BIOLOGICAL AND PHYSICAL CONTROLS OF CO2 FLUX THROUGH SNOW

IN A FORESTED ECOSYSTEM

by

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Fredrick Aaron Rains
January 2013
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ABSTRACT

Soil CO₂ efflux is the dominant component of carbon loss in many temperate forests. Wintertime respiration accounts for a significant contribution of the annual carbon loss to the atmosphere from terrestrial ecosystems, but the magnitude of this flux and physical transport mechanisms through snow are unclear. This research examines wintertime CO₂ flux in a lodgepole pine forest in the Upper Stringer Creek catchment at the Tenderfoot Creek Experimental Forest, Montana, USA. I hypothesized that: 1) CO₂ production and efflux during the winter contributes a significant amount (10-20%) of CO₂ efflux to the atmosphere in the Tenderfoot Creek Experimental Forest; 2) Snow properties, i.e. depth and density, and thereby porosity and tortuosity vary during the winter via snow metamorphosis, thus changing the impedance to flux through the snow medium and CO₂ production increases when the snowpack becomes isothermal during melt due to increased soil moisture and soil temperature. A micrometeorological stations was installed to measure soil water content, soil temperature, incoming and outgoing radiation, albedo, snow depth, snow/soil interface CO₂ concentration, atmospheric CO₂ concentration, three-dimensional wind speed, and above snow/sub-canopy CO₂ flux on a half-hourly basis. In addition, throughout the winters of 2010/2011 and 2011/2012 snow pit analyses was performed in triplicate approximately once monthly and snow depth, density, and temperature were measured in 10-centimeter increments. Three methodological approaches were used to analyze CO₂ flux through the snow pack: Chamber on snow, two-point Fick’s law based diffusivity modeling, and snow-surface/subcanopy eddy covariance. The results of the comparison show a significant difference in measured and estimated flux between methodologies during early and late winter, while demonstrating the Fick’s based model is can accurately estimate up 75% of measured flux during mid-winter. Observations are consistent with advection, in addition to diffusion, as a mechanism of CO₂ transport through snow such that observation strategies that do not account for advection may underestimate wintertime efflux. Furthermore, all three methodologies indicate that wintertime respiration is a major contributor to the annual carbon budget when mean flux rates are compared to growing season flux rates.
CHAPTER 1

INTRODUCTION

Scientific Background

This research quantifies physical controls imposed on soil CO\textsubscript{2} efflux through snow during two full winter seasons (2010/2011, 2011/2012). The primary focus was on snow physical properties i.e. depth and density, and the accumulation and ablation of a seasonal snowpack, and in turn, how these variables affect the rate and timing of CO\textsubscript{2} flux from the soil, through the snowpack into the atmosphere. CO\textsubscript{2} efflux was observed using three techniques – eddy covariance, the flux-gradient method using solid-state probes, and a snow-surface chamber with infrared gas analyzer. This allowed the examination of snowpack properties, and their affects on CO\textsubscript{2} flux.

CO\textsubscript{2} efflux via heterotrophic and autotrophic respiration accounts for the largest portion of carbon loss from the terrestrial system to the atmosphere, producing approximately 80PgC/yr (Raich et al., 2002). The return of CO\textsubscript{2} into the atmosphere during winter impacts the net primary productivity (NPP) of an ecosystem and determines in part whether the ecosystem can be designated a carbon sink or a carbon source. A more in depth understanding of wintertime efflux in our study area and the major controls exerted by a seasonal snowpack, will increase the overall understanding of carbon cycling in forested mountain ecosystems with similar characteristics. Traditionally, the wintertime portion of the carbon cycle was thought to be negligible due to temperature induced slowing of metabolic processes within the micro-organismal
communities found in the soil medium (e.g. Coyne and Kelley, 1971; Steudler et al., 1989; Zimov, Davidov, & Voropaev, 1996). While this is perhaps true in areas that have a shallow, accumulated snowpack, research has shown that deeper snowpacks like those that can be found in the mountainous regions across the Northern hemisphere, can insulate the soil, maintaining a temperature above -6.5 degrees C (Coxson and Parkinson 1987), which is necessary for CO₂ production (Sommerfield et al. 1996).

Much of the northern hemisphere is covered in snow for a significant portion of the year, and soil respiration has been identified as the dominant source of CO₂ input to the atmosphere in many temperate forests (McDowell et al. 2000). As knowledge of the controls over wintertime soil CO₂ flux increases, its importance to the annual ecosystem carbon budget is becoming more widely recognized (Wang et al. 2010). Understanding the drivers and dynamics of soil respiration in winter will lead to a more complete understanding of the carbon cycle. Studies to date have demonstrated the importance of not only climate and snow properties, primarily depth (Monson, 2006) on controlling wintertime CO₂ efflux, but also the role of measurement methodology for generating defensible flux estimates. Furthermore, understanding how vegetative cover affects a seasonal snowpacks physical properties and temporal persistence and in turn how those variables affect wintertime efflux will increase the understanding of how future changes in forest physiognomy may effect carbon efflux. With an increase in disturbances in North American forests from Mountain Pine Beetle (MPB) and fire regimes changing in frequency and severity due in part to a changing climate, management practices are being designed to mitigate the effects of these disturbances as well as the effects of the management practices themselves, i.e. thinning, clear cutting, and the roads needed
access the areas being managed (USDA, National Report on Sustainable Forest-2010).

Although there has been widespread research on the effects management practices on soil carbon pools, the effect of these disturbances, both natural and anthropogenic, on snow accumulation and distribution and the reciprocating affects on winter-time efflux are not fully understood.

There have been a variety of methodological approaches used to study wintertime CO$_2$ efflux in high-latitude and/or mountainous regions. Some earlier research was conducted by Sommerfield (1996) in alpine and subalpine zones at the Glacier Lakes Ecosystem Experiment site in South Central Wyoming, USA. The methodology consisted of installing gas collectors at the soil surface and digging snow pits nearby to determine the snow’s physical properties. The results showed strong CO$_2$ release during winter from both altitudinal zones, with a significantly higher efflux in the subalpine zone, demonstrating the importance of climate to wintertime CO$_2$ efflux.

McDowell et al. (2000) performed a study comparing chamber on snow, chamber on soil surface, and a flux-gradient system in mid-elevation forests in Wyoming, Idaho, and Washington, USA. The researchers found that of the three techniques, the chamber on snow surface measurements were most reliable because they required the least amount of disturbance and made the fewest assumptions. Snow chamber and flux-gradient measurements were very similar when a tortuosity of 0.7-0.9 was used as a diffusional constant in the Fick’s Law calculation.

Other studies have compared the use of various techniques in a variety of locations worldwide. Sullivan (2008, 2010) compared several methodologies while study wintertime flux at tussock tundra and boreal forest sites in Alaska. He installed a flux-
gradient system with a solid-state CO$_2$ sensor array and also used a portable infrared gas analyzer (IRGA) and probe set up that allowed measurements to be taken at the snow surface as well as subniveal measurements to be taken without disturbing the snow directly adjacent to the measurement sites. The researchers also had micrometeorological data from three stations located in the area and a station near the mouth of the watershed they were studying as well as soil temperature at the study plots. Snow physical property data were also collected at each of the study plots. Results demonstrate strong differences between the sites in subniveal concentrations of CO$_2$, as well as the rates of flux, and overall production of CO$_2$ throughout the course of the winter. The tussock tundra site produced 24 g C m$^{-2}$ and the upland boreal forest 75 g C m$^{-2}$ over the course of the study period. Also of significance is the strong correlation (r = .94) of subniveal CO$_2$ values measured using the two methods described above.

