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Temporal Dynamics and Controls of Carbon Dioxide, Ozone, and Nitrogen Oxides in Seasonally Snow-Covered Forest Ecosystems

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Temporal dynamics and controls of carbon dioxide, ozone, and nitrogen oxides in seasonally snow-covered forest ecosystems

by

B. Seok

B.S. & B.A., The Ohio State University, 2003

A thesis submitted to the
Faculty of the Graduate School of the
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This thesis entitled: Temporal dynamics and controls of carbon dioxide, ozone, and nitrogen oxides in seasonally snow-covered forest ecosystems written by B. Seok has been approved for the Department of Atmospheric and Oceanic Sciences

Assoc. Research Prof. Detlev Helmig

Dr. Mark W. Williams

Dr. Darin Toohey

Date ________________

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.
Seok, B. (Ph.D., Atmospheric and Oceanic Sciences)

Temporal dynamics and controls of carbon dioxide, ozone, and nitrogen oxides in seasonally snow-covered forest ecosystems

Thesis directed by Assoc. Research Prof. Detlev Helmig

Understanding how reactive gases interact with the snowpack is important as these gases influence the oxidation capacity of the atmosphere and ozone formation, which is important in understanding the impact of climate change on the Earth system. Trace gas exchange studies conducted in the Polar Regions showed that snow is a highly reactive medium for photochemical reactions, heterogeneous reactions, and physical exchange processes. The impact that snowpack can have on the overlying atmosphere can be significant depending on its location, but the importance of these effects are not yet well quantified. Thus, there is a need to investigate how reactive gases interact with the snowpack at various locations. Yet, the majority of studies investigating the snow-air exchange of reactive gases are done in the Polar Regions and only a handful are done in the mid-latitudes. If we want to be able to accurately predict how the atmospheric oxidation capacity and formation of ozone will respond to climate change, more measurements in the mid-latitude, seasonal snowpack needs to be done.

To address this issue, I conducted trace gas measurements of carbon dioxide, ozone, and nitrogen oxides in two different seasonally snow-covered forest ecosystems. One study site was a high elevation, subalpine forest, and the other study site was a low elevation, deciduous forest. I used a novel, automated measurement system based on the gradient diffusion method (GDM) to determine trace gas fluxes through snow at those sites. This system enabled me to evaluate the assumptions and semi-empirically quantify the errors in GDM. I demonstrated how the uncertainties in calculating average seasonal flux values using GDM can be reduced by statistically combining data from multiple gradient heights. I also found
that wind or pressure induced variations at the snow surface can result in a large (> 30\%) underestimation in inferred flux. Then by analyzing the differences in the dynamics of the trace gases in snow between the high and low elevation sites, I was able to demonstrate and re-emphasize that snow is a complex medium, and that the influence of snow on chemical and biological exchange is highly variable and dependent on climatic conditions and geographical location. For instance, subnivial soil appeared to be the main source of nitrogen oxides at the high elevation site, while atmospheric deposition and photochemistry in the snowpack were the sources of nitrogen oxides at the low elevation site. I also investigated the dynamics of ozone and nitrogen oxides during snow-free conditions at the low elevation site to better understand observations during snow-covered conditions. I discovered that transport of pollutants can strongly influence the dynamics of nitrogen oxides in-snow during snow-covered conditions and in-canopy during snow-free conditions. Finally, preliminary results from model study of trace gas exchange in Polar snowpack suggest that gas-phase chemistry in the snowpack interstitial air is insufficient for explaining the observed dynamics of ozone and nitrogen oxides in snow and that other not yet well understood chemical and physical processes in the snowpack drive these observed variations. These results collectively demonstrate the importance of understanding the biosphere-atmosphere interaction in snow-covered environments.
Dedication

I dedicate this thesis to my parents and brother. Thank you for your unconditional love and support, and encouraging me to pursue what is important in my life.
Acknowledgements

First and foremost, I would like to thank my thesis advisors, Detlev Helmig and Mark Williams, for providing me with the skills to become an independent scientist and being the best mentors I can ever imagine having. Each in their own way have shaped me in to the person who I am today. I think my primary advisor Detlev for giving the opportunities to see the world and pursue my research passions—something that I often boast to my peers. The biggest appreciation that I have for Detlev is the way he calmly handled the numerous turbulent moments that I instigated towards the end of my Ph.D. training. He has probably made the most valuable contributions to my personal growth. I have learned the value of humbleness, the importance of responsibility, and that a dose of skepticism in one’s self is necessary to becoming a successful and influential scientist. Words cannot describe how much I admire his patience, steadfast manner, and meticulous attention to detail, which are all basis of being a great scientist. I will strive to emulate those quality of his has I move forward with my scientific career. I am also extremely blessed to have Mark as an advisor. he has been unconditionally supportive throughout my Ph.D. training. Mark’s full trust in my abilities to do good work and make sound judgment has been instrumental in keeping my enthusiasm in science and hopes to pursue a career in advocating science, i.e., provide a voice for science in societal issues. I am thankful to have these two individuals as my thesis advisors, and I look forward to continuing my working relationship with them.

Next, I would like to thank my thesis committee members: David Noone, Darin Toohey, and Laurens Ganzeveld. I cannot express the amount of gratitude I have for their support,
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Since the beginning of the Industrial Revolution in 1850, human activity has led to a near exponential increase in average global surface temperature. In the 50 years from 1850 to 1899, mean temperature increased by 0.57°C. In contrast, over a five year period from 2001 to 2005, global mean surface temperature increased by 0.95°C. Changes in atmospheric composition, primarily the abundance of greenhouse gases, drove this temperature increase (IPCC, 2007).

Greenhouse gases are trace constituents of the atmosphere (e.g. carbon dioxide and methane) that efficiently absorb longwave radiation emitted by the Earth’s surface, and serve to warm the atmosphere. The natural abundance of greenhouse gases is controlled by interactions between the atmosphere and the other components of the Earth system (i.e. the biosphere, the hydrosphere, and the cryosphere) and the balance of sources and sinks amongst these reservoirs. Human industrial activity perturbs the balances between these interactions (Fig. 1.1).

It has been well-recognized that human activities exert significant direct influence on the biosphere-atmosphere component of the climate system. As such, there has been increasing efforts aimed at investigating the exchange of greenhouse gases in the natural system and responses to climate change. For example, a wide array of tower-based measurement networks (e.g. FLUXNET, NACP, AmeriFlux, NEON) were established to monitor the Net Ecosystem Exchange (NEE) at the ecosystem scale, which provides important information
Figure 1.1: Schematic view of the components of the climate system, their processes and interactions. Taken from IPCC (2007, FAQ 1.2)
on the carbon budget over annual time scales, and its coupling with climate dynamics. However, much of the ecosystem research to date as focused on the growing season due to large instantaneous flux rates during this period (Monson et al., 2006b) and the traditional view that winter is a season of limited biogeochemical activity (Campbell et al., 2005). It was assumed that trace-gas exchanges between the soil and the atmosphere ceased with snow cover or when soil temperatures dropped to 0°C (Steudler et al., 1989; Bouwman, 1990). As a result, most biogeochemical research focused on the growing season, even though, the importance of snow and related cryospheric processes as an ecological driver was known since the early-1990s (Chernov, 1988). This emphasis on ecosystem research during the growing season has led to problems in balancing the annual biogeochemical budget (IPCC, 1990), and thus the perception of winter as a season of suppressed biogeochemical activity was put in to question.

In recent years, these has been a steady shift towards investigating the biogeochemical cycle during the winter season to resolve this imbalance in the budget. By inserting air sampling probes into the snowpack, it was discovered that CO$_2$ concentrations were elevated at the bases of snowpack at high-latitude or high-elevation sites (Kelley et al., 1968; Coyne and Kelley, 1971; Solomon and Cerling, 1987), which suggested continued biological activity even after snow cover and with soil temperature near 0°C (Taylor and Parkinson, 1988; Sommerfeld et al., 1991). The work by Kelley et al. (1968) demonstrated that snow can act as a barrier to CO$_2$ from the soil as it moves to the atmosphere.

Forests are the largest terrestrial carbon sink (Pan et al., 2011), and they cover nearly a third (30%) of the terrestrial surface (MA, 2005). Approximately 45% of the forests experience seasonal snow cover (MA, 2005). Although wintertime measurements of trace gas exchange can be done easily at the tower measurement network sites, over a quarter (26.5%) of the worlds forests are in mountainous or complex terrain (MA, 2005), adding particular difficulty to the use of tower measurement sites, which typically use the eddy covariance technique to measure NEE. Therefore, an alternative approach was needed. This set the ba-
sis for estimating trace gas fluxes between the soil and the atmosphere through the snowpack using techniques based on first-order diffusion models (e.g. Fick’s first law of diffusion) at sites where more sophisticated turbulence-based models (e.g. eddy covariance) could not be applied (Björkman et al., 2010b). This approach enabled the measurements of CO₂ fluxes (among other greenhouse gases such as N₂O and CH₄ in forested regions) and promoted the rapid expansion of measurement sites in different natural ecosystems, for instance high-latitude tundra and permafrost sites (Zimov et al., 1996; Winston et al., 1997; Fahnestock et al., 1998; Welker et al., 2000), high-elevation alpine and subalpine sites (Sommerfeld et al., 1993; Brooks et al., 1996; Brooks and Williams, 1999; Williams et al., 1998; Monson et al., 2005, 2006a; Schindlbacher et al., 2007), and low-elevation agricultural and forested sites (van Bochove et al., 1996; Alm et al., 1999; Groffman et al., 2001; Schurmann et al., 2002; Maljanen et al., 2007). These studies—including those from tower networks—found that a large percentage (as much as 60%) of growing season carbon uptake can be lost during the winter, indicating that wintertime trace gas exchange is important in evaluating the ecosystem annual biogeochemical cycle in order to balance its budget (Sommerfeld et al., 1993, 1996).

It is uncertain how trace gas exchange in the winter will change with the predicted decline in snowpack resulting from continued climate change. Future climate scenarios are predicting decreases in seasonal snow coverage area and snowpack thickness, as well as increased summer rain (Baldwin et al., 2003). In the past 50 years, the Western U.S. has experienced reductions in snowpack (Mote et al., 2005; Hamlet et al., 2005) and higher springtime temperatures (Aguado et al., 1992; Kalra et al., 2008). It is likely that the decline in snowpack will result in modification to plant and microbial metabolism and distributions (Groffman et al., 2001), ultimately changing the biogeochemical cycle and the biosphere-atmosphere interaction.

With uncertainties surrounding future climate change and the ecological responses to that change, research at different spatial and temporal scales is necessary. While the eddy
covariance technique can monitor fluxes at the ecosystem scale, this technique is not able to provide information on the soil and snow processes that control the wintertime fluxes and it cannot be used at sites with complex topography. Snow property measurements, for example depth, density, and age, are essential to compliment ecosystem flux measurements and improve our understanding of ecosystem response to climate change (Williams et al., 2009a). This is where the aforementioned measurement techniques based on first-order diffusion principles can be used to collect wintertime flux data.

A number of measurement techniques based on the diffusion approach have been proposed: soil-chamber measurements (non-steady state, e.g., Davidson et al., 2002; Livingston et al., 2005; Sahoo and Mayya, 2010), snow-chamber measurements, 2-point concentration gradient measurements, and multi-point concentration gradient measurements, each with their pros and cons (McDowell et al., 2000; Schindlbacher et al., 2007; Björkman et al., 2010b). But, there are common drawbacks to all of these diffusion-based approaches. For instance, the estimation of trace-gas fluxes through snow is dependent on the properties of the snowpack, which is normally heterogeneous. Related to this, the diffusion approach is sensitive to the mixing of interstitial air by wind and pressure intrusions into the snowpack known as “wind-pumping” or “pressure-pumping” (Colbeck, 1989; Clarke and Waddington, 1991; Massman et al., 1997). Another common issue with diffusion-based measurement is that they are point-in-space measurements and assume a steady-state emission from the soil (Williams et al., 2009a). Also, seasonal wintertime fluxes are averaged from a limited number of discrete measurements made during the season. There are often large variations among the measurements due to the heterogeneous nature of soil (Suzuki et al., 2006). Therefore, there is a need for quantifying the errors in these measurements techniques based on the properties of snowpack at the study site to help us choose the appropriate measuring method.

Most of the mentioned snowpack trace gas flux studies examined stable greenhouse gases (e.g. CO₂, and to lesser extent N₂O) and very little attention has been given to reactive greenhouse and non-greenhouse gases in these studies (Williams et al., 2009a). Understanding
how reactive gases interact with the snowpack is important as these gases influence the oxidation capacity of the atmosphere and ozone formation, which is important in understanding the impact of climate change on the Earth system (IPCC, 2007). Trace gas exchange studies conducted in the Polar Regions showed that snow is a highly reactive medium for photochemical reactions, heterogeneous reactions, and physical exchange processes (Domine et al., 2008). The impact that snowpack can have on the overlying atmosphere can be significant depending on its location. Complete depletion of ambient ozone was observed over snowpack in the polar coastal regions (Simpson et al., 2007), while snowpack at the South Pole could double the ambient ozone concentration Helmig et al. (2008), we need to investigate how reactive gases interact with the snowpack at various locations.

Among the trace gases studied at Polar sites, surprising discovery was made with nitrogen oxides in snow. Above snow NO\textsubscript{x} measurements yielded very low concentrations (Honrath and Jaffe, 1992), but later NO\textsubscript{x} measurements within the snowpack yielded NO\textsubscript{x} concentrations that were a factor of three to ten times higher than ambient air (Honrath et al., 1999). This triggered the expansion of study sites to determine if NO\textsubscript{x} is also released from snow at other sites (Grannas et al., 2007). In the mid-latitudes, Honrath et al. (2000b,a) measured and proved that NO\textsubscript{x} was produced in snowpack in Michigan. Leading to the hypothesis that production of NO\textsubscript{x} via photochemical reactions in snow was a global process. However, Helmig et al. (2009c) showed that production of NO\textsubscript{x} in sunlit snow can be masked by larger biogeochemical signals particularly emissions of NO from soils. Nitrogen oxides are of particular interest because they play a critical role in regulating the photochemical production of ozone in the troposphere (Crutzen, 1970; Hauglustaine et al., 2001; Crutzen and Lelieveld, 2001). The primary source of nitrogen oxides to the atmosphere is from soils. Over the past century, the nitrogen oxides respired from soils via nitrification or aerobic denitrification from microbes are can be returned to the soil as nitrate through precipitation or snowfall at an increasing rate (Williams and Tonnessen, 2000; Galloway et al., 2008). As the carbon flux studies have provided evidence for an active subnivial respiration, it is
likely that similar nitrogen cycling occurs. Better understanding of the wintertime nitrogen cycle is crucial, because nitrogen availability to the soil is important to predicting future carbon sequestration by terrestrial ecosystems (Reich et al., 2006). Yet, the majority of the studies investigating the NO\textsubscript{x} exchange within the snowpack surface are conducted in the Polar Regions (Honrath et al., 1999; Jones et al., 2000; Beine, 2002; Dibb et al., 2002; Jacobi et al., 2004), where there is no or limited interaction with the biosphere. Thus far, there is only a handful of reported wintertime NO\textsubscript{x} measurement studies done in the mid-latitudes (e.g. Honrath et al., 2000b; Helmig et al., 2009c). More studies investigating the NO\textsubscript{x} exchange within the snowpack surface are needed to supplement the studies in the Polar Regions if we want to be able to predict how the atmospheric oxidative capacity and formation of ozone will respond to climate change.

Ultimately, the goal of conducting various snowpack gas exchange measurements in the field and the in laboratory is to understand the interplay between climate and Earth system dynamics. Through field and laboratory experiments, we can develop theories about the interplay among the components of the Earth system and make predictions on the ecosystem response to climate change. To test our understanding of the Earth system and its response to climate change, we develop numerical models built on mathematical relationships discovered from field and laboratory experiments. Significant development and advances in models have been made these past years, but still, much of the biosphere-atmosphere and cryosphere-atmosphere interaction processes are not adequately represented and not used in the models, we must test our understanding of these interactions using first principle based numerical models. If these comparatively simple models can properly simulate observations, then we can build confidence in our understanding of the interplay of the biosphere and the cryosphere with the atmosphere (Grannas et al., 2007). Modeling studies supported by field observations and laboratory experiments are needed to not only validate the model results, but they needed to determine whether the results are representative for other snow covered locations. This type of research is needed to improve our understanding and develop predic-
tive modeling capabilities and parameterizations of the processes in-snow and interplay with
the atmosphere for inclusion in regional and global atmospheric chemistry models (Thomas
et al., 2012).

In this these, I aim to help narrow the gap in our understanding of the snow-air gas ex-
change and its impact on the overlying atmospheric composition. I do this by first evaluating
an automated trace gas flux through snow measurement system developed to improve the
accuracy and precision of calculating the seasonal trace gas fluxes through snow (Chapter 2).
In the process of evaluating this novel measurement system, I quantify the uncertainties as-
sociated with diffusion-based measurement systems. Specifically, I investigate the effects of
wind-pumping or pressure-pumping on inferred flux values using this diffusion-based mea-
surement system. I also examine the impact on how measurements of snowpack physical
properties can influence the error in the calculated flux. After establishing the performance
of the automated trace gas flux through snow measurement system, I address the applica-
bility of the results from a series of studies conducted at a high elevation site in the Niwot
Ridge Long Term Ecological Research site (“White on Green,” Williams et al., 2009a) to
a low elevation site in northern Michigan (Chapter 3). I also examine the implications of
the results from the Michigan study to climate change. Next, I continue the investigation of
ozone and nitrogen oxides dynamics in the growing season at the Michigan site to compare
and contrast the winter results with snow-free conditions (Chapter 4). At last, I present a
short report on a work-in-progress project on developing a highly parameterized snowpack
trace gas transport module using data collected at Summit, Greenland to improve our under-
standing of gas transport through snow and observed interstitial ozone and nitrogen oxides
at different sites (Chapter 5) before concluding my thesis in Chapter 6.
Chapter 2

An automated system for continuous measurements of trace gas fluxes through snow: An evaluation of the gas diffusion method at a subalpine forest site, Niwot Ridge, Colorado

This chapter has been published in Biogeochemistry as part of the “White on Green” special issue.


2.1 Abstract

An experimental system for sampling trace gas fluxes through seasonal snowpack was deployed at a subalpine site near treeline at Niwot Ridge, Colorado. The sampling manifold was in place throughout the entire snow-covered season for continuous air sampling with minimal disturbance to the snowpack. A series of gases (carbon dioxide, water vapor, nitrous oxide, nitric oxide, ozone, and volatile organic compounds) was determined in interstitial air withdrawn at eight heights in and above the snowpack at approximately hourly intervals. In this chapter, carbon dioxide data from 2007 were used for evaluation of this technique. Ancillary data recorded included snow physical properties, i.e., temperature, pressure, and density. Various vertical concentration gradients were determined from the multiple height measurements, which allowed calculation of vertical gas fluxes through the snowpack using Fick’s first law of diffusion. Comparison of flux results obtained from different height inlet
combinations show that under most conditions fluxes derived from individual gradient intervals agree with the overall median of all data within a factor of 1.5. Winds were found to significantly influence gas concentration and gradients in the snowpack. Under the highest observed wind conditions, concentration gradients and calculated fluxes dropped to as low as 13% of non-wind conditions. Measured differential pressure amplitude exhibited a linear relationship with wind speed. This suggests that wind speed is a sound proxy for assessing advection transport in the snow. Neglecting the wind-pumping effect resulted in considerable underestimation of gas fluxes. An analysis of dependency of fluxes on wind speeds during a three-week period in mid-winter determined that over this period actual gas fluxes were most likely 57% higher than fluxes calculated by the diffusion method, which omits the wind pumping dependency.

2.2 Introduction

Recent research in snow-covered temperature, alpine, and arctic environments shows that subnival (i.e. under the snow) soil respiration can result in substantial fluxes of carbon dioxide ($\text{CO}_2$) through the snowpack (Sommerfeld et al., 1993; Brooks et al., 1996; Zimov et al., 1996; Oechel et al., 1997; Mariko et al., 2000; McDowell et al., 2000; Welker et al., 2000; Roehm and Roulet, 2003; Monson et al., 2005, 2006a). The wintertime $\text{CO}_2$ flux through the snow can contribute in excess of 20% to the annual carbon budget (Winston et al., 1997). To date, studies of trace gas flux through snow have focused primarily on $\text{CO}_2$. These findings suggest that microbial processes in underlying soil similarly may drive the flux of other gases such as nitric oxide (NO), nitrous oxide ($\text{N}_2\text{O}$), and methane ($\text{CH}_4$). Therefore, these processes warrant consideration in the annual ecosystem carbon (C) and nitrogen (N) budgets of seasonally snow-covered ecosystems (Sommerfeld et al., 1993; Brooks et al., 1996; van Bochove et al., 1996; Mast et al., 1998; Yashiro et al., 2006).

The ecological controls on the trace gas fluxes through the seasonal snowpack are still poorly known, in part because of the difficulty in measuring these fluxes and their depen-
dencies during the winter season. The trace gases CO$_2$, CH$_4$, and N$_2$O are greenhouse gases that play important roles in climate forcing. Nitric oxide is a precursor of tropospheric ozone (O$_3$), which is also a greenhouse gas, formed by photochemical reactions. Several studies have pointed out the high sensitivity of respiration, denitrification, and other processes, which produce these gases, to soil temperature under the seasonal snowpack. In turn, the soil temperature tends to increase with increasing snow depth because the insulating quality of snow cover increases with depth (Brooks and Williams, 1999). Consequently, the depth and duration of the seasonal snowpack have been shown to have notable impacts on trace gas exchanges and ecosystem C and N budgets (Williams et al., 1998; Monson et al., 2006a). For these reasons, there is a need to better quantify these processes, their behavior, and dependency on conditions such as snowpack properties, snow chemical composition, and soil biogeochemistry, in order to develop conceptual models for the description of these trace gas fluxes under current and future climate conditions.

The experimental protocols for the measurement of fluxes of trace gases through a seasonal snowpack, which was developed over five winter seasons (2004–2008) at a high elevation subalpine site in the Colorado Rocky Mountains, was improved. Trace gases studied included CO$_2$, nitrogen oxides (NO$_x$=NO + NO$_2$), N$_2$O, O$_3$, and volatile organic compounds (VOCs). The high resolution, multiple season data obtained were used to test the gas diffusion model (DM) method for deriving quantitative C and N winter balances. The DM approach has been the most common method for evaluating trace gas flux through snow (McDowell et al., 2000), as it has a number of advantages over other flux techniques such as chamber methods and eddy covariance measurements. In particular, the mixing ratios of trace gases in the seasonal snowpack are often substantially higher than ambient levels, which results in pronounced mixing ratio gradients. This allows for more robust measurements and experiments appropriate for complex mountainous terrain and wintertime conditions. Furthermore, these snowpack gradient measurements can be conducted without meeting the stringent requirements for homogeneous and flat terrain essential for eddy covariance measurements.
The DM relies on the assumption that gas transfer inside the snowpack is determined by molecular diffusion. However, there are other factors such as pressure-related phenomena that influence gas exchange from the soil through any permeable medium (in particular, snow) to the atmosphere (Massman, 2006). A number of studies (Massman et al., 1997; Jones et al., 1999; Hubbard et al., 2005; Takagi and Nomura, 2005; Suzuki et al., 2006) pointed out the large potential error that may occur when the DM approach is applied to trace gas flux through the snowpack because of the effects of advection or wind-pumping. Yet, quantitative descriptions and corrections of this effect on the flux calculation remain highly uncertain.

In this chapter, I present the experimental approach that was originally developed by my predecessors Bocquet et al. (2007) and improved by me over the last five years for all winter measurements of trace gas fluxes through a seasonal snowpack. Here, I focus on the CO$_2$ flux from 2007, but I believe that this evaluation is applicable to other trace gases and other years. The decision to use CO$_2$ for evaluating this trace gas sampling system was because of the CO$_2$ record has been the longest and most complete of all gases studied to date; the relative precision and accuracy of its analytical measurements were highest, thus minimizing errors from the analytical determination, and the CO$_2$ data offered the highest number of comparison with studies reported in the literature. I evaluated the potential errors in the estimation of CO$_2$ fluxes through snow including sampling frequency, number of measurement heights within the snowpack, and physical properties of the snowpack such as the density of snow. Errors associated with the DM technique will be discussed with particular emphasis on the influence of wind-pumping. Results and discussion of measured gas fluxes and its ecological significance can be found in papers by Filippa et al. (2009) for N$_2$O, Helmig et al. (2009a) for NO$_x$, and Liptzin et al. (2009) for CO$_2$. 
2.2.1 Diffusion model (DM) measurement technique

The DM method appeared to be most suitable for this study, because it allowed continuous long-term measurements throughout the winter season with relatively simple measurement techniques. This method provided a direct approach to measuring the gas transport through the snowpack, since trace gases were sampled from inside the snow. In past research, gases from the snowpack were typically drawn from two levels, the soil-snow interface and the atmosphere above the snow surface, to obtain a vertical profile of the mixing ratio gradient (Jones et al., 1999; Takagi and Nomura, 2005; Monson et al., 2006a; Suzuki et al., 2006). Besides the measurement of trace gases at different heights, the DM method depends on the physical properties of the porous medium. For the snowpack, this involves the measurements of snow depth, density, and temperature. A newer technique not evaluated here involves measurements of gas mixing ratios in the snowpack using nondispersive infrared (NDIR) sensors (Takagi and Nomura, 2005).

The DM method is based on Fick’s first law of diffusion. The underlying theory assumes that the transport of a gas, e.g., CO$_2$, in the snowpack operates primarily in the vertical dimension with fluxes dictated by the concentration differential. Within the horizontal footprint of the CO$_2$ measurement, snow properties are assumed constant in each arbitrary layer of the snowpack, leading to consistent CO$_2$ concentrations (or mixing ratios) at each layer in the snowpack. Thus, CO$_2$ efflux through the snowpack is calculated using the equation

$$F_{CO_2} = -D_{CO_2} \left( \frac{\partial C_{CO_2}}{\partial z} \right), \quad (2.1)$$

where $F_{CO_2}$ is the molecular flux of CO$_2$ ($\mu$mol m$^{-2}$ s$^{-1}$), $D_{CO_2}$ is the diffusivity of CO$_2$ in the snowpack airspace at the $\partial z$ interval (mol m$^2$ s$^{-1}$) and $\frac{\partial C_{CO_2}}{\partial z}$ is the CO$_2$ concentration gradient in the snowpack ($\mu$mol m$^{-3}$). Therefore, the flux of gas is directly proportional to the concentration gradient. This indicates that any changes in the concentration gradient
term will directly change the flux. The diffusivity \( D_{CO_2} \) can be estimated using the relation

\[
D_{CO_2} = \phi \tau D \frac{P_0}{P} \left( \frac{T}{T_0} \right)^{\alpha},
\]

(2.2)

where \( \phi \) is the snowpack porosity, \( \tau \) is the tortuosity coefficient, and \( D \) is the diffusion coefficient of the specific gas under consideration at standard temperature and pressure \((T_0 = 273.15 \text{ K} \text{ and } P_0 = 1013 \text{ hPa}), \text{i.e. } D = 0.1381 \times 10^{-4} \text{ m}^2 \text{ s}^{-1} \text{ for } CO_2, \text{ P is the ambient pressure (hPa), } T \text{ is the snowpack temperature (K), and the exponent } \alpha = 1.81 \text{ is a theoretically set coefficient explained by Massman (1998). Snowpack porosity } \phi \text{ is calculated by}

\[
\phi = 1 - \frac{\rho_{\text{snow}}}{\rho_{\text{ice}}},
\]

(2.3)

where \( \rho_{\text{snow}} \) is the measured density of snow at the \( \partial z \) interval \((\text{kg m}^{-3})\), and \( \rho_{\text{ice}} \) is the density of ice \((917 \text{ kg/m}^3, \text{ Eisenberg and Kauzmann, 2005}). \text{ For the tortuosity constant } \tau, \text{ Du Plessis and Masliyah (1991) developed a theoretical relationship where the tortuosity can be derived from the porosity as}

\[
\tau = \frac{1 - (1 - \phi)^{2/3}}{\phi},
\]

(2.4)

However, I used

\[
\tau = \phi^{1/3},
\]

(2.5)

which is a relationship that was empirically developed from a snowpack in a region similar to my study site (Mast et al., 1998; Hubbard et al., 2005). Some researchers dealt with tortuosity by either ignoring it or by letting it be equal to 1 (Sommerfeld et al., 1993), or compensating for its effect by reducing the calculated flux value by 35% (Fahnestock et al., 1998).

