A Subsurface, Closed-Loop System for Soil Carbon Dioxide and Its Application to the Gradient Efflux Approach

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Carbon dioxide concentrations in the soil can vary both temporally and spatially. Methodology was developed to semicontinuously measure subsurface concentrations of CO₂ using expanded, porous Teflon (ePTFE) tubing. Lengths of ePTFE tubing (7.6 m) were buried at 0.02, 0.1, and 0.18 m below the soil surface in a Harps loam soil (fine-loamy, mixed, superactive, mesic Typic Calciaquoll) in central Iowa, and also positioned directly on the soil surface (0 m). Soil atmospheric gases that diffused through the walls of the tubing were circulated in a closed-loop design through solid-state CO₂ sensors to determine the concentration of CO₂ at each depth. Independent measures of CO₂ concentrations were also determined by sampling the in-line gas stream of the ePTFE system and from samples extracted from gas wells positioned near the buried tubing. Good agreement (r² > 0.95) was observed between the ePTFE system and the independent measures, with the ePTFE having biases of 1.2 and 1.37 times greater than the in-line and gas well samples, respectively. The soil-gas diffusion coefficient of CO₂ (Dₕ) was determined using intact soil cores and values were about 2.5 times less than two popular models used to predict Dₕ in soil. Estimates of CO₂ flux using Fick’s Law, six approaches to determine the vertical CO₂ concentration gradient, and three methods to determine Dₕ ranged from >800 to <1 μmol m⁻² s⁻¹ on Day of the Year 239.5. Although Fick’s Law is commonly used to estimate CO₂ flux from soil, the approach used to determine the vertical CO₂ concentration gradient and method used to determine Dₕ can both include sources of uncertainty.

Abbreviations: AFP, air-filled porosity; DOY, day of the year; ePTFE, expanded, porous Teflon; PE, ultra-high-molecular-weight polyethylene.

Numerous methods have been used to determine CO₂ concentrations beneath the soil surface. Two popular methods include gas wells (Burton and Beauchamp, 1994; Davidson et al., 2006; Drewitt et al., 2005; Risk et al., 2002) and solid-state CO₂ sensors (Chen et al., 2005; Hirano et al., 2003; Jassal et al., 2005; Liang et al., 2004; Tang et al., 2003, 2005; Turcu et al., 2005). Historically, gas wells used for determining CO₂ concentrations were sampled infrequently (i.e., days) while the solid-state CO₂ sensor can be used continuously. An advantage of the automated, continuous measurements from these solid-state sensors is that the dynamic nature of CO₂ concentrations beneath the soil surface can be determined (Jassal et al., 2005; Tang et al., 2003). These solid-state sensors are fixed in a location, however, and may be susceptible to the spatial variability of soil environments. An alternative approach to address both spatial and temporal variability is to bury porous tubing in the soil and circulate the gas that has diffused from the soil atmosphere into the inner tubing volume in a closed-loop through gas analyzers (Gut et al., 1998, 1999, 2002). A common application of soil CO₂ concentration data is to estimate the flux of CO₂ from the soil surface. This calculation is often made using Fick’s Law:

\[ F = D_s \frac{dC}{dz} \approx D_s \frac{\Delta C}{\Delta z} \]

where \( F \) is the flux of CO₂ (μmol m⁻² s⁻¹), \( D_s \) is the soil-gas diffusion coefficient of CO₂ in the soil (m² s⁻¹), \( C \) is the concentration of CO₂ (μmol m⁻³), and \( z \) is the depth below the soil surface (m). Variations in estimated flux may exist from the same data set depending on the approach used to determine the vertical CO₂ gradient and the model used to estimate \( D_s \). Numerous researchers have applied Fick’s Law but many times they fail to report the model used to describe the concentration with depth curve or the depth at which the concentration gradient was determined. When estimating the flux of CO₂ from soil using Fick’s Law, studies have either used published \( D_s \) models (Davidson et al., 2006; Drewitt et al., 2005; Hashimoto and Suzuki, 2002; Pumpanen et al., 2003; Tang et al., 2003, 2005; Turcu et al., 2005) or determined \( D_s \) values specific to...
their soils (Davidson et al., 2006; Hirano et al., 2003; Jassal et al., 2004, 2005; Liang et al., 2004). Jassal et al. (2005) showed mixed agreement between measured and modeled approaches for determining D, whereas Davidson et al. (2006) showed good agreement between a modeled and a measured approach. Underlying assumptions used in the predictive models may not be valid for all soils and can lead to errors when used to determine fluxes.