Bjorkman et al (2010) recently performed a comparative analysis of wintertime efflux sampling methodology in high arctic Svalbard. The researchers compared four different techniques: 1) chamber on snow surface, 2) chamber on soil surface, 3) two-point diffusional measurement, subniveal at soil surface, and snow surface, 4) trace gas through snow times series. Two sites in arctic Svalbard were used, both with similar vegetation and soil characteristics, but with differences in elevation and latitude including the presence of permafrost at the higher latitude site. Furthermore, shallow and deep snow regimes were compared using snow fences. Results demonstrated substantial differences in efflux estimates among different methodologies of up to 2 orders of magnitude. This is cause for concern because these data are often used in climate models and carbon budget calculations (Bjorkman et al, 2010).
The eddy covariance technique has been employed to measure net ecosystem exchange in a variety of locations around the world. Eddy covariance measures net ecosystem exchange (NEE) at a very high frequency (up to 10 times per sec) and can be applied to a various spatial sizes and arrangements based on numerous factors including tower height, topography, micrometeorology, etc. This technique is perhaps best suited to relatively flat, homogenous topography (Bjorkman et al., 2010). However, it has been applied to mountainous terrain as well. Monson (2006) compared eddy covariance data with subniveal chamber and inlet measurements at NIWOT Ridge, Colorado, USA. It was found that soil respiration accounted for 38-45% of total wintertime respiration, and 7-10% of total annual ecosystem respiration. Wang et al, (2010) analyzed winter CO$_2$ flux data from 57 eddy covariance sites at mid and high latitudes across the northern hemisphere. They found that among the variety of ecosystem types compared in their analysis, evergreen needle leaf forest had an “intermediate” level of contribution to the annual carbon budget of 7.4–7.9 gCm$^{-2}$ d$^{-1}$.

Study Objectives

This research will add to the science of land atmosphere interaction and forest ecology through the observation of wintertime soil efflux and the role of snow in the transport of gases to the atmosphere. The affects that snow plays on the major drivers of soil respiration i.e. soil temperature and soil moisture is not wholly understood. Through the measurement of snow properties, soil micrometeorology, subnivean CO$_2$ concentration, and snow-surface efflux of CO$_2$ we may begin to understand relationships that exist between these phenomena. Additionally, quantifying the contribution of
wintertime efflux to the annual carbon budget in our study area will lead to a more complete understanding of the carbon cycle in ecosystems with similar characteristics i.e. vegetation, elevation, and latitude. Furthermore, the comparative analysis of the primary methodologies used in studying wintertime flux will demonstrate the applicability and appropriateness of these methodologies in similar ecosystems in winter.
CHAPTER 2

COLD-SEASON SOIL CO₂ EFFLUX IN A LODGEPOLE PINE ECOSYSTEM

Introduction

The cycling of carbon dioxide (CO₂) between land and the atmosphere is an integral topic in climate science. Soil respiration has been identified as the largest contributor of terrestrial CO₂ efflux, with a magnitude of approximately 80 PgC/yr (Raich et al., 2002). Soil CO₂ flux is the dominant respiratory flux in many temperate forests (McDowell et al. 2000), and most studies focus on observations during seasons when belowground metabolic processes are more active. The wintertime portion of the carbon cycle is often considered to be negligible due to a reduction in the primary drivers of soil respiration, soil temperature, labile carbon and soil liquid water, which lead to a slowing of metabolic processes within the micro-organismal communities found in the soil medium (e.g. Coyne and Kelley, 1971; Steudler et al., 1989). Recent studies have demonstrated, however, that cold season respiration may contribute on the order of 10 - 20% of the annual CO₂ efflux (Larsen et al. 2007b) in many ecosystems with seasonal snow cover. With much of the Northern Hemisphere being covered in snow for a significant portion of the year, wintertime CO₂ flux is increasingly recognized as an important component of the terrestrial carbon cycle (Wang et al. 2010). Understanding the drivers and dynamics of surface-atmosphere CO₂ exchange in winter will lead to a more complete understanding of the carbon cycle.
Soil respiration generally increases with snow depth as a function of soil insulation (Grogan and Jonasson 2006; Larsen et al. 2007a; Monson et al. 2006), suggesting a close interplay between the physical properties of snow and the biological process of soil respiration. Specifically, snow insulates soil, and soil respiration has been quantified at soil temperatures as low as -6.5 degrees C (Coxson and Parkinson 1987) (Suzuki et al., 2006) (Sommerfield et al. 1996). Soil CO₂ efflux therefore responds to changes in snow depth and density throughout the snow-covered season (Monson et al., 2006), but important uncertainties remain in our understanding of how trace gases move through temporally dynamic snowpacks and therefore how to best quantify soil-snow-atmosphere CO₂ transport over time, especially because some systems assume that CO₂ flux through snow is controlled by diffusion when advection may also represent an important transport mechanism (Massman and Frank, 2006).

Several techniques are available for measuring wintertime CO₂ efflux, all of which offer both benefits and disadvantages. Chamber measurements can provide highly accurate flux observations, but may disturb snow structure (especially if snow is removed for a direct soil CO₂ efflux measurement), Chambers also measure over small scales in space and time, and are difficult to automate for continuous measurements during the snow-covered season. Flux-gradient methods based on Fick’s first law of diffusion can readily provide continuous estimates of wintertime soil CO₂ efflux, but models of the conductance of snow to trace gas diffusion rely on uncertain parameterizations (especially regarding tortuosity), and recent studies have demonstrated a non-trivial role of advective transport of trace gas through snow, especially in windier conditions (Bowling and Massman, 2011). The observed relationship between wind and CO₂ efflux
also complicates the application of the eddy covariance technique, which must filter out data collected under conditions of insufficient turbulent flux, often approximated as conditions with insufficient friction velocity \((u^*)\), itself related to wind speed. Few studies to date have combined the eddy covariance method with in situ point and chamber measurements during the snow-covered season [but see Monson et al. (2006)], despite the growing prominence of the eddy covariance methodology for quantifying surface-atmosphere CO$_2$ exchange (Baldocchi et al., 2008).

Despite methodological challenges, measurements of cold season CO$_2$ efflux have demonstrated its importance to the annual carbon budget, and have highlighted the important roles of snow cover, climate, and ecosystem type in determining flux magnitude. Some earlier approaches involved installing gas collectors at the soil surface and digging snow pits nearby to determine its physical properties (Sommerfield et al. 1996). Results showed strong CO$_2$ release during winter from both alpine \((95 \text{ g C m}^{-2} \text{ y}^{-1})\) and subalpine zones \((232 \text{ g C m}^{-2} \text{ y}^{-1})\) with the significantly higher efflux in the subalpine zone attributable to warmer temperatures and higher primary productivity.

Other multi-method comparisons for wintertime CO$_2$ efflux include McDowell et al. (2000), in which chamber on snow, chamber on soil surface, and flux-gradient techniques were compared in mid-elevation forests in Wyoming, Idaho, and Washington, USA. It was found that of the three techniques, the chamber on snow surface measurements were most reliable because they required the least amount of disturbance and made the fewest assumptions, although obtaining continuous measurements across time with chamber techniques on snow remains challenging. Direct flux measurements made via the snow-surface chamber and flux-gradient measurements were very similar.
when a tortuosity of .7-.9 was used in the conductance equation when applying the flux-gradient approach.

Sullivan et al. (2008) and Sullivan (2010) combined a fixed array of solid-state CO₂ sensors with an infrared gas analyzer and probe installation that allowed subnival measurements to be taken with minimal snow disturbance the in tussock tundra and boreal forest ecosystems in Alaska. Results show strong differences between the sites in subnival concentrations of CO₂, as well as the rates of flux, and overall production of CO₂ throughout the course of the winter. The tussock tundra site produced 24 g C m⁻² and the upland boreal forest 75 g C m⁻² over the course of the study period and excellent agreement (r = 0.94) between time series of subnivean CO₂ concentration using the two methods.