2.3 Materials and methods

2.3.1 Site description

This study was conducted at the Soddie site on Niwot Ridge in an open meadow surrounded by ribbon forest just below tree-line near the Continental Divide in the Colorado
Rocky Mountains (40°2′52″N 105°34′15″W, 3345 m above sea level). The site is on a 10° southwest facing slope (Erickson, 2004). It has an underground laboratory 3 m × 9 m × 2.4 m in size, line power, and an array of snow and zero-tension soil lysimeters Williams et al. (2009b). The soil in the open meadow is classified as a mixed Typic Humicryept (Soil Survey Staff, 2006) and the forest vegetation is primarily a mixture of spruce (Picea englemannii) and fir (Abies lasiocarpa) (Williams et al., 2009b). The depth of A horizon is ~34 cm; soil composition is 46% sand, 33% silt, 21% clay, and 31% organic matter in the upper 10 cm. The soil pH ranges between 4.7 and 5.0 (Bowman and Seastedt, 2001).

2.3.2 Trace gas sampling system

Snowpack gas flux studies began in the 2003–2004 winter season and have continued with additional gas and physical snowpack measurements. Williams et al. (2009a) provides the history of the studies. In this chapter, I report the system configuration from the 2006–2007 winter season (from hereon referred to as WI2007), because this season has the most extensive measurements to date. The photographs in Fig. 2.1 and the schematic in Fig. 2.2 depict the multi-inlet snow tower used in WI2007. The snow tower was constructed of square aluminum alloy tubing (3.8 cm × 3.8 cm) with 60 cm long cross bars (1.3 cm × 1.3 cm) at heights of 0 cm, 10 cm, 30 cm, 60 cm, 90 cm, 120 cm, 150 cm and 245 cm above the ground. The tower was installed in fall 2006, and snow was allowed to accumulate around it. The snow pack surrounding the tower was not disturbed throughout the winter season.

Each of the eight cross bars supported a pair of sampling inlets. The inlets were fitted with 25 mm Acrodisc® hydrophobic polytetrafluoroethylene (PTFE) syringe filters (Pall Life Sciences, Ann Arbor, Michigan, USA) to prevent debris from entering the sampling line. Air was drawn at a rate of 1.5 L min⁻¹ to 3 L min⁻¹ from each sampling height depending on the number of chemical measurements conducted. Since the sampling flow was split between the paired inlets, the effective sampling rate per inlet was 0.75 L min⁻¹ to 1.5 L min⁻¹.

The selection of a pair of inlets for sampling at a particular height on the tower was
Figure 2.1: Series of photographs showing the snowpack sampling tower (snow tower). The left picture was taken before the onset of snowfall in autumn 2006. The upper-right picture shows the snow tower buried in \( \sim 2 \text{ m} \) of snow with the top sampling inlet (at 245 cm) above the snowpack on 11 March 2007. The lower-right photo shows the syringe fiber glass filter and the type-E thermocouple mounted to one of the ends of the horizontal cross arms on the snow tower.
Figure 2.2: Schematic diagram of winter 2007 season snowpack sampling tower with plumbing and instrument configuration. The light blue solid line defines the snow surface, and the brown dashed line is the ground. Abbreviations in the legend and diagram reflect the following: C-scrubber = CO$_2$ scrubber, O-scrubber = O$_3$ scrubber, MFC = mass flow controller, F-controller = flow controller, PG = pressure gauge, S-filter = syringe filter, N1 = 320 nmol mol$^{-1}$ N$_2$O standard, N$_2$ = 408 nmol mol$^{-1}$ N$_2$O standard, N3 = 485 nmol mol$^{-1}$ N$_2$O standard, BA = breathing air standard, CO$_2$ = 1% CO$_2$ standard, NO = 0.1% NO standard, P5 = 5% CH$_4$ / 95% Ar carrier gas, the GC-ECD is for N$_2$O measurements. The thermocouples are linked to one of the syringe filters at each level (see Fig. 2.1).
done through an array of eight solenoid valves. Sampling through each pair of inlets was done sequentially from the 245 cm height to the 0 cm height. Each sampling interval was 10 min long, with trace gas contents determined in this gas flow every 10 s. From that record, 1-min averages were calculated for each trace gas, sampling interval, and measurement height. During the transition from one sampling height to the next, concentration readings for both gases adjusted over ∼1 min to the new level at the lower inlet. A complete cycle took 80 min, and there were 18 cycles per day. The manifold used 2-way solenoid valves with PTFE body seals (Cole-Parmer, Vernon Hills, Illinois, USA). All the sampling lines and valves were conditioned over night with a flow of 2 L min$^{-1}$ to 3 L min$^{-1}$ of air containing 200 nmol mol$^{-1}$ to 300 nmol mol$^{-1}$ ozone prior to installation to minimize the loss of O$_3$ in the manifold during subsequent field sampling. All sampling tubes were directed to the underground laboratory, which housed the analytical instruments. Sampling lines were all perfluoroalkoxy (PFA) Teflon®, inner diameter of 3.9 mm and outer-diameter of 6.4 mm (Parker Hannifin, Cleveland, Ohio, USA), with equal lengths of 18 m. Sections of the sampling lines outside the laboratory were wrapped in pipe insulation with a self-controlling water pipe heater to maintain line temperatures slightly above 0 °C. This was done to prevent water from freezing and clogging the sampling lines.

Monitored gases included CO$_2$, H$_2$O, NO$_x$, N$_2$O, and O$_3$. CO$_2$ and H$_2$O were measured using a LI-7000 IRGA (LI-COR Environmental, Lincoln, Nebraska, USA). Nitrogen oxides and O$_3$ were measured using a model 42CTL chemiluminescence NO$_x$ analyzer, and model 49 UV photometric O$_3$ analyzer (Thermo Environmental Instruments, Franklin, Massachusetts, USA), respectively. Nitrous oxide was measured by isothermal gas chromatography with electron capture detection (GC-ECD; Shimadzu GC-8AIE, Shimadzu Scientific Instruments, Columbia, Maryland, USA). On site instrument calibrations for the LI-7000 IRGA, the model 42CTL chemiluminescence NO$_x$ analyzer, and the Shimadzu GC-8AIE were automated. More details on these analytical measurements and calibrations procedures are presented by Filippa et al. (2009) for the GC-8AIE, Helmig et al. (2009a) for the 42CTL, and Liptzin et al. (2009)
for the LI-7000 IRGA. The sampling manifold, calibration system, and data acquisition were controlled through an array of digital input/output modules, temperature input components, and LabVIEW software (National Instruments, Austin, Texas, USA). The GC-ECD signals were acquired through a PeakSimple system (SRI Instruments, Torrance, California, USA).

### 2.3.3 Ancillary data

Temperatures at each sampling height were measured using type-E thermocouples (Omega Engineering, Inc., Stamford, Connecticut, USA) that were covered by white shrink tubing to reduce radiation artifacts. Wind speed, at 6 m above the ground on a meteorological (MET) tower 10 m away, was measured using a 05103-L R. M. Young Wind Monitor (Campbell Scientific, Logan, Utah, USA). Barometric pressure was measured using a CS105 Vaisala PTB101B Barometer (Campbell Scientific, Logan, Utah, USA). Differential pressure between the soil-snow and snow-atmosphere interfaces was collected at the MET tower using a differential pressure sensor (PX277-0.1D5V, Omega Engineering, Inc., Stamford, Connecticut, USA) with 1 Hz sampling rate and 1-min averages stored. The high pressure inlet was placed at 3 m above the soil surface and the low pressure inlet was placed on the ground. Given this setup, if pressure at the ground was greater than at the snow surface, then the resulting pressure gradient was measured as a negative signal.

Readings of snow depth were conducted at 1 to 2-week intervals from calibrated marks on the snow tower. Gaps in the snow depth record were filled by comparing and interpolating the daily snow depth record from the SNOTEL site (University Camp, site 838), 1.5 km from the Soddie. An analysis of the linear correlation between concurrent snow-depth data from these tow sites resulted in a $r^2 = 0.91$. These snow depth data were used for flux calculations including the ambient air measurement data (245 cm). An effective snowpack diffusion distance to the snow surface was determined by calculating the distance from the respective, fixed height inlet pair to this determined snow surface height. Gas measurements from the 245 cm height were assumed to be representative for conditions at the snow-atmosphere
interface. This simplification neglects the concentration gradients between the snow surface and the 245 cm height.

Soil moisture was measured using four CS616-L Water Content Reflectometers (Campbell Scientific, Logan, Utah, USA) with 30 cm long proves installed vertically into the soil in a 1 m radius from the snow tower, following the protocol at the C-1 Ameriflux site on Niwot Ridge (Bowling et al., 2008), with the average of the four sensors used for all further data applications.

Snow density was measured in an adjacent open meadow area ~30 m away from the primary study site with similar vegetation and slope characteristics. Snow pits were dug every 1 to 2 weeks, upslope first and progressed downhill for each new snow pit. Snow properties including depth, density, grain type and size, and stratigraphy were measured using previously published protocols (Williams et al., 1996, 1999).

2.4 Results

2.4.1 Snow physical properties

Continuous snowpack at this site typically develops between the end of October and early November. The seasonal snow cover reached a maximum depth of 2.2 m in March 2007, and all snow had melted by the first week of June (Fig. 2.3). The snowpack development in 2007 was similar to the past five seasons of measurements, where seasonal maximum snowpack depths of 1.8 m to 2.2 m occurred between day of year (DOY) 65 and 85. While there were occasional minor reductions in snowpack depth throughout the winter, with a more significant one occurring during DOY 80 to 85 in 2007, the springtime snow melt with significant and continuous snow depth reductions did not commence until DOY 130. The physical changes associated with this transition are also evident in the temperature and density records.

Snowpack temperatures were usually warmer than ambient air temperatures through-
Figure 2.3: **a** A temporal and vertical development of the snowpack temperature. The black solid line is the snow height above the ground (cm). The color bar is the snowpack temperature (°C). The inverted dark gray triangles denote time when actual snow depth measurements were taken. The gaps in the snow depth data were filled through extrapolating daily snow depth measurements from the SNOTEL site 838 (see text for more detail). **b** Contour plot of snow density (kg m\(^{-3}\)) generated from the biweekly snow pit excavation with 10-cm vertical resolution. The inverted green triangles denote the dates when actual snow density samples were taken. Gaps between sampling periods were filled through linear interpolation.
The average air temperature during the snow-covered period was $-5.2^\circ C$, with minimum of $-25^\circ C$ in mid-winter and an increasing trend in late winter and early spring. The diurnal and daily fluctuations of air temperature progressively damped within the first 10 cm to 50 cm below the snow surface. The temperature at the soil-snow interface increased to about $0^\circ C$ when the snowpack reached a depth of $\sim 12$ cm and remained as such until the end of the season (Fig. 2.3a). At DOY 67, the upper snowpack layers suddenly warmed. The entire snowpack turned isothermal over an eight day period. However, it took another 55 days from that point until significant snow melt occurred.

Snowpack density generally increased over time (Fig. 2.3b). The initial density was approximately 200 kg m$^{-3}$ early in the season; maximum density (500 kg m$^{-3}$) occurred during the snowmelt period. Density normally increased with the depth due to compression caused by the overlying snow. However, at depths below 60 cm, density remained lower and showed little change over time until active snowmelt. This section of the snowpack was composed of kinetic grains (depth hoar), which resists compression.

### 2.4.2 CO$_2$ and H$_2$O vapor mixing ratios within the snowpack

A typical plot of the snowpack mixing ratios of CO$_2$ and H$_2$O vapor during a sampling cycle is presented in Fig. 2.4. After 3 min of the transition between levels, the mixing ratios of CO$_2$ and H$_2$O vapor remained relatively constant for the remainder of the measurement interval. Because of the changing signal during the transition from one inlet to the next, the five points around the transition period were omitted for calculating the gas mixing ratio for each measurement time interval (Fig. 2.4).

### 2.4.3 CO$_2$ fluxes

The time series of calculated daily mean fluxes from all possible gradient combinations for WI2007 is shown in Fig. 2.5. These data show a remarkable variability both between results from different inlet heights and between measurement days. Figure 2.5 also shows the
Figure 2.4: Example of a time series of CO\textsubscript{2} and H\textsubscript{2}O vapor mixing ratios during one sampling cycle on 11 March 2007 with the x-axis scale indicating time from the beginning of the cycle (02:40 MST). The dots are 1-min averages of data collected every 10s. The white dots in each 10-min sampling interval represent the data that were averaged for determining gas concentration gradients (\(\frac{\partial C}{\partial z}\)). The black dots were omitted from the calculation for determining the gas concentration gradient because the values may be compromised during the switching between sampling inlets. The snowpack depth during this sampling cycle was 1.87 m.
median value calculated from all available gradient interval fluxes at a given time. Closer inspection of this record revealed that individual gradient data typically fall within a range of ±50% of the overall median, but it was not uncommon that data from a selected gradient deviated up to 100% from the median. Results derived from measurements at the 0 cm inlet frequently deviated from the other inlet data, with gradients between the 0 cm and 10 cm inlets often being unusually small and on occasion even negative. This behavior was interpreted as this measurement interval being too close to the ground and within the surface roughness layer at this site, where consistent gradients are not well developed. Figure 2.5 also shows the median value calculated from all available gradient interval fluxes at a given time. My estimate of the diffusive CO$_2$ flux based on the seasonal average of the daily mean ranged from 0.58µmol m$^{-2}$ s$^{-1}$ to 1.08µmol m$^{-2}$ s$^{-1}$ in 2007, depending on the pairs of inlets used for the gradient calculation (Fig. 2.5). However, of the 27 gradient combinations, 16 of them gave results between 0.70µmol m$^{-2}$ s$^{-1}$ and 0.90µmol m$^{-2}$ s$^{-1}$. The linear correlation of the all-season data from the 27 gradient combinations illustrated that—not unexpectedly—correlations were highest where gradient intervals overlap due to the autocorrelation in these data. For example, the correlation coefficient for gradients calculated from 90 cm to 60 cm and from 120 cm to 30 cm was 0.99. Furthermore, correlations were high for data from adjacent gradients (see Fig. 4 in Filippa et al. (2009), which graphically displays the corresponding analysis for calculated N$_2$O fluxes from the 90–60 cm vs. the 60–30 cm gradient data), and became weaker the further the gradients were separated vertically. Also, better agreement was generally seen in data from the middle of the snowpack, whereas results from sampling near the bottom and involving measurements from the ambient inlet often showed weaker correlations. The correlation coefficient $r$ was only 0.29 between gradients calculated from 30 cm to 10 cm and from 120 cm to 90 cm. In essence, the linear correlation results of the fluxes were dictated by the concentration gradient, as shown in Eq. 2.1. Absolute correlation values $r$ of 1 or close to 1 between different-height gradients implied that the fluxes through the snowpack were constant, which is a key assumption of the DM. This behavior also implies
that diffusion was the dominant process in the transport of CO$_2$ through the snowpack. The multiple-inlet gradient and flux data illustrate that for the center portion of the snowpack, these conditions (i.e. linear concentration gradients and dominant diffusion transport) were reasonably well met and that the diffusion model was an appropriate tool for estimating fluxes. Consequently, most of the subsequent analyses were done using the data from the 60–30 cm gradient interval. These data showed relatively high correlation with most non-overlapping inlet pair combination (range in $r$ values of 0.29 to 0.80). Furthermore, the 60–30 cm inlet data were the longest and most steady record for the 2005–2006 winter season (hereon as WI2006) and WI2007.

2.5 Discussion

2.5.1 Potential sampling effects

Active sampling from interstitial air in the snowpack represents a disturbance to the natural air transport and this can generate artifacts in the measured snowpack data (Albert et al., 2002; Domine et al., 2008). I evaluated the potential artifact caused by the sampling technique using an approach similar to the one presented by Bowling et al. (2008). My sampling system pulled $\sim$20 L of air from the paired inlets during each sampling interval. The $\sim$10 L of air withdrawn at each inlet, at a snowpack density of 400 kg m$^{-3}$ (which was the seasonal average), and assuming a sphere volume, would yield an effective radius of $\sim$16 cm per inlet of the sampling volume. All, but one, sampling ports were 30 cm apart in the vertical, so there is very little overlap within this radius. (The closer distance between the 0 cm and 10 cm height inlet pairs was the only exception to this requirement.) Based on gas-phase diffusive transport only (Seinfeld and Pandis, 2006, p. 551), I estimated that it would take $\sim$44 min within this volume of air to re-equilibrate to its original condition. This is faster than the 80-min cycle used in my experiment. With increased (decreased) snow density, the re-equilibrium time would increase (decrease), and the sample will reflect a
Figure 2.5: Daily WI2007 CO$_2$ flux for all sampling height combination. The thick black line depicts the daily median flux data calculated from the results of all gradient combinations.
larger (smaller) volume of snowpack. Data from my sampling protocol confirmed the validity of these assumptions. As seen in Fig. 2.4, other than during the transition period, there was comparatively little change in gas mixing ratios during the 10-min sampling interval. This meant that gas sampled during this time remained relatively representative of the given inlet height. Also, closer inspection of these records revealed that the relative change of signal was largest for the 0 cm measurement height, which reflects the fact that the available airspace extends only in one direction; therefore, air that replaced the sampled air volume is expected to be drawn from a larger vertical distance. The larger degree of overlapping sampling volumes for the 0 cm and 10 cm heights explained so some extend the deviating behavior in the observed gradient from these two heights. In summary, my results were in agreement with the findings of Bowling et al. (2008) who re-measured several inlets 25 min after the initial measurement and found no difference in CO$_2$ concentrations or isotopes of carbon and concluded that the advective influence of their sampling under these conditions was negligible.

2.5.2 Dependence of CO$_2$ flux on environmental conditions

In general, CO$_2$ fluxes gradually increased over the snow-covered season, reaching a maximum around the onset of snowmelt. An interesting question was what drove the daily variations in CO$_2$ (Fig. 2.5), and if the change in flux was driven by changes in the source term, i.e., day-to-day changes in the emission of CO$_2$ from soil to the snowpack, or to other physical or chemical processes that influenced the flux calculation. For the investigation of this question, I focused on the 30-day time period between DOY −11 and 19 when the snow depth was relatively constant at $\sim$20 cm (Fig. 2.6a). Over this time span, the soil volumetric water content remained constant at $\sim$0.20 m$^3$ m$^{-3}$ (Fig. 2.6b), and the temperature near the soil-snow interface was always $\sim$0°C (Fig. 2.6d). In contrast to the relatively constant snow depth, snow temperature, and soil moisture content, data for wind speed ranged over more than an order of magnitude from $<0.2$ m s$^{-1}$ to 6 m s$^{-1}$ (Fig. 2.6c). In turn, there was a
tendency that higher wind speeds were associated with lower differential pressures (Fig. 2.6c).
Mixing ratios of CO$_2$ increased from ambient levels at the snow surface ($\sim$385 µmol mol$^{-1}$) to $\sim$4000 µmol mol$^{-1}$ at the bottom of the snowpack (Fig. 2.6e). Comparison between the CO$_2$ mixing ratio and wind speed time series data suggested that CO$_2$ mixing ratios in the snowpack generally decreased with increasing wind speed. For example, between DOY $-6$ and $-5$, at the 10 cm level, CO$_2$ mixing ratios decreased by almost a factor of 2 from 2690 µmol mol$^{-1}$ to 1475 µmol mol$^{-1}$, as wind speed increased from 1.5 m s$^{-1}$ to 5.9 m s$^{-1}$. As a result, calculated CO$_2$ fluxes decreased from 0.67 µmol m$^{-2}$ s$^{-1}$ to 0.16 µmol m$^{-2}$ s$^{-1}$ (Fig. 2.6f).

### 2.5.3 Uncertainties in flux estimates using the diffusion model

Snow permeability and gas transport are related to snow density (Albert and Hardy, 1995; Albert and Shultz, 2002; Albert et al., 2004) as permeability is affected by porosity and tortuosity, even though there is no direct relationship between porosity, tortuosity, and permeability (Hardy et al., 1995). In my flux calculation, gas diffusivity, following Eq. 2.2, was derived indirectly from snow density, as porosity and tortuosity were calculated from the density values (see Eqs. 2.3 and 2.5). For example, the diffusion rate at a density of 250 kg m$^{-3}$ was 87% faster than at a density of 500 kg m$^{-3}$, assuming all other variables were unchanged. Thus, errors in the estimate of CO$_2$ flux through snow caused by incorrect measurements of density varied as density changed. Errors in measuring the density of snow have been estimated at 10 to 15% (Sommerfeld et al., 1996; Hubbard et al., 2005). In my case, the uncertainty in applied density was likely higher, as I applied density data from an adjacent plot, and the biweekly density determinations did not allow for capturing density changes that occurred at higher frequency than this sampling interval. I evaluated how errors in measuring density propagated to errors in estimating the flux of CO$_2$ using errors in the measurement of density of ±10, 20 and 30%. The calculated error increased non-linearly at higher snow densities and with the uncertainty in the determination of snow density.
Figure 2.6: Dataset from DOY −11 to 19. a Snow height from the ground. The gray dots are the actual snow depth measurements. The solid line is the interpolated data based on the daily SNOTEL snow depth measurements (see text for more detail). b Soil moisture data. The line is the average of the four soil moisture sensors surrounding the snow tower in a 1-m radius. c Wind speed (dark blue solid line) and differential pressure (sky-blue solid line). d Temperature data from the snow tower (in and above the snowpack). e CO$_2$ mixing ratio in and above the snowpack measured from the snow tower. The green and red arrows mark the start and end when the instrument range was maxed out at 3000 µmol mol$^{-1}$ at one or more sampling heights. f Calculated flux using the 60–30 cm inlet data without consideration of wind correction.
For instance, a 10% error in the measurement of snow density resulted in an error in the estimated CO$_2$ flux on the order of 5% for a snow density of 300 kg m$^{-3}$ but more than 10% at a density of 500 kg m$^{-3}$. For the range of snow densities encountered during the experiment at the Soddie sites, I estimated that the error in calculating the flux of CO$_2$ ranged from 2 to 9% (Fig. 2.7). Another potential complication in the diffusion flux calculation was the presence of crust and ice layers, which may constitute diffusion barriers that were not considered in the Fick’s law calculation. Snow pit analyses showed that ice layers were uncommon at the site, as snow surface temperatures at this high elevation generally remain below freezing (which avoids freeze-thaw events that form crust and ice layers) until the onset of the spring melt period. There are several reasons why the sampling technique used in this study is rather robust against the influence of inhomogeneous snow density, and ice lenses and crusts. The variation of snowpack density was accounted for in the flux calculation. For each sampling interval, the snowpack density corresponding to that sampling interval and snowpack layer was used to calculate the fluxes. This resolves the temporal and spatial variations the snowpack density would have on the flux. Conceptually, my sampling system in the snowpack was similar to a chamber with open sides giving it horizontally infinite spatial scale. Since ice lenses and crusts do not span over an infinitely large area, gases diffusing through the snowpack would continue to travel around the ice lenses and crusts, and gas concentration at each arbitrary horizontal layer in the snowpack would equilibrate and maintain a distinct concentration gradient. The deviation in flux results from different height intervals affirms (Fig. 2.5) and defines the maximum effect that this error has; as already elucidated above, these data show that flux results generally agreed within a factor of 1.5 from different height intervals.

Errors in the measurement of the snowpack height and the height of the tower arms were also a source of uncertainty when calculating the flux of CO$_2$. All gradient distances within the snowpack were determined by the distance between the tower cross arms. Due to the pressure exhibited from the compacting and creeping snow, some of the cross arms were
Figure 2.7: Sensitivity of calculated CO$_2$ fluxes to estimates of snow density. The propagated errors from porosity and tortuosity estimation resulting in snow density uncertainties estimates of ±10, 20 and 30% are shown as a function of the absolute snow density value.
bent by up to 5 cm, which introduces an error of as much as 15% in the flux calculation. The flux from any inlet to the snow surface depended on the accuracy on the snow depth determination. The associated error would be variable, depending on the time passed from the last visual inspection, and the accuracy of the interpolation from the SNOTEL record. Furthermore, this error relied on the absolute distance of the respective inlet to the snow surface. As this error propagated, its relative value would be larger for inlets closer to the atmosphere than for inlets nearer to the soil surface. I estimated the overall range of the error contributed from uncertainties in the gradient interval to the surface to be on the order of 10 to 100% in the most extreme cases; the latter for inlets very close to the snow surface. Temperature measurements inside the snowpack are expected to have a minor contribution (< 5%) to the error estimate, as snowpack air temperatures were measured with relative high accuracy and showed little variation with time and space (Fig. 2.3). This error may increase slightly nearer to the surface where temperature changes were more pronounced than deeper in the snow.

I also investigated how sampling frequency may bias the flux calculation. Among previous studies, the frequency of measurements varied widely, ranging from as often as half-hourly (Musselman and Massman, 2005) to as few as twice per winter (Hubbard et al., 2005). I used a bootstrap randomization without replacement test to examine the sampling frequency effects (Fig. 2.8). First, I calculated a daytime (09:00–17:00 MST) mean to provide a more realistic comparison to manual sampling protocols. For each sampling frequency the appropriate number of daytime values (ranging from 5 to 120 days) was randomly selected and a mean calculated. This process of calculating means was repeated 1000 times, and the 95% confidence interval was determined as the 25th and 975th mean (Manly, 2007). The 95% confidence limit for the continuous data was 0.69 µmol m⁻² s⁻¹ to 0.82 µmol m⁻² s⁻¹ in 2007. Monthly sampling resulted in an increase in the 95% confidence interval ranging from 0.50 µmol m⁻² s⁻¹ to 1.1 µmol m⁻² s⁻¹. The 95% confidence interval for weekly sampling (30 samples) of 0.69 µmol m⁻² s⁻¹ to 0.82 µmol m⁻² s⁻¹ moved close to the results from this boot-
strap analysis meant that a weekly sampling frequency (i.e. one gradient per week) would give a mean flux value that was within ±10% of the results from the continuous measurements of CO₂ flux.

2.5.4 Assessment of advection on flux calculations

The observed day-to-day variability in calculated fluxes and differences in results from different gradient intervals fully cannot be accounted for even when combing all of the above considered sampling and measurement errors and uncertainties, consequently other factors must contribute to the flux variability. Other research has shown that the CO₂ efflux from snow-covered soils is sensitive to volumetric soil moisture and soil temperature (e.g. Oechel et al., 1997; Winston et al., 1997; Groffman et al., 2006; Monson et al., 2006a). The lack of significant changes in these variables during DOY −11 to 19 (Fig. 2.6) suggests that CO₂ emissions from the soil might be reasonably constant over this 30-day period; it is therefore also unlikely that the variability in the flux data is caused by changes in the CO₂ source term. Hence, I conducted further analysis of the potential role that advection may play in the measured CO₂ mixing ratios and calculated diffusion fluxes in the snowpack.