The soil gradient method has been proposed as an alternative to surface chambers for measuring CO2 flux (Hirano et al., 2003; Tang et al., 2003, 2005; Turcu et al., 2005) and may provide additional information on the CO2 production zones within the soil (Davidson and Trumbore, 1995; Drewitt et al., 2005; Fierer et al., 2005; Hashimoto and Suzuki, 2002; Rik et al., 2002; Schwenndemen and Veldkamp, 2006). The real difference (advantage) of the gradient approach is that it does not alter the soil surface boundary conditions like a chamber does. The objectives of this research were to: (i) propose and evaluate a method to semicontinuously measure CO2 concentrations beneath the soil surface using expanded Teflon (ePTFE) tubing and solid-state sensors; (ii) determine soil-gas diffusion coefficient values for CO2 using intact cores; (iii) using a simple data set, apply these measurements for calculation of CO2 efflux considering several approaches for determining the CO2 concentration gradient.

MATERIALS AND METHODS

Site Description

The study site was located in central Iowa about 10 km south of Ames (41°58′ N, 93°41′ W) in 2005. The soil at the site was a Harps loam, which has a slope range of 0 to 2% and is classified as poorly drained. At the 0- to 18-cm depth, the soil has sand, silt, and clay concentrations of 380, 360, and 260 g kg−1, respectively, a pH of 8.2, organic C concentration of 26.2 g kg−1, a cation exchange capacity of 23.3 cmol c−1 kg−1, and a particle density of 2600 kg m−3 (Oechsner et al., 2001). The soil bulk densities at the 0- to 0.02-, 0.02- to 0.1-, and 0.1- to 0.18-m depths were 920, 1100, and 1290 kg m−3, respectively. The soil had been managed under a corn (Zea mays L.)–soybean (Glycine max [L.] Merr.) rotation for at least 10 yr before the study. After harvest in 2004, the corn residue was chisel plowed and on DOY 126 in 2005 (6 May), the corn residue was further tilled by disking to a depth of 20 cm. Also on DOY 126 the soil was planted to soybean. The soybean was planted in 76-cm rows at a population of 310,000 seeds ha−1 and was harvested on DOY 276 (3 October).

Field Installation of Carbon Dioxide Concentration Tubing

Carbon dioxide concentrations beneath the soil surface were monitored using a modification of the Gut et al. (1998) approach. Here, a closed-loop system using 7.6-m lengths of ePTFE tubing (062404–4, W.L. Gore and Assoc., Elkton, MD) was buried at three depths on DOY 126. The ePTFE tubing had an outer diameter and wall thickness of 9.6 and 0.94 mm, respectively, and a manufacturer-rated porosity of 60%. The tubing was white, smooth to the touch, and could be pinched using finger strength but did not collapse when buried in the soil. DeSutter et al. (2006) previously described this tubing as having a CO2 diffusion coefficient of 1.23 × 10−5 cm2 s−1 at 24°C and a 95% equilibration time (CO2 concentration inside the tubing equilibrating with the CO2 concentration outside the tubing) of <6 min.

The ePTFE tubing was installed at average depths of 0.02, 0.1, and 0.18 m below the soil surface (within the Ap horizon) using a t trenching machine (Trench Master, Brown Manufacturing, Ozark, AL) equipped with a 0.36-m o.d. cutting wheel that was 0.025 m wide. A square trench (1.9 m on each side) was dug so that all four sides intersected the plant rows at a 45° angle, thereby integrating both rows and interrow areas. Using modified hand tools, the 0.18-m-depth ePTFE tubing was positioned so that the center of the tube was 0.18 m below the soil surface. Soil was then back-filled for subsequent installation of tubing centered at the 0.1- and 0.02-m depths. Each end of the buried ePTFE tubing was fitted with 3.2-mm i.d. tubing that was resistant to CO2 diffusion (Bev-A-Line IV, Thermoplastic Processes, Stirling, NJ), which was then routed under the soil surface at respective depths until the instrumentation enclosure was reached. Finally, a 7.6-m length of ePTFE tubing was positioned on the soil surface (0 m) immediately above the buried tubing to assist in monitoring CO2 concentrations at the soil surface. The trenching operation provided only minor additional disturbance following the 0.2-m-deep tillage operation on the previous day. During the study, soil settling in the trench was minimal and similar to that observed in the surrounding soil.