Bjorkman et al. (2010) compared wintertime efflux sampling methodology using chamber on snow & soil surface, two-point diffusional measurements, and trace gas (SF₆) measurements at multiple depths in the snowpack. Two sites in arctic Svalbard were compared, both of which had similar vegetation and soil characteristics, but with significant differences in elevation and latitude including the presence of permafrost at the higher latitude site. Shallow and deep snow regimes were examined and snow fences were created that artificially formed areas of deep snow. CO₂ flux estimates from different methodologies differed by up to 2 orders of magnitude, suggesting that further investigations into measurement methodology are necessary to constrain wintertime CO₂ flux. The divergent efflux estimates are cause for concern because these data are often used in climate models and carbon budget calculations.
Monson et al. (2006) found that wintertime respiration accounted for 7-10% of total annual ecosystem respiration in their study area, and that beneath-snow soil respiration contributed 35-48% to total wintertime respiration. Of particular significance was the snowmelt period when melt water began infiltrating the soil profile. The observation that a slight increase in soil temperature (0.3-0.5°C) resulted in a six-fold increase in respiration indicates that the snowmelt period is highly important to wintertime respiration dynamics.

In the present study, wintertime CO$_2$ efflux observations were made in a lodgepole pine stand in the Tenderfoot Creek Experimental Forest in the Little Belt Mountains of west-central MT during the winter of 2011/2012. Snow-surface chamber, two-point flux gradient, and eddy covariance measurement techniques are compared with a focus on relationships among different techniques during different periods of snowpack development and ablation. Additionally, I examined the significance of wind speed and $u^*$ (friction velocity), the role that they play in measuring wintertime flux via the eddy covariance technique via the Reichstein algorithm (Reichstein et al., 2005), and the possibility that neglecting to account for variables related to atmospheric pressure pumping may lead to an under-estimation of wintertime flux when applying the two-point flux gradient technique which traditionally assumes flux to be via molecular diffusion.

I hypothesized that: 1) CO$_2$ production and efflux during the winter contributes a significant amount (5-10%) (Monson et al., 2006) of CO$_2$ to the atmosphere in the Tenderfoot Creek Experimental Forest, 2) Snow properties, i.e. depth and density, and thereby porosity and tortuosity vary during the winter via snow metamorphosis, thus changing the impediment to flux through the snow medium, 3) CO$_2$ production increases
when the snowpack becomes isothermal during melt due to increased soil moisture and soil temperature.

Methods

Study Location and Characteristics

This study was conducted in the Stringer Creek catchment, a sub-watershed within the Tenderfoot Creek Experimental Forest (TCEF) (lat. 46° 55’ N., long. 110° 52’ W.) in the Little Belt Mountains of west-central Montana, USA. TCEF was established in 1961 and was initially designed as a hydrologic study site. Since 1991, ecological studies have been conducted, often focusing on the sustainability of Lodgepole pine (*Pinus contorta* Dougl.) ecosystems on the east-slope of the Northern Rocky Mountains have been conducted at TCEF. Researchers have developed state-of-the-art approaches for quantifying hillslope and soil hydrology (Jencso et al. 2009) and for quantifying soil C fluxes at point (Pacific et al. 2008; Pacific et al. 2009; Riveros-Iregui et al. 2007; Riveros-Iregui et al. 2008) to whole watershed scales (Riveros-Iregui and McGlynn 2009; Pacific et al. 2010).

TCEF encompasses 3591 ha and elevation ranges from 1840 to 2421 m with a mean of 2205 m. We focus on a forested plot within the Upper Stringer Creek sub-catchment. The Stringer Creek catchment is 555 ha and has a varying range of slope, aspect, and topographic convergence/divergence (Pacific et al., 2007; Farnes et al. 1995).

Average annual precipitation at TCEF is 883 mm, with 52% of annual precipitation falling between October and March, most of which is stored as snow until spring melt. Average snowfall depths at the study sites used in this research average 1-1.5
m and daily mean temperatures in winter range from 1.7 °C in October, to -12.8 °C in January (Farnes et al. 1995). Lodgepole pine is the dominant tree species found at TCEF, with minor contributions of subalpine fir (Abies lasiocarpa), Engelmann spruce (Picea engelmannii), whitebark pine (Pinus albicaulis), and quaking aspen (Populus tremuloides) (Farnes et al. 1995).

Snow Property Analysis

Snow profile pits were dug in triplicate during each visit to the field site (approx. once per month over the course of the winter), no closer than five meters and no further than 50 meters away from the instrumentation arrays. Temperature and snow density were measured at ten cm increments using a Prosnow kit (Snowmetrics, Fort Collins, CO). Pit location was chosen at random upon each visit to the site, and pits were refilled after measurements were taken to minimize disturbance effects.

Micrometeorological Instrumentation

A full suite of micrometeorological sensors was installed on or near the tower. Soil temperature was measured using Type T (Copper-Constantan) thermocouple temperature probe in the soil -5cm below the soil surface. A CS616 soil moisture probe (Campbell Scientific, Logan, UT) was installed at 5cm below ground surface. Incident and outgoing short and long-wave radiation were measured using a NR01 four-component net radiometer (Hukseflux, Delft, The Netherlands), and soil heat flux was measured using a Hukseflux HFP01 heat flux plate placed 5 cm below the soil surface. Temperature and relative humidity were measured using HMP45C temperature/relative humidity sensor (Vaisala, Vantaa, Finland) and subnivean air pressure at the soil surface (i.e. underneath
the snowpack) was measured using a Vaisala PTB110 barometer. Snow depth was recorded using a Campbell Scientific SR50A-L sonic depth sensor (Campbell Scientific). All micrometeorological measurements from the sensor array were recorded using CR3000 and CR1000 data loggers (Campbell Scientific) at a scan interval of one minute and averaged over half-hourly periods.

**Eddy Covariance**

An eddy covariance tower was installed below the forest canopy at the Stringer Creek site in the fall of 2010. The eddy covariance method is used to measure water vapor and CO\textsubscript{2} flux over a footprint that often extends hundreds of meters depending on tower height, topographical characteristics of the site, and meteorological conditions. The tower setup was designed to measure CO\textsubscript{2}/H\textsubscript{2}O fluxes representative of autotrophic (microbial) and heterotrophic (tree and plant root) respiration occurring within the soil profile over a small footprint (Misson et al., 2005), including CO\textsubscript{2} efflux from the snowpack surface during winter. The tower was equipped with an enclosed LI-7200 CO\textsubscript{2}/H\textsubscript{2}O infrared gas analyzer (LiCor, Lincoln, NE, USA) and a CSAT-3 Sonic Anemometer (Campbell Scientific Inc., Logan, Utah) both at 2 m above the ground surface. The tube between the air inlet and the Li-7200 was 100 cm, the tube flow rate was 14.0 L/min, separation between the center of the anemometer path and tube inlet was 25 cm (northward) 5 cm (eastward), 6 cm in the vertical. Measurements were collected at 10 Hz and stored on a CR3000 data logger (Campbell Scientific, Logan, UT). Thirty-minute flux sums were calculated using EddyPro v 4.0 (LiCor, Lincoln, NE, USA). Axes were rotated for tilt correction using double rotation (Lee. et al., 2004), block averaging was
used to de-trend (Moncrieff et al. 2004), and time lag was detected using covariance maximization (Mauder and Foken, 2004). The analytic correction of high-pass filtering effects (Moncrieff et al. 2004) option was selected for the low frequency range and the low-pass filtering option was selected for the high frequency range (Moncrieff et al. 1997). Statistical tests for the raw data screening (Vickers and Mahrt, 1997) were performed under the ‘Statistical Analysis’ option in EddyPro. Spike count/removal options were set allowing for a maximum of 3 consecutive outliers. Accepted spikes in the data were set at 1.0 %. The remaining spikes were replaced by linear interpolation. Standard skewness and kurtosis thresholds were applied.

