A new method for in-situ soil gas diffusivity measurement and applications in the monitoring of subsurface CO$_2$ production

David Risk, Lisa Kellman and Hugo Beltrami

Environmental Sciences Research Centre, St. Francis Xavier University,
Abstract. Subsurface approaches to soil CO\textsubscript{2} monitoring are becoming increasingly important for process studies in terrestrial carbon research. When used in conjunction with a diffusion model to determine CO\textsubscript{2} production, subsurface methods require good estimates of effective soil gas diffusivity (D\textsubscript{e}). Outlined here is a novel membrane probe and continuous flow system for in-situ soil gas diffusivity measurements. Laboratory tests confirm performance across the range of CO\textsubscript{2} diffusivities found in natural soils. Field tests were performed across a range of soil moisture contents by artificially hydrating eight soils over a period of three to seven days. These soils were representative of a range of textural classes in Eastern Nova Scotia, Canada. The absolute values of diffusivity, and also the rate at which diffusivity decreased with increasing soil moisture content were typically quite different from model predictions. When applied to subsurface CO\textsubscript{2} monitoring at two sites, the site-specific diffusivity measurements greatly improved the accuracy of CO\textsubscript{2} production estimates. We observed a consistent and close correspondence between calculated profile CO\textsubscript{2} production and (independently measured) soil CO\textsubscript{2} surface flux. The subsurface CO\textsubscript{2} production estimates acquired using in-situ gas diffusivity measurements allows detailed vertical profile resolution to be constructed over time. The majority of CO\textsubscript{2} was generated at shallow depths, but periodic contributions from deeper depths were important, particularly towards the end of the growing season.
1. Introduction

In temperate forests, soil respiration accounts for approximately half of total forest respiration and is regarded as the least well understood component of landscape carbon balance [Valentini et al., 2000]. Many research efforts have been aimed at determining the physical controls on total soil respiration [Risk et al., 2002a; Lavigne et al., 2003], and to that end, a wide variety of methods have been employed. The large-scale eddy covariance towers that are in operation at many key research sites are not able to resolve CO₂ dynamics at the soil level and surface based CO₂ measurements are required. Subsurface approaches to soil CO₂ monitoring are becoming increasingly popular [Jassal et al., 2005; Drewitt et al., 2005; Tang et al., 2005; Hashimoto and Suzuki, 2002; Hirsch et al., 2004; Hirano et al., 2003; Tang et al., 2003; Risk et al., 2002b; Yoshikawa and Hasegawa, 2000] and while substantially more equipment intensive than surface flux measurements and limited in terms of spatial coverage and averaging, they offer significant advantages for resolving soil gas processes. Advantages include excellent vertical resolution of CO₂ dynamics in the layered soil system, and the ability to estimate instantaneous CO₂ production at specific depths. Such soil CO₂ production estimates are helping to clarify temperature and soil moisture controls on soil respiration processes [Risk et al., 2002a; Drewitt et al., 2005]. This is especially true for shorter time scales when measured surface fluxes may often lag well behind actual CO₂ production due to CO₂ storage in the soil profile [Hirsch et al., 2004].

When used in conjunction with a diffusion model to determine instantaneous CO₂ production [de Jong and Schappert., 1972; Freijer, 1994; Burton and Beauchamp, 1994], sub-
surface methods require good estimates of effective soil gas diffusivity ($D_e$). Concentration profiles of natural or injected $^{222}$Radon [Lehmann et al., 2000] or other tracers [van Bochove et al., 1998] have been used to determine diffusivity in the field, but many researchers defer to empirically-derived approximations that require soil-specific input parameters such as the Millington model [Millington, 1959; McCarthy and Johnson, 1995] or recent improved models [Moldrup, 2004, 2001]. Unfortunately, diffusivity models tend to perform better in some soils than in others. And, more importantly in cases where diffusivity fluctuates periodically, this parameter can control output from the gas production model because modeled diffusivity values may change by an order of magnitude or more during the course of a week, whereas the relative variation in trace gas concentrations is much smaller [Risk et al., 2002b]. There are several approaches that allow for laboratory testing of intact soil cores collected in the field [Jassal et al., 2005]. These have the advantage that soil gas diffusivity can be determined on a relatively small spatial and temporal scales that would be difficult to measure with $^{222}$Rn concentration profiles, and in highly organic substrates such as soil litter that are not clearly dealt with in diffusivity model approximations.

There remains, however, the potential for changes to soil physical properties (e.g. soil aggregation, compaction etc) that could have a large influence on resulting values. It would be desirable to directly evaluate soil gas diffusivity in the field, as this would minimize potential problems with alteration to diffusivity in extracted soil cores and allows for field conditions to be monitored in-situ at the time of soil gas measurement.

