Methane Fluxes at a Temperate Upland Forest in Central Ontario

by

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A thesis submitted in conformity with the requirements for the degree of Master of Science
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Abstract

Methane fluxes were calculated from measurements carried out at a temperate upland forest in Central Ontario using the eddy covariance method over five months in the summer and fall seasons of 2011. Measurements were made by an off-axis integrated cavity output spectrometer Fast Greenhouse Gas Analyzer (FGGA) which simultaneously measured methane (CH$_4$), carbon dioxide (CO$_2$), and water at 10 Hz sampling rates. Observed methane fluxes showed net uptake of methane over the measurement period with an average uptake flux value ($\pm$standard deviation of the mean) of -2.7$\pm$0.13 nmol m$^{-2}$ s$^{-1}$. Methane fluxes showed a diurnal pattern of increased uptake during the day and increasing uptake with seasonal progression. There was also a significant correlation in methane fluxes with soil water content and wind speed. Comparison of the FGGA measurements to those using a static chamber method and canister sampling showed close agreement in flux and mixing ratio values respectively.
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1 Introduction

1.1 Methane as a Greenhouse Gas

The main source of energy to Earth is radiation provided by the Sun which emits light at short wavelengths (ultraviolet, visible, and near-visible light). Due to the colder surface of the Earth compared to the Sun, some of the absorbed incoming solar radiation is transformed into energy at longer wavelengths in the infrared region and emitted back into space. A large portion of this terrestrial radiation is absorbed by the atmosphere and reradiated back to the lower atmosphere and the Earth’s surface. This is commonly known as the greenhouse effect. Greenhouse gases such as water (H₂O), carbon dioxide (CO₂) and methane (CH₄) absorb and reemit terrestrial. An increase in the concentration of these greenhouse gases can lead to an increase in the greenhouse effect results in a global increase in temperature known as atmospheric warming (Jacob, 1999). To better understand the magnitude of these effects, we must quantify how these greenhouse gases are emitted and removed by both anthropogenic and natural means.

Methane is the predominant hydrocarbon in the atmosphere and the third most important greenhouse gas after H₂O and CO₂, having risen by 150% since the pre-industrial era (1750 AD) (Hendriks et al., 2008). Although its abundance is much lower than that of CO₂, its greenhouse gas warming potential (GWP) is 21 times higher per molecule than that of CO₂ over a 100 year time horizon. Methane contributes 18% to the total anthropogenic radiative forcing from greenhouse gases with a current forcing from anthropogenic emissions of 0.48 W m⁻², corresponding to approximately 30% of the radiative forcing from CO₂. Methane has a relatively short atmospheric lifetime of ~12 years compared to CO₂ (IPCC, 2007). A reduction in emissions of CH₄ could help to stabilize atmospheric concentrations, but in order to properly mitigate CH₄, there must be an accurate understanding of the global CH₄ budget. Although both CH₄ and CO₂ measurements were made in this study, the focus will be CH₄ fluxes.
1.1.1 Trends in Atmospheric Methane

Trends in the growth rate of atmospheric CH$_4$ have been much less predictable compared to the steady increase in atmospheric CO$_2$. For the last three decades, CH$_4$ measurements were made at the National Oceanic and Atmospheric Administration Earth System Research Laboratory Global Monitoring Division (NOAA/ESRL-GMD) shown in Figure 1 compiled from 15 different ground stations averaged annually. Methane mixing ratios increased from 1664 ppb in 1984 to 1788 ppb in 1999, although the growth rate decreased from ~14 ppb yr$^{-1}$ to near zero in the same time frame (Dlugokencky et al., 2003) with the exclusion of minor abrupt changes in 1991 and 1998. The increase in CH$_4$ growth rate in 1991 was attributed to the eruption of Mt. Pinatubo which reduced the tropical hydroxyl radical (OH) sink of CH$_4$, and in 1998 to strong warm wet conditions from El Niño in northern wetland regions and increased boreal biomass burning which both may have contributed to an increase in CH$_4$ emissions (Dlugokencky et al., 2009). From 2003 to 2006, CH$_4$ levels were at a near zero growth rate. There has been very little consensus in the scientific community as to why growth rates were stagnant, although reasons have been attributed mainly to a decrease in anthropogenic sources.

Figure 1: Averaged CH$_4$ mixing ratio (top) and annual rate of change (bottom) compiled from 15 different global atmospheric measurement stations (data retrieved from NOAA-GMD, E. J. Dlugokencky).
Dlugokencky et al. (2003) suggested that the decrease in the growth rate could be attributed to the decrease from the fossil fuel sector. Coal and oil extraction dropped by ~30% from their peak values in the 1980s to the mid-1990s. Natural gas extraction also fell by 17% between 1991 and 1997. This was further explored by Aydin et al. using measured ethane in air trapped in perennial snowpack samples from Greenland and Antarctica. Both CH$_4$ and ethane are released from mining, processing, transport and consumption of fossil fuels during use of biofuels and biomass burning. Assuming a fixed methane-to-ethane emission ratio, a history of fossil fuel CH$_4$ emissions could be estimated. In contrast to historical fuel emission history, which showed an increasing trend, Aydin et al. (2011) showed that there was actually a decline of CH$_4$ emissions from fossil fuel use from 1980 – 2000 by almost 30% than previously thought. If true, this would be an important driver in the CH$_4$ slowdown. Kai et al. (2011) offered an alternate explanation that an increase in relatively enriched carbon isotope values from 1979 – 2005 resulted from an increase in isotopically enriched sources such as fossil fuels and biomass burning, or a decrease in isotopically depleted sources such as microbial sources as a result of a drying trend in northern wetlands and rice agriculture. These conflicting results provide an example of the lack of consensus within the community about what has happened with methane sources and sinks over the last three decades (Heimann, 2011).

Even more puzzling was the observed increase in the growth rate of CH$_4$ of ~10 ppb yr$^{-1}$ in early 2007 which was measured almost simultaneously at all 13 ground stations of the Advanced Global Atmospheric Gases Experiment (AGAGE) and the Commonwealth Scientific and Industrial Research Organization (CSIRO) networks which have stations located in both hemispheres. Due to the interhemispheric mixing time of around 1 – 2 years, there must have been an emission increase in both hemispheres assuming negligible changes in OH concentration (Terao et al., 2011). Reasons offered were increased emissions from wetlands resulting from anomalously higher temperatures in the high latitudes regions of the Northern Hemispheres and large precipitation in the northern tropics. However, it was less clear as to why there was an increase in the Southern Hemisphere (Dlugokencky et al., 2009). In order to increase the accuracy of predictions in atmospheric methane concentrations, we must first be able to model methane sources and sinks. The ability to properly model methane dynamics is limited by the lack of reliable measurements of methane fluxes (Clement et al., 1995).
1.2 Sources and Sinks

Methane has both anthropogenic and natural sources which total 503 – 610 Tg CH₄ yr⁻¹. Its natural sources make up approximately 25 – 50% of the total emissions, ranging from 145 – 260 Tg CH₄ yr⁻¹ derived mainly from wetlands which make up ~20 – 40% of the total global emissions of CH₄ (IPCC, 2007). Minor natural sources include termites, geological sources, oceans, hydrates, wild animals, and wildfires. Anthropogenic sources range from 264 – 428 Tg CH₄ yr⁻¹ coming mainly from the energy industry which includes coal mining and gas/oil industry, and from ruminants, landfills and waste, rice agriculture, and biomass burning (IPCC, 2007). Around 85 – 90% of the total sink, which is estimated at 492 – 581 Tg CH₄ yr⁻¹ is through reaction with OH in the troposphere. The remaining 10 – 15% is attributed to removal by stratospheric OH and biological consumption in sub-surface soils (IPCC, 2007). Assuming that the annual mean of atmospheric OH remains relatively constant, the tropospheric and stratospheric sinks also remain relatively constant. In contrast, the soil sink is highly variable and is estimated at around 30 ± 15 Tg CH₄ yr⁻¹ (Curry, 2007), but upscaling from the statistical distribution of measurements gives a much wider range of 7 – 120 Tg CH₄ yr⁻¹ (Smith et al., 2000). Uncertainties in the global CH₄ budget arise from limited observational data coverage and uncertainties in the factors that drive CH₄ source and sink variability (Heimann, 2011).

1.2.1 Methanotrophs and Methanogens in Soils

Methane in ecosystems is produced by methanogenic archaea in waterlogged anaerobic soils and oxidized by methanotrophic bacteria. Both types of microbes can be found in a range of ecosystems such as wetlands, which tend to be net CH₄ sources, and comparatively dry aerobic soils which are net sinks for atmospheric CH₄. Both production and consumption of CH₄ by microbes can occur in many types of soil, with the net effect defined mainly by environmental variables of each ecosystem. This results in high uncertainty and variability in the magnitude and direction of the flux. The natural source can be attributed to methanogens that exist in anaerobic soils that have high water content such as wetlands and rice paddies, but also in relatively drier soils, although typically at much deeper soil depths than methanotrophs near the water table during wet seasons. Although these methanogens are only active in anoxic soil conditions, they are found globally even in aerated soils and rapidly become active under wet conditions (Angel
et al., 2011). Methanogenesis involves the microbial mineralization of organic carbon which is used as an alternative terminal electron acceptor that provides a source of energy for the microbes. The biochemical reaction involves the reduction of a methyl group of CH$_4$. Most methanogens reduce a single substrate such as CO$_2$ into CH$_4$, although some are able to reduce other compounds such as formate, methanol, methylamines or acetate into CH$_4$ such as the cleavage of acetate into CH$_4$ and CO$_2$ (Cohen, 2011).

Although the CH$_4$ soil sink is much smaller compared to that of the tropospheric OH sink, there is a high uncertainty in its magnitude, which is variable depending on soil types and ecosystems, as well as environmental variables. In forest soils, which cover nearly 30% of the Earth’s land surface, methanotrophs can effectively oxidize CH$_4$. These microbial sinks are extremely sensitive to various types of anthropogenic disturbances such as conversion of forest to agriculture, fertilization, soil compaction, acidification, and nitrogen deposition. All of these can result in a much lower rate of oxidation (Reay et al., 2007) which can potentially convert these CH$_4$ sinks into CH$_4$ sources. Methanotrophs are quite unique in that they can utilize CH$_4$ as a sole carbon and energy source. These methanotrophs exist as a variety of species depending on the environment they are in, and each species reacts differently to specific environmental factors. In a broad sense, they can be represented as two distinct types; low- and high-affinity methanotrophs. Low-affinity/high-capacity methanotrophs require high CH$_4$ mixing ratios, typically greater than 1000 ppm and are generally found near waterlogged soils and sediments because they rely on high CH$_4$ found in the presence of methanogens. The second type is high-affinity/low-capacity methanotrophs which convert trace concentrations of CH$_4$, such as those in the atmosphere. Both types of methanotrophs can be active in the same area, but at different soil depths (Reay et al., 2007). In terms of a relatively dry soil ecosystem such as upland forests, high-affinity methanotrophs are typically found in the soil sub-surface region making use of the atmospheric CH$_4$ diffusion through the surface. They are typically most active at 3 – 15 cm in depth (Curry, 2007), although this is dependent on where the soil mineral layer is located. Low-affinity methanotrophs are active at deeper soil depths, typically confined to a narrow band where there is a balance of CH$_4$ diffusing up from methanogens when present, but where there is still enough oxygen diffusing downwards from the atmosphere. The narrow band of low-affinity methanotrophs can move in depth depending on changes in the water table (Reay et al., 2007).
Methane oxidation is primarily defined by the rate of diffusion through the sub-surface soil layer limited by the binary CH₄ diffusion coefficient $D_{CH₄_{soil}}$ (cm² s⁻¹), and secondly by the rate of biological oxidation characterized by a first-order decay rate constant $k$ (s⁻¹) controlled by the activity of the microbes (Curry, 2007).

$$D_{CH₄_{soil}} = D_{CH₄_{air}} \times a \phi^b_g$$  \hspace{1cm} (1)

The CH₄ diffusion coefficient in Equation 1 describes how well CH₄ diffuses through the soil in terms of reaching methanotrophs for oxidation or being transported away from methanogens following emission, where $D_{CH₄_{air}}$ is the diffusion rate in air (0.226 cm² s⁻¹ at 22.5 °C) and $\phi_g$ is the fractional gas-filled soil porosity where $a$ and $b$ are dimensionless coefficients that account for the pore tortuosity and size distribution, respectively, in the soil (Price et al., 2004). These variables are commonly represented by soil texture and type. It has been observed that drier soil profiles containing methanotrophs exhibit a gradient of decreasing CH₄ concentrations with depth, typically from atmospheric concentrations at the surface layer to less than 0.5 ppm at 10 – 30 cm in soil depth meaning that CH₄ oxidation is diffusion-limited. Soil is a three-phase system composed primarily of air, water, and solids. The rate of diffusion in soil is dependent on soil properties and hydrology, because the diffusion of gas through water is 10,000 times slower than diffusion through air (Reay et al., 2007).
Soil texture is characterized by the proportion of clay, silt, and sand composition which directly affects soil porosity. This defines both physical and chemical properties affecting soil respiration, soil water-holding capacity, water movement and gas diffusion in the soil, and ultimately its fertility in terms of being able to provide nutrients to vegetation (Luo and Zhou, 2006). Sandy soils are coarser, consisting of more than 70% sand and less than 15% clay. This type of soil has low water-holding capacity and high porosity. Soils that contain more clay tend to have much higher adsorption and water-holding capacity (Dirk van Elsas et al., 1997). Soil moisture and respiration can be closely correlated in sandy sites, but not as much in sites containing more clay which buffer soil moisture.