The \( u^* \) thresholding algorithm of Reichstein et al. (2005) was applied to the data to explore the dependency of flux magnitude on the friction velocity (\( u^* \)). The routine was applied to the entire dataset, and to nighttime periods only (defined here as periods with solar zenith angle > 90°). The Reichstein et al. (2005) algorithm tests the dependency of \( \text{CO}_2 \) efflux on \( u^* \) using three month subsets of the data. \( \text{CO}_2 \) flux observations are sorted into temperature and \( u^* \) classes and the threshold is determined to be the \( u^* \) value at which mean flux exceeds 95% of mean flux at higher \( u^* \) values after taking into account the role of temperature in determining \( \text{CO}_2 \) flux magnitude.

Subnivean CO\(_2\) Sampling Instrumentation

A subnivean \( \text{CO}_2 \) sampling apparatus (Figure 1.1) was designed and installed in the autumn of 2011. A small diaphragm pump cycled air at 1 L/min through \( \frac{1}{4}'' \) (0.635 cm) vinyl tubing from the ground surface to and from a fixed Vaisala 343 \( \text{CO}_2 \) probe (Vaisala, Helsinki, Finland) situated in an airtight case (Pelican Products Inc., Torrance,
CA, USA) above the snow surface. This design allowed us to prevent the small amount of heat typically produced by solid-state CO$_2$ sensors from disturbing snow properties \textit{in situ} and from inducing advection by continuously removing gas.

Figure 1.1: Gas sampling apparatus. The lowest inlet of the system measured continuously throughout the winter, while the other inlets were used to draw samples with a PP Systems EGM-4 IRGA upon each visit to the site.

**Flux Gradient Method**

The flux gradient method applies Fick's first law of diffusion, which, for the case of CO$_2$ flux, can be written:

$$ F_{CO_2} = -D_{CO_2} \frac{dC}{dz} $$

(1)

where $D_{CO_2}$ is the diffusivity constant of CO$_2$ through a given medium, here the
snowpack, and \( dC \) is the difference in CO\(_2\) concentration between two points separated by a difference in depth \( dz \). This method can be used to describe the rate of flux between any two inlets on the aforementioned sampling apparatus (Figure 1.1), or any one of the inlets and atmospheric/ambient CO\(_2\) concentration at the top of the snowpack. \( D_{CO2} \) was calculated using:

\[
D_{CO2} = [\Phi \tau D(P_0/P)(T/T_0)^\alpha]
\]  

(2)

Where \( D = 0.1381 \times 10^{-4} \text{ m}^2 \text{ s}^{-1} \) for CO\(_2\) at standard temperature and pressure \( (T_0 = 273 \text{ K} \text{ and } P_0 = 1013 \text{ hPa}) \), \( P \) is the ambient barometric pressure (hPa), \( T \) is the snow pack temperature (K), and \( \alpha = 1.81 \) is a theoretical coefficient (Massman, 1998). Snowpack porosity \( (\Phi) \) was calculated using \( \Phi = 1-(\rho_{\text{snow}}/\rho_{\text{ice}}) \) (Eisenberg and Kauzmann, 1969), where \( \rho_{\text{snow}} \) is the mean density of the snowpack and \( \rho_{\text{ice}} \) is 917 kg m\(^{-3}\). The tortuosity constant \( \tau \) is based on an empirical relationship \( (\tau = \Phi^{1/3}) \) developed by Millington (1959), although other studies have investigated tortuosity equations that range from \( \Phi^{1/3} \) to \( \Phi^{2/3} \) (Striegl, 1993). Per this definition, \( 0 < \tau \leq 1 \) as discussed by Massman et al (1997). Tortuosity has been traditionally described as the ratio between the length of a curve \( (L) \) to the distance between the ends of the curve \( (C) \):

\[
\tau = \frac{L}{C}
\]  

(3)

and by definition greater than or equal to one. By the definition used here multiplying \( \tau \) by \( \Phi \) in equation 2 results in a decrease in \( D_{CO2} \), consistent with the effects of a more tortuous path on the diffusion of a gas (Massman et al., 1997).
Manual snow depth, density, and temperature measurements were taken approximately once per month over the course of the winter. I then cross-referenced the manual density measurements with the Onion Park Snotel site, located in TCEF (NRCS.gov), which provided continuous, half hourly, snow density data (Serreze et al. 1999). A < 2% difference was found between our monthly, point measurements and the values obtained from Snotel for those specific points in time at which the manual measurements were taken. I elected to use the Snotel density data, rather than gap fill between our density measurements.

**Snow Chamber**

The PP Systems IRGA was used in conjunction with a snow surface chamber and float (Figure 1.2) for chamber-based measurements of CO$_2$ efflux. The float was constructed of 1.5” (3.81 cm) PVC tubing, wire mesh, and a 10 L PVC dome-shaped chamber (Sterilite, Townsend, MA). Two ports in the chamber allowed a semi-closed loop of ¼ (0.635 cm) " vinyl tubing to be connected to the inlet and outlet ports on the IRGA. A small fan was installed within the chamber to circulate the gas inside the chamber. Use of the snow surface chamber allowed for total flux measurements to be made near the CO$_2$ ladder and eddy covariance tower, with additional sampling near snow profiles. This sampling procedure was performed in triplicate at approximately one-month time intervals during the 2011/2012 winter season.
Figure 1.2: A schematic representation of the snow chamber and float. The float was constructed of .5 inch PVC and wire mesh. The chamber was a dome shaped 10 L PVC chamber.
Results

**Snow Depth, Density, and Water Equivalent**

Snowfall began in late October 2011 and accumulated until snowmelt began in April 2012 (Figure 1.3). Snowmelt began in earnest in mid April, which is very typical for this site. The snowpack melted completely by mid-May at the study site and was followed by a late spring snowstorm that melted within a week. Snow depth reached a maximum of 1.2 m in mid-March. Snowpack density increased over time as snow accumulated and settled with an average range of 2.5 g/cm$^3$ in late December to nearly 4 g/cm$^3$ in early April (Figure 1.4). Although snow crystal structure is highly variable in both time and space, common trends have been observed in continental snowpacks. Some of these trends were observed such as the formation of large grain (1-2mm) depth hoar and facets near the ground surface, and ice lense formation. These structures could in fact influence gas transport in that they may impede vertical diffusion and potentially enhance a later diffusion. For this study, these factors were ignored, and snow density was used as a proxy for calculating diffusion on the vertical plane only.

The snow water equivalent (SWE) at the Onion Park SNOTEL site located within TCEF measured a higher than average peak SWE in 2012 compared the prior 18-year average (Figure 1.3). Although there was slightly above average SWE, the rate of melt was faster than average and the snowpack melted completely nearly 20 days earlier than average.
Figure 1.3: Snow water equivalent (SWE) measurements from the Onion Park SNOTEL site. 2012 showed an above average SWE compared to the eighteen-year average, but a faster melt rate and earlier total melt date we experienced, while 2011 was a higher than average year in terms of SWE and had a 20 day later-than-usual total melt date.

Figure 1.4: Snow depth and density measured manually during the four visits to the site in 2012. This graph was created using linear interpolation and is not a mechanistic model.
Meteorological and Micrometeorological Observations

Average to below-average precipitation and average to warm temperatures prevailed during the winter of 2011/2012 across Montana and most of the Rocky Mountains of the U.S. and Canada. During the period ranging from December 2011 through May 2012, 166 mm of precipitation fell at TCEF and the average air temperature was 2.2 °C. These values varied from the 20th century mean by -2.79 mm of precipitation, while the average temperature was a deviation of +2.9 °C from the 20th century mean for the same period (www.noaa.gov). For the measurement period beginning in late November 2011 and ending in mid-May 2012, air temperatures were typically below 0 °C until early March when daytime temperatures began climbing above freezing (Figure 1.5A). Mean soil temperatures were ca. -1 °C until mid-March when they began climbing above freezing (Figure 1.5B). Available water content in the soil also increased in concert with soil temperature as frozen soil water began to melt and snow water began to percolate into the soil (Figure 1.5C).
Figure 1.5: A) Air temperature at 2 m above the soil surface, B) soil temperature at 5 cm below ground, and C) volumetric soil moisture content (θ) for winter and spring 2011/2012 in a lodgepole pine forest at the Tenderfoot Creek Experimental Forest, MT.

