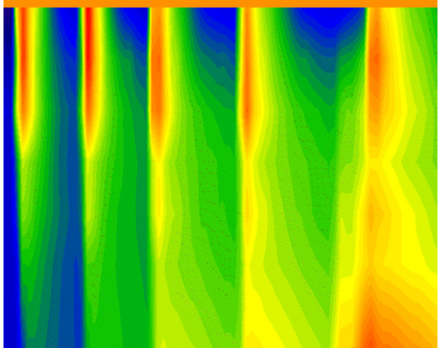
Published January 31, 2014

Original Research



Undetected shallow soil surface application of water can create a temporary reduction in the soil gas diffusion, overestimating gradient-based estimates of soil CO_2 efflux. Measured and modeled effects of soil temperature and water content on subsurface CO_2 concentration and surface efflux are presented using laboratory and field data.

Soil Surface Wetting Effects on Gradient-Based Estimates of Soil Carbon Dioxide Efflux

Jun Fan* and Scott B. Jones

The gradient method is widely used in conjunction with Fick's Law to estimate emissions of soil CO_2. This requires accurate estimation of the soil gas diffusion coefficient (D_P) and the CO_2 concentration gradient, typically from measured water content and CO_2 concentration. Shallow application of water via precipitation or irrigation causes a temporary reduction in the near-surface soil gas diffusion coefficient, which compromises gradient-based flux estimates when undetected by a water content sensor. Our objectives were to analyze the effects of soil surface wetting and temperature on CO_2 concentration and efflux using laboratory and field measurements and to compare four widely used models for estimating D_P. A laboratory test was conducted to determine the effects of water application on the soil CO_2 concentration and the CO_2 efflux calculated with the gradient method. The D_P parameter was very sensitive to the soil water content and was most reliably calculated using a power function model in a Millville silt loam field soil, while both power function and SAPHIR models were similarly reliable in a Kidman fine sandy loam laboratory test. A single CO_2 sensor at a depth of 5 cm with water content monitored at 2.5 cm provided reasonable estimates of the soil CO_2 efflux validated with an automated chamber. We found that under most conditions, the CO_2 concentration gradient in the soil profile is a reasonable estimator of CO_2 flux when measurements of the soil water content and known porosity values are used to estimate the gas diffusion coefficient. However, shallow wetting events require improved monitoring of spatial and temporal changes near the surface or appropriate modeling of hydrodynamics there.

Abbreviations: DOY, Day of the Year; EF, Nash–Sutcliffe efficiency coefficient; SAPHIR, Soil Air Phase Individual Resistances; SWLR, substrate-dependent water-induced linear reduction.

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Vadose Zone J.
doi:10.2136/vzj2013.07.0124
Received 8 July 2013.

Soil respiration and soil surface CO_2 efflux have been studied widely. However, further research into spatiotemporal variations in these parameters and new methods for their measurement are still needed to improve our understanding of the mechanisms affecting gas dynamics and to accurately quantify their variation during soil respiration. Soil CO_2 fluxes have been studied extensively using diverse methods, although it is widely accepted that chamber-based methods are the most appropriate of the available options for use in field studies (Rochette and Hutchinson, 2005). Methods of this kind can be used to investigate spatial variability using portable surface chambers, and the development of automated chamber systems has made it possible to acquire measurements on a continuous basis to study temporal and spatial variations in soil respiration (Bauer et al., 2011).

Many of the previous studies on this topic were based on manual CO_2 soil chamber measurements that often failed to capture fluxes from consecutive days, night measurements, and precipitation events (Vargas et al., 2010). New techniques for the continuous monitoring of soil gas efflux have been developed on an ongoing basis (Risk et al., 2011) to meet the need for methods with high accuracy and low cost. Moreover, the creation of process models such as that described by Pumpanen et al. (2008) or Hydrus-1D (Fan et al., 2012) has been encouraged to improve our understanding of CO_2 effluxes and to facilitate the quantitative interpretation of experimental data. However, a critical mass of continuously measured data will be required to validate these new methods and identify their limitations. In situ gradient-based methods for monitoring soil respiration have recently been improved and hold considerable promise as tools for assessing soil respiration. They enable long-term monitoring of CO_2 output without substantial disturbance of natural CO_2 concentrations and can thus provide detailed information on subsurface CO_2 dynamics (Tang et al., 2003, 2005; Liang et al., 2004; Turcu et al., 2005; Jassal et al., 2005; Yasuda et al., 2008; Maier et al., 2010; Arevalo et al., 2010).

The key parameters that affect the data obtained using gradient approaches are the CO_2 concentration and the soil gas diffusion coefficient (D_p). Many methods have been proposed for estimating D_p (Millington and Quirk, 1961; Thorbjørn et al., 2008; Moldrup et al., 2013). Generally, D_p is a function of the soil water content because gas transport occurs primarily through air-filled soil pores. Highly structured soils can complicate the water content–gas diffusion relationship (Koehler et al., 2010), often exhibiting dual pore systems leading to bimodal diffusion coefficients (Blonquist et al., 2006; Chamindu Deepagoda et al., 2012). Diffusivity–water content relationships in the field were significantly different from those in the laboratory because of soil disturbance or moisture content levels, which cause discrepancies using diffusivity models (Risk et al., 2008). Furthermore, brief periods of precipitation or irrigation pulses can temporarily increase the water content of the near-surface layer, thereby reducing D_p without affecting the soil water content (and thus the D_p value) for the soil layers just below the wetted zone, potentially undetected by water content sensors buried there. Such events may therefore trigger soil respiration in the near-surface zone without impacting respiration activity at greater depths. The usefulness of Fick's Law for predicting soil surface CO_2 effluxes is based on the assumptions of quasi-steady-state conditions and also depends on how well the measured CO_2 concentration gradient represents the driving concentration gradient for CO_2 efflux across the plane of the soil surface (Billings et al., 1998).

DeSutter et al. (2008) used three methods (a curve-fitting approach, linear regression, and finite difference analysis between discrete depths) to estimate the vertical CO_2 concentration gradient in soil based on measured CO_2 concentrations and estimates of soil water content. These methods for determining the CO_2 gradient were used in conjunction with three methods for determining D_p to estimate the CO_2 efflux using Fick's Law. When linear regression was used to compute the slope of the vertical concentration gradients, the flux estimates obtained for periods during and immediately after rainfall events were unreliable because during such periods, the concentration gradient and diffusivity both become very nonlinear. Pumpanen et al. (2008) also found that gradient-based CO_2 flux estimates of this type are useful only during periods when the soil water content is not changing rapidly. Tang et al. (2003) obtained good agreement between the results obtained using the gradient method and chamber measurements in cases where no precipitation occurred during the measured period. Pingintha et al. (2010) reported that the gradient method can yield acceptable results if an appropriate relative gas diffusion coefficient is selected in cases where no precipitation events are involved. However, the distribution of brief and extended precipitation events is likely to affect the relative magnitude of the pulsed CO_2 flux and also its direction (Deng et al., 2011). Unlike the relationship between soil temperature and respiration, the influence of soil moisture on soil C stocks has received relatively little attention despite its important role in regulating soil respiration (Liu et al., 2009). Therefore, Falloon et al. (2011) argued that further research is needed to obtain a better understanding of the soil moisture–respiration relationship.