Soil methane flux by diffusion can be described by the one-dimensional diffusion equation using Fick’s Law of Diffusion and the rate of microbial oxidation shown in Equation 2 where \( J \) is the flux, \( C_{dCH_4} \) and \( C_{0CH_4} \) are the concentration of \( CH_4 \) at soil depth \( z_d \) and at the surface, and \( k_d \) is the first-order \( CH_4 \) oxidation rate constant (Ridgwell et al., 1999).

\[
J(z_d) = D_{CH_4 \text{soil}} \frac{(C_{0CH_4} - C_{dCH_4})}{z_d} = k_d \times C_{dCH_4} \tag{2}
\]

The diffusion rate of \( CH_4 \) should increase depending on the percentage of gas-filled pore space, with the maximum rate occurring when all the pore space is gas-filled. This can also be affected by the size of the pores in the soil, where coarse-textured soil allow for higher \( CH_4 \) diffusion rates compared to finer-textured soils (Reay et al., 2007). This is important because an ecosystem that is typically a \( CH_4 \) sink could easily be converted into a \( CH_4 \) source with increased water content either by natural or anthropogenic means.

This picture is complicated by the biological processes of the microbes themselves, where at extremely low soil water content, the microbial activity can be limited by water stress and soil temperature. Typically \( CH_4 \) uptake is at a maximum when the percentage of water-filled soil pore space is at 25 – 50%. Soil temperature does play a role in microbial oxidation activity, although the effect is relatively weak compared to soil water content (Reay et al., 2007). Methanotrophs have adapted well to the soil habitats in terms of temperature allowing for a large variation in optimal temperature ranges for microbial activity and growth. The optimal temperature for \( CH_4 \) oxidation is 25 °C in peat soils, but oxidation was observed to still occur from 0 – 35 °C although at reduced rates. The oxidation rates between 0 – 5 °C were 10 – 38%
of the maximum rates observed at 25 °C (Friebel et al., 2009). In contrast, the optimal temperature in an Arctic bog hollow ranged from 0 – 10 °C and growth of some microbes declined or failed to grow at temperatures higher than 15 °C (Omelchenko et al., 1993). Other factors that affect CH$_4$ diffusion and microbial oxidation include soil pH and nitrogen content, where oxidation rates are enhanced under more acidic conditions and are inhibited by nitrogen species such as ammonium from fertilizers (Hanson and Hanson, 1996).

Microbial activity has been observed to continue through the winter under snow, as the soil beneath relatively thick snow cover rarely freezes (Jones et al., 2001). Uptake and emission of CH$_4$ have been observed even at low ambient temperatures under snowpack, with emissions observed through the winter in a boreal littoral wetland with ambient temperatures ranging around -5 to -6 °C, contributing to 12 – 28% of the annual CH$_4$ emissions from the area (Larmola et al., 2004). There have also been observations of methanotrophic activity at low temperatures in biofilters, landfills, and arctic wetlands which result in winter uptake of CH$_4$, although these microbes are poorly understood (Siljanen et al., 2012). In a study conducted by Sommerfeld et al. (1993), CH$_4$ uptake was consistently observed during snow-covered periods in the winter in a southeastern Wyoming snow range, where increased uptake was observed mainly during snow-covered periods in the winter.

1.2.2 Previous Methane Flux Measurements

In the past, methane flux measurements have been made using chambers. Although chambers are simple, inexpensive, and suitable for process level studies; the technique has drawbacks such as being labour intensive and lacking temporal and spatial resolution. Since the early 1990’s, meteorological techniques such as the eddy covariance (EC) method have become feasible in making continuous measurement of methane fluxes integrating over a larger area possible by advances in instrumentation (Clement et al., 1995). One of the earliest studies using the EC method to measure methane fluxes was by Fan et al. (1992) using a fast response flame ionization detector and a fast laser methane monitor to measure methane emissions from the southwestern Alaskan tundra. In the same year, Verma et al. (1992) used a tunable diode laser (TDL) spectrometer to measure methane emission fluxes in a Minnesota peatland with further advances on the technique in 1995 by Zahniser et al. that introduced a multipass absorption cell.
Unfortunately, these measurements experienced drift and low sensitivity as well as additional practical drawbacks with requirements of liquid nitrogen used for temperature control, a large optical module, and frequent calibrations (Hendriks et al., 2008). The Quantum Cascade Laser (QCL) spectrometer was an alternative instrument that offered improvements on stability and accuracy for the EC method over TDL spectrometry, but had similar practical limitations. In 1998, O’Keefe et al. offered a new off-axis integrated cavity output spectrometry (OA-ICOS) technique that used highly reflective mirrors within a small optical cell providing a path length of at least two kilometres without practical limitations exhibited by the original TDL technique. The small absorption rates allowed for a large reduction in the transmission laser intensity, thus lowering the power requirement of the instrument making it suitable as a field instrument for EC measurements. In 2008, the OA-ICOS was first tested in the field by Hendriks et al. that showed high precision and system stability. A similar instrumental technique was subsequently used by Smeets et al. in 2009 to measure methane fluxes in a ponderosa pine plantation showing satisfactory flux measurements during the daytime. In 2011, Querino et al. used a fast greenhouse gas analyzer, similar to this instrument used in this thesis, which allowed for simultaneous measurement of CH₄, CO₂, and H₂O in a tropical forest with high sensitivity over eight months. Although not the first, this field measurement in this thesis is one of the few to make methane flux measurements in a temperate forest ecosystem over such a long period of time. In contrast to other studies that have concentrated mainly on methane emitters, such as tropical forests and wetlands, the temperate upland forest has different methane dynamics, where the ecosystem is on average a methane sink.

Examples of soil CH₄ uptake were typically higher in rural forest environments compared to ecosystems that experience higher levels of anthropogenic activity, such as from a pristine New Zealand forest with a CH₄ uptake of 2.1 nmol m⁻² s⁻¹ (Price et al., 2004), a rural temperate deciduous forest of 0.39 – 0.67 nmol m⁻² s⁻¹ (Guckland et al., 2009), a Japanese forest at 1.9 – 2.2 nmol m⁻² s⁻¹ (Ishizuka et al., 2009), and a Pennsylvania temperature deciduous forest at 1.8 nmol CH₄ m⁻² s⁻¹ (Bowden et al., 1999) upscaled from studies conducted using soil chambers or soil core incubation methods of annual averaged values. A study by Wu et al. (2011) showed the long term effects of clear- and selective-cutting in a temperate spruce forest on CH₄ oxidation where clear-cutting resulted in a mean uptake of 0.090 nmol m⁻² s⁻¹ whereas selective cutting was 0.23 nmol m⁻² s⁻¹. Also noted in this study was a large anthropogenic influence and N-saturated
soils which could have also affected CH4 oxidation, as uptake was much lower than those measured at pristine or rural forests. In terms of eddy covariance studies of forest ecosystems, uptake fluxes were measured at 1.8 nmol m\(^{-2}\) s\(^{-1}\) in a pine planation in California (Smeets et al., 2009) and an emission flux of 0.0020 nmol m\(^{-2}\) s\(^{-1}\) in a tropical forest (Querino et al., 2011).

1.2.3 Source in Plants

Laboratory studies by Keppler et al. (2006) have shown significant emissions from vegetation that have been attributed to the plants themselves, rather than microbes. Incubation chambers that contained intact plants exposed to tropical temperatures around 30 – 70 °C showed CH4 production for all plant species studied through some unidentified biochemical pathway in leaf tissues. The estimated CH4 production strength of 62 – 236 Tg yr\(^{-1}\) for living plants and 1 – 7 Tg yr\(^{-1}\) for plant litter (Keppler et al., 2006). This sparked controversy in the scientific community as to whether the global CH4 budget at the time was missing a major natural source.

In 2009, Nisbet et al. used chambers to grow plants in normal and high stress conditions. They showed that only plants in high stress conditions such as exposure to high UV radiation or high temperatures produced CH4 as a result of the cellular breakdown process and that in normal conditions, the only source of CH4 was found to be from plant transpiration of CH4-rich water (Nisbet et al., 2009). However, other studies have shown that plants produced CH4 in non-microbial aerobic conditions. In 2009, Brüggemann et al. found that plant growth in sterile conditions under low-light at room temperature produced 13C-labelled CH4 after feeding plants with 13CO2. Another study published in 2011 by Wang et al. found that fresh leaves and plant tissue in ambient temperatures produced CH4 from non-microbial sources, with fresh and dried leaves collected from outdoors. The interpretation of non-microbial production was based on the assumption that instantaneous production of CH4 in living organisms could not be microbial as methanogens require adequate time to multiple and produce significant amounts of CH4 (Wang et al., 2011). To date, there have been no field measurements that have directly measured methane emissions from plants.
2 Experimental Method

2.1 Site Description

Measurements were made at a 70,000 ha upland temperate forest at the Haliburton Forest and Wildlife Reserve (45°17’11.23”N, 78°32’19.59”W) located in the Great Lakes/ St. Lawrence lowlands forest region of Ontario. The forest is an uneven-aged forest managed under selection system silviculture, and the measurement site has not been harvested since 1996/1997 resulting in a highly heterogeneous canopy structure. The forest region is dominated mainly by *Acer saccharum* Marsh., *Fagus grandifolia* Ehrh., *Tsuga Canadensis* L., and *Betula alleghaniensis* Britt. Measurements were taken from the top of a 32 m tower, 8 m above a medium dense canopy. The forest contains sandy and acidic soils (pH 4.0 – 5.0). A diesel generator was located northeast of the tower which was usually downwind of the measurement tower 100 m away. The generator showed negligible interference for CH$_4$ and CO$_2$ based on simultaneous measurements by the NO$_{xy}$ instrument which recorded obvious spikes.

Figure 3: Picture of the tower and location of measurement site at the Haliburton Forest and Wildlife Reserve, central Ontario, Canada.
2.2 Instrumentation

2.2.1 Eddy Covariance System

An off-axis integrated cavity output spectrometer (OA-ICOS) Fast Greenhouse Gas Analyzer (model 09-0033, FGGA) developed by Los Gatos Research Inc. (Mountain View, CA) was used for continuous simultaneous measurements of CH₄, CO₂, and H₂O to provide a high response rate of 10 Hz required for the eddy covariance (EC) method. The instrument, shown in Figure 4, employs two distributed feedback (DFB) diode lasers, which offer broad tunability, narrow linewidth, and high output power with a wavelength in the near-infrared region around 1.65 µm. The laser uses a grating structure within the semi-conductor which narrows the wavelength spectrum guaranteeing single-frequency emission (Hendriks et al., 2008). This system is known as a closed-path (CP) system because the sample is measured as it is pulled through the optical cell that is closed off from the ambient atmosphere.

The laser beam enters the optical cell at an off-axis geometry making multiple passes within the cavity until the light retraces its path between the highly reflective mirrors making approximately $1\times10^4$ passes where each pass increases the intensity inside the cavity (Hendriks et al., 2008). An added advantage of the instrument is the increased intensity within the optical cell which can be achieved without a high output laser lowering the power requirement of the system. After sufficient laser power is detected leaving the cavity, the laser source is interrupted and the ringdown decay can be measured (Baer et al., 2002). The concentration of the gas species within the cavity can be determined by measuring the fractional absorption of light at the specific resonant wavelength of the gas (Hendriks et al., 2008). The spectral absorbance $\alpha_v$ at specific optical frequency $v$ shown in Equation 3 uses the Beer-Lambert law relating the measured difference in transmission signal ($I$) and reference signal ($I_0$) from the time domain into the optical frequency domain (Mihalcea et al., 1998).

$$\alpha_v = -\ln \left(1 - \frac{I_0 - I}{I_0}\right)$$  (3)

The spectral absorbance is linearly dependent on the mole fraction $X_i$ of the gas species $i$ with $M_i$ overlapping absorption lines shown in Equation 4 where $P$ is total pressure, $T$ is cell temperature, $L$ is the absorption pathlength, $S_{i,j}$ is the temperature-dependent line strength of the line $j$ and species $i$, and $\Phi$ is the lineshape function (Mihalcea et al., 1998).
Typically in diode-laser absorption spectroscopy, the mole fraction can be determined based on the relation shown in Equation 4 by iteratively fitting the measured absorbance to a simulated reference spectroscopic plot which contains relative line positions and line strengths with conditions specific to the instrument (Mihalcea et al., 1998; Kranendonk et al., 2007) taking into account both pressure and temperature measurements made in the optical cell.

$$a_v = PX_iL \sum_{j=1}^{M_i} S_{i,j}(T) \Phi_{i,j}(v - v_{0,i,j}, a_{i,j}) \quad (4)$$

Figure 4: Picture and general schematic of the OA-ICOS FGGA optical cell system.

The OA-ICOS also allows for high sensitivity from the long effective optical path length of 2 – 20 km provided by the optimized off-axis geometry within the optical cell. The instrument can measure at a range of 0.1 – 25 ppm for CH₄ and 200 – 4000 ppm for CO₂. The path length is determined by the time period in which the laser is reflected within the cell and is affected by the reflectivity of the mirrors also known as the mirror ringdown time (MRT). The MRT can decrease due to dirt accumulation on the mirrors in the cell (Hendriks et al., 2008). Sudden drops in the instrument MRT due to particulate accumulation were avoided by using a 7 micron Swagelok stainless steel in-line particulate filter before the inlet of the instrument. The manufacturer advised that for proper measurements, the MRT should not decrease below 3.5 µs
and was observed to remain above 10 µs during the measurement period in the field. The instrument allows for two flow rates options; a low flow rate at ~1 L/min using an internal pump and pressure controller, and a high flow rate which requires an external pump which pumps at ~30 L/min using a coarse pressure control knob. Pressure and temperature measurements were recorded at high frequency within the optical cell using metal foil gauge pressure sensor and fine wire thermocouple.