Field Instrumentation

Gas that diffused into the inner tubing volume of the ePTFE was circulated in a closed-loop through an aboveground instrumentation suite mounted in an environmental enclosure (Fig. 1). Starting with the 0-m depth, the two two-way valves (ET212, Clippard Instrument Lab., Cincinnati, OH) connected to the 0-m ePTFE tubing were energized simultaneously along with the 12-V DC pump (NMP830-KNDC, KNF Neuberger, Trenton, NJ), thus completing a closed-loop. Gas flowed from the ePTFE tubing via the 3.2-mm i.d. tubing, through a six-port manifold (BHH4–06, Clippard Instrument Lab.), filter (1-μm Arco50, Pall Corp., East Hills, NY), and a Nafion air dryer (MD110–48–4, Perma
Clippard), and compressed N2 gas. To further decrease the potential of CO2 sensors were calibrated periodically when the system was not sampling using two three-way valves (C in Fig. 1) (EVO312, Clippard). The 0.6-L chamber was saturated with a known concentration of CO2 (10%) that was monitored by a solid-state CO2 sensor (0–10%, GMT221, Vaisala) and temperature (25°C) following procedures similar to those outlined by Dane and Hopmans (2002). The diffusion of CO2 through the soil was then determined on each soil core in the laboratory using modified techniques of Evans (1965) and Jassal et al. (2005) (Fig. 2). In our approach, a 0.6-L chamber was saturated with a known concentration of CO2 (10%) that was monitored by a solid-state CO2 sensor (0–10%, GMT221, Vaisala) (Fig. 2A). The 10% CO2 gas was used so that the concentration of gas in the headspace was greater than what was determined from soil CO2 concentrations in the field, and thus CO2 produced in the soil and introduced back into the chamber headspace was assumed to be negligible.

After CO2 saturation, the chamber was moved into place over the soil core, which was sealed to a PVC plate using a ring of modeling clay (Fig. 2B). Stopcock grease was used as both a lubricant and sealant between the two PVC plates. Thus, the only outlet for the CO2 was into and through the ePTFE tubing. A six-port manifold, an energized two-way valve, and back into the ePTFE system were also sampled within the same hour as the gas wells following the same sample handling procedures. Carbon dioxide was then determined from the sample using gas chromatography.

Two soil water content sensors (MLx2 Delta-T Theta Probe, Dynamax, Houston, TX) were buried horizontally at the 0.06- and 0.14-m depths, 0.38 m from the plant row, and volumetric water content was estimated hourly using calibration information collected from a previous study at the site (Kaleita et al., 2005). Soil temperature was monitored at the 0.02-, 0.1-, and 0.18-m depths every hour using type-T thermocouples. An automated CO2 efflux chamber (Parkin and Kaspar, 2003) was installed within 2 m of the porous tubing. This chamber measured CO2 flux every hour, coinciding with the measurements of CO2 concentrations in the porous tubing. All instrumentation and data (both porous tube system and efflux chambers) were controlled and collected, respectively, by dataloggers (23X, Campbell Scientific, Logan, UT) and data were offloaded daily via cellular telephone. Twelve-volt DC deep cycle batteries supplemented with solar panels delivered power to the site. A 12-V DC to 24-V DC converter (AVD-34L-SW-12V, Zane International, Grand Junction, CO) was used to power the CO2 sensors. Instrumentation was operated from DOY 164 to 300.

**Measurement of the Carbon Dioxide Soil-Gas Diffusion Coefficient**

Intact soil cores (0.076-m i.d. by 0.076-m height) were removed from the 0.02- to 0.1- and 0.1- to 0.18-m depths in the study area from both the row and interrow locations. All cores were taken within 1.0 m of the tubing. Each core was saturated from below with tap water (25°C). After saturation was complete, cores were placed into pressure cells and pressure was applied to achieve a water potential of −4.9 kPa H2O at constant temperature (25°C) following procedures similar to those outlined by Dane and Hopmans (2002). The diffusion of CO2 through the soil was then determined on each soil core at the site (Kaleita et al., 2005). Soil temperature was monitored at the 0.06- and 0.14-m depths, 0.38 m from the plant row. From each gas well, 2 mL of sample was withdrawn and exhausted to the atmosphere to flush the dead volume in the tubing, after which 10 mL of gas sample was withdrawn from the PE and put into 6-mL gas-tight evacuated serum vials. From an in-line septum, the 0.02-, 0.1-, and 0.18-m closed-loop air streams of the ePTFE system were also sampled within the same hour as the gas wells following the same sample handling procedures. Carbon dioxide was then determined from the sample using gas chromatography.

