Ammonia in Rural and Remote Environments

by

Gregory R. Wentworth

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Graduate Department of Chemistry
University of Toronto

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Department of Chemistry
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Abstract

Ammonia (NH₃) can harm ecosystems through deposition and react in the atmosphere to increase fine particulate (PM₂.₅) levels which impact climate and degrade air quality. Despite an abundance of field studies and modelling efforts there are still large uncertainties regarding the sources, sinks, and transport of NH₃. These uncertainties are magnified in rural and remote regions where measurements are sparse. The Ambient Ion Monitor – Ion Chromatograph (AIM-IC) was deployed on three separate occasions to measure hourly averages of ambient NH₃, SO₂, and HNO₃ as well as PM₂.₅ constituents (NH₄⁺, SO₄²⁻, NO₃⁻). AIM-IC measurements at a rural field in Ontario, in conjunction with soil measurements, revealed that a non-fertilized grassland exhibits bi-directional soil-atmosphere NH₃ exchange. A “morning spike” of NH₃ was occasionally observed around 7:00 to 9:00 local time and was investigated in a subsequent study at a remote park in Colorado. Simultaneous observations of dew composition, dew amount and NH₃ suggested that the frequently observed, yet currently unexplained, morning spike is caused by NH₃ released from evaporating dew.

The AIM-IC was operated aboard a research icebreaker throughout the Canadian Arctic Archipelago. NH₃ ranged between 30-650 ng m⁻³ and was usually sufficient to fully neutralize SO₄²⁻. Low values of NH₄⁺ in the Arctic Ocean and melt ponds revealed they were always a net NH₃ sink. Decomposing seabird guano and wildfires were identified as the primary NH₃ sources.
through the use of a chemical transport model (GEOS-Chem) and particle dispersion model (FLEXPART-WRF). Lastly, AIM-IC measurements from a campaign in the Athabasca Oil Sands Region showed that air masses that had recently passed over bitumen upgrading facilities were enriched in NH$_3$, SO$_2$, HNO$_3$, NH$_4^+$ SO$_4^{2-}$, and NO$_3^-$. Comparison of observed NH$_3$ to that predicted by the Extended – Aerosol Inorganics Model (E-AIM) implies that the aerosol system was in disequilibrium in polluted airmasses.
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This degree has been such a positive and eye-opening experience. I have learned more than I ever thought possible and have been extremely fortunate to be able to travel the world to pursue research I find so interesting. It really has been a fun five years.

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Chapter 1
Introduction

1 Chapter 1

1.1 Ammonia in the Atmosphere

Ammonia (NH$_3$) is the most abundant alkaline gas in the Earth’s atmosphere (Seinfeld and Pandis, 2006). For centuries NH$_3$ has been recognized as an efficient fertilizer and in the 1910s its commercial production surged due to the invention of the Haber-Bosch process (Sutton et al., 2013). The process was initially used to manufacture munitions and explosives but by the 1950s its main utility was the production of nitrogen-containing fertilizers. Prior to this much of the fertilizer for the Western world came from local manure recycling or costly imports of South American guano (seabird excrement) (Sutton et al., 2008). Production of NH$_3$ via the Haber-Bosch process continued to increase until present day and has allowed humankind to produce larger crop yields and a greater abundance of livestock than it would have been able to otherwise. Although beneficial for food security, the increased production of NH$_3$ has perturbed the natural nitrogen cycle and caused unforeseen environmental effects (Galloway et al., 2003; Sutton et al., 2008). As a result the emissions, transformation and deposition of NH$_3$ have been the subject of intensive study over the last four decades. Much of this work has focused on agricultural areas where anthropogenic input of NH$_3$ is high (Massad et al., 2010; Zhang et al., 2010). However, significant knowledge gaps still remain, such as large uncertainties for natural emissions and rudimentary (non-mechanistic) representations of NH$_3$-biosphere interactions in atmospheric chemical transport models (CTMs). This thesis aims to address several of these shortcomings by using field measurements to better understand the cycling of NH$_3$ in rural and remote environments.

1.1.1 Sources

The most recent global estimate for total NH$_3$ emissions is ~65 Tg N yr$^{-1}$ (Sutton et al., 2013). The agricultural sector is the largest contributor with animal husbandry (~9 Tg N yr$^{-1}$) and agricultural soils/crops (~28 Tg N yr$^{-1}$) accounting for over half of total emissions. Other anthropogenic sources include biomass burning (~6 Tg N yr$^{-1}$), fossil fuel burning (~2 Tg N yr$^{-1}$), humans and pets (~3 Tg N yr$^{-1}$) and waste processing (~4 Tg N yr$^{-1}$). Natural sources account for
the remainder: excrement from wild animals (~3 Tg N yr\(^{-1}\)), soils under natural vegetation (~2 Tg N yr\(^{-1}\)) and oceans/volcanoes (~9 Tg N yr\(^{-1}\)). However, these emission estimates are poorly constrained because of the diversity of sources, area-wide nature of emissions (i.e. large spatial extent) and paucity of underlying data (e.g. uncertainties in emission factors, animal statistics) (Pinder et al., 2006). Indeed there are significant differences between global NH\(_3\) emission inventories both in terms of total emissions and source classification (e.g. van Aardenne et al., 2001; Beusen et al., 2008; Bouwman et al., 1997; Dentener and Crutzen, 1994; Sutton et al., 2013). Some regional NH\(_3\) emissions inventories are better studied and more detailed, such as those for the Netherlands (Velthof et al., 2012), Denmark (Geels et al., 2012), Europe (Reis et al., 2009; De Vries et al., 2011), and the United States (Pinder et al., 2008; Reis et al., 2009). The majority of these studies have focused on improving estimates of anthropogenic emissions leading to comparably large uncertainties for natural sources, particularly in remote environments (Reis et al., 2009; Sutton et al., 2013). For instance, one recent study by Paulot et al. (2015) analyzed numerous datasets of atmospheric NH\(_3\) and seawater [NH\(_3\)] (=NH\(_3\) + NH\(_4^+\)) and found that oceanic NH\(_3\) emissions are only ~2.5 Tg N yr\(^{-1}\), significantly smaller than previous, less rigorous estimates (7-23 Tg N yr\(^{-1}\)) that have been used for decades in global inventories. Such large uncertainties in NH\(_3\) sources, especially in remote regions, makes it difficult to model, predict and mitigate environmental impacts of NH\(_3\) (discussed in section 1.1.4).

1.1.2 Sinks

The primary sinks of NH\(_3\) are dry and wet deposition due to its relatively high water solubility and “sticky” nature (Seinfeld and Pandis, 2006). The rate of dry NH\(_3\) deposition is dependent on NH\(_3\) mixing ratios, atmospheric stability, surface type (e.g. forest, grassland, snow) and surface properties (e.g. wetness, acidity). Deposition velocities range between 0.1-10 cm s\(^{-1}\) and are higher for wet, acidic surfaces and turbulent conditions (Schrader and Brümmer, 2014). Wet deposition is episodic as opposed to continuous and its effectiveness for scavenging NH\(_3\) is dictated by droplet size, composition and precipitation rate. NH\(_3\) loss from the atmosphere will be dominated by wet deposition in regions with heavy and frequent precipitation. Reaction with the hydroxyl radical (•OH) is relatively slow (\(k_{\text{OH}} = 1.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) at 298 K) corresponding to a lifetime against •OH oxidation of roughly 72 days at typical mid-latitude boundary layer conditions (Seinfeld and Pandis, 2006). By comparison, lifetime against dry
deposition in a 2000 m boundary layer is on the order of 2 hours to several days depending on meteorological conditions and surface type.

NH₃ can also partition into particles containing sulphuric acid (H₂SO₄) or sulphate (pSO₄²⁻, the dissolution product of H₂SO₄) to produce ammonium sulphate ((NH₄)₂SO₄) and/or ammonium bisulphate (NH₄HSO₄):

\[
\text{NH}_3(g) + \text{H}_2\text{SO}_4(s, aq) \rightarrow \text{NH}_4\text{HSO}_4(s, aq) + \text{NH}_3(g) \rightarrow (\text{NH}_4)_2\text{SO}_4(s, aq) \tag{R1.1}
\]

Although NH₃ reacts preferentially with H₂SO₄/pSO₄²⁻ it can also react with other acidic trace gases (e.g. HNO₃, HCl, organic acids) in a similar fashion:

\[
\text{NH}_3(g) + \text{HNO}_3(g) \leftrightarrow \text{NH}_4\text{NO}_3(s, aq) \tag{R1.2}
\]

\[
\text{NH}_3(g) + \text{HCl}(g) \leftrightarrow \text{NH}_4\text{Cl}(s, aq) \tag{R1.3}
\]

However, these acid-base reactions are reversible, unlike the semi-reversible reaction with pSO₄²⁻, and the NH₃(g) ↔ pNH₄⁺(s,aq) equilibrium is dependent on mixing ratio of the acidic gases, particle composition, temperature, and relative humidity (RH). Therefore reactions R1.2 and R1.3 can be considered reservoirs of NH₃ as opposed to sinks. Typically pNH₄⁺ exists in particulate matter with diameters smaller than 2.5 µm (PM₂.₅) as opposed to coarse particles larger than 2.5 µm in diameter. The main losses of PM₂.₅ are wet and dry deposition, but these deposition rates are slower than for gas-phase NH₃ so pNH₄⁺ can have a total atmospheric lifetime of days to weeks (Seinfeld and Pandis, 2006). As a result, pNH₄⁺ can be transported hundreds or thousands of kilometers and has the potential to influence remote ecosystems far away from NH₃ sources.

### 1.1.3 NH₃ Bi-directional Exchange

Since the early 1980s it has been well-known that NH₃-surface interactions are not simply unidirectional (i.e. deposition only) but instead are bi-directional (i.e. deposition and emission are possible) (Farquhar et al., 1980; Lemon and Van Houtte, 1980). In other words, in each ecosystem there exists surface pools of dissolved NH₃ (e.g. stomata, soil, litter, cuticles, surface water, ocean) available for exchange with the atmosphere. Each surface pool has a compensation
point (χ) which is defined as the atmospheric NH$_3$ mixing ratio below which net emission from the surface pool will occur (Farquhar et al., 1980; Sutton et al., 1995).

The χ framework is derived directly from Henry’s Law equilibrium which quantitatively describes the thermodynamic equilibrium of a given species between a solution and the overlying atmosphere (Sander, 2015). For instance, the Henry’s Law constant (K$_H$) of NH$_3$ is the ratio of the concentration of NH$_3$ in solution ([NH$_3$]$_{(aq)}$) to the partial pressure of NH$_3$ (P$_{NH3}$) above the solution at equilibrium (Sander, 2015):

$$K_H = \frac{[NH_3]_{(aq)}}{P_{NH3}} = 60 \text{ M atm}^{-1} \text{ (at 298 K)} \quad (E1.1)$$

Equation 1.1 is more complicated for species that ionize in solution due to acid-base equilibrium which results in greater solubility and a larger effective K$_H$. The dissociation equilibrium (NH$_3$(aq) $\leftrightarrow$ NH$_4^+$(_aq)) in solution is taken into consideration using the acid dissociation constant (K$_a$) of NH$_4^+$ according to (Bates and Pinching, 1950):

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]_{(aq)}} = 10^{-9.25} \text{ M (at 298K)} \quad (E1.2)$$

Where [NH$_4^+$]$_{(aq)}$ and [H$^+$] are the ammonium and hydronium ion concentrations in solution, respectively. The temperature dependence of E1.1 and E1.2 are governed by the enthalpy of NH$_3$ vaporization (-34.18 kJ mol$^{-1}$) and enthalpy of NH$_4^+$ dissociation (52.21 kJ mol$^{-1}$), respectively, and can be applied using the van’t Hoff equation (Bates and Pinching, 1950; Sander, 2015). By combining E1.1 and E1.2, the temperature dependent equilibrium P$_{NH3}$ (analogous to χ) above a given solution can be predicted using the following equation:

$$P_{NH3} = \chi = 13587 \cdot \Gamma \cdot e^{-\frac{10396 K}{T}} \cdot 10^9 \quad (E1.3)$$

Where χ is given in units of parts per billion (ppb) or nmol mol$^{-1}$ (Nemitz et al., 2001, 2004), Γ is the emission potential (defined as $\Gamma = [NH_4^+]/[H^+]$ in solution), and T is the temperature (in K) of the surface. If χ exceeds the ambient NH$_3$ mixing ratio above the surface pool, then there will be net emission until equilibrium is achieved, and vice versa for net deposition. Surfaces that receive a large input of reactive N (e.g. fertilized agricultural fields, grazing pastures) will have a larger Γ and hence a greater propensity to be a net source of NH$_3$. Surface temperature also has a
strong effect; a ~5 °C increase will result in a doubling of $\chi$ at ambient temperatures (Riddick et al., 2012).

The bi-directional nature of NH$_3$-surface interactions adds significant complexity to estimating NH$_3$ deposition and lifetime since $\chi$ depends on nitrogen status, pH and temperature of the surface. These elements are susceptible to change on short timescales and are influenced by a multitude of biological (e.g. microbial turnover rates, plant type, soil type) and physical (e.g. sunlight, precipitation) factors (Flechard et al., 2013). Furthermore, there can be large variation in $\Gamma$ between surface pools within the same canopy such that one component can be a net source and another can be a net sink. For instance, Bash et al. (2010) found that fertilized soil in a Zea mays (corn) field was a strong source of NH$_3$ but, on average, ~70% of soil NH$_3$ emissions were recaptured by plant stomata. Measuring the rate of surface-air NH$_3$ exchange (i.e. overall net flux) and incorporating bi-directional exchange into models are described in Sections 1.3 and 1.4, respectively.

### 1.1.4 Environmental Impacts

Assessing environmental impacts of NH$_3$ is not trivial due to large uncertainties regarding sources as well as complex loss pathways and surface interactions. Nonetheless, it is well known that N-deposition can impact the ecology and health of ecosystems (Krupa, 2003; Liu et al., 2013). Excessive N-deposition can cause an ecosystem to transition from N-limited to N-saturated resulting in shifts in biodiversity (Bobbink et al., 2010; Wolfe et al., 2003). In addition, N-deposition can harm ecosystems via soil acidification (Fenn et al., 1998) and eutrophication (Burkart and James, 1999). Typically the majority of N-deposition to ecosystems is from NH$_x$ ($=\text{NH}_3+\text{NH}_4^+$) as opposed to other reactive-N species (e.g. NO$_x$, HNO$_3$, organic-N) and effects from NH$_x$ deposition are more adverse (Leith et al., 2002; Sutton et al., 2008). N-deposition is usually evaluated in relation to a site-specific critical load value (deposition rate beyond which negative environmental impacts are observed).

NH$_3$ can increase PM$_{2.5}$ mass by reacting with acidic precursor gases (e.g. HNO$_3$, HCl) or pSO$_4^{2-}$ to produce pNH$_4^+$. Elevated levels of PM$_{2.5}$ are linked to respiratory and cardiovascular disease (Brook et al., 2010; Nawrot et al., 2011; Pope et al., 2002) and cause reduced visibility. In addition to causing negative health effects, the extent of PM$_{2.5}$ neutralization (measure of the relative abundance of pNH$_4^+$ to the sum of acidic species) impacts climate-altering properties of
PM$_{2.5}$ such as scattering efficiency (Martin et al., 2004) and ice-nucleating (IN) ability (Abbatt et al., 2006). Scattering efficiency and IN ability influence climate via the aerosol direct and indirect effect, respectively. Gas-phase NH$_3$ can also impact climate by promoting new particle formation (NPF) via stabilization of sulphuric acid-water clusters (Kirkby et al., 2011). These particles can then grow to sizes that affect incoming solar radiation either directly (via scattering, reflection and absorption) or indirectly by acting as cloud condensation nuclei (CCN) and altering cloud lifetime and albedo. Lastly, certain heterogeneous chemical reactions occurring on PM$_{2.5}$ surfaces can be influenced by the presence of pNH$_4^+$ (Fickert et al., 1999).

Since NH$_3$ has the potential to impact ecosystem health, biodiversity, human health, climate and atmospheric chemistry it is crucial to understand the sources, transport and sinks of NH$_3$. These processes vary spatially and temporally, hence measurements in multiple locations (e.g. urban, agricultural, rural, remote) and at different timescales (e.g. intensive multi-week studies, decadal monitoring networks) are required to gain an adequate understanding of NH$_3$ cycling and its impacts so that effective mitigation strategies and policies can be developed.

### 1.2 Ammonia Measurement Techniques

Ambient mixing ratios of NH$_3$ vary greatly from less than 5 parts per trillion by volume (pptv) in remote regions (e.g. open ocean (Johnson et al., 2008; Norman and Leck, 2005) or northern forests (Janson et al., 2001)) to greater than 500 ppbv near large sources (e.g. wheat field following fertilization (Personne et al., 2015)). At most ground sites NH$_3$ exhibits a distinct diurnal trend with maximum mixing ratios observed mid-day due to the temperature sensitivity of many NH$_3$ sources (Pinder et al., 2006). Another commonly reported feature in many environments is a second NH$_3$ peak in the mid-to-early morning at ~7:00 to 10:00 local time (e.g. Bash et al., 2010; Ellis et al., 2011; Gong et al., 2011; Löflund et al., 2002; Nowak et al., 2006; Walker et al., 2006; Whitehead et al., 2007; Wichink Kruit et al., 2007). Despite the ubiquity of this morning feature there is still uncertainty as to its origin(s), although hypotheses include: plant/soil emissions, dew evaporation, morning traffic, and break-up of the nocturnal boundary layer.

In addition to high-temporal variability, several other factors complicate ambient NH$_3$ sampling, particularly at low mixing ratios. First, NH$_3$ is an inherently “sticky” molecule and is known to experience substantial inlet losses and slow response times (Yokelson et al., 2003). Secondly,
humans are a source of NH$_3$ so care must be taken to prevent contamination in pristine environments (Sutton et al., 2000). Lastly, NH$_3$ undergoes gas/particle partitioning (Section 1.1.2) which can impact NH$_3$ measurements if the inlet and/or sampling technique perturb this equilibrium away from ambient conditions (Mozurkewich, 1993). Therefore, when studying NH$_3$ it is advantageous to also have simultaneous measurements of pNH$_4^+$, pSO$_4^{2-}$ and pNO$_3^-$ as well.

The instruments discussed in this section are by no means an exhaustive list. Techniques pertinent to projects in this thesis are discussed in greater detail, and those which are commonly used but not employed in this work are discussed in less detail.

1.2.1 Traditional (Offline) Techniques

There are several key advantages to offline techniques: low-cost and simplicity. Passive samplers are a subset of offline techniques and are often used for long-term studies in remote environments where supplying power and shelter is difficult. For instance, Adon et al. (2010) created an extensive 10-year monitoring network of NH$_3$ passive samplers across Africa to provide a unique dataset of NH$_3$ concentrations in a region severely underrepresented in the literature. A similar approach yielded simultaneous NH$_3$ measurements (bi-weekly averages) at 74 sites across Southern Ontario and was used to help constrain the regional NH$_3$ emission inventory (Hu et al., 2014; Yao and Zhang, 2013). Such passive sampler networks can provide measurements across a sufficient spatial extent to evaluate regional or global chemical transport models (CTMs) (Puchalski et al., 2011).

Passive samplers consist of a sampling pad impregnated with a sorbent to capture the gas of interest. The rate of accumulation (diffusion) on (to) the pad must be calibrated for prior to deployment and is governed by temperature, RH, pressure, and housing design. After exposure to ambient air the pads are brought back to a lab and extracted into a solution. The total amount of NH$_3$ captured by the pad is quantified as NH$_4^+$ in solution by either a colourmetric or chromatographic method. Their efficacy for measuring NH$_3$ has been validated (e.g. Roadman et al., 2003; Walker et al., 2004) and passive samplers typically have an accuracy better than 20% (Sutton et al., 2001). One major drawback is the slow rate of diffusion which necessitates a lengthy (on the order of weeks) sampling time.
Using a pump to actively draw air through a denuder and/or filters reduces the sampling time required to achieve sufficient sample for analysis. Allen et al. (1988) used two filters in succession to capture pNH$_4^+$ on a coarse (0.5 µm pore diameter), uncoated PTFE filter followed by a coated filter paper impregnated with a 5% phosphoric acid solution to capture NH$_3$. However, this technique is prone to loss of NH$_3$ to the aerosol filter as well as volatilization of NH$_4$NO$_3$ or NH$_4$Cl from the coarse filter and recapture on the second filter. The denuder technique avoids these complications since it relies on accumulation of NH$_3$ on an acid-coated surface (usually glass) via gas-phase diffusion (Ferm, 1979). Particulate ammonium has sufficient inertia to follow the laminar flow through the denuder and, in theory, never contacts the acid-coated surface. Often these two techniques are used in tandem in a denuder/filter pack system (e.g. Benedict et al., 2013; Heald et al., 2012; Koutrakis et al., 1988). These systems contain several denuders coated with different materials to capture both basic (NH$_3$) and acidic (HNO$_3$, HONO, SO$_2$) gases followed by filters to capture PM$_{2.5}$. After sampling (usually for 24-48 hours) the denuders and filters are extracted in the same manner as passive samplers for quantification of NH$_3$, pNH$_4^+$, and other species of interest.

The need to extract samples offline (in a laboratory setting) makes these techniques labor-intensive and time-consuming. Furthermore, significant contamination can be introduced during the preparation, transport and extraction steps. In combination with the need for higher time resolution measurements, many studies use automated, online techniques for quantifying atmospheric NH$_3$.

1.2.2 Modern (Online) Techniques

Numerous online techniques based on wet-chemical analysis have been developed over the last several decades to avoid the limitations of offline sampling. For instance, Keuken et al. (1988) developed the annular Rotating Batch Denuder (RBD) which automatically collects water-soluble gases (NH$_3$, HNO$_3$, HCl, and SO$_2$) onto two wetted rotating annular denuders over the course of 40 min. Each sample is automatically pumped into a vial for subsequent analysis and the denuder coating is regenerated for the next run. Samples are analyzed for NH$_4^+$ (dissolved NH$_3$) using a flow injection analyzer (FIA) and conductivity detector (Genfa and Dasgupta, 2000). FIA is a two-step process: first, sufficient base is added to the solution to convert NH$_4^+$ to gas-phase NH$_3$ which crosses a semi-permeable membrane. Second, NH$_3$ is dissolved in a
counter flow of deionized water and quantified as \( \text{NH}_4^+ \) via conductivity. The acidic gases (HNO\(_3\), HCl, SO\(_2\)) are typically quantified using anion chromatography.

A similar technique is the Ammonia Measurement by ANnular Denuder sampling with online Analysis (AMANDA). It uses three annular wet rotating denuders at separate heights and the denuder solutions are continuously pumped to a FIA for quantification (Wyers et al., 1993). The AMANDA offers improved sampling time (7.5 min for all three heights), better background correction (deionized water used in the stripping solution is constantly monitored), near-continuous data reporting, and the ability to measure concentration gradients with height (see Section 1.3). The AiRRmonia (Mechatronics Instruments, Hoorn, NL) is a commercially available, updated version of the AMANDA (Erisman et al., 2001). Upgrades include a more user-friendly interface/sampling software, Teflon membrane (as opposed to rotating glass denuders), and syringe pumps for better stability of liquid flow rate.

Due to the potential for NH\(_3\) to undergo rapid gas-particle partitioning, it is advantageous for an instrument to simultaneously measure components of \( \text{PM}_{2.5} \) (\( \text{pNH}_4^+ \), \( \text{pSO}_4^{2-} \), \( \text{pNO}_3^- \)) in addition to NH\(_3\). One such instrument is the Wet-Annular Denuder/Steam Jet Aerosol Collector (WAD/SJAC) developed by Trebs et al. (2004). The system collects and analyzes water-soluble gases using a WAD in a manner analogous to the AMANDA (Wyers et al., 1993). Downstream of the WAD is a SJAC (Khlystov et al., 1995; Slanina et al., 2001) which grows \( \text{PM}_{2.5} \) hygroscopically and then collects the supermicron droplets in a reservoir of high purity steam. In other words, the WAD/SJAC components separate then collect water-soluble gases and \( \text{PM}_{2.5} \) in aqueous reservoirs. The solutions are then automatically analyzed for \( \text{NH}_4^+ \) (originally NH\(_3\) or \( \text{pNH}_4^+ \)) and anions (\( \text{SO}_4^{2-} \) for \( \text{SO}_2/\text{pSO}_4^{2-} \), \( \text{NO}_3^- \) for HNO\(_3/\text{pNO}_3^- \), \( \text{NO}_2^- \) for HONO/\( \text{pNO}_2^- \), \( \text{Cl}^- \) for HCl/\( \text{pCl}^- \)) using a FIA and anion chromatograph, respectively. The system is commercially available under the name Monitor for AeRosols and GAses in ambient air (MARGA, Metrohm-Applikon B.V., the Netherlands). The MARGA uses ion chromatography to analyze both channels allowing for a greater suite of cations (e.g. Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\)) to be measured (ten Brink et al., 2007; Rumsey et al., 2014).

The Gas/Particle Ion Chromatograph (GP-IC, Ullah et al., 2006) and Ambient Ion Monitor-Ion Chromatograph (AIM-IC, Markovic et al., 2012) are two other semi-continuous, online systems that automatically quantify both water-soluble gases and ions in \( \text{PM}_{2.5} \) using ion
chromatography. They differ from the WAD/SJAC and MARGA since they both use a parallel-plate wet denuder (PPWD) to scavenge water soluble gases (Takeuchi et al., 2004). The PPWD consists of two membranes (made from either cellulose acetate or nylon) separated by ~2 mm in a polycarbonate housing. The membranes have a solution continually flowing through them. Unlike the WAD or rotating glass denuders, the PPWD is insensitive to orientation and has a rapid replenishment rate. For particle collection the GP-IC has a second channel containing a particle collection system (PCS) downstream of a PM$_{2.5}$ size-cut cyclone and PPWD. The PCS is a continuously wetted filter which traps PM$_{2.5}$ for analysis (coarse particles and gases were removed in the first two stages). One downside to the GP-IC is it uses FIA for NH$_3$ and pNH$_4^+$ analysis so is insensitive to other cations. On the other hand, the AIM-IC uses ion chromatography for both the anion and cation channels so it can quantify a wider range of species, similar to the MARGA.

Since the AIM-IC is the principal measurement technique used for several studies in this thesis (see Chapters 2, 4 and 5) it is described here in detail. As shown in Fig 1.1, the AIM-IC consists of two main components: 1) the AIM 9000D (URG Corp., Chapel Hill, USA) used to separate and collect gases/PM$_{2.5}$, and 2) two IC systems (ICS-2000, Dionex Corp., Sunnyvale, USA) for near-real time quantification of dissolved anions and cations. Ambient air is first pulled through a PM$_{2.5}$ impactor at a rate of 3.0 L min$^{-1}$ to remove coarse particles. Air then enters the parallel plate wet denuder (PPWD) which is continuously regenerated with a dilute H$_2$O$_2$ solution (2-10 mM) in deionized water (DIW). Particles have sufficient inertia to pass through into the particle supersaturation chamber (PSSC) which introduces DIW steam into a glass cyclone. The PSSC efficiently captures and dissolves water-soluble components of PM$_{2.5}$. The impactor, PPWD and PSSC are housed in a custom-made aluminum inlet box and connected to the aqueous reservoirs, sample syringe pumps, air pump and IC systems through a ~20 m heated (40 °C) sampling line (Markovic et al., 2012). This is a significant improvement to the standard commercial set-up since it allows for the dissolution of atmospheric analytes to occur immediately after the impactor. Normally air is pulled through tubing into the trailer housing the entire AIM-IC set-up which can result in significant and hard-to-characterize wall losses for PM$_{2.5}$ and “sticky” gases (e.g. NH$_3$, HNO$_3$). Furthermore, the inlet box can be mounted atop a tower allowing the operators more freedom for choice of sampling location.
Solution containing dissolved gases and PM$_{2.5}$ are pulled through the sampling line separately at 10 mL hr$^{-1}$ resulting in a residence time of 1 hr in the line. Both aqueous samples (10 mL for gases and 10 mL for particles) are then split into four 5 mL glass syringes (Hamilton Co., Reno, USA) – the syringes correspond to the anion gas, anion particle, cation gas and cation particle channels. After one hour of collection each ~5 mL sample is separately injected into an anion and cation IC for quantification. Each IC is calibrated offline by manual injection of aqueous standards several times during each field campaign (usually beginning and end). The IC calibration curves and air flow rate are used to calculate the corresponding atmospheric concentration (in mol m$^{-3}$) of each analyte. In addition, several “zero air experiments” are performed per campaign to characterize the background signal of the AIM-IC. High-purity zero air (AI 0.0 UZ-T, PraxAir, Toronto, Canada) is used to overflow the inlet and the resulting IC signal during this period is used as the AIM-IC background for each analyte. Detection limits are
typically around 1-20 ng m\(^{-3}\) for a wide range of species in PM\(_{2.5}\) (Na\(^{+}\), NH\(_{4}^{+}\), K\(^{+}\), Mg\(^{2+}\), Ca\(^{2+}\), F\(^{-}\), Cl\(^{-}\), NO\(_{2}^{-}\), NO\(_{3}^{-}\), SO\(_{4}^{2-}\), PO\(_{4}^{3-}\), acetate, formate, oxalate) and precursors gases (NH\(_{3}\), HCl, HNO\(_{3}\), HONO, SO\(_{2}\)) as well as some short-chain alkyl amines in both phases (Markovic et al., 2012; VandenBoer et al., 2011, 2012).

The AIM-IC provides near-real time measurements (two hour delay due to collection and analysis) of hourly averages for both water-soluble gases and PM\(_{2.5}\). The system has previously been deployed in a wide range of environments such as Toronto, Canada (VandenBoer et al., 2011), an agricultural region in Southwestern Ontario (Ellis et al., 2011), Bakersfield, California (Markovic et al., 2014), Fort McMurray, Canada (Hsu and Clair, 2015), Ahmedabad, India (Sudheer and Rengarajan, 2015) and Antarctica (Legrand et al., 2012). The system was found to be in good agreement with a co-located Aerosol Mass Spectrometer (AMS, Aerodyne Research Inc., Ballerica, USA) for ambient measurements of pNH\(_{4}^{+}\), pSO\(_{4}^{2-}\) and pNO\(_{3}^{-}\) during the Toronto study (Markovic et al., 2012). Lab experiments have also confirmed the validity of AIM-IC measurements for NH\(_{3}\), pNH\(_{4}^{+}\), SO\(_{2}\), pSO\(_{4}^{2-}\), HNO\(_{3}\) and pNO\(_{3}^{-}\) by flowing known amounts of each analyte into the system at different concentrations and comparing measured versus predicted concentrations (Hsu and Clair, 2015; Markovic et al., 2012).

Other systems have the ability to measure NH\(_{3}\) at much faster timescales (from sub-second to minute). Some of these are spectroscopic instruments which make use of the characteristic rotation-vibrational absorption features of NH\(_{3}\) in the infrared region of the electromagnetic spectrum. For example, a commercially available Cavity Ring Down Spectroscopy (CRDS) instrument (EnviroSense 1000 Analyzer, Picarro Inc., Sunnyvale, USA) is a direct absorption technique that measures the decay of a laser pulse in a highly reflective cavity (Berden et al., 2000). The rate of signal decay (“ring-down time”) can be used to calculate the concentration of NH\(_{3}\) in the cavity. Quantum Cascade Laser Absorption Spectroscopy (QCLAS) also uses the absorption of NH\(_{3}\) at a particular wavelength to measure its ambient mixing ratio. Traditionally the optical cell has been closed-path (e.g. von Bobrutzki et al., 2010), but more recently open-path systems have been designed to avoid inlet and wall losses (Miller et al., 2014). There are several commercial QCLAS systems developed by Aerodyne Inc. capable of measuring NH\(_{3}\) with sub-second frequency, such as the multichannel DUAL-QCLAS (Whitehead et al., 2008) and the compact QCLAS (c-QCLAS, McManus et al., 2007).
Chemical Ionization Mass Spectrometry (CIMS) is another high time resolution and high sensitivity technique that is used to measure ambient NH₃. Ambient air is pulled into the CIMS where it interacts with a reagent ion to selectively ionize species of interest in the air flow. A common reagent ion for NH₃ detection is the protonated acetone dimer (H⁺(C₃H₆O)₂) due to its high selectivity for NH₃ (Nowak et al., 2007). The product ions formed from the interaction of gaseous NH₃ and H⁺(C₃H₆O)₂ are then detected using a mass analyzer.

The measurement technique(s) of choice should have sufficient temporal resolution, precision, and accuracy to answer the scientific hypotheses of interest. For instance, weekly or monthly resolution provided by passive samplers is adequate for analyzing seasonal trends in NH₃ mixing ratio across a large spatial gradient. However, most environmental factors influencing NH₃ mixing ratios and gas-particle partitioning change on the timescale of minutes to hours (e.g. temperature, precipitation, RH, wind direction) so faster resolution is often necessary. Studies using eddy covariance (see Section 1.3) require even more rapid (sub-second) NH₃ measurement frequency that can only be achieved by more complicated, high-end techniques such as the QCLAS.