![Figure 5: Sonic anemometer, IRGA, and inlet tubing secured to the top of the tower.](image)

The closed-path instrument was located in an environmentally controlled building at the bottom of the tower. The FGGA required a dry vacuum scroll pump (Varian TriScroll 300, Palo Alto, California) to pull air at approximately 30 litres per minute through 38 m of 0.95 cm internal diameter PVC black tubing from the top of the tower to maintain sufficient flow for 10 Hz measurements. This increased the power required for the system which was the reason for the use of a power generator. The inlet tubing of the FGGA was 0.7 m away from the sonic anemometer (model CSAT3, Campbell Scientific Inc., Logan, Utah) used for wind direction and wind speed measurements, and a LI-7500 open-path (OP) infrared gas analysis (IRGA) for CO₂ and H₂O measurements (model 7500, LI-COR Inc., Lincoln, Nebraska) secured to a pole extended from the top of the tower directed in a southwesterly direction (215°) on the tower. Data were logged by a micrologger (model CR3000, Campbell Scientific Inc., Logan, Utah) for the instruments and sensors at 10 Hz.
2.2.2 Other Sensors and Measurements

Tower and soil station data were set up and operated by Mike Fuller, Jon Schurman and Sean Thomas from the Department of Forestry, University of Toronto. The tower sensors (Onset Computer Corporation, Bourne, Massachusetts) included temperature, wind direction and magnitude within the canopy, and amount of rain, which was measured at intervals of 5 minutes throughout the measurement period. The soil station located southwest of the tower in mid-level elevation terrain measured soil moisture and temperature. The soil station was not continuously operational throughout the measurement period due to sensor malfunctions, although it measured periods of different environmental conditions throughout the field campaign.

Figure 6: Chamber used in the study with collection syringes the in background.

Carolyn Winsborough and Nathan Basiliko from the Department of Geography, University of Toronto where CH₄, CO₂, and N₂O fluxes were calculated by measurements made from static soil chambers near the tower. The study consisted of a distributed network of soil flux chamber stations established within the footprint of the tower. A permanent collection of 10 cm PVC collars were installed over seven topographical gradients including five sites each; low slope, toe slope, mid-slope, ridge slope, and high slope. On measurement days, 1.5 PVC chambers were secured to each collar, shown in Figure 6. The chamber was first mixed by pumping air in and out of the chamber, and then 30 mL was taken over a 90 minute period at 30
minute intervals using airtight syringes. The samples were analyzed in the laboratory using gas chromatograph/flame ionization detector (GC-FID) (SRI Instruments, Menlo Park, California) to determine the concentrations of the gas sample series to infer a flux for each site. A vent system was not installed with this chamber measurement method.

Figure 7: Stainless steel canisters and passive flow controller with automatic timer at the top of the tower during sampling.

A canister study was also conducted at the tower site August 22 – 24, 2011 using 6 L stainless steel summa polished canisters (Scientific Instruments Specialists, Moscow, Idaho) with passive flow controller with timer shown in Figure 7 integrated over two hour sampling periods during the day, and between 18:00 – 06:00 hours over the nighttime. Samples were collected at three different levels; near ground (5 m), mid-canopy (20 m), and above-canopy (32 m). The samples were brought to the Environment Canada Analysis and Air Quality Section laboratory (AAQS) where the samples were diluted with air and analyzed with a GC-FID 6890 (Agilent, Santa Clara, California) equipped with a 1 mL sample loop. A Valco Bond (VICI, Gig Harbor, Washington) capillary column (VP-molsieve 5A, 30 m, 0.53 mm ID, 15 µm film thickness) was used to separate CH₄. A four point calibration curve using a CH₄ calibration gas was used to determine the concentration of the sample from the peak area of the chromatograms. The dilution factor was then applied to give the proper mixing ratio of CH₄.
2.3 Eddy Covariance Method

The eddy covariance (EC) method uses high frequency fluctuations in wind and an atmospheric scalar to calculate exchange between an ecosystem or surface and the atmosphere. This method can be used to verify climate and ecological models, as well as previous flux measurement techniques applied to specific ecosystems. Looking at a horizontal flow, there are rotating eddies of various sizes with horizontal and vertical components. EC considers only the vertical component which represents only the transfer of the scalar into or out of the ecosystem. The flux is simply the covariance of the instantaneous deviation in vertical wind velocity ($w'$) and the scalar, for example the concentration of the atmospheric species ($c'$), averaged over a specific period of time. This is described by Equation 5 where $\rho_a$ is air density, the overbar represents time averaging, and primes denote fluctuation from the mean (Burba and Anderson, 2010):

$$F = \bar{\rho_a} \cdot \bar{w'}c'$$  \hspace{1cm} (5)

To capture all significant scales of motion contributing to the turbulent transfer of the atmospheric species between the ecosystem and atmosphere, a high sampling frequency is required over a sufficient duration. To capture the high frequency portion of the cospectrum, a sampling rate of at least 10 Hz is required to include the smaller fluctuations. In terms of the low frequency portion, sampling duration must be long enough to sample the larger motions associated with the convective boundary layer, but must not be so long as to be affected by diurnal changes in the gas species. Typically, averaging of atmospheric turbulence is done over an interval of 30 – 60 minutes during the day and may be extended at night due to intermittent turbulence and stable thermal stratification of the atmosphere (Baldocchi, 2003), although it is typical to simply use a 30 minute averaging period. Some major advantages of EC over other flux measurement techniques is that it allows for automated and continuous measurements with high temporal resolution integrated over a representative portion of an ecosystem, which does not directly disturb the surface (Hendriks et al., 2008).

A major drawback is the infrastructure required for site set-up and instrumentation. The requirement of an instrument that has a high time response, sampling frequency, and precision adds an additional cost compared to simpler flux measurement techniques. When available, fast-
response open-path sensors can be used in place of closed-path instrumentation that has a larger power requirement typically requiring a generator or measurements to be made near to available line power, which is not always ideal. The infrastructure of chamber-based flux measurements is much simpler and can be made in any remote area, thus this technique has been more commonly used in the past. Fluxes inferred from chamber measurements can be useful in examining single elements within an ecosystem. Scaling up to the ecosystem level typically requires multiple chamber sites, but there may be limited temporal and spatial resolution. Without verification with another more representative method such as EC, it would be difficult to determine the accuracy of the upscaled ecosystem flux calculated from chamber measurements.

Another drawback of the EC method is that its accurate implementation requires several major assumptions; that the air is fully turbulent, most of the vertical transfer is done by eddies, the process must be stationary within the averaging period, the surface is horizontally level and uniform where the density fluctuation, flow convergence and divergence are negligible, and that the instruments can detect very small changes at high frequency with good precision (Burba and Anderson, 2010). As these assumptions cannot always be met in the field, the quality assurance and control of the data are much more important than simple methods. Data that do not meet these conditions should either be corrected for or removed altogether during the processing of the data to avoid inaccurate flux values. Some of the corrections used in the EC calculations will be discussed below.

2.3.1 Coordinate System

Horizontal momentum flux (τ) is the covariance of the vertical component (w′) and the horizontal component (u′) in this case, the x- or y-axis (Aubinet, 1997). The case of non-horizontally level terrain or a tilted sonic anemometer can lead to large horizontal momentum flux errors introduced from cross contamination of wind velocities, where improper measurement of velocity fluctuations in the vertical component of wind could appear as longitudinal fluctuations. This is corrected using a mean streamline coordinate system with planar fit technique. The coordinates are aligned so that it matches the system where the x-axis is parallel to the local mean wind, the y-axis is on the plane of the local terrain, and the z-axis is perpendicular to the local terrain and orthogonal to the x-axis. The result is a dataset which is in a
true vertical coordinate system independent of the terrain slope and direction to the first order which can then be compared to other level terrain results (Wilczak et al., 2001).

2.3.2 Sensor Separation Corrections

Separation of different sensors in space can lead to a difference in measured turbulent fluctuations and a phase shift. A co-spectral transfer function can be used to calculate the discrepancy in the measurements due to a sensor separation which depends on the angle between the separation path and wind vector. In the case where the separation path is parallel to the wind, or a longitudinal separation, then the two sensors would measure the same turbulent fluctuations but with a phase shift in the measurements. To correct for the longitudinal separation, the sample measurements can be shifted in time to match (Moore, 1986) in which the correction can be included in the determination of the lag time between the sonic anemometer and the instrument. In terms of a separation path that is perpendicular to the wind, or a lateral separation, the fluctuations would be different but with no phase shift. The zero-plane displacement height \( d \) of a vegetated surface is the height at which the wind speed extrapolates to zero (Oke, 1978) and the Monin-Obukhov length \( L \) is the length proportional to the height above the surface where buoyant production of turbulence dominates mechanical production of turbulence (Jacobson, 2005). If the sensor separation is small, defined as less than 10% of the height above the zero-plane displacement in unstable conditions or less than 0.7% of \( L \) in stable conditions as to only affect measured turbulent fluctuations in the inertial sub-range, the velocity cross spectra for isotropic turbulence can be used to describe the transfer function for separate effects in Equation 6; where \( f = ns/u \) is the normalized frequency and \( n \) is frequency (Hz), \( \Gamma \) is the gamma function, \( s \) is the separation distance between the sensors, \( u \) is the horizontal wind velocity, and \( K_{5/6} \) is a modified Bessel function of the second kind (Moore, 1986).

\[
T_s(f) = \frac{2^{1/6}}{\Gamma(5/6)} (2\pi f)^{5/6} K_{5/6}(2\pi f)
\]  

Equation 6 can be simplified into a good working description of the transfer function (Equation 7) from empirical data, which can be used in the flux calculations to take into account the lateral separation of sensors (Lee and Black, 1994).
\[ T_s(f) = e^{-9.9f^{1.5}} \]  

(7)

The transfer function in Equation 7 can be applied as a cospectral correction in the frequency range to estimate the relative flux losses in the high frequency range due to sensor separation by scaling the contribution to the fluxes in the cospectrum. There was a sensor separation between the sonic anemometer with the IRGA sensor of 0.2 m, and with the FGGA tube inlet of 0.6 m.

2.3.3 Tube Damping Effects

In closed-path measurements made where the air is drawn through tubing to the instrument, the tube itself could act as a low-pass filter which could result in the attenuation of high frequency fluctuations. The damping of the fluctuations is due to the radial variation in streamwise air velocity and radial diffusion (Leuning and King, 1992). In 1954, a solution for this effect was first described by Taylor shown in Equation 8, where \( C \) is the concentration as a function of the longitudinal distance down the tube at distance \( x \), \( C_0 \) is the amplitude of the varying concentration at the inlet of the tube, \( k = \frac{2\pi f}{U} \) is the wavenumber (\( k \)) where \( f \) is frequency, \( U \) is the discharge velocity in the tube, and \( \alpha_1 = Dk^2 \) is the attenuation coefficient (Taylor, 1954).

\[ C(x, t) = C_0 \exp(ikx - \alpha_1 t) \]  

(8)

In 1991, this was expanded upon by Lenschow and Raupach shown in Equation 9, where \( C_{in} \) and \( C_{out} \) are the concentration of the species at the inlet and outlet of the tube respectively, and the time taken for the air to travel from \( C_{in} \) to \( C_{out} \) is defined as \( t = \frac{X}{U} \) with \( X \) being the distance travelled by the bulk flow and \( U \) is the discharge velocity in the tube (Lenschow and Raupach, 1991).

\[ \frac{C_{out}}{C_{in}} = e^{-Dk^2X/U} \]  

(9)

From Equation 8, a transfer function shown in Equation 9 can be used to describe the changes in the variance of gas concentration fluctuations dependent on the type of flow in the tubing. In terms of a closed-path system, turbulent flow is typically encountered in the tube due to the higher flow rate. Turbulent flow is defined by the range of Reynolds number between...
Re<sub>c</sub> < Re < 10<sup>5</sup> in which the Reynolds number (Re) is defined by \( Re = \frac{2aU}{\nu} \) where \( \nu \) is the kinematic viscosity, and \( Re_c \) is the critical Reynolds number where flow becomes turbulent (\( Re_c \approx 2300 \)). For this closed-path system at the high flow rate setting, the Reynolds number was calculated at ~7000 defined as turbulent flow. The virtual diffusivity for turbulent flow in Equation 9 is given by \( D = 10.1a\,u_* \), where \( u_* \) is the friction velocity at the tube surface and \( a \) is the tube radius. The empirical Blasius resistance formula \( u_* / U \approx 0.2Re^{-1/8} \) is substituted into Equation 9 to give the transfer function (Leuning and King, 1992) shown in Equation 10 to describe the tube damping effects.

\[
G_t^2(f) = (C_{\text{out}}/C_{\text{in}})^2 = \exp(-160Re^{-1/8}af^2x/U^2)
\] (10)

This correction is applied similarly as the sensor separation correction and affects the high frequency range of the cospectrum in terms of flux losses due to tube damping effects. Depending on the flow rate and tube dimensions, the correction factor could vary, as reported by Leuning and King, their closed-path instrument underestimated the flux by 16% (Leuning and King, 1992).

### 2.3.4 Webb-Pearman-Leuning (WPL) Corrections

Density fluctuations result due to sensible heat and water vapour fluctuations not associated with the net transport of the atmospheric species can give incorrect estimates of the flux. If measurements are made of the density of the species in \textit{in situ} air, corrections are required to correct for these inaccuracies. These corrections can be avoided if measurements are made in the fluctuation of the gas mixing ratio relative to the dry air component (Webb et al., 1980). This assumes that the air is dried before being measured or H<sub>2</sub>O is simultaneously measured. For the FGGA, H<sub>2</sub>O was simultaneously measured and a software algorithm corrected for any dilution effects to report a dry mixing ratio of the gas. The temperature of the gas sample in the optical cell is also continuously measured.