In addition, the soil atmosphere was sampled nine times during the study period using gas wells constructed of 0.08-m lengths of ultra-high-molecular-weight polyethylene (PE) tubing, which was previously described in DeSutter et al. (2006) as PE-3. Each PE tubing had an internal volume of 26 cm3. The PE tubing was fitted with 3.2-mm i.d. tubing (Bev-A-Line IV, Thermoplastic Processes) and a Swagelok union fitted with a rubber septum. Three gas wells were positioned 0.02, 0.1, and 0.18 m below the soil surface at 0, 0.19, and 0.38 m from a soybean row. From each gas well, 2 mL of sample was withdrawn and exhausted to the atmosphere to flush the dead volume in the tubing, after which 10 mL of gas sample was withdrawn from the PE and put into 6-mL gas-tight evacuated serum vials.
dried at 105°C and reweighed to determine soil bulk density and air-filled porosity (AFP) at each water potential. The soil-gas diffusion coefficient of CO\textsubscript{2} through the intact cores ($D_s'$) was calculated for each soil core at each AFP following the methods outlined in Rolston (2002, Section 4.3). The SAS System Version 9.1 (SAS Institute, Cary, NC) was then used to determine the best-fit model between $D_s'$ and AFP. This model was used to estimate $D_s'$ in the field with AFP determined from measured water content and bulk density. The $D_s'$ for the 0- to 0.02-m depth was estimated using the derived model with inputs of bulk density of this soil layer and the measured water content at 0.06 m.

**Estimation of Soil Carbon Dioxide Efflux**

As an example data set, the vertical CO\textsubscript{2} concentration gradient was determined on DOY 237.5 to 244.5 using three approaches: (A1) a power function ($y = a + bx^c$) was fit to CO\textsubscript{2} concentration with depth data and the first derivative was determined at 0 and 0.02 m below the surface (TableCurve Version 4, SPSS, Chicago); (A2) linear regression was fit through the CO\textsubscript{2} concentration with depth data and the CO\textsubscript{2} gradient was determined using the slope of the line; and (A3) concentration data from discrete depth increments below the surface (0.02–0, 0.1–0, and 0.1–0.02 m) were used to calculate the gradient as $\Delta C/\Delta z$. Graphic examples of these three approaches are shown in Fig. 3.

The six approximations used to determine the vertical CO\textsubscript{2} concentration gradient were used in conjunction with three methods to determine $D_s'$ (one measured and two modeled) to estimate the efflux of CO\textsubscript{2} according to Fick's first law of diffusion (Eq. [1]). Hourly values at midday on DOY 237, 239, 241, and 243 were chosen for this comparison, which encompassed time periods both before and after rain. Here we redefine the variables of Eq. [1] so that $F$ is the flux of CO\textsubscript{2} (μmol m\textsuperscript{-2} s\textsuperscript{-1}), $D_s'$ is the soil-temperature-corrected CO\textsubscript{2} soil-gas diffusion coefficient (m\textsuperscript{3} soil air m\textsuperscript{-1} soil s\textsuperscript{-1}), $C$ is the molar concentration of CO\textsubscript{2} in the soil (μmol m\textsuperscript{-3}), and $z$ is the depth below the surface (m). The $D_s'$ values measured from intact cores in the laboratory were adjusted to reflect the temperature dependence of the CO\textsubscript{2} soil-gas diffusion coefficient for each estimate of CO\textsubscript{2} flux using the approach of Fuller et al. (1966):

$$D_s = D_s' \left(\frac{T_{\text{field}}}{T_{\text{lab}}}\right)^{1.75} \quad [2]$$

where $T_{\text{field}}$ is the temperature (K) of the soil at time $t$, and $T_{\text{lab}}$ is the temperature of the soil cores at the determination of $D_s'$ (298.15 K). The two independent models that were used to estimate $D_s'$ were the Moldrup et al. (2000):

$$\frac{D_s}{D_s'} = \left(\frac{2\varepsilon_{100} + 0.04 \varepsilon_{100}}{\varepsilon_{100}}\right)^{1.2+3/3} \quad [3]$$

and the Millington and Quirk (1961):

$$\frac{D_s}{D_s'} = \frac{\varepsilon^{3/3}}{\Phi} \quad [4]$$

where $D_s'$ is the gas diffusion coefficient in free air (m\textsuperscript{3} s\textsuperscript{-1}), $\varepsilon_{100}$ is the soil air-filled porosity at ~100 cm H\textsubscript{2}O water potential (m\textsuperscript{3} soil air m\textsuperscript{-3} soil), $\varepsilon$ is the soil air-filled porosity (m\textsuperscript{3} soil air m\textsuperscript{-3} soil), $b$ is the slope of the soil water retention curve in a log-log coordinate plot and here was 5.82, and $\Phi$ is the soil total porosity (m\textsuperscript{3} m\textsuperscript{-3}).

