Ammonia and Aerosol Emission Impacts: New Insights with Open-path Measurements

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Abstract

Atmospheric aerosols and their precursors have significant influences on Earth’s climate and tropospheric air quality. Aerosol direct and indirect radiative forcing currently constitute the largest uncertainties for future climate change predictions. Anthropogenic aerosols degrade regional air quality, with implications for human health. Aerosol and precursor observations on multiple spatial scales are necessary to understand primary emissions, secondary formation, long-range transport and nitrogen deposition. Ammonia (NH$_3$) is an important gas-phase precursor to fine particulate matter. Recent air quality model simulations show large discrepancies with NH$_3$ observations due to significant emission inventory uncertainties, especially for increasing, highly variable agricultural NH$_3$ emissions. Gas-phase NH$_3$ measurement challenges due to surface adsorption and partitioning in closed-path NH$_3$ sensors have led to a lack of widespread NH$_3$ observations. To improve our understanding of aerosol and NH$_3$ precursor emissions, my dissertation focuses on synthesizing new observations from continental to individual emission plume scales. First, I synthesized multiple aerosol datasets to track the physical and chemical evolution of biomass burning smoke aerosols and quantified how their long-range transport influenced U.S. air quality. Next, I developed and performed rigorous field testing of a quantum cascade laser-based, open-path NH$_3$ instrument capable of high precision (0.15 ppbv NH$_3$), high time resolution (10 Hz) field measurements with minimal sampling biases. Upon validating its field performance, I applied this sensor to perform open-path, mobile measurements of NH$_3$ dairy emission ratios in the Central Valley, California during the NASA DISCOVER-AQ field campaign. Ammonia emission ratios were quantified from individual dairy farms to regional scales through syntheses with aircraft measurements. The final part of my dissertation involved the development and field deployment of a quantum cascade laser-based, open path-integrated methane sensor, which achieved long path length, high precision (0.5% at 1 Hz) measurements in an Arctic field environment. The path-integrated configuration is applicable for future NH$_3$ measurements on comparable spatial scales to regional model simulations. Ultimately, these efforts have implications for understanding aerosol
long-range transport and provide new high resolution, in-situ NH$_3$ measurement capabilities applicable for validating NH$_3$ emission inventories and air quality modeling efforts to constrain NH$_3$ emission influences on air quality.
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Chapter 1

Introduction

1.1 Motivation

Atmospheric aerosols are important species that influence the Earth’s climate system and tropospheric chemistry (Jimenez et al., 2009; Murphy et al., 2013; IPCC, 2013). Aerosol direct and indirect radiative effects include scattering and absorption of solar radiation, aerosol-cloud interactions and influences on precipitation (Rosenfeld et al., 2000; Kaufman et al., 2002; IPCC, 2013). The radiative forcing associated with natural and anthropogenic aerosols currently constitutes the largest uncertainty in future predictions of climate change (IPCC, 2013). Aerosol radiative effects depend on physical, chemical and optical properties. Fine inorganic and organic aerosols scatter solar radiation and black carbon aerosols absorb solar radiation (IPCC, 2013; Murphy et al., 2013). Natural and anthropogenic aerosols are emitted from primary sources and are produced in the atmosphere by nucleation and aerosol growth processes (secondary formation) from precursor emissions of sulfur dioxides (SO$_2$), nitrogen oxides (NO$_x$), ammonia (NH$_3$) and organic species. Global aerosol distributions are non-uniform, leading to regionally variable radiative forcing and indirect effects (Murphy et al., 2013).

Anthropogenic particulate matter loading perturbs troposphere composition, leading to significant and variable impacts on air quality, human and ecosystem health (Pope et al.,
Aerosol particles with aerodynamic dry diameters less than 2.5 μm, known as PM2.5, are of particular concern for human health, as these fine particulates can be carried deep into the human respiratory tract (World Health Organization, 2008). Epidemiological studies have estimated that long-term exposure to combustion-related fine particulate pollution is a significant environmental risk factor for premature mortality associated with cardio-pulmonary diseases and lung cancer (Pope et al., 2002). To protect human health, the United States Environmental Protection Agency (U.S. EPA) has established National Ambient Air Quality Standards (NAAQS) under the Clean Air Act, including regulation of fine and coarse mode particulate matter mass concentrations (U.S. EPA NAAQS). The current standards for PM2.5 set by the U.S. EPA are 35 μg m⁻³ in a 24-hour period (98th percentile, averaged over 3 years) and 15 μg m⁻³ annually averaged over 3 years for secondary PM2.5 (U.S. EPA NAAQS). Although precursor emissions of sulfur dioxide (SO₂) and nitrogen oxides (NOₓ) from fossil fuel combustion have decreased in the U.S. due to Clean Air Act regulations, there is still considerable non-compliance for PM2.5 in many U.S. counties in highly populated, urban metropolitan areas (PM2.5 Standard Nonattainment Areas, 2006). Approximately 66 million people (21% of the U.S. population in 2010) reside in PM2.5 24-hour standard non-attainment counties as of December 2013 (PM2.5 Standard Non-attainment Areas, 2006).

To constrain the influences of aerosols on climate and air quality, observations must be carried out on local, regional and global scales from remote sensing observations of aerosol optical depth (Kaufman et al., 1997) and absorbing aerosols (Torres et al., 2007) to vertical profiles from ground-based and satellite-based aerosol lidars (Welton et al., 2001; Winker et al., 2010). Ground-based chemical composition, physical and optical properties are also measured with sun photometers (AERONET) and speciation sampling (IMPROVE) (Holben et al., 2001; Hyslop and White, 2008). The integration and synthesis of these observations and platforms on various scales is necessary to constrain impacts on aerosol emissions, secondary
formation, transport, transformation and deposition, with implications for air quality, climate and ecosystem health.

In addition to aerosol observations, quantifying the emissions, atmospheric transformations and fate of aerosol precursors is essential to constrain influences on air quality and climate. Ammonia (NH$_3$), the dominant atmospheric base and most abundant reduced nitrogen (N) species in the atmosphere, is an important gas-phase precursor to ammoniated fine particulate matter, as it reacts with acidic species to form ammonium sulfate ((NH$_4$)$_2$SO$_4$) and ammonium nitrate (NH$_4$NO$_3$) aerosols (Nowak et al., 2007; Pinder et al., 2008). Ammonium sulfate accounts for $\sim$47% of PM$_{2.5}$ mass concentrations in the eastern United States (Anderson et al., 2003) and ammoniated aerosols dominate the molar composition of urban aerosols (Jimenez et al., 2009). Ammonia influences inorganic aerosol nucleation and new particle formation (Ball et al., 1999; Hanson and Eisele, 2002; McMurry et al., 2005; Benson et al., 2011) as well as fine inorganic aerosol radiative properties (Martin et al., 2004).

Atmospheric NH$_3$ is a significant N species in the global reactive N cycle. The current rate of anthropogenic nitrogen fixation is more than double the natural rate of terrestrial N fixation, with the Haber-Bosch production of NH$_3$ being a major contributor (IPCC 2007; Erisman et al., 2008; Cansfield et al., 2010). Global NH$_3$ emissions have more than doubled since pre-industrial times, largely due to intensification of agricultural livestock and fertilizer use (Galloway et al., 2003). Ultimately, total ammonia (NH$_x$ = NH$_3$ + NH$_4^+$) is removed from the atmospheric by wet and dry deposition. Condensed phase ammonium (NH$_4^+$) is a dominant form of N in bulk deposition (Fenn et al., 2003; Galloway et al., 2003). Total ammonia deposition contributes to the acidification and eutrophication of natural terrestrial and aquatic ecosystems, with impacts on biodiversity and coastal anoxia (Galloway et al., 2003; Gruber and Galloway, 2008; Bobbink et al., 2010; Canfield et al., 2010). Although mass concentrations of inorganic sulfate and nitrate in U.S. wet deposition measurements have declined in recent decades, NH$_4^+$ wet deposition has increased (Lehmann et al., 2005; Lehmann et al., 2007). As oxidized N deposition declines due to decreases in U.S. NO$_x$
emissions, reduced N is becoming the dominant form of reactive N wet and dry deposition (Mathur and Dennis, 2003; Pinder et al., 2008; Ellis et al., 2013).

Ammonia is emitted from diverse anthropogenic and natural sources with high spatial and temporal variability. Agricultural fertilizer volatilization from cropland soil, and livestock activities are the major NH$_3$ sources, accounting for over 60% of the global inventory (Aneja et al. 2008a; Lamarque et al., 2010). Agricultural NH$_3$ emissions impact air quality and human health. Paulot and Jacob (2013) recently reported that NH$_3$ emissions associated with agricultural food exports significantly increase U.S. population exposure to PM$_{2.5}$. Ammonia is also a by-product of fossil fuel combustion (vehicles and power plants), biomass burning and other minor sources including sewage treatment plants and the ocean (Clarisse et al., 2009; Lamarque et al., 2010). The U.S. EPA currently monitors ambient NH$_3$ concentrations in the Passive Ammonia Monitoring Network (AMoN) at long integration times (2-week measurements) [http://nadp.isws.illinois.edu/amon](http://nadp.isws.illinois.edu/amon). However, NH$_3$ is not currently regulated by the U.S. EPA as a PM$_{2.5}$ precursor. In contrast, NH$_3$ emissions have been effectively regulated in Europe (Gothenburg Protocol, 1999; Aneja et al., 2008b). Recent studies have highlighted the potential for controlling PM$_{2.5}$ cost effectively with NH$_3$ emission reduction policies (Pinder et al., 2007; Wang et al., 2013).

Ammonia emission inventories are highly uncertain, with up to 50% uncertainties in global NH$_3$ emission budgets and even higher uncertainties in many large source regions (Battye et al., 2003; Gilliland et al., 2006; Aneja et al., 2008a; Clarisse et al., 2009). Comparisons between atmospheric model simulations and satellite observations suggest that current NH$_3$ emission inventories are under-estimated (Shephard et al., 2011; Heald et al., 2012; Walker et al., 2012). Gas-phase NH$_3$ has a short tropospheric lifetime of a few hours to a few days, which depends on ambient temperature, relative humidity and aerosol composition (Anderson et al., 2003). More widespread high spatial and temporal resolution atmospheric NH$_3$ observations are essential to validate emission inventories and regional air quality models used to assess
impacts and inform policy actions (Reis et al., 2009; Dennis et al., 2010; Heald et al., 2012; Walker et al., 2012).

Satellite NH$_3$ observations have recently been developed to characterize global and regional NH$_3$ distributions. The NASA Tropospheric Emission Spectrometer (TES) provides 5 x 8 km footprint representative volume mixing ratio retrievals with two overpasses every 16 days (Shephard et al., 2011). The Infrared Atmospheric Sounding Interferometer (IASI) provides twice daily global coverage with a 2200 km swath width and 12 km spatial footprint (Clarisse et al. 2010). Both platforms have measured the spatial and temporal trends of NH$_3$ (Clarisse et al. 2009, Clarisse et al., 2010; Pinder et al., 2011; Shephard et al., 2011). TES provides boundary layer sensitivity (700 hPa), with a detection limit of 1 ppbv NH$_3$ (Pinder et al., 2011). However, these remote measurements have limited spatial resolution for resolving field-scale gradients and do not provide temporal coverage to capture diurnal cycles. In addition, TES retrievals are sensitive to thermal contrast and clouds, which is especially problematic in regions with temperature inversions such as agricultural valleys (Clarisse et al., 2010). The degree to which retrievals represent surface concentrations has not been fully validated (Clarisse et al., 2010).

Despite the need for more sensitive gas phase measurements (Pinder et al. 2008, Battye et al. 2003, Gilliland et al. 2006), atmospheric NH$_3$ is not measured extensively due to significant in-situ measurement challenges (Nowak et al. 2007, von Bobrutzki et al. 2010). Atmospheric NH$_3$ instruments require high (sub-ppbv) sensitivity to measure low atmospheric mole fractions (pptv-ppbv), fast response time and large dynamic range to capture atmospheric variability (von Bobrutzki et al., 2010). Ammonia sensors must also account for gas-phase NH$_3$ surface adsorption effects and condensed-phase partitioning due to changes in temperature and relative humidity between the sampling volume and ambient atmosphere (Yokelson et al., 2003).

Current ground-based, in-situ NH$_3$ measurements are limited in spatial and temporal coverage. Conventional ammonia sensors such as denuders, passive filters and chemical ionization
mass spectrometry lack the requisite selectivity, time resolution and compactness for in-situ ammonia sensing (von Bobrutzki et al., 2010). Laser-based sensors that use reduced pressure cells to isolate atmospheric absorption lines exhibit closed-path artifacts and require high power consumption, limiting widespread deployment in field environments (von Bobrutzki et al., 2010; McManus et al., 2008). There is a strong need to constrain emission inventories and regional models assessing NH$_3$ impacts on PM$_{2.5}$ with new sensing technology that addresses the sampling, resolution and portability requirements.

The NH$_3$ molecule exhibits strong fundamental rotational-vibrational absorption transitions in the mid-infrared spectral region, presenting a promising technique for high sensitivity atmospheric NH$_3$ sensing. Laser absorption spectroscopy is fundamentally based on the Beer-Lambert absorption law as follows (Tittel et al., 2003):

$$I(\nu) = I_o \cdot \exp(-\sum_i (x_i S_i L_i \psi_i(T, P, \nu))),$$

(1.1)

where $I(\nu)$ is the laser intensity received on the detector; $I_o$ is the incident laser optical intensity; $x_i$, $S_i$ and $L_i$ are the number density, absorption line strength and optical path length, respectively, for different absorbing species $i$; and $\psi_i(T, P, \nu)$ is the Voigt line-shape function for absorption feature $i$, a function of temperature, pressure and wave-number $\nu$. The Voigt line-shape function and line strength for the absorption lines probed are obtained using the HIgh-resolution TRANsmission molecular absorption (HITRAN) database. Measurements of incident laser optical power, $I_o$, path length, $L_i$, and light intensity received on the detector, $I(\nu)$, are used to derive $x_i$, the number density of species $i$. Figure 1.1 shows the HITRAN simulated absorption spectrum from 2 to 12 µm for 1 ppbv NH$_3$ ambient mixing ratio in air at atmospheric pressure and 30 m optical path length. The strongest transitions ($\nu_2$) are located between 8-12 µm.

Laser-based absorption spectrometers for gas-phase NH$_3$ have been developed for real-time, selective NH$_3$ detection in the near-infrared, but their sensitivity is limited due to the NH$_3$ overtone bands in the near-infrared, requiring very long path lengths or longer averaging.
times for atmospheric measurements (Claps et al., 2001; Kosterev and Tittel, 2004). Recently, the newly emergent thermoelectrically (TE) cooled, distributed feedback (DFB), single mode, continuous-wave (CW) quantum cascade (QC) lasers operating at room temperature (Faist et al., 1998; Gmachl et al., 2001; Curl et al., 2010) offer the potential for high sensitivity, fast, selective NH$_3$ measurements by probing the strongest fundamental rotational-vibrational lines of NH$_3$ in the mid-IR (Figure 1.1; Curl et al., 2010). QC lasers are reliable, stable mid-IR light sources which can be operated at room temperature (TE-cooling), offer high optical power (1-100 mW) and are capable of continuous tuning across several wave-numbers for high sensitivity absorption spectroscopy of single absorption lines at ambient pressure. High output power QC lasers (1-100 mW) are advantageous to achieve sensitive measurements for both compact and long open-path measurement applications. These advances have led to the

Figure 1.1: Direct absorption HITRAN simulation (Rothman et al., 2009) calculated based on 30 m path length, 296 K, 1013.25 hPa for 1 ppbv NH$_3$ in air.
development of high sensitivity, QC laser-based, closed-path NH$_3$ sensors (Manne et al., 2006; Whitehead et al., 2007; McManus et al., 2008; Manne et al., 2009; Ellis et al., 2010; Gong et al., 2011), which must account for sampling artifacts that limit response time, and require high power consumption for pumps and temperature control systems (Whitehead et al., 2008; von Bobrutzki et al., 2010).

Non-intrusive, open-path sensors have been demonstrated for other trace gases that address the sampling challenges and provide fast response times (Zondlo et al., 2010; McDermitt et al., 2011; Tao et al., 2012b). These systems employ wavelength modulation spectroscopy (WMS), a method similar to direct absorption spectroscopy with the addition of a higher frequency sinusoidal modulation of the laser current (and wavelength). In this technique, the modulated signal is processed by a lock-in amplifier which performs demodulation at the fundamental modulation frequency and integral multiples or harmonics of the fundamental modulation frequency. WMS allows for increased sensitivity by shifting to a higher frequency detection bandwidth to minimize 1/f laser noise. However, these systems have so far only been demonstrated for NH$_3$ field measurements in long path-integrated configurations (Griffith and Galle, 2000; Galle et al., 2000; Mount et al., 2002; Thoma et al., 2005; Volten et al., 2012). Currently, there are significant hurdles for long open-path, laser-based NH$_3$ sensing techniques, including pressure-broadened absorption lineshapes sensitive to changes in environmental temperature and pressure and interferences from broad, overlapping absorption features from other atmospheric species. High sensitivity, compact, low power, open-path NH$_3$ sensing technology is needed for widespread spatial and temporal coverage measurements on stationary and mobile platforms.

During my Ph.D. research, I have contributed to these endeavors by developing and field deploying a new open-path, in-situ NH$_3$ sensing platform. To constrain current uncertainties in NH$_3$ and aerosols emissions, and associated impacts, I focused on new and existing observations at multiple scales, from satellite remote sensing, to vertically-integrated lidar, to ground-based long path-integrated and mobile platform point measurements with open-path
sensors. The long path-integrated surface measurement technique (tested initially for CH\textsubscript{4} detection) is applicable to NH\textsubscript{3} and other important atmospheric trace gases at spatial scales comparable to the grid resolutions of regional air quality models.

1.2 Scientific objectives

In order to better constrain aerosol and precursor emissions, transport and transformation uncertainties, my Ph.D. research has focused on measurements and analyses at multiple scales to address the following scientific questions:

**Question 1:** What are the impacts of long-range transport, physical and chemical evolution of aerosol emissions on regional air quality?

**Question 2:** How can new sensing technology be developed to address the current challenges for NH\textsubscript{3} sensing to achieve high sensitivity, fast, in-situ measurements?

**Question 3:** What is the spatial distribution of agricultural NH\textsubscript{3} emissions and how can spatial mapping capabilities with a mobile, open-path platform be applied to constrain agricultural emission uncertainties?

**Question 4:** How can compact sensing capabilities be extended to long path-integrated spatial measurements with requisite field precision and stability for measurements at scales comparable to regional air quality models?
To answer these questions, I demonstrated that multiple aerosol observation data sets can be used to track the evolution of physical, chemical and optical properties of biomass burning smoke aerosols from typical fires, which were shown to impact air quality thousands of km downwind of the source region (chapter 2). To address the lack of NH$_3$ sensing technology, I led the initial development and field deployments of a QC laser-based, open-path NH$_3$ sensor with sufficient sensitivity and time response for high resolution, in-situ measurements (chapter 3). I performed the first high resolution, mobile measurements of NH$_3$ in an intensive agricultural region and analyzed these measurements in the context of NASA DISCOVER-AQ aircraft measurements to compare bottom-up and top-down approaches for quantifying NH$_3$ agricultural emission ratios. Finally, I developed and field-tested a QC laser-based, long path-integrated sensor (tested initially for CH$_4$ detection) to explore field performance for future NH$_3$ and other trace gas measurements on the spatial scales of regional models.

1.3 Dissertation structure

The objectives of each chapter in this dissertation address solutions to the scientific questions posed in section 1.2 as follows:

Chapter 2. Assessing boreal forest fire smoke aerosol impacts on U.S. air quality: A case study using multiple data sets

This chapter addresses the first objective of the study - namely using the existing network of satellite and ground-based aerosol observations to track the evolution of biomass burning aerosol plumes. This study illustrates the value of synthesizing physical and chemical data sets to constrain the impacts of long-range transport of biomass burning smoke aerosols on air quality thousands of kilometers downwind.
Chapter 3. Open-path, quantum-cascade-laser-based sensor for high-resolution atmospheric ammonia measurements

This chapter addresses the second objective of the study - namely development of an open-path NH$_3$ sensing platform for high resolution measurements with minimal sampling artifacts, applicable to mobile, stationary and eddy-covariance flux measurement applications.

Chapter 4. Agricultural ammonia and methane emissions in the Central Valley, California with open-path mobile measurements

This chapter addresses the third objective of the study - namely characterizing agricultural emissions with high resolution mobile vehicular measurements to assess the spatial distribution of NH$_3$ and CH$_4$ emissions from dairy farms in the Central Valley, California during the DISCOVER-AQ 2013 field campaign.

Chapter 5. Open path-integrated, quantum cascade laser-based sensor for high precision methane measurements

This chapter addresses the fourth objective of the study - namely long-integrated open-path sensing of methane in a harsh field environment to assess field precision and stability capabilities for various future applications, including comparisons with regional models on comparable (kilometer) scales.

1.4 Co-author contributions to publications

All chapters in this dissertation are derived from publications or manuscripts in which I am the lead and first author. Chapters 2 and 3 of this dissertation are published in peer-reviewed journals. Chapter 4 will be submitted to Atmospheric Chemistry and Physics Discussions.
Chapter 5 has been published as a peer-reviewed conference proceeding. Although these publications and manuscripts are all co-authored, the main ideas, descriptions and analyzes presented in this dissertation are based on my own work. My first-authored publications (Chapters 2 and 3) are:


The first-authored conference proceeding (Chapter 5) is:


The manuscript in preparation is:

I was also a co-author on the following publications during my Ph.D. research at Princeton University:


7. Tao, L., K. Sun, M. A. Khan, D. J. Miller, and M. A. Zondlo, Compact and portable open-path sensor for simultaneous measurements of atmospheric N$_2$O using a quantum cascade laser, Optics Express, 20, 28106-28118, 2012.


Chapter 2

Assessing boreal forest fire smoke aerosol impacts on U.S. air quality: A case study using multiple data sets

2.1 Introduction

Biomass burning emissions have significant effects on both air quality and radiative processes through trace gas and aerosol emissions (Crutzen and Andreae, 1990). Globally, open biomass burning contributes 74% of total organic carbon (OC) emissions from combustion sources which is approximately ten times that from fossil fuel sources (Bond et al., 2004). Soot carbon (commonly referred to as black carbon (BC)) and brown carbon from biomass burning emissions absorb solar radiation and are associated with atmospheric brown clouds that can be transported globally (Andreae and Gelencsr, 2006; Ramanathan and Carmichael, 2008). Wild and prescribed forest fires typically generate smoke particle emissions composed mainly of OC and BC. While lower temperature smoldering combustion produces more OC than higher temperature flaming combustion, actual smoke plumes contain particles from both phases (Reid et al., 2005). For boreal forest fires, approximately 40% of combustion originates from the flaming phase and 60% from the smoldering phase (Reid et al., 2005).
A significant fraction of boreal forest fire emissions are injected above the boundary layer into the free troposphere (Leung et al., 2007), with some events injecting aerosols above the tropopause where they can induce stratospheric ozone catalytic destruction. Aerosol plume injection into the free troposphere facilitates long-range transport hundreds or thousands of kilometers downwind, whereas aerosols confined to the atmospheric boundary layer typically influence air quality near the source region (Kahn et al., 2007). This has been observed for Australian forest fires where intense heat and synoptic conditions caused pyro-convective lofting of the aerosol mass into an upper level jet stream (Dirksen et al., 2009). Damoah et al. (2004) documented around the world transport of intense Russian fires in 17 days. Transport of smoke plumes from North American wildfires led to large-scale haze layers over parts of Europe in 1998 (Forster et al., 2001). Detailed aircraft measurements during the 2004 ICARTT-ITOP Experiment also documented North American smoke plumes transported to Central Europe (Petzold et al., 2007).

Biomass burning plumes have significant and uncertain effects on climate with the potential to alter radiative budgets by both direct and indirect aerosol radiative forcing. Hsu et al. (1999) showed that smoke can significantly alter radiative forcing as it reduced the observed surface albedo for Greenland from 90-100% down to 30-40%. Black carbon in smoke transported from Canada to Europe enhanced the aerosol absorption coefficient by two orders of magnitude above background levels (Petzold et al., 2007). Biomass burning aerosols facilitate longer-lived clouds with smaller droplets that inhibit precipitation (Koren et al., 2004). Springtime agricultural burning and wildfires are a potentially significant source of organic and black carbon aerosol for the Arctic, with implications for springtime Arctic warming (Warneke et al., 2010).

Biomass burning emissions can have significant impacts on regional air quality in distant regions. Boreal forest fire emissions impact tropospheric trace gas chemistry, especially through enhancements of CO and O$_3$ (Wotawa and Trainer, 2000; McKeen et al., 2002; Forster et al., 2001; DeBell et al., 2004; Leung et al., 2007; Verma et al., 2009). Jaffe et al. (2004) found that
CO and NO\textsubscript{x} emissions from Siberian biomass burning contributed to exceedances of ozone air quality standards in the Pacific Northwest. Smoke aerosols from biomass burning affect local air quality and as a result, human health (Saarnio et al., 2010; Rittmaster et al., 2006). One of the major concerns for human health are particles with aerodynamic dry diameters less than 2.5 \(\mu\text{m}\) (PM\textsubscript{2.5}) as they can be carried deep into the human respiratory tract (World Health Organization, 2008). The current standards for PM\textsubscript{2.5} set by the U.S. EPA are 35 \(\mu\text{g m}^{-3}\) in a 24-hour period and 12 \(\mu\text{g m}^{-3}\) annually for primary PM\textsubscript{2.5} (U.S. EPA NAAQS). Forest fires are one of the significant sources of PM\textsubscript{2.5} particularly in non-urban areas (Mathur, 2008). In some cases, boreal forest fire emissions can exhibit larger impacts than anthropogenic emissions on Northern Hemisphere midlatitude air quality (Wotawa and Trainer, 2000). Bertschi and Jaffe (2005) studied the episodic transport of Siberian fire plumes to the northwestern United States, reporting enhancements of PM\textsubscript{2.5} affecting regional air quality in the state of Washington.

Canadian fire emissions and impacts on the northeastern U.S. have been studied from the perspectives of chemical composition, transport and atmospheric chemistry interactions focusing on CO enhancements (DeBell et al., 2004) and O\textsubscript{3} formation (McKeen et al., 2002). Canadian forest fire smoke plumes have also been tracked by satellite imagery, back trajectories and ground-based optical property observations (O’Neill et al., 2002). A case study by Colarco et al. (2004) examined an elevated smoke plume from Quebec, Canada eventually entrained into the planetary boundary layer by focusing on mixing and optical properties. Mathur (2008) examined smoke plume transport to the eastern U.S. with a July 2004 case study of the largest fires on record for Alaska using remote sensing satellite data, aircraft and ground-based measurements. They concluded that large boreal forest fires in Canada can have a significant impact on widespread surface particulate matter over the heavily polluted U.S. East Coast. The case study of McKendry et al. (2011) examined medium-range smoke transport from northern California wildfires to the Pacific Northwest, combining ground-based and satellite
observations. Duck et al. (2007) analyzed high altitude forest fire smoke layers, including long-range transport toward the surface.

Most cases studied thus far (Forster et al., 2001; Colarco et al., 2004; DeBell et al., 2004; Bertschi and Jaffe, 2005; Duck et al., 2007; Mathur, 2008) have focused on large, intense fires that occur once every decade or even less frequently such as the July 2004 fires which produced very significant aerosol emissions in Alaska and western Canada as studied by Duck et al. (2007) and Mathur (2008). However, boreal forest fires occur every year. Despite all these studies, the degree to which these annually occurring, less extreme fire events impact air quality, especially long distances (greater than 2500 km) downwind has not been studied. McMillan et al. (2010) highlighted some of the complex challenges for quantifying these biomass burning influences on air quality degradations. From an analysis point of view, medium intensity fires are more difficult to detect and dissociate from other pollutants.