The Webb-Pearman-Leuning (WPL) correction estimates the influence of sensible heat flux (\( H \)) and water vapour flux (\( E \)) on vertical fluxes measured between the fluctuations in density (\( \rho_c' \)) and vertical wind speed (\( w' \)). For an OP system, in which \( H \) and \( E \) affect the
calculated corrected flux \( (F_c) \) of the gas species, Equation 11 is used to correct for these effects where \( \rho_a \) is the density of dry air, \( \mu \) is the ratio of molecular weights of water to dry air, \( \sigma \) is the mean density ratio of water vapour to dry air, and \( T \) is ambient temperature (Suyker and Verma, 1993).

\[
F_c = \overline{w' \rho'_c} + \mu (\overline{\rho_c/\rho_a}) \overline{w' \rho'_v} + (1 + \mu \sigma)(\overline{\rho_c/T}) \overline{w'T'} \tag{11}
\]

From Equation 11, the correction can be altered for a closed-path system with a cell temperature and pressure different from ambient conditions, where \( \overline{P} \) and \( \overline{T} \) are the mean ambient pressure and temperature with subscript \( I \) denoting conditions within the cell, and \( \rho_{ci} \) and \( \rho_{vi} \) are the density of \( C \) and water vapour in the measurement cell (Suyker and Verma, 1993) in Equation 12. This correction in contrast to the one for an OP system does not take into account sensible heat fluctuations.

\[
F_c = (\overline{P}/\overline{P_I})(\overline{T}/\overline{T})[\overline{w' \rho'_{ci}} + \mu (\overline{\rho_{ci}/\rho_a}) \overline{w' \rho'_{vi}}] \tag{12}
\]

The previous correction applies to an instrument that is able to measure water vapour within the cell, but in the case where water vapour is measured by an open-path sensor near the tube inlet of the CP system, the equation can be changed to include the OP latent heat flux term which includes the sensible heat flux correction in Equation 13 (Suyker and Verma, 1993).

\[
F_c = (\overline{P}/\overline{P_I})(\overline{T}/\overline{T})[\overline{w' \rho'_{ci}} + \mu (\overline{\rho_{ci}/\rho_a}) (\overline{w' \rho'_{vi}} + (\overline{\rho_v/T}) \overline{w'T'})] \tag{13}
\]

The inherent problem that arises from using OP sensor water vapour measurements for the latent heat correction is that the measurement of \( \text{H}_2\text{O} \) is made in the free atmosphere does not accurately represent the fluctuations within the CP measurement cell. Although this correction has been used in the past with studies that made CP CH\(_4\) measurements, this was avoided by the FGGA which makes simultaneous \( \text{H}_2\text{O} \) measurements.

Webb et al. (1980) also suggested that the WPL correction could be simplified by simply measuring the mixing ratio of the gas, which allows for the removal of the sensible heat flux corrections. Where the air is not dried, the latent heat flux correction must still be taken into account where \( \overline{\rho} \) is the total density \( (\rho = \rho_a + \rho_v) \), \( \overline{w'C'} \) and \( \overline{w'q'} \) is the fluctuation of the gas and
H₂O mixing ratio, and $\overline{C}$ and $\overline{q}$ are the mean mixing ratio of the gas species $C$ and H₂O respectively (Webb et al., 1980) shown in Equation 14.

$$F_C = \left(\frac{P}{\overline{P}}\right)\left(\frac{T}{\overline{T}}\right)\overline{\rho}\left[w'c' + \left(\frac{\overline{C}}{1 - \overline{q}}\right)w'q'\right]$$

These different WPL corrections were applied in Section 2.4.4 and compared with the flux values calculated from the corrected FGGA mixing ratio measurements with no WPL corrections applied.

### 2.4 Instrumental Stability, Accuracy and Precision

The instrument was tested for its stability, accuracy, and precision before being deployed at the field site, during the field campaign, and after being brought back to the laboratory. A calibration gas (Linde Canada Ltd., Brampton, Ontario) certified at 2.01±0.10 ppm and 371±7 ppm for CH₄ and CO₂ respectively was used to test the accuracy of the instrument. It was connected through a brass tee connection in the inlet line with a vent due to concerns of pressure build-up within the measurement cell. The other end of the inlet line was kept at a positive pressure from the calibration gas output to ensure no ambient air was sucked in. For the low flow calibrations, the calibration gas was introduced at a constant rate of 0.65 litres per minute. The high flow calibration used a dry scroll pump attached to the instrument with the calibration gas output directly from the gas cylinder through the gas regulator which provided a high enough flow rate. An example of one calibration test is shown in Figure 8; the instrument reported an average mixing ratio with the standard deviation over the calibration period of 2.001±0.002 ppm and 370.9±0.3 ppm. Before the instrument was brought to the field, 24 separate low flow calibration runs were conducted over a month, with an average mixing ratio of 1.996±0.003 ppm and 371.2±0.6 ppm for CH₄ and CO₂ respectively which is within the range of uncertainty from the certification of the calibration gas.

No significant differences were observed when the calibration gas was run while the instrument was in the field. The instrument was tested again with the calibration gas after being brought back to the laboratory after the field campaign in November. A high flow calibration was run shown in Figure 9, with an average mixing ratio of 1.998±0.014 ppm and 373.7±2.7
ppm for CH₄ and CO₂ respectively. These values compared well with the calibrations using low flow and tests run before the instrument was brought to the field, with a potential +2 ppm drift in CO₂ which is only a 0.5% change over a 5 month period.

Figure 8: Time series of one calibration at 1 Hz test using low flow setting before the instrument was brought to field site.

The high flow calibration had much higher noise which has been shown to be affected by the high pumping speed resulting in changes in cell pressure and/or increased measurement response. The noise for CH₄ averaged from the calibration tests increased from ±2 ppb using the low flow setting to ±5 ppb at the high flow setting at 1 Hz. With measurements at 10 Hz, the noise averaged at ±14 ppb calculated from tests run at high flow.

Figure 9: Time series of measurements at 10 Hz of calibration gas over 5 minutes sampling at the high flow setting after field measurements.
The instrument was also tested for its accuracy in measuring water using a dewpoint generator (model LI-610, LI-COR Inc., Lincoln, Nebraska) which was attached to the inlet line similarly to the calibration gas tests. The measured H₂O mixing ratio was plotted against the set dew point temperature converted into ppm of H₂O in Figure 10. The FGGA underestimated the mixing ratio of H₂O as relatively humidity was increased, although there was still a linear correlation ($R^2 = 0.9994$). As the accuracy of the dew point generator could not be properly determined, the accuracy of the FGGA was simply judged by the relative values shown in Figure 10 and the underestimation of H₂O was not corrected for within the FGGA. The absolute value of the H₂O mixing ratio was not important in the calculation of the fluxes, although the relative mixing ratio of H₂O to CO₂ and CH₄ was used to correct for dilution and pressure broadening effects described in Section 2.4.2.

![Figure 10: Calibration of water measurements using a Dew Point Generator.](image)

The instrument was also tested for its stability by calculating the Allan variance on the calibration tests. As the integration time increases, the variance resulting from random noise decreases, but when noise caused by instrumental drift begins to influence the measurements, the Allan variance then starts to increase (Hendriks et al., 2008). For 10 Hz measurements made over the course of 10 minutes, there was a decreasing Allan variance over the integration times with no significant increase shown in Figure 11 except for a minor increase in the Allan variance at the integration time of 12.7 s for CH₄. This indicates an influence of instrumental noise for CH₄, in contrast to CO₂ which showed a continuous decrease up to a 100 second integration time.
Figure 11: Time series using high flow setting (top) and Allan variance plot (bottom) of CH$_4$ (left) and CO$_2$ (right) with the line of slope -0.5 indicating the region of uniform spectral density Gaussian noise.

The temperature and pressure stability of the instrument optical cell were also tested. The pressure of the optical cell is controlled by a coarse pressure controller in the instrument. After the cell was adjusted to have a pressure of 138 Torr, there was negligible pressure change recorded. There was an observed low frequency change in the temperature of the measurement cell in Figure 12(a) over a longer period of time affected mainly by the temperature cycles within the instrument shed. Over a 30 minute period Figure 12(b), the ambient temperature ranged from 20.6 °C to 24.1 °C, where the cell temperature only ranged from 22.2 °C to 22.3 °C.

In terms of WPL corrections, when the air is brought to a common temperature and pressure, the $H$ term in the WPL correction can be removed completely due to the attenuation of temperature fluctuations within the tubing (Leuning and Moncrieff, 1990). For turbulent flow, a minimum tubing length required for reducing temperature fluctuations can be determined by $X_{min} = 92aRe^{0.2}$ where $a$ is the inner radius of the tubing and $Re$ is the Reynolds number (Leuning and Judd, 1996). This minimum length assumes tubing with thermally conductive walls, where typically stainless steel tubes which have a thermal conductivity of 16 W/m·K whereas for polyvinyl chloride (PVC) it is only 0.19 W/m·K at 298 °K. The calculated minimum length for the turbulent flow exhibited at approximately 30 L/min is only five meters, whereas 40 meters of PVC tubing was used for measurements in this study. The effects of the CP temperature corrections will be further investigated in Section 2.4.4.
2.4.1 Instrumental Lag Time

When using the covariance of instantaneous deviations in wind and a chemical to calculate the flux, it is important to correct for any offset, or lag, in the time between the measurements of the two. The average lag time of the CP instrument was determined by cross-correlating the measured gas with vertical wind, shown in Figure 13 averaged over 864 half hour intervals or 18 days. The lag time was determined as 4.2 seconds for FGGA measurements of CO₂, CH₄, and H₂O. The correlation coefficient from the peak in the cross-correlation function for CO₂ was much higher than CH₄, thus it was used to identify the lag time for all three gases measured by the FGGA since they should all be the same. This lag time is expected to change as wind speed changes, thus during processing of each half hour interval of data for flux calculations the covariance was calculated for a range of lag times between 2 and 4.2 s, and the time that produced the maximum CO₂ flux was used. For OP CO₂, the average lag time was 0 seconds, which given the proximity of the OP sensor to the sonic anemometer was to be expected compared to the 40 m of tubing used in the CP system.
2.4.2 Water Effects on the Mixing Ratio

In the infrared laser spectroscopy of CO$_2$ and CH$_4$, studies have found a cross-sensitivity of the reported mixing ratios of the gases to atmospheric water vapour in two separate ways; through dilution and pressure broadening effects (Chen et al., 2010; Hiller et al., 2012). The humid mole fraction of the measured gas can be significantly affected by variations in H$_2$O called the dilution effect, where the number of moles of the atmospheric species is divided by the number of moles in wet air. By using a dry mole fraction which is reported by the FGGA, the dilution effect can be taken into account, although this would depend significantly on the accuracy of the correction used by the instrument.

In Figure 14, the difference between the humid mole fraction (light grey) and the reported dry mole fraction (dark grey) represents this dilution effect. The remaining discrepancy between the dry mole fraction and the corrected dry mole fraction (coloured) is attributed to the pressure broadening of the spectral line used to measure the mixing ratios (Chen et al., 2010). Although this effect does not affect the total area of the absorption line, it affects the absorption peak height which is used by the algorithm of the FGGA to calculate concentration. Line broadening effects are proportional to pressure with variations in their magnitudes depending on the absorption line of the analyte molecule and the composition of the gas mixture.
Atmospheric water vapour varies significantly relative to other gases found in the atmosphere that can cause significant changes in the line-broadening effects of the absorption lines of other constituents (Chen et al., 2010). This could lead to systematic errors depending on the amount of H₂O present in the cell. For the FGGA, the pressure broadening effects contributed a ~1.5% discrepancy in the mixing ratio in humid air. However the impact on calculated fluxes (Section 2.4.3) can be larger when there is a strong covariance in vertical wind and H₂O concentration.

The effect of H₂O on both dilution and pressure broadening effects was tested using a similar set-up for the calibrations, with an additional line passing through a gas bubbler containing deionized water. Both lines were run in parallel from the calibration gas source to the instrument inlet line, with a valve controlling flow through a normal line without a gas bubbler. As the flow was restricted for the dry line, more gas was pushed through the gas bubbler which increased the water content in the calibration gas downstream. The change in gas mixing ratio related to the effects of H₂O was measured by taking averages of multiple runs, changing the humidity step-wise between 0 – 26,000 ppm, both from dry to humid and vice versa. An example of one run is shown in Figure 14. This was done to avoid biases that can arise from the solubility of CO₂ in the water which was observed to affect the measured mixing ratio of CO₂ downstream. There was less of an effect observed on the mixing ratio of CH₄.