Some field methods allow assessment of $D_e$ at the soil surface [McIntyre and Philip, 1964]. In waterlogged sediments, a method has been used to determine gas diffusivity based on diffusion of a tracer away from a membrane of known diffusivity [Revsbech et
Similar waterproof gas-permeable diffusion membranes have been applied to soil gas studies [Gut et al., 1981; Hirsch et al., 2002], but they have been used primarily for gas sampling purposes rather than to determine soil gas diffusivity. In these studies, samples have been taken either 1) by pulling soil air through the microporous surface, or 2) by sampling from a volume of air that has been allowed to equilibrate across the membrane. The latter diffusion sampler is well suited to tracer-based gas diffusivity methods if constructed in a continuous flow loop and coupled to a gas detector.

This paper outlines the development, testing and field applications of a membrane probe and continuous flow system for in-situ soil gas diffusivity measurements. This method is designed to determine soil gas diffusivity using diffusion of \( \text{CO}_2 \) across a permeable membrane. Laboratory tests will be presented in addition to soil diffusivity-moisture curves that were obtained from in-situ measurements at eight sites during periods of artificially induced soil hydration. We assumed that diffusivity-moisture curves would be highly site specific, resulting from the range of individual soil characteristics including soil porosity, aggregation, structure, compaction, organic content and especially macropores created by frost, soil organisms or root activity. A subsurface \( \text{CO}_2 \) monitoring program was used to test the robustness of \( \text{CO}_2 \) estimates generated with site-specific diffusivity data, and to examine patterns of \( \text{CO}_2 \) depth contribution over the course of a growing season.

2. Material and methods

2.1. Diffusion probe theory

In a homogeneous semi-infinite, source-free half-space the \( \text{CO}_2 \) gas concentration, \( C \), at any depth due to a time varying concentration at the boundary is governed by the
one-dimensional unsteady gas diffusion equation, which is analogous to the response of
the ground to sudden changes in temperature [Beltrami and Kellman, 2003; Beltrami, 2002]. The concentration anomaly at depth $z$, $C(z,t)$, due to a step change in surface concentration is obtained from the forward model [Crank, 1975]:

$$C(z,t) = \Delta C \text{erfc} \left( \frac{z}{2\sqrt{Dt}} \right), \quad (1)$$

where $\text{erfc}$ is the complementary error function, $D$ is the gas diffusivity, $t$ is time, $z$ is depth (positive downwards) and $\Delta C$ is the concentration at some initial time. At $z = 0$, the rate of change in concentration or loss of diffusing substance from a semi-infinite medium is given by:

$$(\frac{DdC}{dz})_{z=0} = \frac{D\Delta C}{\sqrt{\pi Dt}}. \quad (2)$$

The first term in Eq. 2 is Fick’s first law and equivalent to diffusive mass flux per unit area per unit time, or $(F)$, which is given by integrating the right side of equation (2) with respect to $t$, provided that the concentration $\Delta C$ does not change within a time interval $(0,t)$,

$$F = \int_{0}^{t} \frac{D\Delta C}{\sqrt{\pi Dt}} dt. \quad (3)$$

For known concentration gradients, time intervals and surface areas, diffusivity can be estimated from the following rearrangement of Eq. 3,

$$D = \frac{\pi}{t} \left[ \frac{F}{2\Delta C} \right]^{2} \quad (4)$$
Equation 4 can be used to solve for one-dimensional diffusion of a tracer away from (or to) a membrane where an instantaneous step change in concentration has occurred on one side of its surface, provided that the following conditions are met: 1) One-dimensional diffusion is a reasonable approach given the length to width ratio of the membrane surface, and the shape of the area outside the membrane in which soil gas concentrations are altered by the measurement technique. 2) The diffusive fluxes initiated by the step change in concentration are not of sufficient magnitude to change the concentration of the porous medium. That is, soil concentrations must be well buffered against any concentration changes introduced by the technique. 3) The time interval of measurement following the step change must be as short as possible given the physical limits of the device (time for mixing a continuous flow loop, detector noise, limits of detection). 4) In order to be used in the assessment of soil gas diffusivity, the membrane must have a diffusivity coefficient equal to or greater than that of the surrounding soil. If the membrane limits the rate of diffusion, equation 4 can be used to solve for the diffusivity of the membrane surface.