Estimates of efflux were determined at 1200 h each day from DOY 238.5 to 244.5 using the six approximations of the vertical CO\textsubscript{2} gradient and these three $D_s'$ estimates. These efflux values were compared with effluxes as determined by the automated chamber.

**RESULTS AND DISCUSSION**

**Semicontinuous Measurement with the Closed-Loop System**

Carbon dioxide concentrations ranged from about 21 and 15 mmol mol\textsuperscript{-1} at the 0.02-m depth to >23 mmol mol\textsuperscript{-1} at the 0.18-m depth during the study period (Fig. 4A). The 18-cm depth consistently had the greatest concentration of CO\textsubscript{2}, followed by the 0.1- and 0.02-m depths. Carbon dioxide concentrations at the 0.1- and 0.02-m depth reached maximum values of about 21 and 15 mmol mol\textsuperscript{-1}, respectively, during the study.

![Fig. 4. Average 24-h profiles of (A) CO\textsubscript{2} concentration, (B) volumetric water content, and (C) temperature beneath a Harps loam soil near Ames, IA.](Image)
Carbon dioxide concentrations at the 0-m depth did reach values exceeding 1 mmol mol⁻¹ but were more consistently near 0.5 mmol mol⁻¹.

Large fluctuations in CO₂ concentrations, at all but the 0-m depth, coincided with rainfall events. For example, at the 0.18-m depth, CO₂ concentrations increased from about 8 mmol mol⁻¹ on DOY 220, 1 d before a 3-d rain totaling 106 mm, to nearly 23 mmol mol⁻¹ on DOY 225. These large increases in CO₂ concentrations after rainfall events were seen at all of the subsurface depths. Maximum CO₂ concentrations after rainfall events lagged maximum 6-cm soil moisture values by about 1.5 d (Fig. 4A and 4B). This indicates that surface sealing may not be the only factor increasing subsurface CO₂ concentrations. Other researchers have also observed this pattern and have concluded that surface sealing and decreased Dₛ (Chen et al., 2005; Jassal et al., 2005) as well as increased microbial activity due to increased soil water content (Fierer and Schimel, 2003; Glinski and Stepniewski, 1985) may be responsible. Soil temperatures reached maximum values on about DOY 178 and steadily declined to <10°C near DOY 300 (Fig. 4C). Day-to-day temperature variations did not appear to directly influence CO₂ concentrations, but an overall decline in concentration coincided with the soil temperature decline to <15°C.

Carbon dioxide concentrations determined by sampling the in-line air stream via a septum were slightly greater than concentrations determined from the in-line air stream within the closed-loop sampling scheme (Fig. 5). Correlation between these two independent measures were good (r² = 0.99) but the buried-tubing method was greater by about 1.2 times with respect to all the sampling depths and sampling times. Carbon dioxide extracted from the gas wells also showed good correlation with the buried tubing (r² = 0.95), but CO₂ from the buried tubing was greater by 1.37 when comparing all sampling depths and sampling times. Differences in CO₂ concentrations between the buried tubing and the in-line and gas well samples may be due to the differences in analyzing techniques. The buried-tubing gases were sampled in the field with solid-state sensors and the in-line and gas-well samples were analyzed in the laboratory using gas chromatography. Also, differences between the buried-tubing and gas-well samples may be a function of the buried tubing integrating over 7.6 m whereas the gas wells integrated over only 0.24 m (0.08 m × 3) at respective depths. Overall, good agreement was achieved between the dynamic and static sampling approaches.

**Carbon Dioxide Soil-Gas Diffusion Coefficient**

For this soil, the approach used to determine Dₛ worked very well at pressures less than ∼88.3 kPa H₂O. At pressures greater than ∼88.3 kPa H₂O, however, soil shrinkage was significant and macropores were formed along the soil-ring interface. Average volumetric water contents at the −4.9, −9.8, −49.0, and −88.3 kPa H₂O pressures were 0.41, 0.37, 0.35, and 0.33 m³ m⁻³, respectively. No attempt was made to seal these macropores and determine Dₛ values at higher pressures.