As the FGGA simultaneously reports the mixing ratios CO₂, CH₄, and H₂O, changes in the reported wet air mixing ratio proportional to changes in H₂O were used to determine a proper...
correction described in Equation 15 & 16 to give a corrected dry air mixing ratio (CP-m). The effect was much larger for dilution effects than for pressure broadening effects, although pressure broadening was larger for CO$_2$ than CH$_4$.

\[
[\text{CH}_4]_{\text{dry}} = [\text{CH}_4]_{\text{CP}} + (1.4667 \times 10^{-11} \times [\text{H}_2\text{O}]_{\text{CP}}^2) + (2.0233 \times 10^{-6} \times [\text{H}_2\text{O}]_{\text{CP}}) - 6.3502 \times 10^{-5} \quad (15)
\]

\[
[\text{CO}_2]_{\text{dry}} = [\text{CO}_2]_{\text{CP}} + (1.4937 \times 10^{-10} \times [\text{H}_2\text{O}]_{\text{CP}}^2) + (0.00057335 \times [\text{H}_2\text{O}]_{\text{CP}}) - 0.00035484 \quad (16)
\]

The averaged correction in Equation 15 & 16 for CH$_4$ and CO$_2$ respectively provided, a dry mole fraction of the gas corrected for pressure broadening and dilution, which was tested on the different calibration runs to ensure accuracy. This type of correction has been applied before to cavity ring-down spectroscopy systems (Chen et al., 2010; Hiller et al., 2012), although the correction factors would differ depending on each individual instrument. In Figure 15, the half-hour averaged corrected dry air mixing ratios measured during the field campaign were compared to the uncorrected wet air mixing ratios, where the colour of each point shows H$_2$O mixing ratio.

Figure 15: Correlation plot of corrected mixing ratio of CH$_4$ (left) and CO$_2$ (right) compared to uncorrected wet air mixing ratios.
2.4.3 Water Effects on the Fluxes

The influence of each type of mixing ratio on the calculation of the flux values was also tested using corrected dry air (CP-CDry), uncorrected (reported) dry air (CP-UCDry), and uncorrected wet air (CP-UCWet) mixing ratios. None of the fluxes in this section was corrected for sensible or latent heat fluxes to determine the influence of the pressure broadening effects on the flux values. The CP-UCDry flux values were calculated from the reported dry mixing ratio (shown above to have a ~1.5% discrepancy at higher H2O concentrations). The comparison shown in Figure 16 showed a consistent negative bias of the fluxes in both CP-UCDry and CP-UCWet compared to CP-CDry.

Figure 16: Comparison of CH4 (top) and CO2 (bottom) flux calculated from mixing ratio corrected for dilution and pressure broadening effects to flux calculated from uncorrected dry (left) and wet (right) air mixing ratio.
For both CH$_4$ and CO$_2$, the uncorrected fluxes showed consistently larger flux magnitudes, with the fluxes in CO$_2$ having an increased discrepancy with higher uptake flux values. Methane fluxes showed a larger discrepancy on average, which is mainly due to the much smaller flux values of CH$_4$ compared to CO$_2$. This indicates that CH$_4$ fluxes are much more sensitive to small changes in the mixing ratio that covary with vertical wind.

A diurnal plot was made from the fluxes calculated from CP-CDry, CP-UCDry, and CP-UCWet mixing ratios shown in Figure 17. As the fluxes using CP-UCWet did not apply any H$_2$O corrections, it is obvious in Figure 17 that there is a significant influence during the daytime overestimating the uptake fluxes. Typically in flux calculations using a wet mixing ratio, WPL corrections would be applied to correct for these H$_2$O effects. Although there was little observable diurnal variation in the mixing ratio of H$_2$O in the measurement cell, there were much larger H$_2$O fluxes during the day compared to the night, which could greatly increase the effects of H$_2$O on the fluxes. The daytime overestimation was much less for CP-UCDry fluxes, although there was still a discrepancy between CP-UCDry and CP-CDry fluxes. Although the mixing ratio of CP-UCDry was corrected for the dilution effects of H$_2$O with a reported dry mixing ratio, the pressure broadening effects were not corrected where larger fluctuations in H$_2$O could still affect the fluctuations in the mixing ratio. By correcting for both dilution and pressure broadening effects from H$_2$O, the daytime bias can be corrected.

Figure 17: Averaged diurnal cycles of OP CO$_2$, CP CH$_4$ and CO$_2$ fluxes calculated from uncorrected and corrected mixing ratios for dilution and pressure broadening effects.
2.4.4 WPL Correction Terms and Comparison

To test the accuracy of the flux values, the CP CO₂ fluxes were initially compared to OP CO₂ fluxes to give a rough estimate of the precision of the flux calculations and corrections applied. Although both OP and CP fluxes were processed using a similar program, OP flux calculations used OP sensor measurements for H₂O and temperature with lateral sensor separation, line averaging, and WPL sensible and water vapour fluctuation corrections applied to the fluxes. For CP flux calculations, CP measurements of H₂O in the instrument cell were used and corrected for H₂O effects directly in the mixing ratio rather during flux processing, with corrections applied for high frequency noise. The representative time series in Figure 18 demonstrates the close agreement of the OP and CP flux values, although with some discrepancies in the uptake fluxes during the day.

![Figure 18: CO₂ fluxes from OP (grey) overlapped by CP (red) measurements.](image)

Figure 18: CO₂ fluxes from OP (grey) overlapped by CP (red) measurements.

This discrepancy in the daytime uptake values existed throughout the measurement period shown in the correlation plot in Figure 19, where there was larger uptake in the OP fluxes compared to the CP values. A similar bias was observed by Liu *et al.* (2006) and Serrano-Ortiz *et al.* (2008) where there were 20% higher uptake flux values in the daytime and 15% lower emission flux values in the nighttime measured from fluxes calculated from the measurements made by the OP IRGA compared to the FGGA. Liu found that the increased daytime discrepancy using an OP IRGA could be attributed to the underestimation of sensible heat flux correction term \( H \) through the WPL correction (Liu *et al.*, 2006). Serrano-Ortiz also found that a combination of high sensible heat flux values during the day with additional relative errors from the measured gas density by the OP IRGA could lead to larger propagation of errors in the WPL terms. Error
in the OP IRGA measurement can arise from contamination of the optical windows of the instrument. Due to larger magnitudes of the WPL terms in the daytime and a dependence on the sensible heat flux term, the systematic errors in the WPL correction could lead to selectively systematic errors in the corrected flux values (Serrano-Ortiz et al., 2008). This bias would lead to significant errors in long-term integrations of net ecosystem exchange (NEE). In our data it is difficult to discern whether there was an underestimation of WPL correction terms in the OP calculations or an overestimation of the corrections of H$_2$O effects for the CP calculations which affected the flux values. CP fluxes were further investigated using different correction techniques.

Figure 19: Correlation plot of CO$_2$ flux values from OP and CP measurements.

Given that the WPL correction is the accepted method of correcting the effects of sensible and latent heat fluctuations on fluxes of the measured gases, the accuracy of the corrections of H$_2$O effects in CP-CDry were compared to fluxes calculated from uncorrected mixing ratios using WPL corrections described in Table 1. Although the two correction methods take different approaches, both describe a similar process and the resulting fluxes should be similar. The first method (CP-CDry) is the fluxes described earlier which had no WPL corrections, rather H$_2$O effects were corrected in the mixing ratio. The other methods used WPL corrections on the wet air mixing ratio corrected only for pressure broadening effects in the
The corrections with suffix “-d” converted the mixing ratio into density and then applied WPL corrections. This was done to represent previous studies which measured in density fluctuations rather than mixing ratio and typically lacked simultaneous measurement of H2O within the instrument and instead used OP measurements of H2O and temperature for WPL corrections. OP WPL corrections (OPW-d) used OP ambient H2O measured by the OP IRGA defined by Equation 13 and CP WPL corrections (CPW-d) used FGGA measurements of H2O within the instrument cell defined by Equation 12. CPW-m used the same measurements for the corrections defined by Equation 14, but did not convert the mixing ratio into density. None of the corrections used ambient temperature fluctuation measurements for sensible the heat flux correction of the fluxes, as this did not represent the fluctuations within the measurement cell which could overestimate the correction term. The latent heat correction was also not included in this analysis as the correction term was on average much smaller than the latent heat correction term.

Table 1: Four different methods used to calculate fluxes.

<table>
<thead>
<tr>
<th>Label</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP-CDry</td>
<td><strong>Closed-Path corrected dry</strong> mixing ratio with no WPL corrections (final values)</td>
</tr>
<tr>
<td>OPW-d</td>
<td><strong>Open-Path</strong> Water vapour flux correction using density fluctuation measurements</td>
</tr>
<tr>
<td>CPW-d</td>
<td><strong>Closed-Path</strong> Water vapour flux correction using density fluctuation measurements</td>
</tr>
<tr>
<td>CPW-m</td>
<td><strong>Closed-Path</strong> Water vapour flux correction using mixing ratio measurements</td>
</tr>
</tbody>
</table>

The WPL corrected flux values for CO2 deviated less from CP-CDry than for the same corrections applied to CH4. Between the two gases, CO2 OPW-d ($R^2 = 0.98$) correlated much better than CH4 OPW-d ($R^2 = 0.81$) with CP-CDry in Figure 20a despite having the same corrections. This can be attributed to the much larger CO2 flux magnitudes compared to CH4 fluxes. However, there was a significant difference in correlation between OPW-d and CPW-d with CP-CDry, where visually in Figure 20 both CPW-d and CPW-m compared best with the final flux values CP-CDry. CPW-d and CPW-m fluxes were very close as both used a similar correction method only mainly differing in usage of mixing ratio versus conversion to density. The close agreement of the CPW-d and CPW-m corrections to CP-CDry gives a clear indication of the significance of the correction of the H2O effects applied to the mixing ratio.
The influence of the WPL terms in terms of each gas, and consequently the increased discrepancy for CH$_4$ fluxes using different correction methods compared to CO$_2$ fluxes can be explained by the WPL correction terms. Although WPL correction terms are scaled to the covariance of each gas which can be seen in Equations 11-14, the contribution of each WPL correction term is different. The correction terms were much larger relative to CH$_4$ fluxes than for CO$_2$ fluxes shown as percentages in Table 2. In the daytime, the latent heat term ($E$) was $\sim$40% of the CH$_4$ fluxes whereas was only $\sim$6.7% for CO$_2$. For the sensible heat term, the OP $H$ term was much larger at 16.5% of the CO$_2$ flux compared to the CP $H$ which was only 0.04%. Nighttime values of the $H$ term compared to daytime values were also significantly smaller which indicates a larger contribution of the correction in the daytime. With larger daytime sensible heat fluctuations in the free atmosphere, there is a potential for increased error in the $H$ term which could lead to an overestimation of the correction. The much smaller $H$ term using CP temperature measurements also validates the assumption that the correction term is negligible.
Table 2: Averaged values for each WPL correction term and their percentage of the average flux value of CH$_4$ and CO$_2$ separated by daytime and nighttime.

<table>
<thead>
<tr>
<th></th>
<th>CH$_4$ (nmol m$^{-2}$ s$^{-1}$)</th>
<th>% of CH$_4$ flux</th>
<th>CO$_2$ (µmol m$^{-2}$ s$^{-1}$)</th>
<th>% of CO$_2$ flux</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Daytime Averaged Values</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OP $H$</td>
<td></td>
<td></td>
<td>0.515</td>
<td>17</td>
</tr>
<tr>
<td>CP $H$</td>
<td>-0.00562</td>
<td>0.21</td>
<td>-0.00125</td>
<td>0.040</td>
</tr>
<tr>
<td>OP $E$ (density)</td>
<td>1.12</td>
<td>42</td>
<td>0.219</td>
<td>7.0</td>
</tr>
<tr>
<td>CP $E$ (density)</td>
<td>1.06</td>
<td>40</td>
<td>0.207</td>
<td>6.6</td>
</tr>
<tr>
<td>CP $E$ (mixing ratio)</td>
<td>1.04</td>
<td>39</td>
<td>0.204</td>
<td>6.5</td>
</tr>
<tr>
<td><strong>Nighttime Averaged Values</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OP $H$</td>
<td></td>
<td></td>
<td>-0.446</td>
<td>4.8</td>
</tr>
<tr>
<td>CP $H$</td>
<td>0.000126</td>
<td>0.0052</td>
<td>-0.00115</td>
<td>0.012</td>
</tr>
<tr>
<td>OP $E$ (density)</td>
<td>0.133</td>
<td>5.5</td>
<td>0.0260</td>
<td>0.28</td>
</tr>
<tr>
<td>CP $E$ (density)</td>
<td>0.0780</td>
<td>3.2</td>
<td>0.0156</td>
<td>0.17</td>
</tr>
<tr>
<td>CP $E$ (mixing ratio)</td>
<td>0.0742</td>
<td>3.1</td>
<td>0.0148</td>
<td>0.16</td>
</tr>
</tbody>
</table>

The influence of the correction methods on the diurnal trend of the fluxes was compared, because there was a diurnal trend in both sensible and latent heat fluxes on average increasing during the daytime. In Figure 21, the diurnal trend for all WPL correction types showed close agreement with CP-CDry. Slight variations in the diurnal trend are the be expected because of random spikes which may have arisen during the flux calculations or corrections.

![Figure 21: Averaged diurnal cycles of OP CO$_2$, CP CH$_4$ and CO$_2$ including different WPL correction methods over the entire measurement period.](image-url)
2.5 Flux Quality Assurance and Quality Control (QA/QC)

The accuracy of the flux data was ensured by putting the data through strict regime of QA/QC techniques used during the processing of the data shown in Figure 22.

![Diagram describing the QA/QC methods used on mixing ratio data and during flux processing with the respective percentage of data removed.](image)

Figure 22: Diagram describing the QA/QC methods used on mixing ratio data and during flux processing with the respective percentage of data removed.
During flux processing, the high frequency mixing ratio data was de-spiked removing any data above four standard deviations calculated from ±1500 measurement points and corrected for pressure broadening and dilution effects from the instrumental cross-sensitivity of H₂O. This correction discussed in Section 2.4.2 had a maximum effect of ~1.5% increase on the mixing ratio at the highest measured H₂O periods.