Snowpack ventilation has been shown to be related directly to the high frequency pressure gradients that develop above the surface and inside the snowpack during windy conditions (Albert and Hawley, 2002; Massman and Frank, 2006; Massman, 2006). From the differential pressure data, measured at 1-s resolution, the 10-min mean values (Fig. 2.9a), the standard deviation within each 10-min window (Fig. 2.9b), and the amplitude (Fig. 2.9c) were calculated for the corresponding time window. All three of these graphs show strong correlations between these variables, with the highest degree of correlation seen in the dependency of the standard deviation of the differential pressure data on the 10-min mean wind speed (Fig. 2.9b). Waddington et al. (1996) described that the forcing term, the pressure amplitude, has a 2nd order relationship with wind speed (\(A_{\bar{u}} \propto \bar{u}\), where \(A_{\bar{u}}\) is the amplitude of the mean differential pressure and \(\bar{u}\) is the mean wind speed). However, depending on the
Figure 2.8: Bootstrap randomization without replacement test to examine sampling bias on CO₂ flux calculations. Estimation of 95% confidence interval limits based on the number of days sampled in the randomization. Value at ~120 days is the actual confidence limit based on the measured daily fluxes. The average flux (dashed line) in 2006 and 2007, respectively, were 0.74 µmol m⁻² s⁻¹ and 0.76 µmol m⁻² s⁻¹ using average daily flux data between 09:00 and 17:00 MST.
topography of the surrounding terrain, a 1st order relationship between pressure amplitude and wind speed \( A_p \propto \bar{u} \) may be more appropriate (Massman, 2006). My regression analyses, examining different regression fits, resulted in a best fit (highest \( r^2 \)) for the 1st order relationship between differential pressure amplitude and 10-min mean wind speed (Fig. 2.9c). These analyses showed that the pressure amplitude was directly proportional to wind speed. Thus, it appeared appropriate to use wind speed as the forcing proxy for assessing advection.

In Fig. 2.10a, mixing ratio gradients from the 60–30 cm interval were plotted against the mean hourly wind speed during the measurement interval. With increasing wind speed, the magnitude of the CO\(_2\) mixing ratio gradient became progressively smaller. The mixing ratio gradient reached \(-141\)µmol mol\(^{-1}\) m\(^{-1}\) at the highest recorded winds, while the gradient for zero wind conditions, as extrapolated from the 2nd order polynomial regression fit, was \(-1090\)µmol mol\(^{-1}\) m\(^{-1}\). Mixing ratio gradients varied by a factor of \(\sim 8\) under the wind conditions encountered during this experiment. As the mixing ratio gradient translated proportionally to the final CO\(_2\) flux, the flux results shown in Fig. 2.10b display a similar range of dependency, with calculated flux values at the highest winds dropping to a mere \(1/8^{th}\) of values derived under calm conditions.

Some of my earlier analyses of the diurnal dependency of the CO\(_2\) flux had suggested on average 25% flux increase between early morning and mid-afternoon hours. Figure 2.11 illustrates this analysis by showing the mean hourly deviation from the daily mean flux values (for WI2006 and WI2007) that led to this assumption. The added wind speed data shed new light on this discussion. There was an obvious anti-correlation in the diurnal behavior of winds and calculated flux values, with higher winds coinciding with lower flux values and vice versa. Using the amplitudes of WI2007 data series, the 0.3 m s\(^{-1}\) change in wind speed corresponded to a \(-0.05\)µmol m\(^{-2}\) s\(^{-1}\) change in the diffusion-calculated CO\(_2\) flux. Similarly, for WI2006, a 0.3 m s\(^{-1}\) change in wind speed yielded a 0.03µmol m\(^{-2}\) s\(^{-1}\) change in CO\(_2\) flux. The WI2007 result agreed with Fig. 2.10b, where similarly the slope of the regression function within the linear range predicted a \(-0.06\)µmol m\(^{-2}\) s\(^{-1}\) change in the diffusion-CO\(_2\)
Figure 2.9: Relationship between measures of the pressure fluctuations, representing the effect of wind-pumping, as a function of absolute 10-min average wind. The differential pressure data represent a the mean of 1-s data, b the standard deviation of the 4464 measurements within each 10-min interval, and c the mean value of the amplitudes that were calculated from the recorded maximum and minimum values during each minute. Regression curves shown are the selected best fit results of 1\textsuperscript{st} and 2\textsuperscript{nd} order regression calculations that were examined. The blue curve represent the 95% confidence interval of the regression result.
Figure 2.10: a CO$_2$ concentration gradient ($\frac{\partial CO_2}{\partial z}$) and b CO$_2$ flux derived from inlets at 30 cm and 60 cm and wind speed from DOY -11 to 19 with 2nd order polynomial fit solutions ($y = cx^2 + bx + a$). The blue curves depict the 95% confidence interval for the fits. The $y$-intercept, $a$ term, would represent the CO$_2$ concentration gradient and CO$_2$ flux under zero wind condition.
Figure 2.11: Deviation from daily means of wind speed (left $y$-axis) and CO$_2$ flux (right $y$-axis) for WI2006 and WI2007. The error bars are the standard errors for each bin of data. The CO$_2$ fluxes were calculated from the 60–30 cm concentration gradient for both WI2006 and WI2007.
flux for a 0.3 m s$^{-1}$ wind speed increase. Since results presented in Figs. 2.10b and 2.11 were in qualitative agreement, results from the 30 day period of analysis shown in Fig. 2.10b are expected to be representative for the entire season shown in Fig. 2.11.

Bowling et al. (2008) illustrated that the transport of trace gases through the snowpack at the C-1 Ameriflux site on Niwot Ridge was dominated by diffusion with short-term variability driven by advection. Furthermore, they showed that the influence of diffusion was differentially apparent at greater depths. I evaluated how advection may change the mixing ratios of CO$_2$ between the soil surface and the top of the snowpack by testing the relationship between CO$_2$ mixing ratios at each inlet height and wind speed with 2nd order polynomial solutions ($y = cx^2 + bx + a$) (Fig. 2.12). The regression term $a$, denoting the zero-wind speed snowpack CO$_2$ mixing ratio at each inlet height, linearly increased going from the snow surface towards the bottom of the snowpack. The term $b$ demonstrates the “strength” of the wind’s influence on the CO$_2$ mixing ratio. This value steadily increased towards the soil surface (going deeper into the snow), indicating that the wind effect on absolute CO$_2$ levels was highest at the bottom of the snowpack, where absolute CO$_2$ mixing ratios were the highest. Solutions for $c$ characterized the curvature of the best fit equation. Here, values increased towards the bottom of the snowpack, indicating an increasingly higher sensitivity towards winds deeper in the snow. The quality of the regression fit $r^2$ improved with increasing depth, showing again that the wind-pumping effect was best described by these algorithms at the bottom of the snowpack. Lastly, the 95% confidence interval demonstrated how at higher wind speeds, the uncertainty of CO$_2$ mixing ratio in the snowpack increases.

An important conclusion from these analyses is that measurements made during high wind conditions would have increased errors in calculating CO$_2$ gradients and for flux calculations. Similar to Bowling et al. (2008), my findings showed that advection effects at the bottom of the snowpack were described best by these algorithms.

To demonstrate the bias from wind-pumping on flux results, CO$_2$ fluxes calculated from mixing ratio data, as obtained during actual wind speed conditions encountered during
Figure 2.12: Relationship between CO$_2$ mixing ratio measured at each inlet height above and in the snowpack and wind speed from DOY $-11$ to $19$ with 2$^{nd}$ order polynomial fit ($y = cx^2 + bx + a$). The blue curve shows the 95% confidence interval for the 2$^{nd}$ order fit. Coefficient values printed in red denote cases that are statistically significant ($p < 0.05$). The $y$-intercept, $a$ term, represents the extrapolated CO$_2$ mixing ratio under zero wind condition.
Figure 2.13: Calculated flux under observed and inferred zero wind conditions for different concentration gradient intervals (category axis) from DOY -11 to 19. The wind-corrected condition is derived from CO₂ mixing ratio versus wind speed relationship shown in Fig. 2.12. The medians for each scenario (observed and wind-corrected) are shown in its respective colored solid lines. For observed win, the median flux is 0.54 µmol m⁻² s⁻¹. The median wind-corrected flux is 0.85 µmol m⁻² s⁻¹.
DOY −11 to 19, were compared with fluxes derived from extrapolated gradients for zero wind speed conditions. These latter values were derived from the regression equations (intercept values of the regression solutions presented in Fig. 2.12). Fluxes were calculated in both ways for every sampling interval combination. While results for individual gradients showed a fair degree of variability, overall the findings shown in Fig. 2.13 illustrate that in every case higher flux values were obtained for the wind-corrected calculation. The median flux value calculated from the in situ gradient data of 0.54 µmol m$^{-2}$ s$^{-1}$ accounts to 64% of respective value derived from the wind-corrected calculation (0.85 µmol m$^{-2}$ s$^{-1}$). This finding defines the possible error that is associated with the application of Fick’s law under neglect of wind-pumping effects and the resulting underestimation of flux results.

2.6 Summary and conclusions

I have evaluated the DM method for studying wintertime CO$_2$ fluxes at Niwot Ridge, Colorado. A particular advantage of this method stems from the reduced transfer rate (in comparison to ambient air) in the snowpack, resulting in largely elevated mixing ratios that build up inside the snow. This condition causes gradients in mixing ratios of gases released from the subnival soil, which reach magnitudes that are much larger than above the snow surface. This allows measurement of these gases with relatively simple analytical instruments. Deriving fluxes of these gases requires quantitative description of the gas transport in the airspace of the snowpack. Here, I used the by far most extensive dataset published to date to examine the commonly applied Fick’s law of diffusion approach for computation of fluxes from these data.

Fluxes calculated from all possible gradients from eight inlet heights were found to generally agree within a factor of 1.5 with the overall median. Several factors contribute to variability and uncertainty in these data, with the error in the snow porosity and tortuosity variables, which both are indirectly derived from snow density measurements, being one of the major contributing factors. This research demonstrates how these uncertainties are
reduced when data from several gradient heights can be statistically evaluated and combined for deriving a more representative, average flux value.

Using wind and differential pressure measurements, I was able to develop the constraints from the neglect of wind-pumping on fluxes derived by the diffusion approach. Gas mixing ratios of soil emissions and their snowpack gradients in general declined with increasing winds, causing a negative bias on calculated fluxes, with fluxes calculated at the highest observed winds being less than 13% of those derived under no-wind conditions. Using a 3-week record from mid-winter and averaging over all possible gradient combinations, I determined that fluxes calculated by the diffusion method—neglecting wind-pumping effects—were 36% lower than wind-corrected calculations for conditions at this particular site.
Chapter 3

Wintertime flux measurements of carbon dioxide, ozone, and nitrogen oxides through snow at a hardwood forest in northern Michigan

This chapter is in preparation for submission to *Elementa: Earth and Environmental Science*.


3.1 Abstract

Snowpack-atmosphere gas exchanges of CO$_2$, O$_3$, and NO$_x$ (NO + NO$_2$) were investigated at the University of Michigan Biological Station (UMBS), a mid-latitude, low elevation hardwood forest site, during the 2007 winter season. An automated trace gas sampling system was used to determine trace gases concentrations in the snowpack at multiple depths continuously throughout the snow covered period. The results were compared with the “White on Green” study conducted at the Niwot Ridge (NWT) Long Term Ecological Research site. The average winter CO2 flux ± s.e. at UMBS was $0.54 \pm 0.037 \mu\text{mol m}^{-2} \text{s}^{-1}$ using the gradient diffusion method and at $0.71 \pm 0.012 \mu\text{mol m}^{-2} \text{s}^{-1}$ using the eddy covariance method, and in a similar range as found for NWT. Observed snowpack-O$_3$ exchange was also similar to NWT. However, nitrogen oxides (NO$_x$) fluxes from snow at UMBS were 10 times smaller than those at NWT, and fluxes were bi-directional with the direction of the flux dependent on NO$_x$ concentrations in ambient air. NO$_x$ in snow also showed diurnal dependency on incident radiation. These NO$_x$ dynamics in the snow at UMBS were notably different com-
pared to NWT, and primarily determined by snow-atmosphere interactions rather than by soil NO$_x$ emissions.

### 3.2 Introduction

Winter historically has been perceived as a period of suppressed biogeochemical activity (Campbell et al., 2005). It was assumed that trace-gas exchange between the soil and the atmosphere halted with snow cover or when soil temperatures dropped to below 0°C (Steudler et al., 1989; Bouwman, 1990). However, it was discovered later that CO$_2$ concentrations were elevated at the bases of snowpack at high latitude or high elevation sites (Kelley et al., 1968; Coyne and Kelley, 1971; Solomon and Cerling, 1987), which was indicative of continued biological activity even after snow cover with soil temperatures near 0°C (Taylor and Parkinson, 1988; Sommerfeld et al., 1991). Recent studies showed how snow insulates the soil from ambient air temperatures (Groffman et al., 2001) that microbial activity under snow could stay active until soil temperatures reached below −5°C (Brooks et al., 2005) and that the soil microbial community during snow cover was distinctively different from the growing season (Monson et al., 2006a). These findings challenged the traditional view of winter with respect to the annual biogeochemical cycle.

As the recognition grew that wintertime processes can make important contributions to the annual biogeochemical budget, the number of flux measurements during the snow-covered season increased for different natural ecosystems. For instance, measurements were made at high latitude tundra and permafrost sites (Zimov et al., 1996; Fahnestock et al., 1998; Welker et al., 2000), at high elevation alpine and subalpine sites (Sommerfeld et al., 1993; Brooks et al., 1996; Williams et al., 1998; Schurmann et al., 2002; Monson et al., 2006a,b; Schindlbacher et al., 2007; Bowling et al., 2008; Liptzin et al., 2009), and at low elevation, agricultural and forested sites (van Bochove et al., 1996; Alm et al., 1999; Groffman et al., 2001; Maljanen et al., 2007). Result from these measurements indicated that a large percentage (as much as 60%) of growing season carbon uptake can be lost during the
winter, emphasizing the importance of trace gas exchange through snow for ecosystem functioning and annual biogeochemical budgets (Sommerfeld et al., 1993; Monson et al., 2005; Schindlbacher et al., 2007).

The aforementioned studies examined stable greenhouse gases, i.e., CO₂ and N₂O, with little attention given to reactive gases. From the atmosphere and climate perspective, knowing how reactive trace gases might interact with snow is vital as these gases influence the oxidation capacity of the atmosphere and ozone formation. From the ecological perspective, reactive trace gases, for instance nitrogen oxides, have an important function in various biogeochemical processes such as by influencing the nutritional balance of terrestrial ecosystems (Sparks et al., 2003; Lockwood et al., 2008; Nave et al., 2009) and acid deposition (Schulze et al., 1989). Trace gas exchange studies conducted in the Polar Regions showed that snow is a highly reactive medium for photochemical reactions, heterogeneous reactions, and physical exchange processes (Grannas et al., 2007; Simpson et al., 2007; Domine et al., 2008). As a result, the impact that snow could have on the overlying atmosphere could be important. For example, complete depletion of ambient ozone was observed over the snowpack in the Polar coastal regions (Simpson et al., 2007), while at the South Pole, a doubling in ambient ozone concentration was seen (Helmig et al., 2008). In forested sites, the fate of nitrate—and important source for nitrogen for plants—in the winter is complicated by snow, as it serves as a transporter of (deposited) nitrate (Brooks and Williams, 1999) and a chemical substrate for photochemical conversion of nitrate to nitrogen oxides (Honrath et al., 2000a).

Another motivation is to improve our understanding how declining snowpack due to the changing climate will affect trace gas exchange in the winter. Future climate scenarios are predicting less snow and more summer rain (Barnett et al., 2005). In the past 50 years, the Western U.S—for instance—has experienced reductions in snowpack (Hamlet et al., 2005; Mote et al., 2005) and higher springtime temperatures (Aguado et al., 1992; Kalra et al., 2008). It is likely that the decline in snowpack will result in modification to plant and microbial metabolism and distribution (Groffman et al., 2001), ultimately changing the
The most comprehensive study to date on gas fluxes in snow-covered ecosystems was conducted at the Niwot Ridge (NWT) Long Term Ecological Research site (Williams et al., 2009a). This study included measurements of the stable greenhouse gases CO$_2$ and N$_2$O as well as the more reactive gases NO$_x$, O$_3$, and volatile organic compounds (VOCs) and emphasized both the role of biological activity under the snowpack and chemical reactions within the snowpack. I collected similar measurements at a low elevation site with two goals in mind. One is determining if the results from NWT apply at sites with different snowpack characteristics. The other is to predict how “at-risk” snow can potentially alter the fluxes of trace gases through snow. Here, “at-risk” snow is defined as current snow that is at or near the melting phase during mid-winter conditions. With climate change, “at-risk” snow would melt and not accumulate but precipitation would occur as rain instead. Low elevation sites have warmer wintertime air temperatures than at high elevation sites. Snow at low elevation sites would be “at-risk”, and thus, low elevation sites can serve as proxies to future snow conditions in high elevation sites.

In this study, I measured trace gas in the snowpack at a low elevation, hardwood forest site in Michigan and compared them to similar measurements made at NWT. I hypothesized that soil emissions of CO$_2$ and NO$_x$ would be lower at this low elevation site due to reduced soil microbial activity associated with colder soils below a shallower and less insulating snowpack (Groffman et al., 2001). I also measured trace gases in a second plot in Michigan in which the soil surface was covered with a Tedlar® sheet to determine if the soils were the source of the trace gases in the snowpack.
3.3 Materials and methods

3.3.1 Site description

This study was conducted at the University of Michigan Biological Station (UMBS) AmeriFlux Tower site (45°33′35.0″ N, 84°42′49.6″ W, 234 m ASL) during the snow-covered period from 24 November 2007 to 10 April 2008. The AmeriFlux Tower site is described in detail elsewhere (Schmid et al., 2003; Curtis et al., 2005; Gough et al., 2007; Nave et al., 2009). Briefly, this ecological research site is in a transition zone that is between mixed hardwood and boreal forests with bracken fern (Pteridium aquilinum) dominating the understory. The forest is classified as a deciduous broadleaf forest. The soil is mostly excessively drained spodosols (92.9% sand, 6.5% silt, 0.6% clay, pH 4.8) derived from glacial drift and categorized as entic haplorthods (Pearsall, 1995).

Winter is defined as the period of snow cover. Winter at UMBS starts in November and ends the following year in April. Leaf fall happens in early November. The average winter temperature (from 1979 to 2011) at the site was −0.65°C. Snowfall typically begins in mid-November, but the site has received occasional snowfall in late October. From late November, snow accumulates and persists until early April. Maximum snow depths normally reach just below a meter (average 76 cm). Also, there is on average 270 mm of rainfall in the winter (Vande Kopple, 2011c).

3.3.2 Experimental setup

The gradient diffusion method (GDM) was used for inferring fluxes from chemical gradient measurements. The automated trace gas sampling system of Seok et al. (2009) was modified for use in this study. The system was expanded by a second plot to allow for inferring whether the primary source of measured trace gases was biogenic (i.e. from the soil) or non-biogenic (i.e. from the atmosphere or the snowpack). Two adjacent 3 m × 3 m plots were setup 3 m east of the AmeriFlux tower prior to snowfall. Each of the two plots
were marked off with a PVC-constructed frame (Fig. 3.1). One of the frames was wrapped in Tedlar® sheet (5 m × 5 m, 50 µm thickness; Emco Industrial Plastics, Inc., Cedar Grove, New Jersey, USA) around the bottom and the sides, leaving the top open. The Tedlar® sheet was used to prevent soil emissions and lateral flow of trace gases from the surrounding area to interact with the snowpack in the plot. A small drain was installed at one of the corners to allow snow melt and rain water to drain out of the area. The frame at the other plot was left exposed to permit soil emissions and lateral flow of trace gases into the snowpack in that area. At the center of each plot, a 1 m tall tower with multiple 30 cm long cross bars was erected. The cross bars held a pair of sampling inlets. The tower (or gradient tower) in the plot with the Tedlar® sheet (hereon labeled as the “Tedlar plot”) had its cross bars positioned at 10 cm, 20 cm and 30 cm above the ground in a crisscrossing pattern. Similarly, the gradient tower in the plot without the Tedlar® sheet (hereon as the “natural plot”) had its cross bars placed at 2 cm, 10 cm, 20 cm, 30 cm, 40 cm and 90 cm above the ground also in a crisscrossing pattern. In total, there were nine paired inlets for sampling ambient and snowpack interstitial air. The purpose of having the cross bars in such arrangement was to minimize the potential artifacts caused by active sampling of snowpack interstitial air due to the close proximity of the sampling inlets to each other Albert et al. (2002). After installing the gradient towers, snow was allowed to accumulate naturally around them in their respective plots; the snow was not disturbed in both plots throughout the snow-covered period.

The sampling lines from the nine paired inlets were quarter-inch (3.9 mm inner, 6.4 mm outer) diameter PFA tubing (Parker Hannifin, Cleveland, Ohio, USA) each 10 m long that ran from the inlets to a valve manifold, which was located in a building by the AmeriFlux tower that housed all of the instrumentation and excess tubing. The sampling lines were heated to 1 °C to prevent water vapor from condensing and freezing in the lines. Air was drawn from each paired inlet for 10 min. The switching between the paired inlets was done sequentially starting from the 90 cm paired inlet down to the 2 cm paired inlet in the natural plot, and then it continued on to the 30 cm paired inlet and finished at the 10 cm paired
Figure 3.1: Photos of the experimental setup. Each study plot was 9 m$^2$ marked off by the PVC frame. The plot in the foreground is the natural plot, where soil-snow-air interaction was allowed. The plot in the background is the Tedlar plot, where soil-snow interaction was blocked but snow-air interaction was permitted.
inlet in the Tedlar plot. One cycle through all of the paired inlets took 90 min; this yielded 16 cycles per day.

Sampled air was analyzed for CO$_2$, O$_3$, NO, and NO$_x$ (NO + NO$_2$) every 10 s during each 10 min sampling period. CO$_2$ was analyzed using an infrared gas analyzer (LI-7000; LI-COR, Lincoln, Nebraska, USA). The analyzer was calibrated biweekly following the procedure of Liptzin et al. (2009). A UV absorption monitor (DASIBI 1003-AH) was used to monitor O$_3$ mixing ratios. Prior to deployment of the ozone monitor, it was calibrated according to the method of Brodin et al. (2010). A NO-O$_3$ chemiluminescence analyzer with a molybdenum oxide (MoO) catalyst heated to 325 °C (Model 42C-TL; Thermo Electron Corporation, Franklin, Massachusetts, USA) was used to analyze for NO and NO$_x$. NO$_2$ data were derived by subtracting the measured NO$_x$ from the measured NO data. The analyzer was calibrated biweekly using the procedure of Helmig et al. (2009a). The 1003-AH and the Model 42C-TL each respectively pulled 1.8 ± 0.1 L min$^{-1}$ and 1.2 ± 0.1 L min$^{-1}$ of air through the sampling line, while the LI-7000 used the exhaust from the 1003-AH, therefore it did not require active pulling of air from the sampling line. The resulting total flow through the sampling line was 3.0 ± 0.2 L min$^{-1}$.

Nitric oxide undergoes rapid oxidation through its reaction with O$_3$. Since the mixing ratio of NO is typically two orders of magnitude smaller than O$_3$, care must be taken to avoid NO losses in the sampling lines due to the gas-phase reaction with ambient O$_3$ and to the reaction of NO during transport from the inlet to the analyzer (Helmig et al., 2009a). The theoretical residence time of the trace gases in the sampling line was approximately 1 s. Applying the method of Helmig et al. (2009a), the loss of NO was calculated to be <3% in our sampling lines for any given moment for the O$_3$ levels sampled in ambient air. Because O$_3$ in the snowpack was usually <40 nmol mol$^{-1}$, losses of NO from snowpack interstitial air were expected to be lower than this estimation; consequently, I did not correct for this minor loss of NO in the sampling line.
3.3.3 Environmental parameters

Ambient air and snowpack temperatures were measured using type-E thermocouples, and soil temperature was measured using a type-K thermocouple. From the AmeriFlux tower, ambient air temperature was measured at 2 m above the ground, which is in the understory layer of the UMBS forest (Seok et al., 2013), and soil temperature was measured at 2 cm. In the natural plot, snowpack temperatures were measured at the 2 cm, 10 cm, 20 cm, 30 cm and 40 cm levels on the gradient tower. Similarly, in the Tedlar plot, snowpack temperatures were measured at the 10 cm, 20 cm and 30 cm levels on the gradient tower.

Snowpack depth was read daily through a webcam (LifeCam VX-1000; Microsoft Corporation, Redmond, Washington, USA) pointing to a 1 m stick ruler secured to the ground in the natural plot. Snowpack density was measured in an open area 3 m south of the natural plot. Fifteen snow pits were dug between January and April. Snow properties were measured using protocols described by Williams et al. (1996, 1999).

Rain precipitation was recorded in 30 min intervals at 2 m above the ground from the AmeriFlux tower. Daily snowfall was recorded by the resident biologist at UMBS in accordance of the National Weather Service cooperative observation protocol, i.e., with a 0.093 m² (1 ft²) platform with a meter stick attached, daily snow accumulation was checked each morning at 08:00 EST. Soil moisture was measured using three water reflectometers with 30 cm long probes (CS616-L; Campbell Scientific, Logan, Utah, USA) installed vertically into the soil around the natural plot.

3.3.4 Flux calculations

Gradient diffusion flux

Trace gas fluxes through snow were calculated using a steady-state diffusion model (Fick’s first law of diffusion) based on the vertical concentration gradients through the snow-
pack along with records of snow depth, density, and temperature following the approach of Sommerfeld et al. (1993) as modified by Seok et al. (2009):

\[ F_{\text{diff}} = -\alpha D \phi \tau \left( \frac{T}{273.15} \right)^{1.81} \frac{d\chi}{dz}, \]

(3.1)

where \( F_{\text{diff}} \) is the flux of the trace gas (mol m\(^{-2}\) s\(^{-1}\)), \( \alpha \) is a constant for unit conversion (44.613 mol m\(^{-1}\)), and \( D \) is the diffusion coefficient of the trace gas (m s\(^{-2}\)) (see Table 3.1 for values of \( D \) used for this study). \( \phi \) is the porosity of the snowpack calculated from the bulk density of snow, \( \tau \) is the tortuosity of the snowpack calculated from the porosity according to Du Plessis and Masliyah (1991), and \( T \) is average snow temperature (K). The mole fraction gradient \( (\frac{d\chi}{dz}) \) is the result of a difference in mixing ratio \( (d\chi [\text{mol mol}^{-1}]) \) between sample heights, divided by the distance \( (dz [\text{m}]) \).

Table 3.1: Diffusion coefficients \((D)\) of trace gases used in the gradient diffusion method

<table>
<thead>
<tr>
<th>Gas species</th>
<th>( D \times 10^{-4} \text{ m}^2 \text{ s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)</td>
<td>0.1381</td>
</tr>
<tr>
<td>O(_3)</td>
<td>0.1444</td>
</tr>
<tr>
<td>NO</td>
<td>0.1361</td>
</tr>
<tr>
<td>NO(_2)</td>
<td>0.1802</td>
</tr>
</tbody>
</table>

\(^a\) \( D \) values are from Massman (1998)

Snow density was surveyed 11 times throughout the season. The data gap was filled via interpolation. I used a multiple linear regression to determine the relationship among measured snow density, depth, temperature, and time of snow cover.