When this solution is applied in the field using a testing apparatus, the result is actually the "effective diffusion coefficient", the sum of all soil transport processes occurring during measurement. The probe’s membrane surface and internal volume are subject to the same pressure fluctuations as in surrounding soil that may be induced by factors such as wind pumping, atmospheric pressure changes or temperature fluctuations. These fluctuations are typically considered to be insignificant and diffusion is the dominant soil transport mechanism [Sommerfeld et al., 1993; Hirsch et al., 2004], however, based on this theory the diffusion probe would integrate diffusivity, permeability and all driving forces that can be described by basic diffusion/mass flow theory.
2.2. Physical description of diffusion probe and related components

The most important component of a diffusion probe is the membrane, which must be able to withstand field conditions (i.e. resistant to tearing, waterproof etc) and maximize rates of gas diffusion. In membrane construction, this is accomplished by carefully controlling pore sizes, which are larger than gas molecules of interest but smaller than liquid water molecules (other fluids have different capillarity characteristics). Pore size is relatively fixed among commonly available waterproof-breathable membrane materials but pore counts per unit area vary significantly. A variety of commonly available membranes were tested for diffusive potential in an apparatus consisting of two cylinders of known volume separated by the membrane being tested. Stable CO\textsubscript{2} concentrations were maintained on one side of a membrane of known surface area and CO\textsubscript{2}-free air was circulated at a known rate through the other cylinder and into a Licor LI-7000 IRGA that continuously monitored CO\textsubscript{2} concentration. The gaseous diffusivity coefficient was calculated using the mass fluxes across the membrane once a steady state concentration gradient was attained. Smaller concentration gradients indicated greater membrane diffusivity. Tyvek spun-bonded polyolefin membrane (DuPont) commonly used in building construction was chosen. It was highly tear resistant, waterproof (holds better than 3.5 m water column) and our samples had high rates of diffusivity (CO\textsubscript{2} diffusivity coefficient of $\sim 8.5 \times 10^{-6}$ m\textsuperscript{2}/s), exceeding soil gas transport rates under most normal soil conditions present in Eastern Canada.

Two variations of diffusion probe were built for this study, one for “permanent” deployment, and a “direct push” probe that can be moved between sites easily. Both use 19 mm O.D. machined PVC carriers approximately 125 mm long with four 5 mm x 100 mm
slots along its length, offset from one another by 90°. The individual flow channels are joined using holes drilled in the carrier so that a single loop is formed, with a PVC inlet and outlet tubes that lead to the soil surface. The membrane is bonded to the carrier and covered with a tight-fitting fine stainless steel mesh cylinder for protection and to maintain internal volume against the pressure of the surrounding soil. Both inlet and outlet tubes have Luer Lock valves at their ends.

Both types of probes are installed by drilling a hole into the soil of slightly smaller diameter than the probe, and pushing in the probe. The permanent probes require that the hole is sealed with a mixture of soil and bentonite. Aside from a drive tip, the direct push probes incorporate a 50 cm long extension on the back end of the probe with a fattened section to self-seal the probe in the drilled installation hole. The direct push probes can be hammered in and removed by pulling on the extension, while the permanent probes can only be removed by digging. Both permanent and direct push probes can be installed via the surface (vertical installation) or a pit (horizontal installation). The permanent probes are simple to fabricate and smaller, making them more convenient for lab work. When deployed in the field, they are allowed to settle for 1-2 weeks before making measurements, while the direct push probes can be used immediately as a result of superior hole sealing characteristics.

As shown in Figure 1, the diffusion probe operates in conjunction with a simple closed loop flow system. A small rotary vane pump (Clark Solutions) moves gas through the loop between the probe and infrared gas analyzer (LICOR LI-820 with 5cm optical path). Using two small valves, flow can be diverted through a soda lime column just upstream from the gas analyzer for autozero functions and to scrub CO₂ from the loop. A Campbell Scientific
CR10X-2M datalogger controls all valve and pump functions in addition to logging LI-820 data and performing all final diffusivity calculations. The entire system is housed in a waterproof field portable box. Figure 1 shows a general layout of the diffusivity system components, closed loop gas flows and electrical connections. Differential pressure calculations [Oberg and Jones, 1957] guided system design to minimize pressure gradients that could induce mass flow across the membrane surface. We minimized internal volume and tubing length, chose relatively large diameter tubing and internal orifices, chose a pulseless-flow miniature rotary vane pump (Clark Solutions), and placed flow-limiting components (primarily the valves and column) immediately upstream of the pump so that vacuum would not be present within the probe body. Our configuration resulted in a slow loop flow speed of 2 cm/s under the membrane. Bernoulli simulations of pressure differences across the membrane as a function of gas linear velocity indicated that, for this configuration, trans-membrane flow would be insignificant relative to diffusive flux across the membrane under normal conditions.

Measurement cycles are controlled automatically by the datalogger, and can generally be divided into three parts; concentration, scrub, and recovery. During the first (concentration) part of the measurement period, the logger uses the probe as a reservoir of air that has been allowed to equilibrate to soil conditions, much like Gut et al. (1998). Where the system is left connected to the probe between measurements, the probe is already equilibrated with soil gas concentrations, which is recorded as $\Delta C$. In cases where permanent probes are surveyed occasionally, they are sealed from exchange with atmospheric air during non-sampling periods. When the IRGA and associated tubing are connected to the buried probes and flow is initiated, air in the IRGA is displaced and the IRGA
"sees" only the CO$_2$ that was resident in the probe for approximately 30 seconds before mixing starts, as was established by repeatedly experimenting with probes pre-flushed with known-concentration CO$_2$ gas mixtures. The maximum value attained during this initial 30 second period is recorded as $\Delta C$ in the datalogger memory.