One of the more challenging aspects of implementing gradient-based gas flux measurements is dealing with the impact of short-term, near-surface wetting events. During such events, the initial wetting of the surface and topmost soil layers is followed by a gradual downward redistribution of the water. However, the high water content of the upper soil layers during the event and its immediate aftermath cause significant short-term reductions in their gas diffusivity values, which are underestimated by soil moisture sensors located at greater depths. We therefore suggest that most soil moisture measurement efforts do not place adequate emphasis on monitoring changes in the moisture level, temperature, and nutrient levels in the near-surface layer (i.e., the layer at depths of <1 cm) that are associated with wetting events, resulting in a general overestimation of gas fluxes.

We conducted experiments to obtain a better understanding of the relationship between soil wetting depth and CO_2 efflux. Our objectives were to analyze the effects of soil surface water application in addition to soil temperature on the subsurface concentration and surface efflux of CO_2 using laboratory and field measurements. We also wanted to compare four widely used models for estimating soil gas diffusion coefficients comparing gradient-based estimates of efflux with chamber-based values. While gradient-based methods for CO_2 and other soil gas emissions have been commonly applied in the field, few have paid attention to the near-surface wetting impacts on those gas flux estimates. In this study, we focused on the effects of surface water application on the subsurface soil CO_2 concentration and resulting CO_2 flux estimates to point out errors associated with these conditions. The gradient-based results obtained were compared with those from the surface chamber methods in the laboratory. We also evaluated the chamber method in the field and compared the results using four different diffusion coefficient models.

Materials and Methods

Theoretical Considerations

The surface CO_2 flux (F, μmol m^{-2} s^{-1}) from the soil was computed using Fick's first law of gas diffusion, which depends on the measured mole fraction of CO_2 in the soil, C (μmol mol^{-1}), at a given sensor depth, z (m), and that at the surface, assuming a constant atmospheric CO_2 concentration of $C = 380$ μmol mol^{-1} and a depth of $z = 0$:

$$F = -D_P \frac{dC}{dz} \approx -D_P \frac{\Delta C}{\Delta z} \qquad [1]$$

While a constant atmospheric CO_2 concentration was assumed for convenience, it should be noted that this assumption is not always valid. However, the variation is generally minor and has a minor effect on the results obtained. The water content within the soil layer was measured to provide information on the soil gas diffusivity, D_P (m^2 s^{-1}), which was estimated using four different empirical models. The soil layer thickness is Δz (m), and ΔC (μmol m^{-3}) is the difference in the gas concentrations of the two soil layers being compared. The first model tested for calculating D_P was

$$D_P = D_0 \varepsilon^X \qquad [2]$$

where ε is the air-filled porosity of the soil (cm^3 cm^{-3}) and D_0 (m^2 s^{-1}) is the diffusivity of CO_2 in free air. This function was first suggested by Buckingham (1904), who stated that the empirical parameter X can vary between 2 and 2.5 (Moldrup et al., 2005).

The second tested model is known as the Soil Air Phase Individual Resistances (SAPHIR) model and has the following form:

$$D_P = D_0 \varepsilon^{1+p+w\theta} \qquad [3]$$

where p is a particle shape factor that takes a value between 0 and 1, w is a water-blockage factor that takes a value between 1 and 7 (Thorbjørn et al., 2008), and θ (cm^3 cm^{-3}) is the average soil water content for the soil layer in question.

The third model tested was that of Millington and Quirk (1961):

$$D_P = D_0 \frac{\varepsilon^{10/3}}{\phi^2} \qquad [4]$$

where ϕ is the total soil porosity (cm^3 cm^{-3}).

The fourth tested model, referred to as the structure-dependent water-induced linear reduction (SWLR) model, has the following form:

$$D_P = D_0 \varepsilon^{(1+C_m\phi)} \left(\frac{\varepsilon}{\phi}\right) \qquad [5]$$

where C_m is the media complexity factor, for which Moldrup et al. (2013) recommended $C_m = 1$ for repacked soil conditions and $C_m = 2.1$ for intact soil conditions. The total porosity of the soil was computed as

$$\phi = 1 - \frac{\rho_b}{\rho_m} = \varepsilon + \theta \qquad [6]$$

where ρ_b is the soil's bulk density (g cm^{-3}) and ρ_m is the density of the solid particles within the soil (i.e., 2.65 g cm^{-3}). The effects of temperature and pressure on D_0 can be corrected for using the following expression:

$$D_0 = D_s \left(\frac{T}{T_0}\right)^{1.75} \left(\frac{P_0}{P}\right) \qquad [7]$$

where T is the temperature (K), P is the air pressure (Pa), and D_s is a reference value of D_0 at T_0 (293.15 K) and P_0 (1.013×10^5 Pa); for CO_2, it is equal to 1.47×10^{-5} m^2 s^{-1} (Jones, 1992).

Laboratory Soil Column Experiments

A soil column uniformly packed to a bulk density of 1.48 g cm^{-3} with Kidman fine sandy loam soil (a coarse-loamy, mixed, superactive, mesic Calcic Haploxeroll) was used to study the relationship between soil water dynamics and CO_2 efflux in the laboratory (Fig. 1). The soil texture is listed in Table 1. A similar system was used by Turcu et al. (2005) for preliminary testing of the gradient method. Five CO_2 sensors (GMM 220, Vaisala Corp.) and thermocouples were placed at depths of 5, 10, 15, 30, and 45 cm beneath the soil surface, and time domain reflectometry (TDR) sensors for measuring the water content were installed at depths

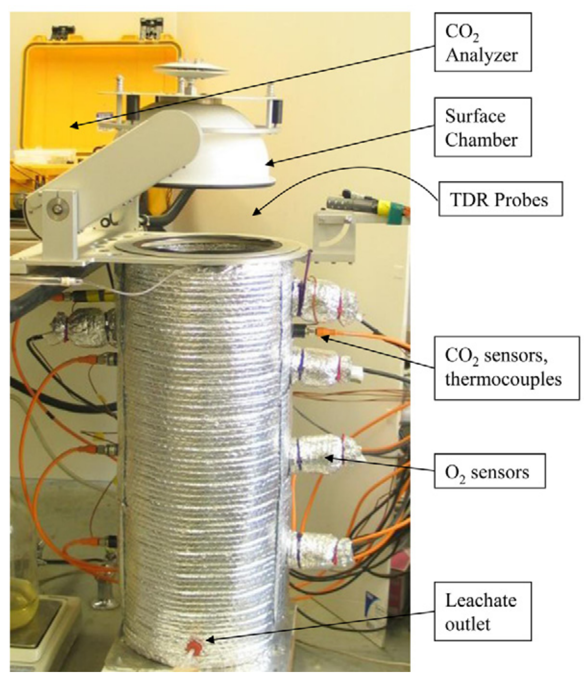

Fig. 1. The laboratory experimental setup showing the surface CO_2 chamber along with five subsurface CO_2 sensors and thermocouples located at depths of 5, 10, 15, 30, and 45 cm beneath the Kidman fine sandy loam soil surface and seven time domain reflectometry probes (at back of column) for water content determination installed at depths of 2.5, 7.5, 12.5, 17.5, 22.5, 27.5, and 37.5 cm. Leachate was collected from a suction lysimeter located at the bottom of the column.

Table 1. Physical characteristics of soils used in the laboratory (Kidman fine sandy loam) and in the field (Millville silt loam) studies.