In post-processing of the fluxes, the data was checked for stationarity within the averaging period and was flagged if it was non-stationary. Co-spectral correction was applied to both CH₄ and CO₂ for the influence of high frequency noise from the instrument on the fluxes (Section 2.5.2). This correction resulted with a reduction in the flux value of ~21% and ~4% averaged over all half-hour periods for CH₄ and CO₂ fluxes respectively. Half-hourly flux data was then removed which were flagged from sonic anemometer errors and intervals which had more than 10% of the data missing. Flux data was then de-spiked with data above eight standard deviations calculated from ±200 flux data points. Furthermore, fluxes with a friction velocity of less than 0.2 m s⁻¹ (Section 2.5.1) and from a wind direction of 0° - 93° (Section 2.5.3) were also removed. These data quality control criteria were applied to the final flux values as well as the flux values in Sections 2.4.3 & 2.4.4, with a total of approximately 37% of the data removed.

Unlike previous studies that used similar techniques discussed in Section 1.2.2, this is one of the first to include dilution and pressure broadening corrections from H₂O cross-sensitivity in the OA-ICOS high frequency data for the field setting. This correction also allowed for the removal of WPL corrections for latent heat flux.

### 2.5.1 Nighttime Atmospheric Stability

The EC method assumes that the atmosphere is fully turbulent where turbulence is responsible for mass transport and development of the equilibrium sublayer. During more atmospherically stable periods, typically during nighttime, the equilibrium sublayer degrades making the measurements not representative of the surface fluxes from the ecosystem resulting in significant flux errors (Anderson and Farrar, 2001). To correct for this, the friction velocity ($u_*$) was used as an index of turbulent momentum fluxes and an indication of stable/unstable atmospheric conditions. When the coordinate system is rotated so that the $x$-axis is aligned with
the direction of surface stress, friction velocity can be defined by Equation 17 where $u'w'$ is the mean vertical flux of the horizontal momentum in the x-axis (Stull, 1988).

$$u_*^2 = \left| u'w' \right|$$  \hspace{1cm} (17)

Fluxes relating to vegetation and soil respiration should be independent of $u_*$, thus any dependence of the fluxes on $u_*$ should be considered an artifact of the method (Aubinet et al., 2012). In this analysis, the same logic is applied to CH$_4$ fluxes, however if there are non-biological controls on the fluxes it may not be completely accurate to make this assumption. In Figure 18, the magnitude of the CH$_4$ fluxes was consistently lower below a $u_*$ of 0.2 m s$^{-1}$. Although this occurred in the daytime as well, there were far less data points in this region of $u_*$ compared to the nighttime, which had less influence on the fluxes.

![Figure 23: Plot of absolute daytime and nighttime CH$_4$ flux values against friction velocity.](image)

This trend was more clear in CO$_2$ fluxes shown in Figure 24, where flux values below a $u_*$ of 0.2 m s$^{-1}$ were overall low flux values at nighttime compared to daytime. This nighttime bias in lower flux values due to flux errors could result in a significant underestimation of emissions at night which can cause a systematic bias, thus potentially giving a significant overestimation in the NEE and budget for a given ecosystem. Both CH$_4$ and CO$_2$ values below a $u_*$ of 0.2 m s$^{-1}$ were completely removed.
Flow distortions can occur from wind blowing through the scaffolding of a lattice tower or even from the sonic anemometer itself. It has been shown that the CSAT3 sonic anemometer had wind speed reductions of 16% for incident wind directions coming directly from behind the anemometer (Friebel et al., 2009), which in our system corresponds to compass directions of 15° - 55°. In combination with the flow distortions from the sonic anemometer, the tower also acted to distort wind flow occurring in the same range of wind directions. These distortions were plotted in Figure 25 with $\sigma_\theta/u_*$ plotted against wind direction, where $\sigma_\theta$ is the standard deviation of wind velocity for each respective axis ($x, y, z$). In the case of no flow distortions, $\sigma_\theta/u_*$ should remain relatively constant from all wind directions. The flow distortion from the posts of the tower are clearly seen in these wind plots which occurred at 10° and 85°. Although there are different techniques to correct for flow distortions, typically the corrections require modeling of the tower and assumptions to be made. For this analysis the data within the range in incident wind direction of 0° - 93° were completely removed from the data processing and flux calculations. This resulted in the largest removal of data during filtering and QA/QC of the data, representing 22.7% of the total data for both CH4 and CO2. As all data from the northwest was removed, care was taken in the interpretation of the data and trends using wind direction.
2.5.3  High Frequency Noise Influence on Cospectra

When an instrument measures at a high frequency, high frequency noise can occur typically as a result of high pumping speed resulting in pressure fluctuations in the measurement cell. This is especially important when the signal-to-noise ratio is low, in the case of CH$_4$ measurements even compared to CO$_2$ made by the same instrument, this can affect the high frequency end of the cospectrum. Fluxes are typically less influenced than mixing ratios by random noise as it should not correlate well with vertical wind variations (Smeets et al., 2009). Instrumental noise can still modify the high frequency region of the cospectrum if the noise level is high enough. To correct for this, the frequency at which noise begins to influence the cospectra must first be determined by averaging multiple ideal half hour intervals.

For the FGGA, noise was observed to have an influence on the cospectra of the measurements. The frequency normalized cospectra in Figure 26 show the contribution of the flux in the raw cospectra compared to the cospectra of sonic temperature ($wT_s$). It assumes that the cospectra of all scalars (ie. temperature, gases) with vertical wind will have the same shape. Compared to the cospectra of temperature, it is obvious that the cospectra of CO$_2$ and CH$_4$ increase in the higher frequencies. Averaged frequency normalized cospectra of 74 daytime intervals in Figure 27 and of 80 nighttime intervals in Figure 28 were used to determine the
frequency above which noise began to influence the cospectra. The smoothed frequency normalized cospectra were bin averaged and the absolute values were used where the flux cospectra were selected from flux periods with similar atmospheric instability ($z/L_{\text{day}} = -0.074 \& z/L_{\text{night}} = +0.18$) and wind speed ($\bar{u}_{\text{day}} = 2.7 \pm 0.5 \& \bar{u}_{\text{night}} = 2.3 \pm 0.5 \text{ m s}^{-1}$).

As seen in the bin averaged cospectra of CH$_4$ and CO$_2$, values started to deviate away from the cospectra of sonic temperature at a positive slope which indicated a contribution of noise to the flux signal. An estimate was determined with a frequency cut-off for CH$_4$ at 0.2 Hz (green dashed line) and for CO$_2$ at 0.5 Hz (red dashed line) shown in Figure 27. Although the frequency at which noise significantly contributes to the cospectra is expected to change for each half-hour interval of data depending on atmospheric stability and wind speed, the estimate was taken from an average of multiple cospectra throughout the measurement period and should be representative of a proper frequency cut-off.

Figure 26: Averaged unsmoothed normalized cospectra of CP CO$_2$ and CH$_4$ and smoothed cospectra of sonic temperature plotted as a function of natural frequency from 74 daytime half-hour runs with an average stability and wind speed range of $z/L = +0.18$ and $\bar{u} = 2.3 \pm 0.5 \text{ m s}^{-1}$.
Figure 27: Averaged smoothed normalized cospectra from 74 daytime ensembles of sonic temperature, OP CO$_2$, and CP CO$_2$ and CH$_4$ plotted as a function of natural frequency with an average stability and wind speed range of $z/L = -0.074$ and $\bar{u} = 2.7 \pm 0.5 \text{ m s}^{-1}$.

Figure 28: Averaged smoothed normalized cospectra from 80 nighttime ensembles of sonic temperature, OP CO$_2$, and CP CO$_2$ and CH$_4$ plotted as a function of natural frequency with an average stability and wind speed range of $z/L = +0.18$ and $\bar{u} = 2.3 \pm 0.5 \text{ m s}^{-1}$.
Assuming cospectral similarity of the scalars, the percent relative contribution to the fluxes within the same frequency range of other scalars such as sonic temperature and OP CO₂ was used as a reference and applied to the cospectrum of the CP CH₄ and CO₂ on a half-hour basis. Described in Equation 18, the correction used the ratio of the area above the cutoff frequency \( \overline{w'T'}_A \) to the area below the cutoff \( \overline{w'T'}_B \) of the raw cospectrum of sonic temperature (or OP CO₂) to vertical wind, and applied this ratio to the area below the cospectrum of the gas species \( \overline{w'c'}_A \) for each half hour. If the area of the cospectrum above the frequency cut-off, considered to be noise, was equal or higher than the flux contribution below the cut-off, then the half-hour flux was flagged and considered to be inaccurate. These data points were flagged but not removed because the magnitudes were relatively smaller than the average fluxes so removal of the data would bias towards larger flux magnitudes.

\[
\overline{w'c'}_{tot} = \left( \overline{w'c'}_A \right) \left( 1 + \frac{\overline{w'T'}_B}{\overline{w'T'}_A} \right)
\]  

(18)

Given the noise of the FGGA, a limit of detection was determined for the flux values based on the influence on instrumental noise on the calculated fluxes. In theory, if a constant mixing ratio is measured for 30 minutes at 10 Hz, the combination of this data with any arbitrary 30 minutes of vertical wind data from the sonic anemometer should result in a flux of zero. Data were obtained from a calibration run using the calibration gas mixed with zero-air on the instrument over 30 minutes at high frequency and processed with vertical wind data from the entire measurement period to determine the limit of detection of the fluxes. Two standard deviations of these flux values is representative of the uncertainty in the calculated flux shown in Figure 30 and was used to determine the limit of detection for CH₄ and CO₂ fluxes of \( ±5.3 \text{ nmol m}^{-2} \text{s}^{-1} \) and \( ±0.94 \text{ µmol m}^{-2} \text{s}^{-1} \) respectively. This is a conservative estimate of the limit of detection because it considers the covariance of noise within the entire cospectrum. These values compared well to the covariance values of the high frequency region determined to be dominated by noise shown as histograms in Figure 29 with a range of noise dominated flux values at approximately \( ~4.5 \text{ nmol m}^{-2} \text{s}^{-1} \) and \( ~0.8 \text{ µmol m}^{-2} \text{s}^{-1} \) for CH₄ and CO₂ respectively. Any values within this range were considered indistinguishable from zero, although were still used during the interpretation of data. There was also no observable diurnal trend in the covariance of the noise cospectrum with vertical wind.
Figure 29: Histogram of the covariance above the frequency cutoff of 0.2 Hz and 0.5 Hz for each gas respectively of CH₄ (a) and CO₂ (b) calculated from a constant mixing ratio from the calibration gas (blue) and naturally varying mixing ratio during the measurement period (red) from each half-hour period.

Figure 30: Histogram of the covariance the entire cospectrum (green) and the covariance above the frequency cutoff of 0.2 Hz and 0.5 Hz (blue) for each gas respectively of CH₄ (a) and CO₂ (b) calculated from a constant mixing ratio from the calibration gas from each half-hour period.
3 Results and Discussion

3.1 Measurement Period

Measurements were made continuously from June 2 until October 24, 2011, with the exception for a period of 5 days from July 5 – 11 when the FGGA was down due to technical problems with the onboard computer in the instrument. The average mixing ratios were 1.92 ppm for CH$_4$ and 391 ppm for CO$_2$ over the entire measurement period. Figure 31 shows the mixing ratios, averaged in 30 minute intervals from the high frequency measurements. There were significant changes in CH$_4$ during the measurement period, with a maximum of 2.08 ppm and a minimum of 1.86 ppm. Changes in wind direction between areas of sinks or sources could cause variations in CH$_4$ mixing ratio. Unlike CO$_2$ which is photosynthesized and respired by vegetation covering large areas with large flux magnitudes, CH$_4$ has relatively much smaller sources and sinks in the area where the measurements were made.

Figure 31: Dry air mixing ratios of CP CO$_2$ (red) and CH$_4$ (green) over the measurement period.

There was a diurnal trend in both CH$_4$ and CO$_2$ averaged over the measurement period shown in Figure 32. Both followed a similar diurnal trend with a minimum in the mid-afternoon at 15:00 and a gradual increase starting at 18:00 which peaked at 6:00 in the early morning. The shape of the diurnal trend for both gases can be partially explained by the accumulation of the surface emissions which collect within the shallow stable boundary layer at nighttime, with the nocturnal layer breaking up as the surface beings heating up diluting the accumulated CH$_4$ and CO$_2$ during the daytime (Culf et al., 1997). For CO$_2$, another important factor is the daytime drawdown as a result of photosynthesis.
Figure 32: Diurnal plot of CP CO₂ and CH₄ mixing ratios during the measurement period.

The diurnal trend for each gas was also separated by month in Figure 33. For CH₄, from June to October, the monthly average difference between the nighttime maximum and mid-day minimum in the mixing ratios was 0.018 ppm, 0.036 ppm, 0.027 ppm, 0.022 ppm, 0.011 ppm respectively. The highest difference was in July and the smallest in October, with a similar trend observed in the CO₂ mixing ratios. Querino et al. observed a similar trend in CH₄ mixing ratio which was attributed to the accumulation of local emissions in the shallow nighttime boundary layer followed by the dilution of the accumulated CH₄ in the daytime as the nocturnal layer broke up (Querino et al., 2011).

Figure 33: Diurnal plot separated by month of CP CH₄ (left) and CO₂ (right) with the average of the entire measurement period (black).
The decrease in diurnal variability of the mixing ratio through the season could be due to a lower daytime boundary height affected by lower surface temperatures in the fall compared to mid-summer. The boundary layer height was not measured during this study, thus the effects of the boundary layer height on fluxes could not be accurately determined. However, the diurnal trend in Figure 34 in the atmospheric stability parameter \( z/L \) separated by month showed that there was little change in the time of break-up in the stable nighttime boundary layer through the season. There also was not a major decrease in average temperatures until mid-October. With an average daytime minimum of 1.916 ppm and a nighttime peak of 1.935 ppm for CH\(_4\), the amplitude of the diurnal cycle was approximately 20 ppb. This corresponds to an increase of \(~1.7 \text{ ppb h}^{-1}\) between sunset and sunrise. If this change is the result of a local surface flux, then there should be a nighttime emission of approximately 2.0 nmol m\(^{-2}\) s\(^{-1}\), assuming an arbitrary stable nighttime boundary layer height of \(~100 \text{ m}\). As will be discussed in Section 3.2.1, this is not consistent with the fluxes measured in the footprint of the tower.