We perform a case study analysis using a suite of relevant ground-based and remote sensing measurements over North America to understand the complex problem of long-range smoke transport by analyzing a less extreme biomass burning event. Our method of synthesizing 9 data sets (5 satellite, 4 ground-based), trajectory model results and meteorological fields allows us to gain a more comprehensive scientific understanding than by any data set individually, especially for analyzing weaker smoke signatures from less extreme events. In the context of a case study, integrating data sets and understanding the processes involved in smoke transport provides a better tool to understand and evaluate complex air quality issues in the eastern U.S. Thus, we track the bulk evolution of biomass burning smoke plumes from a Canadian boreal forest fire event with smoke emission magnitudes comparable to summertime emissions during the previous decade. The analysis includes data (described in section 2) from MODIS, OMI, MISR, CALIOP lidar, AIRS, AERONET CIMEL sky/Sun photometer, MPLNET lidar, IMPROVE and EPA AirNow. We also integrate NCEP/NCAR meteorology and NOAA HYSPLIT trajectories into our analysis. For clarity, we subdivide the analysis into emission and injection heights, synoptic scale meteorology, followed by the Midwestern U.S.
and southern Ontario region and northeastern U.S. region where we analyze optical, chemical and air quality impacts. We discuss our results and provide conclusions on atmospheric implications in the final section.

2.2 Data description

In this section we briefly describe the data sets used in our analysis. More detailed descriptions and in-depth evaluations can be found in the cited references.

2.2.1 Satellite data sets

The Ozone Monitoring Instrument (OMI) onboard the NASA Aura satellite measures Earth’s backscattered radiation in the range 270 - 500 nm. Herman et al. (1997) showed that absorbing aerosols can be detected from the spectral contrast between near UV backscattered radiances. They defined an aerosol index (AI) as

\[ AI = 100[\log_{10}(\frac{I_{360}}{I_{331}})_{measured} - \log_{10}(\frac{I_{360}}{I_{331}})_{calculated}] \]

where \( I_{360} \) and \( I_{331} \) are the backscattering radiances at 360 and 331 nm. The calculated backscattering radiances are for a purely molecular atmosphere (no aerosols). The OMI AI differentiates between absorbing carbonaceous, desert dust and volcanic ash aerosols (the major sources of positive OMI AI) and non-absorbing aerosols, which yield small negative values (Torres et al., 2007). In western Canada, there is no known major source of dust and long-range transport of dust has not been reported during the summer. Consequently, in the absence of dust, positive values of OMI AI are due to carbonaceous aerosols (OC and BC) from fires. The usefulness of the near UV AI to follow smoke plumes has been clearly demonstrated by Hsu et al. (1996, 1999). It is important to note that OMI AI depends on the aerosol layer height, aerosol optical depth and single scattering albedo, which limits its use to qualitative analysis.
The Multiangle Imaging Spectroradiometer (MISR) onboard NASA’s Terra satellite retrieves total column aerosol optical depth in four spectral bands (446, 558, 672 and 866 nm) at nine different viewing zenith angles. Aerosol optical depth (AOD) is defined as the integrated extinction coefficient (aerosol absorption and scattering) over a vertical column of unit cross section. Utilizing a stereo-matching algorithm, altitudes for wildfire smoke and volcanic plumes are routinely retrieved (Kahn et al., 2007). Heights of low smoke plumes near their sources are accurate to a few hundred meters (Mazzoni et al., 2007).

The NASA Moderate Resolution Imaging Spectroradiometer (MODIS) onboard the Sun-synchronous Terra and Aqua satellites retrieves many products from radiances in 36 spectral bands from 0.4 to 14.4 µm. With its large swath width (∓55° view-scan, 2330 km), MODIS provides nearly global daily coverage. Because of its thermal-infrared sensing capability, MODIS is able to detect active fires with high temporal resolution (Justice et al., 2002). Here we use the aerosol optical depth (AOD) at 550 nm. USDA active fire maps [http://activefiremaps.fs.fed.us/] derived from MODIS data are used to quantify actively burned area within 24 hours and burned area since the beginning of the year.

Launched in April 2006, the joint NASA-CNES Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observations (CALIPSO) satellite is part of the NASA A-train satellite constellation. The Cloud-Aerosol Lidar with Orthogonal Polarization (CALIOP) onboard CALIPSO probes the vertical structure and properties of clouds and aerosols globally with day and nighttime observations at 532 and 1064 nm (Winker et al., 2010). To minimize noise, we use total attenuated backscatter measurements at 532 nm (version 3.01) during the nighttime (descending node) to infer aerosol vertical profiles. We also analyze the CALIOP depolarization ratio and vertical feature masks.

The Atmospheric Infrared Sounder (AIRS) onboard NASA’s Aqua satellite retrieves total column trace gas abundances including carbon monoxide (CO) as well as air temperature, water vapor, and cloud properties. Total column CO is retrieved from the 4.55 µm region. The large swath width (1600 km) and cloud-clearing retrievals provide detailed, nearly global
daily CO data that can be used to study transport of mid-tropospheric CO from biomass burning emissions (McMillan et al., 2005, 2010). We use the Aqua AIRS total CO column (10$^{18}$ molecules cm$^{-2}$) ascending node data.

2.2.2 Ground-based observations

The Aerosol Robotic Network (AERONET) makes direct measurements of solar irradiance to retrieve multi-wavelength (visible and near UV) column AOD at 15 minute intervals with a world-wide network of CIMEL sky/Sun photometers (Holben et al., 2001). The aerosol size distribution and optical properties are derived by fitting measurements of Sun radiance and the angular distribution of sky radiances at four wavelengths (440, 670, 870 and 1020 nm) to radiative transfer models (Dubovik and King, 2000; Dubovik et al., 2000). In this study we use only level 2.0 data for AOD and when available for size distributions and single scattering albedo (SSA). Level 2 SSA values are restricted to cases when AOD (440 nm) is greater than 0.4 and Sun elevation angles are above 50°, which excludes anomalously low SSA values (Arola et al., 2010). Level 1.5 data are used for SSA and volume size distributions on July 6 and 9, 2006 when level 2.0 data are not available.

The Micro Pulse Lidar Network (MPLNET) is a ground-based lidar network, collocated with several AERONET Sun photometers, that provides vertical profiles of aerosol and cloud structure (Welton et al., 2001). MPLNET level 1 signal profiles (Campbell et al., 2002; Welton and Campbell, 2002) are used in this study to identify aerosol layer altitudes.

The Interagency Monitoring of PROtected Visual Environments (IMPROVE) program (Malm et al., 1994) has collected aerosol samples starting in 1988 at almost 200 sites located in National Parks of the United States. Mass concentrations of sulfate ($\text{SO}_4^{2-}$), OC, BC, potassium (K) and many other species are measured from PM$_{2.5}$ samples every three days over a 24-hour period (Hyslop and White, 2008).

The U.S. Environmental Protection Agency (EPA) and its state and local government partners maintain networks monitoring the concentration of particulate and gaseous air pol-
lutants at ground level. EPA AirNOW (http://www.airnow.gov) receives PM$_{2.5}$ (and O$_3$) data from over 2,000 ground-based monitoring stations operated by state or local air quality agencies. The PM$_{2.5}$ concentration maps used for our air quality analysis are derived from these data and apply to surface conditions for all reporting monitoring stations on the days analyzed.

2.2.3 Meteorology and transport data

We use NCEP/NCAR reanalysis data (Kalnay et al., 1996) provided by the NOAA/OAR/ESRL PSD, available at http://www.esrl.noaa.gov/psd/data/reanalysis/reanalysis.shtml, to analyze mean daily sea level pressure, specific humidity, precipitation rate and wind fields. Back and forward trajectories generated from the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Hess, 1997) are used to analyze how smoke plumes were transported from central Canada across southern Ontario and the Great Lakes region to the northeastern U.S.

2.3 Results

2.3.1 Emission and injection heights

Boreal forest fires occurred in the Yukon Territory, British Columbia, Alberta, and Saskatchewan provinces in Canada during the summer of 2006. We analyze the fire event with maximum area burned on July 4, 2006 based on the USDA fire maps for July 2006. According to land cover vegetation classification data sets derived from the Advanced Very High Resolution Radiometer (AVHRR) (DeFries and Townshend, 1994), woodland/mixed forest and evergreen forest were the vegetation types burning in these areas of fires.

The 8-day mean emission rates of black carbon, organic carbon and SO$_2$ on a 1x1° grid are given by the Global Fire Emissions Database Version 2 (GFEDv2) (Giglio et al., 2006; van der Werf et al., 2006). Since GFEDv3 currently only provides monthly emissions, we use
GFEDv2 mean 8-day emission rates over a domain of western Canada (50°-70°N; 90°-140°W). To calculate total emissions, we use total grid surface area for non-zero 8-day emission values. This area estimate is on a consistent timescale with the emission values as opposed to using daily USDA fire map burned area estimates. The estimated emissions over the course of 3 days (3x the daily emission rate) of BC, OC and SO$_2$ are 3, 69, and 5 mg m$^{-2}$ respectively. Hence the total emissions of BC, OC and SO$_2$ due to the fires over the course of 3 days are 2, 46, and 4 kilo-tons respectively.

We examine the emissions of carbonaceous aerosols over a domain of western Canada as a metric to compare the magnitude of this fire event with those over the previous decade. Carbonaceous aerosol emissions are defined as total biomass burning black carbon and organic matter (OM) over a domain of western Canada from the GFEDv2 8-day and GFEDv3 monthly emission inventories. In Figure 2.1a, we quantify this fire magnitude metric over the previous 5 years (GFEDv2) and decade (GFEDv3) based on availability of data over these time periods. For reference, the emissions from the July 2004 fires studied by Duck et al. (2007) and Mathur (2008) are indicated by the appropriate arrows and labels in Figure 1a. These fires were the third largest in terms of both 8-day emissions (July 20, 2004) for the previous 5 years and monthly emissions (July 2004) for the previous decade.

Figure 2.1a (left) shows 8-day emissions over western Canada from 2001 - 2006. We focus on the 8-day emissions during the peak fire season in western Canada (June-August) for 2001 - 2006. The July 5, 2006 8-day emissions value is 127.5 kt. This value is approximately one standard deviation ($1\sigma$) above the mean of 47.4 kt ($1\sigma = 76.3$ kt) and larger than $1\sigma$ above the median (12.5 kt) indicating this is a large event. Although this event is the second largest in terms of 8-day emissions for the year 2006, it is only the eleventh largest 8-day emissions value during the peak fire months for 2001 - 2006 with 14% of values higher than the July 5, 2006 emissions. In addition, the maximum 8-day emission value during each summer fire season (June-August) for 2001 - 2006 was larger than the emissions from the fire event we
consider for 4 out of 6 years. Thus, from the perspective of the previous 5 years, this event was large but not unusual.

Figure 2.1 shows monthly carbonaceous aerosol emissions from 1997 - 2007 over western Canada. The July 2006 monthly emissions of 196.5 kt are comparable to the mean of 181.6 kt and within $1\sigma$ of the median of 83.3 kt ($1\sigma = 233.9$ kt) during the peak Canadian fire season (June-August) from 1997 - 2007. July 2006 had the tenth largest monthly emissions out of 30 peak fire months (June-August, 1997 - 2007) considered over this period. In addition, the maximum monthly emissions during June-August from 1997 - 2007 were higher than those for July 2006 in 50% of the fire seasons in the previous 10 years. This indicates that although these are major fires in terms of emissions, fires of even larger magnitude occur quite often in the recent past and this fire event is comparable to the decadal mean emissions for the peak Canadian fire season (June-August). This suggests that there is a great potential for long-range transport of aerosol emissions to frequently influence regional air quality.

MODIS observations on July 4 show a large area of AOD at 550 nm >2 over the fires (Figure 2.1b). MODIS fire counts in Figure 2.1c indicate regions of boreal forest fire burning. OMI AI values near 10 over the fires are shown in Figure 2.1d. These unusually high values likely indicate the presence of elevated aerosol layers. Since there were no significant sources of dust or volcanic ash, it is reasonable to assume the high OMI AI values are due to carbonaceous aerosols from biomass burning.

MISR captured one of the major fires at the western edge of the fire region on July 4, 2006 (MISR plume height project region name 034811-B44-P3). The wind corrected plume height versus distance from the source in Figure 2.2a was retrieved using resources from the MISR Plume Height Climatology Project (http://www.misr.jpl.nasa.gov/getData/accessData/MisrMinxPlumes/). The smoke penetrated into the free troposphere, reaching up to 3 km altitude 25 km away from the source.

The smoke plumes were likely injected both into the boundary layer and the free troposphere at different altitudes. Smoke that remains in the boundary layer is not transported
Figure 2.1: (a) Time series of mean carbonaceous aerosol (OM + BC) emissions (kilo-tons) from (left) GFEDv2 8-day emissions inventory and (right) GFEDv3 monthly emissions inventory over western Canada. Arrows indicate the July 4 fire event and July 2004 fire event studied previously. The dashed line for the monthly emissions plot is the June - August monthly mean emissions value from 1997 - 2007. (b) MODIS Terra aerosol optical depth at 550 nm on July 4, 2006. (c) MODIS fire counts for the period June 30 - July 9, 2006. (d) OMI AI on July 4, 2006 with line indicating CALIOP overpass.
long distances and is potentially removed by deposition processes. Thus, smoke emissions are not transported efficiently in the boundary layer compared with free tropospheric transport. Figure 2.2b shows a family of 8 forward trajectories at 3 different injection heights in the free troposphere originating from the wildfire source region. The forward trajectories originating at 8 km altitude show transport southeastward toward the upper Midwestern U.S. over the course of 2 days and air descending to 5 km altitude. The 5 km injection height forward trajectories show transport toward southern Ontario and the Great Lakes region with a small decrease in altitude down to 4 km altitude. Finally, the 3 km altitude injection height corresponding to the MISR plume height calculation shows transport again to the southeast over southern Ontario. Based on these trajectories, we expect to observe plumes over these regions.
Figure 2.3: CALIOP observations of (left) total attenuated backscatter, (middle) vertical feature mask and (right) depolarization ratio on (a) July 4 on the western edge of aerosol emissions and (b) July 5 over central Canada. Dense cloud/aerosol layers at 8 - 10 km altitude are circled for the July 4 profiles. Aerosol layers at 8 - 11 km altitude are also circled in the July 5 profiles.

with upper level layers reaching the Great Lakes region in 2 days after emissions and lower altitude layers reaching similar locations in 3 or more days following emissions.

CALIOP profiles on July 4 and 5 are shown in Figure 2.3 with the July 4 overpass location indicated in Figure 2.1d for reference. Smoke aerosol features can be seen near 53°N extending from the surface to an altitude of 3 - 4 km above ground level (vertical feature mask in Figure 2.3a) and dense layers at 56°N at 8 - 10 km altitude (Figure 2.3a). Small values of the depolarization ratio indicate that these are smoke aerosols and are not consistent with ice clouds at this high altitude as indicated by the vertical feature mask due to an error in the cloud-aerosol discrimination algorithm. High depolarization ratio values at 10 - 11 km
indicate the presence of a compact cloud (Figure 2.3a, right). The attenuated color ratio (not shown) has large positive values below these features, a signature of dense smoke with larger attenuated backscatter at 532 nm than at 1064 nm. On July 5, an aerosol layer occurs at a similar altitude (8 - 11 km) in the CALIOP profile (Figure 2.3b). A back trajectory (not shown) from this altitude and location at the overpass time indicates that this layer would have been transported from the fire source region at high altitude (8 - 10 km). Therefore, plume injections into the free troposphere occurred at a range of altitudes from 3 - 10 km, with high altitude plumes resulting from different pyro-convective events.

2.3.2 Synoptic scale meteorology

The synoptic scale meteorological conditions control smoke plume transport from the source region. On July 4, 2006, an area of high pressure is over southern Canada with low pressure to the east (Figure 2.4a). This high moves southeast, entering the Midwestern U.S. on July 6 (Figure 2.4b). The smoke plumes were injected into relatively dry air on July 4 with specific humidities of $\sim 0.007 \text{ kg kg}^{-1}$ and no precipitation in the vicinity of emissions. There is a northwesterly flow at 850 hPa in the vicinity of the wildfire region. Mean horizontal winds at 400 hPa (Figure 2.4c) reach magnitudes up to 25 m s$^{-1}$ while winds at 850 hPa reach only 10 m s$^{-1}$. The upper level winds follow the general pattern of the upper tropospheric jets and facilitate efficient wind advection to the Great Lakes region at these upper levels.

Over the Great Lakes and southern Ontario, smoke plumes would be expected to be located between high and low pressure systems on July 6 as shown in Figure 2.4b. The surface high pressure center is displaced from the Midwestern U.S. to the U.S. East Coast. Any smoke north of the high pressure center is expected to be transported southeastward whereas smoke that is northwest or west of the high will be transported eastward or northeastward due to a shift in wind direction. In addition, a cold front formed on July 8 from southern Ontario into the central U.S. and moved eastward, reaching the Great Lakes on July 9 (Figure 2.4d) and the East Coast on July 10 - 11. Any lower level smoke aerosols over the U.S. East Coast would
be potentially removed by precipitation with the slow moving cold front over this region. In subsequent sections, we show that back trajectories for sites observing aerosol features are consistent with these synoptic scale conditions.

### 2.3.3 Southern Canada and Midwestern U.S.

We evaluate aerosol smoke plume characteristics and impacts during transport across southern Ontario and the Midwestern U.S. The OMI AI, used here to identify absorbing aerosols from the fires, shows the biomass burning smoke plume extending from Hudson Bay down to Illinois on July 6, 2006 (Figure 2.5a). The CALIPSO satellite passed over the Great Lakes on July 6 at \( \sim 8 \) UTC, which is almost half a day before the OMI Aura overpass (18:30 UTC).
Figure 2.5: (a) OMI Aerosol Index (AI) on July 6, 2006 with red line indicating track of the CALIPSO satellite. (b) CALIOP vertical feature mask on July 6 showing smoke from 5 - 10 km altitude.

Plume fragments are observed in the CALIOP vertical feature mask from 5 - 8 km altitude between 40-50°N (Figure 2.5b). Large total attenuated backscatter values at 8 - 12 km altitude between 40-55°N are classified as clouds. However, the depolarization ratio values (<0.1) at this altitude are consistent with smoke aerosols and again inconsistent with ice clouds. This evidence leads us to conclude that extensive high altitude smoke layers were present and partially embedded in cirrus clouds. CALIOP also observed a lower aerosol layer (1 - 3 km altitude) further to the south between 35-42°N (Figure 2.5b, far right). These features are not collocated with positive OMI AI values due to the lack of sensitivity of OMI AI to low altitude aerosols.

**Optical properties**

Back trajectories from the AERONET site at Pickle Lake, Ontario (not shown) and forward trajectories from the source region in Figure 2.2b, indicate that the Pickle Lake site is affected by the smoke plume due to transport of air from the west at multiple altitudes. Aerosol optical depths of 1 - 1.5 are measured at the Pickle Lake site on July 6 (Figure 2.6a) and these values are significantly elevated from monthly mean AOD values of ~ 0.3 (Figure 2.6b).
Observations by both MODIS Aqua and Terra also indicate elevated aerosol optical depth (AOD) at 550 nm near unity over Pickle Lake and the nearby region on July 6 (Figure 2.6c and 2.6d). These values are consistent with the collocated AERONET AOD observed at Pickle Lake. The largest optical depths (>2) are observed by MODIS to the northeast of Pickle Lake near Hudson Bay.

There is a dominant accumulation mode observed in the volume size distribution at Pickle Lake on July 6, with a volume mean diameter of 0.2 \( \mu \text{m} \). We note that since Level 2 data is unavailable for July 6, we select Level 1.5 retrievals. The accumulation mode volume concentration maximum at 0.13 \( \mu \text{m}^3 \mu \text{m}^{-2} \) on July 6 is significantly larger than the more
Figure 2.7: (a) Potassium concentration in fine particulate matter across multiple IMPROVE sites in the eastern U.S. on July 7, 10 and 13, 2006 (site locations are black triangles, shading represents interpolated values). (b) Lostwood, North Dakota IMPROVE site aerosol composition data. Note that fine particulate potassium (K) is multiplied by a factor of 100 for comparison with organic mass by carbon (OMC-1.4).

A typical value of 0.007 \( \mu m^3 \mu m^{-2} \) (July 9) indicating the arrival of fine smoke particles. This dominant fine mode has been observed previously for forest fire aerosols (Petzold et al., 2007; Dubovik et al., 2002). In addition, the single scattering albedo (SSA) at 7 am local time on July 6 declines significantly with increasing wavelength (0.93 at 440 nm and 0.86 at 1020 nm). SSA values below 0.9 in the visible and increased absorption as wavelength increases are typical for carbonaceous aerosols.

**Chemical properties**

Reid et al. (2005) have shown that fine particulate potassium (K) concentration is a good marker of biomass burning from fires. Soil fine particles also contain K but these are usually
accompanied by a large coarse mode. Fine particle iron (Fe) is also associated with these soil dust sources. Typically a K/Fe ratio of 0.6 or below indicates contributions from soil dust (Cahill et al., 1986). Potassium concentrations from all IMPROVE sites reporting data on July 7, 10 and 13 with linear interpolation between sites are shown in Figure 2.7a. There is a distinct region of elevated fine particulate K on July 7 stretching from Minnesota to Kansas, reaching values up to 0.16 µg (K) m\(^{-3}\). In this region, K/Fe \(\sim 3\) (well above 0.6), indicating that this potassium enhancement is due to biomass burning. These surface observations of a biomass burning tracer indicate the presence of surface plumes in these regions.

The IMPROVE site at Lostwood, ND is the nearest site to Pickle Lake and the region of enhanced AOD and OMI AI on July 6 which provides full aerosol chemical composition data in early July 2006. Back trajectories from Lostwood, ND (not shown) indicate air is advected from the source region described in section 3 on July 4 and 5. Figure 2.7b shows the 3-day fine particulate chemical composition at Lostwood (ND) for early June to late July 2006. There is a remarkable similarity between the time series of organic mass by carbon (OMC-1.4) and fine mode potassium (K) at Lostwood, ND. Two distinct maxima of OMC-1.4 and fine mode K (scaled up by 100 for comparison with OMC-1.4) are observed. The June 28 maxima are due to previous fires (as seen in OMI AI visualizations for June 28, 2006 and carbonaceous aerosol emissions in Figure 2.1a). Since Lostwood, ND is southwest of Pickle Lake, smoke from the fire event studied here likely reached the Lostwood site first (the July 4 maxima), while the smoke plume is observed at Pickle Lake on July 6. Along with the OMC-1.4 and K maxima, there are smaller enhancements of both ammonium sulfate and elemental (black) carbon (1 µg m\(^{-3}\)). The BC/OC mass ratio is approximately 0.08, consistent with values from past studies for boreal forest fire smoke particles (Reid et al., 2005).

**Air quality impacts**

The quantification of smoke plume impacts on U.S. air quality due to long-range transport is complicated by anthropogenic aerosol sources, plume dispersion and depositional processes.
To estimate a range of possible air quality impacts, we use EPA AirNOW PM$_{2.5}$ concentration observations for the Midwestern U.S. and southern Ontario during the period July 4 - 10, 2006 (U.S. EPA AIRNow archives).

Figure 2.8 shows PM$_{2.5}$ levels reach a maximum in the Midwestern U.S. of 16 - 24 µg m$^{-3}$ on July 8. Time series of daily PM$_{2.5}$ concentrations at four EPA air quality monitoring stations in Minnesota, Michigan and Illinois and two monitoring stations in Southern Ontario (data available at [http://www.airqualityontario.com/history/](http://www.airqualityontario.com/history/)) are shown in Figure 2.9a. Measurements confirm a rise in PM$_{2.5}$ at all sites, albeit none exceeding the 24-hour EPA standard. PM$_{2.5}$ concentrations at the Seney (MI) station reach a maximum of 13.7 µg m$^{-3}$ on July 8. This location also experiences a simultaneous increase in fine particulate potassium, a good tracer of biomass burning (see section 2.3.3). In southern Ontario, the PM$_{2.5}$ maxima at the Sault Saint Marrie and Sudbury (ON) stations are 24 µg m$^{-3}$ and 25 µg m$^{-3}$ respectively. Compared with near background levels, PM$_{2.5}$ values in the Midwestern U.S. increased by 10 - 20 µg m$^{-3}$ during the passage of the plume. The observations at these individual sites show comparable increases as shown in the PM$_{2.5}$ maps (Figure 2.8) indicating that they are...
Figure 2.9: (a) Daily PM$_{2.5}$ concentrations at 6 ground monitoring sites in the Midwestern U.S. and southern Ontario, Canada for the period July 4 - 10, 2006. EPA Michigan Site is EPA site 261630001 and EPA Illinois Site is EPA site 170310052. Data accessed at [http://views.cira.colostate.edu/web/DataWizard/](http://views.cira.colostate.edu/web/DataWizard/). (b) Daily PM$_{2.5}$ concentrations at six ground monitoring sites along U.S. East Coast from July 4 - 16, 2006. Maryland Site 1 is EPA site 240053001; Maryland Site 2 is EPA site 245100035; Maryland Site 3 is EPA site 245100040; New Jersey Site is EPA site 340390004; Virginia Site is EPA site 510590030; West Virginia Site is EPA site 540090005. Data accessed at [http://views.cira.colostate.edu/web/DataWizard/](http://views.cira.colostate.edu/web/DataWizard/). Horizontal dashed line at 35 µg m$^{-3}$ indicates the EPA 24-hour standard for PM$_{2.5}$ concentration exposure. (c) (left) Back trajectory from the Seney, MI monitoring station. (middle) Forward trajectory from the Pickle Lake site showing transport toward the U.S. East Coast on July 10. (right) Back trajectories from three U.S. East Coast site locations collocated with biomass burning tracer (OMC-1.4 and fine mode K) enhancements.
representative of observations in this region. This is expected as the surface site data are used to produce the interpolated maps.

Figure 2.9c (left) shows back trajectories at 200 m AGL from the Seney (MI) monitoring station on July 7 at 6-hour intervals. These results indicate transport from the northwest, the location of plumes on July 5 - 6. These trajectories also indicate the potential for entrainment of smoke plumes into the boundary layer during daytime boundary layer growth. This mechanism may lead to smoke affecting surface PM$_{2.5}$ concentrations.

### 2.3.4 Northeastern U.S.

Positive OMI AI values are observed over a large portion of the U.S. East Coast on July 9, 2006 (Figure 2.10). The CALIOP profile from the CALIPSO satellite overpass on July 9 at $\sim$ 7 UTC (occurring before the OMI Aura overpass at $\sim$ 18:30 UTC) shows substantial aerosol plumes from 5 - 8 km altitude over a large portion of the U.S. East Coast (30-45°N) (Figure 2.10). As before, the depolarization ratio for these features (not shown) is below 0.1. The vertical feature mask (not shown) confirms the presence of aerosols. In the 45-50°N
Figure 2.11: (a) MPLNET lidar profile on July 8 - 10 at the COVE site showing aerosol plumes at 6 - 7 km altitude on July 8 - 9 and at 4 km altitude on July 9 - 10. The periods of reduced signal strength during nighttime (black regions) on July 8 and 9 are caused by condensation on the lidar window. (b) Back trajectories from the Cove site at (left) 6.5 km and (right) 4 km altitude at times corresponding to aerosol layer observations from Figure 11a.

and 35-40°N latitudinal bands, lower aerosol layers are also seen at approximately 1 - 3 km altitude.

**Optical properties**

The AERONET and MPLNET Cove site just off the coast of Virginia also provides useful data on the aerosol optical properties along the U.S. East Coast. We note that Cove is one of only two MPLNET lidar sites along the U.S. East Coast that provide data for July 2006. The other site (GSFC, Greenbelt, MD) provides no lidar data for the time period analyzed (July 8 - 13, 2006). As shown in Figure 2.11, the MPLNET lidar at Cove observes aerosol
layers on July 8 at 6 - 7 km altitude and on July 9 at 3 - 5 km altitude. Figure 2.11b shows two back trajectories arriving at Cove at 4 and 6.5 km altitude respectively (21 UTC July 8 and 00 UTC July 10 respectively). These trajectories show both layers were transported from the source region in central Canada at 5 km and 6 km altitude respectively and reached the Cove site 4 - 5 days later.