Soil	Sand	Silt	Clay	Bulk density	Organic matter	Soil porosity
	———	% ———		$g\ cm^{-3}$	%	
Kidman fine sandy loam	84	8	8	1.48	1.0	0.44
Millville silt loam	24	60	16	1.37	2.5	0.48

of 2.5, 7.5, 12.5, 17.5, 22.5, 27.5, and 37.5 cm. In addition, a pressure sensor (SB-100, Apogee Instrument Inc.), a thermocouple, and a GMM222 CO_2 sensor (range 0–2000 μmol $mol^{-1} \pm 1.5\%$, reading accuracy $\pm 2\%$) were positioned near the column's surface to measure the ambient air pressure, temperature, and CO_2 concentration in the laboratory. The TDR waveforms were measured using a TDR100 sensor connected to an SDMX50 multiplexer (Campbell Scientific). The TDR100 and other sensors mentioned above were connected to a CR1000 datalogger (Campbell Scientific) for data retrieval and storage. A LI-COR long-term CO_2 flux chamber (LI-8100-101) was used to measure the surface CO_2 flux from the soil column on an hourly basis, and the column's initial soil water content was 0.03 $cm^3\ cm^{-3}$. The LI-8100 instrument is an absolute, nondispersive infrared (NDIR) gas analyzer with a measurement range of 0 to 3000 μmol mol^{-1} and a reading accuracy of 1.5%. Surface irrigation was applied by dripping an amount of water equivalent to 10 or 50 mm of precipitation onto the soil surface at defined intervals. Nutrition (1 g of glucose) was added to the irrigation water on Days 46 and 69 to enhance the rate of respiration by the soil microorganisms in the column to modify the CO_2 concentration in the soil profile. Starting on Day 142, 200 cm water head suction was applied to the bottom of the soil column to withdraw leachate-containing water. This was done to maintain the porosity of the soil and avoid saturation of the lower parts of the column.

Field Test

The field study was conducted in Logan, UT, at the Utah Agricultural Experiment Station's Greenville Farm (41°46′1″ N and 111°48′40″ W). The farm receives a mean annual precipitation of 422 mm and its mean annual temperature is 8.6°C. The site thus has a xeric soil moisture regime and a mesic soil temperature regime. The soil at the Greenville Farm is of the Millville series (coarse-silty, carbonatic, mesic Typic Haploxerolls), and its pH is 8.2 because of the wide dissemination of $CaCO_3$ at the site (Table 1). The study was conducted within an established 10- by 10-m pasture research plot with automated irrigation and TDR probes and temperature sensors installed. Both chamber and gradient methods were used to determine the CO_2 efflux within the plot. The soil water content was measured with TDR probes at depths of 5, 10, and 15 cm using a Tektronix 1502B instrument with the WinTDR software package. The soil temperature was measured using thermocouples located at the same depths.

Carbon Dioxide Subsurface Flux Measurement: The Vaisala Probe Calculation Method

Soil subsurface CO_2 concentrations were measured using a GMM222 series CO_2 sensor (Vaisala Corp.), an absolute NDIR gas analyzer that was calibrated for CO_2 concentrations of 0 to 1%. The 0- to 2.5-V output was recorded with a CR1000 datalogger (Campbell Scientific), and the barometric pressure was measured using an SB-100 pressure sensor (Apogee Instrument Inc.). Two GMP222 analyzers were inserted vertically into 1.9-cm (3/4 inch) polyvinyl chloride sleeves, one to a depth of 5 cm and the other to a depth of 15 cm. Pressure and temperature compensation factors (Tang et al., 2003) were computed using

$$C_c = C_m - C_T - C_P \quad [8]$$

where C is the CO_2 concentration in μmol mol^{-1}, and the subscripts c, m, T, and P stand for corrected, measured, temperature correction, and pressure correction;

$$C_P = K_P\left(\frac{P-101.3}{101.3}\right) \quad [9]$$

where P is the measured pressure (Pa), and the pressure coefficient K_P is equal to $1.38C_m$;

$$C_T = 14{,}000\left(K_T - K_T^2\right)\left(\frac{25-T_c}{25}\right) \quad [10]$$

where T_c is the temperature (°C), and the temperature coefficient is given by

$$K_T = A_0 + A_1C_m + A_2C_m^2 + A_3C_m^3 \quad [11]$$

where $A_0 = 3 \times 10^{-3}$, $A_1 = 1.2 \times 10^{-5}$, $A_2 = -1.25 \times 10^{-9}$, and $A_3 = 6 \times 10^{-14}$.

Carbon Dioxide Surface Flux Measurement: The LI-COR Chamber Method

The soil surface CO_2 flux was measured directly at 60-min intervals using the LI-8100-101 long-term CO_2 chamber (LI-COR). The chamber closure duration was 120 s during flux measurement, and a linear model was used to calculate the CO_2 flux values.

Model Performance Evaluation and Parameter Fitting

The Nash–Sutcliffe model efficiency coefficient (EF) was used to assess the predictive power of the gradient method, and the root mean square error (RMSE), a commonly used criterion for model validation, was used to quantify the agreement between the chamber measurements and gradient estimates. The gradient results were inverted to identify appropriate parameters, and the calculated RMSE was used to identify optimal parameters for use with the empirical soil gas diffusivity models.

Results and Discussion

In the following we present soil CO_2 flux results using both gradient-based estimates as well as closed-chamber measurements. These were made first in a laboratory column experiment performed in a Kidman fine sandy loam soil, followed by a field experiment conducted in a Millville silt loam soil.

Laboratory Soil Column Experiment

Surface Wetting Effects on Subsurface Carbon Dioxide Concentration Dynamics

Periodic surface wetting events of 10 and 50 mm were applied to the initially dry soil column surface. Figure 2 shows how the soil water content varied during the experiment, demonstrating the progress of the wetting front as a function of time. The CO_2 concentration increased with depth in parallel with the movement of the wetting front following each wetting event. The temperature profile within the column was relatively stable; the mean temperature was 25.1°C and varied from 20.4 to 29.3°C, with periodic fluctuations when the laboratory air temperature increased. The standard variation was 1.5°C in the whole column during the experimental period. During the first 25 d of the experiment, the lower levels of the column remained relatively dry despite frequent applications of water, and there appeared to be a lower boundary beyond which the wetting front did not progress. Under these conditions, there was a relatively uniform increase in the CO_2 concentration throughout the column profile due to the low gas diffusivity near the column's surface. For example, after 10 d, the wetting front had reached a depth of approximately 20 cm but the CO_2 concentration remained uniform down to a depth of 45 cm. Once the wetting front had reached the depth of the lowest sensor, no additional water was applied during the next 20 d, resulting in the formation of an