Wind direction bringing in air from major CH\(_4\) sources may have also contributed to the variation of CH\(_4\) mixing ratios. In Figure 35, the average mixing ratio in terms of wind direction showed higher mixing ratios with incident wind directions from the south and southwest compared to the other directions. The slope in the change of mixing ratio from 00:00 to 04:00 was also compared with wind direction, with a higher increase in mixing ratio from wind directions also coming from the southwest. With no obvious major sources in the flux footprint
of the tower, larger sources such as Toronto from the southwest could have been a major contributor of CH$_4$ transported into the area. This shows a much larger area of influence on mixing ratio than the expected flux footprint of the tower.

Figure 35: Wind rose plot of bin averaged CH$_4$ mixing ratio (a) and change in CH$_4$ from 00:00 to 04:00 (grey) from the measurement period.

Until the beginning of June, the road conditions were too wet to access the site. This indicated consistent wetness of the soil since the spring thaw. Although the soil was still observed to be wet through June, by July the soil had become drier on average and continued to dry as the season progressed. This was observed in the soil water content measurements made at the soil station near the tower. Unfortunately, the soil station was not continuously in operation through the measurement period, but only during the periods of June 13 – July 4, July 18 – 22, August 21 – Sept 5, and Sept 13 – 21. Correlations made with soil station data were limited to these periods and this effect was taken into consideration when interpreting the data.

In Figure 36, the soil water content can be seen to decrease through the season, averaging much higher in June than in August or September even after rain evens had occurred. The soil temperature remained relatively constant during the periods of soil measurements, even during a cold snap lasting over 4 days in mid-September where ambient temperatures dropped to -9.0 °C, but soil temperatures at 3 cm remained above 7.0 °C. Tower sensors were operational throughout the measurement period. Photosynthetic active radiation remained high until mid-October when levels above the canopy dropped below 500 µE on average.
3.2 Greenhouse Gas Fluxes

Before QA/QC of the flux data, 91% of the measured data was retained. Data was removed during the flux QA/QC, discussed in Chapter 2.5; with 40% of CH4 and 36% of CO2 flux data removed with the final flux values shown in Figure 37 with excluded data in grey. The longer periods of removed data were due to consistent wind ranging from the north to east removed during QA/QC due to flow distortion. Over the measurement period, the average flux values with the standard deviation of the mean were -2.7±0.13 nmol m⁻² s⁻¹ for CH4 and 0.92±0.18 µmol m⁻² s⁻¹ for CO2. The forest was on average a CH4 sink and a slight CO2 source, although this was only during the measurement period and would be inaccurate to upscale these values to an annual flux value due to the large seasonal variability in environmental variables at the tower site. The measurement period excluded the beginning of the growing period before June and the rest of the fall after the end of October before snowfall which could introduce a bias in the average CO2 flux value give the seasonal variability of photosynthetic activity and respiration. In Figure 37, the seasonal variability of CO2 is much clearer than for CH4.
There was a diurnal trend observed in both CH$_4$ and CO$_2$ fluxes in Figure 38. The magnitude of the diurnal cycle for CO$_2$ was much larger than CH$_4$, which had a clear daytime peak in uptake of -10.4 µmol m$^{-2}$ s$^{-1}$ and a mean nighttime emission flux of 9.8 µmol m$^{-2}$ s$^{-1}$. On average, CH$_4$ fluxes were uptake throughout the day, although the magnitude of uptake between 04:00 – 08:00 was less and there were increased uptake fluxes mid-day between 10:00 – 16:00. The minimum in uptake fluxes in the morning could have been due to a reduction in overall uptake during this period and/or increased local emissions. There have been no clear explanations for a diurnal trend in CH$_4$ fluxes, however Querino et al. observed a similar morning peak in their 6 month measurement campaign in a tropical forest (Querino et al., 2011), although on average the forest was a net emitter of CH$_4$. Monthly mean values of CH$_4$ fluxes showed a seasonal evolution; June had a mean flux of -1.1 nmol m$^{-2}$ s$^{-1}$ progressing to a seasonal maximum of -4.0 nmol m$^{-2}$ s$^{-1}$ in September. In October however, the mean flux value dropped to -3.0 nmol m$^{-2}$ s$^{-1}$.
Figure 38: Averaged diurnal cycles of CP CH$_4$ (green) and CO$_2$ (red) over the measurement period, with three times the average limit of detection due to noise (grey).

Figure 39: Monthly average of CH$_4$ and CO$_2$ flux values.

The monthly means of the fluxes were also compared to other environmental variables in Figure 40, where CH$_4$ fluxes showed similar trends to ambient temperature and PAR. Although most likely not directly linked to these variables, PAR and ambient temperature could indicate soil conditions where warmer periods with more sun could indicate drier periods in the soil and vice versa for periods with less sun. The amount of rain for each month matched less in the trend with mean flux values, although higher periods of rainfall in June and October could have caused wetter soils leading to more emissions from methanogens or inhibition of methanotrophic activity due to diffusion limitation and increased anaerobic soil conditions.
3.2.1 Diurnal Trend in CH₄ Fluxes

There was an observed diurnal cycle in CH₄ fluxes over the measurement period, with a decreased magnitude in uptake flux during the morning 05:00 – 07:00 at -0.7 nmol m⁻² s⁻¹ and an increase in uptake during the mid-day between 10:00 – 16:00 with the highest uptake at -4.1 nmol m⁻² s⁻¹. Other studies also observed diurnal trends; for example, Fan et al. observed a diurnal trend of increased CH₄ emissions in the afternoon from an Alaskan subarctic tundra and Edwards et al. observed a similar trend in the Canadian northern wetlands where the increased emissions were attributed to variations in wind direction, the effective footprint of the tower, wind speed which may have induced emissions from lakes and ponds, changes in diurnal temperature in shallow sediments, and disturbance of the surface layer by pressure fluctuations due to turbulence or rain (Fan et al., 1992; Edwards et al., 1994). In a different ecosystem, Hatala et al. also found increased emissions in the afternoon of a Californian rice paddy which was attributed to the increase of gross ecosystem photosynthesis which indicated ecosystem activity on CH₄ fluxes (Hatala et al., 2012). In the forest ecosystem, Querino et al. observed increased CH₄ emissions in the early morning from 07:00 – 10:00 in a Brazilian tropical forest. In contrast, Ueyama et al. observed increased uptake in the afternoon in a Japanese larch forest using relaxed eddy covariance where the uptake was attributed to biological activities such as increased microbial oxidation in the soil during the daytime as these diurnal variations were only observed during the summer during high ecosystem activity (Ueyama et al., 2012). Smeets et al. also observed increased uptake during the daytime in a Californian pine plantation, although fluxes did not correlate with sub-surface temperature or humidity mainly due to constant dry conditions.
(Smeets et al., 2009). Other studies found no diurnal trend in CH$_4$ flux, such as a study conducted by Rinne et al. in a boreal fen in Finland (Rinne et al., 2007) and by Tagesson et al. in the high-arctic wet tundra ecosystem (Tagesson et al., 2012).

The seasonal variation in the diurnal trend in Figure 41 shows the diurnal trends averaged for each month. For CH$_4$ fluxes, the diurnal shape was less apparent, although the morning peak occurred in all the months and the mid-day uptake maximum occurred in July – October. The increased diurnal variability for CH$_4$ fluxes in October shows that the break-up of the nocturnal boundary layer had little effect on the diurnal trend of the fluxes.

![Figure 41: Averaged diurnal cycles for each month of the measurement period of CH$_4$, OP and CP CO$_2$.](image)

It is important to determine some contributing environmental factors to CH$_4$ emissions and uptake in the ecosystem, as minor changes could have major effects on CH$_4$ fluxes. An ecosystem that is predominantly a CH$_4$ sink could be converted into a source or vice versa depending on environmental changes influenced both directly and indirectly by anthropogenic activities. From the observations, it was difficult to discern the influence of each environmental factor on the CH$_4$ fluxes as most variables followed similar diurnal trends, thus correlations were
also made with the flux values. Given the variability of the CH4 fluxes on a half-hour basis, the values were shown in a scatter plot and bin-averaged to give a mean value for a general correlation to the environmental variables. In Figure 42 and Figure 43, the diurnal trend was calculated from periods when the soil station was in operation which was slightly different, but showed a similar trend in both shape and magnitude.

![Figure 42: Diurnal plot (a) and bin-averaged scatter plot (b) of soil temperature at 0, 3, and 10 cm depth compared with CH4 flux.](image)

For soil temperature in Figure 42, temperatures measured at a depth of 3 cm or lower showed very little diurnal variability. However at the surface level, there was a diurnal trend with a minimum at 07:00 of 13.4 °C and a maximum at 15:00 of 15.3 °C which matched well with the diurnal trend of CH4 fluxes. The influence of temperature variations on CH4 fluxes at the soil level would greatly depend on the depth of microbial population. Unfortunately there was no measure of how deep the microbial population was in the soil, but given a potential influence of soil temperature to microbial activity, the methanotrophs should be near the surface. Previous studies have shown microbial populations of methanotrophs near the surface at 3 – 15 cm in depth (Curry, 2007) and is expected to be closer to the surface in this forest given the shallower
soils exhibited in Central Ontario. The diurnal trend in soil temperature above 3 cm showed an inverse trend to CH₄, where an increase in surface soil temperatures resulted in a decrease in CH₄ uptake flux. The relationship between the individual flux values and the soil surface temperature showed a reasonable correlation (R=0.183), with an increase in soil temperature from 11.0 to 23.0 °C resulting in a decrease in average CH₄ uptake from -5.6 to -0.3 nmol m⁻² s⁻¹. However, it is not expected that a small range of moderate temperatures would have such a large effect on microbial activity given the large optimal temperature range for microbes. (Friebel et al., 2009). The relationship seen in the bottom panel of Figure 42 may be the result of each variable having a casual relationship with another factor that has a strong diurnal cycle.

Figure 43: Diurnal plot (a) and bin-averaged scatter plot (b) of soil water content compared with CH₄ flux.

The relationship between SWC to the CH₄ followed previous descriptions of diffusion limitation effects on CH₄ uptake (Reay et al., 2007). With an increase of water in soil, there is a decrease in diffusion through the soil affecting uptake and ultimately with higher SWC, the conversion of the soil from net uptake to net emission of CH₄ is possible if conditions can support methanogens. Given the small diurnal variability in SWC, it is unlikely to be cause of the diurnal trend in CH₄ fluxes although SWC could have a major influence on the seasonal
variation of the fluxes. In Figure 43 at drier soil conditions of 0.16 m$^3$/m$^3$, the averaged flux value was at -6.0 nmol m$^{-2}$ s$^{-1}$, however as SWC increased to 0.21 m$^3$/m$^3$ the uptake flux decreased to near zero with wetter soil conditions which resulted as decreased uptake. Most of the diurnal variations in SWC occur within a small area in the intensive root zone, with SWC decreases observed in the daytime and increases during the nighttime (Werban et al., 2008). The soil station sensor data was probably not strongly affected by the rootzone and therefore our measurements may underestimate the role of SWC in governing the diurnal cycle in methane uptake, especially if microbial activity is predominantly in the root-dominated area.

Figure 44: Diurnal plot (a) and bin-averaged scatter plot (b,c) of wind speed above and in canopy compared with CH$_4$ flux.

The diurnal trend of wind speed both within and above the canopy matched well with the trend in CH$_4$ fluxes shown in Figure 44. The maximum in wind speed occurred at the same time
as the peak in uptake of CH$_4$. Previous studies have shown that advection forced by pressure pumping caused by short-period atmospheric turbulence increased gaseous flux through snowpack (Massman et al., 1995) and landfill soils (McBain et al., 2005) in which the effect was increased when the gas gradients were weak (Massman et al., 1997). Typically these observations showed increased emissions in CO$_2$ and CH$_4$ due to a “pressure pumping effect” which resulted in ebullition or release of CH$_4$ from the surface. In our study however, wind speed correlated well with CH$_4$ uptake where with an increase in wind speed from 0.0 to 3.8 m s$^{-1}$ above the canopy or 0.0 to 1.0 m s$^{-1}$ within the canopy, there was an increase in CH$_4$ flux from 1 to -4.0 nmol m$^{-2}$ s$^{-1}$.

The coarse soils and increased microbial uptake may have allowed for increased aeration to facilitate transport of CH$_4$ and O$_2$-rich air from the atmosphere to the methanotrophs and/or CH$_4$-depleted air out of the soil into the atmosphere. In 2000, Yonemura et al. observed that wind-induced acceleration of gas transport in topsoil could have played a role in gas uptake, where lower levels of uptake were observed during lower wind speed conditions. Although increased uptake due to wind transport has not been widely observed in previous studies, if true, this could prove important as most static chamber measurements have been conducted in enclosed containers which could block transport facilitation from wind. This could lead to an underestimation the flux from the soil into the atmosphere. A diurnal dependence on fluxes could also introduce an error in upscaling fluxes to an ecosystem annual.