The next parts of measurement cycle involve scrubbing and re-equilibration. Circulating air is directed through the valves and into the soda lime column, scrubbing CO$_2$ from the loop. Once loop concentrations are negligible, a normal flow pattern is resumed and the datalogger monitors the recovery of the loop concentrations to ambient soil concentrations at 1 hz. The run is terminated before full equilibration occurs, usually at 15 minutes, which typically corresponds to approximately 25 per cent re-equilibration at normal field diffusivity values. Full re-equilibration is not required for calculations, but greater levels of re-equilibration increase accuracy. The typical 15-minute measurement interval is a reasonable compromise between measurement speed and accuracy, especially when doing survey measurements. The final diffusivity value is calculated based on mass flux of CO$_2$ into the probe over the measurement period, calculated by the change in concentration, loop volume and membrane surface area. This value is written to the datalogger output file.

2.3. Laboratory tests

Several basic laboratory tests were designed to test the general performance of the diffusion probe system. Firstly, experiments were used to determine the constants of membrane area and internal volume of the probe and system to satisfy the requirements of equation 4, which requires measurements of CO$_2$ mass flux, calculated using the change in concentration in a given volume through a given membrane area. Membrane area was
calculated from design drawings and the internal volume of the closed loop was assessed by covering the membrane with impermeable plastic, scrubbing CO₂ from the flow loop, and measuring the dilution of a very small slug volume of injected CO₂ gas. This dilution test was repeated each time physical changes were made to the system.

The first six probes constructed were then tested in media of known diffusivity to determine performance of the system. This test was designed to determine whether a probe-specific calibration factor would be required due to small differences in assembly or materials. Tests were carried out on six probes in two mediums of known CO₂ diffusivity, atmospheric air (1.6x10⁻⁵ m²/s at 25°C) and ultrapure water bubbled with 1000ppm CO₂ for ~24 hrs (1.6x10⁻⁹ m²/s at 25°C). The experiment was repeated four times for each probe in each media.

Further tests using packed columns were conducted to test the diffusivity system. Plastic ABS cylinders 10cm I.D. and 20cm long were packed with pre-wetted sand to achieve 22.5 per cent and 35 per cent volumetric water contents. A stainless steel screen at each end contained the column and the probe was inserted before packing through a hole in the side of the column. Small reservoirs in the end of the column were fitted with inlet and outlet valves through which gas standards of two separate concentrations (2238 ppm and 0 ppm CO₂) (balance N₂) could be introduced to develop a gradient across the column. Inlet and outlet flows were carefully balanced and measured using an Alltech DFC-HR low flow chromatography flowmeter. Static diffusivities were calculated using the mass CO₂ increase in the CO₂-free carrier gas per cross sectional column area as the gas flowed through the reservoir. Diffusivity was measured using the probe after purging the column.
with the standard gas solution. Modeled values were also generated using a modified Millington relationship from *McCarthy and Johnson* [1995],

\[
D_e = \frac{\theta_T D_{fw}}{H} + D_{fg} \theta_T^{10} \theta_g^{10},
\]

where \(D_{fg}\) is the diffusion coefficient in free air, \(D_{fw}\) is the diffusion coefficient in free water, \(\theta_T\), \(\theta_w\) and \(\theta_g\) are the total, water-filled and gas-filled volumetric soil porosity values respectively, and \(H\) is the dimensionless form of Henry’s solubility constant for \(\text{CO}_2\) in water [*Hillel*, 1998]. Porosities were calculated using the bulk density and moisture information. All measurements were conducted within hours of packing the columns to minimize any drying effects.

### 2.4. Field tests

During the summer of 2004, diffusivity-moisture curves were established at eight sites for both the organic matter - mineral interface and at 25 cm depth at eight research sites where subsurface concentrations are being monitored to establish subsurface \(\text{CO}_2\) production rates. Table 1 provides details of the site characteristics.