The best model fit between measured Dₛ and ε was a quartic model: Dₛ = −1.00 × 10⁻⁸ + 3.97 × 10⁻⁵ ε⁴ (R² = 0.98, SE of the model = 0.13). The two published models predicted the Dₛ to be about five times greater than the measured value at ε = 0.25 m³ m⁻³ (Fig. 6), which was about the maximum ε evaluated in this study. Overall, the Moldrup et al. (2000) and Millington and Quirk (1961) models overestimated Dₛ values compared with the actual and modeled Dₛ values. This result differs from Jassal et al. (2005), where the Millington and Quirk (1961) model tended to underestimate measured Dₛ values from a sandy soil.

The field Dₛ determined using this model ranged from about 1.5 to 5.7 × 10⁻⁷ m² s⁻¹ during the study period, with an average Dₛ of about 3.8 × 10⁻⁷ m² s⁻¹ (Fig. 7). The models of Moldrup et al. (2000) and Millington and Quirk (1961) predicted Dₛ values up to 2.5 times greater than the measured approach (Eq. [3]), with season-long averages near 1.1 × 10⁻⁶ and 9.3 × 10⁻⁷ m² s⁻¹, respectively. All models predicted sharp declines in Dₛ after rainfall events due to the decreased ε of the soil.

**Vertical Carbon Dioxide Gradients**

Using a curvilinear approach (Davidson et al., 2006), CO₂ concentration data with depth were observed throughout the experiment but were most pronounced after rainfall events (Fig. 8A and 8B). The power function model C = a + bε³, used to determine the
vertical CO₂ concentration gradient for the curve-fitting approach (A1; Table 1), described the curvilinear CO₂ vertical concentration data very well ($r^2 > 0.99$). The A1 approach yielded the largest vertical CO₂ gradients compared with the other methods when $\Delta C/\Delta z$ was evaluated at $z = 0$ m (Table 1). This approach yielded values ranging from $9.7 \times 10^6$ to $931.5 \times 10^6$ μmol m⁻³ m⁻¹ for DOY 237.5 and 239.5, respectively. This large increase in $\Delta C/\Delta z$ was the result of 32 mm of rain falling between DOY 238.29 and 238.46 (Fig. 8). Evaluating $\Delta C/\Delta z$ at $z = 0.02$ m yielded considerably smaller gradients, where values ranged from $2.2 \times 10^6$ μmol m⁻³ m⁻¹ before the rain to $3.8 \times 10^6$ μmol m⁻³ m⁻¹ 4 d after the rain.

Using the approach of Tang et al. (2003), where the CO₂ gradient was computed as the slope of the linear regression between CO₂ concentration and depth (A2), gradient values were $1.6 \times 10^6$ μmol m⁻³ m⁻¹ before the rain to $2.5 \times 10^6$ μmol m⁻³ m⁻¹ 2 d after the rain. This approach appears inconsistent with the concentration profiles that we observed (Fig. 3 and Fig. 8B). This method may be useful, however, in situations where the concentration gradient with depth is nearly linear, such as in the case of Tang et al. (2003).

The final approach used for determining the vertical CO₂ gradient was the finite-difference approach (A3; Table 1). For this approach, gradients evaluated between 0.02 and 0 m were consistently greater than those computed for either 0.1 to 0 or 0.1 to 0.02 m. The peak gradient was $19.1 \times 10^6$ μmol m⁻³ m⁻¹ on DOY 239.5; the gradient steadily declined to levels observed before the rainfall by DOY 244.5. The gradient from 0.1 to 0.02 m was smallest about 24 h after the rainfall ($1.2 \times 10^6$ μmol m⁻³ m⁻¹) and peaked at $2.2 \times 10^6$ μmol m⁻³ m⁻¹ on DOY 242.5, 4 d after rainfall. This decline in the gradient immediately after the rainfall was caused by similar CO₂ concentrations at the 0.02- and 0.1 m depths, which provides evidence of surface sealing or increased heterotrophic and autotrophic respiration. This approach has an advantage in that only two depths are needed to determine the concentration gradient; however, curvilinear concentration with depth patterns may be undetected using this approach.

### Carbon Dioxide Efflux

Irrespective of the method used to derive $D_v$, estimates of CO₂ efflux using Approach A1 evaluated at $z = 0$ m overestimated efflux by about 600 times that observed with the automated efflux chamber (Table 2). These high estimates of efflux determine the concentration gradient; however, curvilinear concentration with depth patterns may be undetected using this approach.