### 3.2.2 Trends in CH$_4$ fluxes with Wind Direction

In addition to environmental and ecosystem variables that may have affected CH$_4$ fluxes in seasonal trends, the influence of incident wind direction on CH$_4$ fluxes was also investigated. Wind direction did not show any consistent diurnal trend, thus could not have contributed significantly towards the diurnal trend in CH$_4$ fluxes. The measurements were made on a tower which in the immediate area was surrounded by a non-homogenous forest ecosystem. A flux footprint analysis has not been carried out for the site; however it can be estimated that fluxes measured from the tower are influenced by the ecosystem within a 1 km radius or less. Drier areas of forest soils may have acted as net sinks, whereas small wetlands, marshes and lake areas could have been net sources. These areas could have affected the fluxes which were measured
within the footprint of the tower shown in Figure 45 at ~1000 m. There was a small wetland to the southwest and a small lake to the east which drained into Dutton Lake to the southeast. To the north of the tower, the lower elevation areas were a marsh, relatively wetter than the forested areas around the tower. The tower itself was on a higher elevation area compared to the regional area averaging at approximately 500 m.

![Topographic map of the tower site area](image)

**Figure 45:** Topographic map of the tower site area, with the white circle representing a 1 km radius around the tower.

Wind rose plots describing averaged fluxes in terms of wind direction is shown in Figures 46 – 49, with CH₄ uptake (coloured) and emission (grey) fluxes averaged in 15° bins of wind direction where the size of each marker indicates the number of data points within each bin with the axes in flux units of nmol m⁻² s⁻¹. A separate wind rose plot was made indicating predominant wind direction where wind speed was binned from 1 to 5+ m s⁻¹. All fluxes from north to east (0° – 93°) were removed in the flux analysis and thus were ignored in the interpretation of the data. In the averaged data over the entire measurement period in Figure 46, wind came predominantly from the west and north, and showed averaged overall uptake fluxes from all incident wind directions. Fluxes from the westerly direction showed much higher uptake fluxes than from the northwest and southeast. The west of the tower contained primarily forested areas, and from
Figure 45, was at relatively higher elevation compared to the tower which could have provided good conditions for methanotrophic activity in soils. Archer’s Marsh was on the edge of the estimate flux footprint of the tower and emissions from this part of the ecosystem may have been excluded from the flux measurements, although fluxes from this direction on average were much lower in uptake, on average near zero fluxes which showed potential influence of emission in the integration of the ecosystem flux.

![Wind rose plot of average CH$_4$ uptake (coloured) and emission (grey) fluxes (right) and binned wind speed (left) over the entire measurement period.](image)

Unlike most of the other months, in June, the wind came predominantly from the north with low magnitude net emission fluxes shown in Figure 47. Fluxes from other wind directions showed net uptake fluxes with fluxes of lower magnitude than the other months. The highest uptake fluxes came from the southwesterly direction (135° - 165°) which was in the direction of the small lake and Dutton Lake. Only the edges of Dutton Lake were in the 1 km flux footprint of the tower which could have decreased the contribution Dutton Lake had on the fluxes. Lakes have been shown to be net sources (Bastviken et al., 2004) although highly dependent on the water conditions in the lake which can also contain methanotrophs which consume the bulk of the CH$_4$ produced in lakes before reaching the atmosphere (Schubert et al., 2012), as well as the surrounding areas around lakes which could play an additional role in CH$_4$ soil uptake (Tomoaki and Ryusuke, 1999). With relatively drier soils in July compared to June, on average there was net uptake from the west and smaller net emission fluxes from the north. In Figure 47, the
emission fluxes from 235° and 330° – 360° indicated potential influence from the known emission sources of Archer’s Marsh to the north and the small wetlands to the southwest similar to the average flux values from June.

Figure 47: Wind rose plot of average CH₄ uptake (coloured) and emission (grey) fluxes (right) and binned wind speed (left) in June and July.

In August, wind was predominantly from the west and southwest directions shown in Figure 48 with net uptake fluxes of higher magnitude than the previous months. The wind direction dependence of the fluxes in August was similar to July, though the uptake was more significant. For September, the wind direction predominantly came from the north, east, and
southeast which was different from the other months shown in Figure 48. The fluxes were on average higher in magnitude than the previous months. Like the other months, uptake values were lower from the north and southwest from potential sources in the ecosystem. Uptake from the west was also higher with the exclusion of wind from 235° which is the direction of the local small wetlands.

Figure 48: Wind rose plot of average CH₄ uptake (coloured) and emission (grey) fluxes (right) and binned wind speed (left) in August and September.

In October, the wind was predominantly from the west and northeast with overall net uptake from all wind directions shown in Figure 48. Although the flux magnitudes for October
were smaller than September, the flux trends were very similar with lower uptake values from the north, southeast, and at 235° which have all been indicated as directions that contain sources. This indicates that in terms of local sources and sinks; wind direction could play a role in influencing trends in fluxes. The monthly variation of CH₄ fluxes could also be seen in monthly rose plot with increasing magnitude of the fluxes on average, although the monthly variation in flux magnitude affected fluxes from all wind directions.

Figure 49: Wind rose plot of average CH₄ uptake (coloured) and emission (grey) fluxes (right) and binned wind speed (left) in October.

Figure 50: Wind rose of uptake (coloured) and emission (grey) fluxes of CH₄ averaged over the entire measurement period for daytime and nighttime.
Although wind direction showed little consistent diurnal trend, the wind rose plots in Figure 50 averaged by daytime and nighttime through the measurement period showed higher overall uptake values during the daytime, and slightly lower uptake fluxes and some emissions from the southeast in the nighttime.

3.2.3 Comparison of EC and Chamber Study Flux Values

The soil chamber study was conducted alongside the tower measurements which allowed for comparison of flux values between the two measurement techniques. This helps to validate the two methods as well as infer any significant emissions from above ground vegetation which would be indicated by significant discrepancies in terms of calculated fluxes at the tower compared to from the chamber study. In Figure 51, average soil chamber and tower fluxes were calculated for each month of the days when soil chamber measurements were made. The average flux from the soil chambers was calculated from all the toposequences despite very high emission fluxes measured from the low slope chambers. The averaged flux values could not be scaled for the toposequences as the percent contribution of each toposequence could not be readily determined. For August to October, the flux values from the tower were on average higher than chamber measurements.

Figure 51: Bar graph of averaged soil chamber and tower measurement fluxes averaged for each month (left).
However, the flux values for both tower and soil chamber measurements were within the same order of magnitude. Despite sampling from the chambers during the day, the lack of ventilation could have reduced the amount of possible aeration within the chamber underestimating the fluxes measured. Unless there was a serious overestimation of daytime fluxes from the tower measurements, this indicates the potential for a least a 50% underestimation of fluxes from this specific chamber method during the daytime specific to this ecosystem and soil type.

Previous studies have shown known problems with static chamber measurements that have to do with the disturbance of the soil diffusion gradient, which can cause an underestimation of fluxes by 15% in most cases. However the errors can be increased greatly by large pressure differentials from windy conditions and the accuracy of measurements under these conditions need more research. Under-pressurization or over-pressurization of the chamber which are caused by flow restrictions of a lack of or improper design of a vent system in the chamber could lead to significant errors which can be avoided by limiting flow restrictions (Davidson et al., 2002). Additionally, it has been shown that an improper design of the venting system could potentially lead to larger errors than it overcomes (Conen and Smith, 1998). Given the discrepancy in the net uptake flux values shown in this study in the comparison between the tower and soil chamber measurements, and the inherent errors introduced when using a chamber to measure soil fluxes in these types of ecosystems, an underestimation of fluxes could be introduced if data from chamber studies are used in models to upscale from local to ecosystem scale. As soil chambers have been more commonly used in the past, typically datasets from these types of studies have been used to parameterize global models. With recent advances in technology, satellite, aircraft, and ground measurements could be used to verify and compliment chamber measurements to increase the accuracy of global models.

In terms of a significant above ground source, it was difficult to interpret the fluxes due to the potential errors from the chamber flux measurements; however the increased uptake fluxes measured by the FGGA compared to the chamber indicated a lack of significant source contribution above the ground level. Although this is not indicative of all ecosystems, in terms of the temperature forest in Central Ontario, there is little evidence to support significant above ground vegetation sources of CH$_4$ from this study.
3.2.4 Comparison of EC and Canister Study Flux Values

The intensive canister study results matched the FGGA measurements very well. The mixing ratio above the tower averaged over the two hour sampling period from the canister was 1.9199 ppm which was very close to the FGGA measurement averaged over the sample period of time which was 1.9204 ppm. This indicates not only good precision of the FGGA measurements, but also of the correction of the H₂O effects on the instrument as the GC/FID was calibrated and reported using dry air mixing ratio with no H₂O effects. Over the two day period, the average flux calculated from the FGGA was net uptake at -4.6 nmol m⁻² s⁻¹. Measurements made at the three levels gave a vertical profile of CH₄ mixing ratios which were indicative of uptake in Figure 52, with lower CH₄ mixing ratios at the near ground level and higher mixing ratios in the mid- and above canopy levels. The averaged values for sampling periods where measurements at all three levels were successfully made at each level during the two days from near ground to above canopy were 1.871 ppm, 1.902 ppm, and 1.918 ppm. This observed difference in mixing ratio was 16 ppb between above and mid-canopy, 31 ppb between mid-canopy and near ground level, and a 47 ppb difference between near ground and above canopy averaged over the two days.

Figure 52: Vertical gradient of CH₄ mixing ratios at the three different levels.
In Figure 53, the time series of the mixing ratios showed similar values to measurements made by the FGGA. Surprisingly, the canister samples showed decreases around 17:00, similar to the diurnal trend of the increased uptake from the fluxes, although this was not clearly observed from the averaged FGGA measurements. The 12 hour integration sampling period from 18:00 – 06:00 may have been too long to properly represent the mixing ratio within this time, although the long integration sample made on the last day on August 24 showed very close agreement with the different measurement methods. Some data points are missing due to voided samples during the intensive study mainly due to sampler malfunction which occurred more frequently on the first day of sampling.

Figure 53: Time series of the CH₄ mixing ratios from intensive canister study.
4 Conclusions and Future Directions

The five month measurement campaign showed net CH$_4$ uptake with an average flux value of $-2.7\pm0.13$ nmol m$^{-2}$ s$^{-1}$. Care was taken in QA/QC of the measurements and fluxes which included corrections to H$_2$O effects on the FGGA, corrections made to the fluxes in terms of sonic anemometer tilt, nighttime atmospheric stability effects on fluxes, flow distortions from the tower, and high frequency instrumental noise influences on the cospectra. Methane fluxes showed a diurnal pattern with lower uptake flux magnitudes between 04:00 – 08:00 and increased uptake fluxes mid-day between 10:00 – 16:00. Although diurnal trends in terms of increased daytime emissions have been observed in previous studies, diurnal increases uptake has been less common.

This diurnal trend matched with diurnal variations of surface soil temperature and wind speed. Using bin averaged values of the fluxes, we observed a relationship with both soil temperature and wind speed. Soil temperature could have influenced microbial activity and the rate of diffusion of CH$_4$ into the soil, although this has been previously shown to have a minor influence compared to soil water content. Soil water content (SWC) also correlated well with CH$_4$ fluxes, although SWC had little diurnal variation and was more important on a timescale of weeks-months. With an increase in SWC from 0.14 to 0.24 m$^3$/m$^3$, there was a decrease in CH$_4$ uptake. This indicates a diffusion limitation on SWC within the soil and may also indicate activity by methanogens in wet conditions. With increased wind speed measured above or within the canopy, CH$_4$ uptake increased. This indicates the possibility of transport facilitation of CH$_4$ and O$_2$-rich air into the soil and/or CH$_4$-depleted air out of the soil into the atmosphere at high wind speed periods increasing the uptake rate of the soil. If true, this could lead to potential error in chamber flux measurements without proper vents installed in the chamber underestimating the measured daytime fluxes from the soil. Due to the limited dataset and intermittent soil station sensor data, it was difficult to separate environmental variables and their influences on CH$_4$ fluxes, especially with multiple environmental variables exhibiting similar diurnal trends.

Fluxes from the tower EC method compared to the chamber study showed higher uptake fluxes in the later months of the season in August – September which may have been affected by this limitation of wind facilitated transport within the soil. Comparing the chamber flux measurements with the EC tower flux measurements also indicated no significant above ground
contribution of CH$_4$ within this ecosystem. The mixing ratio measurements made by the FGGA also compared well with the canister study over the two day intensive sampling period in August. The three level vertical gradient measured from the canister samples also compared well with the measured fluxes during the two day period showing an average uptake flux of -4.6 nmol m$^{-2}$ s$^{-1}$. During this period, there was an observed increasing gradient of CH$_4$ with the lowest mixing ratios near the ground at 1.858 ppm and the highest above the canopy at 1.920 ppm.

This study showed the accuracy in both CH$_4$ mixing ratio and EC flux measurements over a longer period of time which allowed for comparison with two other measurement techniques. The robust system could make year round measurements given a constant power source. This field campaign lost information on the winter and spring seasons which the measurements would have been invaluable to interpreting seasonal variations and estimating annual flux contributions. Methane uptake studies in forests have been largely overshadowed by emission studies in major contributors such as wetlands, despite the fact that forests take up a much larger land surface and acts as a major sink for atmospheric CH$_4$. A multi-year long term flux measurement study at an upland or boreal forest would provide useful information in terms of carbon budgets and validation of upscaled data for global modeling. A vertical gradient measurement technique would also be invaluable in terms of supporting the flux measurements, as the two day intensive study even as a pilot project showed significant promise towards validating the measurements from the FGGA. Creating a baseline for the forest would also prove invaluable prior to harvesting of the forest to monitor the effects of anthropogenic activity and forestry practices on CH$_4$ fluxes.
References or Bibliography


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