**Eddy covariance flux**

Above canopy flux of CO\(_2\) was determined with the eddy covariance method (ECM). Details on the processing and analysis protocols of the turbulence data for calculating fluxes are described by Schmid et al. (2000, 2003). The fluxes were calculated in 30 min bins, yielding 48 CO\(_2\) flux data points per day.
3.3.5 Data processing

Snowpack-\text{CO}_2 data were analyzed using approaches similar to Liptzin et al. (2009). Daily \text{CO}_2 fluxes were calculated by averaging the 16 flux data points per day for GDM and the 48 flux data points per day for ECM. Environmental variables (snow depth, air temperature, soil temperature, and soil moisture) were tested as predictors of the daily flux using simple linear regression. The seasonal fluxes—calculated by averaging the daily fluxes—from each flux measurement technique were compared using a Mann-Whitney U-test, since the data were not normally distributed and normality could not be achieved with any data transformation technique. The reactive gas data (i.e. \text{O}_3, \text{NO}, and \text{NO}_x) were analyzed to investigate their dependency on irradiance following Helmig et al. (2009a). Data below the limit of detection (LOD) were replaced with LOD/2 for statistical analyses (Helsel, 1990). All statistical analyses were conducted using MATLAB (R2012b Statistical Toolbox, The Mathworks, Inc., Natick, Massachusetts, USA) with a level of significance (\( \alpha \)) of 0.05. Gaps in the data were due to taking the instruments offline for servicing, freezing at the sampling inlets, or damaged switching valves. Results are reported as mean \( \pm 1 \) standard deviation (s.d.) unless otherwise noted.

3.4 Results

3.4.1 Snowpack and soil characteristics

Continuous snow cover over the measurement plots started on DOY 326 (22 November 2007) and ended on DOY 101 (10 April 2008) (Fig. 3.2). From DOY 328 to 11, the snowpack remained relatively shallow (\(< 40 \text{ cm})\). After DOY 11, the snow steadily accumulated until reaching maximum depth of 60 cm on DOY 41. Prior to the onset of snow melt (DOY 90), there were several warm (i.e. above freezing) periods, which usually were associated with rainfall, throughout the winter that led to melting at the snow surface. Subsequent freezing temperatures after these warm period caused the formation of ice features (i.e. crusts, lenses,
or layers) in the snowpack. Also, snowfall and rain events contributed to specific layering in the snowpack. The bulk density of snow increased from 180 kg m\(^{-3}\) mid-season (DOY 11) to 380 kg m\(^{-3}\) at the time of snow melt (DOY 95) (not shown). The average snow density during the entire season was 240 ± 54 kg m\(^{-3}\). Soils at UMBS were relatively dry (< 15% water content), but soil moisture increased to above 25% during snow melt and above 30% during rain events.

The temperature in the snowpack ranged between −5°C and 0°C, with the upper 10 cm of the snowpack occasionally cooling below −5°C, influenced by the overlying air temperature. In contrast, the soil temperature began at 4°C at the start of the measurement period (DOY 328) and steadily decreased to 1°C by the end of January (DOY 25). Afterwards, the soil temperature varied between 1°C and 2°C. These recordings indicate that the soil was insulated from changing air temperature by the overlying snowpack. Air temperature varied widely with a minimum at −23°C and a maximum at 10°C before the snow melt period (DOY 90 to 101). The snowpack temperature turned isothermal during periods when air temperature was above 0°C. When the air temperature dropped below 0°C (e.g. DOY 56 to 65), a strong temperature gradient was formed in the snowpack.

### 3.4.2 Snowpack trace gas mixing ratios

**Carbon dioxide**

Ambient air CO\(_2\) mixing ratios ranged between 394 µmol mol\(^{-1}\) and 424 µmol mol\(^{-1}\) with a median of 404 µmol mol\(^{-1}\) during the study period. CO\(_2\) mixing ratios in the snow were noticeably different between the natural and Tedlar plots (Fig. 3.3a). Mixing ratios of CO\(_2\) in the natural plot snowpack were greater than in ambient air, with generally highest mole fractions closer to the soil. Also, CO\(_2\) in the snowpack rapidly increased after DOY 29, with the highest CO\(_2\) mixing ratio (1850 µmol mol\(^{-1}\)) measured near the soil surface at the 20 cm inlets when snow height was relatively steady at 50 cm. In the Tedlar plot, the
Figure 3.2: Snowpack and soil characteristics and environmental parameters. (a) Air temperature at 2 m. (b) Daily snow depth in the natural plot. The stars denote the locations of the ice features in the snowpack. The dashed lines indicate the levels in which the temperatures and trace gases were measured. (c) Temperatures measured from the gradient tower in the natural plot. (d) Soil temperature at 2 cm depth. (e) Daily snowfall. (f) Daily rainfall. (g) Soil volumetric water content between 0 cm and $-30$ cm.
maximum CO₂ mixing ratio in the snow varied between 394 µmol mol⁻¹ and 424 µmol mol⁻¹ (406 µmol mol⁻¹ median), which was similar as observed in ambient air.

**Ozone**

O₃ measured from both plots yield similar results (Fig. 3.3b). The mixing ratios in ambient air ranged from < 2 nmol mol⁻¹ to 60 nmol mol⁻¹ (28 nmol mol⁻¹ mean). O₃ levels increased during the study period by ∼ 30 nmol mol⁻¹. In both study plots, O₃ mixing ratios in the snow showed similar patterns; they decreased towards the soil, with values below the instrument detection limit of 2 nmol mol⁻¹ near the soil surface.

**Nitric oxide**

There were no apparent differences in NO measured between the two plots (Fig. 3.3c), but statistical analysis indicated that snowpack-NO mixing ratios in the Tedlar plot were significantly greater than in the natural plot (p < 0.05). NO mixing ratios above the snowpack varied between < 0.10 nmol mol⁻¹ and 1 nmol mol⁻¹, but they were mostly below the instrument detection limit of 0.10 nmol mol⁻¹, with the mean and median being 0.10 and < 0.10 nmol mol⁻¹, respectively. There were no apparent concentration gradients within the snowpack, but concentrations were on average ∼ 0.10 nmol mol⁻¹ greater in the snowpack than in ambient air.

**Total nitrogen oxides**

NOₓ also showed little difference between the two plots (Fig. 3.3d). In ambient air NOₓ varied widely between < 0.10 nmol mol⁻¹ and 8 nmol mol⁻¹ (1.2 nmol mol⁻¹ mean). In the snow, NOₓ levels generally decreased toward the soil surface as seen with O₃. The mean mixing ratio in the snow was 0.86 nmol mol⁻¹ for the natural plot and 1.1 nmol mol⁻¹ for the Tedlar plot.
Figure 3.3: Time series of trace gas mixing ratios in ambient air and in snow. (a) CO$_2$, (b) O$_3$, (c) NO, (d) NO$_x$. The legends identified by the “snow-covered” label are data points in the snow measured at the respective inlet levels from the gradient tower.
3.4.3 Snowpack trace gas profiles

Typical vertical snowpack trace gas profiles are presented in Fig. 3.4. The profiles are 20-day mean values constructed using data from DOY 52 to 72, and they are separated by study plot.

**Carbon dioxide**

There was a clear gradient in snowpack-CO$_2$ mixing ratio in the natural plot with considerably higher levels seen closest to the surface. This feature was not observed in the Tedlar plot (Fig. 3.4a). The CO$_2$ gradient indicated that CO$_2$ was transported from the soil surface to the snow surface. The slope of the CO$_2$ gradient in the natural plot was shallower (i.e. larger gradient, faster diffusion) above the 30 cm inlet height. Below the 30 cm inlet height, the gradient slope was steeper (i.e. smaller gradient, slower diffusion).

**Ozone**

Both plots had similar O$_3$ gradient profiles (Fig. 3.4b). Ozone mixing ratios dramatically dropped by 30 nmol mol$^{-1}$ approximately 10 cm below the snow surface, and it continued to decreased at a slower rate towards the soil surface.

**Nitric oxide**

The slopes of the NO gradients from both plots were not significantly different from zero, i.e., there were no discernible concentration gradients ($p < 0.05$ Fig. 3.4c).

**Nitrogen dioxide**

For NO$_2$, there was a clear gradient in the snowpack (Fig. 3.4d) with NO$_2$ generally decreased towards the soil surface. Between the plots, the NO$_2$ profiles were similar.
Figure 3.4: Trace gas profiles in the snowpack by study plot. (a) CO$_2$, (b) O$_3$, (c) NO, and (d) NO$_2$. Data over a 20-day period (DOY 52 to 72), when snow depth was relatively stable (~50 cm), where used to calculate the mean concentrations and their ±1 s.d. (x-error bar) from each height in the snowpack.
3.4.4  Diurnal cycle of snowpack trace gas mixing ratios

Continuing the analysis with the 20-day dataset (DOY 52 to 72) of snowpack trace gases, we examined the relationship between solar radiation and the reactive trace gases (O$_3$, NO, NO$_x$) in the snowpack (Fig. 3.5). The trace gas mole fractions in the snowpack used are from the measurements at the 30 cm inlets. Snow height during this four-day period was ∼50 cm, thus the 30 cm inlets were ∼20 cm below the snow surface.

**Solar radiation**

Solar radiation that was measured above the forest at 46 m above the ground had an average maximum intensity of 325 ± 228 W m$^{-2}$ (Fig. 3.5a).

**Ozone**

O$_3$ mixing ratios in the snowpack did not exhibit a diurnal cycle but ambient air O$_3$ did (Fig. 3.5b). Ambient air O$_3$ increased by 8 nmol mol$^{-1}$ from early morning (∼03:00 EST) to late afternoon (∼15:00 EST).

**Nitric oxide**

Following the solar radiation cycle, NO mixing ratios in the snowpack increased during the day (Fig. 3.5c). Ambient air NO increased by ∼2 nmol mol$^{-1}$ from its nighttime minimum in the morning hours until it reached its maximum at ∼10:00 EST. The daily maximum of NO in the snowpack occurred three to four hours after the ambient airs daily maximum. In the natural plot, NO in the snowpack increased by 0.15 nmol mol$^{-1}$, with maximum occurring between 13:00 and 14:00 EST. In the Tedlar plot, NO in the snowpack increased by 0.40 nmol mol$^{-1}$, with its daily maximum also occurring between 13:00 and 14:00 EST.

**Nitrogen dioxide**

NO$_2$ in the snow also followed the solar radiation cycle, but not as prominently as NO
Figure 3.5: Daily cycle of solar radiation and trace gas mixing ratios in ambient air (from the 90 cm inlet) and in snow (from the 30 cm inlet). (a) Incident radiation measured above the forest at 46 m. (b) O$_3$. (c) NO. (d) NO$_2$. Data over a 20-day period (DOY 52 to 72), when snow depth was relatively stable (∼50 cm), were used to calculate the diurnal averages. The shaded areas indicate the ±1 s.d. of the mean.
(Fig. 3.5d). In both plots, NO₂ in the snow increased from a minimum at ~03:00 EST to its maximum at ~15:00 EST closely resembling the ambient O₃ diurnal pattern. In the natural plot, NO₂ increased by 0.5 nmol mol⁻¹. In the Tedlar plot, NO₂ in the snow increased by 0.8 nmol mol⁻¹.

3.4.5 Snowpack trace gas fluxes

**Carbon dioxide**

In Fig. 3.6a, the CO₂ flux estimate made using ECM (above the forest at 32 m above the ground) is shown for comparison with the CO₂ flux determined by GDM. The CO₂ flux from the natural plot showed a wide spread. The highest CO₂ flux (1.5 μmol m⁻² s⁻¹) from the snow surface was observed late season (DOY 51 to 73), and prior to snowmelt, the lowest flux (0.02 μmol m⁻² s⁻¹) was observed mid-winter. The seasonal average ± standard error (s.e.) was 0.54 ± 0.037 μmol m⁻² s⁻¹. The spread of ECM flux was much narrower than for the GDM. The seasonal average ± s.e. estimated with ECM was 0.71 ± 0.012 μmol m⁻² s⁻¹. The calculated flux was significantly higher using the ECM method (Mann-Whitney, $U = 2401$, $p < 0.05$). The upper limit of the CO₂ fluxes from the Tedlar plot was $< 0.09$ μmol m⁻² s⁻¹. There was no statistically significant relationship between daily CO₂ fluxes estimated using ECM and GDM (Fig. 3.7).

**Nitric oxide**

NO fluxes (Fig. 3.6b) were small and mostly positive. They were largest late winter between DOY 51 and 73. The fluxes ranged from $-0.00014$ nmol m⁻² s⁻¹ to $0.0008$ nmol m⁻² s⁻¹ and from $-0.0003$ nmol m⁻² s⁻¹ to $0.0015$ nmol m⁻² s⁻¹ respectively for the natural and Tedlar plots. The mean ± s.e. NO flux from the natural plot ($0.0003 ± 0.00003$ nmol m⁻² s⁻¹) was less than the mean ± s.e. flux from the Tedlar plot ($0.0005 ± 0.00006$ nmol m⁻² s⁻¹). The difference in fluxes between the plots was statistically significant ($U = 1184$, $p = 0.00227$).
Figure 3.6: Time series of trace gas fluxes through snow and seasonal averages. (a) CO$_2$. (b) NO. (c) NO$_2$. The whisker-box plot on the right column shows the seasonal mean (square symbol) and the median (middle line in the box) flux values. The box lower and upper edges are the 25$^{th}$ and 75$^{th}$ percentiles. The ‘x’ symbols indicate the 1$^{st}$ and 99$^{th}$ percentiles. The ‘-’ symbols indicate the minimum and maximum flux values. Note that the CO$_2$ panel also has the eddy flux (ECM) results.
Figure 3.7: Comparing CO$_2$ flux values calculated using two different methods. Scatter plot of flux calculated using the eddy covariance method (ECM) versus the gradient diffusion method (GDM) color coded by snow-covered periods: early winter (black, DOY 328 to 8), mid-winter (red, DOY 9 to 54), late winter (green, DOY 55 to 94), and snowmelt (blue, DOY 85 to 101).
Nitrogen dioxide

NO₂ fluxes were also small but they were typically negative with large variances. The mean ± s.e. NO₂ flux from the natural plot snowpack was $-0.001 ± 0.0002 \text{nmol m}^{-2} \text{s}^{-1}$ and the flux from the Tedlar plot was $-0.0003 ± 0.0002 \text{nmol m}^{-2} \text{s}^{-1}$. The results between the plots were significantly different ($U = 1206$, $p = 0.00221$).

3.5 Discussion

3.5.1 Non-linearity in snowpack trace gas profiles

Snow acts as a physical barrier for diffusion of trace gases between the soil surface and the atmosphere. While the overall flux through the snowpack is driven by the concentration gradient between the source and the sink, temporal and spatial variability of the flux may be caused by specific snowpack properties (Sommerfeld et al., 1996; Winston et al., 1997; Albert and Perron, 2000), advection (Massman et al., 1997; Albert et al., 2002; Albert and Shultz, 2002; Massman and Frank, 2006; Bowling and Massman, 2011), or temporal and spatial variability in the drivers of soil biogeochemical processes. For reactive trace gases, fast chemical interactions with snow and other gases also affect the flux because these interactions occur on timescales shorter than the transport through the snowpack. The presence of ice layers, lenses, and crusts in and on top of the snowpack can interfere with gas transport through the snowpack. The formation of ice crusts and layers in the snowpack was frequent at UMBS, due to large variations in air temperatures both above and below 0°C and rain events. This appears to be common for sites with similar weather in the winter. For instance, Schindlbacher et al. (2007) observed air temperature ranging from $-19°C$ to 12°C and rain events at their study site, which led to layering and formation of ice features in the snowpack. Schindlbacher et al. (2007) and other studies (e.g, Mast et al., 1998; Björkman et al., 2010a) showed that these ice features did not block trace gas transport but caused non-linearity in the profiles. It is important to consider that the rate at which trace gases are released from
the soil or soil surface is not affected by properties of the snowpack; hence, the actual flux of CO$_2$ from the soil for instance does not change, but instead, the assumptions of the diffusive model used to calculate the flux may need to be revisited.

The non-linearity observed in the CO$_2$ profiles could be attributed to specific layering in the snowpack. It also could be caused by ventilation (Waddington et al., 1996). Albert and Hawley (2002) hypothesized that under low-wind conditions, ventilation rates are comparable to diffusion rates. Subjectively, during the measurement period, I experienced very calm wind conditions. In the 2008 winter season, wind speeds were measured 2 m above the ground next to the natural plot, and median wind speed was <0.3 m s$^{-1}$. Therefore, snowpack ventilation at UMBS is less likely the cause of the observed gas profiles.

Albert et al. (2002) cautioned that active pulling of snowpack interstitial air can cause unwanted ventilation and interference in determining trace gas concentration in the snowpack. The sampling arms were setup to limit the impact of active sampling in snow following the tower setup of Seok et al. (2009) (Fig. 3.1). Despite this, I suspect the non-linear profile in CO$_2$ partly caused by the interference and advection from active sampling. For example, CO$_2$ concentrations at the 20 cm paired inlets would be diluted by the sampling at the 40 cm paired inlets and the 10 cm paired inlets by the 30 cm paired inlets. Therefore, the observed profile below the 30 cm inlet height for CO$_2$ (Fig. 3.4a) may possibly reflect the role of the deployed active sampling methodology. To work around this issue in our flux calculation, I took the top two paired inlets below the snow surface and the ambient air paired inlet to derive the concentration gradient and calculate the flux.

O$_3$ and NO$_2$ are soluble with Henry’s constants on the order of 10$^{-2}$ (Sander, 1999), thus they are considered to be interacting gases with snow. In contrast, NO has a Henry’s constant that is an order of magnitude smaller (Sander, 1999) and is, therefore, considered a gas that does not interact with snow (Bartels-Rausch et al., 2013). Since the dominating species in NO$_x$ at UMBS was NO$_2$, the effective solubility of NO$_x$ would be similar to NO$_2$. From past measurements Helmig et al. (2009a), I expected the O$_3$ profile in snow to resemble
an exponential decay, and this was observed at UMBS (Fig. 3.4b). NO mixing ratios in the
snow were frequently near or below the instrument detection limit, and there was a large
variance in NO mixing ratios (as indicated by the error bars in Fig. 3.4c). This made it
difficult to infer any gradient behavior in the NO profile. The NOx profiles showed good
linearity but also with large variability (Fig. 3.4d). The large variability was likely due to
NO₂ interacting with the liquid water in the snowpack and surrounding snow crystals. As
NO₂ is transported into and through the snowpack, NO₂ can be adsorbed in the liquid water
in the interstitial space of the snowpack and surrounding snow crystals (O’Driscoll et al.,
2008). Also, the reaction with O₃, NO, and other constituents in the snow would lead to flux
divergence as NO₂ is destroyed or produced within the gradient interval. (This also applies
to other reactive trace gases in the snow, i.e., O₃ and NO.) Therefore, GDM is best suited
for calculating non-reactive or conserved trace gases but not for reactive gases. However, I
deemed that using the data from the top inlets under the snow surface was less effected by
snowpack inhomogeneity and utilized these data for a first order of magnitude estimate of
the exchange of these reactive trace gases at the snow surface.

3.5.2 Sources and sinks of snowpack trace gases

Comparing the in-snow trace gas concentrations and fluxes measured from the natural
plot and the Tedlar plot allows me to determine whether or not the soil, the snow, or the
atmosphere act as a source or a sink to those trace gases.

Soils

The fact that the snowpack-CO₂ concentrations in the Tedlar plot were not much
different compared to ambient air CO₂ concentrations (and that the CO₂ fluxes in the Tedlar
plot were nearly zero), while the snowpack-CO₂ concentrations and fluxes in the natural plot
were elevated (Fig. 3.3 and Fig. 3.6) provides two important pieces of information: (1) the
enhanced CO₂ levels observed in the snowpack are due to soil emissions. Common sources
of CO$_2$ from the soil are microbial and root respiration (Winston et al., 1997; Uchida et al., 2005; Monson et al., 2006b), and (2) the Tedlar cover was very effective in preventing gases from the soil entering into the snowpack in this plot.

As previously noted, NO values in the snow were frequently near or below the instrument detection limit. Therefore, it was difficult to infer any gradient behavior for NO. However, as in-snow NO concentrations from the natural plot were similar to the Tedlar plot, I concluded that microbial processes in soil (e.g. nitrification-denitrification) were not the main source of NO. Previous studies at NWT yielded contrary results. At NWT, NO concentrations were largely enhanced in the snowpack, and subniveal soil NO fluxes averaged between 0.05 nmol m$^{-2}$ s$^{-1}$ and 0.08 nmol m$^{-2}$ s$^{-1}$ (Helmig et al., 2009a). To my knowledge, there are no other NO measurements from unfertilized ecosystems in winter to compare. In non-snow covered ecosystems, temperature is thought to be the dominant factor controlling fluxes (Yienger and Levy, 1995). Thus, emissions should be lower in the winter than in the summer at these sites, but the causes for the two order of magnitude difference in NO fluxes between NWT and UMBS is unknown.

Soil is known to take up O$_3$ (Turner et al., 1974; Galbally and Roy, 1980) and NO$_2$ (Stella et al., 2012; Wang et al., 2012). If the removal of O$_3$ and NO$_2$ in snow were caused by soil uptake, then the gradient profiles of O$_3$ and NO$_2$ in both plots would be expected to be different, with lower mixing ratios of O$_3$ and NO$_2$ in the natural plot snowpack. However, concentrations and gradient profiles of O$_3$ and NO$_2$ in both plots were similar. This implies that the soil or soil surface plays only a minor role in the deposition of these gases under snow covered conditions.

**Snow**

The large decrease (>30 nmol mol$^{-1}$) in ozone within the first 20 cm from the snowpack surface once it enters the snowpack from the atmosphere can be attributed to the snow acting as an ozone sink. This also was observed at NWT in the tundra (Bocquet et al., 2007) and
subalpine meadow (Helmig et al., 2009a).

The NO fluxes from the snowpack in the natural plot and the Tedlar plot are both positive (released from the snow to the atmosphere) and similar in magnitude (Fig. 3.6b). Since both plots have similar outward fluxes, we infer that the snowpack is the primary source of NO or serves as the medium for NO production. The NO$_2$ fluxes are bidirectional and of larger magnitude than the NO fluxes. (The bi-directionality of the NO$_2$ fluxes is discussed in a later section.) The source for NO$_2$ in the snow is likely from the photolysis of deposited atmospheric nitrate; given that the concentration levels of NO$_2$ are also higher than NO in the snow, the observed snowpack-NO is likely the secondary product of nitrate photolysis.

The currently accepted nitrate photochemistry in snow is summarized in the following reaction scheme (Frey et al., 2009).

\[
\begin{align*}
\text{NO}_3^- + hv & \rightarrow \text{NO}_2 + O^- \quad (R1) \\
\text{NO}_3^- + hv & \rightarrow \text{NO}_2^- + O(^3\text{P}) \quad (R2) \\
\text{NO}_2^- + hv & \rightarrow \text{NO} + O^- \quad (R3) \\
\text{NO}_2^- + \text{OH} & \rightarrow \text{NO}_2 + \text{OH}^- \quad (R4)
\end{align*}
\]

NO can be produced via the photolysis of nitrite (NO$_2^-$) in snow (R3). It is also produced via photolysis of NO$_2$ as follows (Boxe et al., 2005):

\[
\text{NO}_2 + hv \rightarrow \text{NO} + O(^3\text{P}) \quad (R5)
\]

At night (in the absence of solar radiation), NO$_2$ can hydrolyze to nitrous acid (HONO) and nitric acid (HNO$_3$) (Chu and Anastasio, 2007).

\[
2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{HNO}_3 \quad (R6)
\]

where HNO$_3$ can undergo an autoprotolysis reaction:

\[
2\text{HNO}_3 \rightleftharpoons \text{NO}_2^+ + \text{NO}_3^- + \text{H}_2\text{O} \quad (R7)
\]
The diurnal cycle of NO$_x$ in UMBS snow was similar to that observed in a polar snowpack, where NO$_x$ concentrations in snow increased by a factor of two to three during the day (Peterson and Honrath, 2001). My findings are also consistent with the three-day study conducted by Honrath et al. (2000a) in upper Michigan, where similar diurnal dependency in NO$_x$ in snowpack air was observed. The diurnal NO cycle indicates photochemical production of NO. Likewise, NO$_2$ can also be produced via the photolysis of nitrate (NO$_3^-$) (R1), as evident from the diurnal cycle seen in the data. These diurnal cycles were only observed near the snow surface in the snowpack, which indicates that this photochemistry is most active in the upper layer of the snowpack. At night, the snow can act as a reservoir for deposited NO$_2$ by “storing” it in the form of HONO, HNO$_3$ (R6), and nitrate (R7) and then released it back into the atmosphere during the day from a result of the photolysis of HNO$_3$ or NO$_3^-$ (R1). Furthermore, these results illustrate that the snow acted as a source for these trace gases.

NO and NO$_2$ mole fractions in the snow during the day were $\sim 35\%$ higher in the Tedlar plot than in the natural plot, while the nighttime NO and NO$_2$ in snow levels were similar in both plots. Given the close proximity of the two plots, it was unlikely that the two plots experienced different atmospheric deposition rates or environmental conditions that might explain this difference. A possible explanation could be that the Tedlar plot was exposed to more solar radiation than the natural plot. Although the forest—in most part—was leafless during the winter (leaf area index of 1.5 m$^2$ m$^{-2}$, Seok et al., 2013), the trunks and branches attenuate solar radiation to the forest surface. Consistent with what is expected of solar intensity and O$_3$-NO$_x$ photochemistry, the lower O$_3$ and higher NO and NO$_x$ levels in the Tedlar plot snowpack relative to the natural plot snowpack implies that a higher degree of shading of the natural plot may be a possible cause for the discrepancies in the concentrations of these trace gases between the two plots.

The three to four-hour lag in the NO maximum in the snowpack versus the NO maximum in ambient air can be explained also by the attenuation of solar radiation by the trees.
Lower solar zenith angles are required for minimal shading by the trees and for sufficient amount of solar radiation to reach the snow surface in the forest. As a result, it is during mid-afternoon hours (13:00–14:00 EST) that maximum photochemical reactions can occur. The cause of the morning NO maximum in ambient air is discussed in the following section.

**Atmosphere**

The gradient profile of O$_3$ clearly shows that the source of snowpack-O$_3$ is the atmosphere. For CO$_2$ and NO, the atmosphere is a sink as ambient air concentrations of these trace gases were lower than in-snow concentrations.

The source of nitrate and NO$_2$ for the photochemical reactions of NO$_2$ in the snow is atmospheric. Extensive analyses of air mass transport at UMBS have been done using back trajectory models and correlating pollution concentration with wind direction (Cooper et al., 2001; Thornberry et al., 2001; Seok et al., 2013). Air masses from the south and southwest sectors carry higher levels of pollutants including ammonium and nitrate (Hill et al., 2005). Analyses of my data set showed that during southerly winds, NO$_2$ concentrations were higher above the snow surface than in the snow. This creates a concentration gradient with NO$_2$ transport into the snow as evident in the negative NO$_2$ fluxes (Fig. 3.6c). In contrast, during northerly winds, NO$_2$ concentrations were predominantly lower above the snow surface than in the snow, resulting in reversed NO$_2$ gradients with NO$_2$ release from the snow, hence the observed positive NO$_2$ fluxes (Fig. 3.6c).