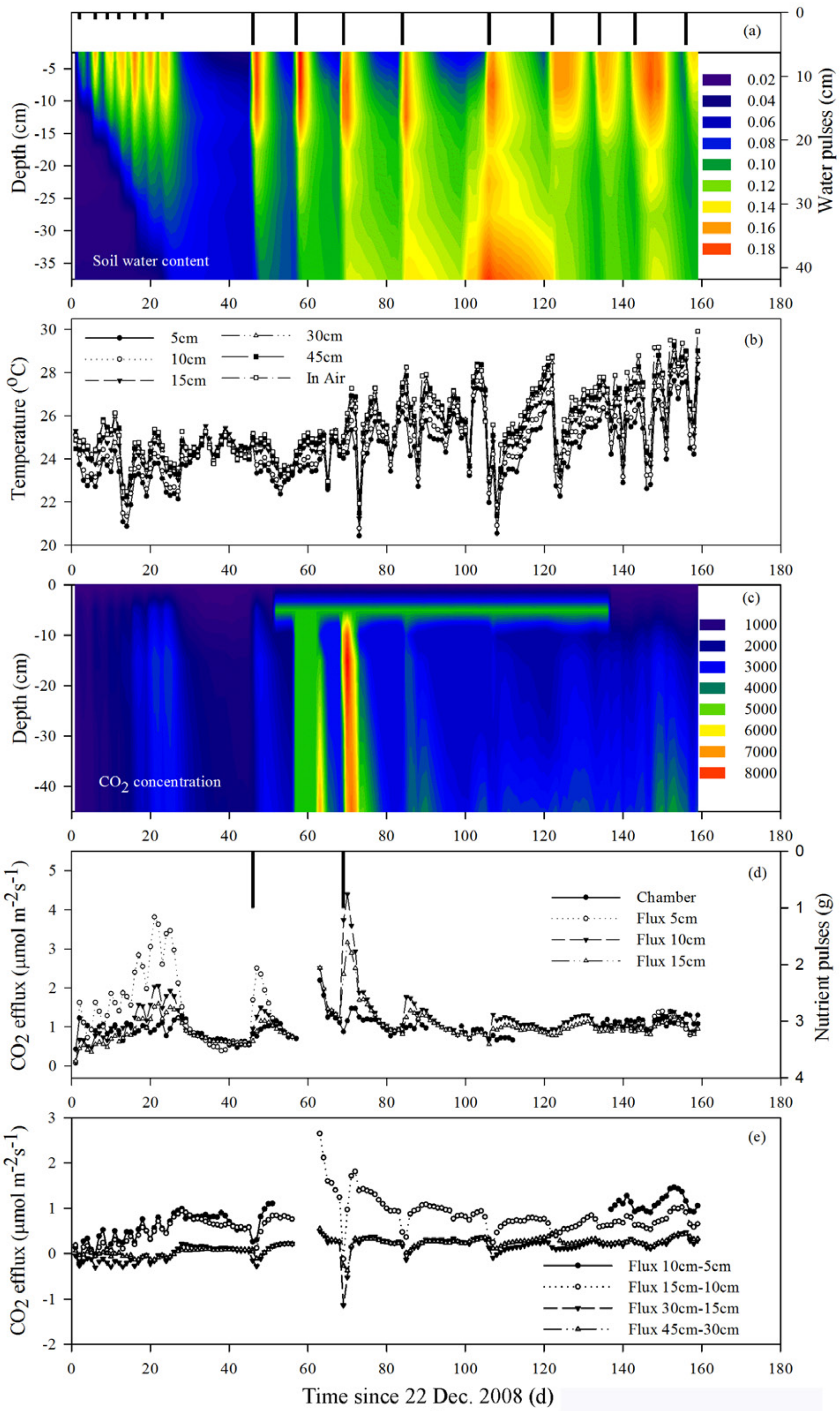

Fig. 2. Temporally varying soil water content profiles (cm^3 cm^{-3}) interpolated between seven time domain reflectometry sampling depths, showing (a) the timing of the water pulses, (b) soil temperature profiles, (c) soil CO_2 concentration profiles (μmol mol^{-1}) interpolated between five subsurface CO_2 sensor locations in addition to one measurement in air, (d) soil CO_2 efflux profiles estimated using different methods, and (e) CO_2 fluxes at different soil depths. The CO_2 flux was calculated using a gradient-based approach using the ambient CO_2 concentration in the laboratory and the measured CO_2 concentrations at depths of 5, 10, and 15 cm using a power model for the soil gas diffusion coefficient D_p where the empirical parameter X = 1.95 (Moldrup et al., 2005). Nutrient solutions were applied to the soil surface on Days 46 and 69.

almost linear CO_2 concentration gradient throughout the column profile. Once the water had reached the deep layers of the soil, it became possible to change the soil's water content profile, meaning that the upper soil layers exhibited greater variations in CO_2 concentration than did the deeper layers due to the periodic application of additional water and evaporation. The CO_2 concentration gradients were always created by the application of additional water pulses (Fig. 2c), and deeper layers had greater CO_2 concentrations than the upper layers. The average CO_2 concentrations at depths of 5, 10, 15, 30, and 45 cm were 1223.5, 1850.0, 2314.1, 2573.4, and 2947.2 μmol mol^{-1}, respectively. The ambient CO_2 concentration in the laboratory was relatively stable, having a mean value of 445.1 μmol mol^{-1} CO_2 during the experimental period (Fig. 2c). The application of nutrient pulses had noticeable effects on the CO_2 concentration profile. The second nutrient pulse produced particularly high CO_2 concentrations because the soil moisture content during the period immediately before the pulse was much greater than had been the case before the first nutrient pulse.

Comparison of Gradient-Based and Surface Chamber Carbon Dioxide Fluxes

Figure 2d shows the surface efflux values calculated using the gradient method based on the ambient CO_2 concentration in the laboratory and the CO_2 concentrations measured at different soil depths. The soil water content had a dramatic impact on the diffusion coefficients when Fick's Law was used to calculate the gas efflux from the soil surface. The gradient method consistently overestimated the CO_2 efflux during and immediately after the application of water to the soil surface (Fig. 2d and 3). Therefore, the CO_2 fluxes calculated using the gradient method during periods of water redistribution and periods when suction was applied to the column were replaced with values obtained from chamber measurements when fitting the gas diffusivity parameters. Table 2 shows that the SAPHIR model yielded the most accurate results and that the power model with $X = 1.95$ and the SWLR model with $C_m = 1.5$ gave comparable results after parameter fitting. However, the Millington and Quirk (1961) model performed relatively poorly. Myklebust et al. (2008) previously reported that there were substantial differences between the results obtained using the gradient and chamber methods in plots planted with an annual semiarid grass, *Bromus tectorum* L., during and immediately after periods of summer rainfall and winter snow.

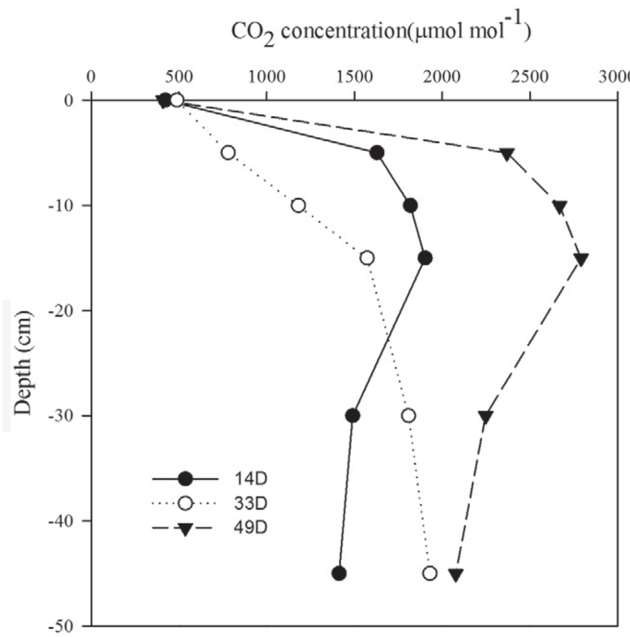

Fig. 3. Carbon dioxide concentration profiles in the Kidman fine sandy loam soil column on Days 14, 33, and 49, illustrating the dynamics of subsurface CO_2 concentration.