1.3 Measuring NH₃ Fluxes

Over the last several decades there has been great interest in measuring air-ecosystem NH₃ fluxes (the rate of mass transfer across an area) in order to assess and constrain bi-directional exchange. The simplest measurement method uses dynamic chambers (DC). With this technique air is pumped through a chamber encapsulating a small section (~30 by 30 cm) of ground/vegetation and NH₃ mixing ratios are measured at both the entrance and exit of the chamber (e.g. David et al., 2009; Husted and Schjoerring, 1995). The flux can then easily be calculated using ΔNH₃, flow rate, and chamber footprint. Advantages to DC include the ability to easily manipulate plant/soil dynamics (e.g. fertilize the soil, shade the plant), ease-of-operation and suitability for examining plant-scale processes. However, extrapolating the data to real, canopy-scale fluxes is complicated by many factors such as wall losses, perturbations in environmental conditions (e.g. light, rainfall, temperature) and unrealistic turbulence.

Another commonly used technique is the aerodynamic gradient method (AGM) that relies on multiple simultaneous measurements of NH₃ to provide a vertical gradient of NH₃ concentrations above the surface (Monteith and Unsworth, 2007). The flux is obtained by multiplying the
difference in NH\textsubscript{3} concentration between two measurement heights and the turbulent diffusion coefficient. The coefficient is an empirical parameterization which describes both the mechanical and turbulent diffusion between the two measurement points. It is often characterized by friction velocity (u*), air temperature and sensible heat flux. The primary advantages of AGM is it does not disturb the ecosystem and is suitable for long-term measurements (Zhang et al., 2010). However, the surface has to be relatively homogeneous over the fetch of the instrument, typically considered to be 100 times the measurement height. Furthermore, concentration gradients between different measurement heights can be small, requiring instruments with high precision. This can be achieved with wet chemical techniques discussed in Section 1.2.2. For example, Wichink Kruit et al. (2007) deployed the GRadient Ammonia High Accuracy Monitor (GRAHAM), which is an updated version of the AMANDA (see Section 1.2.2.), to simultaneously measure NH\textsubscript{3} at three different heights. The GRadient of AErosol and Gases Online Registrator (GRAEGOR) is an analogous instrument based on the MARGA (see Section 1.2.2.) capable of also measuring fluxes of HNO\textsubscript{3}, pNO\textsubscript{3}\textsuperscript{-} and pNH\textsubscript{4}\textsuperscript{+} (Wolff et al., 2010).

Unlike AGM, the Relaxed Eddy Accumulation (REA) technique does not rely on a stability correction function (turbulent diffusion coefficient). Instead, REA samples air at a single measurement height into two separate channels, one for updrafts and one for downdrafts (Businger and Oncley, 1990; Zhu et al., 2000). A valve is triggered by high frequency measurements of vertical wind to control the direction of air flow into the sampling inlet. This allows for the NH\textsubscript{3} measurement technique to have a slower response (~15 min to 1 hr). Fluxes can then be calculated by multiplying the difference in average NH\textsubscript{3} concentrations in the updraft and downdraft by the standard deviation of the vertical wind velocity and an empirical correction parameter. Since only one measurement height is required, REA can be used to study flux divergence by setting up multiple REA systems above the surface. However, substantial errors can arise from small concentration differences between updrafts and downdrafts, especially for small fluxes (Zhang et al., 2010). Hensen et al. (2009) performed an inter-comparison study of fluxes measured by four custom-built REA systems and the mean of several AGM systems described in Milford et al. (2009). All instruments used denuders to collect NH\textsubscript{3} and either conductivity or fluorescence with o-phtalaldehyde for wet chemical analysis. The study occurred in an intensively managed grassland over a four week period during which the grass was cut then fertilized. The REA systems yielded moderate to good correlation with flux estimates from the
AGM systems \((0.30 < r^2 < 0.82)\). The authors concluded that measuring NH\(_3\) fluxes with REA is possible; however, the systems are not yet robust or automated enough for long-term monitoring on the scale of months meaning AGM is still an attractive and more frequently used method.

The Eddy Covariance (EC) method is hailed as the most direct and least empirical option for measuring trace gas fluxes, but it demands extremely fast (up to 10 Hz) sensor response time. Vertical fluxes are calculated as the average product of the instantaneous deviations of a tracer (gas concentration) and vertical wind from the mean values over a typical averaging period of 30 minutes (Baldocchi et al., 1988). EC has been used to measure fluxes of a plethora of trace gases: \( \text{O}_3 \) (e.g. Wohlfahrt et al., 2009), \( \text{CO}_2 \) (e.g. Leuning and Moncrieff, 1990), \( \text{NO}_x \) (e.g. Geddes and Murphy, 2014) and \( \text{CH}_4 \) (e.g. Alberto et al., 2014). Studies using EC to measure NH\(_3\) fluxes are limited due to delayed response times related to the “sticky” nature of NH\(_3\). Sun et al. (2015) avoided inlet and wall losses by using an open-path QCLAS NH\(_3\) sensor developed by Miller et al. (2014). The open-path QC system has a sufficiently short path length to measure NH\(_3\) fluxes through EC with a reported detection limit of \(1.3 \pm 0.5 \text{ ng m}^{-2} \text{ s}^{-1}\) (Sun et al., 2015). This is an improvement on Sintermann et al. (2011) who used a CIMS operating with charged oxygen \((\text{O}_2^+)\) as the reagent ion to measure ambient NH\(_3\) fluxes with a detection limit of \(5 \text{ ng m}^{-2} \text{ s}^{-1}\). The primary reasons for the inferior detection limit are wall/inlet losses of NH\(_3\) as well as an interference with \(\text{H}_2\text{O}\) in the mass spectrometer.

### 1.4 Modelling NH\(_3\) Bi-Directional Exchange

#### 1.4.1 Field-Scale Models

Modelling the interactions between NH\(_3\) and surfaces (whether unidirectional or bi-directional) is most often done using a resistance analogy where the flux between two points \((F_{1,2})\) is calculated as the difference in concentration \((\chi_2 - \chi_1)\) divided by the resistance to transfer between those two points \((R_{1,2})\):

\[
F_{1,2} = \frac{\chi_2 - \chi_1}{R_{1,2}}
\]

An example of a canopy deposition (unidirectional) NH\(_3\) resistance scheme is given in Fig. 1.2a (Flechard et al., 2013). The scheme includes three components that NH\(_3\) can deposit to, each with their own resistance (units of \(\text{s m}^{-1}\)): plant stomata \((R_s)\), cuticle \((R_w)\), and the ground \((R_g)\).
Resistances represent physical or chemical processes that hinder transport between two points. The concentration of NH$_3$ at some point ($z$) above the canopy is given as $\chi_a(z)$. Above-canopy resistances $R_a$ (aerodynamic resistance) and $R_b$ (quasi-laminar resistance) represent the degree of macro- and molecular-scale turbulence, respectively. In this example the canopy compensation point ($\chi_c$) is set equal to zero. As a result, the net flux ($F_t$) can be described by:

$$F_t = -\frac{\chi_a}{R_a + R_b + R_c}$$

(E1.5)

Where a negative flux indicates deposition to the surface, and $R_c$ is the total canopy resistance parameterized as the following resistances in parallel:

$$\frac{1}{R_c} = \frac{1}{R_s} + \frac{1}{R_w} + \frac{1}{R_g}$$

(E1.6)

In this scheme (Fig. 1.2a) the deposition velocity ($v_d$) is calculated as the inverse of the sum of $R_a + R_b + R_c$ and denotes the speed at which NH$_3$ is deposited to the surface. The same framework is used to model the dry deposition of other gas-phase pollutants (e.g. O$_3$, SO$_2$) as well (e.g. Chameides, 1987; Zhang et al., 2003).
Figure 1.2 Surface-atmosphere schemes for net NH$_3$ canopy-scale fluxes for typical (a) deposition only model and (b) bi-directional exchange model for a vegetated surface. Adapted from Flechard et al. (2013).

Figure 1.2(b) is an example of a more complete surface-atmosphere scheme for NH$_3$ since it allows for bi-directional exchange. Net flux between the ecosystem and atmosphere ($F_t$) can be calculated using:

$$F_t = -\frac{\chi_a - \chi(z_0)}{R_a}$$  \hspace{1cm} (E1.7)

Where $\chi(z_0)$ is the NH$_3$ concentration at the top ($z = 0$) of the ecosystem equal to:

$$\chi(z_0) = \frac{\chi_a R_a^{-1} + \chi_g R_g^{-1} + \chi_c R_b^{-1}}{R_a^{-1} + R_b^{-1} + R_g^{-1}}$$  \hspace{1cm} (E1.8)

The terms $\chi_g$ and $R_g$ correspond to the ground (sum of soil and litter) compensation point and resistance, respectively. The canopy compensation point ($\chi_c$) is the critical term to solve for when determining the flux and, in this example, is given by:
\[
\chi_c = \frac{\chi_a}{R_a R_b} + \frac{\chi_s}{(R_a R_s + R_b R_s + R_g R_s)} + \frac{\chi_g}{R_b R_g}
\]

(E1.9)

Where \(\chi_s\), \(R_s\), and \(R_w\) represent the stomata compensation point and resistances to stomatal transfer and cuticular deposition, respectively. Individual fluxes across the foliage (\(F_f\), sum of stomata and cuticle), ground (\(F_g\), sum of soil and litter), stomata (\(F_s\)) and cuticle (\(F_w\)) can be calculated using E1.4 and the appropriate compensation points and resistances. Measurements of \([\text{NH}_4^+]\) and \([\text{H}^+]\) in the leaf apoplastic tissue and soil/litter are used as inputs to calculate \(\chi_s\) and \(\chi_g\), respectively, with E1.3. However, it is important to note that different extraction and measurement techniques lead to significant variability and uncertainty between studies (Cooter et al., 2010; Flechard et al., 2013; Li et al., 2012). Empirical relationships can also be used to predict \(\Gamma\) (and hence \(\chi\)) in studies where surface measurements are either lacking or insufficient to cover the duration of the study. Resistances (\(R_a\), \(R_s\), \(R_g\), \(R_{bg}\), \(R_w\) for Fig. 1.2b) are also calculated via empirically derived equations containing easily measured or estimated parameters (e.g. temperature, RH, leaf area index (LAI), atmospheric composition, land type, plant type, soil moisture). Empirical equations for resistances are derived from model-measurement comparison studies (e.g. Wesely, 1989). Further detail can be found in recent reviews (Flechard et al., 2013; Fowler et al., 2009; Massad et al., 2010; Zhang et al., 2010) which explore the development, optimization and uncertainties of the empirical relations for both resistances and \(\Gamma\).

The 2-layer framework in Fig 1.2b was first proposed by Nemitz et al. (2001) and has since been routinely used in field-scale \(\text{NH}_3\) bi-directional exchange studies (e.g. Cooter et al., 2010; Massad et al., 2010). Variations include simpler schemes, which exclude the soil/litter pool (e.g. Sutton et al., 1995, 1998), as well as more complex schemes which allow for exchange with surface water on plant cuticles (i.e. there exists a \(\chi_w > 0\)) (e.g. Burkhardt et al., 2009; Neirynck and Ceulemans, 2008). The differences in complexity and canopy representation reflect the wide range of ecosystems and surface types that have been studied.

Field-scale studies typically measure \(F_i\) (see section 1.3) and use an iterative approach to parameterize individual components (e.g. \(\Gamma_g\), \(\Gamma_s\), \(R_g\), \(R_s\), \(R_w\)) by minimizing the model/measurement differences for fluxes and/or \(\text{NH}_3\) mixing ratios. Massad et al. (2010) and Zhang et al. (2010) provide extensive reviews and a database of the \(\sim 100\) field-scale studies
which measure or estimate some or all components in Fig. 1.2b. This collation of data has highlighted the need for subsequent studies of surface-air NH₃ exchange in under-represented ecosystems (e.g. natural grasslands, oceans, rain forests, tropical regions). However, it is important to note that empirical relationships and bi-directional schemes derived for one field site often yield large discrepancies between modelled and measured fluxes or NH₃ mixing ratios when used at other sites (Flechard et al., 2013). These site-specific parameterizations result in substantial uncertainties that hinder both the a) predictive capability of these models, and b) implementation of these schemes into larger-scale models.

1.4.2 Large-Scale Chemical Transport Models

The majority of regional and global scale chemical transport models (CTMs) still use deposition-only schemes decoupled from highly uncertain static (i.e. little-to-none temporal variation) emission inventories for NH₃ (Flechard et al., 2013; van Pul et al., 2009). The simplistic deposition scheme is usually derived from Wesely (1989), which parameterizes a pollutant-specific deposition velocity \( v_d \) calculated from an empirical canopy resistance \( R_c \), similar to Fig. 1.2a. Although this de-coupled treatment of NH₃ deposition and emission is incorrect (as shown by a plethora of studies outlined in previous sections) it is advantageous because of its simplicity and low-computational cost.

Only within the last decade have adequate parameterizations been developed to allow for implementation of bi-directional exchange in regional and global scale models. For instance Wichink Kruit et al. (2012) updated the European regional-scale model LOTOS-EUROS to include bi-directional NH₃ exchange using a resistance scheme from Wichink Kruit et al. (2010). The bi-directional scheme allows for exchange with the leaf surface and stomata (i.e. \( \chi_w \) and \( \chi_s \) are > 0). However, the model neglects exchange with a soil compartment (i.e. \( \chi_g = 0 \)) due to large uncertainties in parameterizing \( \Gamma_g \) at a regional-scale – this issue stems from a lack of field-level \( \Gamma_g \) measurements. Parameterizations derived in previous studies were used to model \( R_g \) (Erisman et al., 1994), \( R_s \) (Emberson et al., 2000), \( R_w \) (Sutton and Fowler, 1993), and both \( \Gamma_s \) and \( \Gamma_w \) were calculated from empirical relationships developed by Wichink Kruit et al. (2010). Relative to the base case (deposition only) the updated LOTOS-EUROS modelled higher NH₃ concentrations in nearly all grid cells due primarily to an increased lifetime as a result of slower dry deposition. This shifted NH₃ deposition from source regions (e.g. agricultural areas) to remote regions and
natural environments. Shifting the burden of nitrogen deposition to remote areas highlights the importance of incorporating bidirectional exchange in regional CTMs. The authors also included a compensation point for seawater ($\chi_{\text{water}}$) which resulted in improved model-measurement agreement for NH$_3$ in coastal regions. Overall, including bi-directional exchange better reproduced observed NH$_3$ mixing ratios across much of Europe, albeit with persistent underestimations in agricultural areas and overestimations in rural/remote areas.

Similar improvements were observed in a study by Bash et al. (2013) who coupled CMAQ (Community Multi-scale Air Quality model, a regional-scale CTM for the United States) to EPIC (Environmental Policy Integrated Climate agroecosystem model). The former was modified to allow bi-directional NH$_3$ exchange while the latter estimated soil [NH$_4^+$] and pH based on an inorganic soil nitrogen parameterization (Cooter et al., 2012) calculated from fertilizer application rates, timing and fertilization depth. Hence CMAQ-EPIC has the capability of modelling bi-directional NH$_3$ exchange in addition to providing a more accurate, dynamic and mechanistic representation of agricultural soil NH$_3$ emissions. The resistance scheme mimics Fig. 1.2b (Nemitz et al., 2001) and does not include a leaf surface pool (i.e. $\chi_w = 0$). Resistances were parameterized following Pleim and Ran (2011), with the exception of $R_w$ (Jones et al., 2007). $\Gamma_s$ and $\Gamma_g$ in non-agricultural areas were borrowed from Zhang et al. (2010) and Massad et al. (2010), respectively. Compared to the original CMAQ version (deposition only), CMAQ-EPIC had improved predictions of NH$_3$ wet deposition and ambient pNO$_3^-$ concentrations due to a shift in nitrate/nitric acid equilibrium from increased NH$_3$ levels (Bash et al., 2013).

Recently, Zhu et al. (2015) revised a global CTM (GEOS-Chem) to incorporate bi-directional NH$_3$ exchange as well as diurnal variations in livestock emissions. The scheme is very similar to that used in Bash et al. (2013) with details given elsewhere (Cooter et al., 2010; Pleim et al., 2013). The original version of GEOS-Chem used a static (constant) emission rate from livestock so the authors amended this by making emission rate a function of aerodynamic resistance and surface temperature and including a recently updated inventory for agricultural NH$_3$ emissions (Paulot et al., 2014). Emissions were enhanced during the day and reached a minimum overnight resulting in improved model-measurement comparisons for hourly averaged NH$_3$ mixing ratios. These changes generally increased simulated NH$_3$ mixing ratios and NH$_4^+$ wet deposition, especially in July. On the other hand, the updates were found to have little impact on a persistent overestimation of pNO$_3^-$ in GEOS-Chem in contrast to Bash et al. (2013).
It is noteworthy that although the general approaches of incorporating bi-directional exchange in Bash et al. (2013) and Wichink Kruit et al. (2012) are similar, the authors chose entirely different parameterizations of resistances and emission potentials. They also used slightly different resistance schemes (i.e. $\chi_w$ was lacking in the former and $\chi_g$ in the latter). This highlights the difficulties in generating parameterizations sufficiently representative for a grid cell in a regional or global CTM. Furthermore, the evaluation of such models is complicated by a scarcity of relevant measurements (e.g. $\text{NH}_3$ concentrations, $\text{NH}_3$ wet deposition) particularly in rural and remote areas. In areas where measurements do exist, direct model-measurement comparison is challenging given that point measurements may not be representative of a model grid cell average encompassing tens or hundreds of square kilometers.

Although recent advances in modelling $\text{NH}_3$ bi-directional exchange in large-scale CTMs is promising, the uncertainties in the modelled $\text{NH}_3$/$\text{NH}_5$ cycles are still substantial. Recently, Flechard et al. (2013) identified numerous features and measurements that could be realistically incorporated into or used to improve CTMs with $\text{NH}_3$ bi-directional exchange. Here is an abridged list of suggestions to provide context for work presented in subsequent chapters:

- Reducing uncertainties in emission factors of significant sources (e.g. fertilizer application, animal husbandry) via detailed, process-level studies
- More measurements of $\Gamma_g$ outside of agricultural areas – parameterizations for this term are highly uncertain due to a paucity of measurements
- Improved understanding of canopy-recapture of $\text{NH}_3$ emissions from soil and stomata
- Including leaf surface chemistry into modelling efforts – this will require adequate parameterization of micro- and macroscopic water films on leaf surfaces
- Expanding the datasets used to parameterize surface exchange modelling to include more field measurements for under-represented sources (e.g. natural terrestrial environments, oceans, biomass burning, tropical regions)
1.5 Research Objectives

Atmospheric NH\textsubscript{3} can lead to adverse health effects for both humans and ecosystems, and has the ability to impact climate. Despite its importance, the sources, transport and fate of NH\textsubscript{3} are poorly quantified, partly due to complex surface interactions and a shortage of observational constraints. These uncertainties are exacerbated in rural and remote environments where field studies are few and far between. As a result, there are significant challenges in modelling ambient NH\textsubscript{3} concentrations and NH\textsubscript{3} surface exchange at regional and global scales. Large model uncertainties hinder predictions of deleterious effects imparted by NH\textsubscript{3} and impedes the development of effective strategies to mitigate and regulate NH\textsubscript{3} pollution.

The primary goal of this thesis is to improve our understanding of the sources, sinks and cycling of NH\textsubscript{3} in rural and remote environments through much needed field measurements. Atmospheric NH\textsubscript{3} and other pollutants of interest (pNH\textsubscript{4}\textsuperscript{+}, SO\textsubscript{2}, pSO\textsubscript{4}\textsuperscript{2-}, HNO\textsubscript{3}, and pNO\textsubscript{3}\textsuperscript{-}) were measured in rural Southwestern Ontario (Chapter 2), at a high-elevation site in rural Colorado (Chapter 3), throughout the Canadian Arctic Archipelago (Chapter 4), and in the Athabasca Oil Sands Region (AOSR) of northeastern Alberta (Chapter 5). These atmospheric measurements were combined with simultaneous surface measurements of soil (Chapter 2), dew (Chapter 3) and the ocean/melt ponds (Chapter 4) and atmospheric modelling to help address the following questions:

- How does χ in different surface pools compare to ambient NH\textsubscript{3} in rural and remote environments? Can these surface pools be a significant source of NH\textsubscript{3}?
- What is the variability and magnitude of Γ\textsubscript{g} in non-fertilized fields and is it appropriately parameterized in regional-scale CTMs that allow for bi-directional exchange?
- What factor(s) are responsible for the frequently observed yet currently unexplained morning increase in NH\textsubscript{3}?
- Is dew a significant night-time reservoir and morning source for NH\textsubscript{3}?
- What are the major sources and sinks of NH\textsubscript{3} in the summertime Arctic marine boundary layer?
• Do regional and global CTMs accurately reproduce the abundance, distribution and impacts of NH₃ in rural and remote locations?

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Chapter 2

Soil-atmosphere exchange of ammonia in a non-fertilized grassland: measured emission potentials and inferred fluxes

Sections of this chapter appear in the following peer-reviewed publication:


2 Chapter 2

2.1 Abstract

A 50-day field study was carried out in a semi-natural, non-fertilized grassland in south-western Ontario, Canada during the late summer and early autumn of 2012. The purpose was to explore surface-atmosphere exchange processes of ammonia (NH$_3$) with a focus on bi-directional fluxes between the soil and atmosphere. Measurements of soil pH and ammonium concentration ([NH$_4^+$]) yielded the first direct quantification of soil emission potential ($\Gamma_{\text{soil}} = [\text{NH}_4^+]/[\text{H}^+]$) for this land type, with values ranging from 35 to 1,850 (an average of 290). The soil compensation point, the atmospheric NH$_3$ mixing ratio below which net emission from the soil will occur, exhibited both a seasonal trend and diurnal trend. Higher daytime and August compensation points were attributed to higher soil temperature. Soil-atmosphere fluxes were estimated using NH$_3$ measurements from the Ambient Ion Monitor Ion Chromatograph (AIM-IC) and a simple resistance model. Vegetative effects were neglected due to the short canopy height and significant $\Gamma_{\text{soil}}$. Inferred fluxes were, on average, 2.6 ± 4.5 ng m$^{-2}$ s$^{-1}$ in August (i.e. net emission) and -5.8 ± 3.0 ng m$^{-2}$ s$^{-1}$ in September (i.e. net deposition). These results are in good agreement with the only other bi-directional exchange study in a semi-natural, non-fertilized grassland. A Lagrangian dispersion model (HYSPLIT) was used to calculate air parcel back trajectories throughout the campaign and revealed that NH$_3$ mixing ratios had no directional bias throughout the campaign, unlike the other atmospheric constituents measured. This implies that soil-atmosphere exchange over a non-fertilized grassland can significantly moderate near-surface NH$_3$ concentrations. In addition, we provide indirect evidence that dew and fog evaporation can
cause a morning increase of \([\text{NH}_3]_g\). Implications of our findings on current \(\text{NH}_3\) bi-directional exchange modelling efforts are also discussed.

2.2 Introduction

Atmospheric ammonia (\(\text{NH}_3(g)\)) is the most abundant alkaline gas and is important for many biogeochemical and atmospheric processes (Seinfeld and Pandis, 2006). It neutralizes acidic aerosol, leading to increased mass loadings of fine atmospheric particulate matter (\(\text{PM}_{2.5}\)) which reduces visibility and can cause adverse health effects (Pope et al., 2002). In addition, deposition of \(\text{NH}_3\) and other forms of reactive nitrogen (i.e. \(\text{NO}_x\), \(\text{HNO}_3\)) can lead to eutrophication, soil acidification, and loss of biodiversity in sensitive ecosystems (Krupa, 2003). In urban/agricultural areas runoff of dissolved inorganic nitrogen (DIN) into freshwater ecosystems typically exceeds DIN input from atmospheric deposition by an order of magnitude. However, in rural/remote environments atmospheric deposition can be the dominate DIN source (Lepori and Keck, 2012). \(\text{NH}_3\) is primarily emitted through agricultural activities (i.e. fertilization, animal waste) with minor contributions from transportation and chemical industries (Reis et al., 2009).

\(\text{NH}_3(g)\) exists in equilibrium with aqueous ammonia (\(\text{NH}_3(aq)\)) in surface reservoirs (i.e. apoplastic tissues of plants or soil pore water) that, at least in theory, can be described by the Henry’s law constant (\(K_H\)). The \(\text{NH}_3(aq)\) is also in equilibrium with aqueous-phase ammonium (\(\text{NH}_4^+(aq)\)), governed by the acid dissociation constant (\(K_a\)) of \(\text{NH}_4^+\) and the pH of the solution. The gas-phase concentration above this aqueous phase at thermodynamic equilibrium is known as the compensation point (\(\chi\)) and can, to a first approximation, be predicted according to:

\[
\chi = \frac{K_a \cdot [\text{NH}_4^+(aq)]}{K_H \cdot [\text{H}^+]} \quad (E2.1)
\]

where \([\text{H}^+]\) is the concentration of the hydronium ion in solution. If the atmospheric mixing ratio of \(\text{NH}_3\) over a surface is below this value, net emission from the surface pool is expected until the equilibrium \(\text{NH}_3\) value (i.e. \(\chi\)) is reached and vice versa. In order to account for the temperature dependence of the equilibrium constants, the van’t Hoff equation must be applied so equation E2.1 can be updated to:

\[
\chi = 13,587 \cdot \Gamma \cdot e^{-\frac{10.396K}{T}} \cdot 10^9 \quad (E2.2)
\]
where $T$ is the temperature of the surface reservoir in K, $\Gamma$ is the emission potential equal to the ratio between $[\text{NH}_4^+]$ and $[\text{H}^+]$ in the surface reservoir ($\Gamma = [\text{NH}_4^+]/[\text{H}^+]$), and $\chi$ is given in ppb, or nmol mol$^{-1}$ (Nemitz et al., 2001; Nemitz et al., 2004). A large $\Gamma$ indicates the surface has a high propensity to emit NH$_3$ since it is directly proportional to $\chi$. Values for $K_H$ (10$^{-1.76}$ atm M$^{-1}$) and enthalpy of vaporization (34.18 kJ mol$^{-1}$) at 25 °C were obtained from Dasgupta and Dong (1986). The $K_a$ and enthalpy of dissociation of NH$_4^+$ at 25 °C are 10$^{-9.25}$ M and 52.21 kJ mol$^{-1}$, respectively (Bates and Pinching, 1950).

This conceptual model of a compensation point for NH$_3$ was first suggested by Farquhar et al. (1980). Over the subsequent decades, numerous laboratory and field studies over a wide range of land types have been undertaken to validate and improve this framework. Single-layer exchange models were developed in the 1990s to account for bi-directional exchange with plant stomata and deposition to the cuticle (e.g. Sutton et al. 1993, 1995, 1998). A two-layer model was developed by Nemitz et al. (2001) that also included exchange with the soil. Nemitz et al. (2000) were able to create a multi-layer model that allowed for exchange with different layers within the canopy (i.e. inflorescences, bottom leaves) of oilseed rape. The flux of NH$_3$ ($F_{\text{NH}_3}$) above a surface reservoir can be calculated from $\chi$ with an exchange velocity ($v_{ex}$) using the following:

$$F_{\text{NH}_3} = v_{ex} \cdot (\chi - [\text{NH}_3(g)]) \quad \text{(E2.3)}$$

The $v_{ex}$ (units of m s$^{-1}$) can be parameterized by applying resistances in a series and/or parallel schematic. These resistances represent physical barriers to mass transfer and are analogous to electrical resistances. The number of resistances applied is dependent on how many surface reservoirs are incorporated into the field-scale model. In all cases, aerodynamic ($R_a$) and quasi-laminar ($R_b$) resistances must be considered to account for the turbulence between the surface reservoir and NH$_3$(g) measurement height.

Numerous pathways are present for bi-directional exchange over land: via plant stomata, soil pore water, and ground litter. For each compartment there exists a $\chi$ which is dependent on the surface properties given in equations E2.1 and E2.2. Significant effort has gone into measuring and modelling NH$_3$ fluxes over a wide variety of land types to provide a more thorough understanding of this framework (Massad et al. 2010; Zhang et al., 2010, and references therein).
Canopy-scale resistance models of varying complexity have been developed and successfully employed to mechanistically describe NH$_3$ fluxes (e.g. Nemitz et al. 2001; Personne et al. 2009; Sutton et al. 1995). A detailed list of these models is available in Flechard et al. (2013).

While extremely useful, these mechanistic canopy-scale models are often too complex to be directly incorporated into regional or global chemical transport models. As a result, recent efforts have focused on simplifying previous models by empirically parameterizing certain components (usually $\Gamma$), with either a constant for each land type or a function using parameters (i.e. fertilizer application, regional long-term NH$_3$ concentration) that are easily assimilated into the regional and global models (Bash et al. 2013; Cooter et al. 2010, 2012; Pleim et al. 2013; Wen et al. 2013; Wichink Kruit et al. 2010, 2012). Incorporating bi-directional NH$_3$ exchange in these large scale atmospheric models generally improves model performance. For instance, Bash et al. (2013) reduced the biases and error in both NH$_3$ deposition and aerosol concentration by coupling CMAQ (Community Multiscale Air-Quality) to an agroecosystem model and allowing for bi-directional exchange over the continental United States. Wichink Kruit et al. (2012) incorporated bi-directional exchange in the chemical transport model LOTOS-EUROS and found better agreement between measured and modelled NH$_3$ mixing ratios across Europe, although some domains were still biased low by up to a factor of 2. Large uncertainties still exist for the parameterizations of $\Gamma$ for both stomata and soil over most land types as a result of sparse measurements. Field measurements of soil and vegetation [NH$_4^+$] and [H$^+$], along with atmospheric NH$_3$ mixing ratios are required to evaluate the performance of regional air quality models attempting to parameterize bi-directional exchange.

Reviews by Massad et al. (2010) and Zhang et al. (2010) have summarized the studies to date that have explored bi-directional surface-atmosphere NH$_3$ fluxes over a wide variety of different land types. The majority have focused on biosphere-atmosphere (i.e. stomatal) or canopy-atmosphere (i.e. sum of stomatal, litter and soil) exchange. In the former, both stomatal and cuticular resistances are incorporated (Massad et al., 2010 and references therein). Indeed, there have been a limited number of studies strictly examining soil-atmosphere bi-directional exchange. One reason is that if a dense canopy (i.e. forest or crops) is present, a significant fraction of soil NH$_3$ emissions are expected to be recaptured by the canopy before leaving it (Nemitz et al., 2000). For instance, Walker et al. (2013) estimated that ~76 % of soil NH$_3$
emissions are recaptured by the canopy in a fertilized corn field during peak leaf area index (LAI).

Agricultural fields and fertilized croplands have traditionally been the focus of NH$_3$ bi-directional exchange studies due to their high propensity to emit NH$_3$ (Massad et al. 2010; Zhang et al. 2010 and references therein). Semi-natural and non-fertilized ecosystems have been examined less often. Although these areas are much less likely to be large sources of NH$_3$, they account for a large land fraction and have the potential to impact the quality of atmospheric ammonia predictions from these updated regional scale models. In particular, there have been fewer studies measuring NH$_3$ fluxes over grasslands (e.g. Mosquera et al. 2001; Spindler et al., 2001). Several studies (David et al. 2009; Herrmann et al. 2009; Milford et al. 2001; Sutton et al. 2001, 2009) have explored how different grassland management practices (cutting and fertilization) affect NH$_3$ fluxes; however, all of these studies were performed in fields that had received some degree of fertilization within the last 10 years. To our knowledge, only Wichink Kruit et al. (2007) have investigated NH$_3$ bi-directional exchange over a non-fertilized grassland. The authors used several denuders and the aerodynamic gradient method to measure fluxes above the canopy and then infer both a canopy $\chi$ and $\Gamma$.

Motivated by a lack of measurements in non-fertilized grasslands, this present study aims to measure $\chi$ and $\Gamma$ to provide a better constraint on these values since they are directly employed in current air quality models that represent bi-directional exchange. Atmospheric measurements are then used to estimate a soil-atmosphere flux based on a simple resistance model that has been utilized in the past (e.g. Nemitz et al., 2001). Furthermore, we present evidence that bi-directional exchange over a non-fertilized grassland can significantly impact near-surface NH$_3$ concentrations, and that evaporation of dew can release large quantities of NH$_3$.

2.3 Methods and Materials

2.3.1 Field site

Measurements were obtained from August 12 to October 2, 2012 at a rural site near Egbert, ON located approximately 70 km north of Toronto. The long-term sampling site, Centre for Atmospheric Research Experiments (CARE, 44°13’51”N, 79°46’58”W, 251 m above sea-level), is operated by Environment Canada and situated in an agricultural area. Figure 2.1 shows the
The location of CARE in relation to major Canadian cities and is coloured according to annual NH$_3$ emissions from 2008 (NPRI, 2008). Canada’s National Pollutant Release Inventory (NPRI) does not include soil or vegetative emissions from non-managed ecosystems. The site is located on a sharp transition with high NH$_3$ emissions to the south and negligible emissions to the north. Air masses originating from the south are typically polluted since they pass over urban, industrial and agricultural areas of southern Ontario and the northeastern United States, whereas cleaner air usually arrives from the north (e.g. Rupakheti et al., 2005). As a result, soil-atmosphere exchange of NH$_3$ can be examined under a wide range of atmospheric pollution regimes.