The aforementioned trajectory studies also showed that NO$_2$ is transported into the UMBS forest airspace during the morning hours and that a prominent NO maximum above the forest canopy shortly after sunrise. Seok et al. (2013) concluded that one of the causes of the morning NO maximum (~09:00 EST) is the result of the photolysis of the advected NO$_2$ and that the onset of convective mixing during mid-morning is subsequently diluting the morning NO peak.
3.5.3 Bidirectional exchange of NO$_x$

It is very interesting that the NO$_x$ flux at UMBS is bidirectional at the snow surface unlike at NWT, where NO$_x$ was exclusively released to the atmosphere. Fluxes were negative (or NO$_x$ deposited into the snow surface) during polluted conditions, while fluxes were positive (or NO$_x$ released from the snow surface) during less polluted conditions at UMBS. This behavior is analogous to canopy-NO$_x$ exchanges tied to the effect of a compensation point, in which NO$_x$ is released from the canopy during low pollution conditions and taken up during high pollution conditions (Lerdau et al., 2000; Seok et al., 2013). The compensation point of NO$_x$ is \( \sim 1 \text{nmol mol}^{-1} \) (Lerdau et al., 2000), and this value was applicable for the canopy at UMBS according to the model study by Seok et al. (2013). I analyzed the snowpack-NO$_x$ flux and ambient air NO$_x$ concentration to determine if there is a NO$_x$ compensation point for the UMBS snowpack (Fig. 3.8). The apparent compensation point was estimated to be 0.92 nmol mol$^{-1}$. I found that 84% of the emission flux occurred during low pollution conditions and 70% of the deposition fluxes occurred during high pollution conditions.

3.5.4 Flux method comparison

My analyses comparing the CO$_2$ fluxes calculated from ECM and GDM (Fig. 3.7) illustrate that the two methods do not have a 1:1 relationship at daily time scales. However, ECM and GDM yielded results (ECM: 0.71 µmol m$^{-2}$ s$^{-1}$, GDM: 0.54 µmol m$^{-2}$ s$^{-1}$) that differed by 24% when evaluated over the snow covered period. One explanation for this is that the changes in soil and snow properties influence the calculation and interpretation of GDM fluxes, but over a longer period, the variance in the GDM flux is averaged out. Suzuki et al. (2006) reported that their GDM fluxes were 60% smaller than ECM fluxes, and they attributed this discrepancy to difference in measurement footprint size (i.e. area) and the components of the forest respiration (i.e. soil, understory vegetation, tree trunks/branches,
Figure 3.8: Relationship between NO$_2$ fluxes from the snow surface calculated using the gradient diffusion method and ambient-NO$_2$ above the snow surface. The vertical dash line indicates the compensation point (0.92 nmol mol$^{-1}$), i.e., the ambient air NO$_2$ level where the fluxes shifts between emission and deposition.
and the canopy/leaves). The footprint of GDM is limited to a few square meters and captures soil respiration only, while the footprint of ECM is much wider and includes above snow respiration by evergreen saplings scatter throughout the forest. This difference in footprint and measured components of forest respiration by each method are possible explanations for the larger ECM flux values.

Relationships between the standard environmental parameters (soil moisture, soil temperature, air temperature, and snow depth) and the daily variations in GDM and ECM fluxes of CO$_2$ were investigated by linear and polynomial regression analyses. I did not find any convincing correlation among these variables and the fluxes (Fig. 3.9).

### 3.5.5 Comparing UMBS and NWT

Table 3.2 provides a summary of the results from this study and from the NWT “White on Green” study. The duration of snow cover at UMBS was 100 days shorter than at NWT. Maximum snow depth at UMBS was $\sim 25\%$ of the maximum snow depths observed at NWT. Average air temperature during the snow covered period was similar at $-4^\circ$C for UMBS and $-5^\circ$C for NWT. Despite both sites having similar air temperatures, the soil at UMBS always stayed above freezing (average $1^\circ$C) even with shorter duration of shallower snowpack, which would provide less insulation for the soil. Climatological data show that air temperatures at NWT drop below freezing before the onset of significant snowfall in fall. In contrast, air temperatures at UMBS did not display this behavior. The difference in the timing of when air temperatures dropped and when snowfall occurred between the two sites help explain why both sites have different soil temperatures, despite both sites having similar average wintertime air temperatures.

Snowpack-CO$_2$ levels at UMBS did not reach as high as those measured at NWT ($\sim$1850 µmol mol$^{-1}$ versus $\sim$10 000 µmol mol$^{-1}$). Liptzin et al. (2009) ascribed deep snow (>2 m), high productivity (annual above ground NPP of 750 g m$^{-2}$), and stable soil temperatures at 0°C for the high CO$_2$ mixing ratios in snow at the soil surface. Annual NPP
Figure 3.9: Environmental predictors of daily CO$_2$ fluxes. Fluxes estimated using the gradient diffusion method (GDM) are in squares and using the eddy covariance method (ECM) are in triangles. The solid line is the linear regression fit for GDM; the dashed line is the fit for ECM. Their corresponding slope (s) and $R^2$ values are labeled by their regression line. The text in the red denotes that the slope was not significantly different from zero at the 0.05 level. The snow covered season was divided into early (black, DOY 328 to 8), mid (red, DOY 9 to 54), late (green, DOY 55 to 94), and melt (blue, DOY 85 to 101) periods.
at UMBS is reported to be comparable to similar forest sites at $\sim 1250 \text{ g m}^{-2}$ (Nave et al., 2009). When fine root and below ground NPP are excluded, above ground NPP at UMBS yields $\sim 615 \text{ g m}^{-2}$ (Nave et al., 2009). Thus, the above ground productivity is less than at NWT, but the difference in NPP is not enough to result in an order of magnitude lower maximum CO$_2$ concentration in snow.

The deep snow at NWT creates a stable soil environment allowing for the evolution of a phylogenetically and physiologically unique community of microbes to thrive in the winter soils as cold as $-5 ^\circ\text{C}$ (Brooks et al., 1996; Schadt et al., 2003; Brooks et al., 2005; Monson et al., 2006b; Schmidt et al., 2008). In certain regions of the NWT domain, the soils were covered by “snow molds” (Schadt et al., 2003; Schmidt et al., 2008). These snow molds were found to have high metabolism and growth rates in cold temperatures under snow, and they are thought to contribute to the temperature-sensitive, high CO$_2$ fluxes under snow observed at NWT (Monson et al., 2006b; Schmidt et al., 2008). I am not aware of any wintertime soil microbial studies at UMBS to conclude that the lower CO$_2$ fluxes at UMBS (compared to NWT) is linked to differences in or lower abundance of microbes in the soil.

CO$_2$ flux through snow at UMBS ($0.52 \mu\text{mol m}^{-2} \text{s}^{-1}$) was higher than reported estimates of CO$_2$ flux through snow at other deciduous forest sites that range from $0.22 \mu\text{mol m}^{-2} \text{s}^{-1}$ to $0.37 \mu\text{mol m}^{-2} \text{s}^{-1}$ (Mariko et al., 2000; Mo et al., 2005; Suzuki et al., 2006) and was more comparable to the NWT CO$_2$ flux of $0.71-0.86 \mu\text{mol m}^{-2} \text{s}^{-1}$ (Liptzin et al., 2009) and those found for evergreen forests of $0.32-0.84 \mu\text{mol m}^{-2} \text{s}^{-1}$ (Sommerfeld et al., 1993, 1996; Mast et al., 1998; Hubbard et al., 2005). Despite the relatively high wintertime CO$_2$ flux, this constitutes only $\sim 5\%$ of the annual respiration at UMBS ($1450 \text{ g-C m}^{-2}$). This is similar to reported values of 7-10\% at other deciduous forest sites (Mariko et al., 2000; Mo et al., 2005), but much less than the NWT result of 30\% (Liptzin et al., 2009). This suggests that the UMBS forest is very efficient in CO$_2$ uptake during the growing season and that the wintertime loss is not as important to determining the annual carbon budget as it is for NWT.
The NO emissions might differ between UMBS and NWT because of difference in N cycling. At NWT, nitrate is present in the soil solution throughout the summer, suggesting that nitrification must be occurring (Williams et al., 2009b). While nitrate measurements were not available at UMBS, the forest floor C:N ratio is 28 (Nave et al., 2011). Studies from both Colorado (Rueth and Baron, 2002) and Europe (Gundersen et al., 1998) suggest that N mineralization produces excess nitrate below a C:N ratio of ~ 30. Thus, it may be that the UMBS site is still N limited enough that the rates are low for the N cycling processes that produce NO.

### 3.6 Conclusions

The data did not support the hypothesis that soil emission of CO$_2$ and NOx would be lower at UMBS due to reduced soil microbial activity associated with colder soils below a shallower and less insulating snowpack. Instead, I observed warmer soils and CO$_2$ fluxes in the same order of magnitude as NWT. However, wintertime CO$_2$ emissions were not important in determining the annual C budget at the site, as it constituted only ~ 5% of the annual C budget.

From the Tedlar plot measurements, I validated that the soil was the source for CO$_2$. I also concluded that the snow was a sink for O$_3$ and a medium for bi-directional exchange of NO$_x$ with the atmosphere, much like that observed with forest canopy NO$_x$ exchange. There are two implications of this result. One is that the snowpack acts as a buffer or medium for regulating the reactive nitrogen cycle in forest ecosystems. It has been shown that snow can effectively reduce the effect of atmospheric deposition of pollutants, in particular mercury (Hg$_0$), to watersheds due to re-emission fluxes prior to snow melt (Faïn et al., 2013). Thus, I hypothesize that as snow cover decrease with climate change, the dynamic range in ambient NO$_x$ concentrations over snow-covered regions will increase, i.e., atmospheric levels will exhibit higher maxima and lower minima, and alter the nutrient balance through increased leeching and runoff during rain events. Another implication of the result is that
the interaction that the snowpack has with its overlying atmosphere is not globally uniform. Hence, we must take caution when extrapolating results to other snow covered environments and implementing wintertime biogeochemical processes observed at one site to other sites in model studies.
Table 3.2: Summary of UMBS and NWT results

<table>
<thead>
<tr>
<th>Soil and snow characteristics</th>
<th>UMBS Natural plot</th>
<th>Tedlar plot</th>
<th>NWT (Soddie) Natural plot</th>
</tr>
</thead>
<tbody>
<tr>
<td>Snow cover duration (days)</td>
<td>140</td>
<td>140</td>
<td>220&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Maximum snow depth (cm)</td>
<td>60</td>
<td>60</td>
<td>220&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Snow density (kg m&lt;sup&gt;-3&lt;/sup&gt;)</td>
<td>180–380</td>
<td>180–380</td>
<td>200–500&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Mean ambient air temperature (°C)</td>
<td>−4</td>
<td>−4</td>
<td>−5&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Mean soil temperature (°C)</td>
<td>1</td>
<td>N/A</td>
<td>0&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Soil C:N ratio</td>
<td>28&lt;sup&gt;c&lt;/sup&gt;</td>
<td>N/A</td>
<td>12&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Above ground NPP (g m&lt;sup&gt;−2&lt;/sup&gt;)</td>
<td>615&lt;sup&gt;e&lt;/sup&gt;</td>
<td>N/A</td>
<td>750&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Snow nitrate conc. (µM)</td>
<td>28&lt;sup&gt;f&lt;/sup&gt;</td>
<td>28&lt;sup&gt;f&lt;/sup&gt;</td>
<td>11&lt;sup&gt;g&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Trace gas mixing ratios (mean, min–max)

Above snow

| CO<sub>2</sub> (µmol mol<sup>−1</sup>) | 405, 394–424 | 405, 394–424 | 386<sup>b</sup> |
| O<sub>3</sub> (µmol mol<sup>−1</sup>) | 28, < 2–60   | 28, < 2–60   | 42<sup>h</sup>   |
| NO (µmol mol<sup>−1</sup>)          | 0.10, < 0.1–1| 0.10, < 0.1–1| 1–2<sup>b</sup>  |
| NO<sub>x</sub> (µmol mol<sup>−1</sup>) | 1.2, < 0.1–8 | 1.2, < 0.1–8 | 1–2<sup>b</sup>  |

In snow

| CO<sub>2</sub> (µmol mol<sup>−1</sup>) | Max 1850 | Max 424 | Max 8400<sup>a</sup> |
| O<sub>3</sub> (µmol mol<sup>−1</sup>) | 10, < 2–42 | 11, < 2–53 | < 1–40<sup>b</sup> |
| NO (µmol mol<sup>−1</sup>)          | 0.2, < 0.1–1| 0.23, < 0.1–1.6| < 0.1–14<sup>b</sup> |
| NO<sub>x</sub> (µmol mol<sup>−1</sup>) | 0.86, < 0.1–5| 1.1, < 0.1–5.5| < 0.1–4<sup>b</sup> |

Trace gas fluxes through snow (mean, min–max)

| CO<sub>2</sub> (µmol m<sup>−2</sup>s<sup>−1</sup>) | GDM: 0.54, 0.02–1.5 | 0.02, 0–0.09 | 2006: 0.71, 0.66–1.09<sup>a</sup> |
|                                                 | ECM: 0.71, 0.39–1.3<sup>f</sup> | 0.02, 0–0.09 | 2007: 0.86, 0.58–1.08<sup>a</sup> |
| NO (×10<sup>−3</sup>nmol m<sup>−2</sup>s<sup>−1</sup>) | 0.3, −0.14–0.8 | 0.5, −0.3–1.5 | N/R |
| NO<sub>x</sub> (×10<sup>−3</sup>nmol m<sup>−2</sup>s<sup>−1</sup>) | −0.9, −9–2.6 | −0.3, −6–1.6 | 5–8<sup>b</sup> |

N/A, not applicable; N/R, not reported

<sup>a</sup> Liptzin et al. (2009)
<sup>b</sup> Seok et al. (2009)
<sup>c</sup> Nave et al. (2011)
<sup>d</sup> Hood et al. (2003)
<sup>e</sup> Nave et al. (2009) Derived by subtracting the total NPP with belowground and fine root NPP
<sup>f</sup> Assuming no loss or gain from internal transformation or from dry deposition.
<sup>g</sup> National Atmospheric Deposition Program data (MI09 site for winter 2007)
<sup>h</sup> Williams et al. (2009b)
<sup>1</sup> Helmig et al. (2009a)
<sup>*</sup> Flux above snow determined using the eddy covar. method
Chapter 4

Dynamics of nitrogen oxides and ozone above and within a mixed hardwood forest in northern Michigan

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4.1 Abstract

The dynamic behavior of nitrogen oxides (NO$_x$=NO+NO$_2$) and ozone (O$_3$) above and within the canopy at the University of Michigan Biological Station AmeriFlux (UMBS Flux) site was investigated by continuous multi-height vertical gradient measurements during the summer and the fall of 2008. A daily maximum in nitric oxide (NO) mixing ratios was consistently observed during the morning hours between 06:00 and 09:00 EST above the canopy. Daily NO maxima ranged between 0.1 and 2 ppbv (with a median of 0.3 ppbv), which were 2 to 20 times above the atmospheric background. The sources and causes of the morning NO maximum were evaluated using NO$_x$ and O$_3$ measurements and synoptic and micrometeorological data. Numerical simulations with a multi-layer canopy-exchange model were done to further support this analysis. The observations indicated that the morning NO maximum was caused by the photolysis of NO$_2$ from non-local air masses, which were transported into the canopy from aloft during the morning breakup of the nocturnal boundary layer. The
analysis of simulated process tendencies indicated that the downward turbulent transport of NO\textsubscript{x} into the canopy compensates for the removal of NO\textsubscript{x} through chemistry and dry deposition. The sensitivity of NO\textsubscript{x} and O\textsubscript{3} concentrations to soil and foliage NO\textsubscript{x} emissions was also assessed with the model. Uncertainties associated with the emissions of NO\textsubscript{x} from the soil or from leaf-surface nitrate photolysis did not explain the observed diurnal behavior in NO\textsubscript{x} (and O\textsubscript{3}) and, in particular, the morning peak in NO\textsubscript{x} mixing ratios. However, a \(~30\%\) increase in early morning NO\textsubscript{x} and NO peak mixing ratios was simulated when a foliage exchange NO\textsubscript{2} compensation point was considered. This increase suggests the potential importance of leaf-level, bidirectional exchange of NO\textsubscript{2} in understanding the observed temporal variability in NO\textsubscript{x} at UMBS.

4.2 Introduction

Nitrogen oxides (NO\textsubscript{x}=NO + NO\textsubscript{2}), which originate from combustion, lightning, and soil emissions, play a critical role in regulating the photochemical production of ozone (O\textsubscript{3}) in the troposphere (Crutzen, 1970; Jacob, 2000; Crutzen and Lelieveld, 2001; Hauglustaine et al., 2001). Excessive deposition of NO\textsubscript{x}, which contributes to the total nitrogen input on ecosystems, and exposure of vegetation to toxic levels of O\textsubscript{3} can cause foliage damage; NO\textsubscript{x} deposition is linked to acidification and eutrophication of forests (Mosier et al., 2001; Grunhage et al., 2002).

NO\textsubscript{x} and O\textsubscript{3} concentrations (and fluxes) have been measured in forest ecosystems to quantify NO\textsubscript{x} and O\textsubscript{3} dry deposition in relatively polluted conditions (e.g. CASTNET; US EPA, 2009). Other measurements of NO\textsubscript{x} and O\textsubscript{3} were done to study the role of canopy interactions between biogenic emissions, dry deposition, chemistry, and turbulence in determining bidirectional exchange of NO\textsubscript{x} between more pristine forests and the overlying atmosphere (e.g. Bakwin et al., 1990, 1994; Carroll and Thompson, 1995; Munger et al., 1996; Rummel, 2002). The University of Michigan Biological Station (UMBS) is one of those sites with a history of NO\textsubscript{x} and O\textsubscript{3} measurements since 1997 from the Program for Research on Oxi-
dants: PHotochemistry, Emissions and Transport (PROPHET; Carroll et al., 2001). At the PROPHET site, Thornberry et al. (2001) observed a periodic mixing ratio maximum of NO$_x$ in the morning hours above the forest canopy. A similar behavior was also observed at other forest sites (e.g. Parrish et al., 1993; Munger et al., 1996; Andreae et al., 2002; Farmer and Cohen, 2008). Alaghmand et al. (2011) concluded that to understand the diurnal behavior in NO$_x$ mixing ratios at sites such as UMBS, the combined role of (nocturnal) mixing and transport processes needs to be considered, and this would require the coupling of canopy and boundary layer turbulence models.

In this study, I used the combined analysis of below, within, and above canopy observations and model simulations (1) to investigate the cause for the observed morning peak in NO$_x$ mixing ratios differentiating between the role of local versus distant sources of NO$_x$ and (2) to assess the sensitivity of in-canopy NO$_x$ (and O$_3$) to potentially relevant in-canopy sources and sinks under atmospheric conditions encountered at UMBS. Results are based on an analysis of a five-month data set of NO$_x$, NO, and O$_3$ vertical mixing ratio profiles, which were measured above and within the canopy of the UMBS forest in the summer and the fall of 2008. Simulations with a multi-layer canopy-boundary layer exchange model further supported the analysis.

4.3 Measurements

4.3.1 Site description

This study was conducted from 19 July to 21 November 2008 at the AmeriFlux site in the UMBS domain (45.5932° N, 84.7130° W; Schmid et al., 2003). This site is located in an area rather distant from major anthropogenic sources although it is quite often (~40% of the time) affected by advection of polluted air masses. The nearest metropolitan areas (population > 200000) are Detroit, Michigan, ~350 km to the southeast; Milwaukee, Wisconsin, ~350 km to the southwest; and Chicago, Illinois, ~450 km also to the southwest.
The UMBS forest falls in the transition zone between mixed hardwood and boreal forests with a mean annual (from 1979 to 2009) temperature of 6.7°C and rainfall of 803.4 mm (Vande Kopple, 2011b,a). The pre-settlement forest, dominated by white pine (Pinus strobus), red pine (Pinus resinosa), and hemlock (Tsuga canadensis), was cut around 1880. The area was disturbed repeatedly by fire until 1923. Today, within a 1 km radius of the AmeriFlux tower, the forest is composed mainly of bigtooth aspen (Populus grandidentata) and trembling aspen (Populus tremuloides), but there is also significant representation of maple (Acer rubrum), red oak (Quercus rubra), birch (Betula papyrifera), and beech (Fagus grandifolia). In patches, there is a dense understory of young white pine, up to ~6 m high. The understory layer near the forest floor is dominated by bracken fern (Pteridium aquilinum) and saplings of red maple, red oak, beech, and white pine (Gough et al., 2007).

The forest at UMBS has two distinctive layers: a crown layer and an understory layer (Fig. 4.1). The mean canopy height around the AmeriFlux tower was ~22 m (Schmid et al., 2003). The average seasonal maximum (from 1999 to 2009) of the cumulative single-sided leaf area index (LAI, m² m⁻²) was 3.5. The average seasonal LAI began to decrease in early-October, and it reached its average seasonal minimum of 1.5 by November.

### 4.3.2 Instrumentation

A UV absorbance monitor (DASIBI 1003-AH) was used to measure the mixing ratio of O₃ through the canopy. Before installing the DASIBI at the site, a 5-point calibration was conducted against a TEI 49C monitor (Thermo Environmental Instruments, Inc. (TEI), Franklin, MA, USA), which served as the transfer standard for the calibration. Brodin et al. (2010) describe the calibration of this transfer standard in detail. The calibration of the DASIBI resulted a 1 ppbv offset with a 3% slope correction. The O₃ data from the DASIBI were corrected for this difference. The detection limit of the DASIBI was 1 ppbv.

The mixing ratio of NOₓ was determined with a chemiluminescence analyzer (TEI 42C-TL). This instrument follows the Federal Reference method as designated by the US
Figure 4.1: The forest architecture as vegetation area density profile at UMBS in the summer of 1999, modified from Fig. 2a of Schmid et al. (2003), and a cartoon depiction of the AmeriFlux tower with sensor locations drawn to scale but gas analyzers and housing unit not drawn to scale.
EPA, which is also the most prevalent method of measuring ambient air NO\textsubscript{x} (Demerjian, 2000). The TEI 42C-TL has two channels. The first channel measures nitric oxide (NO) via NO + O\textsubscript{3} chemiluminescence. The second channel measures nitrogen dioxide (NO\textsubscript{2}) by redirecting air through a heated (325 °C) molybdenum converter, which causes NO\textsubscript{2}—and other oxidized nitrogen compounds—to convert to NO. The NO\textsubscript{2} mixing ratio is then determined by subtracting NO, measured in the first channel. There are several interferences in this NO\textsubscript{2} measurement scheme (Steinbacher et al., 2007). The error in the NO\textsubscript{2} measurement increases with rising amounts of interfering gases such as nitrous acid (HONO), peroxyacetyl nitrate (PAN), and alkyl nitrates that contribute to the NO\textsubscript{2}-mode signal. However, in urban environments, NO\textsubscript{x} typically constitutes the largest fraction of oxidized nitrogen compounds (Spicer, 1982; Steinbacher et al., 2007); hence, NO\textsubscript{2} mixing ratios obtained with the TEI 42C-TL will represent a reasonable estimate if the site is influenced by anthropogenic sources. Furthermore, a recent intercomparison of NO\textsubscript{x} measurement techniques showed that NO and NO\textsubscript{2} measured with a molybdenum oxide (MoO) converter instrument yielded values that differed from instruments using other techniques (e.g., photolytical converter) only by 2 and 3%, respectively, for ambient air measurements at a semi-rural site in Germany (Gilge et al., 2013). Before the deployment of the TEI 42C-TL analyzer in the summer of 2008, the instrument was sent to TEI for preventive maintenance. TEI reported the instrument to have a NO\textsubscript{2} conversion efficiency of 99.9\% after servicing it. Ultra-zero air (Airgas Great Lakes, Inc., Royal Oak, MI, USA) was used to establish baseline conditions and for dilution of a NIST-traceable 1 ppmv NO gas standard (Scott-Marrin, Inc., Riverside, CA) to multiple calibration gas levels between 0.5 and 10 ppbv. After propagating the uncertainties of the mass flow controllers and the NO gas standard, I estimated the uncertainty in the NO determination to be \sim 5\%. The signal noise was 0.05 ppbv, which resulted in a detection limit of \sim 0.1 ppbv. The detection limit was determined by taking three times the standard deviation of the blank (the ultra-zero air).

Note that from hereon, I will use NO\textsubscript{2,MO} and NO\textsubscript{x,MO} to indicate that the NO\textsubscript{2} and
NO\textsubscript{x} results in this study are those measured with a MoO converter instrument.

### 4.3.3 Sampling

Vertical mixing ratio profiles of NO\textsubscript{x,MO} and O\textsubscript{3} were measured from the AmeriFlux tower at 4 m, 15 m, 21 m, 25 m, 34 m and 40 m above the ground (Fig. 4.1). Sampling through each inlet was done sequentially from the 40 m height down to the 4 m height. The sampling inlet at a particular height was selected through a manifold constructed of an array of six two-way solenoid valves with polytetrafluoroethylene (PTFE) body seals (Norgren USA, Littleton, CO, USA). Each sampling interval was 5 min long with gas mixing ratios being determined in this flow every minute. A complete cycle took 30 min, thus there were 48 cycles per day.

Perfluoroalkoxy (PFA) inlet funnels with 1 mm grids (Savillex Co., Minnetonka, MN, USA) were used to prevent large debris from being drawn into the sampling line. Single stage 47 mm PFA filter clamps (Savillex Co.) with 5 mm PTFE membrane filter (Millipore Co., Bellerica, MA, USA) were placed upstream of the instrument inlet to prevent fine particles from interfering with NO\textsubscript{x,MO} and O\textsubscript{3} measurements.

All sampling lines, valves, and filters were conditioned for three days with a flow of 2 L min\textsuperscript{-1} of air containing 200 ppbv of O\textsubscript{3} prior to installation. This was done to minimize the loss of O\textsubscript{3} in the manifold during subsequent field sampling. Six equal-length 61 m-long PFA Teflon® tubes with outer diameter of 6.4 mm and inner diameter of 3.6 mm (Parker Hannifin, Cleveland, OH, USA) were used as sampling lines. The excess tubing for the sampling inlets closer to the instruments were coiled and kept in the same housing unit as the instruments.

The flow rate through the DASIBI was 1.8 L min\textsuperscript{-1}, and the TEI 42C-TL flow rate was 1.2 L min\textsuperscript{-1}. Therefore, the total flow rate through each sampling line was 3 L min\textsuperscript{-1}. The theoretical transport time of air samples from the inlet to the gas analyzers was calculated (using tubing dimensions, manifold volume, and purge rate) to be 15 s.
Bias in the sampling lines

All the sampling inlets were inter-compared by bringing them to the 15 m height of the tower. This was done to determine the potential measurement bias, as there are inherent differences in the sampling lines. Mixing ratios of NO and O$_3$ and line pressure were monitored through each line over a 2-day period. The sampling lines varied $<$0.1 ppbv in NO, $<$1 ppbv in O$_3$, and $<$2 kPa in pressure against each other.

Correcting for the loss of NO in the sampling lines

NO undergoes rapid oxidation through its reaction with O$_3$ and other free radicals, e.g., hydroperoxy (HO$_2$) and alkylperoxy (RO$_2$), in the atmosphere. Therefore, it is necessary to correct for the loss of NO during the transport in the sampling line to the analyzer. Since ambient air HO$_2$ and RO$_2$ levels are two to three orders of magnitude smaller than NO (Fuchs et al., 2008), it was assumed they would not affect the sampled NO mixing ratios. The loss of NO due to oxidation by O$_3$ alone was considered in the correction. In the absence of light, NO is oxidized to NO$_2$ by

$$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2,$$

where $k$ is the reaction rate constant ($k = 1.4 \times 10^{-12} e^{-1310/T} \text{[cm}^3\text{molecules}^{-1}\text{s}^{-1]}$, for $T$ between 195 and 308 K; Atkinson et al., 2004).