The direct push diffusivity probes were installed horizontally at the given depths from a dug pit, with the membrane area directly under the center of an artificial “rain” disk of 1 m\(^2\) (r=57 cm) sitting ~20 cm above the soil surface. The underside of this disk was fitted with a 15m coil of PEX tubing with 0.5 mm holes every 5 linear cm. When water was pumped from our 220 liter reservoir into the tubing, the result was an evenly distributed wetting of the soil. A Campbell Scientific CR10X-2M datalogger was used to 1) monitor two CS615 soil moisture probes installed at diffusivity measurement depths, 2) to switch
the pump for a given interval at the start of every hour and to 3) cue the diffusivity systems to measure at the end of each hour. The cumulative depth of precipitation was 21 cm over roughly 35 hours. Soil moisture information was recorded every five minutes, and diffusivity every hour. The entire experiment lasted approximately 40 hours at each site, and was repeated several times at one site (P2) to completely saturate the soil. Calculations suggest that under most field test conditions, each probe’s radial distance of influence was between 3 and 5 cm. This large radial distance suggests that potential small imperfect contact points between soil and membrane would not affect the soil diffusivity estimates. Under these conditions, we can also establish that the membrane’s influence on the measurement is small enough to be neglected (or considered non-limiting). Potential flux across the thin (0.1 mm) high diffusivity membrane is several thousand times faster than through the thickness of soil exploited during the measurement.

To test the measured diffusivity values for calculating subsurface CO$_2$ production, we sampled subsurface CO$_2$ concentrations during the 2004 growing season at two sites, a subset of those at which we established diffusivity-moisture relationships. These sites included a two year-old clearcut (LV3) and an adjacent 80-yr. old mixed hardwood/softwood stand (LV1). Both sites are underlain by sandy soils. Subsurface CO$_2$ was sampled weekly from gas wells made from perforated 2 cm O.D. x 50 cm long rigid PVC tubing covered with Gore-Tex, and with microbore tygon leads running to the surface. They were installed horizontally into soils at 0, 2.5, 5, 10, 20, 35, 50, 75, and 100 cm from a pit that was later backfilled. Samples were stored in 6 ml Exetainer vials (Labco) and concentrations were analyzed using an Licor LI-7000 configured in continuous flow configuration. Soil CO$_2$ surface fluxes were monitored concurrently using a Licor LI-8100 automated flux
chamber. Subsurface CO\textsubscript{2} production was calculated as the difference between CO\textsubscript{2} flux across soil layers, or in other words the outward output from layer \( i \) minus input from layer \( i-1 \) below, from the surface to maximum sampling depth,

\[ p_{\text{CO}_2} = F_i - F_{i-1}, \quad (6) \]

where \( p_{\text{CO}_2} \) is production of CO\textsubscript{2}, \( F \) is CO\textsubscript{2} flux density (g m\(^{-2}\) s\(^{-1}\)) and \( i \) represents a certain soil layer at depth \( z \).

Interlayer flux (\( F \)) is determined from Fick’s Law in one dimension.

\[ F = -D \frac{\partial C}{\partial z}, \quad (7) \]

where \( D \) is the diffusivity (m\(^2\) s\(^{-1}\)), \( C \) is the CO\textsubscript{2} concentration (g m\(^{-3}\)) and \( z \) is depth (m).

Combination of (1) and (2) [Davidson and Trumbore, 1995] yields

\[ p_{\text{CO}_2i} = [D_i \left( \frac{C_i - C_{i-1}}{z} \right)] - [D_{i+1} \left( \frac{C_{i+1} - C_i}{z} \right)], \quad (8) \]

where \( C_i \) and \( D_i \) are the concentration and effective diffusivity for layer \( i \), respectively. Concentrations were corrected for air-filled porosity, so that they would reflect the concentration of CO\textsubscript{2} in a volume of soil, and not soil air as sampled. To constrain the data within the bounds of field measurements, we generated CO\textsubscript{2} production estimates only for dates when moisture fell within the diffusivity-moisture characterizations. The final production estimates are subject to total errors of less than 10% (instrumental error, and Exetainer purging / evacuation / sample transfer.)
3. Results and Discussion

3.1. Laboratory tests

Overall measurement error was determined to be 3-6% of the measured value, which is very small relative to the potential variation between soil gas diffusivity values in dry and wet soils (3-4 orders of magnitude). Small differences between probes contributed to the variation in error, and although we chose not to carry out probe-specific calibrations, they could be useful to further reduce error in very high-resolution applications. The tests carried out in free air were limited by the membrane CO$_2$ diffusivity (approximately $8.5 \times 10^{-6} \text{ m}^2/\text{s}$). In most soils, it is unlikely that the membrane will limit diffusion, but in the unlikely event that measured soil diffusivities are equal to the membrane diffusivity, results will have to be discarded. Figure 2 summarizes performance across a normal range of soil diffusivity values. Assuming a linear relationship between measured and real diffusivities, calibration tests other than those conducted in water and air are not strictly required, as soil CO$_2$ diffusivity values generally fall somewhere between these extremes. But, our column tests using sieved silica sand at two different levels of hydration help to confirm 1) linearity across the measurement range, and 2) correspondence with known values and/or values observed in simultaneous static diffusivity tests.