Eddy Covariance

Eddy covariance measurements were taken on a near-continuous basis beginning in January 2011 though April 2012. The eddy covariance data were partitioned seasonally and the winter of 2011/2012 was partitioned inter-seasonally for comparison (Table 1). The mean flux values indicate that midwinter 2011 mean was 54% of the midwinter 2012 mean. Mid-winter means were 15% and 27% of the summer 2011 mean, indicating that wintertime CO₂ flux accounts for a significant portion of the annual carbon inputs to the atmosphere.

The winter of 2011/2012 was then segmented in five characteristically distinct periods (I-V) with unique snow depth and subnivean CO₂ characteristics: I, early-winter,
when snow was accumulating < 0.5 m deep, II and III, when the snowpack was relatively stable, and depths were > 0.5 m, IV, the snowpack became isothermic and snowmelt began in earnest, and V, when the snowpack was completely melted. Eddy covariance-measured CO$_2$ efflux averaged 0.15 µmol CO$_2$ m$^{-2}$ s$^{-1}$ during the snow accumulation period (periods II and III, called ‘2012a’ in Figure 2.1). Mean CO$_2$ efflux steadily increased and flux measurements became more variable during period IV (Figures 2.1, 2.4 and Table 1). During the snowmelt period, air temperatures that were frequently above 0°C, an increase in soil temperature to above 0°C, and soil moisture measurements that indicated that liquid water was increasingly available (Figure 1.5).

<table>
<thead>
<tr>
<th>Period</th>
<th>Eddy covariance CO$_2$ Flux, µmol CO$_2$ m$^{-2}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I = 11/23-01/18</td>
<td>0.1461 0.0410 1.3108</td>
</tr>
<tr>
<td>II = 01/18-02/16</td>
<td>0.1660 0.0372 1.7093</td>
</tr>
<tr>
<td>III = 02/16-03/16</td>
<td>0.1817 0.0669 0.9815</td>
</tr>
<tr>
<td>IV = 03/16-05/14</td>
<td>0.4187 0.2483 0.3410</td>
</tr>
<tr>
<td>V = 05/14-06/30</td>
<td>0.8303 0.6228 1.3213</td>
</tr>
</tbody>
</table>

Table 1: Mean flux values derived from continuous eddy covariance measurements made from January 2011 through April 2012
Eddy Covariance Quality Control

The u* threshold calculated by the Reichstein et al. (2005) algorithm for summer periods was \textit{ca.} 0.05 m/s, near the mean value determined for multiple subcanopy eddy covariance sites by Misson et al. (2005) (Figure 2.2). The u* threshold during winter periods was determined to be \textit{ca} 0.15 m/s during the winter of 2010/2011 and \textit{ca} 0.2 m/s during the winter of 2011/2012 on account of the saturating relationship between u* and CO₂ flux (Figure 2.3). No dependency of u* on flux-gradient CO₂ flux estimates was found, excluding values of u* less than 0.01 m/s that were observed infrequently.
Figure 2.2: The $u^*$ threshold (m/s) determined using the algorithm of Reichstein et al. (2005) for three month periods of the eddy covariance record for nighttime periods with a solar zenith angle greater than 90°, and for the entire data record.

Figure 2.3: Eddy covariance and flux-gradient CO$_2$ flux measurements as a function of the friction velocity ($u^*$). Eddy covariance data are shown for periods during the snow-free season in 2011 (between day of year [DOY] 182 and 292, during the winter of 2011 (between DOY 18 and DOY 146), during the snow accumulation period in 2012 (2012a), and during the snowmelt period in 2012 (2012b).
Subnivean CO₂ Concentration Observations

The subnivean CO₂ concentration observations exhibited five periods with distinct statistics (Figure 2.1 and Table 1) that were related to snow dynamics. Early-season CO₂ concentrations (Period I) were usually near the atmospheric concentration of ca. 390 ppm with frequent positive excursions and snow depth was consistently ca. 0.4 m during this period. Period II was characterized by steadily increasing CO₂ concentrations with frequent negative excursions to atmospheric values and a snow depth of approximately 0.65 m with infrequent snowfall events. Period III occurred during the peak snow depth period and exhibited slowly increasing subnivean CO₂ concentrations with relatively low variance compared to other periods (Table 1). Subnivean CO₂ concentrations never dropped to atmospheric values during this period. Period IV corresponds to the main snowmelt period and was characterized by the mean daily air temperature warming to above freezing (Figure 1.5), an isothermal snowpack, and extensive variability in subnivean CO₂ concentrations with frequent negative excursions to atmospheric CO₂ concentrations. Both soil temperature and soil water content increased during the transition to Period IV due to an influx of snow water into the soil and frozen soil water melting and becoming more available (Figure 1.5). Period V occurred after snow melted and features a small pulse in CO₂ concentration during the late spring snow event (Figure 2.1).

Flux Gradient

CO₂ flux estimates from the flux gradient approach were analyzed based on the five distinct periods observed in the subnivean CO₂ concentrations (Figure 2.1). The
mean subniveal CO\textsubscript{2} concentration during period I was 427 ppm, and concentrations returned to atmospheric concentration (< 400 ppm) during ca 30\% of the period I measurement record. The mean flux estimate using the Fick’s model for period one was 0.04 µmol CO\textsubscript{2} m\textsuperscript{-2} s\textsuperscript{-1}. As snow depth increased to > 0.4m in periods II and III, subniveal concentrations remained at levels above atmospheric concentration. The mean of the modeled flux for these periods increased three-fold to ca. 0.13 µmol CO\textsubscript{2} m\textsuperscript{-2} s\textsuperscript{-1}.

Subniveal CO\textsubscript{2} concentrations were on average slightly lower during period IV and averaged 0.10 µmol CO\textsubscript{2} m\textsuperscript{-2} s\textsuperscript{-1}, with a higher variance and skewness value (table 1). The flux-gradient approach during period V is not applicable due to lack of snow.

<table>
<thead>
<tr>
<th>Period</th>
<th>Fick’s Model Estimated Flux Statistics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>µ</td>
</tr>
<tr>
<td>I = 11/23-01/18</td>
<td>0.0406</td>
</tr>
<tr>
<td>II = 01/18-02/16</td>
<td>0.1252</td>
</tr>
<tr>
<td>III = 02/16-03/16</td>
<td>0.1344</td>
</tr>
<tr>
<td>IV = 03/16-05/14</td>
<td>0.1012</td>
</tr>
<tr>
<td>V = 05/14-06/30</td>
<td>-0.0771</td>
</tr>
</tbody>
</table>

Table 2: The mean, standard deviation and skewness CO\textsubscript{2} flux estimated by the flux gradient model (units: µmol CO\textsubscript{2} m\textsuperscript{-2} s\textsuperscript{-1}) for statistically distinct periods of the winter 2011/2012 observation record.

Chamber Measurements

Chamber measurements were made during two of the field site visits on January 31, 2012, and the second on April 3, 2012. The mid-winter sampling in late January had a mean of 0.65 µmol CO\textsubscript{2} m\textsuperscript{-2} s\textsuperscript{-1}, and a standard deviation of 0.043 µmol CO\textsubscript{2} m\textsuperscript{-2} s\textsuperscript{-1}. The
springtime measurements made in early April had a mean 1.31 $\mu$mol CO$_2$ m$^{-2}$ s$^{-1}$, approximately double that of the January measurements, and a standard deviation of 0.22 $\mu$mol CO$_2$ m$^{-2}$ s$^{-1}$.