The reaction rate constants were calculated using ambient temperature recorded when the air sample was collected. The conversion rate of NO was then determined from (Eq. 4.1) using the O$_3$ mixing ratio measured at any given moment from the same inlet. From this conversion rate, the percentage of NO lost after 15 s, which was the residence time of the air sample in the tube, was calculated. Up to 32% of the NO was converted to NO$_2$ by O$_3$, depending on the air sample temperature, O$_3$ mixing ratio, and line pressure. The NO mixing ratio was corrected for this loss. NO$_{2,\text{MO}}$ mixing ratios were recalculated accordingly by subtracting the correct NO mixing ratio from the 42C-TL’s output of the NO$_{x,\text{MO}}$ mixing ratio.
4.3.4 Ancillary data

Meteorological instrumentation on the AmeriFlux tower provided the ancillary data used in the analyses (see Schmid et al., 2003, for information about the instruments). Wind speed, wind direction, turbulence, and incoming solar radiation were measured from the 46 m height of the tower (Fig. 1). Turbulence data ($u'$ and $w'$), measured from the 3-D sonic anemometer, were used to calculate the friction velocity ($u_* = -\langle u' w' \rangle^{0.5}$ [m s$^{-1}$]) above the canopy. Temperatures below and above the canopy were measured from temperature sensors at 4, 21, 34, and 46 m on the tower (Fig. 4.1). From the temperature data, temperature lapse rates ($\gamma = (T_{z1} - T_{z2}) / (z_1 - z_2)$[°C m$^{-1}$]) through the canopy (4 and 21 m) and above the canopy (21 and 34 m) were calculated to diagnose atmospheric stability.

4.4 Single column canopy model

4.4.1 Model description and initialization parameters

A multi-layer atmospheric–biosphere exchange model implemented in a single column chemistry–climate model (SCM; Ganzeveld et al., 2002b, 2006, 2008) was used to evaluate the dynamical behavior of NO$_x$ and O$_3$ mixing ratios observed above and within the forest canopy. In contrast to most site-scale atmosphere–biosphere exchange models, the SCM does not use observed meteorological parameters to simulate exchanges. Instead, the SCM determines the dynamic behavior of the system (including the hydrological cycle, boundary layer dynamics, convection, and cloud formation) from initial vertical profiles and surface properties online and reanalysis of weather data (see below).

The atmosphere–biosphere trace gas exchange calculations in the SCM included dry deposition, biogenic emissions, in-canopy chemical transformations, turbulence, and the extinction of radiation within the canopy. All processes were simulated explicitly as a function of the SCMs meteorological, hydrological, and atmospheric chemistry parameters as well as the canopy structure distinguishing a crown layer and an understory layer. Stomatal and
non-stomatal removal in the dry deposition of NO\textsubscript{x} and O\textsubscript{3} (and other gases) is considered in the SCM. The stomatal conductance is calculated from in-canopy radiation profiles and soil moisture status, whereas the non-stomatal removal is a function of cuticular and soil uptake resistances (Ganzeveld and Lelieveld, 1995). The soil biogenic NO emission flux is normally calculated by the SCM according to a modified implementation of the Yienger and Levy (1995) algorithm. However in this study, a range of constant soil NO emission fluxes was applied in a sensitivity analysis with the reference soil NO emission flux being selected based on the observed emission flux of NO from the soil at the site (see Sect. ). The model also considers the potentially relevant contribution to canopy NO\textsubscript{x} by photolysis of nitrate that has accumulated on leaf surfaces (e.g. Zhou et al., 2003, 2011). The emissions of biogenic volatile organic compounds (BVOCs; i.e. isoprene and monoterpenes) are calculated in the SCM according to Guenther et al. (1995) or alternatively with the Model of Emission of Gases and Aerosols from Nature (MEGAN; Guenther et al., 2006). In this study, I applied the Guenther et al. (1995) implementation based on observed emission factors at the leaf-scale reported for this site (Ortega et al., 2007, see Table 1). This results in a simulated canopy isoprene emission flux comparable to that reported by Pressley et al. (2005). Note that the canopy does not act as a uniform source of soil or foliar emissions in the model, but instead, the source and sink strengths change with time and height inside the canopy.

The atmosphere–biosphere exchange simulations also require initialization of a selection of biogeophysical parameters, e.g., LAI, canopy height, surface roughness, and the vertical distribution of biomass (expressed by the leaf area density profile). Values used for these parameters to simulate conditions found at UMBS are also provided in Table 4.1 (and in Fig. 4.1 for the leaf area density profile).

A key feature of the SCM for site-scale evaluation is the consideration of advection and synoptic weather systems. To consider changes in weather, reanalysis data from the European Centre for Medium range Weather Forecast (ECMWF) were applied, which typically results in realistic representation of the site meteorology (Ganzeveld et al., 2006). For the
Table 4.1: Model input parameters for the UMBS AmeriFlux site.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canopy height</td>
<td>m</td>
<td>22</td>
<td>Schmid et al. (2003)</td>
</tr>
<tr>
<td>Surface roughness</td>
<td>m</td>
<td>2.2</td>
<td>Schmid et al. (2003)</td>
</tr>
<tr>
<td>LAI</td>
<td>m² m⁻²</td>
<td>3.5</td>
<td>This study</td>
</tr>
<tr>
<td>Albedo</td>
<td>–</td>
<td>0.15</td>
<td>Hollinger et al. (2010)</td>
</tr>
<tr>
<td>Isoprene emis. factor</td>
<td>µg C g⁻¹ h⁻¹</td>
<td>50</td>
<td>Ortega et al. (2007)</td>
</tr>
<tr>
<td>Monoterpene emis. factor</td>
<td>µg C g⁻¹ h⁻¹</td>
<td>0.7</td>
<td>Ortega et al. (2007)</td>
</tr>
<tr>
<td>Soil NO emis. rate</td>
<td>ng N m⁻² s⁻¹</td>
<td>0.07</td>
<td>Nave et al. (2011)</td>
</tr>
<tr>
<td>Leaf nitrate conc.</td>
<td>nmol cm⁻²</td>
<td>0.83</td>
<td>Zhou et al. (2011)</td>
</tr>
<tr>
<td>O₃ soil uptake rate</td>
<td>cm s⁻¹</td>
<td>0.25</td>
<td>Ganzeveld and Lelieveld (1995)</td>
</tr>
<tr>
<td>Synoptic meteorology</td>
<td>–</td>
<td>ECMWF</td>
<td>Ganzeveld et al. (2006)</td>
</tr>
<tr>
<td>Chem. initialization</td>
<td>–</td>
<td>NOₓ and O₃ mixing ratios</td>
<td>This study</td>
</tr>
</tbody>
</table>

representation of advection of long-lived trace gases, the simulated boundary layer mixing ratios above the canopy (but not those inside and below the canopy) of NOₓ and O₃ in the SCM were “nudged” (forced) towards observed mixing ratios. In this study, the model tracer nudging used a relaxation time of 300 s (for a model time step of 60 s) to capture some of the rapid fluctuations in the observed mixing ratios while avoiding numerical instabilities.

4.4.2 Model run scenarios

Three sets of model runs were performed to evaluate the role of the “biogenic” versus the “anthropogenic” exchange regime in explaining the observed diurnal variability in NOₓ and O₃ at UMBS. All the model runs simulated the month of August observations. Two different model runs focused on the sensitivity to soil NO emissions and on foliage NOₓ emissions by varying the emission rates by 0, 1, 10, and 25 times the default values (see Table 4.1). One other additional simulation focused on the role of leaf-scale bidirectional NOₓ exchanges.
4.5 Results and discussion of observations

4.5.1 Meteorological data

I focus my analysis on observations for the months of August and November. These two months were selected since August represented a state of the forest canopy during a period of highest mean seasonal LAI. In contrast, November was chosen as a period after leaf abscission when the forest canopy was at its lowest mean seasonal LAI.

Weather conditions between July and November in 2008 were typical for UMBS. Temperature variations at UMBS were within the ranges of the temperature normal from 1979 to 2010, but total precipitation during this period was lower than the average climatic conditions. This deviation in total precipitation was not considered anomalous or extreme as they were within 1-standard deviation from the mean (Table 4.2).

Table 4.2: UMBS 1979–2010 climatological data for months when measurements were taken.

<table>
<thead>
<tr>
<th>Month</th>
<th>Temperature (°C)</th>
<th>Precipitation (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Avg. Min</td>
<td>Avg. Max</td>
</tr>
<tr>
<td>Jul</td>
<td>15.1</td>
<td>25.7</td>
</tr>
<tr>
<td>Aug</td>
<td>14.6</td>
<td>24.4</td>
</tr>
<tr>
<td>Sep</td>
<td>10.3</td>
<td>19.8</td>
</tr>
<tr>
<td>Oct</td>
<td>4.3</td>
<td>12.2</td>
</tr>
<tr>
<td>Nov</td>
<td>−0.71</td>
<td>5.3</td>
</tr>
</tbody>
</table>

Figure 4.2 shows the seasonal decline in the daily maximum of incoming solar radiation from July to November (i.e. daytime maxima of ~ 700 W m\(^{-2}\) and ~ 250 W m\(^{-2}\), respectively). Similarly, the daily temperature amplitude above canopy decreased from ~ 11 °C in July to ~ 4 °C in November. The daily amplitude in friction velocity tracks the pattern of the incoming solar radiation with decreasing absolute amplitude (difference between daily minimum and daily maximum) over the five-month period with daytime maxima > 1 m s\(^{-1}\),
indicating intense daytime turbulent exchange and minimum nocturnal friction velocities \( \sim 0.2 \text{ m s}^{-1} \) reflecting the suppressed nighttime mixing conditions.

The monthly average daily cycle of solar radiation, temperature lapse rate, and friction velocity for August and November are shown in Fig. 4.3. Sunrise shifted from 06:00 to 07:30 EST between August and November. Sunset changed from 19:00 EST in August to 17:30 EST in November. The diurnal pattern of the observed above-canopy friction velocity closely followed the solar radiation cycle. Nocturnal friction velocities averaged 0.2 m s\(^{-1}\) in August and 0.4 m s\(^{-1}\) in November, implying inefficient turbulent mixing in the above canopy layer at night. Apparent increases in mixing (or friction velocity) were observed \( \sim 30 \text{ min} \) after sunrise.

Since no direct turbulence measurements inside the canopy were available, temperature lapse rates from the vertical temperature profile measurements (see Sect. 4.3.4) were used, in addition to friction velocity, as a proxy for the efficiency of turbulent mixing inside and above the canopy. These layers were considered to be in the stable regime when the temperature lapse rate (for the canopy layer calculated from observed temperatures at 4 and 21 m and for the above-canopy layer calculated from temperatures observed at 21 and 34 m) was below 0.0098 \( ^\circ \text{C m}^{-1} \), the dry adiabatic lapse rate (denoted as the dashed line in the lapse rate plots; Fig. 4.3). The atmosphere was considered unstable when the lapse rate was above the dry adiabatic lapse rate, and it was considered neutral when the lapse rate equaled the dry adiabatic lapse rate. The fact that changes in the above-canopy lapse rate, which reflect a transition from stable to unstable mixing conditions, coincide with the observed fast increase in friction velocity \( \sim 30 \text{ min} \) after sunrise supports the use of these lapse rates as proxy for mixing conditions.

The daily amplitude (i.e. the difference between daily minimum and maximum) of the lapse rates decreased with a decrease in solar radiation from August to November. This suggests a decreasing role of buoyancy in turbulent exchanges. The timing when atmospheric stability changed varied as a function of the timing of sunrise and sunset implying also
Figure 4.2: The evolution of solar radiation, temperature profile, friction velocity, and the mixing ratio profiles of NO$_x$, NO, and O$_3$ at the UMBS AmeriFlux site from 19 July to 21 November 2008. Missing data were due to taking the instruments offline for calibrations and repairs and due to running intercomparison tests of the sampling inlets. Gaps in the chemical data below the canopy from 27 September onward were due to failures in the 4 and 15 m switching valves.
Figure 4.3: Mean diurnal cycles of solar radiation, temperature lapse rates ($\gamma$), and friction velocity ($u_*$) in the above-canopy layer at UMBS for August and November 2008. The dashed line in the $\gamma$ plots denotes the dry adiabatic lapse rate ($\Gamma_{\text{dry}}$) of 0.0098°C m$^{-1}$. $\gamma < \Gamma_{\text{dry}}$ is stable, $\gamma = \Gamma_{\text{dry}}$ is neutral, and $\gamma > \Gamma_{\text{dry}}$ is unstable.
a dependence of the stability regime on solar radiation.

In August, stable atmospheric conditions were observed at night prior to sunrise through and above the canopy, indicating suppressed mixing between the two layers. Within 30 min after sunrise (~06:30 EST), the lapse rates diverge with enhanced mixing conditions in the above-canopy layer but increasing stability in the canopy layer. This response indicates differential heating of the above-canopy layer and the top of the canopy by the incoming solar radiation. The divergence in the lapse rates also indicates that the layers appear to be decoupled. These conditions suppress vertical mixing and cause accumulation of biogenically produced trace gases inside the canopy. As the sun sets (~19:00 EST), the temperature lapse rates of the two layers converge to a lapse rate reflecting a stable regime.

In November, the mixing of air mass into the canopy layer was strongly suppressed. The canopy layer remained decoupled from the above-canopy layer throughout the day. The above-canopy layer mixing conditions transitioned from a neutral regime to an unstable regime about 30 min after sunrise (~08:00 EST); after sunset (~17:30 EST), the above-canopy layer lapse rate transitioned from unstable to neutral mixing conditions. The canopy layer lapse rate remained stable throughout the day.

4.5.2 Chemical data

Seasonal data

The evolution of NO\textsubscript{x,MO}, NO, and O\textsubscript{3} canopy mixing ratio profiles is shown in Fig. 4.2. Daily amplitudes of NO\textsubscript{x,MO}, NO, and O\textsubscript{3} gradually decreased over the season. For instance, the daily amplitude in NO\textsubscript{x,MO} mixing ratios averaged at 1 ppbv in August, then it declined to 0.5 ppbv in November. However, the daily NO\textsubscript{x,MO} maximum increased with time. The daily NO\textsubscript{x,MO} maxima in August ranged between 0.4 and 10 ppbv with a median of 2 ppbv. For NO, its daily amplitude averaged at 0.3 ppbv in August, and then it declined to 0.2 ppbv in November. The daily NO maximum in August ranged between 0.1 and 2 ppbv with a median
of 0.3 ppbv. O$_3$ varied daily by an average of 20 ppbv in August; the daily amplitude declined to 5 ppbv in November. Its daily maximum ranged between 16 and 66 ppbv with a median of 33 ppbv. These wide ranges in maximum NO$_{x,MO}$ and O$_3$ mixing ratios reflect that this site is influenced by contrasting biogenic and anthropogenic footprints, which may be dependent on season (Cooper et al., 2001).

**Diurnal data**

Mean diurnal vertical mixing ratio profiles of NO$_{x,MO}$, NO, and O$_3$ for August and for November are shown in the color contour plots in Fig. 4.4.

**NO$_x$.** The most prominent feature in the diurnal NO$_{x,MO}$ cycle is the mixing ratio maximum seen during the early morning hours. Elevated NO$_{x,MO}$ was observed throughout and above the canopy, with highest mixing ratios occurring right above the canopy. The diurnal cycle of NO$_{x,MO}$ also shows elevated levels of NO$_{x,MO}$ throughout the canopy during the night (∼ 0.5 to 0.7 ppbv) and lower levels during the latter part of the day (∼ 0.3 ppbv). The daily amplitude in NO$_{x,MO}$ mixing ratio and the magnitude of the morning peak are smaller in November than in August. The differences in the nocturnal NO$_{x,MO}$ mixing ratios between August and November are small.

**NO.** The diurnal variation of NO also clearly shows a morning peak above the canopy after sunrise, coinciding with the morning NO$_{x,MO}$ maximum. This coincidence in timing of the NO peak suggests that this NO is formed from NO$_2$ photodissociation. During the night, despite the previously discussed canopy stratification, observed understory layer NO levels are slightly (< 0.1 ppbv) larger than the above-canopy layer NO levels, which indicates that soil NO emission may have minor influence on the nocturnal NO profile.

**O$_3$.** Ozone increased throughout the daylight hours reaching maxima in the early afternoon. Mixing ratios then began leveling out in the late afternoon and began dropping steadily throughout the evening and night until approximately sunrise time. In the understory layer ozone declined at a faster rate, with ozone loss first occurring right at the forest ground
Figure 4.4: Mean diurnal cycles of NO$_x$, NO, and O$_3$ mixing ratio profiles from the UMBS AmeriFlux site for August and November 2008. The area between the dashed lines in the plots denotes the crown layer. Gaps in the data below the crown layer in November are due to failures in the 4 and 15 m switching valves.
surface, and then from there slowly reaching up to the crown layer. During nighttime ozone mixing ratios above-canopy remained $\sim 10$ ppbv higher than in the understory. Between 08:00 and 09:00 EST, the $O_3$ mixing ratio in the understory rapidly increased to levels measured in the above-canopy layer. During the day, from 10:00 to 17:00 EST, the vertical $O_3$ profile evolved uniformly all throughout below and above the canopy, with average $O_3$ maxima of $\sim 30$ ppbv. It is notable that the temporal evolution of the nighttime $O_3$ loss near the ground coincided with the nighttime accumulation of $NO_{x,MO}$. The main connecting processes here are limited turbulent transport and soil NO emissions explaining the accumulation of $NO_{x,MO}$ near the soil surface. It also partly explains the decrease in $O_3$ due to a reduced resupply of $O_3$ from higher up in the canopy and surface layer. The resupply of $O_3$ is insufficient to compensate for surface deposition and chemical destruction from reaction with soil-emitted NO. The NO mixing ratios are so small that the titration of $O_3$ would only be a minor term in $O_3$ destruction. Similar to the $NO_{x,MO}$ diurnal cycle, the daily amplitude in the $O_3$ mixing ratio was smaller in November than in August.

**Air mass advection**

Figure 4.5 shows a wind-pollution rose of the measured trace gases for August and for November. The length of the wedge corresponds to the frequency of readings from particular wind sectors, while the color corresponds to the magnitude of the pollutant mixing ratios. These wind-pollution roses show that the two predominant wind directions at UMBS are from the southeast (SE; $112^\circ–157^\circ$, occurs $\sim 20\%$) and the northwest (NW; $292^\circ–315^\circ$, occurs $\sim 23\%$), and somewhat less, from the west. The wind distribution did not change much between August and November.

The $O_3$-wind rose plots show enhanced $O_3$ being transported during SE-SW winds ($112^\circ–247^\circ$), most notably for November. During November, elevated $O_3$ levels were also observed during southwest (SW) winds. Relative to $O_3$, $NO_{x,MO}$—and to a lesser extent—NO, display a more pronounced wind direction dependency, with elevated levels clearly
Figure 4.5: Wind-pollution rose for $\text{NO}_x$, $\text{NO}_2$, and $\text{O}_3$ determined for (a) August and for (b) November using data from the 46 m level wind sensor and 34 m level gas inlet (see Fig. 4.1).
being associated to SE and SW wind directions. During NW winds, $\text{NO}_x,\text{MO}$ remained $< 1 \text{ ppbv}$ during most times, whereas SE–SW winds consistently were associated with $\text{NO}_x,\text{MO} > 2 \text{ ppbv}$. There are major urban centers from 350 to 450 km upwind of UMBS in the SE–SW sectors (i.e. Detroit, Milwaukee, and Chicago); these urban areas are likely the source regions for the elevated $\text{NO}_x,\text{MO}$ transported to the site.

The diurnal breakup of the wind roses (Fig. 4.6) shows that the site experienced a diurnal shifting of transport direction. During August, from midnight to 06:00 EST, wind directions were predominantly from the NW and the SE—and occasionally from the W. Winds then gradually shifted to NW and SE–SW. During sunrise (06:00–09:00 EST), wind directions were predominately from the NW and the SE–SW. From the morning hours to after sunset (09:00–21:00 EST), the frequency of SE–SW winds declined and the majority of the winds came from the W–NE directions. During the late evening (21:00–24:00 EST), the frequency of SE wind directions increased leading back to predominately NW and SE winds.

The diurnal frequency of wind directions in November varied from August in that the SE-S wind directions stayed more frequent throughout the night and day (Fig. 4.6). However, from sunrise until after sunset (09:00–21:00 EST), the SE-S wind direction dominance decreased and the frequency of W-NW wind directions increased. The steady frequency of SE-S wind directions in November may contribute to the smaller daily variation observed for $\text{NO}_x,\text{MO}$ and $\text{O}_3$ levels than that observed in August, as winds from these directions tend to bring elevated levels of $\text{NO}_x,\text{MO}$ and $\text{O}_3$ into the region.

The frequency of NO maxima increased during winds from the southerly directions (SE–SW sectors) (06:00–09:00 EST for August; 09:00–12:00 EST for November). Therefore, wind direction seems to be a key factor in the observed variations in gas mixing ratio. Cooper et al. (2001) and Thornberry et al. (2001) also observed higher levels of $\text{NO}_x$ and $\text{O}_3$ during transport from the SE–SW sectors at UMBS. Conversely, they saw lower levels of $\text{NO}_x$ and $\text{O}_3$ with NW winds. Back trajectory analysis done by Cooper et al. (2001) and by Alaghmand et al. (2011) showed that air transported to the site during SE–SW winds had passed through
Figure 4.6: Daily wind roses for (a) August and for (b) November in 4-hourly bins recorded from the UMBS AmeriFlux tower above the canopy at 46 m.
the three major urban areas of Detroit, Milwaukee, and Chicago. The lack of NO\textsubscript{x} increases during NW winds at night indicates the lack of major local emissions from that wind sector (Thornberry et al., 2001). Consequently, these wind flow analyses support the hypothesis that the NO\textsubscript{x,MO} increases seen at UMBS are most likely non-local. The wind-pollution rose and wind rose analyses provide a strong indication that advection plays a major role in the observed morning maxima of NO\textsubscript{x,MO} and NO. This will be further substantiated by the sensitivity analysis with the model for this site presented in Sect. 4.6.2.

### 4.5.3 Seasonal shift of morning NO\textsubscript{x} peak

Figure 4.7 shows the relationship between the time of sunrise and the occurrence of NO\textsubscript{x,MO} and NO maxima from July to November for data falling into the 03:00 to 15:00 EST window (Fig. 4.8). The time of sunrise was determined when the radiation sensor registered > 10 W m\(^{-2}\) increase from its nighttime reading ($\sim 0.1$ W m\(^{-2}\)). The daily sunrise time determinations are not plotted in the figure, but instead the linear regression line fit through the data is shown. The slope of the regression line indicates that the sunrise time shifted $\sim 0.147$ h wk\(^{-1}\). The time of the NO\textsubscript{x,MO} peak was determined from the occurrence of the maximum NO\textsubscript{x,MO} reading at all measurement heights, box-and-whisker plots in Fig. 4.7 show the statistical distribution of the weekly data. The data in Fig. 4.7a clearly illustrate that the majority of the daily NO\textsubscript{x,MO} maxima measured from each tower inlet level occurred within a few hours after sunrise. A linear regression line through the median values of the weekly distribution plot of the daily NO\textsubscript{x,MO} maxima ($y = 0.136x + 7.14$, $r^2 = 0.478$, where $y$ is sunrise time and $x$ is the weekly bin) indicates that the time of the NO\textsubscript{x,MO} maximum shifted by $\sim 0.136$ (standard error $\pm 0.0355$) h wk\(^{-1}\), similar to the change in sunrise time. The difference in the $y$-intercept of the two (sunrise and NO\textsubscript{x,MO} maxima) regression lines can be used as an indicator of the delay of the NO\textsubscript{x,MO} maximum relative to sunrise; the offset between the two regression analyses yields a result of $\sim 2$ h.

Figure 4.7b shows the relationship between sunrise time and the time of maximum
Figure 4.7: The relationship between sunrise and time of observed (a) NO$_{x,MO}$ and (b) NO maxima from 03:00 to 15:00 EST from each sampling inlet. The dashed lines denote the change in time of sunrise over 18 weeks (five months) in 2008 at UMBS (regression: $y = 0.147x + 5.01$, $r^2 = 0.999$). Data for 7 days, staring on 19 July were binned together and are displayed as box-and-whisker plots that depict the mean, median, 25 and 75 percentile, and 5 and 95 percentile values. The solid regression lines were fit to the weekly median data. They denote the average change in when the NO$_{x,MO}$ and the NO maxima were observed (regression: (a) $y = 0.135(SE \pm 0.0355)x + 7.14(SE \pm 0.384)$, $r^2 = 0.478$ and (b) $y = 0.159(SE \pm 0.0321)x + 7.46(SE \pm 0.348)$, $r^2 = 0.605$).
Figure 4.8: Histogram of frequency of time of day for observed (a) NO$_x$ maxima and (b) NO maxima for the five-month measurement period (July to November 2008) at UMBS.
NO. The linear regression through the median weekly NO maxima indicates that the time of NO maximum shifted by $\sim 0.159$ (standard error $\pm 0.0321$) h wk$^{-1}$. The lag between sunrise and when the NO maximum occurs is $\sim 2.5$ h. Notice that this corresponds to a time approximately half an hour after the NO$_{x,MO}$ maximum time.

This analysis suggests that the sunrise time and the occurrence of the NO$_{x,MO}$ maximum are closely linked. Consequently, it appears that solar radiation driven processes, such as thermodynamically driven mixing and photochemistry, are the governing processes in the NO$_{x,MO}$ and NO morning peak occurrence.

4.6 Model results and discussion

4.6.1 Model validation and baseline performance

The model was used to simulate the month of August conditions for UMBS. To assess the performance of the model on simulating the main features of the site-specific micrometeorology and chemical boundary conditions, the results of the simulations were compared against observed incoming solar radiation, above-canopy air temperature at 34 m, above-canopy friction velocity (Fig. 4.9) and the NO$_{x,MO}$ and O$_3$ mixing ratios (Fig. 4.10).

Figure 4.9 shows that the SCM was able to simulate the diurnal cycle in radiation and temperature quite well as reflected by a strong correlation between measured and simulated parameter values ($r^2 > 0.95$). However, the model underestimated the daytime maximum friction velocity with a too strong decrease in turbulence intensity simulated by the model in the afternoon. The latter seems to be due to a misrepresentation of the stability effect for unstable conditions in the SCM. Good agreement between the simulated and observed friction velocity was produced when soil moisture was reduced in the SCM, however, this resulted in simulated temperatures that were 4 $^\circ$C warmer than observations.

Figure 4.10 shows the mean and median diurnal cycles of observed and simulated NO$_{x,MO}$ and O$_3$ mixing ratios. The difference between the mean and median of the observed
Figure 4.9: Observed and modeled (SCM) diurnal variation of solar radiation, above-canopy temperature at 34 m, and above-canopy friction velocity at 46 m for August 2008 at the UMBS AmeriFlux tower. The correlation coefficient, $r^2$, between the observed and the modeled data is noted in each plot.
Figure 4.10: Observed August mean (blue circle) and median (green triangle) diurnal cycle in NO$_x$, MO and O$_3$ mixing ratios above the canopy at 34 m. Also shown are the simulated August mean (red line) diurnal mixing ratios.
data is largest during the midnight to early morning hours (00:00–06:00 EST). This feature indicates that the influence exerted by occasional events with elevated NO$_{x,MO}$ is higher during those hours than during the remainder of the day. O$_3$ shows a similar behavior, but with generally smaller differences between the median and mean mixing ratios. In addition, the difference between the mean and the median mixing ratios reflects the large temporal variability in the observations of air masses that are enhanced in NO$_{x,MO}$ and O$_3$ under suppressed mixing conditions.