3.2. Field tests

Results of field hydration tests show that as Millington and other models predict, diffusivity values fall as soil moisture content rises, giving the diffusivity-moisture curve a negative slope. Table 2 shows the diffusivity-moisture constants from best fit linear regression relationships developed at sites where diffusivity values did not approach those of saturated conditions.
Soils in proximity to one another (all LV sites, all P sites and both CC sites) tended to have roughly similar slopes to the diffusivity-moisture relationship, except where sites have been freshly disturbed, such as the LV3 and P3 clearcut sites. In contrast, organic-mineral (OM) interface and deeper (25cm) diffusivity-moisture curves were not predictably different from one another. In fact the diffusivity values at the OM interface were quite similar to deeper values, although the hydrologic conditions were different, with the OM interface tending to be either drier (LV) or wetter (P,CC) than deeper soils.

During field wetting experiments, we were successful in fully saturating only one soil. At P2, the reservoir was filled three times (over 600 litres total) to verify that saturated diffusivity values generally agreed with the known diffusivity of pure water. Figure 3 shows the results of testing at this site, along with data from the diffusivity model of *McCarthy and Johnson* [1995]. Only at field capacity and saturation do the measured and modeled values agree. In general the measured diffusivity values are much higher and drop precipitously as saturation is approached. This suggests that the most of the diffusive transport occurs via a well drained network of macropores. Where soils did become nearly or fully saturated, a third order polynomial (i.e. Figure 3) provided the best fit. In general, the linear fits are robust (average $r^2$ of over 0.80, n=14) but valid only to some point just below saturation, before the precipitous drop in diffusivity towards diffusion through pure water.

The absolute values of diffusivity and rate at which diffusivity decreased was typically quite different from that predicted by the modified Millington model. Regular light rains kept soils at field capacity all summer, and along with topographic position and drainage, determined the starting moisture value for these field experiments. As summarized in
Table 3, field capacity diffusivity values were higher than modeled values for the LV soils, whereas for most other soils the model over-predicted rates of diffusive transport. The model performance was worse at greater initial moisture contents. We did note a hysteresis effect, where somewhat different diffusivity values were associated with wetting and drying, by analyzing data from the period after the reservoir had emptied. But, soil drying occurs so slowly that we were unable to include this as part of our tests.

Further investigations of the discrepancy between measured and modeled values for all soils revealed that the model error factors (measured-modeled results) could be plotted as a function of soil water content, as shown in Figure 4. Across all site soils, the McCarthy-Millington model \cite{McCarthy and Johnson, 1995} mildly overestimated at small moisture contents, and moderately underestimated diffusivity at high moisture contents. Laboratory testing revealed excellent correspondence in packed sand columns, where pore size and shape was well controlled. In natural settings, however, soil particles are aggregated and distributed heterogeneously. A simple conceptual model may explain the discrepancy between measured and modeled values: Small pores are not well recruited for diffusion because they are plugged with organic matter, cemented into aggregates, filled with capillary water and/or unconnected to one another (high tortuosity). Instead, the network of well-connected and well-drained larger pores in the inter-aggregate space is preferentially recruited for diffusion. The influence of capillary water is smaller in large pores, so that gas diffusivity values do not fall precipitously until near saturation. This macropore network likely remains relatively open as a result of root turnover, seasonal frost, and activity of soil organisms.
3.3. Field application

As shown in Figure 5, measured diffusivity values at sites performed well in field applications when applied in conjunction with subsurface CO$_2$ concentrations and a multilayer CO$_2$ production model. We compared soil CO$_2$ surface flux values (independently measured) with total profile CO$_2$ production rates, under the assumption that production and flux should be roughly equal at most timescales. At both study sites, and as shown in Figure 5, total soil profile CO$_2$ production closely followed soil CO$_2$ surface flux. Although we observe occasional offsets, the flux magnitudes were generally comparable despite the many factors that could cause them to differ, including uncertainties in flux chamber measurements, and soil heterogeneity (CO$_2$ production, diffusion, soil moisture) between the flux collars and subsurface samplers that are 1 m apart. In contrast, the Millington-type model of McCarthy and Johnson [1995] strongly over- or under-predicted diffusivities, depending on the site. As a result, total soil profile production values were unreasonable, either much higher (LV1) or much lower (LV3) than measured surface fluxes. It is clear that site-specific diffusivity values should be employed whenever accurate production values are required or where data will be compared between sites.