**Intercomparison Among Methods**

Each of the three techniques applied in this study resulted in different total seasonal flux estimates and rates. The flux gradient method described up to 75% of eddy covariance-observed flux during periods II and III, but only ca. 25% of eddy covariance-measured flux during periods I and IV. In period V, the Fick’s model was not applicable due to absence of the snow medium. These results indicate that a Fick’s based model approximates eddy covariance-measured fluxes well during winter periods experiencing a snow pack $>$50 cm, and without the occurrence of significant melt periods. The flux-gradient approach substantially underestimated soil CO$_2$ efflux versus the other measurement techniques during the melt periods in our study system. In the instance that the other measurement techniques were more accurate, the flux gradient system would underestimate the importance of this period to the annual carbon balance of our study ecosystem. The large flux underestimates are due in part to the large excursions of subniveal CO$_2$ concentrations to near atmospheric values likely due to preferential flow via tree wells or melt-water pathways, creating a direct link between the soil-snow interface and the atmosphere; in fact, during period IV average subnivean [CO$_2$] averaged over 530 ppm during the hours between midnight and 4 am, but averaged less than 475 ppm between the hours of 3 pm and 7 pm, a difference of over 10%. In other words, there is a preference toward more CO$_2$ buildup underneath the snowpack at night.
Table 3: The mean, standard deviation and skewness for both estimated flux using the Fick’s Model and values measured directly via eddy covariance. Highlighted in red are the periods where the Fick’s model estimated ca. 75% of measured eddy covariance flux.

| Period    | Flux Gradient | | | Eddy Covariance | | |
|-----------|--------------|---|---|----------------|---|
|           | μ    | σ    | Skew | μ    | σ    | Skew |
| I = 11/23-01/18 | 0.0406 | 0.0024 | 0.3001 | 0.1461 | 0.0410 | 1.3108 |
| II = 01/18-02/16 | 0.1252 | 0.0030 | -0.1972 | 0.1660 | 0.0372 | 1.7093 |
| III = 02/16-03/16 | 0.1344 | 0.0013 | 0.4159 | 0.1817 | 0.0669 | 0.9815 |
| IV = 03/16-05/14 | 0.1012 | 0.0097 | 0.7578 | 0.4187 | 0.2483 | 0.3410 |
| V = 05/14-06/30 | -0.0771 | 0.1072 | 1.7227 | 0.8303 | 0.6228 | 1.3213 |

The snow surface chamber measurements were made twice during the winter. The first series of measurements was taken in late January during period III. This was a period with a snowpack that may be considered steady state in the absence of substantial accumulation or ablation. Chamber flux measurements were in good agreement with the eddy covariance measurements during this period, measuring 0.62 μmol CO$_2$ m$^{-2}$ s$^{-1}$ respectively, while the flux gradient model predicted 0.18 μmol CO$_2$ m$^{-2}$ s$^{-1}$. The second series of chamber measurements were made in early April during period IV, which was defined by snowmelt, an isothermal snowpack, and increased soil temperature and available soil water content. The chamber and eddy covariance measured fluxes 1.3 and 0.85 μmol CO$_2$ m$^{-2}$ s$^{-1}$ respectively, while the flux gradient method estimated only a fraction of the measured fluxes at 0.29 μmol CO$_2$ m$^{-2}$ s$^{-1}$.
Figure 2.4: CO$_2$ flux estimates calculated using Fick’s first law of diffusion from observations from a flux-gradient system (red line) and the flux measured with the eddy covariance system (blue dots), and fluxes measured with the chamber method (black dots). A sensitivity analysis of the tortuosity parameter for the flux gradient system is presented as a gray region about the red line. In periods I and IV the Fick’s model underestimated the actual flux by 75%, but in periods II and III it was significantly more accurate, accounting for all but 25% of measured flux.

Discussion

A comparative analysis of the chamber, flux gradient and eddy covariance methodologies used in this study was performed in an effort to determine the accuracy, effectiveness, and applicability of each technique for the purpose of better-understanding controls on wintertime soil CO$_2$ efflux. Results demonstrate that each approach has benefits and disadvantages, with multiple implications for interpreting the contributions
of wintertime CO$_2$ efflux to the carbon balance of lodgepole pine ecosystems. It is important to note that the eddy covariance method is the only method that measures a net CO$_2$ flux, whereas the snow chamber and flux gradient methods measure outgoing, gross flux only. I discuss and compare findings from each methodology after noting how the state of the snowpack during the measurement years influenced eddy covariance observations of carbon efflux.

The snowpack plays an integral role in regulating carbon flux from the soil to the atmosphere through its depth and density and hence tortuosity and porosity (Musselman et al., 2005; Monson et al., 2006a). It also controls to a significant degree the physical drivers of microbial respiration including soil temperature and moisture. The snowpack can insulate the soil, maintaining temperatures that are high enough for soil respiration to occur (Sommerfield et al., 1996; Suzuki et al., 2006). The snowpack can also act as a reservoir for CO$_2$, accumulating gas to orders of magnitude higher than atmospheric concentrations (e.g. Figure 2.1). Shallower continental snowpacks < 0.5 m frequently see subnivean CO$_2$ levels return to atmospheric concentration (Figure 2.1, Bowling & Massman 2011). This can be attributed to a low tortuosity or less diffusive resistance, i.e. less snow for the gas to diffuse through, and potential venting avenues via exposed vegetation or other pathways. Overall production of soil respired CO$_2$ is a critical component when calculating a carbon budget for an area of interest. Therefore, the depth, density, and timing of melt of a snowpack may be significant controllers of CO$_2$ production during the snow-covered season.
Snowpack and Micrometeorological Observations

The winter of 2011/2012 was average in terms of temperature and snowfall when compared to the 20\textsuperscript{th} century averages at TCEF (Farnes et al)(NOAA), but snowfall during 2010/2011 was above average, with consequences for observed CO\textsubscript{2} efflux. Soil heterotrophic and autotrophic respiration varies depending on season, primarily due to soil temperature, and soil moisture content and carbon inputs and stores via vegetation, soil biota, and soil organic matter (Vargas & Allen 2012; Grogan & Chapin, 1999). Therefore, soil respiration will typically be at its maximum during spring and summer, when soil temperature and soil biological activity are at their peak, but I found that mean eddy covariance-measured soil CO\textsubscript{2} efflux during the melt period of 2012 and the late growing season of 2011 with low soil moisture conditions were similar (Table 1). Soil respiration in winter is often thought to be muted, but may be a more substantial contributor to carbon outputs than previously thought (e.g. Oechel et al 1997; Fahnestock et al 1998, 1999; (Grogan & Chapin, 1999; Monson et al., 2006).

Eddy Covariance

The eddy covariance measurements used in this study were made below the forest canopy at 2 m above the forest floor. This sub-canopy tower was designed to measure direct CO\textsubscript{2} flux via soil respiration from the soil surface in the growing season and from the snow surface in winter. Partitioning of forest ecosystem processes such as photosynthesis and respiration with the use of eddy covariance instrumentation placed at different heights in the forest canopy profile in an effective way to measure the source/sink dynamics of a particular site (Misson et al, 2007).
In this study we used half-hourly sub-canopy eddy covariance data to measure the efflux of CO$_2$ via soil respiration to the atmosphere. Additionally, these data were used in a comparative analysis of three differing methodologies (described above) used to measure or estimate snow surface efflux in winter. In order to ensure that the eddy covariance data we collected was accurate quality control measures were taken. In order to have accurate measurements of flux using the eddy covariance technique a sufficient amount of turbulent mixing needs to occur at the level of the instrumentation. The variable used to determine the threshold at which mixing is sufficient $u^*$, which is a measure of turbulent velocity. The threshold itself is at which the concurrent flux value describes 95% of subsequent flux values at higher $u^*$ values. The $u^*$ threshold used in this study was determined using the Reichstein algorithm (Reichstein et al, 2005). For the period ‘summer of 2012’, a $u^*$ value of 0.05 m/s was found. This value matches summer $u^*$ threshold values found in other studies of sub canopy flux measurements (Misson et al, 2007). However, the $u^*$ threshold found for the winter periods of 2011 and 2012, ~0.2m/s, indicating that flux in winter periods show a higher dependency on wind speed (Bowling and Massman, 2011). This observation supports the hypothesis that wind induced diffusion is a contributing factor in wintertime efflux.