Aerosol optical properties on July 9 along the U.S. East Coast are examined using observations from the AERONET sites Maryland (MD) Science Center, Howland (ME), Martha’s Vineyard Coastal Observatory (MA) (MVCO), Billerica (MA), CCNY (New York, NY) and GSFC (Greenbelt, MD). Back trajectories from two of these sites (Figure 2.12a) both show air parcels near the surface (50 m AGL) originated from central Canada on July 4 and 5.
Aerosol optical depths at 500 nm on July 9 at the MD Science Center and Howland (ME) sites are 0.4 and 0.37 respectively. Single scattering albedo decreases with increasing wavelength (Figure 2.12b, left) with values below 0.9 at Howland (ME) and MVCO indicating absorbing aerosols from the smoke plume. Single scattering albedo values at the other sites are above 0.9, indicative of urban aerosols that are likely mixed with OC rich smoke from smoldering combustion as observed by Eck et al. (2003). The volume size distributions (Figure 2.12b, right) exhibit a substantial fine mode at all sites, which is about 5 times that for the coarse mode at MD Science Center and 10 times that at the Howland (ME) site. This enhanced fine mode indicates that either smoke or fine urban aerosols are dominating the aerosol mass loading. These results show the spatial extent of this Canadian smoke plume from Maine to Maryland using data from all AERONET site observations available on July 9, 2006 along the U.S. East Coast.

Chemical properties

Chemical composition data is assessed using the IMPROVE observations of PM$_{2.5}$ organic mass by carbon, fine mode potassium and ammonium sulfate. As shown in Figure 2.13 OMC-1.4 increases significantly on July 10 compared with July 7 in the eastern U.S. Enhancements in fine mode K concentrations near 0.06 $\mu$g K m$^{-3}$ are observed on July 10 across this same region stretching along the U.S. East Coast from New Jersey to Virginia and inland over portions of West Virginia, Ohio and Kentucky (Figure 2.7a). These data suggest that surface plumes are transported to the eastern U.S. while dilution also occurred, leading to a decrease in fine mode K concentrations during transport. This is expected given that these species commonly have much lower mass fractions in aged smoke (Reid et al., 2005). Nevertheless, it is remarkable that IMPROVE aerosol chemical composition observations are capable of detecting smoke plumes at the surface over thousands of kilometers from the source region. Our chemical, optical and trajectory analyzes provide strong evidence that the rise in OMC and fine mode K concentration along the U.S. East Coast can be attributed to smoke from
Figure 2.13: (a) IMPROVE organic mass by carbon (OMC-1.4) concentrations in PM$_{2.5}$ across the eastern U.S. on July 7, 10 and 13, 2006. (b) IMPROVE ammonium sulfate concentrations in PM$_{2.5}$ across the eastern U.S. on July 7, 10 and 13, 2006.

the Canadian fires. Finally, we note that K/Fe $\sim$ 1.6 on July 10 along the U.S. East Coast. This ratio is well above 0.6, indicating that this potassium is due to biomass burning. In contrast, the potassium map in Figure 2.7 for July 13 shows a K/Fe of $\sim$ 0.4 over portions of the southeastern U.S., indicating that the July 13 fine mode K enhancement is not due to biomass burning.

Local and regional aerosol sources between the emissions region in Canada and the U.S. East Coast influence aerosol composition observations. For example, ammonium sulfate concentrations increase dramatically from 2 $\mu$g m$^{-3}$ on July 7 to 15 - 20 $\mu$g m$^{-3}$ on July 10 (Figure 2.8 and 2.13b) over a large portion of the northeastern U.S., including portions of
the U.S. East Coast. The chemical signatures observed suggest that the smoke aerosol was mixed with local and regional anthropogenic sulfate aerosols in these regions. We cannot rule out the possibility of local influences such as urban fossil fuel burning. Alternatively, several studies have shown significant enrichment of secondary inorganic aerosol species, including ammonium, in aged smoke (Reid et al., 2005). Thus, gas to particle conversion of SO$_2$ and ammonia (NH$_3$) fire emissions may also contribute, limited by SO$_2$ oxidation to sulfate which occurs on a one-week timescale (Reid et al., 2005). Chemical transport modeling is an additional tool that could be used to increase the robustness of our results but these models exhibit their own uncertainties. More detailed speciation and higher time resolution (hourly or daily) aerosol chemical composition data would also be useful to fully analyze these mixing and transformation processes.

**Air quality impacts**

The smoke plume affected air quality in the northeastern U.S. where surface PM$_{2.5}$ observations and trajectories are used to characterize these effects. Surface PM$_{2.5}$ concentration observations over the northeastern U.S. from EPA AirNow data are shown in Figure 2.8. PM$_{2.5}$ levels increase from below 13 $\mu$g m$^{-3}$ on July 7 to 30 - 60 $\mu$g m$^{-3}$ PM$_{2.5}$ across a large region in New York State and Pennsylvania on July 10. This is collocated with the July 10 enhancements in ammonium sulfate but not OMC-1.4 or fine mode K which would indicate a biomass burning source. Thus, to evaluate a range of possible smoke aerosol contributions to PM$_{2.5}$, we focus on the region along the U.S. East Coast of collocated enhancements in both fine mode K and OMC-1.4 as shown in Figure 2.7a and 2.13a, respectively. Figure 2.9b shows PM$_{2.5}$ observations at six EPA monitoring sites in Maryland, New Jersey, Virginia and West Virginia (all within this collocated region) which provide daily (or 3-day for VA and WV sites) PM$_{2.5}$ observations. These sites observed PM$_{2.5}$ increases above near background levels of 10 - 30 $\mu$g m$^{-3}$ on July 10 - 12, with the day of maximum concentration depending on the site. All three Maryland sites (in Baltimore County, MD) report PM$_{2.5}$ concentrations
Figure 2.14: (top) MODIS Aqua aerosol optical depth at 550 nm, (middle) OMI AI and (bottom) AIRS total column CO ($10^{18}$ molecules cm$^{-2}$) data on July 6 - 8, 2006.

above the EPA 24-hour standard on July 11 and the New Jersey site observes PM$_{2.5}$ 24-hour standard exceedances on both July 11 and July 12.

Figure 2.9c (middle) shows a forward trajectory from the Pickle Lake site in Ontario originating at 5 km altitude. This trajectory reveals that upper level air is transported toward the surface in a circular trajectory due to a shift in wind direction associated with the anticyclonic circulation (see section 2.3.2). This trajectory reaches the region along the U.S. East Coast of maximum OMC-1.4 and fine mode K on July 10 but the trajectory predicts air parcels remain above the boundary layer and should not reach the surface. This conflicts with our surface observations of smoke and points to inherent trajectory limitations. Although entrainment of plumes into the boundary layer is possible, the trajectories cannot fully account for these turbulent mixing effects. Finally, back trajectories at 500 m AGL from three of the
Figure 2.15: (top) MODIS Aqua aerosol optical depth at 550 nm, (middle) OMI AI and (bottom) AIRS total column CO ($10^{18}$ molecules cm$^{-2}$) data on July 9 - 11, 2006

U.S. East Coast sites used in Figure 2.9b are shown in Figure 2.9c (right). These trajectories also follow a circular path originating from regions to the northwest. However, there are again uncertainties associated with these 5-day back trajectories in horizontal location and altitudes.

2.4 Discussion

2.4.1 Horizontal and vertical transport

A combination of trajectories and CALIOP profiles with MODIS AOD, OMI AI and AIRS CO observations allows us to develop a more comprehensive understanding of the vertical and horizontal extent of smoke plumes during transport. Figures 2.14 and 2.15 show OMI AI, MODIS Aqua AOD and AIRS total column CO on July 6 - 11, 2006. On July 7, OMI
AI has positive values along with elevated MODIS AOD over most of the northeastern U.S. This indicates rapid long-range transport as upper level layers (OMI AI is most sensitive to these) reached the interior northeastern U.S. only 3 days after initial emissions. This area of elevated OMI AI and AOD persists over the northeastern U.S. on July 8. On July 9, the upper layers are observed along the U.S. East Coast (MPLNET Cove and CALIOP profiles) and 2 - 5 km altitude layers are observed over Eastern Canada (CALIOP profiles). In contrast, on July 10 and 11, OMI AI values are zero whereas AOD values remain elevated. This suggests the arrival of lower aerosol layers which are undetectable by OMI AI (due to poor sensitivity to low altitude absorbing aerosols) yet still cause total column AOD to remain elevated. Unfortunately, there is no CALIPSO overpass on July 10 along the U.S. East Coast and no data is available on July 11 or later. However, a CALIOP profile over the southeastern U.S. shows 13 km altitude smoke plume fragments, coincident with regions of elevated AOD on July 10 (Figures 2.14 and 2.15).

Total column carbon monoxide (CO), although not an exclusive tracer for biomass burning, is used as a marker for biomass burning emissions in an air mass not affected by major anthropogenic or other sources. As shown in Figure 14 (bottom), CO enhancements along the U.S. East Coast near the Cove site are observed on July 9, collocated with positive OMI AI values. Another region of increased total column CO occurs over Maine and Eastern Canada on July 10, coincident with elevated AOD (Figures 2.14 and 2.15) and elevated fine mode K (Figures 2.7a) although there are few IMPROVE sites in this region. CO observations also show that plumes were broken into multiple fragments indicating that the extent of smoke plume impacts was likely different at various locations.

From the plume location observations described above, we estimate the mean velocity of smoke plumes from their source to southern Ontario was \( \sim 800 \text{ km d}^{-1} \). From southern Ontario to the U.S. East Coast, upper layers were transported at 600 - 700 km d\(^{-1}\) and reached the U.S. East Coast on July 7 - 8. In contrast, lower layers traveled at 300 - 400 km d\(^{-1}\) and were observed both to the north over Eastern Canada on July 9 - 10 and over
the northeastern U.S. on July 10 - 11. Any of these lower layer plumes incorporated into the atmospheric boundary layer are subject to boundary layer mixing and removal. However, the most efficient removal process is wet removal by precipitation. This may have occurred on July 10 - 11 as some precipitation occurred over the northeastern U.S.

2.4.2 Air quality impact assessments

Despite plume dilution and horizontal separation of plumes, larger PM$_{2.5}$ perturbations are observed in the northeastern U.S. (10 - 30 µg m$^{-3}$) than in the Great Lakes region (10 - 20 µg m$^{-3}$). We can account for this difference by noting that there were predominantly upper level aerosol layers observed over the Great Lakes region, as less smoke had a chance to descend toward the boundary layer. Transport of biomass burning plumes from aloft to ground level has been studied by Duck et al. (2007). They found that synoptic scale meteorological features, a surface ridge of high pressure, can facilitate subsidence of smoke plumes. Based on the trajectory analyzes, smoke could have been easily incorporated into the boundary layer over the northeastern U.S. This transport mechanism can account for the observed surface air quality degradations. In addition, due to spatial heterogeneities in these plumes, some monitoring stations may have missed thicker portions of smoke plumes.

Mixing with local and regional anthropogenic sources can also increase the PM$_{2.5}$ in the northeastern U.S., resulting in a complex problem to discern the contribution from biomass burning with larger anthropogenic PM$_{2.5}$ sources along the U.S. East Coast than over the Great Lakes and southern Ontario. To full quantify and separate out the biomass burning contribution would require chemical transport model simulations and this is beyond the scope of the present study examining aerosol observations. The large PM$_{2.5}$ increases observed in Pennsylvania and New York State on July 10-11 are not solely due to biomass burning aerosols given the large increase in ammonium sulfate along with negligible increases in OMC-1.4 or fine mode K in this region. Midwestern power plant emission plumes and local sources could easily be transported to these regions and contribute to the fine aerosol loading. Nevertheless,
we can conclude that portions of the smoke plume reached the surface along the U.S. East Coast on July 10 in the region of collocated enhancements in OMC-1.4 and fine mode K, contributing to a certain fraction of the PM$_{2.5}$ enhancements observed. This is quite a large region from New Jersey to Virginia along the East Coast and inland into West Virginia, Ohio and Kentucky.

In addition to local anthropogenic sources, atmospheric mixing can play a role in air quality standard exceedances. To assess the influence of high pressure subsidence inversions during this period, we analyzed days (June 26, June 28 and July 7, 2006) with surface high pressure and no collocated smoke from biomass burning and found no enhancements in surface PM$_{2.5}$ concentrations approaching the EPA PM$_{2.5}$ daily standard for exposure. We also note that June 26, 28 and July 7 are all weekdays so any weekend effects (decreased emissions) are not impacting these results. In addition, we observe enhanced PM$_{2.5}$ and other smoke signatures on weekend days July 8 and 9 over portions of the Midwestern U.S. (Figures 2.8 and 2.9a). These weekend days should have lower local backgrounds due to lower vehicular emissions. Therefore, although subsidence inversions due to high pressure over a region can contribute to elevated pollutant concentrations and air quality standard exceedances, this does not occur all the time. Other factors influence PM$_{2.5}$ concentrations, including local emissions, regional and long-range transport.

2.4.3 Data set limitations

When considered separately, each aerosol observation data set used in this analysis is capable of providing only a limited view of the transport of smoke emissions. This leads to uncertainties in efforts to quantify or apportion smoke impacts. For example, using only trajectory analyzes and/or MODIS data, we would not be able to track smoke transport from the free troposphere to the surface due to trajectory uncertainties in vertical location within the boundary layer. MODIS AOD observations alone will not provide data on vertical profiles (CALIOP) or aerosol origin and suffer from interference from clouds. OMI AI cannot provide
observations of absorbing aerosols (smoke) at the surface. The IMPROVE network cannot provide daily (only 3 day) chemical composition data and the sites are limited in spatial coverage. AERONET data on July 10 - 11 over regions of maximum PM$_{2.5}$ are not available but would have been useful to further analyze air quality impacts. AIRS CO cannot distinguish between CO from biomass burning and CO from other anthropogenic sources. The MPLNET Lidar system can provide vertical profiles to identify aerosol layers at only two locations in the eastern U.S. The CALIPSO satellite observations are limited in spatial coverage (narrow swath width), have interferences from clouds and overpass locations are frequently not collocated with other observations for comparisons. Despite these limitations, analyzing numerous tracers and data sets allows one to gain a better overall view of long-range transport leading to potential air quality impacts.

2.5 Atmospheric implications

We have analyzed a case study of smoke plumes from a boreal forest fire in western Canada of a magnitude that has occurred during multiples years in the previous decade. This potentially common event during the summer fire season in central Canada likely contributed to EPA 24-hour PM$_{2.5}$ standard exceedances 3000 km downwind of the source region. Not all boreal forest fire emissions impact U.S. air quality, as their impact on regions far from the source region is contingent upon emission and injection altitudes, meteorology over the fires and downwind, atmospheric mixing and conditions favoring deposition or other aerosol sinks. However, with certain weather patterns allowing for upper altitude plume transport such as those in this case study, there is a real potential for less extreme forest fires to significantly affect air quality in distant regions, a potential that may increase with predicted increases in wildfire frequency and burned area under future climate scenarios (Flannigan et al., 2005; Wotton et al., 2010).

The high altitude aerosols observed over the northeastern U.S. (including CALIOP, MPLNET and OMI AI observations on July 9) can exhibit other influences aside from those related to air quality. Elevated total column aerosol optical depths from smoke can
contribute to significant visibility impairments and regional haze as observed by Pahlow et al. (2005), with implications for the U.S. EPA Regional Haze Rule (U.S. Environmental Protection Agency, 2003). Biomass burning aerosol contributions to regional haze and visibility reductions must be taken into account as noted by Park et al. (2006). In addition, smoke aerosols were observed partially embedded in cirrus clouds at 8-12 km altitude, indicating that aerosol-cloud interactions and potential aerosol effects on ice nucleation and cloud microphysics are important here. Radiative effects due to aerosol absorption, with single scattering albedo values <0.9, may also be significant. Future studies incorporating these observations into radiative transfer models should be useful to fully quantify these effects.

In summary, we demonstrate that surface sites in the Midwestern and northeastern U.S. observed smoke plume signatures, leading to a rise of $\sim 10-20 \, \mu g \, m^{-3} \, PM_{2.5}$ attributable to the smoke along the U.S. East Coast. Trajectory and meteorological analyzes along with biomass burning tracers and other aerosol properties are consistent with smoke. Our results demonstrate the value of integrating the satellite and ground-based measurements used here to develop a larger picture of plume transport and impacts from a large but not unusual magnitude fire event. Due to certain data gaps and uncertainties, no data set by itself accurately depicts the plume horizontal and vertical locations. However, this case study’s value is that the synthesis of data sets allows us to gain a better overall picture of impacts even with no chemical transport model simulations. This tool and technique is thus potentially useful for future studies to assess a range of complex impacts from these less extreme events, some of which may be extended over longer time periods beyond a case study. Thus, the methodology of integrating data sets from the current aerosol observation network in place over North America was able to provide more comprehensive data to evaluate a transient, less extreme event and provide estimates for regional air quality influences over the eastern United States.
2.6 Acknowledgments

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Chapter 3

Open-path, quantum-cascade-laser-based sensor for high-resolution atmospheric ammonia measurements

3.1 Introduction

Atmospheric ammonia (NH$_3$), the third most abundant nitrogen species and dominant atmospheric base, is an important precursor to ammoniated fine particulate matter (Nowak et al., 2007; Pinder et al., 2008). Total NH$_x$, the sum of gas-phase NH$_3$ and particulate ammonium (NH$_4^+$), is an increasingly important component of the reactive nitrogen budget, with implications for human and ecosystem health (Bobbink et al., 2010; Galloway et al., 2003; Pinder et al., 2008). Ammoniated aerosols are a dominant component of inorganic aerosol mass in both clean and urban regions (Jimenez et al., 2009). Gas-phase NH$_3$ measurements are crucial for understanding aerosol nucleation and new particle formation (Ball et al., 1999; Hanson and Eisele, 2002; McMurry et al., 2005; Benson et al., 2011), which facilitate long-range transport.
of aerosol ammonium and nitrate (Nowak et al., 2007; Pinder et al., 2008). Ammoniated sulfate aerosols also play an important role in cirrus cloud nucleation (Tabazadeh and Toon, 1998; Wang et al., 2008), and aerosol–cloud interactions have significant yet highly uncertain radiative effects on climate (Adams et al., 2001; Martin et al., 2004; Solomon et al., 2007).

Anthropogenic NH$_3$ emissions have more than doubled since preindustrial times, largely due to agricultural livestock and fertilizer emissions (Galloway et al., 2003; Battye et al., 2003; Anderson et al., 2003; Aneja et al., 2008a). Uncertainties as large as 50% exist in global NH$_3$ emission budgets due to the spatial and temporal variability of emissions and a lack of in situ measurements for emission inventory validations (Battye et al., 2003; Clarisse et al., 2009). Recent comparisons between measured emissions and concentrations with model inventories found significant discrepancies (Heald et al., 2012; Nowak et al., 2012; Walker et al., 2012).

Gas-phase NH$_3$ has a short atmospheric lifetime of a few hours to a few days, which depends on ambient temperature, relative humidity and aerosol composition (Anderson et al., 2003). High spatial and temporal resolution observations are needed to fully characterize NH$_3$ dynamics, including aerosol nucleation, gas-phase uptake onto particles and volatilization of particulate ammonium (Battye et al., 2003; Nowak et al., 2007; Pinder et al., 2008). In situ NH$_3$ instruments require high (sub-ppbv) sensitivity to measure low atmospheric mole fractions (pptv–ppbv), fast response time and a large dynamic range to capture atmospheric variability (von Bobrutzki et al., 2010). Ammonia sensors must also account for gas-phase NH$_3$ surface adsorption effects and condensed-phase partitioning due to changes in temperature and relative humidity between the sampling volume and ambient atmosphere (Yokelson et al., 2003).

To date, the NH$_3$ measurement challenges have resulted in a variety of different approaches. Conventional offline NH$_3$ sensors (passive filters, denuders and ion chromatography) often have sufficient sensitivity (< 1 ppbv NH$_3$), but have long integration times, lack the requisite selectivity and are labor intensive to analyze (Fehsenfeld et al., 2002; von Bobrutzki et al., 2010; Ellis et al., 2011). Chemical ionization mass spectrometry (CIMS) NH$_3$ instruments have
high time resolution (seconds), selectivity and extremely high sensitivity (<100 pptv NH₃), but require large power consumption (kW) and space (multiple instrument racks) (Nowak et al., 2007; Benson et al., 2010; Sintermann et al., 2011). Laser absorption spectrometers for gas-phase NH₃ have been developed for real-time, high-sensitivity and selective detection. Near-infrared diode lasers have been used for NH₃ detection, but their sensitivity is limited due to the NH₃ overtone bands in the near infrared (Claps et al., 2001; Kosterev and Tittel, 2004).

More recently, advances in room temperature, distributed-feedback quantum cascade (QC) lasers have led to the development of QC-laser-based NH₃ sensors using the strongest NH₃ absorption transitions located in the mid-infrared spectral region (Manne et al., 2006; Whitehead et al., 2007; McManus et al., 2008; Manne et al., 2009; Curl et al., 2010; Ellis et al., 2010; Gong et al., 2011). Although these closed-path systems are highly sensitive (ppbv or sub-ppbv), they suffer from sampling artifacts that limit precision and response time and complicate calibration methods (Whitehead et al., 2008; von Bobrutzki et al., 2010). In addition, these systems are large (usually >100 kg) and require pumps and temperature control systems with high power consumption (usually hundreds of watts).

In contrast to these closed-path systems, non-intrusive open-path designs address the sampling challenges and provide fast response times (Zondlo et al., 2010; McDermitt et al., 2011; Tao et al., 2012b). Peeters et al. (2000) demonstrated laboratory performance of an open-path cavity-enhanced absorption spectrometer for NH₃, but the detection limit was not sufficient for atmospheric measurements. Open-path remote systems employing Fourier transform infrared (FTIR) spectroscopy techniques have been demonstrated for path-integrated field NH₃ measurements, including agricultural flux measurements with single ppbv sensitivity (Griffith and Galle, 2000; Galle et al., 2000). Open-path tunable diode laser absorption spectroscopy (TDLAS) and differential optical absorption spectroscopy (DOAS) systems in remote measurement configurations have been used to measure NH₃ with ppbv detection limits (Thoma et al., 2005; Volten et al., 2012). Mount et al. (2002) demonstrated open-path NH₃ measurements
with a mid-ultraviolet DOAS system and achieved 1 ppbv NH$_3$ sensitivity in 1 s. The high time resolution (> 1 Hz) of this approach illustrated the value of an open-path configuration. However, all of these sensors require long paths rather than compact sensor footprints. Currently, there are significant hurdles for compact, open-path, laser-based NH$_3$ sensing, including pressure-broadened absorption lineshapes sensitive to changes in environmental temperature and pressure and interferences from broad, overlapping absorption features from other atmospheric species.

To address the limitations of closed-path techniques and challenges for a compact, open-path sensing, we demonstrate the performance of compact, open-path, high-sensitivity, QC-laser-based atmospheric NH$_3$ sensor. The sensor probes the fundamental mid-infrared NH$_3$ absorption transitions using a QC laser at 9.06 µm. Multi-harmonic wavelength modulation spectroscopy is used to isolate overlapping absorption features, and an in-line ethylene reference cell is used for online calibration and normalization to account for sensor drift. The system is relatively compact, low power ($\sim$ 50 W), and low mass ($\sim$ 5 kg), with a 10 Hz time resolution and high sensitivity (0.30 ppbv minimum detection limit at 10 Hz). The fast response time and dynamic range capabilities of the open-path system are illustrated. In situ NH$_3$ measurements of emission sources are highlighted.

3.2 Sensor design

3.2.1 Opto-mechanical setup

The open-path, QC-laser-based NH$_3$ sensor is shown schematically in Figure 3.1. Overall, the open-path design is optimized for field portability with a 100 cm $\times$ 10 cm $\times$ 11 cm sensor head and 35 cm $\times$ 33 cm $\times$ 15 cm drive electronics unit. The total sensor head mass is $\sim$ 5 kg, including basic shielding (not shown in Figure 3.1) to protect components in field conditions. The sensor uses a thermo-electrically (TE) cooled, continuous-wave, single-mode, 9.06 µm quantum cascade laser (Alpes Lasers) in a high heat load package, which is detected
by a three-stage, TE-cooled, infrared HgCdTe photodetector (Judson Teledyne). The optomechanical design consists of the laser, collimating lens, in-line ethylene reference cell, steering mirrors, multi-pass optical cell and detector. A Herriott multi-pass cell with spherical mirrors (Herriott et al., 1964) is used to achieve path lengths of 30–60 m in a 70 cm base path. The optimal path length configuration is dependent on the beam size and desired base path. In addition maximizing path length, one must minimize interference fringing which may limit sensitivity for higher path length configurations. The laser beam is directed into the optical cell consisting of two protected silver-coated, 3-inch-diameter spherical mirrors, both with a 6 mm-diameter hole for laser beam entry and exit. We use a configuration with laser and detector components on opposite sides of the optical cell for practical opto-mechanical component design considerations. The QC laser beam size is optimized with focusing mirrors to minimize clipping and distortion effects as the laser beam enters the input hole. A visible alignment laser (HeNe) is used to image the optical spot pattern on the mirrors and couple the QC laser beam into the optical cell. Custom anti-reflection coatings (reflectivity < 0.5 %) are applied to all transmissive optics, including laser and detector housing windows, to minimize signal baseline artifacts due to interference fringes that are unstable with ambient temperature changes.

The QC laser is driven by a low-noise current driver (Wavelength Electronics, QCL500) and thermally controlled with a precise temperature controller (Wavelength Electronics, HTC3000). The QC laser current is modulated with a sawtooth ramp (50 Hz) and higher-frequency (15 kHz) sinusoidal modulation. The QC laser tuning range for NH₃ measurements is 0.52 cm⁻¹, based on the current tuning rate at 50 Hz ramp frequency. Tao et al. (2012a) demonstrated that for the QC laser used here, the current tuning rate decreases with increasing ramp or modulation frequency. Although higher ramp and modulation frequencies should improve sensitivity by minimizing laser excess noise, the decrease in tuning rate at higher frequencies, the broad spectral features probed, and practical QC laser tuning rate limitations prevent us from going to higher frequencies. The tuning rate limitations allow
us to achieve a modulation index of $\sim 1.4$ for NH$_3$ measurements, which is not at the most sensitive, optimal value of 2.2 (Reid and Labrie, 1981).

The detector signal is acquired with a National Instruments data acquisition board (NI-USB 6251) and processed in real time. The 50 Hz raw signal is co-averaged to 2–10 Hz, depending on the field conditions and signal-to-noise ratio (SNR). Multi-harmonic wavelength modulation spectroscopy (WMS) detection is performed with a custom LabVIEW software algorithm, eliminating the need for a bench-top lock-in amplifier, as described in Tao et al. (2012b). The open-path configuration eliminates the need for large pumps that require high power consumption, resulting in significantly lower power consumption ($\sim 50$ W) than existing closed-path NH$_3$ sensors. The laptop computer power consumption (currently $\sim 50$ W) can be
reduced further with alternative, lower-power single-board computers or embedded systems. The system requires no cryogenic cooling, allowing for autonomous field operation.

### 3.2.2 Spectroscopy

![Diagram showing absorption spectra](image)

**Figure 3.2:** (a) Direct absorption HITRAN simulation (Rothman et al., 2009) calculated based on 60 m path length, 296 K, 1013.25 hPa and the following atmospheric mixing ratios: 400 ppmv CO$_2$, 80 ppbv O$_3$, 1800 ppbv CH$_4$, 5 ppbv SO$_2$ and 1 ppbv NH$_3$. Water vapor is not shown for clarity. The arrow indicates the wavelength region selected for open-path NH$_3$ measurements.