#### Table 1. Carbon dioxide concentration gradients determined using: (A1) a curve-fitting approach where $\Delta C/\Delta z$ was evaluated at $z = 0$ and 0.02 m; (A2) linear regression to compute the concentration of the line using all data points; and (A3) using finite difference between discrete depths. Data was evaluated at 1200 h on Days of the Year (DOY) 237 through 244. DOY 238.29 and 238.46, 32 mm of rain was recorded at the site.

<table>
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<th>DOY</th>
<th>A1—$\Delta C/\Delta z \times 10^6$</th>
<th>A2—slope</th>
<th>A3—$\Delta C/\Delta z \times 10^6$</th>
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<td></td>
<td>$z = 0$ $\mu$mol m⁻³ m⁻¹</td>
<td>$z = 0.02$ $\mu$mol m⁻³ m⁻¹</td>
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† Actual values equal reported values times the indicated factor. 
‡ CO₂ profiles were fit to $C = a + bzc$; all $r^2$ values were >0.99. Values were derived by taking the first derivative at $z = 0$.
§ CO₂ profiles were fit to $C = a + bzc$; all $r^2$ values were >0.99. Values were derived by taking the first derivative at $z = 0.02$.
¶ Vertical concentration gradient as determined by using linear regression and computing the slope of the line for CO₂ concentration with depth (Tang et al., 2003). 
# Vertical concentration gradient.
The potential error of using the A2 approach values, even on DOY 237.5 when the concentration profile was when using the modeled surface soil water content in this example. Clearly, the 0.06-m data were not able to accurately describe changes in surface (0–0.02-m) soil water content in this example. Therefore, the Chamber efflux decreased. Using the gradient between 0.02 and 0 m and between 0.1 and 0 m, the two modeled \( D_s \) approaches tended to overestimate efflux compared with the automated chambers on the 2 d following the rain event (Table 2). Efflux was underestimated in all cases compared with the automated chamber using all \( D_s \) approaches and evaluating the gradient between 0.1 and 0.02 m (Table 2).

Using the chamber efflux data and the A3 approach between 0.02 and 0 m, the \( D_s \) values would have needed to be 1.3 \( \times \) 10^{-6}, 7.3 \( \times \) 10^{-8}, 3.0 \( \times \) 10^{-7}, and 6.7 \( \times \) 10^{-7} m^2 s^{-1} for DOY 237.5, 239.5, 241.5, and 243.5, respectively, to correctly estimate the chamber efflux. Using the modeled \( D_s \) formula (Fig. 6) and the above information, estimates of the volumetric water content between 0.02 and 0 m would be 0.22, 0.44, 0.35, and 0.29 m^3 m^{-3} for DOY 237.5, 239.5, 241.5, and 243.5, respectively, which were used for all \( D_s \) estimates in Fig. 7, were 0.28, 0.32, 0.30, and 0.29 m^3 m^{-3} for DOY 237.5, 239.5, 241.5, and 243.5, respectively. Clearly, the 0.06-m data were not able to accurately describe changes in surface (0–0.02-m) soil water content in this example. Surface soil water content was overestimated during periods of drying and underestimated during periods of wetting.

A critical problem of evaluating gas fluxes from the soil surface using (Eq. [1]) is getting accurate estimates of volumetric water content and AFP near the soil surface to use in the \( D_s \) models. Currently, only two methods known to us have been used to determine volumetric water content just below the soil surface

<table>
<thead>
<tr>
<th>DOY</th>
<th>( D_s ) gradient approach</th>
<th>( dC/dz, \ z = 0 ) m</th>
<th>( dC/dz, \ z = 0.02 ) m</th>
<th>( A2—\text{slope} )</th>
<th>( A3—\Delta C/\Delta z, \ 0.02–0 ) m</th>
<th>( \Delta C/\Delta z, \ 0.1–0.02 ) m</th>
<th>( \Delta C/\Delta z, \ 0.1–0.2 ) m</th>
</tr>
</thead>
<tbody>
<tr>
<td>237.5</td>
<td>A1—( dC/dz, \ z = 0 ) m</td>
<td>4.5</td>
<td>1.0</td>
<td>0.7</td>
<td>1.3</td>
<td>5.6</td>
<td>1.9</td>
</tr>
<tr>
<td>239.5</td>
<td>A2—( dC/dz, \ z = 0.02 ) m</td>
<td>1.0</td>
<td>0.8</td>
<td>0.7</td>
<td>0.9</td>
<td>1.1</td>
<td>0.7</td>
</tr>
<tr>
<td>241.5</td>
<td>A3—( \Delta C/\Delta z, \ 0.02–0 ) m</td>
<td>1.3</td>
<td>1.1</td>
<td>1.0</td>
<td>1.4</td>
<td>5.6</td>
<td>1.9</td>
</tr>
<tr>
<td>243.5</td>
<td>( \Delta C/\Delta z, \ 0.1–0.02 ) m</td>
<td>5.6</td>
<td>1.9</td>
<td>1.0</td>
<td>0.4</td>
<td>0.7</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 2. Estimated CO2 efflux from a Harps loam soil using six approaches to determine the vertical CO2 gradient (Table 1) and three methods to estimate the soil-gas diffusion coefficient of CO2 in this soil (Fig. 7) and measured CO2 efflux determined by an automated sampling chamber.
Thus, caution in data interpretation should be used when values of CO$_2$ concentrations in the soil can be achieved using the porous tubing (ePTFE) design outlined here. The advantages of this approach are: semicontinuous, in situ measurements of CO$_2$ concentrations with depth; use of the same sensor(s) in determining CO$_2$ concentrations at all depths; the ability to integrate over a large area; fast equilibration between soil atmosphere and inner tubing volume; and the ability to sample the air stream for other gases. There are also numerous disadvantages, however, including: initial disturbance of the soil at installation; difficulty with size and placement of tubing near the soil surface; the need to remove water or water vapor before CO$_2$ analysis; and the cost of the ePTFE used here, although there are less expensive alternatives (DeSutter et al., 2006).