Figure 2.1 Location of CARE (◊) and major cities in the surrounding area. The map is coloured by annual NH$_3$ emissions according to the 2008 emission inventory.

The site itself is surrounded by 60 hectares of semi-natural, non-fertilized grassland with no overlying canopy. The month of August was relatively dry with cumulative precipitation totalling 8 mm, whereas September had 75 mm of precipitation. The soil sampling area is contained within a radius of 10 m as this is the approximate flux footprint of the air sampling instrumentation explained in section 2.3.4. Fertilizer has not been applied to the soil in at least 15 years. Grass at the site was cut on June 27 but remained uncut for the duration of the study. Over
the course of the study, the grass grew from about 10 cm to a final height of 20 cm. The soil is sandy loam with an organic carbon content of roughly 5% and a cation exchange capacity (CEC) of 22.7 cmol kg\(^{-1}\). The CEC reflects the soil’s ability to retain cations (including NH\(_4^+\)) and at this site is an intermediate value relative to other soils.

### 2.3.2 Bi-directional exchange framework

For surfaces with minimal vegetation and a high soil emission potential (\(\Gamma_{\text{soil}}\)), the exchange between the soil and atmosphere is expected to dominate the bi-directional flux (Personne et al., 2009; Sutton et al., 2009). In these environments, it should be reasonable to estimate the \(v_{\text{ex}}\) by only considering resistances affecting the exchange across the soil-atmosphere interface. As such, \(v_{\text{ex}}\) in this paper is approximated using equation (E2.4) which was derived from Su et al. (2011) who parameterized HONO soil fluxes in a similar fashion. This method is also the same as the two-layer resistance model developed by Nemitz et al. (2001) but neglects the stomatal and cuticular components.

\[
\nu_{\text{ex}} = \frac{1}{R_a + R_b + R_{\text{inc}} + R_{\text{soil}}} \quad (E2.4)
\]

The aerodynamic (\(R_a\)) and quasi-laminar (\(R_b\)) resistances reflect the macro and molecular-scale turbulence, respectively, between the soil and measurement height of NH\(_3\)\(\text{(g)}\). The in canopy (\(R_{\text{inc}}\)) and soil (\(R_{\text{soil}}\)) resistances account for processes within the canopy and at the soil interface that hinder the exchange of gases. According to the theory outlined in Hicks et al. (1987), \(R_a\) and \(R_b\) can be calculated as such:

\[
R_a = \frac{\ln(z_{\text{ref}}) - \ln(z_0)}{\kappa \cdot u_s} \quad (E2.5)
\]

\[
R_b = \frac{2}{\kappa \cdot u_s} \cdot \left(\frac{Sc}{Pr}\right)^{2/3} \quad (E2.6)
\]

where \(z_{\text{ref}}\) is the height of the NH\(_3\) measurement (2.7 m), \(z_0\) the roughness length, equal to 0.05 m for uncut grass (Seinfeld and Pandis, 2006), and the von Karman constant \(\kappa = 0.4\). The Schmidt number (\(Sc = 0.58\)) and Prandtl number (\(Pr = 0.72\)) are taken from Hicks et al. (1987) and
account for the diffusivity of NH$_3$ and heat transfer, respectively. The friction velocity, $u^*$, can be calculated by:

$$u^* = \frac{4}{\sqrt{u'^2 + v'^2}}$$  \hspace{1cm} (E2.7)

where $u'$ and $v'$ are the deviations from the streamline corrected half-hour mean of the horizontal component of wind velocity and $w'$ is the vertical component (Wilczak et al., 2001).

Parameterizations for $R_{\text{inc}}$ and $R_{\text{soil}}$ vary and are empirically determined through measurements of net vertical flux above a given bulk surface. The former is found to be dependent on the canopy height, season and land use whereas the latter is primarily dictated by the Henry’s law constant and reactivity of the pollutant. For the present study, values of $R_{\text{inc}} = 100$ s m$^{-1}$ and $R_{\text{soil}} = 60$ s m$^{-1}$ are employed based on the work by Wesely (1989). These values correspond to resistances for a range land in midsummer with lush vegetation and a soil pH of 6.

It should be reiterated that using equations E2.3 to E2.7 to estimate soil-atmosphere NH$_3$ fluxes neglects any vegetative effects (e.g. recapture of NH$_3$, stomatal emission) and that this serves only as an approximation of NH$_3$ fluxes between the soil and the atmosphere.

### 2.3.3 Soil measurements

Measurements of soil [NH$_4^+$], pH and temperature were necessary to calculate the $\chi$. Soil cores were collected in triplicate on six days during the campaign, all within 30 feet of the atmospheric measurement inlet. The sampling methodology outlined below is based on work done by Li et al. (2012) and van Miegroet (1995). Samples were collected six times throughout the campaign on the days listed in Table 2.1. Sites 1, 2 and 3 correspond to small (~1 m$^2$) areas 10 m west, directly below, and 10 m east of the sonic anemometer, respectively. The soil was sampled more frequently towards the end of the campaign since meteorology (i.e. precipitation, air temperature) was more variable and was expected to perturb the $\Gamma_{\text{soil}}$ to a greater extent than in August when meteorological conditions were more consistent. Specifically, the ranges in air and soil temperature were larger in September than in August. After removing grass and any residual litter (of which there was very little), a PVC tube (2” inner diameter) was inserted into the ground to a depth of 10 cm and a soil core was removed by pulling out the tube with a soil core intact. Each core was thoroughly mixed and an ~8 g subsample was immediately placed into a
pre-weighed extract solution (50 mL of 0.25 % KCl w/w) and transported on ice back to the lab for analysis. After shaking for 30 minutes, extracts were gravity filtered (ashless filter #40, Whatman Ltd., Maidstone, UK) then sent through a 0.2 μm PES membrane syringe filter (Pall Ion Chromatography Acrodisc®, VWR International, Mississauga, ON). Ammonium, nitrate, and nitrite were then quantified using two Ion Chromatograph (IC) ICS-2000 systems (Dionex Inc., Sunnyvale, CA) operated with suppressed conductivity detection and reagent-free eluent (potassium hydroxide for anions, methanesulphonic acid for cations). Gradient elution schemes were optimized so that analyte peaks were baseline resolved. CS12A analytical and CG12A guard columns were used for the cation IC, and AS19 analytical and AG19 guard columns for the anion IC. In both cases, 25 μL loops were used. ICs were calibrated by injection of commercially available (Dionex Corp., Sunnyvale, CA) mixed standards of 7 anions (F⁻, Cl⁻, NO₂⁻, Br⁻, NO₃⁻, SO₄²⁻, PO₄³⁻) and 6 cations (Li⁺, Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺). Serial dilutions of the standards in matrix-matched 0.25 % KCl allowed for a five-point calibration which yielded reasonable calibration curves (slope of R² > 0.99) for all analytes. Extraction with a 0.25 % KCl solution proved sufficient to desorb all accessible ions in the soil matrix, yet dilute enough to allow for quantification of NH₄⁺ and NO₃⁻ in every sample. The inherent assumption is that the extract solution sufficiently mimics the ability of soil pore water to liberate NH₄⁺ ions from the soil matrix to participate in soil-air exchange. An additional extraction into deionized water (DIW) was performed on one set of soil samples. The [NH₄⁺] measured in the DIW extract was between 30-45% of that measured with the KCl extraction. Extraction into DIW is an absolute lower bound on soil [NH₄⁺] since higher ionic strength solutions will desorb more NH₄⁺ via ion displacement, and soil pore water has a much higher ionic strength than DIW. Flechard et al. (2013) and Cooter et al. (2010) have suggested fundamental analytical research is required to assess the validity of this assumption, but this is outside the scope of this current study. A field blank was run with every triplicate to account for any contamination (always less than 1 % of the measured soil [NH₄⁺]) from sample handling and extraction.

Soil pH is the negative logarithm of the activity of hydronium ions dissolved in soil pore water and was measured by mixing ~10 g of soil with an equal mass of deionized water (1:1 soil:DIW slurry). A standard pH electrode (SympHony 14002-782, VWR International, Mississauga, ON) was immediately immersed in the slurry until a stable pH reading was obtained. This was done in triplicate for each soil core and an average pH for each was calculated. Performing the pH
measurements in a saline solution of 0.25 % KCl desorbs more H\(^+\) and was found to lower the pH reading by up to 1 unit relative to extraction into deionized water, which has been reported previously (e.g. Walker et al., 2014). Soil temperature was logged hourly using 5 \textit{in situ} sensors (iButtons, Maxim Integrated, San Jose, CA) placed 10 cm deep dispersed across the 30 foot radius of the soil sampling area. Moisture content was determined gravimetrically for a subsample (\(\sim 3 \text{ g}\)) of each core by drying in an oven at 105 \(^\circ\text{C}\) for at least 24 hours.

2.3.4 Atmospheric measurements

Ambient NH\(_3\)\((g)\) mixing ratios were needed to infer both the direction and magnitude of soil-atmosphere fluxes. Measurements of NH\(_4^+\), SO\(_4^{2-}\), NO\(_3^-\) in PM\(_{2.5}\) and their precursor gases (SO\(_2\), and HNO\(_3\)) were also important to aid in interpretation of air mass trajectory. These water-soluble gases and ions in PM\(_{2.5}\) were measured continuously on-line every hour with the Ambient Ion Monitor-Ion Chromatograph (AIM-IC) system (Model 9000D, URG Corp., Chapel Hill, NC). The set-up has been explained in detail elsewhere (Markovic et al., 2012) and is described here only briefly. Ambient air is pulled at 3 L min\(^{-1}\) through a PM\(_{2.5}\) impactor to remove coarse particles. Gases are stripped from the sample flow by a liquid parallel plate denuder with a 2 mM H\(_2\)O\(_2\) solution continuously flowing over the surface. Particles have sufficient inertia to pass through the denuder assembly and enter a supersaturated steam condensation coil where they are grown hygroscopically and collected as an aqueous solution. The aqueous sample then travels through a 22 m sample line to the IC systems where the \(\sim 5 \text{ mL}\) aliquots (collected over an hour) are separately injected and quantified for water soluble ions. The inlet box was mounted on a tower 3 m above the ground.

The AIM-IC was deployed using CS17 and AS19 analytical columns, CG17 and AG19 guard columns and TCC-ULP1 and TAC-ULP1 concentrator columns. Suppressed conductivity detection and reagent-free gradient elution were used. Five-point calibrations were performed at the beginning, middle and end of the campaign. Standard solutions of known concentration were made by serial dilution of commercially available standards of mixed anions and cations discussed in the previous section.

Backgrounds were acquired by overflowing the inlet with high purity zero air for 24 hours and averaging the peak area signal acquired. This average peak area was subtracted from the peak areas obtained while sampling ambient air. Detection limits were determined by taking 3 times
the standard deviation of the peak area during the final twenty hours of the zero air experiment and converting it to either a mixing ratio or mass loading using the calibration curves and assuming a flow of 3 L min$^{-1}$, pressure of 760 mmHg and temperature of 298 K.

Atmospheric species of primary interest for this study are NH$_4^+$, SO$_4^{2-}$, NO$_3^-$ in PM$_{2.5}$ and their precursor gases (NH$_3$, SO$_2$, and HNO$_3$), for which the limits of detection were 0.2, 0.003 and 0.008 ppb for NH$_3$, SO$_2$, and HNO$_3$, respectively. For NH$_4^+$, SO$_4^{2-}$ and NO$_3^-$ in the particle phase the detection limits were 0.025, 0.04 and 0.04 μg m$^{-3}$, respectively.

Friction velocity ($u^*$) parameters were calculated from wind velocity measured with a 3-D sonic anemometer (model CSAT3, Campbell Scientific, Logan, UT) operating at 10 Hz. Hourly relative humidity (RH) and air temperature (in °C) at CARE were measured by an Environment Canada weather station located 20 m north of the sonic anemometer. This data was obtained from the Environment Canada website (http://climate.weather.gc.ca/data_index_e.html).

The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model was used to compute 48-hour back trajectories throughout the campaign in order to assess air parcel history (Draxler and Rolph, 2013). The model was run four times per day with parcels arriving at a height of 100 m above CARE at 2:00, 8:00, 14:00 and 20:00 local time. Resolution of the meteorology model (EDAS) was set to 40 by 40 km.

## 2.4 Results and Discussion

### 2.4.1 Soil emission potential measurements

Figure 2.2 shows the measured $\Gamma_{\text{soil}}$ for the six soil sampling dates in this study. Soil [NH$_4^+$] and pH measurements used to determine the $\Gamma_{\text{soil}}$ are shown in Table 2.1. The variation in $\Gamma_{\text{soil}}$ was up to an order of magnitude on some days (August 13$^{\text{th}}$ and September 20$^{\text{th}}$) yet was more consistent on others (i.e. September 13$^{\text{th}}$ and 25$^{\text{th}}$). Both August dates have the highest $\Gamma_{\text{soil}}$ suggesting there might be some seasonal variability, as has been observed for stomatal emission potentials ($\Gamma_{\text{stom}}$) (Loubet et al., 2002). However, a similar trend cannot be confirmed for this study due to the relatively short time frame and the inherent heterogeneity of soil. Also shown in Fig. 2.2 is the range of ground emission potentials ($\Gamma_g$) in grasslands suggested by Zhang et al. (2010). $\Gamma_g$ includes both soil and litter, but during this study there was a negligible amount of litter on the ground, therefore $\Gamma_g$ and $\Gamma_{\text{soil}}$ should be analogous. The suggested range in $\Gamma_g$ (2,000 to 200,000)
is based on 14 values from six studies, all of which were in fertilized grasslands. Of these studies, only two (David et al. 2009; Mattsson et al. 2009) directly measured $\Gamma_g$, whereas the other four either inferred it from measurements of dead or dying leaves (Herrmann et al. 2009; Mattsson and Schjoerring, 2003) or modelled it (Burkhardt et al. 2009; Personne et al. 2009). All the $\Gamma_{\text{soil}}$ values (35 to 1,850) measured in this study are below the range from Zhang et al. (2010) review, likely because the field at CARE is non-fertilized and so has a lower N-content.

Suggested ranges of $\Gamma_g$ from Zhang et al. (2010) for various land types were recently incorporated into a regional air quality model (STILT-Chem) by Wen et al. (2013) to allow for bi-directional exchange. The authors found the updated model, using $\Gamma_g = 2,000$ over grasslands, overestimates $\text{NH}_3(g)$ in sites with lower $\text{NH}_3(g)$ concentrations (i.e. CARE). This could be a consequence of overestimating $\Gamma_g$ in these regions, as implied by the $\Gamma_{\text{soil}}$ measurements given here.

**Figure 2.2** Soil emission potentials ($\Gamma_{\text{soil}}$) measured throughout this study. Black circles represent the average of three measurements $\pm 1\sigma$. A review by Zhang et al. (2010) suggests $\Gamma$ ranges for ground ($\Gamma_g$) and stomata ($\Gamma_{\text{stom}}$) for low and high nitrogen input grasslands. These ranges are shown in brown ($\Gamma_g$) and green ($\Gamma_{\text{stom}}$).
Table 2.1 Soil parameters measured in Egbert, ON

<table>
<thead>
<tr>
<th>Date</th>
<th>Site</th>
<th>[NH$_4^+$] (mg/kg wet soil)</th>
<th>pH (1:1 slurry soil:deionized water)</th>
<th>Average $\Gamma_{\text{soil}}$ ($\pm 1\sigma$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>August 13</td>
<td>1</td>
<td>1.4</td>
<td>6.9</td>
<td>978 ± 750</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.67</td>
<td>7.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.85</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>August 28</td>
<td>1</td>
<td>1.43</td>
<td>6.6</td>
<td>290 ± 110</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.31</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.87</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
<td>September 13</td>
<td>1</td>
<td>1.31</td>
<td>5.81</td>
<td>51 ± 20</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.17</td>
<td>6.87</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.51</td>
<td>6.09</td>
<td></td>
</tr>
<tr>
<td>September 20</td>
<td>1</td>
<td>1.01</td>
<td>5.8</td>
<td>176 ± 140</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.89</td>
<td>6.81</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.94</td>
<td>6.53</td>
<td></td>
</tr>
<tr>
<td>September 25</td>
<td>1</td>
<td>2.1</td>
<td>6.22</td>
<td>172 ± 43</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.6</td>
<td>6.57</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.93</td>
<td>6.59</td>
<td></td>
</tr>
<tr>
<td>September 27</td>
<td>1</td>
<td>0.61</td>
<td>6.16</td>
<td>91 ± 40</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.46</td>
<td>6.59</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.25</td>
<td>6.95</td>
<td></td>
</tr>
</tbody>
</table>

Massad et al. (2010) have carried out a similar review and suggest that $\Gamma_g$ be parameterized as 500 in non-fertilized, semi-natural environments without vegetation. To our knowledge, the
results presented here represent the first values of $\Gamma_{\text{soil}}$ directly measured in a non-fertilized grassland. These measurements underscore the importance of distinguishing between fields that receive fertilization and those that do not. The $\Gamma_g$ range from Zhang et al. (2010) is not applicable to the field at CARE, whereas the estimation ($\Gamma_g = 500$) from Massad et al. (2010) is more suitable.

It is worth comparing $\Gamma_{\text{soil}}$ to the range of stomatal emission potentials ($\Gamma_{\text{stom}}$) in grasslands proposed by Zhang et al. (2010) (Fig. 2.2, green line). $\Gamma_{\text{stom}}$ values (300 to 3,000) are based on roughly 50 measurements from over two dozen studies which reflect the narrower range in $\Gamma_{\text{stom}}$ compared to $\Gamma_g$. Massad et al. (2010) also parameterized $\Gamma_{\text{stom}}$, but did so by empirically fitting measurements to total annual N input instead of using a constant value for each land use type. These suggested $\Gamma_{\text{stom}}$ values from each review are on the same order as the $\Gamma_{\text{soil}}$ measured in this study, suggesting that in a non-fertilized field the soil and vegetation might have a very similar propensity to either emit or uptake $\text{NH}_3$ (i.e. they likely have similar $\chi$).

### 2.4.2 Inferred soil compensation point and fluxes

A linear interpolation of $\Gamma_{\text{soil}}$ between the six sampling dates in combination with hourly soil temperature measurements were used to generate a time series of soil compensation point ($\chi_{\text{soil}}$, black trace in Fig. 2.3a) according to equation E2.2. The shaded region around $\chi_{\text{soil}}$ was calculated from a linear interpolation of $\pm 1\sigma$ in $\Gamma_{\text{soil}}$ measurements and therefore reflects the uncertainty in $\chi_{\text{soil}}$ attributed to variability in soil pH and $[\text{NH}_4^+]$. Hourly gas-phase $\text{NH}_3$ measured by the AIM-IC (orange trace) is also shown. These two traces frequently cross meaning that repeated switching between soil emission and atmospheric deposition is predicted. There is a clear decline in $\chi_{\text{soil}}$ throughout the campaign that is mostly attributable to a decrease in soil temperature ($T_{\text{soil}}$) as shown by the grey trace at the top of Fig. 2.3a. Precipitation can also be important factor for $\text{NH}_3$ fluxes – both Cooter et al. (2010) and Walker et al. (2013) observed emission “pulses” of $\text{NH}_3$ over agricultural soils within 24 hours after rainfall. Elevated $[\text{NH}_3]$ levels are seen on August 13, August 28, and September 22 following 0.4 mm, 5.0 mm and 10.9 mm of rain. Reasons for this could include increased soil $\text{NH}_4^+$ available for exchange, increased diffusion of $\text{NH}_3$ through soil, and/or increased N inputs to the surface as a result of wet deposition.
Figure 2.3 (a) Time series of NH$_3$ mixing ratio ([NH$_3$], orange trace), $\chi$$_{\text{soil}}$ (black trace), daily cumulative rainfall (blue markers) and soil temperature ($T$$_{\text{soil}}$, grey trace) throughout the campaign. $\chi$$_{\text{soil}}$ was calculated using a linear interpolation of $\Gamma$$_{\text{soil}}$ and hourly soil temperature measurements. The shaded region around $\chi$$_{\text{soil}}$ was calculated by linear interpolation of $\pm$ 1σ of $\Gamma$$_{\text{soil}}$ and reflects the uncertainty in $\chi$$_{\text{soil}}$ as a result of uncertainty in $\Gamma$$_{\text{soil}}$ measurements. (b) and (c) show time of day plots for the average [NH$_3$], $\chi$$_{\text{soil}}$, and difference between the two ($\chi$$_{\text{soil}}$ − [NH$_3$], red trace) for August and September, respectively. Errors bars in (b) and (c) represent $\pm$ 1σ, and are only included for the difference trace for clarity.

There is a diurnal trend in $\chi$$_{\text{soil}}$ with lower values during the night time that is a consequence of $T$$_{\text{soil}}$ and has been observed before for stomatal compensation points (Van Hove et al., 2002). It is possible there is a diurnal trend in $\Gamma$$_{\text{soil}}$ that is not captured by the periodic soil sampling regime. However, this is unlikely since additional measurements from a nearby site found that spatial heterogeneity in soil [NH$_4^+$] was much larger than the temporal variability in 24 soil grabs taken 6 hours apart (soil grabs were in triplicate) over the course of two days.
The $\chi_{\text{soil}}$ diurnal trends are more evident in Figs. 2.3b and 2.3c, which show time-of-day plots for August and September, respectively. During both months, NH$_3$ peaks between 8:00-10:00 in the morning and is typically at a minimum during the evening where it plateaus at around 2 ppb, which has been observed previously in the region (e.g. Ellis et al. 2011). Mixing ratios were fairly similar in both months, although the morning peak in August was larger than in September. On the other hand, $\chi_{\text{soil}}$ values were significantly lower in September as a result of lower soil temperatures. Accordingly, the diurnal profiles of the difference between $\chi_{\text{soil}}$ and [NH$_3$] (red trace) in Figs. 2.3b and 2.3c are distinct. In August, the difference between $\chi_{\text{soil}}$ and [NH$_3$] is positive throughout the majority of the day (excluding 7:00-11:00 in the morning) indicating a net flux from the soil to the atmosphere. On the other hand, in September the difference is negative throughout the entire day meaning the soil is a continuous sink for atmospheric NH$_3$. This suggests a clear transition from the soil being a net source to a net sink for NH$_3$ due to lower soil temperatures. It should be noted that grass senescence had not yet begun and that there was no appreciable accumulation of litter, which has been shown to act as a strong source of NH$_3$ (e.g. David et al. 2009; Mattsson et al. 2009; Mattsson and Schjoerring, 2003).

In order to determine the magnitude of this exchange, the $v_{\text{ex}}$ was estimated using equations E2.4 to E2.7 and the flux was calculated from equation E2.3. The diurnal profile of NH$_3$ fluxes (in ng m$^{-2}$ s$^{-1}$) for both months is shown in Fig. 2.4. Throughout August there is an average net NH$_3$ emission from the soil of 2.6 ± 4.5 ng m$^{-2}$ s$^{-1}$. In September, there was an average net deposition of 5.8 ± 3.0 ng m$^{-2}$ s$^{-1}$ from the atmosphere to the surface. Average fluxes measured by Wichink Kruit et al. (2007) were 4 ng m$^{-2}$ s$^{-1}$ in summer and -24 ng m$^{-2}$ s$^{-1}$ in autumn, which are on the same order of the flux values estimated in this study. Wichink Kruit et al. (2007) used their measured fluxes to infer a canopy emission potential ($\Gamma_{\text{canopy}}$) using data points where cuticular deposition can be neglected (dry conditions) and stomatal exchange is dominant (daytime). Exchange with the soil is neglected in their study due to the low soil pH (about pH = 5); however, this would not be a valid assumption in this study as the soil pH at CARE is about 7, as shown in Table 2.1. Nonetheless, the inferred $\Gamma_{\text{canopy}}$ was 2,200 and is higher than the $\Gamma_{\text{soil}}$ measured in this study. At least to a first approximation, it appears that NH$_3$ fluxes in both these non-fertilized fields are comparable. The larger deposition in the autumn in Wichink Kruit et al. (2007) is likely attributable to higher NH$_3$ mixing ratios (~9 ppb average versus ~2 ppb
September average in this study). It is noteworthy that both sites are considered the same land type but likely have very different canopy-level processes driving NH$_3$ fluxes. Specifically, the soil in Wichink Kruit et al. (2007) had a sufficiently low pH (~5) to suppress appreciable soil-to-atmosphere exchange, which is not the case at CARE. Furthermore, a review by Schlesinger and Hartley (1992) estimate volatilization rates of NH$_3$ from undisturbed grasslands are between 0.3 and 30 ng m$^{-2}$ s$^{-1}$, which encompasses the values from this work and that of Wichink Kruit et al. (2007).

![Figure 2.4](image)

**Figure 2.4** Time of day plot showing the average hourly NH$_3$ flux in August (orange trace) and September (brown trace). A positive flux indicates emission from the soil, whereas a negative flux indicates deposition from the atmosphere.

It is also important to consider wet deposition when assessing net exchange of NH$_3$ between the atmosphere and an ecosystem. The Canadian Air and Precipitation Monitoring Network (CAPMoN) collects daily precipitation samples at CARE and reports the results on line ([http://www.on.ec.gc.ca/capmon/login/login.aspx](http://www.on.ec.gc.ca/capmon/login/login.aspx)). The average NH$_4^+$ wet deposition rates from 2001-2011 for August and September are 12.4 ± 4.6 ng m$^{-2}$ s$^{-1}$ and 11.3 ± 5.4 ng m$^{-2}$ s$^{-1}$, respectively. In the context of our results (fluxes of 2.6 ± 4.5 ng m$^{-2}$ s$^{-1}$ in August and -5.8 ± 3.0 ng m$^{-2}$ s$^{-1}$ in September), the site at CARE has net NH$_3$ deposition in both months when one considers both wet deposition and bi-directional exchange. In other words, the magnitude of wet deposition fluxes is roughly 2-5 times larger than the magnitude of bi-directional exchange. However, it is important to note that wet deposition occurs in discrete events, whereas dry exchange is continuous.
2.4.3 Evidence for bi-directional exchange

Since CARE lies on a sharp gradient between high NH₃ emissions to the south and low emissions to north (Fig. 2.1), one might expect air masses from the north to be lower in NH₃ relative to air masses from the south. Similarly, the greater level of anthropogenic activity south of CARE suggests an enrichment of anthropogenic pollutants (i.e. SO₂, SO₄²⁻, HNO₃ and NO₃⁻) in air masses from the south. In order to interrogate this hypothesis, 2-day back trajectories were calculated using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model for every six hours throughout the study. Each 6-hour time stamp was then classified as having had the air mass pass through Toronto (a box defined from 43.5-44.0’N by 79.0-80.0’N), or having originated from the North (spent more than half its time above 44.23’N) or the South (spent more than half its time below 44.23’N and not passing through Toronto). Results from this analysis are shown in Fig. 2.5 and yield a distinct directional bias for all species except NH₃; air masses passing through Toronto are clearly enhanced in SO₂, HNO₃, NH₄⁺, SO₄²⁻ and NO₃⁻ but not NH₃. A lack of directional bias for NH₃ could be explained by proximity to a large NH₃ source, but as seen in Fig. 2.1 there is a sharp regional (tens of kilometres) gradient in the emissions inventory suggesting that no such local source exists. A more likely explanation is that bi-directional exchange of NH₃ between the surface and atmosphere modulates near-surface NH₃ mixing ratios sufficiently to eliminate any directional bias that would result from traditional emission sources.
Considering the relatively low $\Gamma_{\text{soil}}$ and small magnitude of soil fluxes, it is reasonable to ask whether such an exchange could have a noticeable effect on observed NH$_3$ mixing ratios. First, a simple calculation was performed to see if the soil reservoir contained enough NH$_4^+$ to sustain fluxes during the month of August. To do this, the following assumptions were made: NH$_3$ exchange occurs in the top 10 cm of soil, the soil is equilibrating a 1000 m atmospheric boundary layer and soil density is 1.5 g cm$^{-3}$. Figure 2.6 shows that even during peak soil emission in the afternoon, less than 1% of the soil NH$_4^+$ pool is required to equilibrate the entire boundary layer. Furthermore, much of this lost soil NH$_4^+$ would be regained during the inferred morning deposition event. Considering that the turnover time for most soil NH$_4^+$ pools is on the order of a day (Booth et al., 2005) it is safe to assume that there is sufficient NH$_4^+$ in non-fertilized grasslands to maintain fluxes to the atmosphere.
Figure 2.6 Estimated percent of the soil NH₄⁺ pool required to equilibrate with the boundary layer (assumed to be 1000 m) using the average fluxes during August. It was assumed that the top 10cm of soil exchanges and the density of soil is 1.5 g cm⁻³. Positive values indicate fluxes are from the soil to the atmosphere (i.e. the soil is losing NH₄⁺).

Second, this exchange could only sufficiently impact NH₃ mixing ratios if it occurs quickly enough. To test this, fast (0.005 m s⁻¹, at 14:00) and slow (0.003 m s⁻¹, at 1:00) average exchange velocities from August were used to calculate the time it would take the system (soil and atmosphere) to arrive halfway to equilibrium with an atmospheric height of 1000 m as well as with the height at which AIM-IC measurements were made (3 m). For 1000 m, the timescale is calculated to be between 40 and 62 hours for the fast and slow $v_{ex}$, respectively. However, for a height of 3 m, only 7 and 11 minutes are required to get halfway to equilibrium. Although this calculation neglects vertical mixing beyond 3 m (which will occur), these short timescales suggest soil-atmosphere exchange is an important component of observed negative [NH₃(g)] gradients with height. In other words, soil-atmosphere exchange over non-fertilized grasslands has the ability to strongly influence near-surface NH₃ despite the low Γ_soil (relative to fertilized fields) whereas the impact on NH₃ levels throughout the boundary layer is dampened due to slower exchange.

2.4.4 Morning increase of NH₃

A morning increase in NH₃(g) between 8:00-10:00 is clearly evident in Figs. 2.3b and 2.3c and has been observed elsewhere (e.g. Bash et al., 2010; Ellis et al., 2011; Flechard et al., 2013; Nowak et al., 2006; Wichink Kruit et al., 2007). The factors contributing to this phenomenon at
CARE are not entirely clear but may include one or more of: dew evaporation, volatilization of particulate NH$_4$NO$_3$, emission from plants/soil, and/or mixing down of NH$_3$ rich air entrained above the nocturnal boundary layer. Wichink Kruit et al. (2007) observed a similarly timed increase that coincided with a decrease in leaf wetness. Furthermore, Flechard et al. (1999) and Bussink et al. (1996) found that water layers sorbed on leaves can store significant quantities of NH$_3$ even at an RH below 100%. Although no leaf wetness sensor was employed during this study, we use night time RH as a surrogate for dew and fog formation. Figure 2.7 shows the difference between the morning NH$_x$ ($\equiv$NH$_3$(g)+NH$_4^+$ (particle)) and the average overnight NH$_x$ concentration. NH$_x$ was chosen to eliminate any bias caused by volatilisation of NH$_4$NO$_3$(p) to NH$_3$(g) and HNO$_3$(g) as temperatures rise. Mornings following a night during which RH was above 0.9 had an average $\Delta$NH$_x$ of 207 ± 37 nmol m$^{-3}$, whereas increases during mornings following drier nights (RH < 0.9) were about half that with an average of 94 ± 16 nmol m$^{-3}$. Although the RH benchmark of 0.9 only serves as a surrogate for dew formation, this finding does suggest that pools of surface water (i.e. dew or fog), which form on nights that have a high RH, can act as significant NH$_x$ reservoirs that release NH$_3$ upon evaporation in the mid-morning. This is corroborated by measurements from Burkhardt et al. (2009) who report an approximate water film thickness of 0.1 mm during dew events and an average dew [NH$_4^+$] of 3.5 mg kg$^{-1}$ in a grassland canopy. If all of the NH$_4^+$ were to be released as NH$_3$(g) upon dew evaporation, this reservoir would release about 20 μmol m$^{-2}$ of NH$_3$(g) into the atmosphere, which corresponds to an increase of 20 nmol m$^{-3}$ throughout a 1000 m boundary layer, equivalent to an increase in mixing ratio of 0.5 ppb. Such a release could have a significant impact on near surface NH$_3$(g) measurements and manifest itself as a large morning increase of NH$_3$(g). The role of dew and fog as a night-time reservoir definitely merits further investigation and could be an important process within this bi-directional framework.
Figure 2.7 The magnitude of the morning NH\textsubscript{x} (=NH\textsubscript{3}(g)+NH\textsubscript{4}\textsuperscript{+}(particle)) peak subtracted by the night time (0:00-6:00) NH\textsubscript{x} average versus the average night time relative humidity. The latter was used as a surrogate for dew formation. The average ΔNH\textsubscript{x} (± 1σ\textsubscript{mean}) both above and below RH = 0.9 are shown inset in the figure.