The strongest NH$_3$ absorption transitions occur in the mid-infrared spectral region near 10.3 $\mu$m and are probed by other QC laser absorption spectrometers (McManus et al., 2008; Gong et al., 2011). However, this spectral region is not optimal for open-path detection, due to the carbon dioxide (CO$_2$) and water vapor (H$_2$O) pressure-broadened absorption lines that overlap with the NH$_3$ absorption lines. The most optimal absorption feature for open-path
NH$_3$ detection is at 9.06 µm, a region between the strong absorption bands of N$_2$O below 8.9 µm and absorption bands of CO$_2$ and O$_3$ above 9.1 µm, as illustrated in Figure 3.2. The selected absorption feature is $\sim 50\%$ weaker than the stronger NH$_3$ features near 9.5 µm, but the spectral clarity at 9.06 µm allows for higher sensitivity. Figure 2a shows spectra simulated using the HITRAN database in the 9.06 µm region for 1 ppbv NH$_3$ and typical ambient mixing ratios of atmospheric absorbers at 296 K and 1013.25 hPa for a 60 m optical path length. The NH$_3$ absorption feature at 9.06 µm in Figure 3.3a is a superposition of six overlapping absorption transitions. This feature overlaps with the minimum of a neighboring H$_2$O absorption feature, producing a direct absorption baseline. Owen et al. (2013) performed spectroscopic studies on relevant atmospheric absorbers in this region at reduced pressure to characterize the interferences. For open-path detection at ambient pressures, wavelength modulation spectroscopy is a well-suited detection technique for spectral resolution of these weak, overlapping absorption features (Schilt et al., 2003; Zondlo et al., 2010). As shown in Figure 3.3b, second harmonic (2f) detection minimizes the water vapor absorption baseline and improves sensitivity and selectivity (Reid and Labrie, 1981). Other atmospheric species such as CO$_2$, O$_3$ and SO$_2$ also absorb in this region below $\sim 5 \times 10^{-5}$ fractional absorption.

We note that polluted conditions are illustrated in Figure 3.3 (5 ppbv SO$_2$ and 80 ppbv O$_3$) to represent ambient conditions with possible interferences. However, the NH$_3$ absorption at 9.06 µm for 1 ppbv NH$_3$ is greater than five times the absorption of these species in this spectral region. Overall, the only significant interfering species for 2f detection at 9.06 µm is H$_2$O, which is addressed in the following section. The O$_3$ absorption baseline begins to interfere significantly for NH$_3$ mole fractions below 100 pptv.

### 3.2.3 Ammonia mole fraction retrieval

The ammonia mole fraction is retrieved with real-time spectral fitting at 10 Hz. We simulate the direct absorption signal recorded by the detector with multiple Voigt lineshape profiles
Figure 3.3: (a) Direct absorption HITRAN simulation (Rothman et al., 2009) calculated based on 60 m path length, 296 K, 1013.25 hPa and the following atmospheric mixing ratios: 400 ppmv CO$_2$, 80 ppbv O$_3$, 1800 ppbv CH$_4$, 5 ppbv SO$_2$, 1 ppbv NH$_3$ and 2% H$_2$O; (b) second harmonic spectrum calculated with same species showing reduction of the water vapor baseline. Ozone and CH$_4$ do not appear in the second harmonic spectrum as they are flat baselines. The black dotted lines in (a) and (b) denote the total absorption of all species simulated.

for all relevant absorption transitions within the laser scan range as follows:

$$ D = \chi \cdot I(t) \cdot \exp\left(-\sum_i (x_i S_i L_i \psi_i(T, P, v(t)))\right), $$

(3.1)
where $\chi$ is the detector collection efficiency; $I(t)$ is the laser intensity function; $x_i$, $S_i$ and $L_i$ are the number density, absorption line strength and path length, respectively, for different absorbing species $i$; and $\psi_i(T,P,\nu(t))$ is the Voigt lineshape function for absorption feature $i$, a function of temperature, pressure and wavenumber $\nu(t)$. This signal is multiplied by a reference signal at the $n$th harmonic and passed through a virtual lock-in amplifier based on a numerical wavelength modulation spectroscopy model (Tao et al., 2012b). A least-squares fitting routine is implemented to produce fitting coefficients for mole fraction, DC signal offset, linear and second-order polynomial baselines. The second-order polynomial baseline fitting accounts for baseline effects, including detector nonlinearity, intensity modulation and interference fringing. The spectroscopic parameters used in the fitting routine for the NH$_3$ absorption lines of interest have been measured experimentally by Sun et al. (2013), and generally agree to within 10% of HITRAN. Ambient temperature and pressure are measured with a digital temperature sensor (HYT 271, $\pm0.2^\circ$C accuracy) and digital pressure sensor (MS5803-01BA, $\pm0.5$ hPa accuracy) at 1 Hz and updated in real time for the fitting routine. An in-line ethylene reference cell is inserted into the optical path as explained in the section below.

Water vapor introduces multiple, minor potential interferences for the 2f NH$_3$ retrieval. The average ambient H$_2$O mixing ratio for a given region and time period of sensor field deployment is used for spectral fitting of the H$_2$O absorption baseline and used to calculate absorption line widths to account for H$_2$O broadening using the coefficients measured by Owen et al. (2013). On short timescales, the variability of ambient H$_2$O vapor (a few hundred ppmv) has a negligible ($<0.5\%$) impact on the 2f NH$_3$ retrieval. For larger changes of water vapor, the H$_2$O mixing ratio is updated in the spectral fitting using routine meteorological data.

### 3.2.4 In-line reference cell

The NH$_3$ and ethylene absorption features (centered at 1103.46 cm$^{-1}$ and 1103.36 cm$^{-1}$, respectively) are fit simultaneously both in second (2f) and eighth (8f) harmonics. The multi-
Figure 3.4: Ammonia 2f (left) and ethylene 8f (right) spectra recorded at 10 Hz with real-time fitting results (dotted lines) and residuals. The 2f NH$_3$ signal was recorded for ambient laboratory conditions of 19.0 ppbv NH$_3$. The two arrows in the 2f plot denote the locations of the two extra troughs due to the ethylene reference signal.

The harmonic approach separates the overlapping, broad ambient NH$_3$ absorption feature from the narrower ethylene reference signal as demonstrated by Sun et al. (2013). Figure 3.4 shows representative 2f and 8f spectra along with fitting results and residuals for a 19.0 ppbv ambient NH$_3$ signal. The 2f signal has two extra troughs, indicated by arrows, due to the ethylene absorption overlapped with the ambient NH$_3$ signal. The eighth harmonic (8f) is used for ethylene reference signal detection to achieve optimal separation between ambient NH$_3$ and ethylene reference signals. The 8f signal isolates the relatively narrow, reduced pressure ethylene reference signal, with negligible influence from ambient NH$_3$ absorption at 8f. We do not use harmonic orders higher than 8f due to limits of signal-to-noise ratio, since the signal intensity decreases as harmonic order increases. The even harmonic orders are advantageous since the maximum of the WMS function occurs at the spectral line center, which is useful for line-locking procedures.

We implement an online spectroscopic calibration method using ethylene, which exhibits negligible adsorption artifacts compared with NH$_3$. We do not use an NH$_3$ reference calibration
cell due to adsorption artifacts associated with changes in cell temperature and pressure. In addition, when ambient and reference absorption features of the same species are overlapping, separating changes in mole fraction from changes in the reference signal becomes difficult. The in-line ethylene reference cell contains 1.5% ethylene in nitrogen at 50 hPa total pressure in a 3 cm length. The ethylene mixing ratio was chosen to be comparable to NH$_3$ signals at ppbv levels. Spectroscopic parameters of both NH$_3$ and ethylene absorption features have been measured and compared with the HITRAN database to evaluate the calibration accuracy. Sun et al. (2013) has demonstrated this ethylene signal can serve as a reference of NH$_3$ mole fraction in real time, with an overall calibration accuracy of ±20%.

In addition to calibration, the in-line ethylene reference signal is especially advantageous as it provides normalization for sources of instrument drift. Normalization for sensor drift is essential for open-path systems exposed directly to changing environmental conditions, which lead to undesirable or unknown opto-mechanical and electronic responses such as optical interference fringes, electrical component drift, laser and detector instabilities and light attenuation due to precipitation. In addition, the sharp peaks and troughs of the 8f signal are used for line-locking via laser current adjustment to account for thermal drifts of the laser wavelength. This improves the drift during a typical ∼10°C diurnal ambient temperature cycle from 0.04 cm$^{-1}$ to < 0.005 cm$^{-1}$.

3.2.5 Calibration

We also perform offline absolute calibration using NH$_3$ direct absorption measurements. Prior verification of path length was performed and uncertainties in the HITRAN parameters for these NH$_3$ absorption lines were previously characterized (Sun et al., 2013). Owen et al. (2013) also studied these absorption transitions and reported lineshape parameter uncertainties of <10%. The standard NH$_3$ mole fractions for calibration of our WMS retrieval are calculated based on a direct absorption fitting using these calibrated HITRAN parameters. The absolute accuracy of this offline calibration method (±10%) is comparable to current
high-sensitivity, state-of-the-art NH$_3$ sensors. For example, the pulsed QC-laser-based NH$_3$ instrument demonstrated by McManus et al. (2008) has a typical concentration uncertainty of 5–20%. Nowak et al. (2007) found uncertainties in CIMS NH$_3$ measurements to be ±25–30% during field operation. Sintermann et al. (2011) found calibration accuracy of ~5% for a CIMS NH$_3$ instrument.

![Figure 3.5: Calibration curve derived from direct absorption measurements for various NH$_3$ gas standard mole fractions at atmospheric pressure. Inset: linear fitting of calibration curve for mole fractions below 120 ppbv NH$_3$. Error bars for each calibration point are ±10% for each measurement method (direct absorption and 2f retrieval).](image)

We perform absolute calibration offline using direct absorption spectroscopy as a reference method to measure NH$_3$ mole fraction independent of our WMS NH$_3$ retrieval based on 2f detection. The open-path optical cell is enclosed in a polyethylene calibration tube, into which a flow of 25 ppmv NH$_3$ in N$_2$ is introduced. This 25 ppmv NH$_3$ standard mixing ratio is decreased incrementally by dilution with dry air and each calibration point is recorded in both
2f and direct absorption as shown in Fig. 4. The horizontal axis is the NH$_3$ standard mole fraction derived from direct absorption measurements. The vertical axis displays the retrieved NH$_3$ mole fraction based on 2f spectral fitting with the online spectroscopic calibration method described in Sect. 2.3. We note that the calibration is performed at mole fractions much less than that of the original 25 ppmv NH$_3$ standard. Therefore, we use HITRAN parameters appropriate for NH$_3$ in dry air. The mole fraction retrieval is derived from nonlinear Voigt lineshape fitting of the direct absorption spectra along with measured ambient temperature and pressure, and assumes the mole fraction is linearly proportional to the fractional absorption for typical (ppbv) atmospheric NH$_3$ mole fractions. However, the retrieved mole fraction does not scale linearly with the standard mole fraction due to strong absorption nonlinearity at mole fractions $>$ 100 ppbv NH$_3$. Therefore, we fit a third-order polynomial to calibrate the retrieved mole fraction as shown in Figure 3.5. The linearity of retrieved mole fraction is shown in the inset plot of Figure 3.5 for mole fractions below $\sim$ 120 ppbv NH$_3$. In this regime, we can assume absorption is linear with number concentration (and mole fraction assuming constant temperature and pressure) based on the Beer Lambert law weak absorption limit. A linear best-fit line in this range yields $R^2 = 0.99$, in agreement with the weak absorption limit. The surface adsorption and partitioning artifacts associated with NH$_3$ calibrations present unique challenges which limit accuracy, especially for low ambient mole fractions. Our accuracy is constrained by the uncertainty in the HITRAN parameters for the NH$_3$ absorption features, which is estimated to be $\sim$ 10% (Sun et al., 2013).

Calibration of the zero NH$_3$ baseline offset is also important when retrieving NH$_3$ mole fractions near the detection limit. The zero calibration point is obtained by flushing the calibration tube with dry air and coating the calibration tube surfaces with a concentrated ($\sim$ 20 wt%) citric acid solution to minimize NH$_3$ desorption effects. We note that true zero NH$_3$ conditions are very difficult to achieve for any NH$_3$ instrument, due to surface adsorption and partitioning artifacts as well as residual NH$_3$ found in dry air. We perform zero calibrations prior to, during, and following field deployments, along with the full calibration
procedure described above. Based on these zero calibrations, our absolute uncertainty in the zero calibration is 0.20 ppbv NH₃. It is important to note that each time zero calibration is performed, there is additional uncertainty due to differences in the amount of residual NH₃ in the calibration tube. Thus, 0.20 ppbv is an upper limit to our estimate of the zero calibration uncertainty. This metric defines an absolute accuracy at low NH₃ mole fractions, due to uncertainty in the zero calibration point. Thus, the total estimated uncertainty is 0.20 ppbv NH₃ ± 10% of the ambient NH₃ measurement.

3.3 Field deployments

The open-path NH₃ sensor has been field-deployed in a wide range of environments to test system performance under real-world, field conditions. While laboratory performance and validation is essential (section 3.4), in-situ sensor performance must be validated under field conditions, where surprises and challenges for sensor operation in the field are brought to light. Open-path designs require optical and electronic system components to be directly exposed to environmental conditions exterior to the sensor, introducing unique considerations to optimize these systems. Field deployment testing is an iterative process, wherein the weakest sensor components (usually unknown prior to deployment) are identified. These weaknesses are addressed with laboratory improvements and subsequently re-evaluated in the field.

The field deployment conditions included hot, dusty, and dry conditions in the San Joaquin Valley, California; >40°C ambient temperatures and high humidity (mid-20°C dew points) in Princeton, New Jersey; and cold, rain and dew conditions in Baltimore and Beltsville, Maryland (Miller et al., 2012). The major weaknesses identified included temperature cycling-induced alignment instabilities, laser and detector temperature control issues, and interference fringes drifting with ambient temperature. As shown by the evolution of the open-path NH₃ sensor design from a bread-board to field-ready prototype (Figure 3.6), these field deployments led to improvements in the opto-mechanical design to address temperature cycling effects and laser and detector thermal stability. The optical cell structure and mirror mounting were
custom designed with carbon fiber rods to minimize temperature cycling effects (Miller et al., 2012). In the following subsections, the results of field testing during CALNEX 2010, the MIRTHE-SLIP field campaigns (2011 - 2012) and mobile platform campaigns including NASA DISCOVER-AQ 2013 and CARE-Beijing-NCP 2013, are highlighted. Sensor temperature stability metrics during these field campaigns are summarized in Table 3.1.

Figure 3.6: Open-path NH$_3$ sensor photos illustrating the evolution and maturity of the sensor design, from the first prototypes in June 2010 (NOAA CALNEX 2010), October 2011 (MIRTHE SLIP UMBC), and April 2012 (MIRTHE SLIP Beltsville), to the mobile measurement-ready prototypes in January 2013 (DISCOVER-AQ SJV 2013) and May 2013 (CARE-Beijing NCP 2013).
Table 3.1: Summary of field campaign \(\text{NH}_3\) sensor temperature stability.

<table>
<thead>
<tr>
<th>Field campaign</th>
<th>Air temperature range (^\circ\text{C})</th>
<th>Laser temperature (^\circ\text{C})</th>
<th>Laser wavelength drift (\text{cm}^{-1})</th>
<th>Line-locking</th>
<th>Optical alignment stable</th>
</tr>
</thead>
<tbody>
<tr>
<td>CALNEX 2010</td>
<td>15-40</td>
<td>24</td>
<td>0.017</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>SLIP UMBC</td>
<td>0-20</td>
<td>19</td>
<td>–</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>SLIP Beltsville</td>
<td>10-25</td>
<td>19</td>
<td>0.04</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>SLIP Princeton</td>
<td>0-10</td>
<td>19</td>
<td>&lt;0.005</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>DISCOVER-AQ</td>
<td>10-20</td>
<td>19</td>
<td>&lt;0.005</td>
<td>Yes</td>
<td>Somewhat</td>
</tr>
<tr>
<td>CARE-Beijing</td>
<td>25-45</td>
<td>19</td>
<td>&lt;0.005</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

### 3.3.1 CALNEX 2010

The first open-path \(\text{NH}_3\) sensor breadboard prototype was deployed in hot, dusty, and dry conditions during the NOAA CALNEX 2010 field campaign at the Bakersfield, California ground supersite. The CALNEX 2010 field campaign focused on atmospheric species and processes in CALifornia at the NEXus of air quality and climate change, including \(\text{NH}_3\) [2010 CalNex Science and Implementation Plan]. The entire open-path sensor was deployed on a tower (third level at \(\sim 9.4\) m above ground level) during June 2010, as shown in Figure 3.7.

Sensor performance was assessed during this initial deployment. The laser operated at a temperature of 24\(^\circ\text{C}\) in a laboratory laser housing (LLH) (Alpes Lasers), with laser line-center drift of only \(\sim 0.017\) \(\text{cm}^{-1}\) during a 17\(^\circ\text{C}\) diurnal temperature change (Figure 3.8). The challenges encountered during this deployment included optical alignment drift with temperature, detector temperature control instability in extreme heat (40\(^\circ\text{C}\)), optical interference fringing limiting detection sensitivity, and current driver operation above the recommended maximum operating temperature.

### 3.3.2 MIRTHE SLIP field deployments

The MIRTHE SLIP grant provided the opportunity for three field deployments of the open-path \(\text{NH}_3\) sensor to assess field performance and improve the sensor design from the initial
Figure 3.7: Bakersfield, California ground supersite tower during the NOAA CALNEX 2010 field campaign. The open-path NH$_3$ prototype sensor was deployed on the third level, as indicated by the red circle.

prototype. Initial field performance of the large breadboard setup with sensor noise and drifts during the CALNEX 2010 field deployment resulted in sensor design refinements, including miniaturization of the breadboard configuration and laser housing with high-heat-load (HHL) packaging, implementation of the in-line ethylene reference cell approach, and integration of the LABVIEW data acquisition and processing algorithms. Field deployments were conducted as part of the Baltimore Ecosystem Study (BES) at the University of Maryland Baltimore County (UMBC) in October 2011, at the Maryland Department of Environment (MDE) - Howard University atmospheric monitoring site in Beltsville, Maryland (April 2012), and at the Princeton Broadmead testbed site (Princeton, New Jersey) in October-November 2012. The open-path sensor design was optimized following these deployments to improve
the thermal stability and improvements were subsequently field-tested during the Princeton Broadmead site deployment.

During the CALNEX 2010 campaign, a bulky LLH QC laser housing was used with a separate external, broadband, anti-reflection (AR) coated collimating lens, resulting in poor beam quality and large beam size that contributed to significant optical interference fringing when coupled into the multi-pass optical cell. To improve this, we installed a HHL-packaged QC laser with an integrated, AR-coated collimating lens. HHL packaging should provide better beam quality and stability in a more compact housing footprint. However, QC laser
temperature control stability for HHL commercial packaging is important to assess in diverse field environments, especially when operating the laser temperature (∼19°C) near ambient temperature. Figure 3.9a shows the laser line-center drifted by ∼0.04 cm⁻¹ (0.2°C laser temperature increase per degree decrease in air temperature) as the HHL-packaged QC laser TEC compensated for a typical 18°C diurnal temperature cycle in Beltsville, Maryland. This drift is significantly worse than during CALNEX 2010 for a similar (17°C) diurnal temperature cycle. The laser wavelength drift is strongly influenced by the ambient temperature contributing to a thermal gradient between the thermistor temperature measurement in the HHL housing and the actual laser temperature. This drift was improved by active temperature line-locking (set point change) and current offset line-locking using the narrow ethylene reference 6f peak. Figure 3.9b shows the long-term stability over multiple days during the Princeton Broadmead deployment within 0.005 cm⁻¹, one order of magnitude better than the previous deployment in Beltsville, Maryland.

Another limitation encountered during CALNEX 2010 and the MIRTHE SLIP campaigns was the large changes in light intensity received on the detector, especially with direct exposure to solar radiation. While retrievals are normalized for light intensity, large changes in light intensity will result in non-linear normalization and lead to artifact drifts in concentration measurements. Figure 3.10a illustrates changes in light intensity on the detector (using 1f DC intensity) of >50% with ambient air temperature changes and solar heating for a typical 10°C diurnal temperature cycle in Beltsville, Maryland. The detector temperature is assumed to remain constant at the TEC set-point (-55°C) under conditions where the heat sink is effective at detector cooling. These light intensity variations are due to thermal expansion and contraction of stainless steel rods supporting the multi-pass optical cell and mirror mounts. Optical alignment stability was optimized with a new robust opto-mechanical design replacing stainless steel rods with carbon rods. Figure 3.10b shows the improved stability of the light intensity (<20% changes in detector signal full scale or 1f DC value) during the Princeton Broadmead deployment.
The sensor performance during the MIRTHE SLIP UMBC and Beltsville, Maryland field deployments revealed major sources of instrument drift. Larger laser temperature drifts due to ambient temperature changes were observed with an HHL-packaged QC laser compared with the LLH QC laser used during CALNEX 2010. In addition, the influence of ambient temperatures on stability of the optical system alignment, first identified during CAINEX 2010, were also observed. Finally, during all MIRTHE SLIP campaigns, the sensor sensitivity and stability were affected by optical interference fringes, which distort the retrieved spectrum used for spectral fitting and are unstable with ambient temperature changes. Typically, these
artifacts result from transmissive optics in the optical system, or scattering of the laser beam at input holes or within the optical cell. We identified possible contributions to interference fringing from the broadband, AR-coated detector, laser housing, and reference cell windows, as well as the collimated beam size comparable to the optical cell input hole size.
3.3.3 Mobile measurement campaigns

The open-path sensor was integrated onto a multi-sensor, mobile vehicular platform. The details of this system are discussed in chapter 4. Initial mobile field tests during the MIRTHE SLIP campaign in November 2012 revealed sensitivity to vibration for on-road measurements, during which alignment could not be maintained. These sensitivity issues were initially linked to clamping of individual components to the optical breadboard. The entire system was subsequently re-designed as one aluminum piece, as shown in the January 2013 configuration (Figure 3.6). The broadband, AR-coated windows were replaced with custom AR-coated windows (> 99.5% transmission at 9 µm), resulting in a minimal, stable signal baseline, even with ambient temperature changes on the car-top. This new design implemented during the DISCOVER-AQ SJV 2013 field campaign.

The main limitations for this mobile system involved temperature-induced optical alignment drifts, which were linked to the sensitivity of the cylindrical cell (Silver, 2005) to temperature and vibration effects on the car-top. A new design with a Herriott optical cell (Herriott et al., 1964) and single rail to connect the entire opto-mechanical system was implemented during the CARE-Beijing-NCP 2013 field campaign in Beijing, China (June 2013). This system exhibited negligible alignment changes due to solar heating and temperature changes on the car-top. In addition, this system hosted mirrors heat sunk to the system, maintaining temperature high enough to avoid dew formation on the mirrors. Detector temperature control was insured by efficient heat sinking to entire system. Finally, the CARE-Beijing NCP 2013 field campaign was conducted in Beijing, China under conditions where the mirror surfaces were coated with a thin layer of particles that significantly attenuated light intensity after only a few hours of driving. New metal mirrors with a robust surface have been subsequently installed which are easily and repeatedly cleaned under these adverse conditions.
3.4 Sensor performance

3.4.1 Precision

To investigate precision and stability of the open-path NH₃ sensor, Allan deviation analyses (Werle et al., 1993) are performed on NH₃ and ethylene reference signal time series. We compare the drift characteristics of the ambient and reference signals to determine the optimal integration time for normalization by the ethylene reference signal. For this analysis, we normalize both NH₃ and ethylene retrievals by the 1f DC value to account for changes in light intensity on the detector. The NH₃ mole fraction and air temperature are variable in the laboratory during the recorded time series, whereas the ethylene mixing ratio in the reference cell is essentially constant.

Figure 3.11: Allan deviation plot of 14.6 ppbv NH₃ and the associated time series data recorded at 10 Hz over the course of 5.5 h.
Figure 3.11 shows the Allan deviation plot for NH$_3$ measurements, with a mean mixing ratio of 14.6 ppbv NH$_3$ recorded in the laboratory at 10 Hz time resolution. The precision is $\sim$1 %, or 0.15 ppbv NH$_3$, at 10 Hz. The precision is similar at 1 Hz integration time. The minimum precision is $\sim$15 pptv NH$_3$ for an integration time of $\sim$200 s, beyond which drift dominates the Allan deviation. The 10 Hz precision is maintained out to timescales greater than 1 h. We note that while the 2f NH$_3$ signal is fit in real time at 10 Hz, the data acquisition is synchronized by the 1 Hz GPS pulse-per-second signal and the current line-locking scheme also at 1 Hz, which results in a transition from 100 % to an effective 10 % duty cycle from 0.1 s to 1 s integration time. We also note that the corresponding offset is consistent with a $\sqrt{10}$ decrease in Allan deviation resulting from a 10 % duty cycle (Werle et al., 1993) at 1 Hz and longer timescales.

The Allan deviation plot for the ethylene reference signal recorded at 1 Hz time resolution is shown in Figure 3.12. Ethylene signals are co-averaged to 1 Hz time resolution to improve the signal-to-noise ratio at the higher (8f) harmonics. The precision of the ethylene signal is $\sim$1 % at 1 Hz, comparable to that for NH$_3$. The precision improves as integration time increases, but interference fringing at the higher harmonics (8f) and laser thermal drift limit this improvement for integration times $>$ 100 s. The minimum of the NH$_3$ Allan deviation in Fig. 6 occurs at an integration time of $\sim$200 s. Thus, a 200 s integration time is optimal for normalization by the ethylene reference signal to account for drift in the NH$_3$ signal. Note that the data in Figures 3.11 and 3.12 show drift of $\sim$1 % or less at 3000 s integration time, which is much lower than the overall accuracy ($\pm$10 %). In this case, the in-line ethylene reference signal is of marginal value under relatively constant laboratory conditions. However, the in-line ethylene signal is an important method to account for much larger system drifts expected under rapidly changing field conditions and over longer timescales (days).
3.4.2 Minimum detection limit

The minimum detection limit of the NH$_3$ sensor was determined by the measuring $2\sigma$ of the background zero ammonia signal time series. The short-term noise is expected to be the limiting factor for the minimum detection limit, as the Allan deviation plot shown in Figure 3.11 indicates precision better than the 10 Hz precision on long timescales.

We analyze the spectral fitting at 1 ppbv NH$_3$ mole fraction with baseline subtraction to estimate the spectral noise levels. Figure 3.13a shows a 1.0 ppbv NH$_3$ signal with spectral fitting and residuals. Figure 3.13b illustrates the base functions for the full spectral fit in Figure 3.13a, with contributions from NH$_3$, ethylene and the polynomial baseline. Based on the height of the baseline-subtracted 2f NH$_3$ signal and the residuals of the fit to this baseline-
Figure 3.13: (a) Second harmonic spectrum of 1.0 ppbv NH$_3$ signal at ambient pressure recorded at 1 Hz along with spectral fitting results and residuals; (b) Base functions used in spectral fitting in (a) as follows: 2f NH$_3$ lineshape (top), 2f ethylene lineshape (middle) and polynomial baseline (bottom).

subtracted signal, the SNR for this spectrum is $\sim 7.6$, corresponding to a spectral noise level ($2\sigma$) of 0.26 ppbv NH$_3$ at 1 Hz. The interference due to O$_3$ and CO$_2$ absorption lines is $\sim 20\%$ of the 1 ppbv NH$_3$ signal (see Sect. 2.2), which is smaller than the baseline spectral noise ($\sim 26\%$). We note that this estimate is derived from only one spectrum and may not be representative of the temporal variability of the background noise, which is expected to be dominated by optical interference fringing and electronic noise.