The air temperature in the laboratory setting was relatively stable, suggesting that the observed variation in the production and transport of CO_2 within the soil column was primarily due to the periodic applications of water and the resulting changes in the soil's diffusion coefficient. In fact, the laboratory temperature had little effect on the CO_2 concentration and CO_2 efflux observed during the study period (Fig. 2). The gradient method based on the differences between the CO_2 concentrations at depths of 0 and 5 cm significantly overestimated the soil CO_2 efflux during periods when water was applied to the soil surface and especially in the aftermath of irrigation. This is probably due to temporary increases in the soil microbial activity (Fig. 2d). When the soil CO_2 concentration difference between depths of 0 and 10 or 0 and 15 cm was used in the Fick's Law calculations, the corresponding discrepancies were much less pronounced because the changes in the CO_2 concentration at deeper levels of the column were much less pronounced (Fig. 2d).

The gradient method significantly overestimated the CO_2 flux following the application of a nutrient-containing solution to the surface on Day 69 because in this case the CO_2 gradient increased significantly in parallel with the soil's water content. The CO_2 concentration increased with depth between 15 and 45 cm due to this

Table 2. Root mean squared error (RMSE) and Nash–Sutcliffe model efficiency coefficient (EF) values for the gradient and chamber methods using the power, Soil Air Phase Individual Resistances (SAPHIR), Millington and Quirk (1961) (MQ), and structure-dependent water-induced linear reduction (SWLR) models of gas diffusivity. The lower the RMSE, the better the model fit to the data. The closer the EF value is to 1, the more accurate the model is in describing the data. Italics indicate the lowest RMSE and largest EF values for each soil.

Parameter	Power	SAPHIR	MQ	SWLR
	Kidman fine sandy loam			
RMSE	*0.17*	*0.17*	0.22	0.18
EF	0.51	*0.52*	0.24	0.47
Fitting parameters	$X = 1.95$	$p = 0.83$, $w = 1.1$	13/4	$C_m = 1.5$
	Millville silt loam			
RMSE	*0.21*	0.29	0.48	0.34
EF	*0.88*	0.77	0.37	0.68
Fitting parameters	$X = 2.05$	$p = 0.83$, $w = 1.1$	10/3	$C_m = 1.3$

nutrient pulse, which stimulated microbial respiration and caused the establishment of an inverse concentration gradient deeper in the soil profile (Fig. 2e). The application of nutrients can thus have significant effects on increasing biochemical processes that occur within the soil, and the resulting increased fluxes may be underestimated by chamber-based methods because they can cause very rapid increases in the chamber pressure. An analysis of the gas fluxes within the soil profile showed that the surface CO_2 levels are sensitive to the production of CO_2 at depths of up to 15 cm (Fig. 2e). The 5-cm CO_2 sensor failed between Days 52 and 137, and so the 0- to 10-cm gradient was used when comparing the two methods for this period.

Criteria for Accepting Gradient-Based Estimates

With the exception of the initial wetting period (through Day 20) and the periods immediately following the application of a nutrient solution on Day 46 and 69, the CO_2 concentration increased with depth throughout the experimental period, as seen in Fig. 2c and 2d. Representative CO_2 concentration profiles are shown in Fig. 3, which clearly shows that the highest CO_2 concentrations on Days 14 and 49 occurred between 10 and 15 cm. In each of these cases, water had recently been applied, and a nutrient solution had been applied 3 d before Day 49, causing the peak surface CO_2 concentration to increase by almost 50% relative to that on Day 14.

Another consequence of having the highest CO_2 concentrations within the profile near the surface where wetting recently occurred is that it caused CO_2 to diffuse both upward and downward within the column, thereby increasing its concentration at depths where CO_2 production may not necessarily have increased. On Day 33, the peak concentration occurred at the bottom of the column. This may have been due to the drying of the near-surface layer, which would increase gas diffusion and thereby facilitate reductions in the near-surface CO_2 concentration, as seen in the Day 33 profile. It is notable that there was still a significant change in the slope of the concentration profile at depths of 10 to 15 cm for the Day 33 data. Short-term increases in the soil water content thus led to unstable CO_2 concentration profiles and also often caused the CO_2 efflux to be overestimated by the gradient method in cases where the volumetric water content was >0.10 $cm^3\ cm^{-3}$ within 5 to 7 d of treatment with 50 mm of water.

The results obtained with the gradient method were reasonably accurate in cases where at least 5 to 7 d had passed since the last application of water, even when the soil moisture content was >0.10 $cm^3\ cm^{-3}$ (Fig. 4), because under such conditions the CO_2 concentration did not vary so much with depth. Moreover, when suction was applied to remove water from the bottom of the column, the results obtained with the gradient method became more accurate because the water in the soil's pores was replaced with CO_2. Water pulses did not significantly affect the CO_2 concentration gradient during these periods (Fig. 2c) and so the gradient method did not

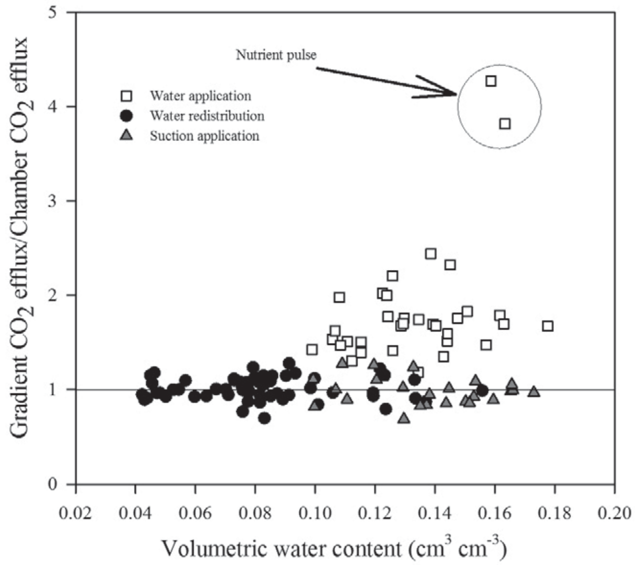

Fig. 4. Effects of the averaged volumetric water content at 2.5 and 7.5 cm on the correlation of the gradient method estimates of the CO_2 efflux vs. chamber estimates between 0 and 10 cm. The water application data points indicate the estimated CO_2 effluxes for periods of 5 to 7 d after the application of water, while the water redistribution data points indicate estimated CO_2 effluxes 5 to 7 d before the application of a water pulse. The suction application data points indicate the estimated CO_2 effluxes during periods when soil water was removed from the bottom of the column by applying 200 cm of water head suction.

significantly overestimate CO_2 efflux even when the soil water content was >0.10 $cm^3\ cm^{-3}$ (Fig. 4). Billings et al. (1998) also found that the 20-cm concentration gradient did not adequately represent the near-surface gradient, resulting in flux estimates that did not match experimental measurements in cases where the soil moisture content was >0.15 $cm^3\ cm^{-3}$ at a well-drained upland site. Other researchers have concluded that surface sealing and decreased D_s values (Jassal et al., 2005), along with increases in microbial activity due to the increased soil water content, may be responsible for errors in gradient-based estimates (DeSutter et al., 2008).

So while the gradient-based method provides reasonable estimates under most conditions in addition to providing valuable insight for understanding depth-dependent soil respiration processes, there are limitations to this method. It appears that use of the gradient-based method during and shortly after any wetting of the surface may be inappropriate because of the resulting increase in the CO_2 concentration within the upper soil layers. The wetting of the upper soil layers reduces gas diffusion upward, causing a buildup of CO_2 in the soil profile and a possible diffusion of CO_2 downward. The resulting concentration gradient is thus temporarily inflated and so the estimated diffusion coefficient, which depends on the measured near-surface water content, may or may not be accurately represented. To accurately compute diffusion coefficients based on water content measurements, one must have very accurate data acquired close to the surface where wetting begins. Most sensors are not capable of near-surface measurements and are generally located at greater depths (5–10 cm) below the surface. There are thus two important sources of error in such cases, namely the increased CO_2 concentration gradient and the lack of a "sensed" decrease in the diffusion coefficient due to the water content increase. These errors are illustrated in Fig. 4.