Since NH\textsubscript{x} morning increases plateau at ~100 nmol m\textsuperscript{-3} at an RH below 0.85, there are likely other contributing factor(s) that lead to this morning enhancement of NH\textsubscript{3}. Bash et al. (2010) observed a similar morning rise over a fertilized corn field and attributed it to plant and/or soil processes. However, CARE contains significantly less vegetation and is non-fertilized. Walker et al. (2013) suggest surface-air NH\textsubscript{3} exchange is impacted by ions that can accumulate in dew as well as the pH of the dew. In addition, Fig. 2.4 reveals there are predicted deposition fluxes to the soil during the morning. It is highly unlikely that a substantial rise in Γ\textsubscript{soil} could occur over the span of a few hours. Stomatal emission cannot be conclusively ruled out as a significant contribution. However, if this were an important factor one would expect sunrise (when stomata open) and the spike to coincide, but given that sunrise at CARE was between 6:00 and 7:15 throughout the campaign, stomatal emission is not likely to be the driving factor behind this trend at CARE. It is also possible this morning increase is linked to the break-up of the nocturnal boundary layer, as observed by Walker et al. (2006) who measured surface NH\textsubscript{3} fluxes over a fertilized soy bean field. Observations from this study rule out soil emissions and suggest that dew/fog evaporation plays a key role in enhancing morning NH\textsubscript{3} mixing ratios.

2.5 Conclusions

Measurements of Γ\textsubscript{soil} and T\textsubscript{soil} in a non-fertilized grassland were used to construct a time series of χ\textsubscript{soil} over a 50-day period. Γ\textsubscript{soil} ranged from 35 to 1,850 with an average value of 290 which is well below the 2,000 < Γ\textsubscript{g} < 200,000 suggestion by Zhang et al. (2010) for grasslands. Zhang et
al. (2010) recommended this range based on field studies exclusively in fertilized grasslands, which is likely the reason $\Gamma_g$ values in this study are lower. Indeed the distinction between fertilization and non-fertilization is critical in accurately assessing bi-directional exchange. Our findings are more in line with the parameterizations of Massad et al. (2010) who suggest a $\Gamma_g$ of 500 for semi-natural, non-fertilized areas without vegetation. Seasonal and diurnal trends in $\chi_{\text{soil}}$ were observed with lower values at night and in September due to decreases in $T_{\text{soil}}$.

Fluxes of NH$_3$ between the soil and atmosphere were estimated using [NH$_{3(g)}$] measurements and a simple resistance scheme that neglects the influence of vegetation. August fluxes were primarily upwards, except between 7:00-11:00, and resulted in an average emission of $2.6 \pm 4.5$ ng m$^{-2}$ s$^{-1}$ from the soil. September was characterized by exclusive deposition from the atmosphere at a rate of $5.8 \pm 3.0$ ng m$^{-2}$ s$^{-1}$. These values are fairly similar to fluxes measured by Wichink Kruit et al. (2007) who reported fluxes of 4 and -24 ng m$^{-2}$ s$^{-1}$ in the summer and autumn, respectively.

HYSPLIT analysis revealed that air masses passing through Toronto were enriched in atmospheric pollutants, except NH$_3$. Since CARE lies on a sharp gradient of high emissions to the south and low emission to the north, this lack of directional bias implies that bi-directional exchange efficiently modulates NH$_3$ mixing ratios. Back-of-the-envelope calculations confirm that: (1) the reservoir of NH$_4^+$ in soil of non-fertilized grasslands is large enough to sustain fluxes to the atmosphere, and (2) fluxes are rapid enough to impact surface concentrations on a relevant timescale.

Figure 2.7 suggests that dew and fog evaporation can enhance the frequently observed morning increase in NH$_3$. It is unlikely that soil emissions contribute to this increase as deposition to the soil is predicted during the morning.

More research is needed to explore seasonal and annual trends in $\Gamma_{\text{soil}}$, $\Gamma_{\text{stomata}}$ and $\chi_{\text{canopy}}$ across all land types, particularly those lacking in measurements. Since regional scale models require these parameters as direct inputs there is great utility in taking a “bottom-up” approach (i.e. measuring $\Gamma$ instead of inferring it from flux data). Even though non-fertilized fields have lower nitrogen content, evidence provided here suggests surface-atmosphere exchange can still affect near-surface concentrations and that this process should be considered when measuring ambient NH$_3$ over non-fertilized surfaces. The role of fog and dew as a night-time reservoir for water-
soluble gases also requires further attention as it may greatly enhance morning NH$_3$
concentrations and is currently not incorporated in models.

2.6 Contributions

The field study at CARE was developed jointly by Gregory Wentworth, Phillip Gregoire, Alex
Tevlin and Jennifer Murphy. The AIM-IC was operated by Gregory Wentworth and Phillip
Gregoire during the study with help from Carol Cheyne and Rachel Hems for set-up and
calibration. Soil samples were collected and analyzed by Gregory Wentworth, Phillip Gregoire,
Carol Cheyne and Rachel Hems. AIM-IC data was processed by Gregory Wentworth and Phillip
Gregoire while the sonic anemometer output was generated and processed by Alex Tevlin.
HYSPLIT back trajectories were performed by Carol Cheyne. The manuscript listed at the
beginning of this chapter was written by Gregory Wentworth with critical comments and insight
from Jennifer Murphy.

2.7 References

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Chapter 3  
The role of dew as a nighttime reservoir and morning source for atmospheric ammonia  

Sections of this chapter appear in the following peer-reviewed publication:


3 Chapter 3  
3.1 Abstract  
Several field studies have proposed that the volatilization of NH$_3$ from evaporating dew is responsible for an early morning pulse of ammonia frequently observed in the atmospheric boundary layer. Laboratory studies conducted on synthetic dew showed that the fraction of ammonium (NH$_4^+$) released as gas-phase ammonia (NH$_3$) during evaporation is dependent on the relative abundances of anions and cations in the dew. Hence, the fraction of NH$_3$ released during dew evaporation (Frac(NH$_3$)) can be predicted given dew composition and pH. Twelve separate ambient dew samples were collected at a remote high elevation grassland site in Colorado from 28 May to 11 August, 2015. Average [NH$_4^+$] and pH were 26 μM and 5.2, respectively, and were on the lower end of dew [NH$_4^+$] and pH observations reported in the literature. Ambient dew mass (in g m$^{-2}$) was monitored with a dewmeter, which continuously measured the mass of a tray containing artificial turf representative of the grass canopy to track the accumulation and evaporation of dew. Simultaneous measurements of ambient NH$_3$ indicated that a morning increase in NH$_3$ was coincident in time with dew evaporation, and that either a plateau or decrease in NH$_3$ occurred once the dew had completely evaporated. This morning increase in NH$_3$ was never observed on mornings without surface wetness (neither dew nor rain, representing one-quarter of mornings during the study period). Dew composition was used to determine an average Frac(NH$_3$) of 0.94, suggesting that nearly all NH$_4^+$ is released back to the
boundary layer as NH$_3$ during evaporation at this site. An average NH$_3$ emission of 6.2 ng m$^{-2}$ s$^{-1}$ during dew evaporation was calculated using total dew volume ($V_{dew}$) and evaporation time ($t_{evap}$), and represents a significant morning flux in a non-fertilized grassland. Assuming a boundary layer height of 150 m, the average mole ratio of NH$_4^+$ in dew to NH$_3$ in the boundary layer at sunrise is roughly 1.6 ± 0.7. Furthermore, the observed loss of NH$_3$ during nights with dew is approximately equal to the observed amount of NH$_4^+$ sequestered in dew at the onset of evaporation. Hence, there is strong evidence that dew is both a significant night-time reservoir and strong morning source of NH$_3$. The possibility of rain evaporation as a source of NH$_3$, as well as dew evaporation influencing species of similar water solubility (acetic acid, formic acid, and HONO) is also discussed. If release of NH$_3$ from dew and rain evaporation is pervasive in many environments, then estimates of NH$_3$ dry deposition and NH$_x$ (≡NH$_3$ + NH$_4^+$) wet deposition may be overestimated by models that assume that all NH$_x$ deposited in rain and dew remains at the surface.

### 3.2 Introduction

Ammonia (NH$_3$) is the most prevalent alkaline gas in the atmosphere and has important implications for both climate and air quality (Seinfeld and Pandis, 2006). For instance, NH$_3$ partitions to acidic fine particulate matter (PM$_{2.5}$, aerosol with diameter < 2.5 μm) to form particulate-phase ammonium (NH$_4^+$), which alters aerosol properties such as hygroscopicity (Petters and Kreidenweis, 2007) and scattering efficiency (Martin et al., 2004). High atmospheric loadings of PM$_{2.5}$ can lead to adverse health effects (Pope et al., 2002) as well as reduced visibility. NH$_3$ is primarily emitted to the atmosphere through agricultural activities (e.g. fertilization, animal husbandry) in addition to natural sources (e.g. soil, vegetation, oceans, volcanoes, wildfires) and other anthropogenic sources (waste/sewage, vehicles and industry) (Reis et al., 2009). Deposition of atmospheric NH$_x$ (≡NH$_3$ + NH$_4^+$) can cause eutrophication and soil acidification in sensitive ecosystems (Krupa, 2003). Hence, there is great interest in being able to accurately model sources, sinks and reservoirs of NH$_x$.

A common feature in the diurnal cycle of atmospheric NH$_3$ mixing ratios is a morning increase or “spike” that typically occurs around 7:00-10:00. Frequently observed in many environments, current hypotheses to explain the morning NH$_3$ increase include dew evaporation (Gong et al., 2011; Wentworth et al., 2014; Wichink Kruit et al., 2007), plant and/or soil emissions (Bash et
al., 2010; Ellis et al., 2011), mixing down of NH$_3$-rich air during the break-up of the nocturnal boundary layer (Walker et al., 2006) and automobile emissions during morning rush hour (Gong et al., 2011; Löflund et al., 2002; Nowak et al., 2006; Whitehead et al., 2007). Several field studies have indicated that NH$_3$ desorption from microscopic water films on leaf surfaces can yield significant fluxes (Burkhardt et al., 2009; Flechard et al., 1999; Neirynck and Ceulemans, 2008; Sutton et al., 1998); therefore, it is reasonable to suggest that macroscopic dew droplets have the same effect. Wentworth et al. (2014) observed a larger morning increase following nights with high relative humidity (RH, a surrogate for dew) and Wichink Kruit et al. (2007) found increasing upward fluxes as soon as the canopy began to dry as measured by a leaf wetness sensor.

Dew generally forms during calm, clear nights when radiative cooling of the surface favours the condensation of water (Richards, 2004). Formation typically starts shortly after sunset and lasts until sunrise when surface heating and a drop in RH initiate evaporation. Over the last five decades, several dozen studies have characterized dew composition and have found that NH$_4^+$ is a ubiquitous constituent of dew and, in some environments, can be the most abundant cation (e.g. Polkowska et al., 2008; Wagner et al., 1992; Yaalon and Ganor, 1968; Yadav and Kumar, 2014). Average [NH$_4^+$] reported in dew ranges from 25 μM (Lekouch et al., 2010) to 1600 μM (Yadav and Kumar, 2014). The composition of dew is primarily controlled by dissolution of water soluble gases (e.g. NH$_3$, HNO$_3$, CO$_2$, SO$_2$) and deposition of coarse mode particles (larger than PM$_{2.5}$ but smaller than 10 μm in diameter) (Takeuchi, 2003).

Field-scale models typically allow NH$_3$ to only deposit on leaf cuticles (i.e. it cannot desorb) and use an empirically-derived function of RH and cuticle acidity to calculate a cuticle deposition velocity. This parameterization accounts for enhanced deposition to acidic water films on leaf surfaces. There are only a handful of field-scale NH$_3$ models that allow for desorption of NH$_3$ from drying water films on leaf cuticles (Burkhardt et al., 2009; Flechard et al., 1999; Neirynck and Ceulemans, 2008; Sutton et al., 1998). Three of these studies (Flechard et al., 1999; Neirynck and Ceulemans, 2008; Sutton et al., 1998) compared models with and without cuticle desorption and found that allowing for NH$_3$ emission from water films on cuticles agrees better with observed fluxes during the morning. Other field-scale measurements attribute discrepancies between measured and modelled morning fluxes to NH$_3$ emission during the drying of canopies (e.g. Bash et al., 2010; Walker et al., 2013; Wyers and Erisman, 1998). Most larger scale
(regional or global) chemical transport models (CTMs) still employ highly simplified deposition schemes for NH$_3$ using look-up tables for deposition velocity and canopy resistance terms (Wesely, 1989). In other words, they treat deposition and emission of NH$_3$ independently despite abundant field evidence that these processes are often highly coupled. However, some recent studies have successfully incorporated a bi-directional NH$_3$ exchange framework into regional and global CTMs (Bash et al., 2013; Wichink Kruit et al., 2012; Zhu et al., 2015).

Although most NH$_3$ surface-air exchange studies account for enhanced deposition to microscopic water films and several even model NH$_3$ desorption, far fewer have attempted to assess the role that macroscopic dew has on influencing NH$_3$ fluxes. This partly stems from the inherent difficulty in measuring dew amount, composition, and pH. Only a few NH$_3$ surface-air exchange studies have attempted to measure dew composition and pH, and did so by manually collecting enough individual droplets in pipettes to perform bulk analyses (Bash et al., 2010; Burkhardt et al., 2009; Walker et al., 2013). To constrain dew amount, Burkhardt et al. (2009) used an empirically-derived relationship to approximate water film thickness from a leaf wetness sensor. Walker et al. (2013) estimated dew amount by difference in water mass between wet and dried leaves. Both studies acknowledge the large uncertainties associated with these methods for estimating total dew amount in the canopy. Regardless, Walker et al. (2013) estimated a maximum flux of 17.6 ng NH$_3$ m$^{-2}$ s$^{-1}$ from dew evaporation in a fertilized corn canopy. One key assumption in this calculation is that all of the NH$_4^+$ present in dew is released as NH$_3$ during evaporation.

Few studies have examined the fate of semi-volatile solutes (e.g. NH$_4^+$/NH$_3$, NO$_2$/HONO, acetate/acetic acid etc…) in rain, cloud, fog or dew during droplet evaporation. Takenaka et al. (2009) studied the chemistry of drying aqueous salts in a series of lab experiments and found that the fraction of “volatile” anions (which they operationally defined as NO$_2^-$, acetate, and formate) remaining on the surface as a salt upon evaporation depends on the relative equivalents of “non-volatile” cations (Na$^+$, K$^+$, Mg$^{2+}$ and Ca$^{2+}$) and “non-volatile” anions (Cl$^-$, NO$_3^-$, and SO$_4^{2-}$). The fraction of volatile anion ($X^-$) that is released during evaporation (as HX$_{(g)}$) can then be predicted using the following equation (Takenaka et al., 2009):

\[
\text{Frac}(X) = \frac{[X_i] - (\Sigma \text{cations} - \Sigma \text{anions})}{[X_i]} \tag{E3.1}
\]
where Frac($X$) is the fraction of the initial anion released to the atmosphere during evaporation, $[X]_i$ is the initial equivalents of “volatile” anion $X$, and $\Sigma$ cations and $\Sigma$ anions are the sums of “non-volatile” cations and anions, respectively. The authors performed numerous experiments for NO$_2^-$, acetate, and formate under a wide range of solute concentrations and pH values and found that equation E3.1 was consistently able to predict the fraction of each constituent liberated during evaporation of aqueous salt solutions. Although not the focus of the work, Takenaka et al. (2009) also performed some evaporation experiments on solutions containing NH$_4^+$ and were able to predict Frac(NH$_3$) with an analogous equation:

$$Frac(NH_3) = \frac{[NH_4^+]_i - (\Sigma anions - \Sigma cations)}{[NH_4^+]_i}$$ (E3.2)

where $[NH_4^+]_i$ is the initial ammonium concentration in the solution.

Few field studies have simultaneously quantified both dew and atmospheric composition. He et al. (2006) observed HONO emission from a drying forest canopy and performed lab studies to show that, on average, ~90% of NO$_2^-$ was released as HONO during droplet evaporation. Rubio et al. (2009, 2012) found positive correlations between formaldehyde, phenols and HONO in dew and the atmosphere. However, none of these studies, or those mentioned earlier for NH$_3$, accurately measured dew amount (in g m$^{-2}$) on the surface, so the relative abundances of the analyte in the dew and gas-phase could not be reliably calculated.

Therefore, great uncertainty exists regarding the influence of dew on boundary layer composition, particularly with respect to NH$_3$ mixing ratios. Motivated by the paucity of data on dew-atmosphere NH$_3$ fluxes, as well as uncertainties about the origin(s) of the frequently observed yet currently unexplained morning NH$_3$ spike, the specific goals of this study were to:

1) Determine the fate of NH$_4^+$ during dew evaporation (Section 3.4.1). What is the ratio of NH$_x$ released as NH$_3$ versus NH$_4^+$ remaining on the surface as a non-volatile salt? What factor(s) govern this ratio?

2) Simultaneously quantify dew amount, NH$_3$ mixing ratio, and dew composition at the onset of evaporation at a field site (Section 3.4.2).

3) Use measurements from 1) and 2) to calculate the relative abundance of NH$_4^+$ in dew and NH$_3$ in the boundary layer, as well as NH$_3$ fluxes from dew evaporation (Section 3.4.3). Is
dew a significant night-time sink or reservoir for NH$_3$? Is NH$_3$ release from dew an important morning source?

4) Evaluate if NH$_3$ is also released during rain evaporation (Section 3.4.4).

5) Assess the impact of dew evaporation for other water-soluble gases (Section 3.4.5).

### 3.3 Methods and Materials

#### 3.3.1 Drying chamber

A drying chamber was used to determine the fraction of NH$_4^+$ lost as NH$_3$ during droplet evaporation and was based on the set-up used by Takenaka et al. (2009). The set-up consists of a zero air cylinder (AI Z300, Airgas) and mass flow controller which deliver zero air at a controlled flow rate into a drying chamber (URG-2000-30H, URG Corp.) containing droplets of synthetic dew. Downstream of the drying chamber is an annular denuder (URG-2000-30, URG Corp.) coated with a phosphorous acid solution (10 g H$_3$PO$_3$ in 100 mL deionized water and 900 mL HPLC grade methanol) to capture any NH$_3$ emitted during dew drying.

At the beginning of each experiment, 26 droplets (20 μL each) of synthetic dew were deposited in the drying chamber and dried over the course of several hours by exposure to a flow of 2 L min$^{-1}$ of zero air. Immediately after the last droplet had dried, the residue remaining in the chamber was extracted twice using two separate 10 mL aliquots of deionized water (18.2 MΩ cm$^{-1}$) and vigorous washing. The second aliquot always contained <10% of each analyte relative to the first aliquot. The annular denuder was extracted by adding 10 mL of deionized water and rotating for 10 minutes. Concentrations of ions in all three extracts were quantified using ion chromatography (IC) systems (DX-500, Dionex Inc.) and an isocratic elution scheme (1.8/1.7 mM Na$_2$CO$_3$/NaHCO$_3$ solution for anions and 0.020 mM methanesulphonic acid solution for cations). The pH of the dew was determined using a commercial pH meter (Orion Model 250A, Thermo Scientific). The fraction of each analyte remaining in the salt residue was then calculated, as well as the fraction of ammonium lost as NH$_3$ based on the total NH$_x$ amount measured in the three aliquots.

Experimental parameters (composition, pH and drying time) were varied to determine the factor(s) responsible for the fraction of NH$_3$ that is released from dew as it dries. Synthetic dew was prepared by dissolving salts in deionized water to the desired concentration. All salts were
reagent grade, obtained from Sigma Aldrich and used without further purification. The pH was then adjusted with either concentrated acid (HCl) or base (NaOH). A total of nine different synthetic dews were prepared to mimic ambient dew composition reported from previous studies (e.g. Lekouch et al., 2010; Takenaka et al., 2003; Yadav and Kumar, 2014). The pH and concentrations of the nine synthetic dews are listed in appendix Table A1.

Synthetic dew was deposited as 20 μL droplets, which corresponds to a hemi-spherical diameter of ~4.25 mm. Takeuchi et al. (2002) found that the diameter of most dew droplets range from 0.8 to 1.0 mm in diameter; however, applying such small droplets would bring the concentration of the extracts below detection limit. In order to maintain solute concentrations relevant to ambient dew, but generate sufficient signal for analysis, it was necessary to use 20 μL droplets. The impact of larger droplet size on NH₃ liberation was tested by performing several drying experiments on four 140 μL drops (~8.1 mm in diameter). These larger droplets had no effect on the fraction of NH₃ emitted relative to the 20 μL droplets.

3.3.2 Field Site

Ambient measurements of dew composition, dew volume and gas-phase NH₃ were obtained at a field site situated on the eastern edge of Rocky Mountain National Park (RMNP) in Northern Colorado (40.2783° N, 105.5457° W; 2784 m a.s.l.) from 28 May to 31 August, 2015. The field site is remote with the nearest town (Estes Park, CO, population ~6,000) located approximately 14 km north. This site is also used by the Interagency Monitoring of Protected Visual Environments (IMPROVE) and EPA Clean Air Status and Trends Network (CASTNet) programs for air quality monitoring and has been the location of extensive studies on nitrogen deposition (Beem et al., 2010; Benedict et al., 2013a) and atmospheric reactive nitrogen (Benedict et al., 2013b). The field site is a grassland clearing approximately 150 m in diameter surrounded by a mixed aspen and pine forest (average summertime maximum leaf area index of 1.5). In addition, excessive nitrogen deposition at RMNP has been linked to ecological impacts including changes in diatom assemblages (Baron, 2006; Wolfe et al., 2003) and shifts in the abundance of some alpine plant species (Bowman et al., 2012). Recently, Nanus et al. (2012) suggested that the critical load for nitrogen deposition (a value beyond which negative ecological impacts are observed) has been exceeded in ~21% of the Rocky Mountains. The existing body of
knowledge regarding reactive nitrogen at RMNP makes this site ideal to examine how dew-atmosphere interactions affect NH$_3$ in the boundary layer as well as its deposition.

### 3.3.3 Atmospheric measurements

NH$_3$ was measured using a Picarro G1103 Analyzer, a cavity ringdown spectroscopy instrument. The inlet line was 3.56 cm diameter Teflon tubing located approximately 2.5 m above ground level. The entire length of the 0.61 m inlet line was insulated and heated to 40°C to minimize wall losses. A filter (Picarro P/N S1021) was placed on the end of the inlet to prevent particles from entering the instrument. The filter was also heated which may have caused NH$_4$NO$_3$ to volatilize from the filter or air stream resulting in an overestimation of the ammonia concentration. However, a previous study at the site found that, on average, only a small fraction of particulate NH$_4^+$ exists as NH$_4$NO$_3$ during the summer (Benedict et al., 2013b). Furthermore, the same study found that NH$_3$ was the majority of the NH$_x$ (≡NH$_3$ + NH$_4^+$) loading. Hence, it is unlikely that there is a large interference from NH$_4$NO$_3$ volatilization.

Calibrations were performed twice during the field deployment using MKS mass flow controllers, a certified 2 ppm NH$_3$ cylinder (AirGas), and a zero air source (Teledyne Zero Air Generator Model 701). The calibration gas was split between the Picarro and a phosphorous acid (10% w/v) coated denuder to act as a check of the concentration. The denuder was sampled at 2 L min$^{-1}$ and the total volume was recorded using a dry gas meter. The concentration determined by the denuder was used as the “true” concentration in the calibration curve.

Meteorological measurements were made at the site by a 10 m tower operated by the National Park Service. Measurements are reported at 1 hour intervals for solar radiation, temperature, wind speed, wind direction, standard deviation of the wind direction over the period, relative humidity, and rainfall.

### 3.3.4 Dew measurements

Ambient dew samples at RMNP were gathered using a dew collector with a design similar to Guan et al. (2014). The collector was built in-house and consists of a wooden base that supports a 7 cm-thick polystyrene foam block with an area of 48 x 60 cm. The top surface of the polystyrene block is covered by a 0.2 mm-thick polytetrafluoroethylene (Teflon®) sheet. The Teflon® sheet is parallel to the ground at a height of 30 cm. During the night the Teflon® sheet
undergoes radiative cooling while the polystyrene insulates the sheet from below. This results in dew formation on the Teflon® surface which can be manually collected into clean sample bottles the following morning using a pre-cleaned scraper and funnel. The emissivity of Teflon® is 0.94 (Baldridge et al., 2009) and is very similar to that of vegetation (0.95) (Guan et al., 2014).

The dew collector was deployed before dusk on nights that had a forecast favourable for dew formation (high relative humidity, light winds, and clear skies). The Teflon® surface was cleaned immediately before deployment in a two-step process: 1) splashing ~1 L of deionized water across the surface, followed by 2) squirting ~30 mL of deionized water on the surface and scraping it off using a plastic scraper. The latter step was repeated 10 times, and the 10th rinse was collected and used as a field blank for dew collected the following morning. Prior to dew collection, the funnel and scraper were rinsed 10 times with deionized water. This cleaning procedure proved sufficient and is similar to prior studies using a similar collector (e.g. Okochi et al., 2008; Wagner et al., 1992). Dew samples were collected into 15 mL polypropylene sample bottles in order to minimize headspace during transport and storage.

If rain had occurred during the night, then rain samples were also collected off of the dew collector in a similar fashion the following morning. Rain samples were unambiguously identified using data from the dewmeter described below.

Chemical analyses of all dew samples were performed within 6 hours of collection, with the exception of one sample which was stored at 4 °C and analysed 48 hours later. The concentration of ions (Na+, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, NO₂⁻, NO₃⁻, SO₄²⁻, PO₄³⁻, acetate, formate and oxalate) in dew samples was determined through ion chromatography and pH was measured with a pH meter, as outlined in section 3.3.1. The total organic carbon (TOC) and inorganic carbon (IC) were quantified with a commercial TOC analyser (TOC-VCSH, Shimadzu Corp.) equipped with a total nitrogen (TN) analyser (TNM-1, Shimadzu Corp.) for quantification of TN. Concentrations of analytes in ambient dew samples were background corrected by subtracting the volume-weighted concentration in the tenth rinse collected the prior evening which is likely an upper bound for the background signal given that some volatile solutes will be scavenged from the air during application and collection of the rinse.

It was also necessary to quantify the volume of dew (V_dew) that formed each night. The dew collector is not suitable since V_dew obtained from the collector is not necessarily representative of
\( V_{\text{dew}} \) that forms naturally on the grassland canopy at RMNP. Numerous methods and instruments exist to measure \( V_{\text{dew}} \); for instance, the cloth-plate method (Ye et al., 2007), lysimeter-related instruments (Grimmond et al., 1992; Price and Clark, 2014), and eddy-correlation techniques (Moro et al., 2007). Although there is no standard method to measure \( V_{\text{dew}} \), Richards (2004) provides a detailed overview of various techniques that have been used to collect and quantify dew.

For this study, we constructed a dewmeter similar to that of Price and Clark (2014). The design consists of a circular collection tray (diameter of 35 cm) that is attached to the top of an analytical balance (HRB 3002, LWC Measurements). The balance has a resolution of 0.01 g and a maximum load of 3000 g. The tray contains artificial turf that is intended to be representative of the grass at the RMNP field site during the early part of the growing season. The balance was contained in a weatherproof box with a hole cut in the lid to accommodate the tray/turf. The mass on top of the balance was recorded to a laptop at a rate of 5 Hz so that the mass of dew was continuously monitored as it formed and evaporated. The data were averaged to 10 min to achieve better signal-to-noise.

Price and Clark (2014) performed an extensive characterization of the dewmeter and compared dew formation/evaporation on co-located dewmeters containing real turf and artificial turf. The authors found that \( V_{\text{dew}} \) and the dew deposition rate were identical between the two turfs. In other words, the radiative properties and surface area of artificial turf sufficiently mimic real turf such that artificial turf can be used as a surrogate to quantify \( V_{\text{dew}} \) and its temporal evolution. The advantage of using artificial turf is that there are no changes in mass due to evapotranspiration during the daytime. The dewmeter is also capable of quantifying rainfall and its evaporation. However, if the rainfall is too intense (\( \geq 2 \text{ mm} \)) then the tray becomes flooded and must be replaced with a dry tray/turf.

### 3.3.5 Flux calculation

\( \text{NH}_3 \) fluxes from dew evaporation were calculated using the following equation:

\[
F_{\text{NH}_3} = \left( \frac{[\text{NH}_3^+]}{t_{\text{evap}}} \right) \cdot V_{\text{dew}} \cdot \text{Frac}(\text{NH}_3) \cdot 17,031
\]  
(E3.3)
where $F_{NH3}$ is the average emission flux (in ng m$^{-2}$ s$^{-1}$) during dew drying, $[NH_4^+]$ is the concentration of ammonium in dew (in μM), $V_{dew}$ is the volume of dew in the canopy (in L m$^{-2}$), $t_{evap}$ is the time it takes for dew to evaporate (in s), $\text{Frac}(NH_3)$ is the fraction of $NH_4^+$ in the dew that is released as NH$_3$, and 17,031 is to convert μmol to ng. It is important to note that equation E3.3 yields the average $F_{NH3}$ during evaporation and cannot account for any variations in $F_{NH3}$ over the evaporation period. The dewmeter was used to record $V_{dew}$ and $t_{evap}$, whereas sample from the dew collector was used to quantify $[NH_4^+]$ and calculate $\text{Frac}(NH_3)$. The dewmeter is automated and was deployed continuously from 22 June until 31 August (and intermittently between 27 May and 21 June), whereas the dew collector requires manual cleaning and collection so was only deployed when forecasts were favourable for dew formation.

3.4 Results and Discussion

3.4.1 Fraction of NH$_3$ that evaporates from drying dew

We tested the validity of equation E3.2 by performing a series of drying experiments similar to Takenaka et al. (2009) but specifically targeting conditions relevant for dew (i.e. composition and drying time). Takenaka et al. (2009) used solutions in the mM range with drying times of ~9 h, whereas natural dew is typically less concentrated (μM range) and usually dries within a few hours. The composition of synthetic dew (appendix Table A1) and drying time (~2.5 h) in this work are a better representation of natural dew.

Figure 3.1 shows the measured $\text{Frac}(NH_3)$ versus predicted $\text{Frac}(NH_3)$ from an updated form of equation E3.2 (see below for details) for the nine synthetic dews. Drying experiments were performed three times per dew composition, and error bars in Fig. 3.1 denote the standard deviation between replicates. The amount of NH$_3$ ($\equiv NH_4^+ + NH_3$) recovered was always within 20% of the amount of NH$_4^+$ added at the beginning of the experiment. There is good agreement between the measured and predicted $\text{Frac}(NH_3)$ which is mostly consistent with the findings of Takenaka et al. (2009) with a few key differences: 1) the majority of acetate and formate remained as a salt after evaporation, 2) HCO$_3^-$ was an important constituent in the anion balance, and 3) the pKa of each substance must be considered. Although acetic acid, formic acid, and carbonic acid are relatively volatile, the conjugate bases can (and do) form non-volatile salts upon evaporation if there is an excess of cations. Furthermore, if the pH is near or less than the pKa of the acids then a significant fraction will be neutral (protonated) and unable to form a salt.
Hence, we update the definition of $\Sigma$ anions in equation E3.2 to include acetate, formate, and bicarbonate (also reflected in Fig. 3.1) which yields much better agreement in predicted versus measured Frac(NH$_3$).

**Figure 3.1** Fraction of NH$_3$ liberated during drying experiments versus the fraction predicted according to an updated equation E3.2 to include acetate, formate, CO$_3^{2-}$ and HCO$_3^{-}$ in the anion balance. Excluding these anions significantly reduces the correlation. Error bars represent ±σ from three experiments per synthetic dew. The dashed line is the 1:1 line.