Background concentrations are difficult to determine for NH$_3$ in an open-path configuration, in large part due to the need to enclose the sensor, leading to adsorption and desorption effects with typical laboratory mole fractions greater than 10 ppbv NH$_3$. To achieve a zero NH$_3$ background signal and examine the time series characteristics of the noise and spectral
fitting, we conducted additional experiments inside a pressure-regulated chamber. The calibration tube and the entire sensor head were placed inside a larger chamber with its inside walls coated with the citric acid solution. The larger chamber was pumped to a reduced pressure of 100 hPa. Even though the sensor was at 100 hPa, we maintained the same modulation amplitude as at ambient pressures. The absorption features of NH$_3$ and other relevant species are therefore overmodulated (effective modulation index $>5$ for NH$_3$ at 100 hPa), effectively broadening and decreasing the 2f signal height by 67% compared to ambient pressures. The overmodulated 2f NH$_3$ signal is used to calculate the background noise, since it minimizes the influences of residual NH$_3$ on the 2f signal. We also verified that there was negligible residual NH$_3$ in the chamber by switching to lower modulation amplitude appropriate for 100 hPa. Figure 3.14 shows the 2f spectrum recorded at 100 hPa under these conditions, which is effec-

![Second harmonic spectrum at reduced pressure (100 hPa) with zero NH$_3$ signal recorded at 10 Hz time resolution.](image)
tively representative of etalon and electrical noise. It is assumed here that etalons, determined by the free spectral range of various transmissive optics, are not affected by pressure changes since the whole sensing system is enclosed inside the chamber. We fit the background signals to the ambient pressure lineshape function to examine how the spectral fit to the background (which should nominally be zero) changes over time. The noise-equivalent limit, defined as $1\sigma$ of the background signal time series, is 0.15 ppbv NH$_3$ at 10 Hz and the minimum detection limit ($2\sigma$) is 0.30 ppbv NH$_3$ at 10 Hz. This detection limit is also consistent with the measurement precision shown in Sect. 3.2 and the spectral noise analysis described above.

We note that other potential methods to achieve background measurements have limitations for our system. One approach is tuning the laser to a different wavelength region. However, the QC laser used here has a limited tuning range and this method will produce a different baseline due to changes in laser optical power, detector response and interference fringing. In addition, there are other absorbing species (e.g., H$_2$O, CO$_2$, O$_3$, SO$_2$) that will contribute to the spectroscopic baseline on either side of the NH$_3$ spectral feature of interest.

### 3.4.3 Time response

We demonstrate the dynamic response of the open-path configuration. Figure 3.15 shows the time series of NH$_3$ mixing ratios measured in the field on a mobile vehicular platform at a dairy farm over the course of $\sim$3 min at 5 Hz time resolution. During this time series, an order-of-magnitude decrease in mixing ratio from $\sim$2.0 ppmv NH$_3$ to 200 ppbv NH$_3$ is observed within 1 s. The inset plot of Figure 3.15 shows a 5 s portion of this time series on a logarithmic $y$ scale to emphasize the two-order-of-magnitude change in mixing ratio. During this time period, the sensor records an increase from $\sim$200 to $\sim$900 ppbv NH$_3$ in 1 s followed by a decrease in mixing ratio ($\sim$900 to $\sim$200 ppbv NH$_3$) in 0.8 s. The mixing ratio decreases by two orders of magnitude to background levels ($\sim$10 ppbv NH$_3$) within 2 s following the ppmv maximum as the sensor left the farm and was no longer sampling the emission plume. This demonstrates
the fast response time of the open-path sensor for two-order-of-magnitude change in mixing ratio in a very short (2s) time period.

Figure 3.15: Mobile, open-path NH$_3$ measurements of in situ dairy farm sources recorded at 5 Hz. The inset plot shows a 5 s portion of this 5 Hz time series on a logarithmic y scale to emphasize the two-order-of-magnitude change in NH$_3$ mixing ratios.

We also demonstrate the time response for smaller mixing ratio enhancements. Figure 3.16 shows a time series of mobile measurements on the highway recorded at 2 Hz time resolution. There are two enhancements observed due to vehicle traffic emissions on the highway. For the first spike at 15:45:40 local time, the sensor recorded an increase of 10 ppbv NH$_3$ (13.0 to 23.0 ppbv) in 1 s. For the second maximum at 15:49:30 local time, the decrease in mixing ratio from 16.0 to 10.0 ppbv following the transient spike is also recorded in 1 s. These measurements demonstrate similar fast response for a lower range of mixing ratios.
Figure 3.16: On-road, mobile, open-path NH$_3$ measurements of highway vehicle emissions recorded at 2 Hz. The response time at ppbv NH$_3$ mixing ratios is demonstrated for the emission spikes at 15:45:40 and 15:49:30 local time.

Ammonia surface adsorption and desorption effects in closed-path sensors typically limit the response time (for several hundred ppbv NH$_3$ changes) to a few seconds, resulting in attenuation of high-frequency concentration fluctuations (Yokelson et al., 2003; Nowak et al., 2007; McManus et al., 2008; Whitehead et al., 2008; Ellis et al., 2010; Gong et al., 2011). The time response of closed-path sensors is often defined by the initial time constant for gas exchange and the slower surface adsorption time constant (e.g., $\sim0.4$ s and $\sim15$ s, respectively, for a QC-TDLAS instrument) (Ellis et al., 2010). For long-term stationary monitoring applications, this time response is sufficient since data are averaged to minutes or longer timescales. However, for mobile platform measurements of transient emissions with
order-of-magnitude changes in mixing ratios, as well as eddy covariance flux measurements, a
time response of at least 1 Hz, as demonstrated for this open-path sensor, is critical.

### 3.4.4 Field measurements

We performed high time resolution (5 Hz) open-path NH$_3$, mobile measurements on the road
and at a local animal farm (pigs, turkeys) in central New Jersey to measure vehicular and
agricultural emissions. All field NH$_3$ measurements are corrected for water vapor dilution and
expressed as mixing ratios in dry air. Simultaneous measurements of a vehicle emission tracer
carbon monoxide (CO) by a separate QC-laser-based sensor (Tao et al., 2012b) were used to
identify these emission sources. Figure 3.17a shows the time series of NH$_3$ measurements at
the animal farm. High mixing ratios above 1 ppmv NH$_3$ are observed and do not correlate
with CO, which remained at near background mixing ratio at the animal farm. Figure 3.17b
illustrates on-road vehicle NH$_3$ emission measurements, with maximum mixing ratios of $\sim$ 60
- 120 ppbv NH$_3$, depending on vehicle type and driving conditions. The enhancements in
NH$_3$ mixing ratio (Figure 3.17b) correlate with on-road CO measurements. These time series
demonstrate the open-path NH$_3$ sensor is capable of performing high time resolution field
measurements to capture various emission sources.

The field measurements of NH$_3$ and the non-adsorbing gas CO shown in Figure 3.17b
illustrate that there is no delay between the spikes of these two species, which occur on
timescales of seconds, due to vehicle exhaust emissions. Other field measurements performed
in tunnels (not shown here) indicate that open-path measurements of non-adsorbing gases,
such as CO$_2$, can serve as an indicator of true mixing ratio decay at the tunnel exit. Our open-
path NH$_3$ measurements show no delay compared with CO$_2$ in this case. This further supports
our conclusion that the surface adsorption time constant for our open-path NH$_3$ measurement
is significantly reduced at these measurement timescales compared with previous closed-path
sensors.
Figure 3.17: (a) Time series of NH$_3$ measurements at an animal farm in central New Jersey; (b) on-road measurements in the Princeton, New Jersey area, with transient spikes correlated with CO emissions from vehicles.

3.5 Discussion

The NH$_3$ sensor noise-equivalent limit corresponds to a fractional absorption of $\sim 3 \times 10^{-5}$, comparable (within a factor of 3) with typical, field-deployable laser-based systems (Tittel et al., 2003). The detection limit and precision are limited by electrical noise and optical interference fringing, a dominant noise source in many laser absorption spectroscopy systems (Dharamsi et al., 1998; Werle, 2011). The dominant electrical noise sources are the power supplies used for the detector preamplifier and laser current driver. The dominant interference fringes in our system are due to the back reflections from transmissive optics (laser collimating lens and zinc selenide windows for laser, detector and reference cell packages) and QC laser beam quality for the multi-pass optical cell. Our current efforts focus on improving beam quality of the QC laser high heat load packages and optimizing transmissive optics with custom anti-reflective coatings. We note that the ultimate detection sensitivity is also constrained by other uncertainties, including the ability to isolate spectral interferences from CO$_2$ and O$_3$ absorption features near 9.06 $\mu$m when approaching the 100 pptv range.

The 2f signal baseline also affects calibration and zero offset measurements. This baseline is due to a combination of detector nonlinearity, intensity modulation and optical fringing.
Further investigations on the long-term stability of this baseline under field conditions will be necessary to characterize the variability of the zero calibration and ultimately improve uncertainties at low mole fractions. This uncertainty is currently the most significant limitation for our open-path NH$_3$ sensor. Signal baseline variability due to temperature changes is of particular concern for open-path systems, where the temperature cannot be controlled due to direct exposure of optical components and power limitations on field platforms.

The laser tuning capabilities also limit the desired sensitivity for open-path detection of the broad NH$_3$ absorption feature. The optimal modulation index for 2f detection ($m = 2.2$ as shown by Reid and Labrie, 1981) cannot be reached with the current QC laser used in our system due to limited current tuning range, which decreases with increasing modulation frequency (Tao et al., 2012a). We can only achieve a modulation index of $\sim 1.4$ for NH$_3$ measurements. To address this issue, the integration of new QC lasers with twice the current tuning range is an ongoing effort.

Despite these limitations, we demonstrate a sensor platform capable of high-sensitivity, high time resolution atmospheric NH$_3$ field measurements. Future autonomous field operation of this sensor for long-term stationary measurements will require further weather-proofing of the prototype sensor for protection from precipitation, dust and insects. These measures are particularly important for the optical cell mirrors, which must be directly exposed to environmental conditions.

### 3.6 Conclusions

We present the instrument performance of a compact, low-power, field-deployable, open-path NH$_3$ sensor. The system uses a QC laser at 9.06 $\mu$m, multi-pass Herriott cell, multi-harmonic wavelength modulation spectroscopy and an in-line ethylene reference cell. No cryogens are required due to the capabilities of TE-cooled, continuous-wave, distributed-feedback QC lasers and HgCdTe photodetectors. Our open-path NH$_3$ sensor has the requisite capabilities for ground-based atmospheric measurements, with a precision and noise-equivalent limit of
0.15 ppbv NH$_3$ at 10 Hz and total accuracy of 0.20 ppbv NH$_3$ ± 10%. The sensor is capable of measuring a large dynamic range of NH$_3$ mixing ratios due to in situ emission sources. The fast (10 Hz) time resolution of the open-path system can be used to capture transient NH$_3$ sources with a short surface adsorption time constant. This is demonstrated by comparing the open-path NH$_3$ sensor response with the simultaneous time response of collocated sensors measuring nonadsorbing species.

It is important to note that surface sampling artifacts in closed-path sensors are typically reduced by minimizing inlet length, optimizing inlet coatings, inlet heating and maintaining high flow rates through small sampling volumes or other special sampling systems (Whitehead et al., 2008; Bianchi et al., 2012). Some of these measures increase power demands and limit portability for a variety of field platforms. In contrast, our open-path approach is advantageous in that it has minimal sampling artifacts and does not require pumps or heaters, allowing for a lower-power, portable design.

### 3.6.1 Applications

The compact, low-power design provides unique capabilities for stationary sensing and mobile platform spatial mapping of NH$_3$ mixing ratios. In addition, the open-path sensor precision, stability and time resolution (10 Hz) make it suitable for future eddy covariance NH$_3$ flux measurements. Future investigations will focus on long-term inter-comparisons with existing commercial, atmospheric NH$_3$ sensors and demonstration of open-path eddy covariance NH$_3$ flux measurements. Future measurement applications for this open-path sensor include NH$_3$ emission measurements in agricultural and urban regions to validate emission inventories.

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Chapter 4

Ammonia and methane dairy emissions in the Central Valley, California with open-path, mobile measurements

4.1 Introduction

Atmospheric ammonia (NH$_3$) is a gas-phase precursor to fine particulate matter (PM$_{2.5}$), with implications for air quality and climate change (IPCC, 2013; Aneja et al., 2008). Ammonia contributes to new particle formation (Benson et al., 2011) and secondary inorganic aerosol growth with implications for long-range transport of condensed-phase nitrogen species (Pinder et al., 2008; Nowak et al., 2010). Ammonium (NH$_4^+$) is a dominant PM$_{2.5}$ mass and molar constituent in urban and agricultural regions (Anderson et al., 2003; Jimenez et al., 2009) with implications for human health (Pope et al., 2002). Global NH$_3$ emissions have more than doubled since pre-industrial times, largely due to agricultural activity intensification (Galloway et al., 2003). Livestock operations are responsible for \(\sim\)55% of U.S. anthropogenic
NH$_3$ emissions (Aneja et al., 2008; Clarisse et al., 2009). Reduced nitrogen in the form of total ammonia (NH$_x$ = NH$_3$ + NH$_4^+$) is becoming the dominant form of reactive nitrogen deposition to ecosystems in the United States (Ellis et al., 2013). These trends contribute to critical load exceedances of nitrogen deposition to ecosystems downwind of intense agricultural NH$_3$ sources, including regions of California (Sierra Nevada) and Colorado (Rocky Mountains) (Fenn et al. 2010; Pardo et al., 2011; Day et al., 2012).

Agricultural NH$_3$ emissions contribute to PM$_{2.5}$ loading in the Central (San Joaquin) Valley of California and regions downwind. The U.S. EPA National Ambient Air Quality standards (NAAQS) are frequently violated in the Central Valley, with PM$_{2.5}$ exceedances occurring especially during cool, stagnant conditions in winter (Watson and Chow, 2002; SJVAQPCD, 2012; Kelly et al., 2013). Ammonium nitrate (NH$_4$NO$_3$) constitutes a significant component (often >50%) of PM$_{2.5}$ mass composition in the Central Valley (Watson and Chow, 2002; Lurmann et al., 2006). Secondary NH$_4$NO$_3$ formation has been observed at high altitudes and in the Central Valley boundary layer due to excess NH$_3$ that neutralizes both sulfate and nitrate (Neumann et al., 2003). Nowak et al. (2012) observed that conditions downwind of livestock (dairy) facilities in California favored NH$_4$NO$_3$ formation due to spatially concentrated NH$_3$ sources in the South Coast Air Basin (SoCAB). However, recent aerosol modeling efforts under-predicted observed surface nitrate (NO$_3^-$) and NH$_4^+$ concentrations in the Central Valley (Walker et al., 2012; Heald et al., 2012). Walker et al. (2012) found a 79% low bias in simulated NH$_3$ compared with satellite observations over the Central Valley. These discrepancies were attributed to NH$_3$ and nitric acid (HNO$_3$) source under-estimations. Recently, regional air quality model simulations greatly under-predicted NH$_3$ concentrations compared with low altitude aircraft observations over the Central Valley Tulare dairy farm region (Kelly et al., 2013). Ammonia emission under-estimations, especially in agricultural valleys, are considered to be a significant contributor to multiple model-measurement discrepancies (Reis et al., 2009; Clarisse et al., 2009; Shephard et al., 2011; Heald et al., 2012).
Uncertain NH$_3$ emissions must be constrained to improve inorganic aerosol model simulations (Gilliland et al., 2006; Walker et al., 2012).

The Central Valley of California is known for a high density of confined dairy facilities with approximately 1.8 million lactating dairy cows on $\sim$ 1700 dairy farms as of 2012. Cow density per dairy feedlot has also increased during the last few decades (CDFA, 2013). Tulare County is the most productive dairy region in the United States, with $\sim$500,000 dairy cows at open-lot or open-freestall facilities (CDFA, 2013). These dairy farms contribute significant NH$_3$ emissions from NH$_4^+$ volatilization due to urea hydrolysis in urine excreted onto dairy farm surfaces and manure management (lagoons, solid manure storage and land application) (Hristov et al., 2011). According to recent satellite observations, the Central Valley has the largest ammonia column abundance in world, with the highest boundary layer concentrations around Tulare County (Clarisse et al., 2010). Other important trace gases emitted from dairy farm sources include methane (CH$_4$), nitrous oxide (N$_2$O) and volatile organic compounds (VOCs) (Shaw et al., 2007). Methane, a potent greenhouse gas, is a known tracer of dairy emissions from cows (enteric fermentation) and manure management (Owen et al., 2014).

Dairy NH$_3$ emission estimates are highly variable and uncertain. Nowak et al. (2012) recently used a top-down aircraft measurement approach to constrain SoCAB dairy emissions and found that the California Air Resources Board (CARB) emission inventory underestimated NH$_3$ emissions by 3-20 times. Ammonia emission factors are highly variable in space and time, depending on a variety of environmental factors (temperature, wind, humidity) and agricultural practices such as manure management, dairy housing and feeding methods (Beusen et al., 2008; Hristov et al., 2011). Gas-phase NH$_3$ has a short and highly variable atmospheric lifetime of $\sim$12 hours (Xu and Penner, 2012), dependent on factors including aerosol composition, temperature and relative humidity. Dry deposition of gas-phase NH$_3$ is another important sink, depending on meteorological conditions and surface properties influencing deposition velocities. In-situ observations suggest that agricultural NH$_3$ emissions and deposition fluxes are highly variable within model grid cells of 5 km horizontal resolution.
(Dragosits et al., 2002; Day et al., 2012). Dairy feedlot areas contain spatially heterogeneous sources of NH$_3$ and CH$_4$, including open-lot corrals or free-stalls, anaerobic lagoons and solid manure storage (Hristov et al., 2011). Processed-based modeling efforts simulating emission variability have large uncertainties (~40%) due to assumptions on farming practices and no constraints from in-situ measurements (Pinder et al. 2004; Li et al., 2012). Widespread in-situ NH$_3$ measurements are scarce with no routine NH$_3$ monitoring networks in the Central Valley (Clarisse et al., 2010). Field observations applicable to the Central Valley are extremely limited, with only one study on an individual open-lot dairy farm in Tulare County during winter (Cassel et al., 2005).

Individual dairy farm measurements in other regions have been used to estimate NH$_3$ dairy emissions using a variety of in-situ measurement techniques (Hristov et al., 2011). Static and dynamic flux chamber techniques have been implemented to quantify emissions at discrete locations (Mukhtar et al., 2008; Parker et al., 2013; Leytem et al., 2013) but have insufficient spatial coverage for sampling spatially heterogeneous dairy source regions. In addition, NH$_3$ adsorbs to chamber surfaces, introducing potential chamber sampling artifacts. Passive filters measure NH$_3$ at long integration times but are also subject to partitioning artifacts. Micro-meteorological methods using point and integrated sensors, including flux gradient (Cassel et al., 2005), relaxed eddy accumulation (Baum and Ham, 2009) and eddy covariance flux methods (Brodeur et al., 2009) can provide farm-scale flux measurements. Relatively few eddy covariance NH$_3$ flux measurements have been attempted, as closed-path instruments have surface adsorption and partitioning artifacts that limit instrument response times (Whitehead et al., 2008; Sintermann et al., 2011). In addition, these techniques derive average fluxes for a farm-scale spatial footprint, but cannot spatially resolve emission heterogeneities within a feedlot, nor are they capable of sampling many farms in an agricultural region. Open path-integrated NH$_3$ measurements have been performed with diode laser-based absorption spectroscopy (Flesch et al., 2007), differential optical absorption spectroscopy (Mount et al., 2002) and open-path Fourier transform infrared spectrometry (Griffith and Galle, 2000; Bjorneberg
et al., 2009). These techniques are commonly coupled with inverse dispersion models (Flesch et al., 2007; Leytem et al., 2013) to estimate individual feedlot emissions, but require wind condition and emission uniformity assumptions (Flesch et al., 2007). Existing techniques have measured the temporal variability of emissions from daily to seasonal timescales for multiple feedlot sections of individual farms. Emission factors (EFs) derived from these stationary measurements are not necessarily representative of regionally and temporally variable agricultural emissions (Cassel et al., 2005; Hristov et al., 2011).

Regional-scale agricultural emission estimates have been conducted using top-down approaches for species including CH$_4$ (Peischl et al., 2012). Nowak et al. (2012) used a top-down mass-balance approach with aircraft measurements on two days in the SoCAB to quantify regional NH$_3$ dairy emissions. The typical aircraft measurement spatial resolution ($\sim$100 m) provides an integrated view of regional plumes (Nowak et al., 2012). Top-down approaches are subject to uncertainties and constraints due to wind and boundary-layer condition requirements to derive fluxes, resulting in snapshot regional emission estimates (Cambaliza et al., 2013). In addition, the origin of variable emission estimates across multiple flights and spatial variability within the mass-balance region are not well understood.

Few measurements with adequate spatial resolution and coverage have been conducted to quantify spatial emission distributions (Aneja et al. 2008). Satellite NH$_3$ retrievals have derived spatial distributions and identified hotspots in the Tulare County region of the Central Valley, but the retrievals (> 5 km spatial resolution) cannot resolve field-scale heterogeneities, nor continuously monitor emission distributions (Clarisse et al., 2009; Clarisse et al., 2010). The boundary layer sensitivity of satellite NH$_3$ retrievals depends on thermal contrast, which is especially problematic for winter day-time conditions in the Central Valley (Clarisse et al., 2010).

Mobile vehicular platforms equipped with fast-response sensors have been deployed previously to quantify spatial emission distributions from urban and industrial sources (Kolb et al., 2004; Wang et al., 2011; Brantley et al., 2013). Mobile measurements of multiple species
are applicable for quantifying emission ratios, source identification and source apportionment in mixed source regions (Petron et al., 2012; Farrell et al., 2013). However, few agricultural mobile measurements have been performed. Hensen et al. (2006) reported mobile CH$_4$ plume measurements downwind of 20 farms, demonstrating the value of mobile measurements to sample localized agricultural plumes with fast-response sensors. However, spatially extensive high resolution mobile agricultural NH$_3$ measurements have not been reported in the literature. Existing studies are limited to mobile “trolley” NH$_3$ measurements at relatively low (30 s) time resolution over a few hundred meters of one farm (Hensen et al., 2009) and a two-day mobile survey with a closed-path commercial NH$_3$ analyzer (Day et al., 2012). Although this limited spatial survey qualitatively illustrated substantial NH$_3$ spatial variability in a feed-lot region, multiple gases were not measured and emission ratios or absolute emissions were not quantified. Closed-path NH$_3$ sampling also introduces adsorption and partitioning artifacts that limit time response, especially for high NH$_3$ mixing ratios near agricultural sources. Although high time response, open-path sensors have been developed, they have so far only been deployed in path-integrated configurations for stationary agricultural NH$_3$ measurements (Flesch et al., 2007), leading to a lack of spatial emission measurements in intense agricultural regions. There is an urgent need for high time resolution, fast-response NH$_3$ mobile measurements to constrain dairy emissions and evaluate top-down approaches for regional NH$_3$ emission estimates.

To characterize NH$_3$ dairy emissions, we measure the spatial distributions of NH$_3$ and CH$_4$ in an intensive dairy farm region of the Central Valley, California. These measurements are used to quantify NH$_3$ emission ratios (ERs) with respect to CH$_4$, a longer-lived dairy emission tracer. Field-scale ERs are compared with regional aircraft observations in this intense agricultural source region. High resolution, open-path NH$_3$ measurements are performed in the Tulare County dairy region during the NASA DISCOVER-AQ field campaign in winter 2013. The open-path, fast time-response NH$_3$ sensor demonstrated by Miller et al. (2014) is integrated into a novel, multi-gas, mobile platform on a passenger vehicle for simultaneous
open-path measurements of NH$_3$, CH$_4$, N$_2$O, CO and H$_2$O, meteorological data, and GPS location. We find high spatial variability of NH$_3$ and CH$_4$ mixing ratios, with maxima localized downwind of individual dairy farms and mean background NH$_3$ and CH$_4$ mixing ratios enhanced in the Tulare dairy region. The median NH$_3$:CH$_4$ ER is $0.15 \pm 0.03$ ppmv ppmv$^{-1}$, with a heavy-tailed distribution of extreme maxima, encompassing environmental and spatial activity emissions variation for both species. For 93 downwind farm plumes sampled, 62% had statistically significant linear correlation between NH$_3$ and CH$_4$. A case study analysis illustrated ER spatial heterogeneities for multiple farm sections. The mobile measurement median NH$_3$:CH$_4$ ER was comparable to aircraft integrated ERs derived from NASA P3-B aircraft regional transects, but less extreme values (25% lower 95 percentiles) were observed for the aircraft integrated ERs. The in-situ mobile ERs are put in the context of relevant literature studies for dairy sources in this region. The surface mobile measurements provide the first evaluation of NH$_3$ ER statistical distributions across multiple dairy farms to expand on previous individual farm studies. The results have implications for NH$_3$ emission inventory validations and for future top-down estimates of regional agricultural NH$_3$ emissions.

4.2 Methodology

4.2.1 Mobile platform

Mobile measurements of NH$_3$, CH$_4$, CO$_2$, N$_2$O, CO and H$_2$O were performed with four open-path sensors mounted on a Chevy Impala, a typical sedan passenger car. A brief overview of the system, (depicted in Figure 4.1) is described here with further details in Tao et al. (2014). The mobile platform was designed with two 91 cm x 30 cm breadboards mounted on the base of a car rack, secured on top of the passenger vehicle. The mobile platform sensor specifications are shown in Table 4.1. The sensors have been described elsewhere (McDermitt et al., 2011; Tao et al., 2012b; Miller et al., 2014) and only brief descriptions are included here. Ammonia, nitrous oxide (N$_2$O) and carbon monoxide (CO) were measured with two open-path, quan-
tum cascade laser-based sensors employing wavelength modulation absorption spectroscopy at 9.06 µm and 4.54 µm respectively (Tao et al., 2012b; Miller et al., 2014). Commercial, open-path analyzers for CH₄ (LICOR LI-7700 analyzer) and CO₂ (LICOR LI-7500 CO₂/H₂O analyzer) were also equipped on the mobile platform. Meteorological parameters (temperature, pressure, relative humidity) were measured with a portable weather station (Vaisala WXT520). Geolocation, vehicle speed, and driving direction were recorded with a GPS unit (GlobalSat EM-406a). Road conditions were recorded by two GoPro Hero3 cameras mounted on the platform. The entire sensor platform operated on two 12 V car batteries, with a total run time on full charge of ~12 hours. The open-path sensor mirrors were shielded from large dust particles, insects and light precipitation. Real-time, online calibration was insured by an in-line ethylene reference cell signal in the NH₃ system to within ±20% accuracy (Sun et al., 2013) and an in-line acetylene reference cell signal in the N₂O/CO system (Tao et al., 2012). The in-line reference cell absorption signal was continuously probed to account for sensor drift. Off-line NH₃ calibration was also performed between field measurements, based on the methods described in Miller et al. (2014). Methane and CO₂ measurements were calibrated with a NOAA WMD calibration standard.

Table 4.1: Summary of the open-path mobile platform sensor specifications, metrics and references containing further details.

<table>
<thead>
<tr>
<th>Species</th>
<th>Precision</th>
<th>Mass</th>
<th>Power</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>0.15 ppbv</td>
<td>15 kg</td>
<td>50 W</td>
<td>Miller et al. (2014)</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.07 ppbv</td>
<td>10 kg</td>
<td>40 W</td>
<td>Tao et al. (2012b)</td>
</tr>
<tr>
<td>CO</td>
<td>0.2 ppbv</td>
<td>-</td>
<td>-</td>
<td>Tao et al. (2012b)</td>
</tr>
<tr>
<td>CH₄</td>
<td>2 ppbv</td>
<td>4 kg</td>
<td>15 W</td>
<td>McDermitt et al. (2011)</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.1 ppmv</td>
<td>2 kg</td>
<td>5 W</td>
<td>LICOR</td>
</tr>
<tr>
<td>H₂O</td>
<td>&lt; 1%</td>
<td>-</td>
<td>-</td>
<td>LICOR</td>
</tr>
<tr>
<td>T,P,RH</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Vaisala</td>
</tr>
</tbody>
</table>

Open-path NH₃ sensing is inherently advantageous for mobile platforms. The high time resolution (>1 Hz) and fast response time (≥ 1 Hz) of the open-path sensor is especially advantageous for capturing transient concentration changes. For typical driving speeds of
40-110 km h\(^{-1}\) during these mobile measurements, the spatial resolution of the 1 s mobile measurements is \(\sim 10-30\) m. Miller et al. (2014) demonstrated fast time-response, open-path NH\(_3\) measurements at a dairy farm for two-order-of-magnitude changes in mixing ratios and comparable to the simultaneous response for on-road vehicle emission measurements of non-adsorbing tracers (CO\(_2\) and CO). The open-path configuration eliminates the need for powerful pumps, allowing multiple sensors to be run simultaneously. The collocation of open-path sensors for multiple gases within the same spatial footprint on the car-top allows for emission source identification and makes it straightforward to calculate NH\(_3\) emission ratios with respect to non-adsorbing tracers such as CH\(_4\).
Table 4.2: On-road measurement conditions for Central Valley measurements used in this study.