A point of interest that should also be considered is the outside diameter of the tubing and how this may affect overall tubing depth. In this study, the center of the ePTFE tubing was positioned at the target depths of 0.02, 0.1, and 0.18 m. However, using the 0.02-m position as an example, the tubing depth ranged from 0.015 to 0.025 m below the surface, leaving 50% of the tubing above and below the target depth. Surface roughness at the time of installation may also complicate the determination of the exact tubing depth at installation. This uncertainty may affect the calculated concentration gradient and the estimate of efflux.

Although not observed in this study, trenching may alter the soil physical structure. Following heavy rains, the trenched soil may settle, have a reduction in macroporosity, and hardsetting may occur after drying (Karunatilake and van Es, 2002). These results may affect the estimates of $D_s$ and ultimately the depth of the tubing. The soil used in this study was tilled before installation of the tubing and there was no visual evidence of soil settling. The likelihood of soil settling after trenching in undisturbed soils (i.e., prairie, forest, no-till agriculture) is great, however, and thus increased care should be taken when assessing both $D_s$ and tubing depth in the trench compared with the surrounding soil.

Using CO$_2$ concentration data with depth with the objective of determining CO$_2$ efflux using Fick’s Law (Eq. [1]) can be challenging. The ability to accurately estimate CO$_2$ efflux hinges on both accurate $D_s$ values and accurate vertical concentration gradients. Not only must gradient and $D_s$ be estimated accurately, they must be estimated for the soil depth for which the CO$_2$ efflux is to be calculated. For example, if CO$_2$ efflux from the soil surface is of interest, then the $D_s$ and $dC/dz$ must be estimated for the surface or near-surface soil. Use of average soil profile $D_s$ or $dC/dz$ may not yield representative estimates of surface CO$_2$ emissions.

Soil-specific $D_s$ values determined for our soil were about 2.5 times less than those predicted using two popular $D_s$ models. Thus, caution in data interpretation should be used when values of $D_s$ are not determined independently, as done here and elsewhere using intact cores (Jassal et al., 2005) or in situ field methods (Lai et al., 1976; McIntyre and Philip, 1964; Rolston et al., 1991).

Depending on the approach used and the depth of interest, gradients may vary widely (Table 1). Determining vertical concentration gradients using linear regression was not useful after a rainfall event but may be more applicable during dry soil conditions. The finite-difference approach is the most straightforward but has the potential to misrepresent curvilinear concentration patterns with depth.

Overall, this experiment points to many questions that remain about estimating CO$_2$ flux within and from the soil using the gradient approach. Future research is needed to improve the reliability of the gradient flux approach, including new methods for determining the $D_s$ of surface soils (0–0.02 m), quantifying the number and placement of tubing and sensors for determining CO$_2$ concentrations with depth, the use of automated flux chambers to help define the proper gradient approach and $D_s$ determination, and application of sensors to determine the water content in surface soils (0–0.02 m). Even with the above concerns, the gradient approach can be a tool to estimate gas efflux or, although not a focus of this research, the most useful application of this approach may be to determine gas production zones within the soil. When using the trenching method in areas where disturbance of the soil is not possible or is impractical, aboveground chamber methods should strongly be considered.

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REFERENCES