Since ion chromatography quantifies the total amount of each species (i.e. both charged and neutral forms) it is necessary to use pH and the acid dissociation constant ($K_a$) for each species to calculate the ionic fraction of each. Furthermore, Takenaka et al. (2009) recommend including carbonate/bicarbonate in the ion balance for field samples. The authors did not account for CO$_2$-equilibria since their lab experiments were performed under strict CO$_2$-free conditions, whereas our synthetic dew samples had sufficient exposure to lab air to equilibrate with atmospheric CO$_2$ (~500 ppm in the lab) as verified by subsequent inorganic carbon measurements (section 3.3.4). Hence, we calculated the amount of HCO$_3^{-}$ and CO$_3^{2-}$ in synthetic dew using pH and carbonate equilibria assuming $P_{CO2} = 500$ ppm. Charge imbalance calculated in equation E3.2 is a result of CO$_2$ dissolving (or outgassing if a large quantity of bicarbonate/carbonate salt was added) as well as the addition of HCl or NaOH. Subsequent research should be conducted to determine whether there is an upper limit on observed Frac(NH$_3$).
3.4.2 Dew parameters

A total of 12 dew samples for chemical analysis were collected at RMNP over the study period. The equivalent concentrations of ions are given in Fig. 3.2 and TOC, IC, TN, pH and Frac(NH$_3$) in Table 3.1. Average values of [NH$_4^+$] in dew found in the literature span several orders of magnitude ranging from 25 μM in coastal Croatia (Lekouch et al., 2010) to 1600 μM in urban India (Yadav and Kumar, 2014). Dew at RMNP is at the lower end of this range with median [NH$_4^+$] = 28 μM. In general, the concentrations of all species in RMNP dew are lower than most previous studies (e.g. Singh et al., 2006; Takenaka et al., 2003; Wagner et al., 1992). This is due to the remoteness of RMNP resulting in low levels of coarse mode aerosol and water-soluble gases which tend to control the composition of dew via deposition and dissolution (Takeuchi, 2003; Wagner et al., 1992). The dominant cations in dew at RMNP are Ca$^{2+}$ and NH$_4^+$. The former is likely from the deposition of coarse mode soil and/or dust particles and the latter from gas-phase dissolution of NH$_3$. Acetate and formate are the major anions and may be the result of dissolution of acetic and formic acid (Wagner et al., 1992) and/or the products of aqueous-phase oxidation of semi-volatile organics (SVOCs, e.g. aldehydes) which has been observed in cloud and fog water (Herckes et al., 2007, 2013; Munger et al., 1989). The area surrounding the field site is heavily forested and the boundary layer is likely rich in biogenic SVOCs which could explain the high TOC content in the dew (average = 6.23 mg C L$^{-1}$). The ability for dew to act as a medium for aqueous-phase oxidation of SVOCs is outside the scope of this paper but warrants further investigation.
**Table 3.1** Total Organic Carbon (TOC), Total Nitrogen (TN), Inorganic Carbon (IC), pH, the ratio of measured to predicted [NH$_4^+$] in dew, and parameters pertinent to NH$_3$ flux calculations in the field dew samples

<table>
<thead>
<tr>
<th>Date</th>
<th>TOC (mg C L$^{-1}$)</th>
<th>IC (mg C L$^{-1}$)</th>
<th>TN (mg N L$^{-1}$)</th>
<th>pH</th>
<th>Frac(NH$_3$)</th>
<th>$V_{dew}$ (mL m$^{-2}$)</th>
<th>$t_{evap}$ (s)</th>
<th>Flux (ng m$^{-2}$ s$^{-1}$)</th>
<th>[NH$<em>4^+$]$</em>{\text{meas}}$/[NH$<em>4^+$]$</em>{\text{eqm}}$</th>
</tr>
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<tr>
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<td>0.52</td>
<td>0.05</td>
<td>5.46</td>
<td>1.0</td>
<td>79.8</td>
<td>6000</td>
<td>2.4</td>
<td>0.02</td>
</tr>
<tr>
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<td>0.32</td>
<td>5.65</td>
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<td>6600</td>
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<tr>
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<td>0.61</td>
<td>5.35</td>
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<td>167.2</td>
<td>10800</td>
<td>7.3</td>
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<td>06/27</td>
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<td>0.59</td>
<td>0.62</td>
<td>5.70</td>
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<td>0.95</td>
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<tr>
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<td>0.32</td>
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<td>1.0</td>
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</tr>
<tr>
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<td>1.0</td>
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</tr>
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<td>5.80</td>
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<td>92.2</td>
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</tr>
<tr>
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<td>0.80</td>
<td>5.34</td>
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<td>6.9</td>
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<tr>
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<td>0.85</td>
<td>4.67</td>
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<td>14400</td>
<td>4.2</td>
<td>0.02</td>
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<td><strong>Avg</strong></td>
<td><strong>6.23</strong></td>
<td><strong>0.42</strong></td>
<td><strong>0.85</strong></td>
<td><strong>5.19</strong></td>
<td><strong>0.94</strong></td>
<td><strong>134.8</strong></td>
<td><strong>10250</strong></td>
<td><strong>6.2</strong></td>
<td><strong>0.04</strong></td>
</tr>
</tbody>
</table>

**Figure 3.2** Ionic composition (in µN) of ambient dew collected at RMNP.
The average pH of dew at RMNP was 5.19 (median = 5.34) which is on the lower range of what has been reported for dew. For instance, Yaalon and Ganor (1968) and Xu et al. (2015) found median dew pH of 7.7 and 6.72 in Jerusalem and Changchun, China, respectively. Whereas Pierson et al. (1986) reported an average dew pH of 4.0 at a rural site in Pennsylvania in a region containing several coal-fired power plants. Given the remoteness of RMNP and low ionic concentrations, CO₂ dissolution plays an important role in governing dew pH. Acidic dews are considered to enhance deposition of NH₃ and hinder that of certain weakly acidic gases (e.g. SO₂, organic acids) (Chameides, 1987; Okochi et al., 1996). In addition, the average summertime NH₃ mixing ratio at RMNP is about a factor of 3 higher than that of HNO₃ (Benedict et al., 2013b) which is roughly the same ratio as NH₄⁺:NO₃⁻ in dew measured in this study.

Figure 3.2 reveals a persistent ion imbalance for ambient dew samples. On average, about 25% more anion is needed to achieve ion balance with the measured cations. This implies that some anions are unaccounted for in the system. Possible explanations include: 1) longer chain organic acids (e.g. succinate, maleate, malonate, and pyruvate) and/or 2) silicates from wind-blown dust.

Equation E3.2 was used to calculate Frac(NH₃) for ambient dew samples (average = 0.94). Only three of the twelve samples had a Frac(NH₃) less than 1 meaning that, in most cases, all of the NH₄⁺ present is predicted to volatilize as NH₃ during dew evaporation. It is important to note that acetate, formate, and HCO₃⁻ were included in the Σanion budget in contrast to Takenaka et al. (2009). If the aforementioned anions were not included in the Frac(NH₃) calculation then all dew samples would have Frac(NH₃) = 1.

The high Frac(NH₃) has an important implication for N-deposition: NH₃ that is dry deposited onto a surface wetted with dew does not necessarily contribute to N-deposition. In other words, NH₃ deposited into dew overnight should not necessarily be counted towards the total N-deposition budget for a given ecosystem. The consequence of this implication likely extends beyond RMNP and merits additional field measurements of dew to calculate Frac(NH₃) in other environments (e.g. agricultural, urban, and rural). To our knowledge, this is the first field study to quantify the extent to which NH₄⁺ is released as NH₃ during dew evaporation. Additional research is needed to examine the effects of: 1) salts already present on vegetative surfaces on dew composition, 2) dew transfer from leaf to soil prior to evaporation, and 3) different canopies (e.g. forest, tall grass) on the amount and timing of dew accumulation and evaporation.
3.4.3 Dew-atmosphere NH₃ fluxes

In this section we examine how the formation and evaporation of dew impacts NH₃ in the boundary layer. Figure 3.3 shows time series (from 19:00 to 11:00 the following day) of dew mass (g m⁻²), air temperature (°C) and NH₃ mixing ratio (ppbv) on four separate nights with dew. One feature common to all four panels is the increase of NH₃ at the onset of dew evaporation followed by a plateau or decrease of NH₃ once the surface had dried completely. The features in Fig. 3.3 are representative of the other 29 nights on which dew formed during the study period (27 May to 31 August). It should be noted that in Fig. 3.3c and 3.3d, the start of the morning NH₃ increase is slightly delayed from the onset of dew evaporation. This may be attributed to canopy growth over the course of the campaign – during May and June (Figs. 3.3a and 3.3b) the grassland canopy was relatively short (~5 cm) and roughly the same height as the artificial turf on the dewmeter. However, during July (Fig. 3.3c) and August (Fig. 3.3d) the canopy had grown significantly (up to ~30 cm) providing significant shade to lower parts of the grass such that dew finished evaporating off the dewmeter prior to complete drying of the canopy. This would also cause an underestimation of dew amount by the dewmeter towards the end of the measurement period.
Figure 3.3 Dew accumulation (blue, g m$^{-2}$), NH$_3$ mixing ratio (orange, ppbv) and air temperature (red, °C) overnight on a) 22 June, b) 27 June, c) 21 July and d) 9 August 2015. The black line in (b) is the best fit for the NH$_3$ mixing ratio to an exponential decay function (see equation E3.4) between 20:00 and the onset of dew evaporation.

The consistent timing between dew evaporation and the increase in NH$_3$ mixing ratio is strong evidence that dew evaporation and the early morning NH$_3$ increases are linked, but other phenomena must be considered. For instance, it is well known that NH$_3$ emissions from plant stomata and soil are heavily temperature dependent and increase at higher temperatures (Massad et al., 2010; Sutton et al., 2013; Zhang et al., 2010). However, NH$_3$ decreases after dew evaporation ceases, despite a continued increase in temperature, suggesting that this morning
increase is not from stomata or soil emissions. Another possible explanation is reduced deposition after dew evaporation since wet canopies provide a lower resistance to deposition for water-soluble gases (e.g. NH$_3$) relative to dry canopies (Fowler et al., 2009; Neirynck and Ceulemans, 2008); however, this scenario requires other continuous source(s) of NH$_3$. If this were the mechanism responsible for morning NH$_3$ increases then one would expect a plateau in NH$_3$ after canopy drying. However, Figs. 3.3a, 3.3b, and 3.3d all show NH$_3$ decreases after dew evaporation. In addition, RMNP is sufficiently remote that morning NH$_3$ increases cannot be from rush-hour traffic or industrial sources.

It is also useful to consider the behaviour of NH$_3$ on mornings without dew. Of the 72 nights on which the dewmeter was deployed and functioning, there was night-time rain on 23 of the nights, and no surface wetness (neither rain nor dew) at sunrise on 16 nights. Typically, dew formation began around 20:30 and it had completely evaporated by 9:00 the following morning. Figure 3.4 compares NH$_3$ mixing ratios from 4:00 to 11:00 on mornings with dew (Fig. 3.4a) and without dew or rain (Fig 3.4b). The clear morning NH$_3$ increase only happens on mornings with dew, further supporting the hypothesis that dew evaporation has a significant influence on near-surface NH$_3$ mixing ratios. The traces in Fig. 3.4 are coloured according to the average NH$_3$ mixing ratio the previous night (from 19:00 to 21:00). The magnitude of the morning increase is related to the amount of NH$_3$ present the previous night suggesting that most of the NH$_4^+$ in dew is a result of NH$_3$ dissolution. This is additional evidence that NH$_3$ deposited in dew overnight at RMNP is recycled back to the atmosphere the following morning upon evaporation, and should not be counted towards total N-deposition. In other words, the dew acts as a temporary reservoir for atmospheric ammonia and the cycle of dew formation and evaporation has a strong influence on boundary layer NH$_3$ concentrations.
Figure 3.4 Time series of NH₃ mixing ratio (in ppb) from 4:00 to 11:00 on (a) mornings with dew and (b) mornings with no surface wetness. Traces are coloured according to the average NH₃ mixing ratio measured the previous night between 19:00 to 21:00.

Table 3.1 shows the calculated NH₃ fluxes from dew during evaporation (average = 6.2 ng m⁻² s⁻¹) as well as the relevant parameters required for flux calculations (tₑᵥₐₚ, Frac(NH₃), and Vₑₜₐₜ). To our knowledge, only two studies to date have reported NH₃ fluxes in a non-fertilized grassland. Wichink Kruit et al. (2007) used the aerodynamic gradient method to measure a daily average summertime NH₃ flux of 4 ng m⁻² s⁻¹ in a field in the Netherlands, whereas Wentworth et al. (2014) inferred a daily average soil emission flux of 2.6 ng m⁻² s⁻¹ during August in a rural field near Toronto, Canada using simultaneous soil and atmospheric measurements and a simple resistance model. In the context of these previous studies over the same land type, the dew-related NH₃ fluxes at RMNP are significant. Furthermore, it is likely that dew-related NH₃ fluxes would be substantially larger at the other field sites given that NH₃ mixing ratios were a factor of 3-10 higher which would result in higher dew [NH₄⁺].

It is likely that during some periods the emission/deposition footprint of the atmospheric and dew measurements extends beyond the grassland clearing and into the surrounding forest. While we did not find that the overnight loss rate of ammonia depended on dew amount, the deposition rate of ammonia likely depends on surface type, so estimates of moles of NH₃ deposited per m² from the dew collector may not be representative of the surrounding forest. Upslope and downslope
flow conditions could also explain some of the variability in nocturnal NH$_3$ since the latter is prevalent during the nighttime and delivers cleaner air from the west of RMNP. Subsequent work should be performed to examine the representativeness of grassland dew measurements to the larger surrounding ecosystem.

For the 12 dew samples listed in Table 3.1, a simple calculation was performed to estimate the moles of NH$_4^+$ contained in dew relative to the moles of NH$_3$ in the boundary layer. Particulate NH$_4^+$ is not considered due to its low mass loadings at RMNP (Benedict et al., 2013b). The $\mu$mol m$^{-2}$ of NH$_4^+$ in dew at the onset of evaporation was calculated by multiplying $V_{\text{dew}}$ by dew $[\text{NH}_4^+]$. One inherent assumption is that $[\text{NH}_4^+]_{\text{dew}}$ on the collector is representative of the dew on the dewmeter. An equivalent mole loading (also in $\mu$mol m$^{-2}$) of NH$_3$ in the boundary layer was calculated by first converting the measured mixing ratio from ppbv to $\mu$mol m$^{-3}$, and then multiplying by an assumed boundary layer depth of 150 m. The average ratio of NH$_4^+_{\text{dew}}$:NH$_3$$_{\text{BL}}$ is 1.6 ± 0.7 for the 12 dew samples collected. In other words, on a per mole basis there is nearly double the NH$_4^+$ in dew than there is NH$_3$ in a 150 m deep boundary layer. Unfortunately, there are no measurements at RMNP that allow a better constraint of the boundary layer height. Assuming a smaller (larger) boundary layer height would increase (decrease) the NH$_4^+_{\text{dew}}$:NH$_3$$_{\text{BL}}$ ratio.

The measured loss of NH$_3$ (in ppbv) during dew nights was used to estimate the sink of NH$_3$ (in $\mu$mol m$^{-2}$) between the onset of dew formation and evaporation. This loss was estimated in a similar fashion as above assuming: 1) 150 m nocturnal boundary layer, 2) no reactive sinks (e.g. NH$_4$NO$_3$ formation), 3) no exchange with the free troposphere, and 4) no influence from horizontal advection (i.e. upslope/downslope flow) on NH$_3$. Figure 3.5 shows a correlation plot of estimated NH$_3$ lost on dew nights versus the observed NH$_4^+$ accumulated in dew. The good correlation and near-unity slope (0.71) show that there is approximate mass closure between NH$_3$ lost overnight and NH$_3$ sequestered by dew. Although these calculations are simplistic it is evident that, on average, dew sequesters a significant portion (estimated at nearly two-thirds) of NH$_3$ over the course of the night. Subsequent studies on dew-atmosphere interactions should include measurements of boundary layer height so a more thorough mass balance calculation can be performed.
Figure 3.5 Estimated NH$_3$ lost overnight assuming a 150 m boundary layer versus measured NH$_4^+$ accumulated in dew by the onset of evaporation. The red line is the best fit line (forced through the origin) and the dashed grey line is the 1:1 line.

The loss rate of NH$_3$ on dew nights versus dry nights was examined by fitting the NH$_3$ mixing ratio to an exponential decay function between 20:00 and 9:00 (or dew evaporation) on the 46 nights in Fig. 3.4. The fit function used was:

$$[\text{NH}_3]_t = [\text{NH}_3]_{\text{sunset}} e^{-kt} + [\text{NH}_3]_{\text{overnight}}$$ (E.3.4)

where $[\text{NH}_3]_t$ is the mixing ratio of NH$_3$ at time $t$, $[\text{NH}_3]_{\text{sunset}}$ is the mixing ratio at 20:00, $[\text{NH}_3]_{\text{overnight}}$ is the plateau in nocturnal NH$_3$ mixing ratio, and $k$ is an empirical fit parameter representing the apparent first-order loss rate constant of NH$_3$. An example of the fit is shown by the black trace in Fig. 3.3b.

The average NH$_3$ loss rate constant on dew nights was 1.33 ± 0.5 x 10$^{-4}$ s$^{-1}$ compared to 1.35 ± 0.3 x 10$^{-4}$ s$^{-1}$ on dry nights. In other words, there is no significant difference in the rate of NH$_3$ loss on dew versus non-dew nights. This implies that dew does not actually enhance NH$_3$ deposition under these conditions, suggesting that the aerodynamic and quasi-laminar resistances dominate over surface resistances. The average nocturnal wind speed on dew nights was lower than on dry nights (1.3 m s$^{-1}$ versus 2.2 m s$^{-1}$). Lower wind speeds typically result in a higher $R_a$
and $R_p$. It is possible that increased aerodynamic and quasi-laminar resistances on dew nights are partially compensated for by a lower surface resistance due to dew, such that the overall canopy resistance is similar on dew nights and dry nights. Average nocturnal wind direction was from the NW (i.e. downslope flow) on both dew nights (307°) and dry nights (313°). The average nocturnal maximum for RH was 75% on dew nights and only 53% on dry nights. The lower wind speeds and higher RH on dew nights are consistent with the meteorological conditions favourable for dew formation.

Deposition of NH$_3$ on dry nights could be to either leaf cuticles and/or soil pore water. However, it is not possible to unambiguously attribute the nocturnal NH$_3$ loss solely to deposition. Enhanced downslope flow of cleaner air on dry nights cannot be ruled out as a contributor to nocturnal NH$_3$ loss. Since NH$_3$ deposition is independent of dew amount, there could be a large discrepancy between [NH$_4^+$] for dew on the dewmeter versus the dew collector if $V_{dew}$ is significantly different on the two surfaces. However, the campaign averages of $V_{dew}$ on the dewmeter (Table 3.1) and are within 10% of dew volume obtained off the collector (data not shown) so [NH$_4^+$] is likely similar for dew on both platforms.

Since most of the NH$_4^+$ in dew volatilizes and the presence of dew does not affect NH$_3$ deposition overnight, the net impact is a reduction in the overall removal of NH$_3$. As a result, the atmospheric lifetime and range of NH$_3$ transport will be extended.

### 3.4.4 Potential influence from rain evaporation

Numerous studies have reported rapid increases of near-surface NH$_3$ within 1-2 h after some rain events (e.g. Cooter et al., 2010; Walker et al., 2013; Wentworth et al., 2014). Given the findings discussed in the previous section, one possible explanation is the emission of NH$_3$ from drying rain droplets. However, unlike dew, some difficult-to-predict fraction of rain will permeate through the soil thus preventing or delaying the release of NH$_3$. Nonetheless, we attempt to qualitatively explore this hypothesis by examining the Frac(NH$_3$) of four rain samples collected at RMNP as well as the behaviour of NH$_3$ during rainfall evaporation. Rain samples were collected with the same procedure used to collect dew, which differs from the usual method of capturing precipitation via an automated precipitation bucket (e.g. Benedict et al., 2013a). The precipitation bucket is normally equipped with an O-ring and lid to prevent dry deposition and dissolution of water-soluble gases when it is not precipitating. On the other hand, precipitation
on the dew collector surface was left exposed and its composition is influenced by dry deposition and gas-phase dissolution until it was collected at the onset of evaporation.

Appendix Table A2 gives the concentration of ions measured in rain samples. In general, concentrations of ions are comparable between dew and rain samples, with the exception of \( \text{NH}_4^+ \), \( \text{SO}_4^{2-} \) and \( \text{NO}_3^- \), which are a factor of 2-4 times more concentrated in rain samples. The enhancement of these species in rain may reflect additional in-cloud and below-cloud scavenging of gases (\( \text{NH}_3 \), \( \text{HNO}_3 \) and \( \text{SO}_2 \)) and PM\(_{2.5} \) aloft. Another possibility is that rain generally forms during upslope conditions which coincide with more polluted air masses from east of RMNP, whereas dew typically forms during downslope (cleaner) conditions. Numerous studies have compared dew composition to rain composition and, in general, have found that concentrations are enhanced in dew relative to rain (e.g. Polkowska et al., 2008; Wagner et al., 1992). However, Pierson et al. (1986) reported dew composition to be similar to, but more dilute than rain at a rural site in Pennsylvania.

Appendix Table A3 shows the TOC, IC, TN, pH and calculated Frac(\( \text{NH}_3 \)) for the four rain samples. Rain samples were more acidic (average pH = 4.54) than dew samples (average pH = 5.19). The average Frac(\( \text{NH}_3 \)) for rain samples was 0.66 suggesting that, on average, roughly two-thirds of \( \text{NH}_4^+ \) contained in precipitation on surfaces should be liberated as \( \text{NH}_3 \) upon evaporation. This could pose a significant flux of \( \text{NH}_3 \) to the boundary layer; however, since the fraction of rain that remains on surfaces after rainfall where it can readily evaporate is not constrained, only an upper estimate on \( \text{NH}_3 \) fluxes from drying rain can be calculated (21.2 ± 13 ng m\(^{-2}\) s\(^{-1}\)). This value was calculated in same manner as the dew samples and assumes all rainfall evaporates.

Figure 3.6 shows time series of rain accumulation (g m\(^{-2}\)), air temperature (°C) and \( \text{NH}_3 \) mixing ratio (ppbv) on four separate days with observed rainfall. The rain accumulation was measured with the dewfall meter; 1000 g m\(^{-2}\) of accumulation is equivalent to 1 mm of rainfall. Rainfall in excess of 2000 g m\(^{-2}\) flooded the collection tray and could not be reliably recorded by the dewmeter. On 24 June (Fig. 3.6a) there were three light rainfalls at 15:00, 16:00 and 19:00. The first event at 15:00 was accompanied by a rapid decrease in \( \text{NH}_3 \) likely due to scavenging by rain droplets; however, this was not observed for the other two rainfalls that day. For the second rain event in Fig. 3.6a (at 16:00) a substantial increase in \( \text{NH}_3 \) (from 0.5 to 1.5 ppbv) was observed.
during evaporation and is consistent with NH₃ liberation from evaporating rain. However, evaporation of the other rain events on 24 June (Fig. 3.6a) as well as those on 27 June (Fig. 3.6b) and 11 July (Fig. 3.6c) are not associated with concomitant increases in NH₃, implying that these rain evaporation events did not release NH₃. The evaporation of a more substantial rainfall on 13 August (Fig. 3.6d) is associated with a temporary rise in NH₃ until evaporation ceases at sundown. The instances of rain evaporation not associated with NH₃ increases could be due to rain with a low Frac(NH₃), an insignificant amount of NH₄⁺ in the rain, more atmospheric dilution than dew mornings due to higher turbulence, and/or significant rain penetration into the soil.
Figure 3.6 Rain accumulation (blue, g m⁻²), NH₃ mixing ratio (orange, ppbv) and air temperature (red, °C) during the afternoon and evening on a) 24 June, b) 27 June, c) 11 July and d) 13 August 2015. 100 g m⁻² is equivalent to 0.1 mm of rain.

The results from Fig. 3.6 are consistent with previous literature showing NH₃ increase immediately following only some rainfall events (Cooter et al., 2010; Walker et al., 2013; Wentworth et al., 2014). The timing of some rain evaporation events with NH₃ increases, as well as the high Frac(NH₃) (average = 0.66) of the four measured rain samples suggests it is possible for rain evaporation from surfaces to be a substantial source of NH₃. Neirynck and Ceulemans
(2008) reported NH$_3$ increases concomitant with a drying forest canopy (after rainfall) as measured by a leaf wetness sensor.

Currently, all NH$_4^+$ collected in precipitation samples is counted towards N deposition. However, if a fraction of NH$_4^+$ in rainfall is emitted as NH$_3$ during evaporation then N-deposition could be overestimated. At RMNP, wet deposition of NH$_x$ and dry deposition of NH$_3$ account for 35% and 18%, respectively, of total reactive nitrogen deposition to the site (Benedict et al., 2013a). This budget does not take into account any re-emission of NH$_3$ from drying rain. This budget also does not explicitly account for ammonia uptake or emission during dew formation and evaporation. A more extensive suite of dew and rainfall measurements is necessary to quantify the impact of evaporation on annual N-deposition budgets at RMNP.

### 3.4.5 Implications for other gases

Other water-soluble gases with similar or larger effective Henry’s law constants ($K_{Heff}$) to NH$_3$ are likely influenced by dew and rain evaporation as well, provided that the relative abundance of counter-ions allows for volatilization during evaporation. $K_{Heff}$ is the equilibrium constant for describing gas-aqueous partitioning and accounts for chemical equilibria in solution. Since acid-base equilibria are pH dependent, the $K_{Heff}$ for acidic and basic species is also pH dependent (Sander, 2015). $K_{Heff}$ of NH$_3$ was calculated for the twelve dew samples using data from Sander (2015) to determine the temperature-dependent Henry’s law constant ($K_H$) and from Bates and Pinching (1950) for the temperature-dependent acid dissociation constant ($K_a$) of NH$_4^+$ required for the calculation of $K_{Heff}$. During the study, dew $K_{Heff}$ spanned two orders of magnitude and ranged from 4.5x$10^5$ to 2.7x$10^7$ M atm$^{-1}$. These high values are indicative of the high water solubility of NH$_3$ at the observed pHs and temperatures. Chameides (1987) used a simple resistance model to show that deposition of gas-phase species with $K_{Heff} > 10^5$ M atm$^{-1}$ to wetted surfaces (i.e. dew) will be limited by the aerodynamic resistance since the surface resistance is negligible for such highly water-soluble species. In other words, it is likely that dew will be a significant night-time sink for other trace gas species with $K_{Heff} > 10^5$ M atm$^{-1}$ since the dissolution into dew is controlled by aerodynamic processes independent of the identity of the gas.

Table 3.1 shows the ratio of [NH$_4^+$] measured in dew to the concentration predicted from equilibrium calculations using $K_{Heff}$ and measured NH$_3$ mixing ratio at the onset of evaporation.
The average ratio is low (0.04) meaning the dew is not close to being saturated with NH$_4^+$. Since NH$_3$ is highly water-soluble, it is likely that a significant aerodynamic resistance prevents NH$_4^+$ saturation in dew droplets overnight as opposed to a high surface resistance.

It has been suggested that dew can act as a reservoir for phenol, nitrophenols, formaldehyde and HONO based on observations of these species in dew in Santiago, Chile (Rubio et al., 2009, 2012). Zhou et al. (2002) found a correlation between high night-time RH (a surrogate for dew formation) and HONO increases the following morning coincident with a decrease in RH. A follow-up study (He et al., 2006) confirmed aqueous solutions mimicking dew can release >90% of NO$_2^-$ as HONO upon evaporation and observed similar HONO pulses during canopy drying at a rural forest site in Michigan. Indeed, there is some evidence in the literature that water-soluble gases (primarily HONO) exhibit a similar behaviour to NH$_3$ during dew formation and evaporation observed in this study.

Table 3.2 shows the calculated $K_H^{\text{eff}}$ (at 10 °C) for common water-soluble gases that could be influenced by dew formation/evaporation. This table is by no means exhaustive, but highlights the important role dew may have as a night-time reservoir and morning source for gases other than NH$_3$. Formic acid (HCOOH), acetic acid (CH$_3$COOH), nitrous acid (HONO) and nitric acid (HNO$_3$) all have increasing $K_H^{\text{eff}}$ with increasing pH since a more basic solution will promote dissociation of the acid into its conjugate base. The average pH of dew at RMNP (~5.2) is likely sufficiently acidic for HONO to experience a surface resistance ($K_H^{\text{eff}} \ll 10^5$ M atm$^{-1}$) which would limit its transport across the dew-air interface. This is consistent with the low average [NO$_2^-$] (0.2 μM) in dew at RMNP, although this might simply reflect low HONO mixing ratios at the remote RMNP site.
Table 3.2 $K_{H}^{\text{eff}}$ of NH$_3$ and other water-soluble gases at 10°C and various pHs

<table>
<thead>
<tr>
<th>Gas</th>
<th>pH</th>
<th>$K_{H}^{\text{eff}}$ (M atm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$ (ammonia)</td>
<td>4.5</td>
<td>2.1x10$^7$</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>6.7x10$^5$</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>2.1x10$^4$</td>
</tr>
<tr>
<td>HCOOH (formic acid)</td>
<td>4.5</td>
<td>1.1x10$^5$</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>2.8x10$^6$</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>8.9x10$^7$</td>
</tr>
<tr>
<td>CH$_3$COOH (acetic acid)</td>
<td>4.5</td>
<td>1.9x10$^4$</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>2.3x10$^5$</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>7.0x10$^6$</td>
</tr>
<tr>
<td>HONO (nitrous acid)</td>
<td>4.5</td>
<td>1.3x10$^5$</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>3.9x10$^4$</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>1.2x10$^6$</td>
</tr>
<tr>
<td>HNO$_3$ (nitric acid)</td>
<td>4.5</td>
<td>5.3x10$^{12}$</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>1.7x10$^{14}$</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>5.3x10$^{15}$</td>
</tr>
</tbody>
</table>

Future field studies on these species should include simultaneous measurements of dew composition, dew amount, and gas phase mixing ratios to determine whether dew is an important night-time reservoir and morning source. The latter will be dependent on the fraction of gas released upon dew evaporation, which requires further investigation specific to each gas. Based on the findings in this work and Takenaka et al. (2009) it is likely that acidic semi-volatiles (e.g. acetic acid, formic acid, HONO) will be retained as salts during dew evaporation at RMNP due to the excess of cations.

3.5 Conclusions

Laboratory experiments involving synthetic dew were performed to determine the factor(s) controlling the fraction of NH$_4^+$ released as NH$_3$ upon dew evaporation. Results were mostly consistent with Takenaka et al. (2009) who found that the amount of NH$_3$ that volatilized from
drying aqueous solutions is governed by the relative abundances of NH$_4^+$ and excess “non-volatile” anions ($\sum$anions - $\sum$cations). However, our findings suggest that acetate, formate and HCO$_3^-$ should also be counted towards the anion budget. Hence, the Frac(NH$_3$) released from a drying dew sample can be predicted given the ionic composition and pH.

A dewmeter (for dew amount, deployed continuously from 22 June to 31 August) and dew collector (for dew composition, deployed successfully on 12 occasions) were set up at a remote field site in Colorado. Dew was relatively dilute compared to previous studies and had an average [NH$_4^+$] of 26 μM and pH of 5.2 at sunrise. Simple calculations revealed that dew can act as a significant night-time reservoir of NH$_3$. At the onset of dew evaporation there was, on average, roughly twice as much NH$_4^+$ in dew as NH$_3$ in the boundary layer. Furthermore, the observed NH$_3$ loss overnight was roughly equivalent to the amount of NH$_4^+$ that accumulated in dew by sunrise. Dew composition was used to calculate an average Frac(NH$_3$) of 0.94 suggesting that the vast majority of NH$_3$ sequestered in dew overnight is emitted during evaporation shortly after sunrise. Mornings with dew experience a large increase in NH$_3$ coincident with dew evaporation. Once the dew has completely evaporated, NH$_3$ mixing ratios either plateau or decrease. Fluxes of NH$_3$ from dew averaged 6.2 ± 5 ng m$^{-2}$ s$^{-1}$ during evaporation and were calculated using measured [NH$_4^+$], $V_{\text{dew}}$, $t_{\text{evap}}$ and Frac(NH$_3$). These fluxes are substantial compared to previously reported fluxes in non-fertilized grasslands (Wentworth et al., 2014; Wichink Kruit et al., 2007). Mornings without any surface wetness (neither dew nor rain) never experienced a sharp increase in NH$_3$. Dew-related NH$_3$ fluxes are likely much more substantial in urban and agricultural areas where NH$_3$ and [NH$_4^+$] in dew are significantly higher than at RMNP.

Morning increases of NH$_3$ frequently observed at RMNP (and other sites) are very likely the result of NH$_3$ emissions during dew evaporation. This hypothesis is supported by: 1) coincident timing of morning NH$_3$ increases/decreases at the start/completion of dew evaporation, 2) lack of NH$_3$ morning increase on every non-dew morning, 3) significant NH$_3$ fluxes calculated from dew, 4) relative abundances of NH$_4^+$ in dew and NH$_3$ in the boundary layer, and 5) approximate mass balance closure between NH$_3$ lost overnight and NH$_4^+$ accumulated in dew. The phenomenon of dew “recycling” atmospheric NH$_3$ could lead to an overestimation of NH$_3$ dry deposition in some ecosystems since dew formed overnight can take up much of the near-surface ammonia and then release most of it again in the morning upon evaporation. Such phenomena
are generally not considered in current models of NH₃ dry deposition. In addition, nocturnal loss rates of NH₃ were unaffected by the presence of dew. Our results suggest the net effect of dew is to reduce the overall removal of NH₃ and prolong its atmospheric lifetime as long as the dew composition yields a high Frac(NH₃).

Similar behaviour (coincident timing of NH₃ increases and evaporation) was occasionally observed for rain. Analysis of four rain samples yielded an average Frac(NH₃) of 0.66 suggesting NH₃ can be released from evaporation of rain in RMNP as well. However, due to the limited number of samples and lack of constraint for amount of rain sequestered below ground it is currently impossible to be even semi-quantitative about potential NH₃ fluxes from rain evaporation. This uncertainty merits further research since NH₃ wet deposition does not account for re-release of NH₃ from evaporation. Subsequent studies should also examine: 1) the role of biological processes on surface water composition (e.g. stomatal exchange, modification via microbes) and 2) influence of guttation (leaf exudate) on surface-air NH₃ exchange.