The simulated diurnal means of NO$_{x,MO}$ and O$_3$ in Fig. 4.10 include the contribution by advection as the model was nudged towards the observed above-canopy NO$_{x,MO}$ and O$_3$ mixing ratios. In other words, the simulations reflect the net result of the explicitly resolved sources, sinks, and vertical exchange processes complemented by the implicitly added “advection” term, which considers changes in chemical composition of air advected to the site. Consequently, the simulated diurnal O$_3$ above-canopy layer mixing ratios (Fig. 4.10) nearly resemble the observed data as anticipated. In contrast, agreement between simulated and observed mean NO$_{x,MO}$ is less. The disagreement is greatest in the early morning hours, where simulated NO$_x$ is $\sim 0.3$ ppbv smaller compared to the observed peak mixing ratio of $\sim 1.5$ ppbv. The fact that the model output shows better agreement with the median data suggests that the morning NO$_{x,MO}$ peak seen in the August mean data reflects the role of some large peak values associated with individual transport events, which are underrepresented by the model. Apparently, these events are not captured by the model for the selected nudging relaxation time of 300 s. This underestimation of the above-canopy layer NO$_{x,MO}$ peak mixing ratios has obvious consequences for explanation of the observed early morning peak in NO, which I discuss in later sections.
4.6.2 Sensitivity of the above and within canopy morning NO\textsubscript{x} peak

**Soil emissions**

The sensitivity of NO\textsubscript{x}, NO, and O\textsubscript{3} to soil NO emissions is shown in Fig. 4.11 as the difference between observed and simulated diurnal mixing ratio profiles ($\Delta = \text{simulated} - \text{observed}$). The soil NO emission rates tested include a “zero” soil NO emissions flux ($0 \times$; Fig. 4.11b), a soil NO emission flux reflecting reported values ($0.07 \text{ng N m}^{-2} \text{s}^{-1}$, Table 4.1) $1 \times$, $10 \times$, and $25 \times$ increases of the reported values Fig. 4.11c, d, e). Note that the $25 \times$ case is most likely an unrealistic and extreme case, as it is significantly larger than what was measured (Nave et al., 2011), but it was applied here for the purpose of testing the sensitivity of the model. In addition, these simulations on the soil NO\textsubscript{x} emission influence did not include any NO\textsubscript{x} contribution by foliage emissions. In Fig. 4.11b–e, a positive delta value implies that the model overestimates measured mixing ratios, while a negative delta value means an underestimation in the simulated mixing ratio.

**NO\textsubscript{x}**. The observed nighttime minimum of NO\textsubscript{x,MO} seen in the data (Fig. 4.11a) near the forest floor points at the role of understory sinks of NO\textsubscript{x,MO}, e.g., surface deposition or chemical destruction, of a magnitude larger compared to the soil NO\textsubscript{x,MO} source. The $0 \times$ and $1 \times$ soil NO emission flux simulations resulted in NO\textsubscript{x} profiles that are similar to each other and resemble the observed data. Apparently, NO\textsubscript{x} in the crown and above-canopy layers is rather insensitive to the magnitude of the soil NO emission flux. Even the further increases of the NO soil flux ($10 \times$ and $25 \times$) did not produce noticeable changes to the NO\textsubscript{x} profiles, except in the understory layer. For the $1 \times$ soil NO\textsubscript{x} source, the model predicted NO\textsubscript{x} minimum mixing ratios of $\sim 0.3 \text{ppbv}$ in the understory layer in the early night compared to observed understory NO\textsubscript{x,MO} levels of $\sim 0.7 \text{ppbv}$. This suggests that the model NO soil flux that I selected for this study—based on observed soil NO emission fluxes—appears to be too small. The $10 \times$ simulation of $0.7 \text{ng N m}^{-2} \text{s}^{-1}$ actually results in a better agreement between
simulated and observed NO\textsubscript{x} inside the canopy. This finding concurs with Alaghmand et al. (2011), who applied a soil NO flux at UMBS of \( \sim 180 \text{ nmol m}^{-2} \text{h}^{-1} \) (\( \sim 0.7 \text{ ng N m}^{-2} \text{s}^{-1} \)) in their work. They based this number on an unpublished dataset from Carleton (2003). I use NO effluxes of \( \sim 0.2 \mu\text{g N m}^{-2} \text{h}^{-1} \) (or \( \sim 0.07 \text{ ng N m}^{-2} \text{s}^{-1} \)) measured around the AmeriFlux site in the summer of 2008 by Nave et al. (2011). At sunrise, the model predicted an increase in NO\textsubscript{x} mixing ratios throughout the canopy, whereas the observations showed mainly an increase in NO\textsubscript{x} above the canopy (Fig. 4.11a, b). Observed NO\textsubscript{x,MO} mixing ratios were as large as 1.5 ppbv, while the model predicted above-canopy maximum NO\textsubscript{x} mixing ratios up to \( \sim 1 \text{ ppbv} \), even for the 10\( \times \) soil emission case. The model predicted minimum NO\textsubscript{x} mixing ratios in the canopy layer in the late afternoon and evening consistent with the data from 12:00 to 18:00 EST. For the “unreasonably” high 25\( \times \) soil emission case, the model predicted levels of NO\textsubscript{x} near the forest surface about 1 ppbv larger than observed during the night. Yet even with this high soil NO\textsubscript{x} flux, there was no improvement in the representation of the above-canopy early morning NO\textsubscript{x} peak.

\textbf{NO.} For all soil NO flux scenarios, the daytime NO mixing ratio profiles were slightly overestimated in the canopy layer. The model simulated NO canopy mixing ratios reasonably well for all soil NO emission cases with differences of < 0.05 ppbv. However, the model underestimated the nocturnal NO mixing ratios in the crown and above-canopy layers by > 0.05 ppbv. The 25\( \times \) soil emission case shows some enhancement in the simulated NO mixing ratios in the understory layer, but the NO increase is only confined to the understory layer, whereas the observations showed nocturnal NO mixing ratios of \( \sim 0.1 \text{ ppbv} \) throughout the canopy. The simulations show a similar above-canopy NO peak as seen in the data. However, the NO maxima simulated by the model are 0.05 to 0.1 ppbv lower than observed. During afternoon hours, the model over-predicts NO by 0.05–0.1 ppbv throughout the canopy. Again, the increase in the soil NO\textsubscript{x} flux exerted little influence on the above-canopy morning NO peak formation.

\textbf{O\textsubscript{3}.} Regardless of the changes in soil emission rates, the model reasonably predicted
Figure 4.11: (a) The observed mean diurnal mixing ratio profiles of NO$_x$, NO, and O$_3$. Plots (b) through (e) depict the difference between the observed and simulated mean ($\Delta = \text{simulated} - \text{observed}$) diurnal cycle of the mixing ratio profiles of these gases as a function of soil NO emission for August 2008. (b) Case for “zero” soil emission. (c) Case for default soil emission (1 × 0.07 ng N m$^{-2}$ s$^{-1}$; see Table 1). (d) Case for 10 times the default soil emission (10×). (e) Case for 25 times the soil emission (25×).
absolute O₃ levels, the mixing ratio profiles of O₃, and the timing of the breakup of the nighttime O₃ gradient at sunrise. The SCM underestimated O₃ mixing ratios in the understory layer at sunrise (06:00–09:00 EST) and during the late evening and nighttime (18:00–24:00 EST). This effect may be related to an overestimation of canopy sinks (e.g., foliage or soil deposition, chemical destruction) or an underestimation of downward turbulent transport inside the canopy (Fig. 4.9, Sect. 4.6.1).

**Foliage emissions**

Hanson and Lindberg (1991) compiled a report showing evidence for deposition of NOₓ onto surfaces such as leaves, bark, and soil. It is possible that residual NO₂ could be “trapped” in the canopy via deposition onto leaves. At sunrise, the deposited NO₂, either as NO₂ or in the form of HONO or HNO₃, would undergo photolysis to ultimately create NO above the canopy. The sensitivity of NOₓ, NO, and O₃ to a foliage NOₓ emission flux is shown in Fig. 4.12. The foliage NOₓ emission rates are based on leaf nitrate content reported by Zhou et al. (2011) (see Table 4.1), where I assumed that photolysis of nitrate on the surface of the leaves results in foliage NO₂ and HONO emissions (hence, referred to as foliage NOₓ emissions). The simulated cases include a “zero” foliage NOₓ emissions flux (0×; Fig. 4.12b), an assumed foliage NOₓ emissions flux based on the reported leaf nitrate value (0.83 nmol cm⁻², Table 4.1) (1×; Fig. 4.12c), and increased foliage NOₓ emission fluxes based on 10 and 25 times increases in the reported leaf nitrate levels (10× and 25×, see Table 4.1; Fig. 4.12d, e). In Fig. 4.12b–e, a positive delta value means that the model has overestimated the mixing ratio, while a negative delta implies an underestimation in the simulated mixing ratio value.

**NOₓ.** The increase in foliage NOₓ emissions causes increasing NOₓ mixing ratios during the sunlit daytime hours, with most of this NOₓ growth seen in the understory layer where NOₓ accumulates due to slower removal by transport, chemistry, and deposition. For the 10× and 25× simulation cases, resulting NOₓ mixing ratios are far above the observed
Figure 4.12: Similar to Fig. 4.11 but for sensitivity towards foliage NOx emission. (a) The observed mean diurnal mixing ratio profiles, (b) case for “zero” foliage emission, (c) 1× case, (d) 10× case, (e) 25× case.
data. These comparisons do not provide evidence that foliage emission have a determining influence on the above-canopy morning $\text{NO}_x,\text{MO}$ peak.

**NO.** NO results are similar to $\text{NO}_x$, except that the effect on NO is not constrained to the understory layer but is notable throughout the canopy and above-canopy layer. Yet again, increasing the foliage $\text{NO}_x$ emission rate above the default value yields atmospheric NO levels that exceed the observations.

**O}_3.** Increasing the foliage $\text{NO}_x$ flux had little influence on the $\text{O}_3$ mixing ratios. Likewise to the sensitivity of soil NO emissions (Sect. ), the underestimation of $\text{O}_3$ in the understory layer during sunrise and late evening hours seen in the comparison between the observed and the simulated values is insensitive to changes in foliage $\text{NO}_x$ flux.

**Leaf-scale bidirectional exchanges of $\text{NO}_2**

To further diagnose the contribution of the different processes that influence the diurnal variability in $\text{NO}_x,\text{MO}$, the simulated process tendencies for the default conditions (expressed in ppbv hr$^{-1}$) are shown for the crown layer in Fig. 4.13a, and for the understory layer in Fig. 4.13b. From Fig. 4.13a it can be inferred that changes in the crown layer $\text{NO}_x$ mixing ratio are dominated by daytime downward turbulent transport into the canopy (shown as positive turbulence tendency). This downward transport compensates for chemical destruction and dry deposition. Figure 4.13b also shows the contribution from soil emission, which provides a constant but relatively minor contribution in the overall net tendency. This confirms the low sensitivity of $\text{NO}_x$ at UMBS to the soil emission source. It is interesting to see that the net tendency after sunrise appears to be controlled primarily by turbulent transport and dry deposition (Fig. 4.13). Meanwhile, the chemistry becomes a relevant sink $\sim 1.5$ h after sunrise. The SCM calculates $\text{NO}_x$ dry deposition in the multi-layer canopy model from the leaf uptake resistance. This leaf uptake resistance includes non-stomatal and stomatal resistances, and it is calculated from radiation and moisture status in series with an assumed mesophyll resistance. In the default setup of the SCM, the $\text{NO}_2$ mesophyll resistance has
a value such that the NO$_2$ dry deposition to vegetation is $\sim 2/3$ the O$_3$ dry deposition velocity, while NO leaf uptake is negligible (Ganzeveld and Lelieveld, 1995).

However, studies have shown that there exists a NO$_2$ compensation point defined as the ambient NO$_2$ mixing ratio at which the net exchange between a plant and the atmosphere is zero (e.g. Rondon et al., 1993; Rondon and Granat, 1994; Lerdau et al., 2000; Ganzeveld et al., 2002a; Chaparro-Suarez et al., 2011). The NO$_2$ compensation point can be viewed as a dynamic process. The canopy foliage can become a source or a sink depending on the ambient NO$_2$ mixing ratio. This contrasts the foliage emission via nitrate photolysis, described in Sect. , which always functions as a source term (i.e. always resulting in a positive NO$_x$ flux). The NO$_2$ gas exchange is a pure physical process, solely driven by ambient air mixing ratio levels. The compensation point mechanism was added on top of the foliage emission flux in these simulations.

A leaf-scale NO$_2$ compensation point of 1 ppbv was used in the simulation. This compensation point value was selected after conducting a sensitivity analysis (not shown) aiming to reproduce the observed trace gas levels throughout the day. With inclusion of this NO$_2$ compensation point in the SCM, a relatively large NO$_x$ foliage emissions flux, exceeding the dry deposition term, was simulated (Fig. 4.14). Having this compensation point reverses the net tendency at $\sim$06:00 EST from a negative (see Fig. 4.13a) to a positive tendency (Fig. 4.14). Comparing Fig. 4.13a and Fig. 4.14, one would expect the turbulence tendency to be the same for both simulations. However, inclusion of a NO$_2$ compensation point changes the sources and sinks; consequently, this changes the mixing ratios in the simulation. Therefore, the turbulent transport tendency (along with the concentration gradients and fluxes) will change accordingly, but the turbulent transport term, derived from the eddy diffusivity, in the SCM remained the same for the two cases. The simulated increases in atmospheric NO$_x$ and NO mixing ratios associated with this 1 ppbv NO$_2$ compensation point is illustrated in Fig. 4.15. First of all, there is an improved simulation of absolute mixing ratios with maximum increases in NO$_x$ of $\sim$ 0.3 ppbv and in NO of $\sim$ 0.05 ppbv in the crown layer
Figure 4.13: Simulated August mean diurnal cycle in NO\textsubscript{x} process tendencies (ppbv h\textsuperscript{-1}) of emissions (red solid line), dry deposition (green long-dashed line), chemistry (blue short-dashed line), turbulent transport (maroon dashed line), and the net tendency (black solid line) (a) in the crown layer and (b) in the understory layer.
Moreover, the better match in the timing of the NO\textsubscript{x} and NO maxima associated with these changes in leaf-level NO\textsubscript{2} exchange (i.e. the NO\textsubscript{2} compensation point) points towards this effect having a possible important contribution to the above canopy morning NO maximum.

At this time, there are no leaf-level experimental data available from this site to further substantiate the assumption that NO\textsubscript{2} compensation point might play an important role in the dynamics of NO\textsubscript{x} at UMBS. However, after demonstrating the significant changes in absolute mixing ratios as well as temporal variability in NO\textsubscript{x}, studies of the role of this foliage source of NO\textsubscript{x}, warrant further investigation.

4.6.3 Synthesis

Based on my air mass transport analysis, I conclude that advection and entrainment of polluted air masses in addition to local scale atmosphere-biosphere exchanges play an integral role in the observed NO\textsubscript{x} dynamics at UMBS. Advection of NO\textsubscript{x} and O\textsubscript{3} in the model was achieved by nudging the model layer above the canopy towards observation. Nudging the model allows me to assess the effects that local processes and non-local sources of pollution have on the temporal variability in NO\textsubscript{x} and O\textsubscript{3} within and below the canopy under observed conditions. As such, this study—including the presented model analysis—adds to that by Alaghmand et al. (2011), who analyzed the relative contributions of in-canopy air versus the supply of NO\textsubscript{x} and other pollutants through advection and entrainment of residual layer air masses at UMBS solely based on observations.

The 3 h lag in the NO maximum after sunrise suggests that this maximum could be associated (1) with entrainment of polluted air masses higher up in the residual layer or (2) with advection of pollution from an anthropogenic source area at an upwind distance resembling a 3 h transport time. Observed vertical gradients and meteorological data imply mixing ratios in the understory layer are depleted by chemical reaction and deposition and replenished by downward mixing of elevated mixing ratios from above the canopy. Alagh-
Figure 4.14: Similar to Fig. 4.13a but showing the simulated August mean diurnal cycle in NO\textsubscript{x} process tendencies (ppbv h\textsuperscript{-1}) for the crown layer for an assumed NO\textsubscript{2} compensation point of 1 ppbv.
Figure 4.15: Simulated August diurnal vertical profiles of NO\textsubscript{x}, NO, and O\textsubscript{3} mixing ratios using (a) default parameters and (b) parameters with 1 ppbv NO\textsubscript{2} compensation point. (c) The difference between simulation considering NO\textsubscript{2} compensation point and the default.
mand et al. (2011) suggested that downward mixing of localized polluted air masses did not contribute to the morning NO$_x$ maximum. Rather, they proposed that long-range transport of aged polluted air masses explain the observed NO$_x$ peak. In cases where the air mass did not flow through major sources of NO$_x$, they attributed the morning NO$_x$ maximum to local soil NO$_x$ emissions. Alaghmand et al. (2011) found that in the early morning hours (hours prior to 06:00 EST) $\sim$ 57% of the time, NO$_x$ mixing ratios were greater below than above canopy. Thus, they postulated that there is sufficient accumulation of NO$_x$ below canopy and if this NO$_x$ was to mix upward with the breakdown of the nocturnal boundary layer, it would contribute to the observed NO$_x$ maximum at sunrise. However, my observations and simulations showed little or no accumulation of NO in the understory layer, thus providing no evidence that soil NO emissions could influence the morning NO$_x$ maximum.

Munger et al. (1996) showed that HNO$_3$ could mix into the canopy layer at sunrise with the breakdown of the nocturnal boundary layer, but efficient deposition of total oxidized nitrogen (NO$_y$) would prevent HNO$_3$ to accumulate in the understory layer. If there was a sufficient amount of HNO$_3$ (or HONO) present on the surface of the canopy leaves, then photolysis upon sunrise could account for some of the increase in NO$_x$ mixing ratios during that time. My simulations showed that foliage emissions of NO$_x$ via nitrate photolysis alone could not explain the observed NO$_x$ maximum in the morning. In fact, it appears that the diurnal behavior is not properly represented including this foliage NO$_x$ source from nitrate photolysis. However, when considering the NO$_2$ compensation point at the leaf-scale of the canopy, the simulated results were closer to the observed, suggesting that the NO$_2$ compensation point mechanism may be important in explaining the dynamics of NO$_x$ at UMBS.

The below-to-above canopy O$_3$ dynamics in August reflects the combined role of in-canopy and boundary layer photochemistry and turbulent transport resulting in entrainment of free tropospheric air masses enhanced in O$_3$ compensating for canopy deposition. During the night, O$_3$ titration through its reaction with NO reduces below canopy O$_3$ levels. However,
the observed NO levels below canopy were generally about two orders of magnitude smaller compared to O$_3$ implying that other sinks, e.g., ozonolysis of very reactive BVOCs (Kurpius and Goldstein, 2003), and dry deposition likely contribute to the apparent significant ozone sink in the understory. Bryan et al. (2012) also conducted a model study for this site and concluded that deposition was the primary sink for ozone in the canopy layer.

The simulation of dry deposition in the model is based on the selected fixed cuticular, soil and other substrate resistances according to Ganzeveld and Lelieveld (1995). Recent studies (e.g. Zhang et al., 2002; Altimir et al., 2004, 2006) have shown a potentially important role of non-stomatal uptake of O$_3$ as a function of moisture conditions. To investigate the potential impact of such an enhanced removal by wet surfaces, I conducted an additional simulation in which I used the relative humidity (RH) of the simulated surface layer as a proxy for canopy wetness (Altimir et al., 2006) (note that the model actually calculates the wet skin fraction, i.e., the fraction of vegetation that is wetted by dewfall and rain interception). I introduced a reduced cuticular resistance scaled between the default maximum resistance of $10^5$ s m$^{-1}$ for a RH $< 70\%$ and an assumed leaf-scale minimum cuticular resistance of 1500 s m$^{-1}$ for a RH $> 95\%$; in between a RH of 70–95\%, a linear scaling between the minimum and maximum resistance was applied. Selection of the minimum cuticular resistance is based on the reported canopy-scale $V_{dO_3}$ between 0.1 and 0.3 cm s$^{-1}$ (Altimir et al., 2006, and references therein), resembling a canopy uptake resistance on the order of 500 s m$^{-1}$, and an LAI for this site on the order of 3–3.5 m$^2$ m$^{-2}$. Applying this substantially smaller non-stomatal uptake resistance as a function of RH resulted in simulated canopy O$_3$ mixing ratios, that were up to $\sim$ 13 ppbv smaller compared to the observed mixing ratios during nocturnal conditions. This indicates that this enhanced O$_3$ removal mechanism is not a good representation for this site. However, it is known that non-stomatal ozone conductance represents over half of the total ozone flux at this site (Hogg et al., 2007). It is uncertain what drives the non-stomatal uptake of ozone. Kurpius and Goldstein (2003) suggested that this would be driven by temperature dependence in BVOC emissions in which ozone scavenging
BVOCs would remove the ozone. In any case, my measurements do not allow me to partition between stomatal and non-stomatal uptake, and determining the drivers of the non-stomatal uptake is beyond the scope of this study.

Differences between the daytime August and November O$_3$ mixing ratios could reflect the combined effect of different boundary layer dynamics (see Fig. 4.3), with a reduced entrainment of free troposphere air masses enriched in O$_3$ in November compared to August. A reduced photochemistry in November is partly compensated by a reduced November O$_3$ sink associated with a decrease in dry deposition.

In summary, the observed morning NO maximum appears to be caused by the photolysis of NO$_2$ and leaf-level bidirectional exchanges of NO$_2$ may contribute to the observed NO$_x$ dynamics. NO$_2$ arises primarily from anthropogenic sources, and it is transported into the UMBS canopy by advection and entrainment.

4.7 Summary and conclusions

The dynamical behavior in NO$_x$ and O$_3$ at a deciduous forest site at UMBS was investigated. I observed consistent occurrences of NO and NO$_{x,MO}$ diurnal maxima above the canopy during the five-month measurement period from mid-summer to late-fall. These occurrences continued after leaf fall, which implies that the observed diurnal maxima of NO and NO$_{x,MO}$ are not controlled exclusively by biochemical processes in the canopy, but they are influenced also by processes not linked to the canopy. To determine the possible controls on the observed NO and NO$_{x,MO}$ diurnal maxima, I combined concentration gradient and micrometeorological measurements with a canopy-boundary layer exchange model for a detailed analysis of the role of local sources and sinks (i.e. biogenic emissions, dry deposition, and chemistry) and turbulent transport versus the role of advection.

According to my data analyses, the morning NO maximum at UMBS is associated with the increase in solar radiation after sunrise and most likely due to the photolysis of NO$_{2,MO}$. The model simulations indicate that soil NO emissions are not sufficient to explain the
morning NO\textsubscript{x,MO} peak concentrations. Also, sensitivity analyses with the SCM showed that foliage NO\textsubscript{x} emissions via nitrate photolysis do not appear to explain the observed morning NO\textsubscript{x,MO} (and NO) maxima above the canopy as these processes yielded a misrepresentation of the observed diurnal variability in NO\textsubscript{x,MO}. Instead, the SCM analyses suggest that a leaf-level NO\textsubscript{2} compensation point seems to play a role in the observed NO and NO\textsubscript{x,MO} dynamics.

Observed and simulated NO\textsubscript{x} data indicate that the morning NO\textsubscript{x,MO} maximum is associated with local and non-local transport events. The sensitivity analysis of the SCM and the analysis of air mass advection suggest that despite UMBS being located in a relatively remote area far from major urban sites, most of the NO\textsubscript{x,MO} seen at UMBS is of anthropogenic origin and that its impact is significant on the chemistry observed at the site.

To understand the dynamics of NO\textsubscript{x} at UMBS, leaf-scale processes should be considered in addition to large scale advection, boundary layer dynamics, and entrainment. Therefore, more studies on leaf-scale processes and their effect on the biosphere-atmosphere exchange are needed for further evaluation of this question.
Chapter 5

Evaluation of snowpack $O_3$ and $NO_x$ exchange at Summit, Greenland in a single-column chemistry-climate model

5.1 Abstract

In this chapter, I present an ongoing model study that evaluates the current representation of snowpack $O_3$ and $NO_x$ exchange in a single-column chemistry model using observation data from Summit, Greenland. The simulated results of the micrometeorology showed strong correlation ($r > 0.75$) to observation indicating that the basic micrometerology of the model is good. However, discrepancies between observed and simulated outgoing radiation and air temperature suggest that further tuning of the micrometeorology is required for more accurate simulation of the dynamics observed at Summit. A model experiment was done to determine whether gas-phase chemistry alone could explain observed variations in snowpack $O_3$ and $NO_x$ concentrations. Preliminary result from the model experiment indicates that gas-phase chemistry alone could not describe observed $O_3$ and $NO_x$ dynamics in snow. Only when a substrate-scale removal term was prescribed, the model was able to simulate observed $O_3$ gradients and deposition velocities in the snowpack. This meant that there are other chemical and physical processes involved in the observed behavior of $O_3$ and $NO_x$ in the snowpack. Further development of the model is needed, which incorporates chemical and physical processes not yet implemented in the model, to ultimately study the global impact of climate change on snow-air gas exchange.
5.2 Introduction

There is a strong effort to build models with the best detailed representation of the chemistry in the snowpack (e.g. Thomas et al., 2011), but often the progress that can be made is limited because we have not yet established a solid understanding of the chemical and physical mechanisms of the reactive trace gases (Grannas et al., 2007). While we may focus on developing models detailing the chemistry on and in the snow crystal surfaces, there is a need for us to synthesize what currently is known and incorporate this into 3-D atmospheric chemistry transport models to investigate the impacts of snow photochemistry globally in relation to pollution and climate change. Therefore, not only should we developing detailed snowpack chemistry models, we also need to develop sufficiently simple models that can capture the observed variations among field measurements.

In efforts to develop a unified 1-D model that can be incorporated into a 3-D global climate model, the initial process is to evaluate and improve the gas transport mechanism in snow. I will show in this chapter that gas transport is more important than the chemistry in interpreting the observed trace gas variability in and above the snowpack. In Chapter 2, I showed the importance of wind-pumping in ventilating the snowpack, and its influence on inferring gradient diffusion flux through the snow. Domine and Shepson (2002) estimated that the volume of the whole atmosphere can pass through the upper 10 cm of the snowpack, which covers \( \sim 33\% \) of the Earth’s surface, on a time scale of \( \sim 3 \) months. Combined with the knowledge of that snow is a medium for photochemical reactions (Grannas et al., 2007), the global impact that snow can have on the overlying atmosphere is huge.

In this chapter, I will present an ongoing study in which I evaluate the current the representation of snowpack \( \text{O}_3 \) and \( \text{NO}_x \) exchange in a single-column chemistry-climate model (SCM). The objectives of this study were to develop and evaluate a process-based representation of snowpack \( \text{O}_3 \) and \( \text{NO}_x \) exchanges at Summit, Greenland for implementation in global chemistry-climate models; to determine key \( \text{O}_3 \) and \( \text{NO}_x \) chemical reactions in the
snowpack; and to better describe the connections between air-snow O$_3$ and NO$_x$ exchanges on the tropospheric O$_3$ budget at Summit, Greenland.