In summary, water and nutrient pulses reduced the agreement between the gradient- and chamber-based methods for CO_2 flux estimation. It is not always clear which of the two methods yields more reliable results because while the chamber method is expected to be the most reliable, it may underestimate CO_2 fluxes during periods when the CO_2 concentration increases rapidly. The gradient method clearly provides unique information regarding gas concentration and fluxes within the soil profile that are not detected using the chamber method.

Field Experiment

Water and Temperature Effects on Carbon Dioxide Dynamics

During the study period, the subsurface CO_2 concentrations were much greater than the atmospheric CO_2 concentration. The daily mean CO_2 concentrations at depths of 5 and 15 cm varied significantly (Fig. 5c); the trends in both cases were similar, but the fluctuations at 5 cm were much more pronounced and more sensitive to surface wetting from precipitation. The daily mean CO_2 concentration at a depth of 5 cm varied between 1548.1 and 4299.1 μmol mol^{-1}, with a 48-d average of 2256.3 μmol mol^{-1}. The corresponding values measured at a depth of 15 cm were 3065.3 to 5401.9 μmol mol^{-1} for the range and 4053.7 μmol mol^{-1}, respectively. The daily mean soil temperature at the three depths studied decreased from 21.9 to 3.7°C during the experimental period (Fig. 5b), but the variation in the temperature curve did not match that in the daily mean CO_2 concentration curves.

The rainfall volume significantly affected the soil water content, soil temperature, and soil CO_2 concentration. In keeping with the laboratory results, the rainfall had different effects on the soil CO_2 concentration at different depths because precipitation can both stimulate CO_2 production and reduce the air-filled porosity of the soil. The subsurface CO_2 concentration increases when its rate of surface dissipation decreases due to the filling of soil pores with water (Jassal et al., 2005; Daly et al., 2008). The volumetric water content of the soil at all three studied depths increased significantly following rainfall events that occurred on DOY 278, 279, and 307 (Fig. 5a). Precipitation also caused significant reductions in soil temperature. There were no distinct differences between the temperatures of the different soil layers or between their measured water contents (Fig. 5a and 5b). This means that there were no pronounced gradients of temperature or soil water content during the course of the field experiment.

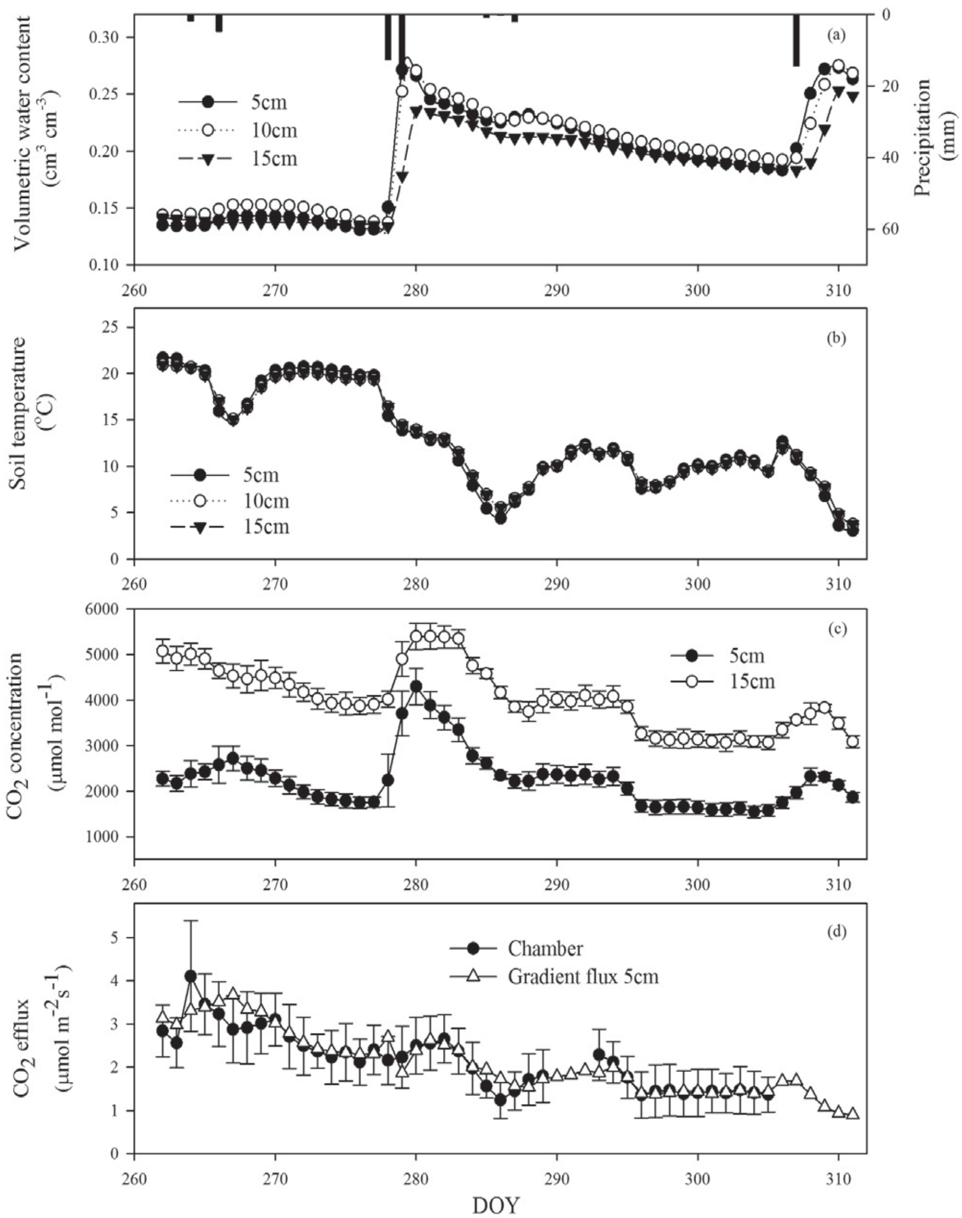

Fig. 5. The Millville silt loam field soil (a) CO_2 concentration, (b) temperature, and (c) water content at different depths, and (d) the daily average CO_2 efflux measured by the LI-8100 chamber method (DOY is Day of the Year).

Carbon Dioxide Efflux Measured by the Chamber Method and Its Correlation with Soil Temperatures

The soil CO_2 effluxes measured by the chamber method decreased from DOY 240 to DOY 310 and varied with soil temperature (Fig. 5b and 5d). Although measurements were unavailable for 5 d of the experimental period, the available data clearly show that precipitation events had complex effects on the measured CO_2 efflux. Small rainfall pulses can trigger soil CO_2 effluxes, and precipitation events did generally increase the soil CO_2 efflux in this study. However, the soil temperature decreased significantly on days with rainfall events, and the soil CO_2 efflux correlated strongly with soil temperature. Therefore, the stimulation of CO_2 efflux by rainwater may be counteracted by reductions in the soil temperature.