Additional field measurements quantifying NH₃ release from dew and rain evaporation are needed to determine how relevant these phenomena are for modulating NH₃ mixing ratios and N-deposition in different environments (e.g. urban, rural, agricultural). Although the majority of NH₄⁺ in dew was released back to the atmosphere at RMNP, this is not necessarily the case at other locations. For instance, environments with HNO₃ deposition exceeding NH₃ deposition to dew would cause a low (or zero) Frac(NH₃). In addition, a tall canopy can recapture near-surface NH₃ emissions and might modulate emissions from dew drying in the lower canopy (Walker et al., 2013). Regardless, the ability for dew to act as a morning source of NH₃ is currently absent from atmospheric models, with the exception of a few field-scale models based on the work of Flechard et al. (1999). The observations from this study suggest dew imparts a large influence on boundary layer NH₃; hence, future work should also focus on developing model parameterizations for NH₃ uptake during dew formation and release from evaporating dew.

To our knowledge, this is the first study to quantitatively examine the influence of dew on any water-soluble gas by simultaneously measuring dew amount, dew composition and atmospheric composition. Although NH₃ is the focus of this work, gases with similar K_H^eff (>10⁵ M atm⁻¹) might be influenced by dew formation and evaporation in a comparable manner. Such species include, but are not limited to, acetic acid, formic acid, HONO and HNO₃. Methodology similar
to this study should be used to conduct quantitative field studies for the aforementioned species to better understand the dynamic influence of dew on boundary layer composition.

3.6 Contributions

The laboratory experiments were devised and carried out by Gregory Wentworth. The dewmeter and dew collector were also constructed and maintained by Gregory Wentworth. Sample collection and analysis was primarily done by Gregory Wentworth with help from Katherine Benedict and Evelyn Bangs. Field site logistics were provided by Katherine Benedict and Jeffrey Collett. The manuscript referenced at the beginning of this chapter was written by Gregory Wentworth, with substantial input from Jennifer Murphy, Katherine Benedict and Jeffrey Collett.

3.7 References


3.8 Appendix A

Table A1. Concentrations (in μM) of ions in the nine synthetic dews

<table>
<thead>
<tr>
<th>Dew</th>
<th>Na⁺</th>
<th>NH₄⁺</th>
<th>K⁺</th>
<th>Ca²⁺</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>Ac⁻</th>
<th>Form⁻</th>
<th>*HCO₃⁻</th>
<th>pH</th>
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<tr>
<td>A</td>
<td>214</td>
<td>232</td>
<td>44</td>
<td>78</td>
<td>166</td>
<td>44</td>
<td>90</td>
<td>18</td>
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<td>100</td>
<td>6.87</td>
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<tr>
<td>B</td>
<td>177</td>
<td>319</td>
<td>0</td>
<td>96</td>
<td>214</td>
<td>260</td>
<td>98</td>
<td>51</td>
<td>46</td>
<td>6</td>
<td>5.64</td>
</tr>
<tr>
<td>C</td>
<td>408</td>
<td>283</td>
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<td>100</td>
<td>200</td>
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<td>100</td>
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<td>20</td>
<td>123</td>
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<tr>
<td>D</td>
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<td>99</td>
<td>49</td>
<td>43</td>
<td>302</td>
<td>7.35</td>
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</table>

*Calculated using carbonate equilibria, pH and assuming P₅CO₂ = 500 ppm

Table A2. Concentration (in μM) of ionic species in rain samples

<table>
<thead>
<tr>
<th>Date</th>
<th>Na⁺</th>
<th>NH₄⁺</th>
<th>K⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>Ac⁻</th>
<th>Form⁻</th>
<th>Cl⁻</th>
<th>NO₂⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>HPO₄²⁻</th>
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<tr>
<td>06/15</td>
<td>5.8</td>
<td>67.2</td>
<td>3.2</td>
<td>1.8</td>
<td>9.4</td>
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<td>5.9</td>
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<td>23.6</td>
<td>4.5</td>
<td>0.9</td>
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<tr>
<td>06/16</td>
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<td>1.0</td>
<td>1.4</td>
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<td>0</td>
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<td>0</td>
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<tr>
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Table A3. Total Organic Carbon (TOC), Total Nitrogen (TN), Inorganic Carbon (IC), pH, and Frac(NH₃) for rain samples

<table>
<thead>
<tr>
<th>Date</th>
<th>TOC (mg C L⁻¹)</th>
<th>IC (mg C L⁻¹)</th>
<th>TN (mg N L⁻¹)</th>
<th>pH</th>
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Chapter 4
Ammonia in the summertime Arctic marine boundary layer: sources sinks and implications

Sections of this chapter appear in the following peer-reviewed publication:


4 Chapter 4

4.1 Abstract

Continuous hourly measurements of gas-phase ammonia (NH$_3$) were taken from 13 July to 7 August 2014 on a research cruise throughout Baffin Bay and the eastern Canadian Arctic Archipelago. Concentrations ranged from 30 to 650 ng m$^{-3}$ (40-870 pptv) with the highest values recorded in Lancaster Sound (74°13’ N, 84°00’ W). Simultaneous measurements of total ammonium ([NH$_4$]), pH and temperature in the ocean and in melt ponds were used to compute the compensation point ($\chi$), which is the ambient NH$_3$ concentration at which surface-air fluxes change direction. Ambient NH$_3$ was usually several orders of magnitude larger than both $\chi_{\text{ocean}}$ and $\chi_{\text{MP}}$ (<0.4 to 10 ng m$^{-3}$) indicating these surface pools are net sinks of NH$_3$. Flux calculations estimate average net downward fluxes of 1.4 and 1.1 ng m$^{-2}$ s$^{-1}$ for the open ocean and melt ponds, respectively. Sufficient NH$_3$ was present to neutralize non-sea salt sulphate (nss-SO$_4^{2-}$) in the boundary layer during most of the study. This finding was corroborated with a historical data set of PM$_{2.5}$ composition from Alert, Nunavut (82°30’ N, 62°20’ W) wherein the median ratio of NH$_4^+/\text{nss-SO}_4^{2-}$ equivalents was greater than 0.75 in June, July and August. The GEOS-Chem chemical transport model was employed to examine the impact of NH$_3$ emissions from seabird guano on boundary-layer composition and nss-SO$_4^{2-}$ neutralization. A GEOS-Chem simulation without seabird emissions underestimated boundary layer NH$_3$ by several orders of magnitude and yielded highly acidic aerosol. A simulation that included seabird NH$_3$ emissions was in better agreement with observations for both NH$_3$ concentrations and nss-SO$_4^{2-}$. 

neutralization. This is strong evidence that seabird colonies are significant sources of NH$_3$ in the summertime Arctic, and are ubiquitous enough to impact atmospheric composition across the entire Baffin Bay region. Large wildfires in the Northwest Territories were likely an important source of NH$_3$, but their influence was probably limited to the Central Canadian Arctic. Implications of seabird-derived N-deposition to terrestrial and aquatic ecosystems are also discussed.

4.2 Introduction

Ammonia (NH$_3$(g)) is the dominant alkaline gas in the atmosphere and is an important component of the global nitrogen cycle. Its transport and deposition can have harmful effects for N-sensitive ecosystems such as eutrophication, loss of biodiversity and soil acidification (Krupa, 2003). The presence of NH$_3$(g) can impact climate by increasing rates of new particle formation via stabilization of sulphuric acid clusters (Kirkby et al., 2011). Gas-phase NH$_3$ is also able to partition to acidic fine particulate matter (PM$_{2.5}$) to form particulate-phase ammonium (NH$_4^+(p)$), which alters various aerosol properties, such as scattering efficiency (Martin et al., 2004), hygroscopicity (Petters and Kreidenweis, 2007), ice nucleating ability (Abbatt et al., 2006) and heterogeneous chemistry occurring on surfaces (Fickert et al., 1999).

As a result, the accurate quantification of the magnitude and location of NH$_3$(g) sources is important for chemical transport models (CTMs). The major anthropogenic source is agriculture (fertilization and animal husbandry) with biomass burning, transport and industry being minor contributors (Reis et al., 2009). Natural sources include soils, vegetation, oceans and animal excreta (Sutton et al., 2013). Estimates for the annual global emissions of NH$_3$(g) range from 35 to 54 Tg N yr$^{-1}$; however, large uncertainties exist for these values due to the area-wide nature (emissions spread over a large spatial extent) and poor characterization of many sources. In remote marine environments, the ocean is thought to be the dominant source of NH$_3$(g) to the marine boundary layer and delivers an estimated 6-8 Tg N yr$^{-1}$ to the atmosphere globally (Sutton et al., 2013). The dominant sources of oceanic NH$_x$ (≡NH$_3$ + NH$_4^+$) include remineralization of organic matter by bacteria and phytoplankton excretion (Carpenter et al., 2012). However, NH$_x$ is an extremely labile nutrient for microbes such that assimilation by phytoplankton and bacteria prevents significant accumulation in surface waters. Nonetheless, there exists a pool of dissolved ammonia (NH$_3$(sw)) available for exchange with the atmosphere.
In order to compute sea-air NH₃ fluxes, simultaneous measurements of both atmospheric NH₃(g) and oceanic NHₓ are required. These measurements are extremely challenging due to low ambient concentrations and complications arising from making ship-based measurements (e.g. proximity to human activity can cause artefacts). As a result, to our knowledge only six previous studies have simultaneously quantified both [NH₃(g)] and oceanic [NHₓ], leading to extremely large uncertainties for both the direction and magnitude of global sea-air NH₃ fluxes (Asman et al., 1994; Geernaert et al., 1998; Gibb et al., 1999; Johnson et al., 2008; Quinn et al., 1988, 1990). Johnson et al. (2008) provided the most recent data set and summarized the previous studies to show that the open ocean can be both a net source and a net sink of NH₃(g), with sea surface temperature (SST) being a key determinant for the direction of flux. Colder SST reduces the emission potential due to increased solubility of NH₃ (because of both reduced NH₃(aq) volatility and increased partitioning of NH₃(aq) to NH₄⁺(aq)); hence, at higher latitudes the open ocean is more likely to act as a net sink (Johnson et al., 2008). Of the six previous studies, only Johnson et al. (2008) quantified NH₃ fluxes above the Arctic Circle (66°33’ N) during a summer time study in the Norwegian Sea. Therefore additional measurements of sea-air NH₃ fluxes in the High Arctic are invaluable for improving constraints on oceanic NH₃ emissions.

During the summertime, freshwater melt ponds are a ubiquitous feature on top of melting Arctic sea ice and can comprise up to 80% of the sea ice surface (Lüthje et al., 2006). These melt ponds form from melting sea ice and are anywhere from a few cm to over 1 m deep. They are chemically distinct from the bulk ocean owing to their low salinity and physical separation from the ocean mixed layer by sea ice or stratification. To our knowledge, no studies to date have attempted to quantify melt pond-air NH₃(g) fluxes despite the abundant presence of melt ponds in the summertime Arctic.

Quantifying sea-air and melt pond-air NH₃ exchange in the Arctic will help elucidate the role these processes play as either sources or sinks in the Arctic nitrogen cycle. Many terrestrial Arctic ecosystems are N-limited and highly sensitive to perturbations in N-input (Shaver and Chapin III, 1980), thus Arctic soils and vegetation are unlikely to represent important sources of atmospheric ammonia. Major sources at lower latitudes include agriculture, vegetation, transport and industry (Reis et al., 2009; Sutton et al., 2013) but these are expected to contribute minimally north of the Arctic Circle. Since the lifetime of NH₃(g) is typically less than 24 h, long-range transport from lower latitudes is likely not important (Lefer et al., 1999). Substantial NH₃
emissions have been measured from both seabird guano (Blackall et al., 2007) and seal excreta (Theobald et al., 2006) so large colonies may be relevant point sources throughout the Arctic region. Biomass burning can also inject significant quantities of NH$_3$ into the free troposphere and/or boundary layer (Bouwman et al., 1997). Although vegetation in the High Arctic is sparse, there can be large wildfires in boreal regions, and emissions may be transported poleward. The potential for the ocean and melt ponds to act as sources to the atmosphere will depend on the relative importance of sources and sinks within the atmosphere and the aqueous systems.

NH$_3$ emission to the atmosphere can affect the extent of non-sea salt sulphate (nss-SO$_{4}^{2-}$) neutralization, which has implications for N-transport (Lefer et al., 1999). Therefore, it is important to also consider the relative abundances of atmospheric NH$_x$ and nss-SO$_{4}^{2-}$. The dominant source of the latter in the summertime Arctic is oxidation of dimethylsulphide (DMS) emitted from the Arctic Ocean (Leaitch et al., 2013; Sharma et al., 1999, 2012). Measurements of PM$_{2.5}$ composition in the summertime Arctic marine boundary layer are rare (e.g. Chang et al., 2011; Leck et al., 2001). Previous chemical transport model (CTM) studies with GEOS-Chem predict highly acidic aerosol (i.e. nss-SO$_{4}^{2-}$ >> NH$_3$) with negligible amounts of NH$_3(g)$ throughout the summertime Arctic boundary layer (Breider et al., 2014).

The region for this study is the eastern Canadian Arctic Archipelago where ship-based atmospheric (NH$_3(g)$, NH$_4^+(p)$, SO$_{4}^{2-}(p)$) and oceanic ([NH$_x$], pH, SST) measurements were taken over a 4-week period in July and August, 2014. To our knowledge, this study presents the first measurements of NH$_3(g)$ in the Canadian Arctic. Motivated by a lack of atmospheric and oceanic measurements in the region, as well as substantial uncertainties in sea-air and melt pond-air NH$_3$ fluxes, the specific goals of this study were the following:

1) to simultaneously quantify NH$_3(g)$ and oceanic/melt pond [NH$_x$] to infer surface-air NH$_3$ fluxes
2) to assess the relative abundances of NH$_3(g)$, NH$_4^+(p)$ and SO$_{4}^{2-}(p)$ to determine the extent of SO$_{4}^{2-}(p)$ neutralization
3) to elucidate the major sources and sinks of atmospheric NH$_3$ throughout the summertime Arctic marine boundary layer
4) and to evaluate whether atmospheric NH$_x$ deposition could be an important N-input to aquatic and terrestrial Arctic ecosystems
4.3 Methods and Materials

4.3.1 2014 CCGS Amundsen Cruise

Measurements were taken aboard the Canadian Coast Guard Ship Amundsen between 13 July and 7 August 2014 as part of the Network on Climate and Aerosols: Addressing Key Uncertainties in Remote Canadian Environments (NETCARE). The CCGS Amundsen departed from Québec City, Québec on 8 July 2014 and sailed throughout the eastern Canadian Archipelago heading as far north as 81.47 °N eventually reaching Kugluktuk, Nunavut on 13 August 2014. A detailed map of the ship’s route for this leg is shown in Fig. 4.1 along with the ship’s position at the start of selected days. All times are given in coordinated universal time (UTC).

Figure 4.1 CCGS Amundsen ship track coloured by gas-phase NH$_3$ concentrations measured by the AIM-IC. Invalid measurements (e.g. instrument troubleshooting, influenced by ship) are purple along the ship track. Units of ng m$^{-3}$ were chosen as a convenience for flux calculations. At STP, 100 ng m$^{-3}$ ≈ 130 pptv. Relevant landmarks are also labelled. Dates and arrows indicate the position of the ship at 0:00 UTC on that day.
4.3.2 Atmospheric measurements

Ambient levels of water-soluble ions in PM$_{2.5}$ (NH$_4^+$, SO$_4^{2-}$, and NO$_3^-$) and their precursor gases (NH$_3$, SO$_2$, and HNO$_3$) were measured using the Ambient Ion Monitor-Ion Chromatograph (AIM-IC) system (Model 9000D, URG Corp., Chapel Hill, NC). The AIM-IC is a continuous on-line system which provides simultaneous gas-phase and particle-phase measurements with hourly time resolution. The system has been adapted to locate the gas and particle separation and collection hardware as close as possible to the inlet sampling point (Markovic et al., 2012).

Ambient air is pulled through a PM$_{2.5}$ impactor to remove coarse (>2.5 μm in diameter) particles at a flow of 3 L min$^{-1}$. Air then enters a parallel plate wet denuder where water-soluble gases are dissolved in a 2 mM H$_2$O$_2$ solution (to enhance the solubility of SO$_2$) which is continuously flowing across the denuder membranes. The remaining PM$_{2.5}$ particles have sufficient inertia to pass through the denuder into a supersaturation chamber where they are collected as an aqueous solution via hygroscopic growth. These components were contained within an aluminum inlet box that was mounted to the hull near the bow of the ship (about 4 m back of the bow). The height of the inlet was 1 m above the deck. Influence from ship-generated sea spray was likely minimal due to the benign nature of the summertime Arctic Ocean, in addition to the PM$_{2.5}$ impactor designed to remove coarse particles. The aqueous solutions collected in the inlet box were pulled down a 22 m sample line through a conduit leading to the IC systems which were housed in a laboratory below deck. Half of each ~10 mL aqueous aliquot (representing 1 hour of sampling) was then separately injected onto both a cation IC and anion IC for quantification of water-soluble ions.

The IC systems (ICS-2000, Dionex Inc., Sunnyvale, CA) were operated using CS17/AS11-HC analytical columns, CG17/AG11-HC guard columns and TCC-ULP1/TAC-ULP1 concentrator columns for improved detection limits. Reagent-free gradient elution schemes and suppressed conductivity were also employed. Aqueous standards of known concentration were prepared via serial dilution of commercially available mixed standards (Dionex Corp., Sunnyvale, CA) containing six cations (P/N 040187) and seven anions (P/N 056933). Manual injection of these standards yielded reasonable ($R^2 > 0.99$) six-point calibration curves.

During the campaign, three zero-air overflow experiments were performed to quantify the background signal of each analyte measured during AIM-IC ambient sampling. For each
experiment the inlet was overflowed with high purity zero air (AI 0.0 UZ-T, PraxAir, Toronto, ON) at 4.5 L min$^{-1}$ for 18 hours. The average peak area during the final 8 hours of each experiment was used as a background and subtracted from each ambient measurement. Detection limits were calculated by taking 3 times the standard deviation of each analyte peak area during the final 8 hours of each zero air overflow. This value was then converted to either a mixing ratio or mass loading assuming standard temperature and pressure (STP). Detection limits for species of interest during the cruise were 29 ng m$^{-3}$ (NH$_3$), 17 pptv (SO$_2$), 8 pptv (HNO$_3$), 12 ng m$^{-3}$ (NH$_4^+$), 36 ng m$^{-3}$ (SO$_4^{2-}$), and 64 ng m$^{-3}$ (NO$_3^-$). For the convenience of flux calculations, NH$_3$ values are reported in ng m$^{-3}$ (at STP 100 ng m$^{-3}$ NH$_3$ $\approx$ 130 pptv).

Standard meteorological parameters were measured using a Vaisala HMP45C212 sensor for temperature, an RM Young model 61205V transducer for pressure, and an RM Young Model 05103 wind monitor for wind speed and direction located at the bow ship of the ship at a height of 8.2 to 9.4 m above the deck. Data were averaged to 1-hour to match the time resolution of the AIM-IC. In order to remove any influence from activities aboard the ship, gas-phase measurements are only reported if the following conditions were met: 1) average hourly ship speed $>$ 4 knots (~7.4 km h$^{-1}$), 2) average hourly apparent wind direction $\pm$ 90° of the bow, and 3) standard deviation of apparent wind direction $<$ 36°. Similar cut-offs for speed and wind direction have been used in previous studies of NH$_3$ in the marine boundary layer (e.g. Johnson et al., 2008; Norman and Leck, 2005).

**4.3.3 Surface measurements**

A total of 37 surface ocean and 9 melt pond samples were collected throughout the study. Melt pond samples were collected directly into a cooler jug using an electrical pump fixed on a telescopic arm. The water was sampled as far from the side of the melt pond as possible, between 1 and 2 m depending on the size of the melt pond. Temperature was measured in situ with a VWR high-precision thermometer and total aqueous [NH$_3$] was determined within 10 h of sampling using a fluorometric technique that measures the fluorescence of an ammonium-orthophthaldialdehyde complex to quantify NH$_3$ in seawater (Holmes et al., 1999). This technique has been optimized for low concentrations and complex matrices. The method detection limit was 20 nM. Surface ocean samples were obtained with a Rosette sampler equipped with GO-FLOW bottles and a CTD (Seabird Electronics SBE911+) recording temperature. Total aqueous
[NH₃] was determined as above within 1 hour of sampling. Surface water temperature along the
ship’s track was continuously measured by a thermosalinograph (Seabird Electronics SBE 45)
connected to the seawater inlet. For the purposes of flux calculations, the ocean pH and salinity
were assumed to be 8.1 and 35 g kg⁻¹, respectively, which are representative for the region of
interest (Takahashi et al., 2014). These assumptions have been made previously and were not
found to be a major source of uncertainty when calculating sea-air NH₃ fluxes (Johnson et al.,
2008). The melt pond pHs were measured using a pH-meter within four hours of sampling. A
three point calibration of the pH probe (Orion™ Model 91-72, Thermo Scientific) was
performed using commercially available pH 4.01, 7.00 and 10.00 buffers. Salinity of the melt
ponds were determined with a WTW Cond 330i handheld conductivity meter.

4.3.4 Flux calculations

The direction of sea-air NH₃ fluxes can be assessed by comparing ambient measurements of
NH₃(g) to the atmospheric mixing ratio predicted from Henry’s Law equilibrium calculations
using seawater [NH₃] and surface temperature measurements (e.g. Asman et al., 1994; Johnson
et al., 2008; Quinn et al., 1988, 1996). This equilibrium NH₃ concentration signifies the ambient
value at which the net flux changes direction, and is known as the compensation point (denoted
χ). In other words, one expects a net downwards flux if ambient NH₃(g) exceeds χ and a net
upward flux if it is below χ. The magnitude of these fluxes are commonly computed using the
“two-phase” model first developed by Liss and Slater (1974), which describes the sea-air transfer
of gases as being controlled by molecular diffusion on either side of the interface. The transfer of
NH₃ across this interface is predominantly dictated by the air-side transfer velocity, given the
relatively high water solubility of NH₃ (Liss, 1983). Hence, the equation to calculate sea-air NH₃
fluxes is as follows:

\[ F_{NH₃} = k_g \cdot (\chi - NH₃(g)) \cdot 17.03 \]  (E4.1)

where \( F_{NH₃} \) is the sea-air flux of NH₃ (ng m⁻² s⁻¹), \( k_g \) is the air-side transfer velocity (m s⁻¹),
NH₃(g) is the measured ammonia concentration (nmol m⁻³), \( \chi \) is the compensation point (nmol m⁻³),
and the molecular weight of 17.03 g mol⁻¹ is to convert nmol to ng. Numerous
parameterizations exist for \( k_g \) with varying degrees of complexity (Johnson, 2010). Here we
adopt the approach established by Duce et al. (1991):
\[ k_g = \frac{u}{770 + 45 \cdot MW^{1/3}} \]  
(E4.2)

where \( u \) is the wind speed (m s\(^{-1}\)) and MW is the molecular weight of the gas of interest (17.03 for NH\(_3\)). Although simple, this parameterization has been used previously to estimate sea-air NH\(_3\) fluxes (e.g. Johnson et al., 2008) and has been shown to be in good agreement (within 20\% ) with a more complex scheme, particularly at lower wind speeds (Johnson, 2010). The following equation is used to calculate \( \chi \):

\[ \chi = K_H \cdot [NH_{3(sw)}] \]  
(E4.3)

where \( K_H \) is the Henry’s law constant (dimensionless) and \([NH_{3(sw)}]\) is the concentration of dissolved ammonia in the surface pool (nmol m\(^{-3}\)). The temperature-dependent equation for \( K_H \) is (McKee, 2001):

\[ K_H = \frac{1}{17.93 \cdot \frac{T}{273.15} \cdot e^{(\frac{4092}{T} - 9.70)}} \]  
(E4.4)

where \( T \) is the surface temperature (in K). The following equation is used to relate the NH\(_{3(sw)}\) to the concentration of total dissolved NH\(_x\) (\([NH_{x(sw)}]\)), which is the value actually measured by the procedure outlined in section 4.3.3:

\[ [NH_{3(sw)}] = \frac{[NH_{x(sw)}] \cdot K_a}{10^{-pH} + K_a} \]  
(E4.5)

where \( K_a \) is the acid dissociation constant of NH\(_4^+\). The \( pK_a \) (≡ \(-\log K_a\)) is calculated according to Bell et al. (2008), which provides an empirical correction for salinity (S, dimensionless) at a given temperature (T, in °C):

\[ pK_a = 10.0423 + 0.003071 \cdot S - 0.031556 \cdot T \]  
(E4.6)

Equations E4.2 and E4.4 closely follow that of Johnson et al. (2008) but are sufficiently similar to analogous approaches for calculating \( K_H \) and \( k_g \) used in other sea-air NH\(_3\) exchange studies (e.g. Asman et al., 1994; Gibb et al., 1999; Quinn et al., 1992). Johnson (2004) reported that
fluxes calculated with these various schemes usually agree within 2%. Melt pond-air exchange was also examined using equations E4.1 to E4.6.

4.3.5 GEOS-Chem

The GEOS-Chem chemical transport model (www.geos-chem.org) is used to aid in the interpretation of the atmospheric measurements. We use GEOS-Chem version 9-02 at 2°x2.5° resolution globally, and with 47 vertical layers between the surface and 0.01 hPa. The assimilated meteorology is taken from the NASA Global Modelling and Assimilation Office (GMAO) Goddard Earth Observing System version 5.11.0 (GEOS-FP) assimilated meteorology product. Boundary layer mixing uses the non-local scheme implemented by Lin and McElroy (2010). Our simulations use 2014 meteorology and allow a 2-month spin-up prior to the simulation.

The GEOS-Chem model includes a detailed oxidant-aerosol tropospheric chemistry mechanism as originally described by Bey et al. (2001). Simulated aerosol species include sulphate-nitrate-ammonium (Park et al., 2004; Park et al., 2006), carbonaceous aerosols (Park et al., 2003; Liao et al., 2007), dust (Fairlie et al., 2007; Fairlie et al., 2010) and sea salt (Alexander et al., 2005). The sulphate-nitrate-ammonium chemistry uses the ISORROPIA II thermodynamic model (Fountoukis and Nenes, 2007), which partitions ammonia and nitric acid between the gas and aerosol phases. For our simulations, the natural NH₃ emissions are from Bouwman et al. (1997) and biomass burning emissions are from the Quick Fire Emissions Dataset (QFED2) (Darmenov and da Silva, 2013), which provides daily open fire emissions at 0.1° x 0.1° resolution. Anthropogenic NH₃ emissions are from Bouwman et al. (1997). The model includes natural and anthropogenic sources of SO₂ (van Donkelaar et al., 2008; Fisher et al., 2011) and DMS emissions based on the Nightingale (2000) formulation and oceanic DMS concentrations from Lana et al. (2011). Oxidation of SO₂ occurs in clouds by reaction with H₂O₂ and O₃ and in the gas phase with OH (Alexander et al., 2009) and DMS oxidation occurs by reaction with OH and NO₃.

GEOS-Chem simulates both wet and dry removal of aerosols and gases. Dry deposition follows a standard resistance in series scheme (Wesley, 1989) with an aerosol dry deposition velocity of 0.03 cm s⁻¹ over snow and ice (Fisher et al., 2011). Wet removal in GEOS-Chem takes place in large-scale clouds and convective updrafts (Liu et al., 2001). In-cloud scavenging of hydrophilic
species takes place at temperatures warmer than 258K, and hydrophobic black carbon and dust are also removed at temperatures colder than 258K (Wang et al., 2011).

4.3.6 FLEXPART-WRF

FLEXPART-WRF (Brioude et al., 2013, website: flexpart.eu/wiki/FpLimitedareaWrf) is a Lagrangian particle dispersion model based on FLEXPART (Stohl et al., 2005) that is driven by meteorology from the Weather Research and Forecasting (WRF) Model (Skamarock et al., 2005). Here we use FLEXPART-WRF run in backward mode to study the emissions source regions and transport pathways influencing ship-based ammonia measurements. A WRF simulation for the summer 2014 NETCARE campaign was performed using WRF 3.5.1 with initial and boundary conditions provided by the operational analysis (0.25° x 0.25° resolution) from European Centre for Medium-Range Weather Forecasts (ECMWF). Parameterizations and options for the WRF simulations are given in Table 4.1. The WRF model was run from 1 July 2014 to 13 August 2014 and nudged to ECMWF winds, temperature, and humidity every 6 hours above the atmospheric boundary layer. The WRF run was evaluated using meteorological measurements made onboard the Amundsen and from the Polar-6 aircraft flights during this period. FLEXPART-WRF was run in backward mode to produce retroplume output that is proportional to the residence time of the particles in a given volume of air. Runs were performed using the location of the ship, with one model run performed every 15 minutes while the ship was in the model domain (13 July-13 August 2014). For each run, 100,000 particles were released at the ship location (100 m extent horizontally and vertically) and the FLEXPART-WRF was run backwards for 7 days prior to release. The output provides retroplume information (the residence time of air prior to sampling) which is used to calculate the potential emission sensitivities (PES) integrated over the seven days prior to sampling by instruments aboard the Amundsen.
Table 4.1 Parameterizations and options used for the NETCARE WRF simulations

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<td>Land surface</td>
<td>Unified Noah Land Surface Model (Tewari et al., 2004)*</td>
</tr>
<tr>
<td>Microphysics</td>
<td>WRF Single-Moment 5-class scheme (Hong, Dudhia, and Chen, 2004)</td>
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<tr>
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<td>Goddard Shortwave Scheme (Chou and Suarez, 1994)</td>
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<td>Cumulus parameterization</td>
<td>Kain–Fritsch Scheme (Kain, 2004)</td>
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</table>

*with corrected calculation of skin temperature over sea ice when snow melting is occurring, see http://www2.mmm.ucar.edu/wrf/users/wrfv3.7/updatess-3.7.1.html.

4.4 Results and Discussion

4.4.1 Surface-atmosphere NH₃ fluxes

Figure 4.1 shows the ambient NH₃(g) concentrations measured by the AIM-IC throughout the cruise. Measured values of NH₃(g) range between 30-650 ng m⁻³ with the highest values occurring in Lancaster Sound as the ship was steaming eastward into Baffin Bay. Only two measurements of NH₃ were below the detection limit (29 ng m⁻³) throughout the entire cruise. NH₃ consistently exceeded 100 ng m⁻³ during later parts of the cruise along the eastern shores of Ellesmere Island and western shores of Greenland. Lower values (<100 ng m⁻³) were observed at the beginning of the campaign along the eastern shores of Baffin Island. Measurements of NH₃(g) in the marine boundary layer at northern latitudes (>50°N) are sparse; however the concentrations measured in this study are within the few previously reported ranges for the regions above 50 °N. Johnson et al. (2008) reported NH₃(g) between 20-300 ng m⁻³ in the
Norwegian Sea during spring and summer, but a lower range (20-90 ng m\(^{-3}\)) in the northern North Sea in winter. In the southern North Sea, Asman et al. (1994) measured higher values (30-1500 ng m\(^{-3}\)) in a study lasting from February to October.

The relevant measurements needed to calculate \(\chi\) for both the open ocean and melt ponds are listed in Appendix Tables B1 and B2, respectively. Only four unique co-ordinates are listed for the nine melt pond samples because multiple melt ponds were sampled at each location. Roughly half of the surface ocean samples had [NH\(_x\)] below the detection limit (20 nM) and in general values were significantly lower than in the melt ponds. Open ocean samples ranged from <20 to 380 nM whereas seven of the nine melt pond samples were between 640 to 1260 nM (with the other two below detection limit). These concentrations and their spatial variability are typical for the region during summer (Martin et al. 2010).

Parameters listed in Appendix Tables B1 and B2 were input into equations E4.3 to E4.6 to calculate \(\chi\) for both the surface ocean and melt pond samples. For samples with [NH\(_x\)] below the detection limit, a value of 10 nM (half of the detection limit) was assumed. A comparison of the calculated compensation points for the ocean (\(\chi_{\text{ocean}}\)) and melt ponds (\(\chi_{\text{MP}}\)) are shown in Fig. 4.2. Also shown is the range for the nearest valid measurement (see section 4.3.2) of ambient NH\(_3(g)\). The NH\(_3(g)\) concentration taken during the hour of surface sampling could not be used since the ship remained stationary for up to 12 hours while melt pond or ocean work was being conducted. Hence, the NH\(_3(g)\) measurement from several hours prior (as the ship approached the surface sampling site) had to be used. This approach should not significantly impact the analysis given that the ambient levels of NH\(_3(g)\) were observed to be fairly uniform from one hour to the next (i.e. no rapid spikes of NH\(_3(g)\) were measured). Shown in lighter yellow are the ranges of NH\(_3(g)\) observed over the entire study (~30-650 ng m\(^{-3}\)). Figure 4.2 clearly shows that the ambient concentrations of NH\(_3(g)\) exceed both \(\chi_{\text{ocean}}\) and \(\chi_{\text{MP}}\) by several orders of magnitude throughout the entire region. This conclusively demonstrates that during the summertime, the ocean and melt ponds are net sinks of atmospheric NH\(_3(g)\). This finding is consistent with Johnson et al. (2008) who found a tendency for downward net fluxes at higher latitudes, primarily as a result of colder sea surface temperatures. Assuming an upper limit for the ocean pH of 8.2 would increase \(\chi_{\text{ocean}}\) by less than 20 %. 
Figure 4.2 Box-and-whisker plot showing the observed ranges of $\chi$ (on a log scale) for both the ocean surface (dark blue) and melt ponds (light blue). The range of NH$_3$ measured by the AIM-IC near the time of surface sampling is shown in darker yellow whereas NH$_3$ over the entire campaign is shown in lighter yellow. The box represents 25$^{th}$ to 75$^{th}$ percentile while the line within the box denotes the median. Whiskers extend to the 10$^{th}$ and 90$^{th}$ percentile.