5.3 Model description

The 1-D SCM used in this study is based on a modified version of the canopy model of Ganzeveld et al. (2002b). The physics and dynamics of the SCM was based on subcomponents of a chemistry-climate model ECHAM4 coupled with a regional atmospheric climate model RACMO. The chemistry scheme of the SCM, based on ECHAM4’s atmospheric chemistry scheme, considers natural and anthropogenic emissions, gas-phase and cloud water chemistry, turbulent and convective transport, and wet and dry depositions.

The SCM used the European Center for Medium-range Weather Forecast (ECMWF) reanalysis data to simulate advection of wind, temperature, humidity, and liquid water content. The SCM chemistry module was initialized with observed (i.e. user input) free troposphere trace gas concentration, which allowed the SCM to simulate advection of long-lived tracer.

Details on the structure and layout of the model is provided by Ganzeveld et al. (2002b), but briefly I will highlight the modifications made to the SCM for this study. The model column was partitioned into 63 layers. The upper 60 layers represented the atmosphere. Then, there were two snowpack layers and one ice layer in the lower part of the column (Fig. 5.1). The snowpack module uses a 2-layer scheme based on a well tested 2-layer canopy model scheme (Ganzeveld et al., 2002b).

The following schemes or parameterization (i.e. wind pumping, gas adsorption on ice crystal, and light transmission in snow) were added in the SCM for this study. For taking into account of the wind-pumping effects, the snowpack ventilation scheme of Toyota et al. (2013) was implemented, which is commonly used in other snowpack chemistry models (e.g.
Figure 5.1: Layout of the snowpack module is based on a 2-layer canopy model scheme by Ganzeveld et al. (2002b). The total snowpack thickness is 0.6 m and is divided into two layers of equal 0.3 m thickness. Transport (pink arrows) between each layer is solved analytically.
Thomas et al., 2011; Liao and Tan, 2008) as follows:

\[ U = \frac{6k \rho_{\text{air}} h}{\pi \mu \lambda} \sqrt{\frac{\alpha^2 + 1}{\alpha}} \left( C_1 \exp \left( -\frac{z}{\delta} \right) - C_2 \exp \left( \frac{z}{\delta} \right) \right) \]  \hspace{1cm} (5.1)

where \( \delta = \frac{\alpha}{\sqrt{\alpha^2 + 1}} \frac{\lambda}{2\pi} \), \( C_1 = \frac{\exp \left( \frac{H_s}{x_p} \right)}{\exp \left( \frac{H_s}{x_p} \right) + \exp \left( -\frac{H_s}{x_p} \right)} \), and \( C_2 = \frac{-\exp \left( \frac{H_s}{x_p} \right)}{\exp \left( \frac{H_s}{x_p} \right) + \exp \left( -\frac{H_s}{x_p} \right)} \). \( U \) is the wind pumping speed, \( k \) is snowpack permeability, \( \mu \) is the dynamic viscosity of air, \( u \) is surface wind speed measured at 2 m above snow surface, \( \rho_{\text{air}} \) is air density, \( h \) is the relief amplitude of the snow surface, \( \lambda \) is the relief wavelength of the snow surface, \( \alpha \) is the horizontal aspect ratio of the relief that is the horizontal axis divided by the relief wavelength, \( z \) is the measurement distance from the snow surface, and \( H_s \) is the average snow depth.

The snow surface area (SSA) parameterization was taken from Fig. 5 of Domine et al. (2008) as such:

\[ y = -308.2 \ln x - 205.96 \]  \hspace{1cm} (5.2)

where \( y \) is the SSA (cm g\(^{-2}\)) and \( x \) is snowpack density (g m\(^{-1}\)). Adsorption of trace gases to the ice crystal surface was implemented based on a semi-empirical approach by Herbert et al. (2006) as shown:

\[ f = \frac{1}{1 + r_{sp} \times K_{ia} \times SSA} \]  \hspace{1cm} (5.3)

where \( f \) is the relative fraction of the chemical in the snow pore space, \( r_{sp} = \rho_{s}^{1-\phi} \) is the ice-to-air ratio (kg m\(^{-1}\)) with \( \rho_{s} \) being snow density (kg m\(^{-1}\)) and \( \phi \) being snow porosity, \( K_{ia} \) is the interfacial-air partitioning coefficient (m m\(^{-3}\)), and SSA is the snow surface area (Eq. 5.2). Light transmission in snow is important for photochemistry. The SCM used the light transmission in snow scheme described by Lee-Taylor (2002).

5.4 Model validation

5.4.1 Model initialization

The snowpack chemistry was initialized with averaged nitrate (NO\(_3^-\)) concentrations and \( J_{\text{NO}_3^-} \) values reported by Honrath et al. (2002) (Table 5.1).
The wind pumping module required snow surface microtopography data. I used the following: surface relief height, length, and width: 0.23 m, 2.2 m and 1.3 m, which I roughly estimated from photographic images of the snow surface taken at Summit in 2008 (not shown). The dependency of topographic data for the wind pumping module is a significant weakness as the topographic information of snow covered sites is not well documented and the surface continuously changes with time. In future studies, I intend to develop a more simplified wind pumping module based on the differential pressure and wind speed data analysis that I have done in Chapter 2, which I showed that wind speed and differential pressure amplitude are linearly correlated. Further investigation will be done to build a mathematical model of the relationship among wind speed, differential pressure amplitude, and snowpack ventilation. The advantage of my scheme will be independent of the snow surface topography, but because the scheme will be based on empirical data from a high elevation, subalpine site, the applicability of the scheme may be limited.

5.4.2 Micrometeorology validation

To properly simulate mass flux, the micrometeorology in the model needs to be correct. The basic micrometeorology of the SCM has been tested and tuned previously by Niemendal (2008). I was able to verify that the model is able to predict the micrometeorology at Summit fairly well ($r > 0.75$, Fig. 5.2). Simulated maximum temperatures were overestimated, whereas simulated outgoing radiation was underestimated. The discrepancy in these two parameters indicates that the atmospheric stability functions and the heat and momentum fluxes used in the model requires further tuning to correctly simulate conditions at Summit. Further investigation is required to resolve the discrepancies of the micrometeorology in the model. However, given the good correlation between the observed and simulated results, I deemed that the model was able to sufficiently represent the micrometeorological conditions at Summit for this study.
Figure 5.2: Comparing simulated results with measurements from the field. (A) Wind speed at 8.5 m above the snow surface. (B) Temperature at 2 m above the snow surface. (C) Incoming shortwave radiation. (D) Outgoing shortwave radiation. The $r$ value is the linear correlation coefficient between the measured and the simulated.
5.4.3 Chemistry validation

Two model experiments were conducted to validate the representation of the chemistry in the SCM. First, I tested if the snowpack-NO$_3^-$ concentration and $J_{NO_3}$ values from Honrath et al. (2002) would result in proper order of magnitude NO and NO$_2$ in the snow. Second, I evaluated if gas-phase NO$_x$ chemistry was sufficient enough to explain most of the O$_3$ removal in snow.

Initializing the snowpack NO$_3^-$ concentration and $J_{NO_3}$ using values reported by Honrath et al. (2002) resulted in a factor of 2–3 overestimation in NO and NO$_2$. The model was able to properly simulate the observed O$_3$ enhancement (days 17–18) in the upper snow layer (Fig. 5.3a). Diurnal timing of NO in the snowpack were captured in the simulation (Fig. 5.3b). The enhancement in NO$_2$ concentrations at the $-0.45$ m depth in the snowpack relative to the 0.15 m depth was also properly simulated (Fig. 5.3c).

Table 5.2 provides an estimate of how much gas-phase NO$_x$-O$_3$ chemistry alone explains for the observed O$_3$ removal. Simulation with only NO$_x$-O$_3$ chemistry explains $\sim 10\%$ of observed ozone gradient. The other 90% requires additional sink (e.g. sticking or quasi-liquid layer chemistry not yet incorporated) at each snow grain surface (referred to as substrate-scale removal, SSR). SSR have been scaled to $0.0005$ cm s$^{-1}$ to reproduce observed O$_3$ gradient using the snow surface area index on the order of 22 m, this can be compared with the bulk snowpack removal rate, but it does not result in proper fluxes suggesting that further evaluation of turbulent and diffusion transport is needed.

This implies that NO$_x$-O$_3$ chemistry plays a minor role in O$_3$ destruction in the snow and that there are other sinks that contribute significantly to the snowpack uptake of O$_3$, such as halogen, quasi-liquid layer (QLL), organics, and other yet unknown physical and chemical processes. This finding compliments the results from a model study by Grannas et al. (2002), who evaluated how much of the measured trace gases over snow could be explained by gas-phase chemistry. For NO$_x$, Grannas et al. (2002) found that gas-phase chemistry could only
Figure 5.3: Measured and simulated $O_3$, NO, NO$_2$ concentrations in the snowpack in April 14–20 (22 for model), 2009. The color contour plots on the left are measured concentrations in the snowpack. The line plots on the right are simulated concentrations in the snowpack at depths 0.15 m and 0.45 m from the snow surface.
explain \sim 5\% of the measured NO\textsubscript{x} concentration over snow. Combining the imposed SSR and NO\textsubscript{x}-O\textsubscript{3} chemistry in the model run results in bulk snowpack O\textsubscript{3} $V_d$ within range of $-0.01 \text{ cm s}^{-1}$ to $0.01 \text{ cm s}^{-1}$ in Spring at Summit reported by Helmig et al. (2009b).

By evaluating the tendencies (the rate of change of O\textsubscript{3} over time at a given point in space), the drivers of O\textsubscript{3} removal in the snow can be determined. Fig. 5.4 shows that net O\textsubscript{3} tendencies is driven by turbulence. Therefore, proper simulation of micrometeorology is key! However, chemistry becomes important when contribution from turbulence is low.

![Figure 5.4: Processes that drive simulated O\textsubscript{3} tendencies at 8.5 m above the snowpack at Summit, Greenland.](image)

Within the currently considered chemical processes of O\textsubscript{3} tendencies, the NO\textsubscript{x}-O\textsubscript{3} reaction mechanism dominates the net chemical tendency in and above the snowpack (Fig. 5.5). Above the snowpack, the NO\textsubscript{x}-O\textsubscript{3} reaction mechanism plays a role in O3 production (Fig. 5.5a). In the snowpack, NO\textsubscript{x}-O\textsubscript{3} reaction mechanism is a O3 sink (Notice that in Fig. 5.5b, the NO\textsubscript{x}-O\textsubscript{3} line is under the chemical tendency line).
Figure 5.5: Chemical reactions that drive the chemical processes of the $O_3$ tendencies (A) above the snowpack at 8.5 m and (B) at −0.15 m from the snow surface.
5.5 Conclusions and outlook

Further development of the model is required to address the deficiencies in the representation of the micrometeorology and gas transport through snow in the SCM. However, the preliminary results presented in this chapter indicate that basic representation of the micrometeorology in the SCM is good \( r > 0.75 \) when correlated to observations. From the first set of model experiments, I am able to conclude that NO\textsubscript{x}-O\textsubscript{3} gas-phase chemistry alone is insufficient in explaining the observed O\textsubscript{3} uptake to snow. Only when a SSR value of 0.0005 cm/s was prescribed, the model was able simulate observed O\textsubscript{3} concentration gradients and deposition velocities. The implication of the SSR is that there are other chemical and physical processes in the snowpack that contributes to the removal of O\textsubscript{3}. Heterogeneous QLL chemistry in snowpack chemistry model studies is a currently active topic of discussion, and there is an effort to improve the description of QLL chemistry in snow (e.g. Boxe and Saiz-Lopez, 2008; Thomas et al., 2011; Grannas et al., 2007; Domine and Shepson, 2002). Thus, the next step in this model development work will be to investigate the aqueous phase chemistry scheme of the SCM and improve the representation of QLL chemistry in the model. Through these incremental steps in model development, the ultimate goal of the project that is to determine the response of climate change on snowpack-O\textsubscript{3} exchange at the global scale can be achieved.
Table 5.1: Reported nitrate concentrations in snow. The value used to initialize the SCM’s nitrate concentration was taken from Honrath et al. (2002).

<table>
<thead>
<tr>
<th>[NO$_3^-$] ($\times 10^{20}$ molec m$^{-2}$)</th>
<th>$J_{NO_3-NO_x}$ ($\times 10^{-6}$ 1/s)</th>
<th>Location</th>
<th>Reference</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6</td>
<td>N/R</td>
<td>Svalbard</td>
<td>Beine et al. (2003)</td>
<td>Total conc.</td>
</tr>
<tr>
<td>3.6</td>
<td>N/R</td>
<td>Summit</td>
<td>Dibb et al. (1998)</td>
<td>Average inventory value</td>
</tr>
<tr>
<td>7.2</td>
<td>N/R</td>
<td>Summit</td>
<td>Dibb et al. (1998)</td>
<td>Average snow surface (top 50 cm) conc.</td>
</tr>
<tr>
<td>7.2–48</td>
<td>3.5</td>
<td>Summit</td>
<td>Honrath et al. (2002)</td>
<td>Max photolysis during the day</td>
</tr>
<tr>
<td>26</td>
<td>1.3</td>
<td>Summit</td>
<td>Honrath et al. (2002)</td>
<td>Average values</td>
</tr>
<tr>
<td>18</td>
<td>0.83</td>
<td>Summit</td>
<td>Jacobi and Hilker (2007)</td>
<td>Conc. value from Dibb et al. (1998)</td>
</tr>
<tr>
<td>21–30</td>
<td>N/R</td>
<td>Summit</td>
<td>Thomas et al. (2011)</td>
<td>From Dibb et al. measured in summer 2008</td>
</tr>
<tr>
<td>6.9–9.4</td>
<td>N/R</td>
<td>Dome C</td>
<td>Frey et al. (2009)</td>
<td>Value from personal comm. with Dibb</td>
</tr>
<tr>
<td>36</td>
<td>N/R</td>
<td>South Pole</td>
<td>Liao and Tan (2008)</td>
<td></td>
</tr>
</tbody>
</table>

N/R, not reported

Table 5.2: Average simulated and observed O$_3$ gradients, $\Delta$O$_3 = [O_3]_{8.5m} - [O_3]_{0.15m}$, and its resulting bulk snowpack-O$_3$ deposition velocities, $V_d$, for April 14–20, 2009. Substrate-scale removal rate, SSR, represent additional sinks in the snowpack (not yet incorporated in the model) to result in simulated $\Delta$O$_3$ that was close to observed $\Delta$O$_3$.

<table>
<thead>
<tr>
<th>Simulated NO$_x$-O$_3$ chem. + SSR</th>
<th>Only SSR ($= 0.0005$ cm$^{-1}$)</th>
<th>Only NO$_x$-O$_3$ chem.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta$O$_3$ (ppbv)</td>
<td>Measured</td>
<td></td>
</tr>
<tr>
<td>7.50</td>
<td>7.38</td>
<td>6.76</td>
</tr>
<tr>
<td>$V_d$ (cm/s)</td>
<td>$\leq 0.01^a$</td>
<td>$2.1 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

$^a$ Helmig et al. (2009b)
Chapter 6

Conclusions

6.1 Summary and key findings

The presence of snow can influence the composition of near-surface air. Quantifying and understanding the chemical and physical processes that occur in snow as trace gases are transported through it are important for predicting how climate change will affect the atmosphere and the biogeochemical cycle at regional and global scales. To achieve this, snow-air gas exchange studies need to be conducted at various snow-covered locations. Historical goals for evaluating techniques of analyzing ice cores have limited snow-air interaction studies of reactive trace gases to Polar sites. And, in the mid-latitude sites, trace gas fluxes were measured during the snow-covered period for the purpose of balancing the biogeochemical budget, as the winter season was ignored by ecologists (Williams et al., 2009a; Campbell et al., 2005). But, there is great value in making flux measurements of reactive gases in mid-latitude sites for two main reasons. First, Polar studies showed that snow is a highly reactive medium for photochemical reactions, heterogeneous reactions, and physical exchange processes (Domine et al., 2008). Due to this property of the snow, as previously mentioned, snow can greatly perturb the overlying atmosphere. This effect will not be limited to just Polar snowpack but for all snow. Second, a snow-air gas exchange study of reactive gases conducted at a mid-latitude, high elevation site (Helmig et al., 2009c) demonstrated that certain photochemical processes observed in Polar snowpack can be masked by biogeochemical processes under the snow. As a result, the impact that mid-latitude snow can have on
its overlying atmosphere can be very different from Polar snow.

In my thesis, I used a novel in-snow trace gas sampling system based on the gradient diffusion method (GDM) to measure trace gas fluxes of CO$_2$, O$_3$, and NO$_x$ through snow at two different forest ecosystems: a high elevation subalpine forest (NWT LTER) and a low elevation deciduous forest (UMBS). I focused on forested ecosystems because forests are the largest terrestrial sink for carbon (Pan et al., 2011) and cover nearly 30% of the Earth’s surface with 45% of forests experiencing seasonal snow cover (MA, 2005). I investigated the possible impact of climate change on snowpack trace gas fluxes at the NWT LTER site by examining the applicability of the results from that study to the findings at the UMBS site.

GDM is a commonly used approach for calculating trace gas fluxes through snow in sites for multiple reasons. One reason is the relative simplicity and low costs associated with it. The other reason is it allows for better process-based understanding of trace gas movement through snow. GDM allows for flux measurements in areas where direct flux measurement techniques such as the eddy covariance method cannot be used. In fact, over a quarter (26.5%) of the worlds forests are in mountainous or complex terrain (MA, 2005). Therefore, the use of GDM for estimating wintertime fluxes requires thorough evaluation.

In Chapter 2 and 3, I evaluated the GDM and quantified the errors associated with the method when inferring trace gas fluxes through snow. The major contributing factors to the uncertainty and variability in the inferred flux data are the error in measuring the snow physical properties. The errors from these measurements non-linearly propagates in the process of calculating the flux. This is due to the porosity and tortuosity terms being indirectly derived from the snow density measurements. I demonstrated how these uncertainties are reduced when data from several gradient heights are statistically evaluated and combined for deriving a more representative, average flux value. Also, measurements of trace gas concentrations at the soil-snow interface are most sensitive to wind-pumping effects, which was theorized by Massman et al. (1997) from a model study. I also determined that wind-pumping led to a large (<30%) underestimation of the calculated flux supporting the
results of Suzuki et al. (2006). The correlation analysis of differential pressure and wind speeds yield that these two parameters are directly related. This finding will contribute to model development and parameterization of trace gas movement through snow.

The automated in-snow trace gas sampling system that I introduced in Chapter 2 has been used with great success for measuring not only CO$_2$ (Liptzin et al., 2009; Seok et al., 2009, Chapter 3), O$_3$ (Helmig et al., 2009b,c, Chapter 3), and NO$_x$ (Helmig et al., 2009c, Chapter 3), but for other trace gases such as N$_2$O (Filippa et al., 2009), Hg$_0$ (Faïn et al., 2013; Van Dam et al., 2013), and volatile organic compounds (Helmig et al., 2009a). One notable success using this sampling system is from the Hg$_0$ study of Faïn et al. (2013). This study demonstrated that photochemical production of Hg$_0$ occurs throughout the entire winter and that snow effectively reduces the effects of atmospheric mercury deposition to watersheds due to reemission fluxes prior to snow melt. Van Dam et al. (2013) used the in-snow measurements (from the in-snow sampling system) to supplement their investigation of O$_3$ and Hg$_0$ depletion events observed at Toolik Lake, Alaska. The successes and discoveries from these studies using this in-snow sampling system has led to a new 2-year project at Toolik Lake, Alaska for further investigation of the Hg$_0$ dynamics in and above the snowpack (Helmig, personal communication). Also, variations of the sampling system have been used by others (e.g. Aaltonen et al., 2012; Merbold et al., 2013; Miao et al., 2012; Sullivan et al., 2012; Wang et al., 2013; Zhu et al., 2012), and the sampling system has made important technical contributions on gaining insights about the dynamics of snowpack gas exchange in diverse snow-covered environments.

In Chapters 3 and 4, I investigated the dynamics of O$_3$ and NO$_x$ during snow-covered and snow-free conditions at a low elevation forest site (UMBS). Despite UMBS being located in a relatively remote area far from major urban sites, most of the NOx seen at UMBS were determined to have anthropogenic origins through the analysis of air mass advection, and the urban source NO$_x$ had a significant impact on the chemistry observed at the site based on model sensitivity analysis. The most important finding that I have made is that the snowpack
behaves analogously to the canopy with respect to NO\textsubscript{x} concentrations. The potential for the canopy to act as a sink or a source depending on the ambient air NO\textsubscript{2} concentration is known, and this dynamic behavior of the canopy poses a major challenge in closing the NO\textsubscript{x} budget known as the “NO\textsubscript{2} flux conundrum” (Lerdau et al., 2000). In addition to the model study during snow-free conditions (Chapter 4), the discrepancy between simulated and observed NO\textsubscript{2} concentrations at UMBS could be explained by simulating a leaf-level bidirectional exchange of NO\textsubscript{2} in the model. This implied that the leaf-level NO\textsubscript{2} compensation point in the canopy plays an important role in the observed dynamics of NO\textsubscript{x}.

Honrath et al. (2000b) showed that mid-latitude snow can produce NO\textsubscript{x} and questioned to what degree snow photochemistry was active under more polluted conditions. In Chapter 3, this question was partly addressed with monitoring of NO\textsubscript{x} concentrations in and above the snowpack. NO\textsubscript{x} concentrations in the snowpack showed a strong diurnal signal with elevated concentrations during the day, implicating photochemical production and supporting the results of (Honrath et al., 2000b). But under more polluted conditions, the deposition of NO\textsubscript{x} in the snow surface was observed. This has potentially strong implications on the chemistry of NO\textsubscript{x} and oxidative capacity of the atmosphere in snow-covered forested sites influenced by air masses from urban and industrial regions. This dynamics behavior of the snowpack on the snow-air exchange of NO\textsubscript{x} with respect to ambient air concentrations adds to the already complex and highly uncertain NO\textsubscript{2} flux between the atmosphere and the biosphere.

Lastly, in Chapter 5, the preliminary results from the model study reiterated the complexities and the unknowns in snow-air gas exchange for reactive gases. NO\textsubscript{x} gas-phase chemistry in interstitial air failed to explain O\textsubscript{3} uptake to snow, and only when a substrate-scale removal term was prescribed, the model was able to simulate observed in-snow O\textsubscript{3} concentration gradient and deposition velocities. This implies that there are other chemical and physical processes in the snowpack that contribute to the removal of O\textsubscript{3}. Further investigation of the chemical processes are required, but first, proper representation of the physical
processes, i.e., the micrometeorology and the gas transport through snow, is needed.

6.2 Concluding remarks

The findings presented in this thesis collectively demonstrate the importance of understanding the biosphere-atmosphere interaction in snow-covered environments. Some of the results in this thesis already have contributed to subsequent research on quantitative evaluation and understanding of the mechanisms of trace gas fluxes through snow (e.g. Bowling and Massman, 2011; Huwald et al., 2012; Maier et al., 2011, 2012). Future climate change will have profound effects on the atmospheric composition and the gas exchange in forested ecosystems. To accurately predict how changes in the atmosphere and snow cover will affect ecosystem carbon and nitrogen uptake, we must continue to develop and improve measurement systems for determining trace gas fluxes through snow (Björkman et al., 2010b) and develop field and laboratory experiments that will help our understanding of temporal dynamics and controls of fluxes measured at different scales. Modeling studies supported by field observations and laboratory experiments are needed to validate the model results and to determine whether the results are representative for other locations. This will help us develop predictive modeling capabilities and parameterizations of processes in-snow and interplay with the atmosphere for inclusion in regional and global atmospheric chemistry models (Thomas et al., 2012). Thus, we will be able to better assess the impact of climate change on the Earth system.

6.3 Future outlook

The core of my thesis has been making field observations. With the data that I have collected, the next set of research projects should focus on model development and validation. There are many observed phenomena that cannot be explained with the data that I have collected without additional field measurements or through model studies. First conducting model studies will be more beneficial as results from these studies can aid in planning for
Thus far, there are no reported models that unify the biogeochemical processes in soil and the physical and chemical processes in snow. The most recent models or modules used in chemistry-climate models still deal with snow processes and soil processes separately. Current biogeochemical modules used in chemistry-climate models heavily depend on soil temperature or soil moisture for simulating emissions of trace gases from soil (e.g. Li et al., 2000). This dependence usually results in zero emissions from soils when temperatures are at freezing or below freezing, or underestimation of fluxes during snow-covered periods due to snowpack ventilation (as discussed in Chapters 2 and 3, and in Seok et al., 2009; Björkman et al., 2010b; Takagi and Nomura, 2005; Massman and Frank, 2006; Massman, 2006; Bowling and Massman, 2011). Now, there are studies numerous studies that show there is continued soil emission in snow-covered areas, and the processes that drive these emissions under snow and ventilation in snow must be accounted for in estimating wintertime fluxes (e.g. Brooks et al., 1996; Monson et al., 2006b; Liptzin et al., 2009; Bowling and Massman, 2011; Seok et al., 2009; Takagi and Nomura, 2005). Therefore, it is necessary to incorporate the findings from these studies into the chemistry-climate models.

It is also necessary to include the known chemistry and physical processes that occur through snow in the chemistry-climate models, because as previously noted, snow is a medium for various chemical reactions. The latest set of snowpack chemistry models (e.g. Thomas et al., 2011; Liao and Tan, 2008; Toyota et al., 2013, and Chapter 5) strive to enhance our understanding of the chemical and physical processes that occur in the snowpack and its impact on the overlying atmosphere. The model that I am helping develop (Chapter 5) is focused on improving the physical processes in snow. As shown in Chapter 5, physical processes (i.e. trace gas transport, dry deposition) in snow are the contributors in observed chemical dynamics. Liao and Tan (2008) and Toyota et al. (2013) mention the importance of correctly simulating the physical processes in snow as this determines the distribution of trace gases that ultimately affect the chemical processes. The questions of how much detail
is required and which processes should be emphasized more in the model development are
hotly debated topics in the modeling community (AICI Conference 2013). There has been
a general tendency towards focusing on improving the chemistry in snowpack models since
Grannas et al. (2002) showed that gas-phase only chemistry was insufficient for explaining
the observed chemical concentrations (Domine and Shepson, 2002). As a result, Thomas
et al. (2011) and Toyota et al. (2013) included a detailed chemistry module in their models.
This limited their simulation duration to two to three-days due to differences in chemical and
physical processes time scales. Chemical reactions require significantly shorter time steps (<
1 s) than physical processes (~minutes, hours, and longer). This makes it computationally
expensive to conduct simulations over an extended period by model runtime (Toyota et al.,
2013). Thus, Thomas et al. (2011) and Toyota et al. (2013) had to set the physical processes
constant through the simulation period and could only investigate periods when the atmo-
spheric conditions did not vary. Despite these limitations, Thomas et al. (2011) were able
to show that mechanisms based on first principles can correctly describe the coupled atmo-
spheric and in-snow chemical processes. The model of Toyota et al. (2013) was more detailed
than Thomas et al. (2011) in both chemical and physical processes. Toyota et al. (2013)
concluded that the added details in their model only provided limited improvement in un-
derstanding of the significance of unknown chemical interactions and in comparison to their
past model study, even a simplified snow-air interaction scheme could successfully simulate
observations. This implies that providing more elaborate chemical and physical mechanisms
in these snowpack chemistry models is not necessarily beneficial. However, detailed model
studies as those by Thomas et al. (2011) and Toyota et al. (2013) are required for us to
prioritize the mechanisms that are most important and that should be incorporated into
chemistry-climate models. It is essential that we build on our current knowledge in de-
veloping and improving models for assessing the impact that climate change will have on the
Earth system.


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