<table>
<thead>
<tr>
<th>Days in 2013</th>
<th>Start time (PST)</th>
<th>End time (PST)</th>
<th>Driving distance (km)</th>
<th>Air temperature (°C)</th>
<th>Wind direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>January 28</td>
<td>13:23</td>
<td>16:10</td>
<td>129</td>
<td>11-13</td>
<td>WSW</td>
</tr>
<tr>
<td>January 29</td>
<td>10:45</td>
<td>19:21</td>
<td>306</td>
<td>9-16</td>
<td>W</td>
</tr>
<tr>
<td>January 30</td>
<td>10:59</td>
<td>17:10</td>
<td>164</td>
<td>12-18</td>
<td>WSW</td>
</tr>
<tr>
<td>January 31</td>
<td>11:21</td>
<td>17:18</td>
<td>185</td>
<td>14.5-19.5</td>
<td>NW</td>
</tr>
<tr>
<td>February 1</td>
<td>8:58</td>
<td>16:46</td>
<td>269</td>
<td>10.5-19</td>
<td>NW</td>
</tr>
</tbody>
</table>

4.2.2 Data sets

Mobile measurements

We focus on a subset of mobile measurements performed during NASA DISCOVER-AQ 2013 on five days (January 28 to February 1, 2013) in the vicinity of ~500 dairy farms located in Tulare and Kings Counties, California. The mobile measurement routes for the entire field campaign are shown in Figure 4.2. Daily measurement durations and conditions are listed in Table 4.2. Number density retrievals of NH$_3$, CO$_2$, CO and CH$_4$ used in the analysis were corrected for water vapor dilution (using H$_2$O, temperature and pressure measurements) to obtain dry mixing ratios of all species. The raw (5 Hz) mixing ratio measurements were averaged to 1 s data synchronized to the GPS time stamp. The 1 s time series of NH$_3$ and the associated tracer mixing ratios were synchronized with each other to within 1 s using the cross-correlation method (Choi et al., 2012). Thresholds were applied to eliminate data with insufficient light intensity signals due to rain, dust or insects in the optical path or deposited on the optical cell mirrors. Carbon monoxide enhancements above background exceeding 500 ppbv were used as the criteria to remove measurements contaminated by combustion-related NH$_3$ or CH$_4$ sources, including from our own or nearby vehicles.
Figure 4.2: Mobile measurement routes over 12 days during the NASA DISCOVER-AQ 2013 field campaign in January-February 2013. The colors represent the routes covered on each day, with total spatial coverage of $\sim$4300 km. The inset shows measurement routes in the Tulare County region. The white points denote locations of dairy farms (California Department of Water Resources Land use data set).
NASA DISCOVER-AQ 2013 measurements

The NASA Deriving Information on Surface conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ) field campaign took place in the Central Valley, California during winter 2013 (DISCOVER-AQ website). Ground-based and airborne measurements, including transects and vertical profiles (spirals and missed approaches), were conducted in the Central Valley dairy region during this campaign. We use the NASA P-3B aircraft measurements on concurrent days with mobile measurement data coverage (January 30, 31 and February 1, 2013). The following merged P3-B airborne data sets were used for the analyses in section 4.3.4. Gas-phase NH$_3$ was measured with a Picarro cavity ringdown spectrometer (Nowak, NOAA) with mixing ratios reported every 3 seconds, a time response of 8-20 s and total uncertainty of ± (35% + 1.0 ppbv) NH$_3$. Methane mixing ratios were measured at 1 s resolution with a DACOM instrument to within 2 ppbv accuracy (Diskin, NASA). Condensed phase NH$_4^+$ measurements recorded by a PILS-IC (Anderson, NASA) with 240 s response time within 20% accuracy were used to calculate NH$_x$.

Wind simulations

The prevailing wind direction is necessary for isolation of downwind measurements. Although the Vaisala weather station measures wind speed and direction, it is biased due to turbulent conditions at the surface. Therefore, for prevailing wind, we use Weather Research and Forecasting (WRF) model simulations of 4 km, hourly resolution wind vectors at 10 m above ground level (Z. Liu, personal communication), from which hourly mean prevailing wind speed and direction were calculated. Ground-level wind observations (Trevino, San Joaquin Valley Unified Air Pollution Control District) at the Porterville, Visalia and Corcoran, California ground sites were also used to validate the WRF simulated wind speed and direction.
4.2.3 Emission ratio calculation

The emission ratios (ERs) were estimated using NH$_3$, CH$_4$ and CO$_2$ mixing ratios above local background for measurements performed directly downwind of individual dairy farms. To account for regional background variability, the time series were separated into a slowly varying background and rapidly changing emission peaks. The background trends were obtained using the 1 percentile over a 400 s moving time window over the 1 s time series, similar to a method used previously (Bukowiecki et al., 2002). The time window was chosen to be larger than the time scale for typical cross-wind plume sampling (~100 s) obtained by the cross-correlation method (Choi et al., 2012), while not too large such that the background would be smoothed and under-estimated. The sensitivity of time window choice is explained in section 4.3.2 below. The low (<5) percentiles are insensitive (within 2%) to large spikes, as shown previously (Hudda et al., 2013). Figure 4.3 illustrates the background trend estimates for a representative time series of CH$_4$ mixing ratio measurements. The enhancement mixing ratios above background were calculated as $\Delta$NH$_3$ = NH$_3$ (measured) - NH$_3$ (background trend) and similarly for $\Delta$CH$_4$ and $\Delta$CO$_2$. The $\Delta$NH$_3$/$\Delta$CH$_4$ and $\Delta$CH$_4$/$\Delta$CO$_2$ emission ratios were calculated and are abbreviated here as NH$_3$:CH$_4$ and CH$_4$:CO$_2$ respectively. Empirical cutoffs of 4 ppbv $\Delta$NH$_3$ and 125 ppbv $\Delta$CH$_4$ were selected to exclude data close to the background levels that may result in negative or spuriously large ER values. The ER sensitivity to a factor of two change in the empirical cutoff choice is < 4%.

Downwind measurements were selected based on the wind vectors and horizontal sampling distance from the dairy farms. The WRF wind simulations were linearly interpolated to the dairy farm (centroid) locations. Dairy farm locations were obtained using the California Department of Water Resources land use dataset for Tulare County in 2007 (386 dairy farms) and Kings County in 2003 (199 dairy farms). The mobile platform sampled in the vicinity of 494 dairy farms in these two counties, shown as white points in Figure 4.2. Google Earth imagery from August 2012 was used to verify the locations manually. A few dairy locations were updated (added or removed) as appropriate. The distance between each mobile mea-
Figure 4.3: Representative time series of mobile CH₄ measurements, along with background trend fitting (1 percentile over 400 s moving time window) and data points (red) selected downwind of dairy farms.

measuremnt data point and the closest dairy farm edge was calculated. To minimize potential low biases for the emission ratios due to NH₃ losses (deposition and partitioning) at longer sampling distances, we imposed a distance limit for measurements defined as those sampled downwind. The range of spatial sampling was chosen as 600 - 1200 m downwind, calculated using 600 s transport time based on the wind speed simulations to account for variable transport times from the dairy farm sources. We note that the lifetime of gas-phase NH₃ is on the order of hours. The deposition and aerosol partitioning sinks vary with aerosol composition, temperature, relative humidity and other meteorological conditions. For the Central Valley winter conditions, we expect NH₃ condensed phase partitioning and gas-phase dry deposition to be the dominant gas-phase NH₃ sinks. Methane has a much longer lifetime (∼12 years)
Figure 4.4: (a) Map depicting downwind data point isolation. The mobile measurement route (blue), dairy farm polygons locations (yellow) and wind vectors at time of passing a given dairy farm are indicated; (b) The corresponding map, as in (a), for the entire sampling region over four days (January 29-February 1, 2013).

and can therefore be used as a longer-lived tracer for dairy emissions on the temporal and spatial scales of our measurements.

The method described above isolated measurements performed downwind of 93 dairy plumes with collocated NH$_3$ and CH$_4$ measurements on four days. Figure 4.4 shows the mobile measurement routes and isolated downwind data points, as well as the dairy farms polygons. The wind vectors in Figure 4.4a indicate the wind speed and direction during the hour when the mobile platform measured near a given farm.

4.3 Results

4.3.1 Spatial variability

We find high spatial variability of NH$_3$ and CH$_4$ mixing ratios in the Tulare dairy region. Figure 4.5 illustrates the NH$_3$ mixing ratio spatial variability, with maxima $>500$ ppbv NH$_3$. 
Figure 4.5: Mobile spatial measurements of NH$_3$ mixing ratios (5 s averages of 1 s data for optimal display) on Google Earth imagery of the Tulare County region for January 28 - February 1, 2013. The peak mixing ratios reach above the colorscale (> 200 ppbv NH$_3$) and are denoted by the peak heights on the map.

Figure 4.6 shows a closer view of on-road NH$_3$ mixing ratio measurements. Four plumes reaching maxima above ~500 ppbv NH$_3$ are observed directly downwind of four dairy farms, with no detectable plumes when sampling upwind of other nearby farms. In addition, the left-most plume measurements show spatial gradients in concentration for different regions on the farm. This spatial heterogeneity is investigated further with a case study in section 4.3.3.

The background trend time series obtained by the methods in section 4.2.3 were used to derive the temporal and spatial variability of background mixing ratios. Figure 4.7a shows the diurnal variability of background NH$_3$ and CH$_4$ in the Tulare dairy region. The diurnal variability of both gases is influenced by boundary layer mixing. The highest mixing ratios are observed for NH$_3$ and CH$_4$ in the morning (before 11:00 PST) when the boundary layer is not well-mixed and emissions accumulate near the surface. The lowest mixing ratios occur during afternoon (12:00 - 17:00 PST) with well-mixed turbulent boundary layer conditions.

A sampling period with relatively constant background mixing ratios, the well-mixed boundary layer period (12:00 - 17:00 PST), was selected for spatial background maps. Figure 4.7b shows spatial background maps of NH$_3$ and CH$_4$ with spatially averaging at 5 x 7
Figure 4.6: An example of on-road measurements (January 28, 2013) directly downwind of 4 dairy farms (white points) at 1 s time resolution. The left-most plume shows fine structure and spatial heterogeneity of NH\textsubscript{3} mixing ratios within one dairy farm plume.

km grid resolution and linear interpolation. This horizontal scale is selected to be comparable to satellite retrievals (NASA TES) and regional air quality model simulations (CMAQ). Both species are enhanced in the dairy region, but the spatial distributions are different. The maximum NH\textsubscript{3} background (∼35 ppbv) is more than a factor of 4 larger than regional background (<10 ppbv) in the Central Valley outside of the dairy region. Methane shows smaller relative enhancements (∼35%), with maximum background of ∼2.7 ppmv CH\textsubscript{4} in the dairy region and regional background < 2 ppmv CH\textsubscript{4}. These spatial maps illustrate the importance of dairy source contributions to enhanced NH\textsubscript{3} and CH\textsubscript{4} background mixing ratios in this high source region.

4.3.2 Emission ratio statistics

The NH\textsubscript{3}:CH\textsubscript{4} ERs are derived based on the methods described in section 4.2.3. Figure 4.8a shows the distribution of NH\textsubscript{3}:CH\textsubscript{4} ER values, obtained by dividing each data point sampling within 93 downwind plumes. The median ER is 0.15 ± 0.03 ppmv ppmv\textsuperscript{-1} and the geometric
Figure 4.7: (a) Box-whisker plots of the background mixing ratio diurnal cycles for \( \text{NH}_3 \) and \( \text{CH}_4 \) in the Tulare dairy region. The boxes represent 25, 50 and 75 percentiles and whiskers represent 5 and 95 percentiles. The blue points and lines represent the arithmetic means. The data are binned by equal number of data points and most sampling is performed during midday. Local time is Pacific Standard Time (PST). (b) Spatial maps of \( \text{NH}_3 \) and \( \text{CH}_4 \) background mixing ratios for measurements performed between 12:00 - 17:00 PST on January 29 - February 1, 2013. The data are spatially averaged on a 7 x 5 km grid and linearly interpolated. The black lines denote the locations of mobile measurements. The triangles denote the locations of Visalia, Porterville, Corcoran and Hanford, California (clockwise from upper right triangle) as reference locations.
mean is 0.16 ± 0.03 ppmv ppmv⁻¹. The histogram shows a highly asymmetric distribution (skewness = 5.46) with a heavy-tail for values above the median, indicative of a small number of high NH₃ emitters relative to CH₄. The arithmetic mean (0.29 ppmv ppmv⁻¹) is much higher and not appropriate for ratio averaging in this analysis. We analyze statistics across multiple dairy farms with linear least squares regression to assess the statistical significance of the linear correlation of the two species in each emission plume. We find 58 downwind plumes (62%) had statistically significant linear correlation (p<0.05) between ∆NH₃ and ∆CH₄. However, 38% of farm plumes sampled (35 plumes) had no linear correlation. The lack of correlation at certain farms is due to a variety of factors, including variable NH₃ and CH₄ sources resulting in different spatial emission signatures within a dairy farm area that are resolved when sampling at 10-30 m horizontal resolution at close proximity (<100 m downwind).

**Emission ratio uncertainties**

Emission ratio uncertainties and biases originate from multiple factors including concentration measurement uncertainties (±20% for NH₃ and ~1% for CH₄), choice of parameters for ER calculations, the degree of correlation, mixing of multiple emission plumes and NH₃ losses (addressed in the following section). Sensitivity analyses were performed to quantify potential biases due to background trend fitting parameters and the maximum distance chosen for sampling emissions. Other potential biases due to non-dairy farm emission sources were also assessed. We varied the time window for the background trend from 100 s to 1100 s. Window sizes larger than ~1000 s will lead to ER over-estimation. The time window chosen (400 s) is a factor of four higher than the typical time scales for cross-wind sampling of individual plumes (~100 s or 1-3 km). For the range tested (100-1000 s time windows), the ER sensitivity to changes in time window is ~5%. The isolation method verified that the observations used for ERs were only representative of dairy emissions, minimizing any contributions from non-dairy (e.g. fertilizer) NH₃ sources. In addition, mobile measurements in regions of significant
non-agricultural CH$_4$ sources (e.g. Bakersfield petrochemical activities) were removed. It was assumed that the dominant CH$_4$ enhancements originated from dairy farm sources for these isolated plume measurements. Overall, we find these potential biases are at most ±10%, which is within the measurement uncertainty. In addition, the range of observed ERs (at least twice the median value) is much greater than the uncertainties due to these biases.

**Spatial extent of emission plumes**

As noted above, there is potential for NH$_3$ losses in high mixing ratio plumes due to its short lifetime relative to CH$_4$, leading to a bias in NH$_3$:CH$_4$ ERs as a function of the sampling distance. To evaluate this potential bias, we aggregate all enhancement mixing ratios for NH$_3$
Figure 4.9: Box-whisker plots of enhancement mixing ratios of (a) $\Delta$NH$_3$ and (b) $\Delta$CH$_4$ as function of distance downwind of the closest dairy farm edge. The plot is binned by equal number of data points sampled at a given distance. The bins are clustered at distances near zero due to the large number of data points at close proximity.
and CH₄ as a function of distance to the closest dairy farm edge (Figure 4.9). Based on a statistical viewpoint across all farm plumes, extreme maxima (ΔNH₃ >1 ppmv) are typically observed within 200 m distance from the dairy farms, with smaller enhancements (<100 ppbv NH₃) observed at longer distances. This is in agreement with the maps in Figures 4.5 and 4.6 showing very localized downwind plumes. For the longer-lived species CH₄, the highest downwind mixing ratio enhancements are observed within 400 m distance from the dairy farms.

In most cases, the mobile measurements sample cross-sections perpendicular to the wind through dairy emission plumes in the vicinity of multiple dairies, but cannot assess the entire spatial decay of an individual plume. Figure 4.10 depicts a unique case study of an individual dairy farm plume sampled approximately parallel to the wind direction on Route 99, a northwest/southeast highway in the Central Valley. The NH₃ mixing ratio spatial measurements and prevailing wind direction for this case study are shown in Figure 4.10a. With no other dairy farm plumes sampled within 5 km downwind in this region, the plume is assumed to originate from this one dairy farm. The NH₃ and CH₄ plumes extend ∼3.9 km downwind before reaching regional background. Although it is assumed that turbulent dispersion is comparable for both species, NH₃ dry deposition fluxes are potentially significant in high mixing ratio plumes. Figure 4.10b shows the NH₃:CH₄ ERs as a function of distance downwind of this dairy farm. Although the plume is detectable up to ∼3.9 km downwind, the NH₃ enhancements begin to decline relative to CH₄ at ∼1.3 km downwind. The ER decreases by ∼30% between the closest downwind measurements (400 m) and 3 km downwind. We expect gas-phase NH₃ partitioning losses to be <10%, based on well-mixed boundary layer NH₄⁺ aircraft measurements in this region (section 4.3.4). Therefore, to account for the 30% loss in this case study, we estimate that at least 20% of the NH₃ emitted is lost to dry deposition within the first 3 km downwind of this dairy farm plume. This case study result shows the potential for significant depositional losses, especially for much higher concentration plumes observed in this dataset.
Figure 4.10: (a) Ammonia mixing ratio spatial measurement (1 s data) sampling one dairy farm plume on January 31, 2013 (12:43 PST), with the measurement route (Route 99) approximately parallel to the wind direction (indicated by the arrow). (b) $\Delta \text{NH}_3/\Delta \text{CH}_4$ emission ratios (1 s time resolution) for the plume in (a), as a function of distance from the dairy farm source. The error bars indicate the measurement uncertainty ($\pm 20\%$) and the red box-whiskers indicate the variability of measurements for the data in each distance bin.
4.3.3 Spatial heterogeneity case study

Fine-scale mobile measurements can resolve heterogeneities at sub-farm scales to categorize multiple sections within typical dairy farms. Figure 4.11a shows the NH₃ spatial distribution for a snapshot (∼23 minutes) of multiple transects and circles around one dairy farm during the evening hours, with low wind (stagnant) conditions. The NH₃ mixing ratios have high spatial variability with distinct hotspot regions observed downwind. Figure 4.11b shows three distinct regions of this farm: dairy corrals with dairy cows, an anaerobic lagoon for liquid manure management and solid piles of manure or soil. Figure 4.11c illustrates the mixing ratio profiles of NH₃, CH₄, N₂O and CO₂. Methane maxima are observed at the anaerobic lagoon (up to 80 ppmv CH₄), N₂O maxima at the solid manure piles (up to 600 ppbv N₂O), and NH₃ and CO₂ maxima at the dairy corral and soil manure piles. These profiles are consistent for multiple transects.

We analyze the NH₃:CH₄ and CH₄:CO₂ emission ratios downwind of the three sections to evaluate sub-farm-scale ER variability. The regional backgrounds (assumed to be constant during the transect time period) are estimated using the minimum mixing ratios observed within the corresponding farm sections. Figure 4.12a shows linear correlations at the dairy corral and solid manure regions. Ammonia, CH₄ and CO₂ are well-correlated at the dairy corral (R²=0.71) and show a much weaker correlation at the solid manure piles (R²=0.33 for CH₄:CO₂). The CH₄:CO₂ correlation is expected for the dairy corral due to the collocation of CH₄ enteric fermentation emissions from cows and exhaled CO₂ from their breath. Extremely high CH₄ enhancements are observed at the anaerobic lagoon and no strong correlations with NH₃ or CO₂ (Figure 4.12a). Figure 4.12b shows the ER percentiles for each section. Addition of an anaerobic lagoon to a dairy farm decreases the NH₃:CH₄ ER estimate for the entire dairy farm due to the higher anaerobic lagoon CH₄ emissions found in this case study. The solid manure section shows extreme maxima, with higher NH₃ enhancements for a portion of the solid manure pile section.
Figure 4.11: (a) Ammonia mixing ratio spatial distribution (with Google Earth imagery) sampling multiple passes during the evening of January 29, 2013, around one dairy farm (1 s measurements). The arrow indicates the prevailing wind vector (northwest wind direction). (b) Google Earth imagery of the dairy farm sampled in (a), with sections labeled as follows: dairy corrals (I), anaerobic lagoon (II) and sold manure piles (III). The length of the farm is $\sim$ 1600 m. (c) Spatial distributions of NH$_3$, CH$_4$, N$_2$O and CO$_2$ mixing ratios along the downwind edge of the dairy farm. The sections corresponding to those in (b) are labeled in the time series (I, II, III). Multiple passes were sampled for a total of $\sim$ 23 minutes. The red lines denote the 5 and 95 percentiles within each bin of equal number of data points.
Figure 4.12: (a) Correlation plots of $\Delta$NH$_3$/ΔCH$_4$ (right) and ΔCH$_4$/ΔCO$_2$ (left) corresponding to data downwind of each farm section (I, II, III) defined in Figure 11. Least squares linear regression fits (zero-intercept) are shown for sections I and III and the table lists the fitting results. (c) Box-whisker plots of percentiles and arithmetic mean (black point) emission ratios for each farm section ($\Delta$NH$_3$/ΔCH$_4$ at right; ΔCH$_4$/ΔCO$_2$ at left).

Based on the integrated mixing ratio enhancements across these three sections, $\sim$50% of total CH$_4$ emissions originated from the anaerobic lagoon, which only comprises $\sim$12% of the farm area. Lagoon sources must be accounted for when quantifying whole dairy farm ERs. Only $\sim$25% of CH$_4$ emissions were observed from the dairy corral ($\sim$40% of the farm area). In contrast, NH$_3$ enhancements from the dairy corral contributed $\sim$45% of total emissions and negligible anaerobic lagoon emission contributions. This is consistent with previous dairy farm emission case studies identifying dairy corrals surfaces as the dominant NH$_3$ dairy emission source, relative to anaerobic lagoons during the winter (Cassel et al., 2005; Mukhtar et al., 2008; Leytem et al. 2013). The different sources within an individual farm and close sampling
proximity where emissions are not sufficiently mixed are likely the reason for only 62% of farm plumes with statistically significant correlations.

### 4.3.4 Aircraft integrated emission ratios

The NASA P3-B airborne NH$_3$ and CH$_4$ measurements provide an integrated view of mixing ratio gradients and boundary layer vertical distributions within the regional-scale Tulare dairy region emission plumes. Surface mobile measurements were collocated with “missed approaches” of the NASA P3-B aircraft at Porterville, Visalia and Corcoran airports on three days (January 30, 31 and February 1, 2013). The mobile platform was positioned within 400 m of the runway during the missed approaches and sampled the local region around the airports to assess surface spatial variability. Figure 4.13 shows the vertical distributions (50 m vertical bins) along with surface measurements. We find comparable CH$_4$ mixing ratios for airborne and surface measurements. The Visalia mid-afternoon missed approach (Figure 4.13b) shows higher CH$_4$ at the surface, indicative of surface sources. Ammonia vertical profiles and surface measurements show clear differences. During the mid-afternoon, surface measurements are considerably lower than the minimum altitude airborne observations (Figure 4.13b,c). Since the aircraft horizontal coverage during the missed approach is much larger than the mobile measurements, there is potential for large spatial (horizontal) variability within the missed approach path. The Visalia mid-afternoon missed approach data (Figure 4.13b) shows NH$_3$ mixing ratios increase from north to south (higher NH$_3$ on the ascent), a clear difference between the two legs of this missed approach. The surface measurements are comparable to the northern (descending) leg of this missed approach. The Corcoran missed approach (Figure 4.13c) shows large surface NH$_3$ measurement variability, since this airport is very close to nearby dairy farm sources. In addition, there are large absolute measurement uncertainties of the high (> 50 ppbv NH$_3$) boundary layer airborne observations in this high source region. These discrepancies are potentially linked to closed-path sampling biases due to the aircraft sampling ~110 ppbv boundary layer NH$_3$ plumes to the east of Corcoran two minutes before
Figure 4.13: Airborne vertical profile measurements and surface mobile platform measurements at NASA P3-B missed approaches. The error bars for NH$_3$ airborne data indicate the measurement uncertainty (± 35%); the CH$_4$ airborne data whiskers represent ± 1 standard deviation within 50 m vertical bins; the surface measurement red bars represent ± 1 standard deviation for surface measurements within the airport vicinity: (a) Visalia Municipal Airport on January 30, 2013 (12:30 PST), 90 m minimum GPS altitude, with mobile platform ∼ 350 m from runway, (b) Visalia Municipal Airport on January 31, 2013 (15:08 PST), 92 m minimum GPS altitude, with mobile platform ∼ 200 m from runway, (c) Corcoran Airport on February 1, 2013 (14:05 PST), 50 m minimum GPS altitude, with mobile platform ∼ 45 m from runway.
the Corcoran missed approach. However, further investigation on the response time of the airborne NH$_3$ measurement for >100 ppbv NH$_3$ is necessary to fully quantify this potential bias.

The aircraft transects across the dairy region provide an integrated view of regional farm emission plumes and can be used to estimate a regional plume emission ratio. We calculate the integrated boundary layer NH$_x$:CH$_4$ emission ratios as a function of altitude in this region using the north-south P3-B aircraft transects (performed three times per day) from Fresno to Bakersfield, California (Figure 4.14a). This transect passes directly through the dairy region at low altitude (400-600 m), with a missed approach in the middle of the transect at Visalia Municipal Airport. The upwind background vertical distribution was derived from the Fresno missed approach. In this region, ~26% of the boundary layer NH$_x$ is in the condensed phase as NH$_4^+$, which adds ~2 ppbv to the overall NH$_x$ background. It is assumed that data points within each 50 m vertical bin have the same background value to account for any fine structure in the Fresno profile resulting from local effects. The boundary layer is well-mixed for the upwind profiles and the background values (not shown) are approximately the same for all altitudes. The domain for ER estimation was restricted to eliminate the Bakersfield region with oil and gas-related CH$_4$ sources. Due to sampling a few hundred meters above the surface, we expect NH$_3$ partitioning to occur on the time scales of vertical transport from the surface to the transect altitude. Therefore, we use NH$_x$ instead of gas phase NH$_3$ to calculate the NH$_x$:CH$_4$ ER. Figure 4.15 shows the percent contribution of gas-phase NH$_3$ to NH$_x$ for the transect locations, based on available NH$_4^+$ data. With a response time of 240 s, the NH$_4^+$ measurements range from 2.5 - 4.5 ppbv along the transect. At least 85% of NH$_x$ is in the gas phase in the dairy region (> 90% for the higher temperature conditions of transect 3), with somewhat smaller (80-85%) contribution to the north. Similar empirical cutoffs as for the mobile platform (10 ppbv ΔNH$_3$ and 100 ppbv ΔCH$_4$) were selected to exclude data close to the background levels. The aircraft ER is insensitive to these cutoffs to within 3%.
Figure 4.14: (a) NASA P3-B aircraft transects from Fresno to Bakersfield, California, which are flown from north to south (three times per day) at 400-600 m altitude, with a missed approach (\(~90\) m minimum GPS altitude) at Visalia Municipal Airport. Data for transect 2 (12:00 PST) on January 30, 2013 is shown (NH$_3$ at left; CH$_4$ at right). Wind direction and distance scales are indicated. The white points denote dairy farm locations (California Department of Water Resources). (b) Latitudinal (horizontal) gradients of NH$_x$ = NH$_3$ + NH$_4^+$ and CH$_4$ as a function of latitude for the transect shown in (a). Note the time delay for the NH$_x$ decay on the ascending portion of the Visalia missed approach during transect 1. (c) Vertical distributions of arithmetic mean enhancement mixing ratios (\(\Delta\)NH$_x$ at left; \(\Delta\)CH$_4$ at right) within 50 m vertical bins.
Figure 4.15: Percent of total ammonia (NH\textsubscript{x}) in the gas phase, as a function of latitude, for transects 2 and 3 (see Figure 14) used to calculate the aircraft integrated $\Delta$NH\textsubscript{3}/$\Delta$CH\textsubscript{4} emission ratios.