To illustrate seasonal CO$_2$ dynamics in the soil profile as calculated with in-situ diffusivities, we plotted depth-specific contributions to total profile CO$_2$ production for both sites throughout 2004 (Figure 6). The bulk of soil profile production was observed high in the soil profile (approx. 90% in the first 10 cm), despite clear site differences between the intact forest at LV1 and 3-yr. old (root free) harvest at LV3. Short term variation and seasonal trends can be seen, especially the increasing importance of production deep in the soil profile in late 2004.
4. Conclusions

A new portable membrane probe and system to rapidly measure CO$_2$ diffusivity in the field has been tested successfully in the laboratory, and applied to quantification of diffusivity rates as a function of moisture content at eight field sites. Diffusivity-moisture relationships at field sites were highly significant and where soils weren’t brought to full saturation, they were best described by a linear fit. At high soil moisture contents, we observed a strong departure from this linear behavior, with very rapid decreases in soil gas diffusivity near saturation. In these circumstances, site-specific polynomial relationships provided the best overall fit across the measured soil volumetric water contents.

In the laboratory, measured, modeled and known rates of diffusivity agreed well with one another, but in the field, the diffusivity model over- or under-predicted diffusivity by up to two orders of magnitude. Field values were in agreement only at soil saturation, when diffusive transport takes place mainly through the water phase. Across all sites, the discrepancies between measured and modeled results at moderate and low moisture contents were found to depend on the soil moisture content itself. One possible explanation for this behavior in field soils is the preferential recruitment of large pores for diffusive transport.

Field application of the diffusivity technique in our monitoring program clarified the advantage of the measured diffusivity values over model-generated values. Use of model-generated values translated into significant error in CO$_2$ production estimates. The in-situ diffusivity measurements boosted the accuracy and effectiveness of the in-situ monitoring program, and demonstrated that diffusion in complex natural soil structures must be
quantified on a site-specific basis, preferably using an in-situ method such as the one described here.

The application of this system to the measurement of vertical soil profile contributions to CO$_2$ production can be used to accurately resolve differences in vertical contributions over time at field sites. This has the potential to contribute to our evaluation of subsurface CO$_2$ processes, in particular the independent responses of shallow vs. deep soil organic matter pools to the alterations in the physical environment.

The effort spent refining subsurface monitoring methods are worth the trouble, as they are able to deliver increased detail for carbon monitoring and other trace gas studies. They become particularly attractive because of probes now on the market (e.g. Vaisala) that can be deployed in the subsurface to monitor concentration profiles continuously, for costs competitive with commercially available surface flux measurement systems. In fact, the concentration profile approach may hold advantages for continuous monitoring of respiration particularly in remote and/or extreme environments, where moving parts on the surface aren’t a potential threat to reliability. The diffusivity approach described here is flexible in embodiment, and could likely be integrated into the small package of a CO$_2$ probe. This will help improve results from all types of subsurface trace gas studies, whether used for the purposes of budgeting or to elucidate information on soil processes.

**Acknowledgments.** This research was funded by Natural Sciences and Engineering Research Council of Canada (NSERC), the Canadian Fundation for Climate and Atmospheric Sciences (CFCAS), the Atlantic Canada Opportunities Agency (ACOA) and the Geological Society of America (GSA), through research grants to D. Risk, L. Kellman and H. Beltrami. Thanks to Krista Kavanaugh for expertise during laboratory testing. We
would like to thank anonymous reviewers for their suggestions, which greatly strengthened this manuscript.
References


Drewitt, G.B., Black, T.A., Jassal, R.S. (2005), Using measurements of soil CO$_2$ efflux and concentrations to infer the depth distribution of CO$_2$ production in a forest soil *Cdn. J. Soil Sci.* 85, 213-221.


Tang, J., D. D. Baldocchi, Y. Qi, and L. Xu (2003), Assessing soil CO₂ efflux using continuous measurements of CO₂ within the soil profile with small solid-state sensors,

Valentini, R., and 30 others (2000), Respiration is the main determinant of carbon balance in European forests, Nature 404, 861-865.


Table 1. Site characteristic including aboveground vegetation, and soil textural information.

Data from Cann and Hilchey [1954].

