanchez-Canete 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 nondiffusive 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; Sanchez-Canete et al., 2013a]. All of these nondiffusive 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 $F_{\text{soil}}$ 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 flux networks [McFarlane et al., 2014]. At the ecosystem scale, the measurement of net ecosystem CO$_2$ exchange (NEE) can be partitioned into ecosystem respiration ($R_{\text{eco}}$) 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 ($R_{\text{eco}}$) and gross ecosystem production (GEP) [Barr et al., 2013]. Furthermore, $R_{\text{eco}}$ consists of a belowground
component, $F_{\text{soil}}$, and an aboveground component attributed to plant respiration. $F_{\text{soil}}$ 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 $F_{\text{soil}}$ 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 $F_{\text{soil}}$ is generally the largest flux contributing to $R_{\text{eco}}$, few studies have compared both fluxes. Reported estimates of the relative contribution of $F_{\text{soil}}$ to $R_{\text{eco}}$ range between 48% and 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 al. [2000] used continuous $F_{\text{soil}}$ measures during the whole year; the other authors obtained annual $F_{\text{soil}}$ from extrapolation of low-frequency measures using manual chambers. Clearly, the $F_{\text{soil}}$ contribution is strongly dependent on the ecosystem and we need to produce accurate long-term estimates of $F_{\text{soil}}$ across changing environmental conditions to improve our understanding of its contribution to $R_{\text{eco}}$.

5. Conclusions

An accurate depiction of CO$_2$ production and diffusion processes in soil is a key uncertainty in obtaining accurate measurements of $F_{\text{soil}}$. 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 $F_{\text{soil}}$ 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 nondiffusive 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 $F_{\text{soil}}$ (e.g., using a portable chamber) can result in an adequate gas transfer model that generates accurate $F_{\text{soil}}$ estimates. Therefore, we recommend that future $F_{\text{soil}}$ studies use a combination of the GM and targeted manual or automatic $F_{\text{soil}}$ chamber measurements to build the gas transfer model in situ and produce accurate long-term estimates of $F_{\text{soil}}$.

References