Subnivean CO$_2$ Observations and the Flux Gradient Method

This study demonstrates that the flux gradient method can provide relatively accurate estimates of wintertime CO$_2$ efflux under certain conditions, assuming that eddy covariance and chamber measurements are closer to true flux, although we note that the eddy covariance system is likely to underestimate true flux given that our eddy
covariance system is unable to resolve flux transporting eddies with characteristic time scales less than 0.1 s (1/10 Hz). Under the assumption that the eddy covariance flux measurements are more accurate than the flux gradient estimates, the flux gradient method is most accurate during periods in mid-winter when the snowpack is relatively deep (> 0.5 m, periods II and III) after initial snowfall (period I) and before significant melt is experienced (period IV, figure 2.4). During periods II and III the flux gradient method estimated 75% of the mean values (Table 1) obtained using the eddy covariance and chamber techniques. I will discuss sources of uncertainty in measurements during periods II and III when the snowpack was approximately steady state before discussing additional sources of uncertainty during periods I and IV when the snowpack was short and/or melting.

The potential 25% negative bias experienced by the flux gradient system, again assuming that the eddy covariance and chamber methods make fewer assumptions about flux measurements and thereby may be more accurate, may be attributed to a number of potential mechanisms. Snow height and density measurements are highly accurate with proper technique, but both differ across space. Snowpack height, \(dz\) in equation 1, was measured continuously using a SR50A sonic distance sensor (Campbell Scientific) with a highly precise spatial resolution of 0.25 mm and a vertical accuracy of \(+/-1\) cm or 0.4% of the distance to the target. This measurement of snow depth, effectively at a point, contrasts the variable height of the snowpack within the variable eddy covariance flux footprint with the height of the snowpack at the points where chamber measurements were made and where snow pits were dug. Using snow pit observations as a surrogate for spatial variability of snow depth at the study site, I can test if the sonic distance sensor
observations are representative of snow depth in the area of the flux tower, noting also that uncertainties in $dz$ will scale inversely with estimates of $F_{CO2}$ following equation 1.

The mean observed snow pit depth did not differ by more than 5.4 cm from the sonic distance sensor measurements, with a mean difference of 1.6 cm noting that the sonic distance sensor has an accuracy of 1 cm. For a snow depth of 1 m, the uncertainties in $F_{CO2}$ that these uncertainties in depth incur are on the order of 1 to 6 %, and are not likely to be a dominant source of error in the flux gradient estimates at our site, which are estimated to be on the order of at least 25% for periods II and III.

Another source of uncertainty in the flux gradient calculation is the subnivean/atmospheric gradient in CO$_2$ concentration, $dC$. Uncertainties in the measurements of atmospheric [CO$_2$] by the Li-Cor 7200 infrared gas analyzer are on the order of 1% and are unlikely to be a dominant contributor to uncertainty in the $F_{CO2}$ calculation. The Vaisala GMP343 used for subnivean [CO$_2$] measurements has uncertainties on the order of 3% within the temperature range of -40 °C to 60 °C, and on the order of 10ppm + 5% within the pressure range of 700 hPa to 1300 hPa. Combined, uncertainty in $dC$ measurements is unlikely to be greater than 10%, and any biases in $dC$ scale linearly with $F_{CO2}$. Likely uncertainties in the measurements of the gradient $dC/dz$ are alone insufficient to explain the proposed 25% negative bias in $F_{CO2}$ estimates from the flux gradient system during periods II and III.

On the other hand, models for $D_{CO2}$ contain numerous sources of bias that may contribute to the proposed underestimation of $F_{CO2}$. Temperature and pressure adjustments to the atmospheric diffusivity of CO$_2$ ($D$, equation 2) are unlikely to contribute substantial uncertainty to $D_{CO2}$ and thereby $F_{CO2}$ if these inputs are measured
within a few percent of the true value. The Eisenberg and Kauzmann (1969) model for $\Phi$ is theoretically consistent because it describes the percent of air space in a snowpack under the assumption that snow density measurements account for the liquid and solid phases of water in the snow, the remainder is the air space within the snow, and that a snowpack without gaseous or liquid components is ice. It is reasonable to assume that these assumptions hold at the snowpack scale, and therefore that uncertainties in the snow density measurement, rather than the equation itself, is the dominant source of uncertainty in $\Phi$. Field measurements of snow density with proper practice are likely accurate to within 5-10% if care is taken with the snow pit or snow tube measurements. It is important to note that these uncertainties, whereas small, also factor in to the calculation of $\tau$.

Models for $\tau$ show satisfactory agreement to field observations and theoretical expectations (Millington 1959; Millington and Quirk 1961) and have been found to be appropriate descriptors of trace gas fluxes in soil and snow (Striegl and Ishii, 1989), but may contain uncertainties that may bias the $F_{CO2}$ estimate. Using ($\tau = \Phi^{1/3}$), I found tortuosity values ranging from 0.74-0.94 for the entire study period, with a mean of 0.92 for periods II and III. In other words, the entire range of observed $\tau$ differs by ca. 30%, and the flux gradient and eddy covariance systems differed by an average of ca. 25% during periods II and III. A 25% upward adjustment to the median tortuosity value of 0.9 equals ca. 1.1, which exceeds the range possible values of $\tau$ noted in the Methods section (Massman et al., 1997). A sensitivity analysis of $\tau$ between a range of observed values between 0.74 and 0.94 (Mast et al., 1998; Sommerfield et al., 1993) was unable to explain the discrepancy between flux gradient estimates and eddy covariance
observations (Figure 2.4), leading to the conclusion that variation in tortuosity alone cannot account for the under estimation of $F_{CO2}$ when using the flux gradient model. Furthermore, I combined inference from measurement systems and set equation 1 to equal eddy covariance-measured CO$_2$ flux to calculate $\tau$. The mean estimate of $\tau$ that results is greater than one, further suggesting that a model for diffusion alone is insufficient to account for eddy covariance CO$_2$ flux observations. It is important to note that eddy covariance uncertainty is on the order of 10-15% (Goulden et al., 1997), which again does not explain the full discrepancy between measurement systems.

A final explanation for the underestimation observed in periods II and III is that the flux gradient method does not account for an enhanced diffusion (i.e. advection), which is caused by wind induced pressure pumping of the air space (Bowling and Massman 2009). From our observations (Figure 2.4), mean $F_{CO2}$ and eddy covariance flux observations were approximately equal within a range of $u_*$ values between ca. 0.03 m/s and 0.15 m/s. $F_{CO2}$ estimates were characteristically smaller than eddy covariance measurements above this range, suggesting that wind-enhanced gas transport likely played a role in the underestimation of $F_{CO2}$. In fact, Bowling and Massman (2011) were able to explain the dynamics of stable isotopic composition within the snowpack at their Niwot Ridge study site by adjusting flux-gradient estimates of CO$_2$ efflux for variations in wind speed such that wind speeds >10 m/s measured above the canopy. Their upward adjustment based on wind speed resulted in a 20-30% increase in flux. Mean wind speed at the Onion Park SNOTEL site was only 1.43 m/s during 2011. Above canopy windspeeds will likely be higher than those measured by the SNOTEL site at onion park; therefore I instead found a 30% enhancement of mean CO$_2$ efflux using a subcanopy $u^*$.
value of 0.13 m/s during periods II and III over the mean value at the minimum summertime threshold of 0.05 m/s (Figure 2.3). Results demonstrate an important role of wind velocity within the canopy air space in determining the magnitude of eddy covariance-measured CO$_2$ efflux, a topic that I return to below.