The NH\textsubscript{x} and CH\textsubscript{4} distributions for all 3 transects on January 30, 2013 are shown in Figure 4.14b,c. The latitudinal profiles both show distinct enhancements in the dairy farm region (Figure 4.14b). A correlation plot of NH\textsubscript{x} and CH\textsubscript{4} (not shown) indicates a hysteresis effect due to response time of the closed-path airborne NH\textsubscript{3} measurement relative to the airborne CH\textsubscript{4} measurement, leading to a low ER bias when entering the regional dairy farm plume and high bias when exiting the region. We restrict our calculation to the dairy region only to account for this potential bias. These entering and exiting biases are opposite in sign and when combined balance the geometric mean ER result to within 3%. This time response artifact is also apparent for the ascending portion of the morning transect missed approach (Figure 4.14b at left) due to the high concentration layer below 200 m altitude. Therefore, we use the descending portion of the missed approach measurements for the ER calculation.
The \( \text{NH}_2: \text{CH}_4 \) ER vertical distributions for all three transects on January 30, 2013 are illustrated in Figure 4.16a. The vertical distribution is indicative of a well-mixed boundary layer up to at least 500 m altitude for transects 2 and 3. We note that no ER values are reported above 200 m altitude for the morning transect 1 due to negligible \( \text{CH}_4 \) enhancements relative to the upwind background profile at these altitudes. At all altitudes up to 500 m, the \( \text{NH}_2: \text{CH}_4 \) ER increases from the morning to the afternoon transect, but for most altitudes these differences are within the measurement uncertainties.

To assess the validity of regional plume ER estimates, we compare the aircraft integrated \( \text{NH}_2: \text{CH}_4 \) ER distributions with those calculated from the surface mobile measurements (\( \text{NH}_3: \text{CH}_4 \)) of individual plumes. We find comparable geometric mean ERs for aircraft and surface measurements (Figure 4.16b). A comparison of the percentile distributions for both measurements indicates that surface measurements have much larger extreme maxima (heavier tailed distribution) with a 95 percentile a factor of four higher than the aircraft integrated emission ratios. This difference is expected as the surface measurements provide a local view of individual plume variability with higher (10-30 m) spatial resolution, whereas the aircraft measurements provide a regionally averaged (100-300 m spatial resolution) view of many plumes. We note that sensitivity analyses indicate that within the range of chosen empirical cutoffs, these cutoffs do not significantly influence the 95 percentile values.

4.3.5 Emission ratio literature comparisons

Dairy emission estimates for \( \text{NH}_3 \), \( \text{CH}_4 \) and \( \text{CO}_2 \) were compiled from the published literature. Multiple studies have separately quantified individual dairy farm \( \text{NH}_3 \) or \( \text{CH}_4 \) emissions during winter (Cassel et al., 2005; Hensen et al., 2006; Mukhtar et al., 2008; Hensen et al., 2009; Owen et al., 2014 and references therein). We limit our selection of studies to those that estimate \( \text{NH}_3 \) and \( \text{CH}_4 \) emissions at the same farm, since there is added variability when comparing emission factors across different locations and environmental conditions. Since no such studies have been performed in the Tulare County region, we choose studies with
Figure 4.16: (a) Vertical profiles of the emission ratios for all transects on January 30, 2013, displayed as the geometric means within 50 m vertical bins. The error bars indicate the measurement uncertainty (±40%). (c) Comparison of percentiles and geometric means for emission ratios derived from surface mobile (left) and aircraft measurements (right). The literature study emission ratios shown in Table 4.3 are indicated by the colored diamonds.
comparable air temperatures conditions and open-lot or open-freestall dairy types similar to Tulare dairy farms. We calculate the ERs by dividing the literature reported NH\(_3\) and CH\(_4\) emissions (kg d\(^{-1}\)) and converting to molar fractions.

Table 4.3: Comparison of mobile emission ratios with relevant dairy emission case studies in the published literature.

<table>
<thead>
<tr>
<th>Published Emissions</th>
<th>(\Delta\text{NH}_3/\Delta\text{CH}_4) [ppmv ppmv(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current study (mobile) median</td>
<td>0.15 ± 0.03</td>
</tr>
<tr>
<td>Current study (mobile) geometric mean</td>
<td>0.16 ± 0.03</td>
</tr>
<tr>
<td>Bjorneberg et al. (2009)</td>
<td>0.10</td>
</tr>
<tr>
<td>Leytem et al. (2011)</td>
<td>0.24</td>
</tr>
<tr>
<td>Leytem et al. (2013)</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Table 4.3 summarizes the present study ER results and the literature estimates. The median and geometric mean NH\(_3\):CH\(_4\) ERs derived from our mobile measurements are consistent with multiple past studies. We observed large variability of ERs across 93 dairy farm plumes (Figure 4.8). It is important to note that Leytem et al. (2011 and 2013) published winter measurements at temperature ranges much lower than that observed during winter in the Central Valley dairy region (Table 4.2). The winter ERs derived from Leytem et al. (2013) are a factor of three lower than springtime values. Therefore, these winter measurements are not be applicable for comparison with our mobile measurements and the springtime values with more comparable temperatures are reported in Table 4.3 for these studies. Finally, the CH\(_4\):CO\(_2\) ER (0.06 ppmv ppmv\(^{-1}\)) for the open-lot dairy average springtime measurements by Leytem et al. (2011) is comparable to the dairy corral ER obtained for the case study in Figure 4.12.
4.4 Discussion

4.4.1 Mobile measurement emission ratios

The high spatial resolution surface mobile measurements illustrated the large variability and range of NH$_3$ mixing ratios observed near large dairy emission sources. However, surface measurements during day-time only capture cross-sections of farm plumes and do not sample the entire spatial extent of plumes, as they generally mix vertically due to vertical dispersion in turbulent day-time boundary layer conditions (Dennis et al., 2010). Thus, the ΔNH$_3$ absolute magnitudes do not correlate with total NH$_3$ emissions, since turbulent diffusivity at the time of passing the farm will influence the absolute magnitude. By quantifying ΔNH$_3$ with respect to another emission tracer (ΔCH$_4$) using an emission ratio approach, we normalize for these plume mixing dynamics. It is important to note that the emission ratios cannot be used to directly estimate the distribution of total emissions of either species, as they both vary considerably in space and time. However, each farm sampled is a point source within typical gridded emission inventories on the spatial scales of several kilometers. Thus, these emission ratios are directly applicable to comparisons with NH$_3$ and CH$_4$ inventories.

The mobile platform spatial measurements occurred under real-world conditions at multiple locations, providing a statistical estimation of ER spatial variability (Figure 4.11). Multiple factors may contribute to the observed variability, including environmental conditions (e.g. temperature, wind) and farming activities such as the number of lactating and dry cows on a dairy farm (Sun et al., 2008) and manure management (Owen et al., 2014). The mobile measurements sampled two counties (Tulare and Kings) with the highest total dairy farm NH$_3$ emissions in the United States. According to inventory models, these measurements occurred during the seasonal minimum of dairy emissions (January-February) (Pinder et al., 2004). However, due to higher Central Valley temperatures, NH$_3$ emission factors applicable to colder winter regions are not applicable to our sampling period (Walker et al., 2012).
We used the high resolution mobile data set to quantify sub-farm-scale ERs for multiple sections of a case study dairy farm. Although previous measurements have shown manure management, primarily from anaerobic lagoons, to be the dominant CH$_4$ dairy source (95%) and the largest greenhouse gas source from California agriculture, no field measurements of anaerobic lagoon CH$_4$ emissions have been performed in California (Owen et al. 2014). Although we did not quantify total CH$_4$ emissions, the case study showed large anaerobic lagoon contributions to total CH$_4$ dairy emissions. Approximately two thirds (66%) of Tulare County dairy farms have anaerobic lagoons (Owen et al., 2014). Therefore, the observed NH$_3$:CH$_4$ ER variability likely includes different manure management activities.

The sampling proximity to dairy farm sources can influence ER estimates and correlations. High concentrations decrease with distance from these sources due to dispersion and dry deposition (Day et al., 2012). Turbulent dispersion is assumed to be similar for NH$_3$ and CH$_4$, whereas NH$_3$ is shorter-lived and expected to be lost via dry deposition. Due to the excess NH$_3$ in the Central Valley, the partitioning loss of gas-phase NH$_3$ to inorganic aerosol is relatively small (<10%). However, dry deposition is potentially significant due to the high mixing ratios observed in surface plumes and the high deposition velocities of NH$_3$. Previous studies modeling dry deposition have shown a range of values for the percent of emissions lost at distances downwind: ∼40% loss within 230 m downwind with large model uncertainties (Hensen et al., 2009); ∼8-15% dry deposited within 12 km grid cell (Dennis et al., 2010). The case study in section 4.3.2 shows 20-30% of the NH$_3$ was lost to dry deposition within ∼3 km downwind. However, restricting data to 600-1200 m from dairy farm centroids minimizes this bias. Further investigation of the spatially variable dry deposition velocities in this region is necessary to better constrain this bias. Finally, linear correlation between ∆NH$_3$ and ∆CH$_4$ was not observed for all emission plumes. The lack of correlation is related to spatial differences in sources and variability of activities since the mobile measurements capture snapshots of each emission plume.
4.4.2 Aircraft measurement emission ratios

The aircraft integrated ERs for two transects were used to assess the regional ER approach in the context of surface ER measurements. The NH$_3$:CH$_4$ ER was consistently larger in the mid-afternoon transect relative to the morning or mid-day, but the difference is within the measurement uncertainty for altitudes below 400 m. This trend is potentially linked to higher NH$_3$ surface emissions in the mid-afternoon due to increased solar heating relative to CH$_4$ emissions. However, further investigation is needed to evaluate the robustness of this trend on multiple days and across other transects in the dairy region. In addition, the aircraft-derived ER estimates have multiple uncertainties. For instance, the extent to which the Fresno background vertical profile represents the background within the dairy region along this transect is uncertain and requires further validation.

There are multiple differences between surface mobile and aircraft plume measurements. We expect dry deposition to remove some NH$_3$, resulting in a lower ER than surface measurements for downwind aircraft transects. Future aircraft top-down NH$_3$ emission estimates must consider under-sampling of surface plumes with much higher spatial variability than observed at higher altitudes. Finally, we note that while CH$_4$:CO$_2$ ERs can be obtained for individual surface plumes (Figure 4.12), the regional aircraft CO$_2$ measurements show no enhancements in the dairy farm region, but clearly shows urban area enhancements. This represents an advantage of mobile measurements, since the aircraft integrated sampling cannot resolve these individual dairy CO$_2$ plumes within a regional background of other sources.

4.5 Summary and conclusions

We characterized the spatial distributions of NH$_3$ and CH$_4$ in the Tulare County dairy region during the NASA DISCOVER-AQ 2013 field campaign. High resolution, open-path, mobile measurements were used to quantify NH$_3$:CH$_4$ emission ratios, demonstrating the value of fast-response, simultaneous measurements of multiple gases on a vehicular platform. We observed
high spatial variability of NH$_3$ mixing ratios, with maxima localized downwind of individual dairy farms. The statistics of NH$_3$:CH$_4$ emission ratios for 93 downwind dairy farm plumes were evaluated, with a heavy-tailed distribution and 62% of farm plumes with statistically significant linear correlation between ΔNH$_3$ and ΔCH$_4$. The ER was shown to vary with distance from the source, indicative of NH$_3$ losses within plumes relative to the longer-lived CH$_4$. Based on a case study plume, >20% of the NH$_3$ was lost within 3 km downwind. A dairy farm case study illustrated spatially variable ERs for dairy corral, anaerobic lagoon and solid manure pile dairy farm sections with high resolution sampling at close proximity (<100 m). These findings highlight the importance of anaerobic lagoon CH$_4$ sources, which must be accounted for in dairy emission inventories.

We also quantified regional plume ERs (NH$_x$:CH$_4$) based on boundary layer aircraft measurements. The mobile-derived ERs were comparable (in median value) to previous relevant in-situ studies and to the aircraft-integrated ER geometric mean values. However, the mobile measurements showed much larger variability and extreme values of the distribution. The mobile surface ER estimates are valuable to constrain biases and uncertainties in regional NH$_3$ emission estimates using top-down approaches. These include background variability within the source region (Figure 4.7) and the potential for dry depositional losses (Figure 4.10) that influence aircraft measurements downwind of the entire source region. Although modeling results have constrained dry deposition fluxes, deposition velocities are spatially and temporally variable. These factors must be evaluated in future investigations.

4.6 Future work

Future investigations will explore the inter-annual variability, seasonality and diurnal variability at individual farms. The mobile measurement approach can be coupled and collocated with open-path eddy covariance flux measurements and vertically-resolved in-situ NH$_3$ measurements to gain a better understanding of NH$_3$ emission plume structures for constraining total agricultural NH$_3$ emissions in space and time. The mobile surface ER statistics pre-
Presented here are applicable to improving NH$_3$ emission spatial allocations in future inventories. With potentially better constraints on CH$_4$ emissions derived from inventory model or aircraft measurements in this region, future analyses can couple CH$_4$ emission estimates with the measured NH$_3$:CH$_4$ emission ratios to estimate total NH$_3$ emissions. In addition to total emission magnitudes, spatial distributions of dairy farm sources are important for improving modeling efforts for spatially variable, hotspot NH$_3$ and CH$_4$ distributions. Aerosol and air quality model simulations must represent NH$_3$ spatial distributions correctly to quantify fine particle loading in the Central Valley and evaluate agricultural emission impacts on air quality.

4.7 Acknowledgements

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Chapter 5

Open path-integrated, quantum cascade laser-based sensor for high precision methane measurements

5.1 Introduction

Atmospheric trace gas measurements of air pollutants and greenhouse gases can be performed with fixed stationary sensors (such as the compact open-path sensor described in Chapter 3), equipped on mobile platforms for spatial measurements (as described in Chapter 4), or conducted as remote sensing measurements using open path-integrated configurations. While the fixed and mobile-based sensors only probe a small volume of air at any given time, the path-integrated approach captures variability across larger spatial scales simultaneously. These measurements can be used to calculate fluxes (Griffith and Gale, 2000) and have been coupled with inverse dispersion models (Flesch et al., 2007). Regional air quality models typically simulate trace gas distributions at single kilometer-scale grid resolution (Dennis et al., 2010; Kelly et al., 2013). Multiple point sensor measurements performed using sensor networks must be aggregated to these grid scales for direct comparison, but sensor locations must be properly distributed to avoid sampling biases. Previous comparisons between point measurements and
model grid scale estimates have shown potential discrepancies due to sampling biases (Heald et al., 2012, Walker et al., 2012). Satellite retrieval comparisons with in-situ point measurements must use appropriate spatial and temporal averaging windows to account for differences in sampling paradigms between point and volume measurements (Diao et al., 2013). This is especially problematic for species with large spatial heterogeneities, as illustrated by the mobile NH$_3$ measurements discussed in Chapter 4. Thus, it is advantageous to perform measurements on comparable spatial scales as regional model simulations for more straightforward model-measurement comparisons and validations.

Open path-integrated sensing platforms are applicable to a variety of trace gases important for air quality and climate change, including NH$_3$ and CH$_4$. The applications of open path-integrated monitoring include quantifying agricultural emissions and characterizing spatial locations and distributions of leaks from petrochemical and industrial activities (e.g. natural gas infrastructure; hydraulic fracturing wells; waste facilities). Current emission inventories for these sources are highly uncertain (Thoma et al., 2005; Gibson et al., 2006; Miller et al., 2013). These sources often occur as fugitive, spatially distributed and heterogeneous emissions (Thoma et al., 2005). Traditional point measurements likely under-estimate these emissions, as they miss transient hotspots or isolated leaks (Gibson et al., 2006). This open path-integrated sampling strategy is especially advantageous for high time resolution monitoring of hotspot or leakage emissions and for species (such as NH$_3$) that adsorb to surfaces and partition into condensed phases (Yokelson et al., 2003). Open path-integrated systems have been previously deployed to measure NH$_3$ emissions from highly uncertain agricultural sources (Galle et al., 2000; Childers et al., 2001; Mount et al., 2002; Desjardins et al., 2004; Thoma et al., 2005).

To address these issues, I explored the feasibility of long-path, integrated measurements by developing a quantum cascade laser-based instrument. For this study, I focused on atmospheric methane (CH$_4$) detection because of its stringent high precision and stability measurement requirements. In this way, sensor performance issues can be identified during field measurements, whereas drift and noise may be difficult to quantify for an extremely variable
trace gas species such as NH$_3$. Atmospheric CH$_4$ is a potent greenhouse gas responsible for approximately 20% of total radiative forcing, with a global warming potential 21-25 times that of CO$_2$ over 100 years (IPCC, 2007; Montzka et al., 2011). Methane also plays important roles in tropospheric chemistry, including tropospheric ozone formation (Isaksen et al., 2011). Global, annual mean CH$_4$ mixing ratios (1803 ± 2 ppbv in 2011) have been increasing, following a temporary leveling in the late 1990s (IPCC 2013; Rigby et al., 2008; Isaksen et al., 2011). The dominant removal mechanism for methane in the troposphere is oxidation by the hydroxyl radical (OH) and stratospheric oxidation results in enhanced stratospheric water vapor production (Isaksen et al., 2011; IPCC, 2013). While the total atmospheric burden of CH$_4$ is well constrained, many CH$_4$ sources are poorly quantified, with large uncertainties for both anthropogenic and natural emission sources (EPA, 2011; Dlugokencky et al., 2011; Montzka et al., 2011).

Anthropogenic CH$_4$ sources include petrochemical activities (Miller et al., 2013) such as hydraulic fracturing (Howarth et al., 2011, Petron et al., 2012, Karion et al., 2013) and agricultural activities such as enteric fermentation, manure management and rice cultivation (Peischl et al., 2012; Owen et al., 2014). Natural sources include wetlands, termites, lakes and permafrost peatlands (EPA, 2011). These emission sources are all spatially heterogeneous and also vary in time. Global climate change may be accelerating natural CH$_4$ emissions from organic carbon-rich permafrost in rapidly warming Arctic regions (Cole et al., 2007; Tranvik et al., 2009; IPCC, 2013). Recently, significant CH$_4$ emissions have been observed from Arctic lakes (Walter et al., 2007), at the onset of freezing of the tundra (Mastepanov et al., 2008), from sediment on the Arctic shelf (Shakhova et al., 2010), and from surface waters of the Arctic Ocean (Kort et al., 2012). However, Arctic lake CH$_4$ emissions are very difficult to quantify with existing point measurement sampling methods, since they occur as transient hotspots emissions (Walter et al., 2008). Currently, there is a growing need to quantify these natural and highly variable CH$_4$ sources with high spatial and temporal coverage in-situ measurements.
Field CH$_4$ measurements require high precision and stability, large spatial and temporal coverage, and robust, low-power sensing platforms for operation in remote field environments. Previous measurement techniques have stability and field deployment limitations. Conventional monitoring methods include flux chambers that use offline gas chromatography analysis. These techniques are highly precise, but flux chambers provide discrete point measurements in space and time, which cannot fully characterize the spatial variability of heterogeneous, distributed CH$_4$ sources. Eddy covariance flux measurements (with closed or open-path analyzers) can quantify CH$_4$ fluxes over large spatial footprints (Eugster and Plüss, 2010; McDermitt et al., 2011; Peltola et al., 2013), but cannot resolve the spatial heterogeneities of emissions within that footprint region. Methane measurements have been performed with point sensors in field environments including the Arctic (Eugster and Kling, 2012). Suto and Inoue (2010) demonstrated an in-situ, portable atmospheric CH$_4$ sensor with 30 second averaged mole fractions varying by ± 2 ppbv CH$_4$ and long-term stability for over 1 week. However, compact, laser-based point sensors under-sample transient emission hotspots and require a moving platform or tower for extensive spatial measurements.

Open path-integrated, in-situ CH$_4$ techniques are ideal tools to address these observational requirements. Open-path Fourier transform infrared (OP/FTIR) spectrometry techniques have shown precision of 10 - 20 ppbv CH$_4$ for 10 s measurements (Goode et al., 1999; Griffiths and Galle, 2000). These systems have been deployed in the field at path lengths of 100s of meters for CH$_4$ emission measurements from agricultural facilities (Galle et al., 2000; Childers et al., 2001). However, OP/FTIR instruments have limited sensitivity and reliability for longer path lengths in the field (Bacsik et al., 2005). Tunable diode laser systems such as GasFinder MC (Boreal Laser Inc.) have shown sensitivities under laboratory conditions of $\sim$1 ppm.m, corresponding to $\sim$1 ppbv CH$_4$ precision for a 1 km round-trip path length. These systems have been deployed in the field to measure agricultural CH$_4$ emissions (Desjardins et al., 2004). However, the precision is defined under laboratory conditions up to 750 m path lengths, rather than field conditions for longer (> 1 km) path lengths. In addition, the long-
term stability of this system has not been evaluated in a changing field environment, such as the Arctic. Tunable diode laser absorption spectroscopy (TDLAS) CH$_4$ sensors have also been developed for laser scanning applications to detect natural gas leakage (Gibson et al., 2006, Xia et al., 2008) and measure fugitive emission fluxes (Thoma et al., 2005). Xia et al. (2008) demonstrated a minimum detection limit of 1.1 ppm \textbullet m for CH$_4$ with a 120 m optical path length. However, the sensor drift was not tested in the field. Brooke et al. (2012) demonstrated 144 km open path CO$_2$ measurements across two mountaintops using relatively low power diode lasers and claimed the technique is easily extended to CH$_4$ measurements.

Open path-integrated, quantum cascade (QC) laser-based instruments for trace gases such as ozone have been deployed at kilometer-scale path lengths (Taslakov et al., 2006), but long-term field stability of this measurement was not investigated. Currently, there have been no open path-integrated sensors demonstrated with the capability to perform high precision and high stability CH$_4$ measurements at kilometer-scale path lengths in real-world field environments, such as in the remote Arctic. Thus, compact, low power, open path-integrated sensing technology is needed for high precision and high stability measurements in a range of field environments.

To address the precision, stability and field robustness requirements for spatially integrated CH$_4$ measurements, I developed and deployed an open-path QC laser-based CH$_4$ sensor for long path length (hundreds of meters) measurements across an Arctic lake. The QC laser has high optical power ($\sim 40$ mW) for high precision sensing at long path lengths, with low ($< 100$ W) electrical power requirements, advantageous for operation in a remote field environment. High short-term precision (0.5 % in 1 s) for CH$_4$ mixing ratio measurements at 459 m total path length was achieved at Toolik Lake, Alaska with measurement stability of 1% for up to 1 hour with an N$_2$O in-line reference cell. Robust field operation was demonstrated through precipitation events. The sensor was intercompared with a commercial point sensor (LICOR LI-7700 CH$_4$ analyzer) and correlated well with the point measurements when accounting for the spatial scale differences between measurements.
5.2 Sensor design

The open path-integrated QC laser-based sensor schematic is shown in Figure 5.1a with photos of the sensor prototype in the field in Figure 5.1b. A high optical power (∼ 40 mW), 8 µm QC laser (AdTech Optics) was used to probe a strong mid-infrared transition of CH₄. In comparison with point measurement techniques, probing the strongest CH₄ absorption line is not optimal for long path length configurations due to optical saturation. Therefore, an absorption line was selected at 8 µm to avoid absorption saturation at long (> 10 m) path lengths. The QC laser was operated in a continuous wave mode at 22°C, with a thermoelectric (TE) cooler and temperature-controller (ILX LDT5980). Recirculating chilled coolant (Koolance coolant; Thermocube chiller) was used for stable operation of the TE-cooled element. The laser current was controlled by a Wavelength Electronics current source (QCL-500). A Newtonian telescope was employed to launch and receive the QC laser light with one corner-cube retro-reflector (Newport Optics) placed at a selected distance away from the telescope in a transmitter-retro-reflector-receiver configuration. A visible green laser (532 nm) was co-aligned with the infrared beam to facilitate long distance alignments to the retro-reflector. The received light was focused onto a TE-cooled mercury cadmium telluride (MCT) detector (Vigo Systems). A National Instruments data acquisition board (NI-6251) acquired the detector signal, which was transmitted to a laptop computer. The detector signal was processed by a custom, LABVIEW-based algorithm that performs multi-harmonic, wavelength modulation spectroscopy and real-time spectral fitting (Tao et al., 2012). Water vapor (H₂O) mixing ratio was measured nearby for water vapor dilution and air density corrections.

High-precision CH₄ measurements are important to resolve relatively small ambient CH₄ mixing ratio variations. For open-path measurements where environmental conditions are constantly changing within the sampling volume, maintaining stability is also essential. Small sensor drifts over time can appear as real mixing ratio fluctuations but may instead originate from sensor system instabilities (e.g. detector or laser temperature fluctuations, electronics temperature-dependencies, optical interference fringing). To account for these drifts, an in-line
Figure 5.1: (a) Schematic of the open path-integrated QC laser-based sensor. The QC laser beam is co-aligned with a visible laser for long path length alignments to a retroreflector. A Newtonian telescope configuration is used with light collection onto a TE-cooled MCT detector. QCL = Quantum cascade laser; M = mirror, DCM = dichroic mirror. (b) Photo of open path-integrated sensor prototype deployed at the Princeton Broadmead site (left) and this sensor (shielded from precipitation) along with LI-7700 CH$_4$ analyzer during field inter-comparison at the Princeton Broadmead site (right).
reference absorption signal was simultaneously monitored, along with the ambient CH₄ signal. The reference cell was placed in the same optical path, eliminating differences between sample and reference paths (Sun et al., 2013). This inline technique has previously been demonstrated for atmospheric NH₃ (Sun et al., 2013; Miller et al., 2014) and N₂O measurements (Tao et al., 2012). As shown in the HITRAN simulated spectra (Figure 5.2), the short (5 cm length) sealed reference cell (1% N₂O in N₂ at a reduced pressure of 50 hPa) yields a stronger absorbance and narrower line-width than the pressure-broadened, ambient N₂O absorption signal. While ambient (atmospheric) N₂O would nominally impact the reference signal, the narrow line-width of the reference signal and higher harmonic detection minimize this potential interference as discussed below.

Wavelength modulation spectroscopy, in which a high frequency sinusoidal modulation is superimposed on the laser current tuning function, was used for high-sensitivity detection. Linear current tuning was implemented to scan across the spectral features of CH₄ and the reference signal of N₂O (Figure 5.2). The detector signal was demodulated at harmonics of the modulation frequency (40 kHz) to minimize laser excess noise by shifting the detection bandwidth to higher frequencies (Schilt et al., 2003). Figure 5.3 shows the 2f and 6f spectra in this wavelength range. The second harmonic (2f) was used for ambient CH₄ detection with the CH₄ absorption line at lower wavelength without interference from other species such as N₂O (Figure 5.3a). The sixth harmonic (6f) signal was used for detection of the in-line N₂O reference absorption line (Figure 5.3b). The sixth harmonic shows much less sensitivity to interferences from adjacent ambient pressure-broadened absorption lines. Therefore, changes in the broad CH₄ absorption signal or ambient N₂O have minimal impact on the inline reference N₂O signal. Figure 5.4 shows the 2f CH₄ spectrum (1 s) and 6f N₂O reference spectrum (30 s) recorded in the field with real-time spectral fitting. These spectra demonstrate excellent spectral fitting quality recorded at 459 m total path length. The 2f spectral fitting residuals are ~ 3% of the CH₄ absorption signal height and 6f residuals are ~ 9% of the N₂O reference absorption signal height, consistent with lower signal to noise ratios at higher harmonics.
Figure 5.2: Direct absorption simulation based on HITRAN (Rothman et al., 2009) of the 8 \( \mu \text{m} \) region. The following conditions are used for simulation: 1.9 ppmv CH\(_4\), 325 ppbv N\(_2\)O, 390 ppmv CO\(_2\) (all at ambient pressure of 1013 hPa and path length of 300 m) and 1% N\(_2\)O in N\(_2\) at reduced pressure (50 hPa) and 5 cm path length. Total absorption is shown by the dotted black line.