Figure 4.3 shows the magnitude of the sea-air and melt pond-air flux of NH$_3$. Average net downward fluxes of 1.4 ng m$^{-2}$ s$^{-1}$ and 1.1 ng m$^{-2}$ s$^{-1}$ were calculated for the open ocean and melt ponds, respectively using equations E4.1 and E4.2. Net fluxes were exclusively downwards (net deposition into the ocean and melt ponds) due to the relative abundances of NH$_3$ and NH$_4^+$ in these surface pools as well as cold surface temperatures as suggested by Johnson et al. (2008). It is unlikely that this represents a significant input of NH$_4^+$ into the open ocean except in cases of extremely low [NH$_3$]. A simple calculation assuming a mixed layer depth of 25 m results in an increase of only $\sim$0.3 nM d$^{-1}$ to the ocean (assuming complete mixing and no loss pathways). However, for the much shallower melt ponds (assumed depth of 0.25 m) the same calculation yields an input of $\sim$22 nM d$^{-1}$. Furthermore, this does not account for atmospheric inputs from either wet deposition or dry deposition of particulate NH$_4^+$, and these melt ponds are cut-off from the upwelling currents in the ocean which deliver reactive N to the surface. Rates of nitrification, mineralization and N$_2$-fixation in the open ocean and melt ponds would help put this atmospheric
input into perspective and give insight as to whether or not it is an important process in the nitrogen cycle in these environments.

![Box-and-whisker plot](image)

**Figure 4.3** Box-and-whisker plot of the estimated fluxes into the open ocean and melt ponds. The percentiles are represented in the same fashion as Fig. 4.2.

### 4.4.2 Sulphate neutralization

The extent of neutralization of PM$_{2.5}$ influences aerosol properties as discussed previously. Figure 4.4 depicts the relative abundances (in neq m$^{-3}$) of gas-phase ammonia and particulate-phase ammonium and sulphate. It is important to note that the value for sulphate is total PM$_{2.5}$ sulphate as opposed to non-sea salt sulphate (nss-SO$_4^{2-}$), which is commonly reported for marine boundary layer studies. High and variable backgrounds of Na$^+$ from the AIM-IC prevented the calculation of nss-SO$_4^{2-}$, hence this data set provides an upper limit for nss-SO$_4^{2-}$. Given the low wind speeds (< 5 m s$^{-1}$) that dominated the campaign, it is likely the nss-SO$_4^{2-}$ ≈ SO$_4^{2-}$ since the contribution from sea salt to PM$_{2.5}$ was likely small. It should also be noted that measurements of SO$_2$, HNO$_3$ and NO$_3^-$ were almost always below their respective detection limits.
Particle loadings of NH$_4^+$ and SO$_4^{2-}$ were extremely low (typically < 5 neq m$^{-3}$) throughout the duration of the cruise. During the first third of the cruise (before 18 July), gas-phase NH$_3$ was also low and neutralization (i.e. the ratio NH$_4^+$:SO$_4^{2-}$ in units of equivalents) was ambiguous due to numerous values near or below detection limit. On the other hand, after 25 July the nanoequivalents of NH$_3(g)$ were substantially higher than either NH$_4^+$ or SO$_4^{2-}$ (i.e. NH$_4$ ≈ NH$_3$), which implies a nearly neutralized sulphate aerosol. It is important to note that a nearly neutralized aerosol does not equate to an aerosol with a pH of 7 since aerosol pH is highly sensitive to liquid water content as well as the precise NH$_4^+$:SO$_4^{2-}$ ratio. An aerosol with NH$_4^+$:SO$_4^{2-}$ approaching 1 can still have an acidic pH. For example, a deliquesced ammonium sulphate particle containing 20 neq m$^{-3}$ of SO$_4^{2-}$ and 19.98 neq m$^{-3}$ NH$_4^+$ at 85% RH will have a pH of ~3.1 under equilibrium conditions despite having an NH$_4^+$:SO$_4^{2-}$ equivalents ratio of 0.999.

Figure 4.5 shows the distribution of the NH$_4^+$:nss-SO$_4^{2-}$ ratio (on a per equivalent basis) measured in Alert, Nunavut (82.50 °N, 62.33 °W) as a function of month from 1996-2011. Weekly averaged PM$_{2.5}$ speciation measurements at Alert are made by Environment Canada and are available on-line (Environment Canada, 2014). The contribution from NO$_3^-$ is minor and has not been included in this analysis. In warm environments volatilization of NH$_4$NO$_3$ off of filters can cause an underestimation of NH$_4^+$, but this is not expected to be an issue in Alert due to cold weather and low loadings of NH$_4$NO$_3$. During July and August the nss-SO$_4^{2-}$ is, on average, completely neutralized by the NH$_4^+$ in PM$_{2.5}$ as shown by a median neutralization ratio approaching 1 during these months. This implies there is sufficient NH$_3(g)$ throughout the region.
to neutralize nss-SO$_4^{2-}$ produced from DMS oxidation which is consistent with the measurements shown in Fig. 4.4. However, there is no denuder upstream of the Hi-Vol filters to remove NH$_3$ so the observed NH$_4^+$.SO$_4^{2-}$ ratio (Fig. 4.5) may be higher than for ambient PM$_{2.5}$. This effect is difficult to characterize, but if it is important then it is still evidence for the abundance of NH$_3$ in the summertime Arctic boundary layer. Lastly, Johnson and Bell (2008) show that a sufficiently neutralized sulphate aerosol will tend to ‘push’ gas-phase NH$_3$ into the ocean in the aerosol-gas-ocean system, also consistent with Fig. 4.3. The AIM-IC and Alert measurements are both inconsistent with a previous study that used GEOS-Chem to predict a highly acidic aerosol and insignificant gas-phase ammonia (NH$_x \approx$ NH$_4^+$) throughout the summertime Arctic marine boundary layer (Breider et al., 2014). This inconsistency implies a missing process in a widely used CTM that we investigate further below.

![Figure 4.5](image)

**Figure 4.5** Box-and-whisker plot of neutralization (defined as NH$_4^+$/2*nss-SO$_4^{2-}$) for 15 years (1996-2011) of weekly PM$_{2.5}$ speciation measurements taken in Alert, Nunavut. The percentiles are represented in the same fashion as Fig. 4.2.

### 4.4.3 Evidence for the importance of seabird guano

Observations collected onboard the *Amundsen* and in Alert strongly suggest a significant source of NH$_3$ in the Baffin Bay region. Decomposition of uric acid in seabird guano (excreta) has been recognized as a significant source of NH$_3$ where large colonies exist (Blackall et al., 2007;
Wilson et al., 2004). However, studies measuring NH$_3$ from seabird colonies are limited due to the remoteness of most colonies and technical challenges in quantifying NH$_3$ in isolated locations (Blackall et al., 2007). The few studies that have been done have focused on colonies located in the United Kingdom (Blackall et al., 2004; Wilson et al., 2004), Antarctica (e.g. Legrand et al., 1998; Zhu et al., 2011) and remote tropical islands (Riddick et al., 2014; Schmidt et al., 2010). Recently, Riddick et al. (2012a) developed a global inventory to estimate the magnitude and spatial distribution of NH$_3$(g) from seabird guano. The authors employed a bioenergetics model, first developed by Wilson et al. (2004), to calculate the NH$_3$(g) emissions (in g bird$^{-1}$ yr$^{-1}$) for 323 different seabird species. After compiling a list detailing the populations and locations of 33,225 colonies, they were able to estimate global annual emissions between 97-442 Gg NH$_3$ per year. Although this is less than 2% of total global NH$_3$(g) emissions, it can be the dominant source in remote regions where seabird populations are large and other sources are negligible.

In order to assess the impact of seabird guano on NH$_3$ across the Baffin Bay region, seabird colony NH$_3$ emissions were implemented in the GEOS-Chem model, and the impact on monthly mean surface layer NH$_3$ was examined. The NH$_3$ emissions inventory used in the standard GEOS-Chem v9-02 (and in many other CTMs) is from Bouwman et al. (1997) and does not include seabird emissions. Paulot et al. (2015) recently showed the oceanic emissions from this original inventory are roughly a factor of 3 too high since the initial inventory assumes atmospheric NH$_3$ is equal to zero. The Riddick et al. (2012a, b) seabird colony NH$_3$ emissions inventory (scenario 3) was added to the original inventory in GEOS-Chem following Paulot et al. (2015). Scenario 3 was chosen since this represented the midpoint between the minimum and maximum emissions of scenario 1 and 2, respectively. Close inspection of this seabird inventory revealed that some large seabird colonies in our study region were not accounted for. To investigate this, the spatial co-ordinates of northern colonies (>50 °N) in the Riddick et al. (2012a) inventory were cross-referenced against colonies in the on-line Circumpolar Seabird Data Portal (Seabird Information Network, 2015). Annual emissions for large colonies in the seabird data portal were calculated in the same manner as in Riddick et al. (2012a). In total, there were 42 colonies present in the seabird data portal but absent in the Riddick inventory in the region north of 50 °N. These additional emissions were added to the inventory we implemented in GEOS-Chem. These colonies totaled 7.5 Gg NH$_3$ year$^{-1}$ (approximately one quarter of the
existing emissions north of 50 °N) and were primarily in Siberia and western Alaska. The Riddick et al. (2012a) bioenergetics model only counts emissions that occur during breeding season and while the seabirds are at the colony. Hence, the annual emission estimates (Gg NH$_3$ year$^{-1}$) per colony were temporally allocated evenly between the 15 May to 15 September. This period is when the majority of seabirds in the Baffin Bay region are nesting (e.g. Gaston et al., 2005; Mallory and Forbes, 2007; McLaren, 1982). One limitation to this approach is that it does not account for additional temporal variations in NH$_3$ emissions. For instance, moisture increases the rate of uric acid degradation, and fluxes of NH$_3$ from guano have been observed to increase 10-fold for up to a day after rain events (Riddick et al., 2014).

Figure 4.6 shows the July mean output for surface layer NH$_3$ mixing ratio both without (Fig. 4.6a) and with (Fig. 4.6b) seabird emissions, along with the NH$_3$(g) measured by the AIM-IC denoted by circles in Fig. 4.6a. Comparing the top two panels reveals that seabird emissions make a substantial impact on modelled NH$_3$ levels in the boundary layer. Much better model-measurement agreement is achieved with the inclusion of the seabird colonies. Without the seabird emissions, NH$_3$ mixing ratios are underpredicted by several orders of magnitude. Surface NH$_3$ is still underpredicted in Fig. 4.6b (with guano NH$_3$ emissions) which could be the result of modelled emissions being independent of rainfall, which can substantially increase NH$_3$ emissions. Episodic rainfall was persistent throughout the latter half of the campaign. Other contributing factors may include the following: challenges in representing boundary layer mixing, uncertainties in deposition rates, comparing monthly averages (GEOS-Chem) to ambient hourly measurements, missing/underestimated bird colonies, and/or excreta from other fauna (e.g. seals, caribou, musk-ox) absent in the updated inventory. The bottom two panels (Figs. 4.6c and 4.6d) show the influence of seabirds on the ammonium to non-sea salt sulphate ratio.

Without seabirds (Fig. 4.6c) the ratio is less than 0.3 throughout most of the study region, which is inconsistent with the abundance of NH$_3$ relative to SO$_4^{2-}$ measured by the AIM-IC. Adding the seabird emissions (Fig. 4.6d) increases the ratio to above 0.7 in most grid cells along the ship track. Although the high ratio (July average is ~1) observed at Alert (denoted by the star in Figs. 4.6c and 4.6d) is underestimated in the GEOS-Chem simulation, the bias is reduced by nearly a factor of 2 (from 0.32 to 0.57) when seabird emissions are included.
Wildfires are also a source of NH$_3$ to the free troposphere and/or boundary layer. Particularly strong wildfire events were persistent in the Northwest Territories (NWT) during the study period. Blue circles in Fig. 4.7 show the location and average fire radiative power (representative of fire strength) of wildfires across the Arctic from July 20-26. It was constructed using data from NASA’s Fire Information Resource Management System (FIRMS) database (NASA, 2015). We used FLEXPART-WRF retro plumes to assess the importance of wildfire NH$_3$ emissions, as well as to further corroborate the influence of seabird guano.

**Figure 4.6** GEOS-Chem simulation of NH$_3$ mixing ratio (ppb) of the July monthly mean surface layer for (a) no seabird emissions and (b) with seabird emissions. Circles in (a) represent the ship track coloured by NH$_3$ measurements. Panels (c) and (d) show GEOS-Chem simulations for the ammonium to non-sea salt sulphate ratio during the same period for (c) no seabird emissions and (d) with seabird emissions. The star indicates the average ratio observed at Alert during July.
Figure 4.7 PES plots of FLEXPART-WRF 7-day retroplumes from the ship’s location on (a) 14 July 00:00, (b) 26 July 00:00, (c) 2 August 00:00, (d) 3 August 00:00 and (e) 4 August 00:00. The ship track is shown in black and the ship location at the release time is indicated in red. Colours show the airmass residence time prior to arrival at the ship (PES) in seconds. The plume centroid locations at 1 and 2 days (the approximate lifetime of NH₃) before release are shown (numbers 1 and 2). Purple circles represent the location of bird colonies with the size of each circle indicating the magnitude of estimated NH₃ emissions (in Mg NH₃ yr⁻¹). Blue circles show the location of wildfires from the NASA FIRMS measurements of fire radiative power from July 20-26 (in MW). The bottom panel is a time series of NH₃(g) and particle-phase NH₄⁺ and SO₄²⁻ measured by the AIM-IC with arrows indicating times of retroplume initiation in the upper panels. The NASA FIRMS data set was provided by LANCE FIRMS operated by NASA/GSFC/ESDIS with funding from NASA/HQ.

The significant impact of seabird colonies on [NH₃(g)] is supported by the analysis of FLEXPART-WRF retro plumes shown in Fig. 4.7. Periods of low [NH₃(g)] (bottom panel in Fig.
4.7) correspond to air masses that spent at least the last 48 hours over the ocean and/or aloft above the MBL (~500 m) where NH$_3$ sources are negligible. This is clearly shown in Fig. 4.7a where the air mass sampled on 14 July 00:00 (UTC) spent the previous 96 hours in the MBL over Baffin Bay, consistent with low [NH$_3(g)$]. In contrast, on 26 July 00:00 (Fig. 4.7b) air had recently passed over seabird colonies (purple circles) surrounding Lancaster Sound as well as wildfires in the Northwest Territories (NWT) on mainland Canada (blue circles), coincident with the large increase in [NH$_3(g)$]. A similar NH$_3(g)$ peak occurs on 3 August that can also be examined by using a retro plume analysis. Low NH$_3(g)$ values observed on the morning of 2 August agree with Fig. 4.7c showing the air originating from the MBL over Baffin Bay. At 3 August 00:00 (Fig. 4.7d) the air had spent the last 12 hours in the boundary layer of western Greenland where large seabird colonies exist. However, by 4 August 00:00 (Fig. 4.7e) the retro plume shifted such that air is now originating from primarily above the boundary layer (altitude plots not shown) leading to a decrease in NH$_3(g)$. In addition from August 2 to 4 the ship was north of 79° N and in the eastern Canadian Arctic, hence it is unlikely that this increase in NH$_3$ can be attributed to wildfires given how far removed this region is from wildfires in the NWT. While Fig. 4.7 only highlights five examples from the study period, retro plumes throughout the entire campaign also support the hypothesis that NH$_3(g)$ in the MBL originates primarily from seabird colonies (for the Eastern Canadian Arctic) with contributions from wildfires in some regions (central Canadian Arctic). All NH$_3(g)$ spikes in the time series can be attributed to air that had recently passed over seabird colonies and/or wildfires, whereas low values coincide with air masses from either the open ocean or free troposphere not influenced by wildfires.

To further investigate the potential influence of wildfires on NH$_3$ in the Arctic MBL, GEOS-Chem simulations were performed using a wildfire emissions inventory for 2014 (QFED2). Simulations with/without wildfires and with/without seabirds revealed that in Lancaster Sound (along 74° N) roughly 40% and 55% of the boundary layer NH$_3$ can be attributed to seabirds and wildfires, respectively. In other words, air sampled in Lancaster Sound (20 July to 27 July) was likely influenced by wildfires in NWT in addition to seabird guano. On the other hand, north of Lancaster Sound, contributions from seabirds and wildfires to surface layer NH$_3$ were approximately 95% and 5%, respectively. Wildfires in the NWT are an important but episodic source of summertime NH$_3$ in the Canadian Arctic. This is due to periodic transport events associated with this source that is located remote to our study region. Whereas, seabird colonies
are a local, and persistent source of NH\textsubscript{3} from May to September. Given the observation of consistently neutralized sulfate in Alert each summer, and the large interannual variability and episodic wildfire influence, emissions from migratory seabirds are likely to be a significant contributor to NH\textsubscript{3} abundance in the Arctic marine boundary layer.

4.4.4 Implications for N-deposition to ecosystems

Previous studies have highlighted the important role that seabird-derived N can play in the nitrogen cycle of ecosystems adjacent to bird colonies due to large deposition rates of NH\textsubscript{3} and NH\textsubscript{4}\textsuperscript{+} (e.g. Anderson and Polis, 1999; Lindeboom, 1984). However, little attention has been paid to the effects of seabird-derived N on deposition at the regional scale. In this section, we consider the importance of seabird-derived nitrogen as an input of reactive N to Arctic ecosystems. These ecosystems tend to be N-limited during the summer and hence have a large sensitivity to N input (Shaver and Chapin III, 1980). In terrestrial ecosystems, soil N availability is a key factor in determining both plant community structure (McKane et al., 2002) and greenhouse gas emissions from soil (Stewart et al., 2012).

Nitrogen (N\textsubscript{2}) fixation via microbes is thought to be the primary N input to remote Arctic terrestrial ecosystems (e.g. Cleveland et al., 1999; Hobara et al., 2006; Stewart et al., 2014). Numerous field studies have been conducted to estimate N\textsubscript{2}-fixation rates via the acetylene reduction technique (Hardy et al., 1968). The N\textsubscript{2}-fixation rates for most terrestrial Arctic sites fall within the range of 10 to 120 mg N m\textsuperscript{-2} yr\textsuperscript{-1} (Hobara et al., 2006). However, highly variable rates (due to spatial heterogeneity of microbial populations) and assumptions in the acetylene reduction technique yield high degrees of uncertainty for N\textsubscript{2}-fixation rates (Stewart et al., 2014).

Total atmospheric N-deposition (wet and dry) in the Arctic is thought to be smaller than fixation, with typical ranges from 8 to 56 mg N m\textsuperscript{-2} yr\textsuperscript{-1} (Van Cleve and Alexander, 1981). Only a few N\textsubscript{2}-fixation studies also quantify wet deposition, with dry deposition being ignored altogether (e.g. Hobara et al., 2006). Nonetheless, in certain Arctic regions atmospheric deposition may exceed N\textsubscript{2}-fixation in soils (DeLuca et al., 2008). These processes are coupled since large inputs of NH\textsubscript{4}\textsuperscript{+} have been shown to inhibit N\textsubscript{2}-fixation in certain microbial species and lichens (Chapin and Bledsoe, 1992).
Figure 4.8 shows results from the GEOS-Chem simulation of total NH$_x$ (≡NH$_3$ + NH$_4^+$) deposition (both wet and dry) for the months May to September (inclusive) both without (Fig. 4.8a) and with (Fig. 4.8b) seabird NH$_3$ emissions. The difference in total NH$_x$ deposition for birds and no birds is shown in Fig. 4.8c (absolute difference) and Fig. 4.8d (percent difference). Areas near large colonies are heavily influenced by seabird guano with NH$_x$ deposition from seabirds exceeding 10 mg N m$^{-2}$ yr$^{-1}$, particularly in western Greenland and near the mouth of Lancaster Sound. The majority of NH$_x$ deposition is caused by NH$_3$ as opposed to NH$_4^+$. Most regions in Fig. 4.8b are on the lower end of the annual N-deposition rate of 8 to 56 mg N m$^{-2}$ yr$^{-1}$ suggested by Van Cleve and Alexander (1981). However, there are two important distinctions: the latter is an estimate of total N-deposition and annual input. Estimates in Fig. 4.8 might be more useful for comparing N-deposition to N$_2$-fixation since it captures deposition only during the growing season, and NH$_x$ is likely the dominant form of atmospheric reactive N in the summertime Arctic boundary layer. Furthermore, Fig. 4.8b provides information on regions where N-deposition rates could be comparable to input from terrestrial N$_2$-fixation (>10 mg N m$^{-2}$ yr$^{-1}$) which can help inform subsequent studies exploring N-cycling in the region. According to Hobara et al. (2006), Arctic terrestrial N$_2$-fixation only occurs from May to September (inclusive) and peaks in July, similar to migration patterns of Arctic seabirds.
Estimates of N2-fixation rates in the Arctic Ocean mixed layer are even sparser than estimates for terrestrial ecosystems. To our knowledge, only Blais et al. (2012) have measured oceanic N2-fixation in the summertime Arctic Ocean mixed layer. The authors found that open ocean N2-fixation rates averaged 0.12 nM d\(^{-1}\) in the upper 50 m of the water column throughout the Beaufort Sea to Baffin Bay. For the period of May to September (inclusive) this represents an input of approximately 13 mg N m\(^{-2}\) which is comparable to inputs we calculate from guano-derived NH\(_3\) in regions close to seabird colonies as shown in Fig. 4.8b.
4.5 Conclusions

Simultaneous measurements of atmospheric and oceanic composition in the eastern Canadian Arctic revealed that the summertime Arctic Ocean and melt ponds were net sinks of NH$_3$(g). Concentrations of NH$_3$(g) ranging from 30 to 650 ng m$^{-3}$ were observed and represent the first reported measurements of NH$_3$(g) in the Canadian Arctic. An average downward flux of 1.4 ng m$^{-2}$ s$^{-1}$ into the Arctic Ocean was calculated, consistent with previous studies showing that higher latitude waters are a net NH$_3$ sink (Johnson et al., 2008). Melt ponds had a smaller net downward flux (1.1 ng m$^{-2}$ s$^{-1}$) as well as a slightly higher $\chi$ as compared to the open ocean (median 2 ng m$^{-3}$ versus 0.8 ng m$^{-3}$). To our knowledge, this is the first study to estimate melt pond-air NH$_3$ exchange despite the ubiquitous presence of melt ponds throughout the summertime Arctic.

On a nanoequivalent basis, NH$_3$(g) values were significantly greater (up to an order of magnitude more) than both NH$_4^+$ and SO$_4^{2-}$. This finding was consistent with a 15-year historical data set of weekly PM$_{2.5}$ composition from Alert, NU which showed that nss-SO$_4^{2-}$ is, on average, completely neutralized by NH$_4^+$ during July and August. These measurements imply strong regional source(s) of NH$_3$(g) in the eastern Canadian Arctic Archipelago that are sufficient to neutralize nss-SO$_4^{2-}$ produced from DMS oxidation. Our surface-air flux estimates show that the Arctic Ocean and melt ponds are not responsible for NH$_3$(g) in the marine boundary layer.

It is also noteworthy that even though these melt ponds have significantly higher [NH$_x$] than the open ocean (average of 670 nM versus 55 nM), $\chi_{MP}$ is only marginally higher. More acidic pHs and slightly lower temperatures mitigate the effect of higher [NH$_x$] on $\chi$. Chemical transport models (CTMs) that explicitly account for bi-directional NH$_3$ exchange typically require $\chi$ as a predefined model input (e.g. Bash et al., 2013; Wichink Kruit et al., 2012). Therefore, from a modelling standpoint, similar values of $\chi_{ocean}$ and $\chi_{MP}$ are convenient since they can be parameterized in a similar fashion which would remove the need for CTMs to resolve the spatial extent and temporal evolution of melt ponds to properly model surface-atmosphere NH$_3$ exchange in the summertime Arctic.

To investigate the impact of NH$_3$ emissions from seabird guano, we examined GEOS-Chem simulations both with and without seabird colony NH$_3$ emissions. The seabird NH$_3$ emission inventory developed by Riddick et al. (2012a) was updated for this study to include northern colonies (>50 °N) that had been overlooked in the original inventory. Without the seabirds,
GEOS-Chem underestimated NH$_{3(g)}$ by several orders of magnitude and predicted highly acidic aerosol at the surface in July, which is in direct contrast to our measurements. The inclusion of seabird emissions provided much better agreement with NH$_{3(g)}$ observations and yielded more neutralized aerosol throughout most of the Baffin Bay region. The importance of seabird NH$_3$ emissions is also supported by analysis of FLEXPART-WRF retro plumes throughout the study period. Air masses enriched in NH$_{3(g)}$ had recently passed through regions with seabird colonies whereas periods of low NH$_{3(g)}$ involved air masses originating from the open ocean or above the boundary layer. Together, these models provide strong evidence that seabird colonies are the dominant and persistent local source of NH$_{3(g)}$ in the summertime Arctic. FLEXPART-WRF and GEOS-Chem were also used to assess the influence of wildfires on NH$_3$. Wildfires are an important but episodic source of NH$_3$ to the Arctic due to ongoing changes in transport patterns and fire intensity. Further work should be done to examine the inter-annual influence of NH$_3$ emissions from wildfires in the NWT on other regions in the Arctic.

Deposition estimates of NH$_x$ from GEOS-Chem during the seabird nesting season (May to September) exceed 10 mg N m$^{-2}$ season$^{-1}$ in grid cells close to large seabird colonies, which is on the lower end of microbial N$_2$-fixation in Arctic tundra (Hobara et al., 2006). Hence, in some regions seabird-derived NH$_x$ could be a significant N-input to terrestrial Arctic ecosystems which are typically very N-sensitive. Estimates of NH$_3$ fluxes into the open ocean are unlikely to be an important input of reactive-N except for waters close to large seabird colonies; however, these fluxes may be important for the N-cycle in the much shallower melt ponds.

There is strong evidence that seabird colonies are likely the dominant and persistent source of NH$_{3(g)}$ to the summertime Arctic boundary layer. Emissions appear to be significant enough to at least partially neutralize nss-SO$_4^{2-}$ throughout most of the study region, in contrast to previous model simulations that did not consider seabird colony emissions. Further research is required to better constrain the location, population, and NH$_3$ emissions of Arctic seabird colonies. It is also important to quantify meteorological effects (e.g. rainfall, wind speed) on seabird emissions. The NH$_3$ emissions inventory in CTMs should be updated to include seabird emissions with correct representation of the breeding season so that emissions only occur when seabirds are nesting. Summertime measurements of atmospheric NH$_x$ elsewhere in the Arctic are needed to assess whether the impacts of seabirds observed in this study (substantial NH$_{3(g)}$, nss-SO$_4^{2-}$ neutralization, and N-deposition) are relevant to the entire Arctic.
4.6 Contributions

Gregory Wentworth was responsible for operating the AIM-IC, in addition to processing, analyzing, and interpreting the atmospheric field measurements aboard the Amundsen. Jonathan Gagnon, Jean-Sébastien Côté and Isabelle Courchesne collected and analyzed the oceanic and melt pond samples. Maurice Levasseur and Jean-Éric Tremblay were principal mission scientists during the cruise and helped interpret oceanic and melt pond data. Betty Croft performed all GEOS-Chem simulations and helped Jeffrey Pierce, Randall Martin, and Gregory Wentworth perform model-measurement comparisons. The updates to the seabird NH₃ emissions inventory using the CSDP were completed by Gregory Wentworth. FLEXPART-WRF simulations and interpretation were performed by Jennie Thomas. Alert filter data were collected and posted online by Desiree Toom-Sauntry, Alina Chivulescu and Sangeeta Sharma. The principal investigator for NETCARE was Jonathan Abbatt. The manuscript referenced at the beginning of this chapter was written by Gregory Wentworth with significant contributions from Jennifer Murphy, Betty Croft, Jonathan Gagnon, and Jennie Thomas.

4.7 References


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4.8 Appendix B

Table B1. Surface ocean parameters relevant for determining surface-air NH₃ exchange

<table>
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Table B2. Melt pond parameters relevant for determining surface-air NH$_3$ exchange

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Chapter 5
Ammonia and aerosol acidity in the Athabasca Oil Sands Region

Contributing authors: Wentworth, G. R., Murphy, J. G., Willis, M. D., Lee, A. K. Y., Abbatt, J. P. D., Li, S.-M., and Brook, J. R.

5 Chapter 5

5.1 Abstract

A four-week intensive field campaign was carried out in the Athabasca Oil Sands Region (AOSR) of north-eastern Alberta to investigate the regional emissions, transport and transformation of atmospheric pollutants. The Ambient Ion Monitor-Ion Chromatograph (AIM-IC) system measured hourly averages of water-soluble inorganic ions in PM$_{2.5}$ ($\text{NH}_4^+$, $\text{SO}_4^{2-}$, $\text{NO}_3^-$) and associated precursor gases ($\text{NH}_3$, $\text{SO}_2$, $\text{HNO}_3$) between 13 August and 8 September 2013. The ground site experienced relatively clean air masses arriving from the west but was occasionally impacted by polluted plumes from the direction of the AOSR upgrading facilities. Observations were grouped into two regimes: plume-influenced and non-plume-influenced (background) periods. The former were characterized by elevated levels of $\text{SO}_2$ (up to 45 ppbv), $\text{SO}_4^{2-}$ (up to 17 $\mu$g m$^{-3}$), $\text{NH}_3$ (up to 2.5 ppbv) and $\text{NH}_4^+$ (up to 3.5 $\mu$g m$^{-3}$). During background periods all the aforementioned species were below 0.2 $\mu$g m$^{-3}$ or 0.2 ppbv, except $\text{NH}_3$ which exhibited a unimodal diurnal maximum peaking at ~1 ppbv, on average, around noon.

Measurements from an Aerosol Mass Spectrometer (AMS) were used to complement AIM-IC data to examine particle pH during plume-influenced periods. The Extended – Aerosol Inorganic Model (E-AIM) was used to investigate the aerosol $\text{NH}_3$-$\text{NH}_4^+$-$\text{SO}_4^{2-}$-$\text{HNO}_3$-$\text{NO}_3^-$-$\text{H}_2\text{O}$ system and calculate particle pH. E-AIM predicted particle pH between -0.16 and 2.07 assuming a deliquesced particle and not allowing gas-particle partitioning. Predicted equilibrium $\text{NH}_3$ mixing ratios above these particles were several orders of magnitude lower than observations which implies that the aerosol system is out of equilibrium. Further work is required to better constrain $\text{NH}_3$ sources in the AOSR, as well as to elucidate the cause of the apparent disequilibrium diagnosed by E-AIM during the peak of plume-influenced periods. Implications for acid deposition downwind and modelling air quality are also discussed.
5.2 Introduction

The Athabasca Oil Sands Region (AOSR) is an area in north-eastern Alberta encompassing ~144,000 km² and containing one of the largest proven fossil fuel reserves in the world (~2.7 x10⁷ m³). Oil production was 2.2 million barrels per day (bpd) in 2014 and by 2030 is expected to increase to 4.0 million bpd (CAPP, 2015). The deposits mostly lie under boreal forest and muskeg, although surface mining, tailings ponds and upgrading facilities are common across the AOSR. The Wood Buffalo Environmental Association (WBEA; www.wbea.org) has monitored air quality throughout the region for nearly two decades with a primary monitoring goal of ensuring industrial compliance with the Alberta Air Quality Objectives. Various criteria air contaminants (CACs) are routinely monitored by WBEA, including sulphur dioxide (SO₂), nitrogen dioxide (NO₂), ozone (O₃), ammonia (NH₃), total reduced sulphur (TRS), and mass of fine particulate matter (smaller than 2.5 μm in diameter, PM₂.₅) (Percy, 2013). Targeted atmospheric field studies have examined other air pollutants in the AOSR, such as polycyclic aromatic compounds (PACs; Hsu et al., 2015; Schuster et al., 2015) and volatile organic compounds (VOCs; Shephard et al., 2015; Simpson et al., 2010).