During periods of low snow and snow melt (periods I and IV) the flux gradient method is likely less accurate, estimating 25% of the eddy covariance obtained mean for the same period, and again assuming that the eddy covariance measurement is a more accurate representation of the true flux. Observations are due to a number of mechanisms including snow depths of < 0.5 m in period I, which appears to allow rapid venting of subnivean CO$_2$ to the atmosphere in our case. The flux gradient system also underestimated flux during period IV due in part to frequent excursions of subnivean CO$_2$ to near-atmospheric values. A plausible explanation may be the creation of preferential flow pathways through the snow pack via macropores created by snow-surface melt-water percolation. Later during the melt period when the snowpack was shallower, the exposure of understory vegetation and other preferential flow paths allow gas to escape rapidly to the atmosphere unobstructed rather than via diffusion through the snowpack matrix. These conditions violate the assumptions of the flux gradient methodology that gas is transported from soil surface to atmosphere via diffusion (equation 1). As seen in figure 2.4, during period IV when snowmelt begins in earnest subniveal CO$_2$ reaches a peak, but also experiences a high level of variation (Table 1). Taking these observations into account, we have determined that the flux gradient method is most appropriately applied in mid-winter situations at our study site.
Snow Chamber Measurements

The snow chamber technique is potentially the most accurate means of sampling flux from the snow surface (McDowell et al., 1998) because one physically samples the increase in $\text{CO}_2$ concentration over time in a known volume and makes no assumptions about the resistance of the snowpack to gas transport nor the characteristic time scales of flux-transporting eddies in the atmosphere. A primary drawback of chamber techniques is that one must be physically present at the field site to perform manual sampling or design a complicated automated chamber system that must account for changes in snow depth across the snow-covered season. Such a system will likely have large power requirements, which may additionally limit applicability in areas where grid access is unavailable and alternate power sources may be difficult to access. Other potential drawbacks include disturbing the snowpack near the chamber measurement site via footprints etc. in the snow. This could change the subnivean pressure dynamics resulting in unnatural diffusion within the snowpack.

Chamber flux measurements closely matched eddy covariance flux measurements in mid winter when snow levels exceeded 0.5 m (Figure 2.3), but exceeded eddy covariance during snowmelt (period IV). T-tests performed on both chamber and eddy covariance data during each sampling date revealed no significant difference ($<5\%$) for both the mid winter and the snowmelt sampling dates. Where site access is a non-issue, chamber techniques provide a relatively low cost and very accurate means of snow surface flux sampling.
Additional Sources of Uncertainty

Over the course of the winter a significant layer of depth hoar ~20cm (large grain, faceted snow crystals) formed at the study site at the base of the snowpack. The poorly bonded, large grained nature of this layer may provide an avenue for lateral gas diffusion via macropore space between the grains. The formation of depth hoar is a very common occurrence in continental snowpacks. Typically depth hoar forms early in the winter season when snowpacks are shallow, and nights are cold, allowing for a high vapor pressure gradient within the snowpack, and a negative temperature gradient from ground to air. The transport of water vapor and other gaseous constituents through the snowpack results in snow crystal metamorphosis (and often the formation of depth hoar) via sublimation (Giddings and LaChapelle, 1962).

For the purposes of this study lateral gas diffusion was ignored, and diffusion was assumed to occur on the vertical plane only. This may have led to an over-estimation when using the flux gradient model due to the fact it was assumed that all of the CO$_2$ produced in the soil diffused vertically to the snow surface, when in reality, concentration differences on the lateral plane may have resulted in lateral diffusion. Additionally, mean snowpack density and temperature were used for the purpose of modeling and estimating the diffusion of CO$_2$ through the snowpack using the flux gradient model. In fact, snowpack properties such as density, temperature, and structure are highly variable both temporally and spatially. Although mean snowpack density and temperature were measured on a half hourly time scale, accounting for much of the temporal variability, the snowpack was assumed to be spatially heterogeneous for comparison with the eddy covariance flux footprint.
Furthermore, differences in temperature and density as it varied with snowpack stratigraphy were ignored, as these variables were calculated as means for the entire snow profile. This may lead to potential error, as ice lenses and other structures in the snowpack that may have acted as either impediments to diffusion or avenues to a more rapid diffusion were ignored, although I note that ice lenses were not observed during the measurement period.

The potential for error using the eddy covariance technique is high due to the complex nature of the methodology and instrumentation. Measurements made are not perfect due to the fact that major assumptions are and errors may be introduced do to physical phenomena, instrument problems, and issues with terrain and topography. Many procedures were made (see Methods: Eddy Covariance) to correct for these sources of error.
CHAPTER 3

SUMMARY

The measurement of CO$_2$ efflux during winter in mountainous regions poses a challenge itself in that no particular methodology has proven to be the most effective. In situ systems such as eddy covariance and the flux gradient method require costly power systems and instrumentation, while manual measurements such as the snow chamber technique require the researcher to be physically present. This study sought to compare and contrast these techniques in an effort to determine the most effective and efficient means of measuring wintertime efflux. Overall, the flux gradient method provides a temporally resolute dataset at a relatively low cost when compared to the eddy covariance system. It also requires less maintenance the eddy covariance system and less time in the field when compared with the chamber technique. It is important to note that the eddy covariance system is the only method used in this study that measures net ecosystem CO$_2$ flux, and that the chamber and flux gradient methods measure only outgoing, gross efflux.

Wintertime CO$_2$ efflux has proven to be an important contributor to the annual carbon cycle at Tenderfoot Creek Experimental Forest, and many other ecosystems. As climate changes affect temperature and precipitation patterns we can expect the primary drivers of soil respiration to change in concert. Understanding the role that snow plays in these processes and how changes in winter weather regimes might affect the primary drivers of soil respiration could become an increasingly important factor in the global carbon budget. Additionally, determining the most efficient and cost effective means of
measuring these processes will allow researchers to conduct more in depth and widespread inquiries into the evolution of wintertime CO₂ flux processes.

This study compared three different methodologies for the purpose of finding the effectiveness and applicability of each technique, while also attempting to quantify the wintertime portion of CO₂ efflux at the study site. The three methodologies used were 1) The eddy covariance method, 2) The snow surface chamber method, and 3) the flux gradient method.

Results from each of the techniques show that snow surface efflux is most stable (less variable) in mid winter when snowpacks are >.5m and have not begun to experience significant melt. Additionally, each method demonstrated that wintertime efflux is a major contributor of CO₂ from earth to the atmosphere as relatively high rates of flux were found when compared to summertime flux rates.

When comparing the three techniques in terms of applicability, cost effectiveness and accuracy certain characteristics of each technique standout.

1) In situ methods such as the flux gradient and eddy covariance methods are more appropriate to remote, backcountry study areas in that they don't require a physical presence in the field in order to obtain measurements, as does the chamber technique. The in situ techniques therefore save time and travel expenses.

2) The chamber measurement is potentially the most accurate point efflux measurement technique as it makes the fewest assumptions. Although extrapolating the point measurements made to a larger scale is one major assumption that is made using this technique.
3) The eddy covariance method, although the most costly, provides the highest resolution measurement of efflux on a temporal scale, has a larger footprint than the other methods, and also measures net CO$_2$ efflux, rather than strictly outgoing gross efflux.

4) The flux gradient model is based on relatively low cost instrumentation, and does not require a physical presence to make measurements. However, this model assumes a vertical diffusion of CO$_2$ through snow and does not account for other physical drivers of diffusion such as wind-enhanced diffusion. If the model can be calibrated to account for enhanced diffusion it could potentially be a cost effective and accurate means of estimating wintertime efflux in remote areas.

In conclusion, the results from this study show that wintertime efflux is an important contributor to the annual carbon cycle in forested mountain ecosystems. The means by which a researcher chooses to measure this process will likely depend on the nature of the study site, accessibility, and the financial resources available.
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