The long open-path QC laser-based sensor was calibrated in the Arctic field environment using seven air samples taken along the laser path, which were subsequently analyzed off-line using gas chromatography (GC). The accuracy of this method is \( \pm 2\% \) due to the gas standard uncertainties used for the GC calibration curve. During the field inter-comparison, CH\(_4\) mixing ratios were calibrated by linearly scaling the retrieval with LICOR LI-7700 CH\(_4\) analyzer measurements, as discussed in section 5.4.2.
Figure 5.3: (a) Second harmonic spectra simulated using HITRAN database (Rothman et al., 2009). The ambient signals are at 1000 hPa and N$_2$O reference signal at 50 hPa (over-modulated) and 5 cm length. The mixing ratios are as follows: 1.9 ppmv CH$_4$, 325 ppbv ambient N$_2$O, 1% N$_2$O reference in N$_2$ (reference). The path length simulated for ambient signals is that for the Princeton Broadmead site deployment (240 m). Total absorption is shown by the dotted black line. (b) Sixth harmonic (6f) signal of the same conditions described in (a), showing the isolation of the narrow N$_2$O reference signal at higher harmonics.

5.3 Field sites

The QC laser-based CH$_4$ sensor was deployed over a two-week period (August 14 - 29, 2012) across Toolik Lake at the NSF Toolik Field Station in Alaska [68° 38’ N, 149° 36’ W]. The sensor was located inside a wooden shelter in order to protect it from precipitation events, wind and insects. The input and output beams passed through an opening in the shelter of $\sim 15$ cm by 15 cm. Electronic line power was provided from a laboratory building at the field station. The sensor was deployed on the south side of Toolik Lake. The retro-reflector, attached to a tripod, was placed at three locations across the lake, as shown in Figure 5.5. The one-way distances between the sensor and the retro-reflector are shown in Figure 5.5, corresponding to round-trip distances of 458 m, 756 m, and 1288 m respectively. High optical power and minimal laser beam divergence (0.35 mrad) were both critical for long (> 500 m) distance measurements. Alignment across the lake was achieved using the visible (532 nm) laser and a spotting scope. The laser light traversed across the lake at approximately
Figure 5.4: (a) Ambient methane 2f signal (1 second averaging) recorded in the field at Toolik Lake along with the real-time fitted spectrum. Note the residuals of the spectral fit are plotted on a smaller voltage range than the ambient spectrum to better illustrate the spectral noise. (b) 6f signal of N$_2$O reference cell signal recorded with 30 second averaging in the field at Toolik Lake, along with the real-time fitted spectrum and spectral fitting residuals.

one meter above the water surface. The system remained well-aligned for the duration of measurements.

A one-week inter-comparison experiment was conducted at the Princeton Broadmead test-bed site in March 2013 with a commercial open-path CH$_4$ analyzer (LICOR LI-7700) designed for point (rather than path-integrated) measurements (McDermitt et al., 2011). The LICOR LI-7700 has a 1 s precision of 2 ppbv CH$_4$ and long-term drift (over hours) of $\sim$20 ppbv CH$_4$. 
Figure 5.5: Three long path lengths implemented across Toolik Lake, Alaska during the summer 2012 deployment. The retro-reflector was relocated to the yellow, blue and green locations to achieve these path lengths during separate phases of the field campaign. The distances shown are one-way distances.
5.4 Field performance

5.4.1 Precision and stability

Figure 5.6 shows the Allan deviation plot for ambient CH$_4$ mixing ratios recorded at 1 s in the field at Toolik Lake, Alaska. The relative Allan deviation is 0.5% at 1 s integration time, equivalent to $\sim$10 ppbv CH$_4$, for a 459 m path length implemented for this measurement. Since the measurements in Figure 5.6 include the effects of real, atmospheric variability, 0.5% is an upper limit for instrument precision with contributions from instrument noise and real atmospheric variability. The short-term precision for measurements at the longest path length implemented (1.29 km round-trip) is expected to degrade by $\sim$25% compared with the results in Figure 5.6 (459 m path length), due to lower light intensity on the detector with a larger beam incident on the retro-reflector at longer path lengths.

At longer time-scales, long-term drift dominates the Allan deviation plot in Figure 5.6, suggesting that calibration is needed on these timescales to ensure accuracy. Figure 5.7 shows the relative Allan deviation plot of the raw 6f N$_2$O signal in the field. The reference signal shows that drift on timescales up to $10^4$ s remains below the 1 s precision (2.5%). The precision of the 6f N$_2$O reference signal is slightly worse than the 2f CH$_4$ precision due to the intrinsically lower signal-to-noise ratio of 6f signals. Thirty-second averaging of the N$_2$O reference cell was implemented to be consistent with the precision of the 2f CH$_4$ measurement. Based on the Allan deviation plot in Figure 5.7, the in-line approach can account for an instrument drift within 1%, up to 1 hour time-scales.

In order to perform Arctic field measurements, it is critical that the sensor be able to function through a range of environmental conditions, including significant temperature cycling, wind and precipitation events (rain and snow). It is important to note that although open-path measurement data quality may inevitably be degraded due to precipitation, a field sensor must be capable of autonomous operation through these precipitation events. During the deployment period, environmental conditions included a range of air temperatures (-1°C to
Figure 5.6: Allan deviation plot of ambient 1 s CH₄ data. The ambient data was recorded over ~ 7 hours across Toolik Lake at a 459 m round trip path length.

19°C), snowfall (15.6 mm snow accumulation on August 27), and variable wind speed reaching up to 9.3 m s⁻¹. The system operated unattended through this range of environmental conditions and maintained excellent thermal control with the laser temperature remaining stable at 22°C through all weather and wind conditions. During the deployment period, heavy snowfall (precipitation rate > 0.2 mm hr⁻¹) took place, which resulted in the sensor losing signal primarily due to snow accumulation inside the retro-reflector housing. With the addition of a precipitation shield, the signal and data quality was immediately recovered following the snowfall period.
Figure 5.7: Relative Allan deviation plot of in-line N₂O reference signal (1 s) recorded over ~10 hours in the field at Toolik Lake, Alaska.

5.4.2 Field intercomparison

The open path-integrated QC laser-based sensor and LICOR LI-7700 point sensor were deployed at the Princeton Broadmead site for simultaneous diurnal measurements of ambient CH₄ mixing ratios. Figures 5.8 and 5.9 show the effects of snowfall and rainfall on both sensors during this deployment. The open path-integrated QC laser sensor recovered light intensity without any intervention following a snowfall event (Figure 5.8). Moderate rainfall resulted in small attenuation of light intensity on the detector for the open path-integrated QC laser sensor, which did not significantly degrade data quality during this period. At the same time, the LICOR LI-7700 mirrors became wet and could not perform measurements during the rainfall (Figure 5.9).
Figure 5.8: The effect of snowfall on the signal strength of the open path-integrated QC laser sensor at the Princeton Broadmead test-bed site in March 2013.

The open path-integrated QC laser-based sensor was aligned to a total (round-trip) path length of 240 m. Note that the two sensors have different sampling footprints, so that sufficient time averaging of measurements is necessary to allow for well-mixed conditions along the integrated path for inter-comparison. Figure 5.10 shows 1 s measurements and Figure 5.11 shows one-hour averaged measurements for both sensors during the field deployment. The time series of 1 s measurements in Figure 5.10 shows a comparable short-term precision for both sensors. Figure 5.11 illustrates that the 1-hour averaged measurements by the open path-integrated and point sensors both captured a large variation in ambient CH$_4$ mixing ratios ($\sim$ 200 ppbv CH$_4$).
Figure 5.9: Effects of rainfall on the signal strengths of two different open-path sensors, the QCL-based sensor and the Licor LI-7700 analyzer at the Princeton Broadmead site.

5.5 Discussion

High precision, open path-integrated measurements with a QC laser-based CH$_4$ sensor were performed in an Arctic field environment. The equivalent fractional absorbance for a 1 s measurement (or 1 Hz bandwidth) is $7 \times 10^{-4}$ (at 459 m path length). The limiting factors in this sensor system for precision and stability are due to optical interference fringing from uncoated reference cell and detector windows, and electronic noise from drive electronics. The 1 s precision was limited to 1% when the reference cell was installed, due to light attenuation from the reference cell and detector windows with no anti-reflection coatings. In addition, the beam divergence prevented collection of all light on the retro-reflector, further degrading received power and limiting precision. Future refinements of the sensor system will improve this noise level to reach higher precision measurements closer to the $10^{-5}$ absorbance noise.
level in typical laser-based systems (Tittel et al., 2003) by implementing custom anti-reflection coatings on all sensor window components and installing a beam expander to improve beam divergence at long path lengths.

Typical short-term CH$_4$ mixing ratio fluctuations measured by other CH$_4$ sensors above Arctic lakes are larger than our stated 1 s precision of 10 ppbv CH$_4$. Eugster and Kling (2012) performed summer season CH$_4$ measurements at Toolik Lake and found 6-hour averaged mixing ratio variations of $\sim$50 ppbv CH$_4$. Higher mixing ratio variations are expected with higher time resolution (i.e. 1 s) measurements. Therefore, we expect that 10 ppbv CH$_4$ precision would be sufficient to capture large mixing ratio changes on short timescales. However, the mean diurnal cycle at Toolik Lake showed a total variability of $\sim$10 - 15 ppbv CH$_4$ with 1 hour averaging (Eugster and Kling, 2012). The Allan deviation for our CH$_4$ measurements
Figure 5.11: Inter-comparison of open path-integrated QC laser sensor and LICOR LI-7700 analyzer at the Princeton Broadmead site with 1 hour averaged measurements. The whiskers represent the standard deviation of 1 s measurements during the 1 hour time averaging window.

with 1 hour integration time (including atmospheric variability) is 20 ppbv CH$_4$ (Figure 5.6). Long-term drifts are likely to be much worse on timescales longer than $10^4$ s. For example, a diurnal cycle of CH$_4$ measurements with the open path-integrated QC laser-based sensor showed artifact oscillations in the time series, even when normalizing by the N$_2$O reference signal, due to interference fringing and laser thermal drift. Therefore, for future measurements, improvements in long-term stability would be necessary to measure CH$_4$ diurnal cycles in these field environments.

In theory, the in-line reference cell can be used to maintain sensor stability by separating tiny instabilities in the system from real atmospheric CH$_4$ mixing ratio changes and provides a narrow line-width signal at 6f for line-locking to mitigate laser thermal drifts. However, there is another CH$_4$ absorption feature that overlaps with the N$_2$O reference signal (Figure 5.3),
representing a potential interference for the \( N_2O \) reference signal even with multi-harmonic spectral fitting. This is especially of concern when measuring high \( CH_4 \) mixing ratios near emission sources or for longer path lengths. This spectroscopic 6f interference will be investigated in future experiments.

Finally, while open path-integrated sensor for \( CH_4 \) detection at 8 \( \mu \)m were achieved in an Arctic field environment, this open path-integrated sensing configuration can be applied for other trace gas measurements such as \( NH_3 \) by using a different wavelength laser (9.06 \( \mu \)m) and ethylene in-line reference cell. This would be similar to the detection method described in Chapter 3 and Miller et al. (2014) but in a long optical path configuration. The main considerations for implementing this system for open path-integrated \( NH_3 \) measurements would be accounting for potential optical saturation near large source regions at kilometer-scale path lengths, sufficient laser optical power (ideally 10s of mW), collimation for adequate received optical power, and custom optical coatings for 9.06 \( \mu \)m. Based on previous mobile \( NH_3 \) measurements presented in Chapter 4 near large sources, we expect much larger relative changes in \( NH_3 \) mixing ratios than for \( CH_4 \). The precision and accuracy requirements for atmospheric \( NH_3 \) detection are also not as strict as for \( CH_4 \).

### 5.6 Summary

The open path-integrated quantum cascade laser-based \( CH_4 \) sensor was designed for field operation in an Arctic field environment. The QC laser beam was successfully aligned across Toolik Lake in August 2012 at round-trip distances up to 1.29 km. High precision (0.5 % in 1 s) measurements were achieved. Robust field measurement capabilities were demonstrated, including operation in both snowfall and rainfall events. The open path-integrated sensor inter-compared well with a commercial \( CH_4 \) sensor and captured large variations in ambient mixing ratios during the inter-comparison experiment.
5.6.1 Future applications

This proof-of-concept field deployment demonstrated the capabilities of open path-integrated, QC laser-based sensing in Arctic and other field environments. Future designs will incorporate several refinements to address noise and drift sources discussed above, as well as miniaturization and weather-proofing. This technology is directly applicable for agricultural emission characterization, as well as leak detection from natural gas, industrial or waste facility activities. In particular, there is an urgent need to better constrain climate impacts of CH$_4$ natural gas leakage (Alvarez et al., 2012). These stationary remote monitoring capabilities can also be combined with other measurement configurations. For example, mobile measurements of agricultural emissions (such as in Chapter 4) can be performed in the vicinity of stationary open path-integrated measurements. Since open path-integrated sensors can be deployed for long-term monitoring, combining these measurement platforms can allow for assessments of both spatial and temporal emission variations. Finally, open path-integrated measurements at long (kilometer) path lengths can be directly compared with regional air quality model simulations to constrain model uncertainties and validate modeled emission inventories.

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Chapter 6

Conclusions and implications for future studies

6.1 Summary and conclusions

In this final chapter, I summarize the major findings and conclusions of each chapter:

6.1.1 Aerosol data set synthesis to assess long-range transport and air quality impacts from biomass burning smoke emissions

Biomass burning aerosol emissions have wide-ranging influences on air quality and radiative processes. Aerosol emissions can be transported long distances (thousands of kilometers) downwind and impact surface air quality. However, typical medium-intensity biomass burning smoke plumes are difficult to detect and distinguish from other pollutants, especially long distances downwind of the source region. Aerosol observations on multiple spatial scales from ground-based to column and vertically-resolved measurements are required to constrain these impacts. In Chapter 2, I addressed these issues by analyzing a case study of smoke plumes from a typical summer boreal forest fire in western Canada. In this study, I integrated a suite of relevant ground-based and remote sensing aerosol measurements over North America to
track smoke plume physical and chemical evolution and long-range transport. The observed
smoke plumes contributed an increase of $\sim 10-20 \mu g m^{-3}$ PM$_{2.5}$ and EPA 24-hour PM$_{2.5}$
standard exceedances along the U.S. East Coast, 3000 km downwind of the source region.
The synthesis of multiple data sets enabled a more comprehensive understanding than any
individual data set considered separately. These results imply that long-range transport of
typical boreal forest fires can have significant influences on U.S. air quality, which may increase
due to predicted increases in wildfire frequency under future climate change.

6.1.2 Open-path, quantum cascade laser-based ammonia sensing
technology for high resolution, in-situ measurements

Atmospheric NH$_3$ is an important fine aerosol precursor with increasing, highly variable an-
thropogenic emission sources. Currently, there is a lack of widespread in-situ NH$_3$ measure-
ments due to measurement challenges, including surface adsorption and partitioning artifacts
in common, high resolution closed-path NH$_3$ sensors. In Chapter 3, I addressed the challenges
for in-situ NH$_3$ sensing by developing and field testing a quantum cascade laser-based, open-
path NH$_3$ instrument capable of high precision (0.15 ppbv NH$_3$), high time resolution (10
Hz) field measurements in a compact ($\sim 15$ kg), low power ($\sim 50$ W) sensor footprint. This
novel, open-path sensor probes fundamental mid-infrared NH$_3$ absorption transitions with a
quantum cascade laser at 9.06 $\mu m$. Multi-harmonic wavelength modulation spectroscopy is
used to isolate overlapping absorption features. An in-line ethylene reference cell is used for
online calibration ($\pm 20\%$) and normalization to account for sensor drift. The open-path
configuration minimizes sampling biases due to adsorption or gas-particle phase partitioning
common in existing, in-situ NH$_3$ sensors. This approach does not require powerful pumps
or temperature control systems, allowing for a lower-power, portable design applicable to a
range of stationary and mobile field measurement platforms. Thus, the compact, open-path
sensing technology presented in Chapter 3 is a significant advance for in-situ atmospheric NH$_3$
measurement capabilities to constrain uncertain and highly variable NH$_3$ emission sources.
6.1.3 Ammonia dairy emission ratio analyses based on open-path, mobile NH\textsubscript{3} and CH\textsubscript{4} measurements in the Central Valley, California

Agricultural NH\textsubscript{3} emissions are significant, yet highly uncertain due to high spatial and temporal variability and a lack of wide-spread in-situ measurements. The spatial variability of intensive agricultural emission sources is important for assessing impacts on ammoniated aerosol formation. There is an urgent need for high time resolution, fast-response, extensive spatial NH\textsubscript{3} measurements to constrain dairy emission sources in high source regions such as the Central Valley, California. In Chapter 4, I characterized NH\textsubscript{3} dairy emission spatial variability by performing novel, open-path, mobile measurements of NH\textsubscript{3} and CH\textsubscript{4} in the intensive Tulare dairy farm region of the Central Valley. High spatial variability of NH\textsubscript{3} and CH\textsubscript{4} mixing ratios was observed, with maxima localized downwind of individual dairy farms and mean background NH\textsubscript{3} and CH\textsubscript{4} mixing ratios enhanced in the Tulare dairy region. The median NH\textsubscript{3}:CH\textsubscript{4} emission ratio observed was 0.16 ± 0.03 ppmv ppmv\textsuperscript{−1}, with a heavy-tailed distribution of extreme maxima. A case study analysis illustrated spatial variability of emission ratios at sub-farm scales. These results provide a new evaluation of NH\textsubscript{3} emission ratio statistical distributions across multiple dairy farms to expand on previous individual farm studies. The mobile measurement median NH\textsubscript{3}:CH\textsubscript{4} emission ratio was comparable to aircraft integrated emission ratios derived from collocated DISCOVER-AQ P3-B aircraft transects, but less extreme values were observed for the aircraft integrated emission ratio distribution. This comparison has implications for evaluating field-scale measurements in the context of regional aircraft observations in this intense agricultural source region.
6.1.4 Open path-integrated, quantum cascade laser-based sensor development for harsh field environments

Atmospheric measurements on spatially integrated scales are advantageous for capturing variability across larger spatial scales than traditional point measurements. Currently, there have been no open path-integrated sensors demonstrated with the capabilities for high precision and high stability field measurements at kilometer-scale path lengths in real-world field environments. In Chapter 5, I developed and field tested a novel open-path, quantum cascade laser-based CH$_4$ sensor for long path-integrated sensing in an Arctic field environment. I focused on atmospheric CH$_4$ detection due to the stringent precision and stability requirements for atmospheric measurements. High short-term precision (0.5 % in 1 s) and 1% stability for up to 1 hour with an N$_2$O in-line reference cell were achieved for 459 m path length CH$_4$ measurements at Toolik Lake, Alaska. The open path-integrated QC laser sensor intercompared well with a commercial point sensor for one-hour averaged measurements. The high optical power QC laser provided high precision sensing capabilities at long optical path lengths up to 1.29 km, with low electrical power requirements. These features are advantageous for operation in a remote field environment. The open path-integrated technology is applicable for future NH$_3$ measurements on spatial scales comparable to regional model resolutions.

6.2 Implications for future studies

6.2.1 Implications for assessing aerosol emission and long-range transport impacts with multi-scale aerosol observations

As discussed in Chapter 2, synthesizing multiple aerosol observation data sets is an advantageous approach to constrain biomass burning smoke aerosol emission long-range transport and air quality influences. This approach provides a framework for synthesizing satellite and ground-based physical, chemical and optical aerosol measurements with trajectory model re-
sults and meteorological fields using the existing aerosol observation network that operates continuously over North America. This technique implemented in Chapter 2 is valuable for future studies over longer (seasonal to annual) timescales to assess temporal and spatial variability of aerosol plume transport, transformation and downwind impacts. Future chemical transport model simulations of aerosol plume evolution can be validated by comparisons with the multiple aerosol data set approach. In addition, future model simulations can provide a more complete picture by filling inherent observational gaps in each in-situ or remote sensing data set.

The ability to track smoke plume long-range transport has implications for assessing air quality degradations from anthropogenic and natural aerosol sources. In particular, the combination of HYSPLIT back trajectories and CALIOP vertical profiles analyzed in Chapter 2 provided an opportunity to constrain both vertical and horizontal plume extent. As illustrated in Chapter 2, upper level plumes must be entrained into the boundary layer to influence surface air quality. Methods to track vertical transport and incorporation of aerosol plumes into the boundary layer are especially advantageous for future analyses. This is particularly important for plumes mixed with other local and regional sources, which are difficult to discern and quantify using any aerosol data set individually.

The smoke plume observations in this study have implications for modeling efforts to constrain uncertain biomass burning aerosol influences on air quality and climate. In particular, as discussed in Chapter 2, high altitude absorbing smoke aerosols were embedded in clouds. These results have implications for future radiative transfer model simulations to fully quantify uncertain indirect radiative effects of elevated biomass burning smoke aerosols. In addition, elevated total column aerosol optical depths cause significant visibility impairments and regional haze. Future studies can use the observations from our case study to evaluate the impacts of typical, medium-intensity boreal forest fires on U.S. regional haze with implications for regulations in pristine regions. Finally, this case study has implications for future
climate change impacts on wildfire frequency and the associated trends in episodic air quality degradation events.

6.2.2 Implications for future high resolution, open-path ammonia emission flux measurements

The compact, open-path, quantum cascade laser-based atmospheric NH$_3$ sensing capabilities described in Chapter 3 provide unique opportunities for future measurement applications to address NH$_3$ emission uncertainties. The open-path configuration provides fast (> 1 Hz) time response field measurements with minimal sampling biases, a clear advantage compared with existing high resolution, closed-path NH$_3$ sensors. This platform does not require powerful pumps or temperature control systems commonly implemented in state-of-the-art, closed-path NH$_3$ sensing systems. These components introduce additional challenges for long-term unattended field operation. The in-line reference cell approach provides continuous calibration to account for the challenges of drifts due to changing environmental conditions in open-path sampling cells. This technology is capable of significantly advancing in-situ NH$_3$ measurement capabilities for future NH$_3$ mobile and stationary emission flux measurements.

The open-path sensor precision (0.15 ppbv NH$_3$ at 10 Hz) and high time resolution (10 Hz) make it suitable for future open-path NH$_3$ eddy covariance flux measurements. Relatively few eddy-covariance NH$_3$ flux measurements have been attempted due to the lack of fast time response (> 1 Hz) analyzers. Significant limitations exist for recent measurements, including attenuation of high frequency concentration fluctuations (Whitehead et al., 2008) and flux under-estimations due to sampling inlet hysteresis effects with rapidly changing NH$_3$ concentrations (ppbv to ppmv) observed near emission sources (Brodeur et al., 2009; Sintermann et al., 2011). The high time resolution (10 Hz) and minimal adsorption time constant illustrated in Chapters 3 and 4 allow for future eddy covariance flux measurements to study NH$_3$ emission fluxes across the spatial footprint of a feedlot or other distributed NH$_3$ source regions. These measurements are applicable for constraining NH$_3$ emission temporal
variability as a function of environmental conditions and agricultural activities to expand on the spatial measurements performed in Chapter 4.

The path-integrated and eddy covariance applications discussed Chapter 5 and above are advantageous for stationary, long-term measurements to quantify the temporal variability across a farm scale spatial footprint. The path-integrated sensor demonstrated for CH\textsubscript{4} measurements (Chapter 5) can be applied for agricultural emission measurements of CH\textsubscript{4} and easily extended to NH\textsubscript{3} measurements. For high concentrations observed near feedlots (Chapter 4), much lower paths lengths than demonstrated in Chapter 5 would be necessary to achieve comparable sensitivities.

The mobile and path-integrated measurement approaches can also be coupled with open-path eddy covariance flux and vertically-resolved NH\textsubscript{3} measurements in future investigations. The mobile measurements can probe horizontal plume structures upwind and downwind of sources and estimate NH\textsubscript{3} deposition losses, as explained in Chapter 4. Currently, NH\textsubscript{3} emission plume vertical structures are highly uncertain, with essentially no vertically-resolved measurements in the surface layer above agricultural livestock facilities. Vertical distributions are essential for constraining plume dispersion model parameters. The low power, compact NH\textsubscript{3} sensor (Chapter 3) is applicable for future deployments on airborne platforms (helicopter, tethered balloon or unmanned aerial systems) for horizontal and vertically-resolved, open-path NH\textsubscript{3} measurements. Future studies combining surface mobile and path-integrated techniques with airborne measurements will offer comprehensive capabilities to quantify both spatial and temporal emission distributions. These capabilities have implications for informing agricultural best management practices for future NH\textsubscript{3} emission mitigation strategies.

6.2.3 Implications for validations of ammonia satellite retrievals, emission inventories and air quality models

The spatial and temporal variability of NH\textsubscript{3} emissions is highly uncertain, with a lack of widespread in-situ NH\textsubscript{3} observations to validate emission inventories, model simulations and
satellite retrievals. The path-integrated and mobile measurement capabilities presented in Chapters 4 and 5 are applicable for future measurement comparisons on comparable spatial scales to satellite retrievals (e.g. 5 x 8 km satellite footprint), emissions inventory and model grid cells (e.g. 4 km CMAQ regional model). The implications for each of these comparisons are described below.

**Satellite retrieval validations**

Ground-based, open-path NH$_3$ measurements are applicable for validating recently developed tropospheric NH$_3$ satellite retrievals. As discussed in Chapter 1, TES and IASI satellite observations can provide large spatial coverage NH$_3$ retrievals, but suffer from some limitations and uncertainties. NASA TES can estimate NH$_3$ representative volume mixing ratios (RVMRs) sensitive to the boundary layer, but the retrieval is uncertain due to limited detection limit (e.g. $\sim 1$ ppbv) and contamination due to thermal inversions and clouds. Ground-based validations are urgently needed to quantify retrieval errors (Clarisse et al., 2010). The mobile measurements presented in Chapter 4 are applicable to future studies comparing the satellite retrieval transects with mobile measurement transects. This is particularly advantageous for validations in large source regions such as the Central Valley, California or the North China Plain where boundary layer thermal structure and aerosol haze influence retrieval sensitivities. In addition, mobile measurements performed over a relatively short time period can resolve NH$_3$ spatial variability within satellite retrieval footprints. Comprehensive retrieval validations are promising for more reliable, long-term and extensive spatial NH$_3$ monitoring in the future.

**Emission inventory validations**

Efforts to quantify NH$_3$ distributions with global and regional air quality model simulations have shown large discrepancies with observations due to significant emission inventory uncertainties. Future spatial and temporal NH$_3$ measurements have implications for constraining
the spatial allocation of emissions in model inventories, which currently rely on emission factors and parameterize farm activity distributions. The sub-farm scale emission ratio analyses in Chapter 4 also have implications for representing the sub-farm scale variability in emission inventories that currently assume a single emission factor value. In particular, the distribution of manure management activities across feedlots in agricultural regions can be further constrained with high resolution mobile measurements similar to those presented in Chapter 4.

**Air quality model comparisons**

Future modeling studies on aerosol precursor impacts must be constrained by comparisons with in-situ observations. Open-path NH$_3$ measurements on spatial scales comparable to model grid resolutions are advantageous to assess the predictive power of air quality models simulating inorganic aerosol loading. The mobile surface measurements presented in Chapter 4 are applicable to improving the representation of modeled NH$_3$ concentration spatial gradients. In addition, long-term stationary measurements harnessing path-integrated sensing capabilities have implications for assessing the degree to which models can accurately represent diurnal, seasonal and inter-annual NH$_3$ concentration variations. Finally, model simulations constrained by NH$_3$ observations are valuable to assess reduced nitrogen deposition trends and ecosystem impacts.

Ultimately, future observations are essential for accurately predicting air quality and aerosol impacts due to aerosol precursor emissions. Future analyses coupling measurements with regional air quality models are important to evaluate the impacts of NH$_3$ emissions on PM$_{2.5}$ and the associated policy implications. Reliable in-situ NH$_3$ observational constraints for fine particulate matter formation will be extremely valuable in the future to evaluate influences on air quality and climate.
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