<table>
<thead>
<tr>
<th>Site</th>
<th>Vegetation Type</th>
<th>Max Porosity</th>
<th>Sand</th>
<th>Silt/Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>LV1</td>
<td>Forest</td>
<td>45</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td>LV2</td>
<td>Selective Cut</td>
<td>45</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td>LV3</td>
<td>Clear Cut (2001)</td>
<td>45</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td>CCF</td>
<td>Field</td>
<td>45</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>CCW</td>
<td>Forest</td>
<td>45</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>P1</td>
<td>Field</td>
<td>50</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>P2</td>
<td>Forest</td>
<td>50</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>P3</td>
<td>Clear Cut (2001)</td>
<td>50</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>Site</td>
<td>Depth (cm)</td>
<td>Linear Slope</td>
<td>Linear Intercept</td>
<td>Linear r²</td>
</tr>
<tr>
<td>-------</td>
<td>------------</td>
<td>---------------</td>
<td>------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>LV1</td>
<td>OM interface</td>
<td>-1.1823</td>
<td>0.7506</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>-1.2028</td>
<td>0.8200</td>
<td>0.89</td>
</tr>
<tr>
<td>LV2</td>
<td>OM interface</td>
<td>-1.8450</td>
<td>0.8077</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>-0.9267</td>
<td>0.7522</td>
<td>0.71</td>
</tr>
<tr>
<td>LV3</td>
<td>OM interface</td>
<td>-9.3390</td>
<td>3.4206</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>-1.8346</td>
<td>0.9599</td>
<td>0.74</td>
</tr>
<tr>
<td>CCF</td>
<td>OM interface</td>
<td>-0.5666</td>
<td>0.4464</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>-4.7419</td>
<td>1.4387</td>
<td>0.72</td>
</tr>
<tr>
<td>CCW</td>
<td>OM interface</td>
<td>-1.9489</td>
<td>0.9988</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>-7.0188</td>
<td>1.7716</td>
<td>0.92</td>
</tr>
<tr>
<td>P1</td>
<td>OM interface</td>
<td>na</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>-1.6574</td>
<td>0.9015</td>
<td>0.90</td>
</tr>
<tr>
<td>P2</td>
<td>OM interface</td>
<td>na</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>-0.4232</td>
<td>0.3873</td>
<td>0.84</td>
</tr>
<tr>
<td>P3</td>
<td>OM interface</td>
<td>-28.3110</td>
<td>5.0238</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>-40.3300</td>
<td>5.9479</td>
<td>0.97</td>
</tr>
</tbody>
</table>

**Table 2.** Constants and regression significance for diffusivity-moisture curves at all sites, both for mineral (25cm) and OM-interface depths. Where data is not available (na), polynomial fits were applied.
Table 3. Initial soil volumetric water contents at the start of rain experiments (field conditions), and corresponding soil CO\textsubscript{2} diffusivity values (both measured and modeled). Despite a wide range in initial soil moisture conditions, measured field diffusivity values generally fell within one order of magnitude. The modified Millington model of McCarthy and Johnson (1995) predicts a much wider variation in diffusivity than is seen in field settings. The "error factor" (field D\textsubscript{e}/model D\textsubscript{e}) was high at high initial soil moisture conditions, and low where initial soil moisture was also low.
Figure 1. Schematic of diffusivity system, showing components, electrical connections and closed loop gas flow (clockwise direction). The reader will appreciate that other probe designs would also be suitable.

Figure 2. Measured diffusivities plotted against theoretical diffusivity for various testing media; pure water, pure air (known diffusivities) and sand columns of different moisture content (diffusivity predicted by modified Millington of McCarthy and Johnson [1995] or by static method). The 1:1 line is shown, and error bars are not shown because they would not be graphically resolvable.

Figure 3. Diffusivity-moisture curve for P2, the only site that was fully saturated during the course of field testing. Approximately 120 field data points are shown, many of which overlap. Open squares show modified Millington model diffusivity estimates [McCarthy and Johnson, 1995] for the same soil (total porosity was estimated at 45%). Millington and measured values converge at saturation, but at intermediate soil moisture contents, measured diffusion is significantly higher than the model estimate.

Figure 4. Diffusivity error factors (measured modeled D) as a function of soil volumetric water content. Data is for mineral soils (25cm depth) at all six sites where test data were fit linearly. Data for each site are only plotted for the measured ranges of volumetric water content. The McCarthy/Millington model overestimated at small moisture contents, and underestimated diffusivity at high moisture contents. This trend was evident at all sites.
**Figure 5.** Measured surface fluxes plotted through the 2004 sampling season relative to total profile soil CO$_2$ production as calculated using the measured (probe) and modeled (Millington-type) diffusivities. For both sites shown, measured-D production corresponds well to observed surface fluxes, but possible lags are evident. Use of Millington diffusivities resulted in errors of up to 2x, and were site specific. The errors could be positive or negative in sign as shown by the shaded area.

**Figure 6.** Depth-specific contributions to total profile CO$_2$ production for a range of dates in 2004. Most of the production at both sites was observed high in the soil profile (approx. 90% in the first 10 cm), despite differences in site soils and surface characteristics. Short term variation and seasonal trends can also be seen, especially the increasing importance of production deep in the soil profile towards the end of 2004.
Field-portable enclosure

IRGA (LIcor LI-820) → Datalogger (CR10x-2M) → 12V → Pump → Soda Lime

Soil surface

Membrane probe (permanent burial type), shown with membrane (light shading) and stainless mesh (dark shading)

Membrane probe internals. Gas flow passes along linear flow paths along one side of membrane carrier, then along other side.
Soil CO$_2$ Diffusivity (m$^2$/s x 10$^6$)

Soil Water Content (v/v)

$y = -264.1x^3 + 220.56x^2 - 61.699x + 6.4106$

$R^2 = 0.9392$
$y = 0.0267e^{16.645x}$

$R^2 = 0.8244$