A measure of the rate of change of CO_2 production as a result of increasing the temperature by 10°C is known as the Q_{10} value. Estimates of Q_{10} using an exponential equation were fit to plots of the daily mean CO_2 efflux against the soil temperature at depths of 5 and 15 cm and found to be 1.98 and 1.87, respectively. The CO_2 flux from the 15-cm soil layer to the 5-cm layer exhibited an exponential dependence on the soil temperature at 15 cm; similar results have previously been reported by Hirano et al. (2003). This relationship was also observed when examining the data for depths of 5 and 10 cm because the measured temperatures at 5, 10, and 15 cm did not differ significantly.

Comparison of Four Diffusion Coefficient Models

Four models for estimating the soil gas diffusion coefficients were evaluated. As mentioned by other researchers (e.g., Risk et al., 2008; Pingintha et al., 2010), all of the calculated diffusion coefficients were affected significantly by the soil water content, and their values differed substantially from one another in some cases (Fig. 6). The estimated CO_2 effluxes obtained using D_p values calculated with the different models were compared with the experimental measurements, and the estimated CO_2 effluxes were fitted to the experimental curves to identify optimal parameter values for the power function (Eq. [2]) and SAPHIR (Eq. [3]) models (Table 2). The best results were obtained using the power function model with a value of 2.05 for the parameter X. This yielded an RMSE of 0.21 μmol m^{-2} s^{-1} and a maximal EF value of 0.88 when comparing the gradient and chamber fluxes. It was impossible to identify optimal values for the parameters used in the Millington and Quirk (1961) model (Eq. [4]) because it consistently and significantly under- or overestimated the D_p value at various soil water levels no matter what parameter values were used (Fig. 6). Tang et al. (2003) also found that this model consistently underestimated the CO_2 efflux. It thus appears that while the Millington and Quirk (1961) model may often provide reasonable predictions for more sandy soils with relatively low porosity, it is not reliable for all soil types and porosities (Moldrup et al., 2004). The SAPHIR model overestimated the D_p value (using parameter values of p = 0.83 and w = 1.1) when the soil water content was <0.17 cm^3 cm^{-3}. When this model was used with the gradient method and the resulting estimated CO_2 effluxes were compared with those determined by the chamber method, the RMSE and EF values were 0.29 μmol m^{-2} s^{-1} and 0.77, respectively. The SWLR model also overestimated the D_p value (using C_m = 1.3) when the soil water content was <0.17 cm^3 cm^{-3}. This clearly shows the importance of selecting an appropriate D_p model when using the gradient method. Pingintha et al. (2010) drew similar conclusions based on a comparison of six gas diffusion coefficient models.

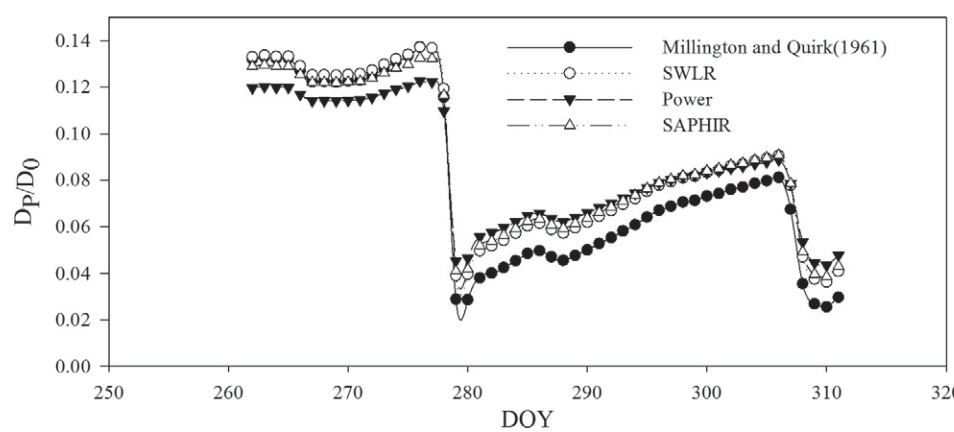

Fig. 6. Gas diffusion coefficient estimates in the Millville silt loam field soil obtained using the Millington and Quirk (1961), structure-dependent water-induced linear reduction (SWLR), power-law, and Soil Air Phase Individual Resistances (SAPHIR) analytical models (DOY is Day of the Year).

The estimated CO_2 effluxes obtained using two different D_p models (the power function model and SAPHIR) and those based on data from CO_2 sensors at various depths in conjunction with the power function model were compared with chamber measurements of the CO_2 efflux (Fig. 7). The CO_2 effluxes estimated using the power model based on a constant atmospheric CO_2 concentration of 380 μmol mol^{-1} and sensor measurements of the CO_2 concentration at a depth of 5 cm were in good agreement with those measured using the chamber method. In this case, a simple power model was sufficient to provide estimates that agreed well with experimental measurements (Fig. 7), yielding a RMSE of 0.21 μmol m^{-2} s^{-1} and an EF of 0.88. Because CO_2 storage can lead to much higher nighttime concentrations in the atmosphere (i.e., Jarvis et al., 1997), we also calculated using a concentration of 450 μmol mol^{-1} instead of 380 μmol mol^{-1} to test the magnitude of the differences, finding a RMSE

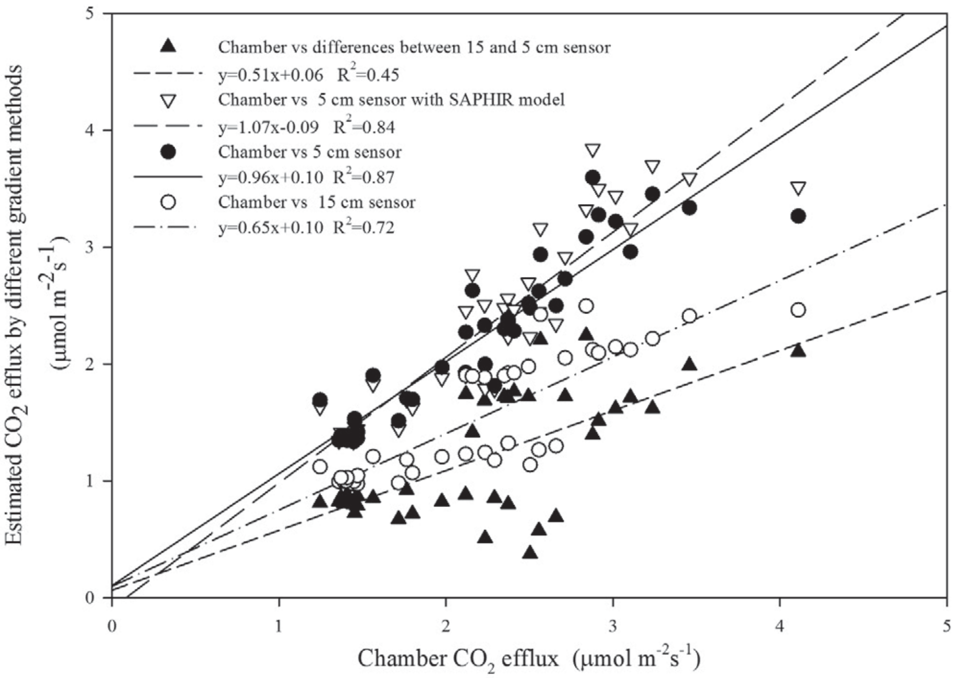

Fig. 7. Linear relationships between the CO_2 efflux levels measured using the LI-8100 chamber and the CO_2 effluxes estimated using the gradient method. In the gradient calculations, the soil gas diffusivity was estimated using a power model (Eq. [2]) at depths of 5 and 15 cm and between these depths. Data from the sensor at a depth of 5 cm were also used in conjunction with soil gas diffusivity estimates obtained with the Soil Air Phase Individual Resistances (SAPHIR) model (Eq. [3]).

of 0.26 μmol m^{-2} s^{-1} and an EF of 0.85, which demonstrated that the absolute value of the constant surface CO_2 concentration played a minor role in the results.

Efflux estimates based on data from a sensor at a depth of 15 cm did not correlate well with chamber measurements and did not respond strongly to rainfall events. This may be due to inaccuracies in the measured soil water content at this depth and the variation in the CO_2 concentration within the soil profile. The soil water content and temperature change more rapidly at the soil surface than they do at greater depths, and the response magnitude at a depth of 15 cm are relatively attenuated in comparison. Moreover, the transport of CO_2 between the surface layer and the 15-cm layer may be slow due to the distance between them. It should be noted that the D_p value was calculated based on the average water content measured using sensors at depths of 5, 10, and 15 cm. This may introduce error into the calculated level of gas transported in the 0- to 15-cm soil layers because the wettest soil water content layer will limit gas diffusion owing to its minimal air-filled porosity. The CO_2 flux from the 15-cm soil layer to the 5-cm layer (i.e., the difference between the values measured using the sensors at these depths) was less pronounced than the CO_2 flux between either depth and the surface, which may arise due to microbial respiration near the soil surface, where plant roots and microorganisms are more abundant and water content variation is greater.

Comparison of Gradient-Based and Surface Chamber Carbon Dioxide Flux Estimates

Surface wetting (e.g., precipitation, irrigation) impacts on CO_2 effluxes measured using the chamber and gradient methods are variable. For example, the CO_2 concentration generally increases rapidly due to infiltration of rainwater into the soil and then decreases gradually as a result of drainage and drying. In general, the amount of CO_2 transported through the water-filled pores is negligible compared to the amount produced by respiration within the soil (Pumpanen et al., 2008). Increases in the CO_2 concentration caused by brief rainfall events were observed at the soil surface (0–5 cm) and were accompanied by increases in CO_2 efflux measured using the chamber method. However, the CO_2 concentration at a depth of 5 cm may lag behind these changes, a trend that would be even more pronounced at 15 cm. In addition it appears that heavy rainfall reduced the soil temperature while also filling the soil's pores with water.

These processes have opposing effects on the rate of respiration in the soil, and so there was no rapid increase in the CO_2 efflux measured by the chamber method during heavy rainfall events. Notably, although 6.5 mm of precipitation fell on DOY 264 and 266, this did not appreciably reduce the D_p value (Fig. 6). However, the CO_2 concentration at 5 cm increased, possibly due to the upward movement of CO_2 from lower layers, where the D_p was unaffected by the rainfall. Under these conditions, the CO_2 efflux estimated using the gradient method increased but that measured using the chamber method decreased because of the significant fall in the soil temperature. Following a rainfall event in which 29.5 mm of precipitation fell on the study site, the D_p value decreased significantly. The resulting obstruction of gas exchange between the atmosphere and soil caused significant increases in the soil CO_2 concentration and reductions in the CO_2 flux due to a sharp decrease in surface gas diffusivity that was followed by an accumulation of CO_2 in the soil. Another low-intensity rainfall event (involving a total of 2.8 mm of precipitation across DOY 285, 286, and 287) seemed to increase the soil CO_2 concentration and CO_2 efflux, although these changes were primarily attributed to a significant increase in the soil temperature that occurred at the same time. On DOY 307, 14.5 mm of rain fell, causing a sharp increase in the CO_2 efflux. In the aftermath of rainfall events, the soil moisture content reduced due to infiltration and redistribution or evapotranspiration at the surface, and the resulting increased surface diffusivity allowed a larger gas flux across the soil–atmosphere interface, removing CO_2 that would have accumulated due to microbial production (Fig. 5a and 7). Similar results have been reported previously (e.g., Turcu et al., 2005). Although the results obtained using the gradient and chamber methods were generally in good agreement for this field study, the gradient method overestimated the CO_2 efflux following the rainfall events of DOY 264, 266, 278, 279, 285, 286, and 287 because the rainfall modified the soil CO_2 concentration profile. In particular, during low-intensity rainfall events (such as those of DOY 264, 266, 285, 286, and 287), the soil surface pores were blocked and the resulting large gradients caused the CO_2 efflux to be overestimated.

Application of Criteria

Consistent with the laboratory results, the gradient method overestimated the CO_2 efflux during and immediately after rainfall events, which were infrequent. Although gradient measurements are ideally calibrated against chamber-based measurements, we found the near-surface estimates of flux to be well correlated with chamber-based results except during periods of surface wetting. The gradient method can also provide internal soil profile estimates of gas flux (e.g., between 15 and 5 cm), which has proven useful for understanding CO_2 production spatially within the profile (Arevalo et al., 2010). Chambers should be used with caution during rainfall events because the infiltration of wetting fronts from outside the chamber can induce a mass flow of gases into the chamber (Rochette and Hutchinson, 2005). It is therefore difficult to accurately estimate CO_2 fluxes during and shortly after wetting events in the field, but the use of a numerical process-based model such as Hydrus-1D or inverse analysis of the soil CO_2 profile method (Koehler et al., 2010) can provide insightful simulations for such conditions.

Conclusions

The gradient method is a powerful tool for studying and understanding the dynamic variations in soil CO_2 levels and the production of CO_2 within the soil with little disturbance to the subsurface environment. When used in conjunction with a simple power model for estimating the gas diffusion coefficient, the gradient method produces CO_2 efflux estimates in agreement with those obtained using the chamber method. Abrupt increases in the near-surface soil water content between the surface and the nearest sensor can result in overestimates of CO_2 efflux due to the increased gradient without adequate information on the reduction in gas diffusion due to increased soil water content. Because there is currently no method that can reliably determine CO_2 fluxes during rainfall events in the field, it is difficult to determine the accuracy of the gradient method under these conditions. The results of our laboratory soil column experiment demonstrated that the gradient method overestimated CO_2 efflux during and immediately after the application of water. Where CO_2 and water content are accurately measured and the soil porosity is well defined, the gradient method can provide accurate gas flux estimates. The relatively low cost and simplicity of the instruments make it a useful tool for studying soil processes associated with the soil CO_2 concentration. Based on our results, CO_2 sensors placed at a depth of 5 cm yielded reliable CO_2 effluxes provided that the soil water content and temperature were well represented. However, surface wetting (precipitation, irrigation) can modify the soil CO_2 concentration distribution significantly, creating nonlinear CO_2 concentration profiles. Under such conditions, the results obtained using Fick's Law may become unreliable. Data from the gradient method should therefore be considered questionable during periods when water is applied, but were found to be accurate when the soil CO_2 concentration was steady (e.g., when the soil water content was not changing and there was no rainfall). We therefore recommend, as a minimum installation, a single CO_2 sensor at a depth of 5 cm and a soil water sensor at 2.5 cm for estimating CO_2 effluxes other than during wetting events. Additional CO_2 sensors can be useful for identifying situations when there is a significant variation in the CO_2 concentration as a function of depth, suggesting periods when data obtained using the gradient method may be invalid.

Acknowledgments

This research was supported by the National Natural Science Foundation of China (41271239 and 51239009) and by the Utah Agricultural Experiment Station, Utah State University, Logan, approved as Journal Paper 8611. We express appreciation to the reviewers and AEs for their help improving this paper and we thank William Mace and Marcos Chalas for their assistance with the laboratory and field experiments.

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