Significant anthropogenic point sources of SO₂ and NOₓ, as well as mobile NOₓ sources, exist in the AOSR (Environment Canada, 2013). These gases are oxidized in the atmosphere to form sulphuric acid (H₂SO₄) and nitric acid (HNO₃), which lead to the production of particle-phase sulphate (SO₄²⁻) and nitrate (NO₃⁻), respectively (Seinfeld and Pandis, 2006). NH₃ is the most abundant alkaline gas in the troposphere and is able to neutralize these acidic PM₂.₅ species depending on their relative amounts in air. The neutralization reaction of NH₃ with deliquesced acidic particles yields particle-phase ammonium (NH₄⁺), and gas-particle equilibrium can be established on the order of minutes for submicron particles (Huntzicker et al., 1980; Meng and Seinfeld, 1996). However, some laboratory studies show equilibration can be retarded by the presence of hydrophobic organic coatings (Daumer et al., 1992; Liggio et al., 2011). These coatings can add a substantial kinetic limitation to mass transfer of NH₃ across the gas-particle interface. The extent of neutralization influences several properties of PM₂.₅ including hygroscopicity (Petters and Kreidenweis, 2007) and ice nucleation potential (Abbatt et al., 2006), and some evidence suggests that less neutralized PM₂.₅ is more harmful to human health (Kelly and Fussell, 2012).
Globally, NH$_3$ is primarily emitted from agricultural activities with smaller contributions from industry, transport, and natural sources such as biomass burning (Reis et al., 2009). However, in the AOSR there is minimal agriculture and, according to the 2013 National Pollutant Release Inventory (NPRI), industrial anthropogenic NH$_3$ emissions in the area are roughly 30 times smaller, by mass, than SO$_2$ emissions (or a factor of 8 on the basis on moles) (Environment Canada, 2013). Natural emissions of NH$_3$ from soil and vegetation are known to be relatively significant in remote environments (Sutton et al., 2000, 2013) but have yet to be quantified in the AOSR. Hsu and Clair (2015) also found that air quality in the AOSR can be influenced by regional wildfires during the summer months.

The large uncertainties regarding the magnitude and spatial and temporal distributions of natural NH$_3$ sources and limited number of NH$_3$ datasets in the AOSR (Hsu and Clair, 2015; Shephard et al., 2015) provide motivation for subsequent measurements of NH$_3$ and its impact on particle acidity. This chapter presents measurements taken during the intensive 2013 Fort McMurray Oil Sands Strategic Investigation of Local Sources (FOSSILS) study. The specific goals of this chapter are to:

1) Determine typical concentrations of NH$_3$, NH$_4^+$, SO$_2$, SO$_4^{2-}$, HNO$_3$ and NO$_3^-$ and compare measurements to previous studies at other ground sites in the AOSR.
2) Assess the influence of anthropogenic activities on air quality. To what extent are pollutant levels enhanced in air masses impacted by oil sands emissions?
3) Examine particle acidity and whether sufficient NH$_3$ exists to neutralize SO$_4^{2-}$ and NO$_3^-$. 
4) Explore the implications that particle acidity, neutralization and NH$_3$ have for modelling air quality in the AOSR.

5.3 Materials and Methods

5.3.1 Field Site (AMS13)
The FOSSILS intensive campaign included two air monitoring stations (AMS13 and AMS1) in addition to concurrent airborne measurements (Gordon et al., 2015; Liggio et al., 2016). The primary goals of the study were to elucidate the sources, transport and transformations of atmospheric pollutants in the AOSR. An extensive suite of instrumentation was deployed at AMS13 from 7 August 2013 until 12 September 2013 (Fioletov et al., 2016; Tokarek et al., 2014).
Figure 5.1 shows the location of AMS13 and AMS1 within the AOSR. Mining operations and bitumen upgrading facilities are ~5 km to the south and north of both sites. AMS13 (57.1492° N, 111.6422° W, ~270 m a.s.l.) was the most extensively instrumented ground site and is surrounded by boreal forest, with dominant winds from the west, which deliver relatively clean air masses. However, the site was occasionally impacted by anthropogenic emissions from nearby facilities. This made it possible to sample both clean and polluted air masses, and assess the influence of emissions from these facilities on air quality and atmospheric chemistry. Table 5.1 lists the 2013 emissions for NH₃, SO₂, and NO₂ from three major facilities in the AOSR (Environment Canada, 2013).

**Table 5.1** 2013 NPRI emissions (in tonnes) of NH₃, SO₂ and NO₂ from major AOSR facilities

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<th>NO₂</th>
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<td>1 093</td>
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Figure 5.1 Location of the FOSSILS ground sites (AMS1 and AMS13, red pins) and major upgrading facilities (green houses) in the AOSR. Open mines, active mines, and tailings ponds are shown in green, red, and blue, respectively. Boundaries of the AOSR are shown in yellow. (Image credit: Jasmin Schuster)

5.3.2 Ambient Ion Monitor-Ion Chromatograph (AIM-IC)

The Ambient Ion Monitor-Ion Chromatograph (AIM-IC) system was operated at AMS13 from 13 August until 8 September 2013. The AIM-IC was housed in a temperature-controlled trailer and its inlet box was attached to a pole extending above the trailer to a height of 4.55 m above ground (i.e. sampling height of 4.55 m). Since the AIM-IC has been discussed in previous chapters and publications (e.g. Markovic et al., 2012; Wentworth et al., 2014) it is described here only briefly.

The AIM-IC consists of two Ion Chromatographs (ICS-2000, Dionex Inc.) that simultaneously quantify water-soluble ions in PM$_{2.5}$ and precursor gases that have been collected (dissolved) in
~5 mL aliquots of deionized water using an Ambient Ion Monitor (URG-9000D, URG Corp.). The system measured hourly averages of NH$_3$, NH$_4^+$, SO$_2$, SO$_4^{2-}$, HNO$_3$, and NO$_3^-$ with detection limits of 40 pptv, 9 ng m$^{-3}$, 2 pptv, 5 ng m$^{-3}$, 20 pptv, and 10 ng m$^{-3}$, respectively, during FOSSILS. Detection limits were determined by overflowing the AIM-IC inlet with high purity zero air for 15 hours and calculating three standard deviations (3σ) of the peak area for each analyte in the ion chromatograms during the last 8 hours. The 3σ value was then converted to either a mixing ratio (gas-phase) or mass loading (particle-phase) assuming a temperature of 298 K and pressure of 760 mm Hg. The average analyte peak area during the last 8 hours was used a background and subtracted from each ambient measurement.

The ICs were calibrated offline at the beginning and end of the campaign using a set of 5 aqueous standards of known concentration prepared via serial dilution in deionized water (18.2 MΩ cm$^{-1}$). Suppressed conductivity detection and reagent-free gradient elution schemes were used for both IC systems. The ICs were operated with CS/CG17 and AS/AG19 analytical/guard columns. Both were equipped with pre-concentrator columns (TCC-ULP1 and TAC-ULP1, Dionex Inc.) which allowed for improved detection limits relative to a sample loop.

The AIM-IC is also capable of detecting gas-phase and particulate-phase amines (VandenBoer et al., 2011). During FOSSILS the gas-phase detection limits were determined for six amines: methylamine (110 pptv), ethylamine (0.44 pptv), dimethylamine (0.68 pptv), triethylamine (0.46 pptv) and trimethylamine plus diethylamine (TMA+DEA, 0.49 pptv). The peaks for TMA and DEA could not be separated using the elution scheme described above. Amines were never observed above detection limits during the campaign.

Submicron aerosol composition measurements from an Aerodyne Aerosol Mass Spectrometer (AMS) were also examined and used to complement the AIM-IC dataset. The instrument is a high-resolution time-of-flight AMS with an IR-laser for vaporizing refractory black carbon (Lee et al., 2015). The AMS was housed in a separate trailer at AMS13 and sampled aerosol within the size range of ~80-1000 nm. It should be noted that the AIM-IC has a larger size cut-off (particle diameter < 2.5 µm). Data were collected with 2 minute time resolution and corrected using a composition-dependent collection efficiency (Middlebrook et al., 2012). The AMS has been described previously in great detail (Onasch et al., 2012).
5.3.3 Extended – Aerosol Inorganics Model (E-AIM)

The Extended – Aerosol Inorganics Model (E-AIM) is a thermodynamic model that can be used to calculate gas/liquid/solid partitioning of common inorganic and organic aerosol species at equilibrium (Wexler and Clegg, 2002). The equations for calculating solute and solvent activities are based on the earlier work of Clegg et al. (1992). The model is accessible on-line and available at: http://www.aim.env.uea.ac.uk/aim/aim.php. E-AIM is used in this chapter to assess the degree to which acidic components of PM$_{2.5}$ (SO$_4^{2-}$ and NO$_3^-$) are neutralized by NH$_4^+$, and how consistent the measured aerosol H$^+$-NH$_3$-NH$_4^+$-SO$_4^{2-}$-HNO$_3$-NO$_3^-$-H$_2$O system is with thermodynamic equilibria predicted from E-AIM.

The chemical model (Model II) was used since it can model the species of interest under conditions ranging from temperatures of 180 to 330 K and RH from 0.1 to 1.0. Model inputs are ambient relative humidity, pressure, temperature and the measured mole loadings (mol m$^{-3}$ of air) of SO$_4^{2-}$, NO$_3^-$, HNO$_3$(g), NH$_4^+$, and NH$_3$(g). Aerosol ion balance is achieved by inputting either sufficient H$^+$ or OH$^-$ to achieve electroneutrality. For this work, the formation of solids was turned off (i.e. deliquesced aerosol is assumed) and partitioning of NH$_3$ and HNO$_3$ was allowed, unless otherwise stated. Pertinent model output consists of molalities, mole fractions, and activity coefficients for aqueous (particle) species at equilibrium, in addition to equilibrium partial pressures of gases. Equilibrium for the system is achieved when the total Gibbs free energy is at a minimum, and is calculated using equations for aqueous phase activity coefficients and gas-liquid (Henry’s law, K$_H$) and solid-liquid (K$_{eq}$) equilibrium constants. The E-AIM output was also used to calculate particle pH by taking the negative logarithm of the activity of H$^+$, calculated as the product between H$^+$ molality and its activity coefficient. E-AIM calculations were performed for every hour during the campaign for which the necessary AIM-IC (or AMS) and meteorology data were available and valid (above detection limits).

5.4 Results and Discussion

5.4.1 Gases and Plume-Influenced Periods

The hourly measurements of SO$_2$, NH$_3$ and HNO$_3$ during FOSSILS are shown in Fig. 5.2. Campaign ranges (averages) were <0.002 to 47 (1.20) ppbv for SO$_2$, <0.04 to 3.0 (0.61) ppbv for NH$_3$, and <0.02 to 0.55 (0.05) ppbv for HNO$_3$. The averages are within a factor of four of the
measurements from Hsu and Clair (2015), who performed a field study in 2013 at a site in Fort McMurray roughly 60 km south of AMS13. Hsu and Clair (2015) operated the same model of AIM-IC instrument and reported summer (May to October) averages of 0.47 ppbv (SO$_2$), 2.5 ppbv (NH$_3$), and 0.09 ppbv (HNO$_3$). The higher SO$_2$ mixing ratios observed in our study can be explained by the proximity of AMS13 to the upgrading facilities (relative to Fort McMurray), which are known to be large point sources of SO$_2$ (e.g. McLinden et al., 2012; Percy, 2013; Simpson et al., 2010). Another possibility is the fact that Fort McMurray is located within the Athabasca River valley preventing it from intercepting the elevated stack plumes from the facilities under typical meteorological conditions. The higher average summertime NH$_3$ mixing ratio from Hsu and Clair (2015) could be a consequence of the Fort McMurray sampling site (population ~60,000) being more influenced from residential and transportation sources of NH$_3$. Previous field studies in forested areas similar to AMS13 have observed summertime NH$_3$ averages around 1 ppbv, consistent with measurements from our study (e.g. García-gómez et al., 2016; Hansen et al., 2015). NH$_3$ mixing ratio exhibited a midday peak at AMS13, likely due to the significant temperature-dependence of biospheric NH$_3$ emissions (Flechard et al., 2013).

**Figure 5.2** Hourly averaged mixing ratios of water-soluble gases measured by the AIM-IC during FOSSILS. SO$_2$ is on the left axis; NH$_3$ and HNO$_3$ are on the right axis.

Atmospheric measurements at AMS13 can be divided into two regimes: plume influenced and non-plume influenced times. Elevated SO$_2$ is a suitable metric to distinguish between these two regimes since the three facilities within the vicinity of AMS13 have large annual SO$_2$ emissions (Table 5.1). Furthermore, natural emissions of SO$_2$ and its precursors (reduced sulphur) are negligible relative to these large anthropogenic point sources. Hence, a “plume-influenced” day
was defined as a day which $\text{SO}_2$ exceeded 0.5 ppbv for at least one hour. All other days were considered “non-plume” or “background” days. Plume-influenced periods correspond to the specific times during each plume day when $\text{SO}_2$ was greater than 0.5 ppbv, and usually occurred in the afternoon.

Figure 5.3a shows that plume-influenced air masses enriched in $\text{SO}_2$ typically arrived from the east-southeast (ESE). These air masses did not arrive directly from due south or north because the Athabasca River created a valley flow and funnelled polluted air to AMS13 from the ESE. A clear enhancement in $\text{SO}_2$, $\text{NH}_3$ and $\text{HNO}_3$ was seen on plume-influenced afternoons (Fig. 5.3b). Average afternoon $\text{NH}_3$ mixing ratios were roughly twice as high on plume influenced afternoons which suggests: 1) mining related source(s) of $\text{NH}_3$, and 2) a significant regional background of $\text{NH}_3$ that reaches an average daily maximum of 1 ppbv around midday. In 2013, Syncrude Mildred Lake reported atmospheric $\text{NH}_3$ emissions of 1,436 tonnes, in comparison to much smaller values for Suncor (1.3 tonnes) and CNRL Horizon (1.1 tonnes) (Environment Canada, 2013). Insufficient detail is given in the NPRI to determine whether these emissions are from point sources (stack) or fugitive (near-ground) emissions.

Figure 5.3 (a) Rose plot of $\text{SO}_2$ (red) and $\text{NH}_3$ (orange) average mixing ratio (in ppb) as a function of wind direction. (b) Time-of-day plot comparing hourly average mixing ratio of water-soluble gases on plume (solid lines) and non-plume (dashed lines) influenced days.
Shephard et al. (2015) used the Tropospheric Emission Spectrometer (TES) and airborne measurements from FOSSILS to investigate NH$_3$ in the AOSR. The magnitude of the representative volumetric mixing ratio of NH$_3$ retrieved at 965 hPa from the satellite and the in situ mixing ratios measured by an aircraft instrument were consistent (within a factor of 2) with AIM-IC observations. The authors also used a regional air quality (GEM-MACH) to interrogate potential NH$_3$ sources. In airmasses that were not influenced by industrial plumes, the model drastically underpredicted NH$_3$ mixing ratios (average <0.05 ppbv with values never exceeding 0.2 ppbv). This version of GEM-MACH does not include bi-directional NH$_3$ exchange, a diurnal emission profile, or natural sources of NH$_3$. This large model-measurement discrepancy underscores the importance of using robust surface-atmosphere parameterizations for NH$_3$ in remote environments.

5.4.2 PM$_{2.5}$ and Particle Acidity

AIM-IC hourly averages of SO$_4^{2-}$, NH$_4^+$, and NO$_3^-$ in PM$_{2.5}$ along with organic mass loading measured by the AMS are presented in the lower panel of Fig. 5.4. Particle loadings of inorganic ions were extremely low (< 0.15 µg m$^{-3}$) except during plume-influenced periods, when a substantial increase in SO$_4^{2-}$ was observed, along with notable increases of NH$_4^+$ and NO$_3^-$. The top panel in Fig. 5.4 shows the calculated mole loading of H$^+$ in PM$_{2.5}$, which is a surrogate for particle acidity. Since particle H$^+$ loading cannot be measured directly, it was inferred from ion balance ($\equiv 2*$SO$_4^{2-}$ + NO$_3^-$ - NH$_4^+$) using both AIM-IC (black trace) and AMS (purple trace) measurements. During plume events it is clear that the aerosol does not contain sufficient NH$_4^+$ to neutralize SO$_4^{2-}$ and NO$_3^-$ despite the presence of NH$_3$ (Fig. 5.2). However, the co-existence of NH$_3$ and acidic particles does not necessarily imply a lack of equilibrium for deliquesced particles – we explore this further below.
Another metric for particle acidity is particle pH which can be calculated using the output of thermodynamic equilibrium models (e.g. Zhang et al., 2007). Unlike using ion balance to assess particle acidity, particle pH is not directly dependent on total particle loading. Particle pH was investigated during the peak of six plume-influenced periods (i.e. the hour during plume days which had the highest SO₂, denoted by grey circles in Fig. 5.4) using the activity coefficient and particle H⁺ molality predicted by E-AIM. Table 5.2 shows the equilibrium particle pH calculated using two separate conditions: 1) no gas-particle partitioning and 2) allowing gas-particle partitioning. The former holds the particle mole loading constant (i.e. NH₄⁺ and NO₃⁻ are fixed at the measured value) and E-AIM reports an equilibrium partial pressure of NH₃ and HNO₃ above the particle. The latter represents particles that have equilibrated with the measured NH₃ and HNO₃ (i.e. NH₃/NH₄⁺ and HNO₃/NO₃⁻ partition to achieve respective equilibria). In both cases the particles were assumed to be deliquesced. E-AIM calculations were performed using both AIM-IC particle measurements (top rows) and AMS particle measurements (bottom rows). When applicable, AIM-IC measurements of HNO₃ and NH₃ were used.
Table 5.2 Calculated particle pH during plume-influenced periods both with and without gas-particle partitioning, as well as equilibrium NH$_3$ (no partitioning) and measured NH$_3$. Calculations using particle data from both the AIM-IC (top rows) and AMS (bottom rows) are shown.

<table>
<thead>
<tr>
<th>Measurement Hour (local)</th>
<th>pH (without g/p partitioning)</th>
<th>Calculated NH$_3$ (ppbv)</th>
<th>pH (with g/p partitioning)</th>
<th>Measured NH$_3$ (ppbv)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Calculated with AIM-IC PM$_{2.5}$ Data</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23 Aug 18:00</td>
<td>-0.16</td>
<td>0.001</td>
<td>1.56</td>
<td>0.32</td>
</tr>
<tr>
<td>24 Aug 15:00</td>
<td>0.42</td>
<td>0.006</td>
<td>2.55</td>
<td>1.7</td>
</tr>
<tr>
<td>26 Aug 15:00</td>
<td>1.04</td>
<td>0.002</td>
<td>2.67</td>
<td>1.7</td>
</tr>
<tr>
<td>3 Sep 14:00</td>
<td>-0.01</td>
<td>0.0007</td>
<td>2.13</td>
<td>0.58</td>
</tr>
<tr>
<td>4 Sep 14:00</td>
<td>-0.06</td>
<td>0.001</td>
<td>2.66</td>
<td>1.9</td>
</tr>
<tr>
<td>7 Sep 13:00</td>
<td>0.63</td>
<td>0.009</td>
<td>2.81</td>
<td>1.1</td>
</tr>
<tr>
<td><strong>Calculated with AMS PM$_{1}$ Data</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23 Aug 18:00</td>
<td>0.25</td>
<td>0.006</td>
<td>1.88</td>
<td>0.32</td>
</tr>
<tr>
<td>24 Aug 15:00</td>
<td>2.07</td>
<td>0.26</td>
<td>2.89</td>
<td>1.7</td>
</tr>
<tr>
<td>26 Aug 15:00</td>
<td>1.68</td>
<td>0.01</td>
<td>3.62</td>
<td>1.7</td>
</tr>
<tr>
<td>3 Sep 14:00</td>
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<td>0.09</td>
<td>2.58</td>
<td>0.58</td>
</tr>
<tr>
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<td>0.1</td>
<td>2.75</td>
<td>1.9</td>
</tr>
<tr>
<td>7 Sep 13:00</td>
<td>No Data</td>
<td>No Data</td>
<td>No Data</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Also in Table 5.2 is the calculated equilibrium mixing ratio of NH$_3$ above the particle without gas-particle partitioning, as well as the measured NH$_3$ mixing ratio. Comparing these two values...
provides an indication of how “close” the NH$_3$-NH$_4^+$-SO$_4^{2-}$-HNO$_3$-NO$_3^-$-H$_2$O system is to equilibrium. For instance, if the calculated and measured NH$_3$ are similar then the measured aerosol system has approached thermodynamic equilibrium. A robust analysis of particle pH during non-plume periods was complicated by PM$_{2.5}$ measurements near the detection limits since particle pH is extremely sensitive to the precise ion balance.

When gas-particle partitioning was allowed, the particle pH ranged from 1.56 to 2.81 for the AIM-IC data and 1.88 to 3.62 for the AMS particle data, consistent with reported literature values that are typically between 0 and 3 (e.g. Guo et al., 2015). When gas-particle partitioning was not allowed, pH values calculated by E-AIM were about 1 to 2 pH units lower since NH$_3$ could not partition to the particle to neutralize acidic species.

Using the AIM-IC data, calculated NH$_3$ mixing ratios in equilibrium above the particle without partitioning are roughly 3 orders of magnitude smaller than observed values. This large discrepancy implies that the measured NH$_3$-NH$_4^+$-SO$_4^{2-}$-HNO$_3$-NO$_3^-$-H$_2$O system is in disequilibrium for these plume-influenced periods. In other words, according to equilibrium there exists sufficient NH$_3$ to further neutralize the acidic particles (i.e. some NH$_3$ should partition to the particle to achieve equilibrium). An analogous comparison using the AMS particle data yields similar results, although the difference is only about 1-2 orders of magnitude. The apparent disequilibrium between the particle and NH$_3$ is unusual considering that gas-particle equilibrium for volatile species (e.g. NH$_3$) should be achieved on the timescale of seconds or minutes for submicron particles (Meng and Seinfeld, 1996). Below we investigate possible explanations for this apparent disequilibrium.

Organic coatings have been shown to retard the uptake of NH$_3$ into acidic sulphate particles (Daumer et al., 1992). Liggio et al. (2011) demonstrated that sulphuric acid particles with a hydrophobic organic coating can take hours to days to achieve a steady-state NH$_4^+$:SO$_4^{2-}$ ratio. These laboratory experiments were performed under low RH conditions (20-40%), leading to a more viscous particle which further hinders NH$_3$/NH$_4^+$ equilibration. The RH during the peak of plume-influenced periods was 38-44% (except 26 August was 71%). As shown in Fig. 5.4., the organic mass loading in PM$_1$ was ~10-15 µg m$^{-3}$ during plume-influenced periods and ~3-5 µg m$^{-3}$ during background times. The relatively low RH and enhanced organic loading mean that the presence of a viscous organic coating on PM$_{2.5}$ is plausible.
Another explanation for the apparent disequilibrium in the measurements is the exclusion of base cations (e.g. \( \text{Ca}^{2+}, \text{Mg}^{2+} \)) in the prescribed ion balance. If present, these base cations could account for the remaining neutralization (i.e. less \( H^+ \) is required for electroneutrality).

Unfortunately the AIM-IC backgrounds for \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) were high and variable during the campaign which prevented quantification of these species in PM\(_{2.5}\). Since the particle pH is so sensitive to the relative abundances of \( \text{NH}_4^+ \), \( \text{SO}_4^{2-} \) and \( \text{NO}_3^- \), instrument biases and sensitivity uncertainties could also be a contributing factor. However, for this effect to be significant, both instruments would have to be biased towards underpredicting aerosol neutralization by overestimating \( \text{SO}_4^{2-} \) and \( \text{NO}_3^- \) and/or underestimating \( \text{NH}_4^+ \). It is also possible that \( \text{NH}_3 \) and the acidic particles have had insufficient mixing time to approach equilibrium. For instance, if the source(s) of \( \text{NH}_3 \) were at the surface (e.g. tailings ponds, soil, vegetation) then acidic particles produced/emitted aloft could have an inadequate amount of time to mix before being sampled by the AIM-IC and AMS. Lastly, it is possible that the ambient particles were not deliquesced which would invalidate the calculations in Table 5.2.

Further work is required to ascertain whether the \( \text{NH}_3\text{-NH}_4^+\text{-SO}_4^{2-}\text{-HNO}_3\text{-NO}_3^-\text{-H}_2\text{O} \) disequilibrium is a real phenomenon during plume-influenced periods, or whether it is an artefact (from e.g. persistent instrument bias towards underpredicting \( \text{NH}_4^+ \) or exclusion of base cations).

### 5.4.3 Estimating Plume Age

Plume processing time (age) can be qualitatively examined using the \( \text{SO}_4^{2-}:\text{SO}_2 \) ratio in the plume. Since \( \text{SO}_2 \) is irreversibly oxidized to \( \text{SO}_4^{2-} \) the ratio in an air mass increases with time from emission (Karamchandani and Seigneur, 1999). However, this approach is only qualitative since there exist numerous pathways for \( \text{SO}_2 \) oxidation and the rate of \( \text{SO}_4^{2-} \) formation varies according to oxidant concentrations and meteorology (Lee et al., 2011; Stein and Saylor, 2012). In addition, the two species have different deposition rates.

Figure 5.5a shows the ambient mole equivalents loading of \( \text{SO}_2 \) (solid line) and \( \text{SO}_4^{2-} \) (dashed lined), as well as the molar \( \text{SO}_4^{2-}:\text{SO}_2 \) ratio calculated during the peak of each plume-influenced period. With the exception of 26 August, the ratio ranges from 0.04 to 0.11. These ratios are similar to those in fresh stack emissions measured aboard the aircraft only several hundred metres downwind of the upgrading facilities. This suggests that air masses during these five plume-influenced periods contain relatively fresh anthropogenic emissions, which have not
undergone significant oxidation by the time they arrive at AMS13. This lack of oxidative processing is consistent with the relatively short distance (~5-20 km) between the upgrading facilities and field site.

![Figure 5](image)

**Figure 5.5** Time series of (a) SO$_2$ (solid) and SO$_4^{2-}$ (dashed) mole equivalents and (b) SO$_x$ (=SO$_4^{2-}$ + SO$_2$, red) and NH$_x$ (=NH$_4^+$ + NH$_3$, orange) mole equivalents. Values above each plume-influenced period indicate the average (a) SO$_4^{2-}$:SO$_2$ mole and (b) NH$_x$:SO$_x$ ratio during the peak of the plume-influenced period corrected for background NH$_x$.

In contrast, the plume-influenced period on 26 August had a SO$_4^{2-}$:SO$_2$ ratio of 0.74. Another difference on 26 August is the wind direction at AMS13 was ENE as opposed to the ESE. The Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Stein et al., 2015) was used to assess air mass back-trajectories for each plume-influenced period. The 26 August back-trajectory (not shown) was consistent with the air mass having meandered around (i.e. variable wind speed and direction) the AOSR the previous day and subsequently arrived at AMS13 during the afternoon of 26 August. The wind direction and HYSPLIT analyses and the high SO$_4^{2-}$:SO$_2$ ratio suggest the plume-influenced air mass on 26 August contained AOSR emissions that have undergone significant oxidation relative to other episodes.

Figure 5.5b is a time series of SO$_x$ (=SO$_4^{2-}$ + SO$_2$) and NH$_x$ (=NH$_3$ + NH$_4^+$) along with the NH$_x$:SO$_x$ ratio during each plume-influenced period. The NH$_x$:SO$_x$ ratio was corrected for background NH$_x$ by subtracting the average NH$_x$ mole loading during that given time on non-
plume influenced days (Figure 5.3b). The molar \( \text{NH}_3: \text{SO}_2 \) air emission ratio reported in Table 5.1 are 0.09 (Syncrude ML), \( 1 \times 10^{-3} \) (CNRL Horizon) and \( 3 \times 10^{-4} \) (Suncor B&M). With the exception of Syncrude, these ratios are significantly lower than what was observed during the plume-influenced periods. This is consistent with additional (i.e. natural or unreported anthropogenic) sources of \( \text{NH}_3 \) throughout the AOSR. It is also consistent if Syncrude is the major source of anthropogenic emissions during plume-influenced periods at AMS13. The influence of \( \text{NH}_3 \) volatilization from on-site disposal and the exclusion of direct \( \text{SO}_4^{2-} \) emissions will affect the estimated emissions ratios, although direct \( \text{SO}_4^{2-} \) emissions are likely negligible. The strong temperature dependency of \( \text{NH}_3 \) volatilization may also cause a large seasonal effect in the \( \text{NH}_3: \text{SO}_2 \) emissions ratio.

Figure 5.4 (top) and Table 5.2 reveal that the 26 August plume-influenced period contains acidic particles that are perturbed from thermodynamic equilibrium as evaluated by the E-AIM calculations. Hence, it is unlikely that insufficient gas-particle mixing time is the cause of disequilibrium in the measured aerosol system. If it were, then of the six plume-influenced periods the polluted air mass on 26 August should have the aerosol system that is closest to equilibrium due to its longer atmospheric lifetime.

5.4.4 Implications for \( \text{NH}_x \) Partitioning and Modelling

Figure 5.6a shows that background air masses (light orange bars) generally have a higher gas fraction of \( \text{NH}_x (\equiv \text{NH}_3 + \text{NH}_4^+) \) than plume-influenced periods (difference between dark and light bars). In other words, \( \text{NH}_3 \) partitions into acidic particles during plume-influenced periods. This phenomenon is unsurprising and has been previously observed in the AOSR (Hsu and Clair, 2015). The partitioning of \( \text{HNO}_3 \) appeared to be unaffected (Fig. 5.6b) since the distribution of \( \text{HNO}_3 \) gas fraction is similar when plume-influenced air masses are excluded. It is possible that additional aerosol water and increased acidity have offsetting effects for \( \text{HNO}_3 \) partitioning during plume times, since the former would favour particle \( \text{NO}_3^- \) while the latter would not. The shift in \( \text{NH}_x \) partitioning has implications for \( \text{NH}_x \) transport and N-deposition since \( \text{NH}_4^+ \) in \( \text{PM}_{2.5} \) has an atmospheric lifetime on the order of days to weeks meaning it can be transported greater distances than \( \text{NH}_3 \) (Lefer et al., 1999; Paulot et al., 2014).
The extent of aerosol neutralization is important for particle processes such as scattering efficiency (Martin et al., 2004), hygroscopicity (Petters and Kreidenweis, 2007) and ice-nucleating ability (Abbatt et al., 2006). Furthermore, acid deposition can have harmful effects for sensitive ecosystems with a low critical load for acidic species. The boreal forests of northern Saskatchewan are particularly sensitive to acid deposition and are only hundreds kilometres downwind of the AOSR (Whitfield and Watmough, 2012). Therefore it is imperative to understand the NH₃ partitioning and apparent disequilibrium of NH₃ in the aerosol system since it can affect particle acidity and the amount of NH₃ deposited downwind of the AOSR. Further work is required to ascertain whether the NH₃ disequilibrium is the result of a chemical phenomenon (e.g. hydrophobic organic coatings), physical phenomenon (e.g. insufficient mixing time) or simply a methodological artefact (e.g. exclusion of mineral cations from the ion balance). If the inorganic gas-particle system is not close to equilibrium in the AOSR, then there are significant implications for regional air quality models used to study the region since these models assume thermodynamic equilibrium when calculating partitioning of semi-volatile species.
5.5 Conclusions

Simultaneous measurements of water-soluble gases (NH$_3$, SO$_2$, HNO$_3$) and the corresponding constituents in PM$_{2.5}$ (NH$_4^+$, SO$_4^{2-}$, NO$_3^-$) were made over a four week period as part of an intensive air quality study in the AOSR. Campaign averages of NH$_3$ (0.61 ppbv), SO$_2$ (1.20 ppbv), HNO$_3$ (0.05 ppbv), NH$_4^+$ (0.19 µg m$^{-3}$), SO$_4^{2-}$ (0.48 µg m$^{-3}$), and NO$_3^-$ (0.04 µg m$^{-3}$) were in good agreement with regional summertime averages reported by Hsu and Clair (2015). All species were elevated during plume-influenced periods (defined as >0.5 ppbv SO$_2$), especially SO$_2$ and SO$_4^{2-}$. A significant background NH$_3$ mixing ratio was observed (~1 ppbv at midday) and is inconsistent with previous GEM-MACH output predicting a regional background of <0.05 ppbv (Shephard et al., 2015).

During these plume-influenced periods, particles were acidic despite the presence of free gas-phase NH$_3$ in excess of the calculated equilibrium NH$_3$ partial pressure above these particles. Both AIM-IC and AMS measurements were input into E-AIM to calculate particle pH both with ($1.56 < $pH$ < 3.62$) and without ($-0.16 < $pH$ < 2.07$) gas-particle partitioning allowed. Predicted NH$_3$ mixing ratios above the particles (without partitioning) were several orders of magnitude lower than AIM-IC observations, suggesting the aerosol system was far from thermodynamic equilibrium. One possible explanation is the presence of a viscous hydrophobic organic coating on particles that slow equilibration. It is also possible that the exclusion of basic cations (e.g. Ca$^{2+}$ and Mg$^{2+}$) are responsible for an artificially large estimate of H$^+$ mole loading. Instrument bias (e.g. persistent underestimation of neutralization) cannot be conclusively ruled out, but is unlikely since two independent particle data sets (AIM-IC and AMS) generated similar results.

The plume-influenced period on 26 August had a high SO$_4^{2-}$:SO$_2$ ratio, indicating it had likely undergone significant aging. This event contained particles that were highly acidic ($pH$ $\approx$ 1.04 to 1.68 when gas-particle partitioning was turned off). If aerosol in plume-influenced air masses remain highly acidic, then acid-sensitive soils downwind of the AOSR could be at risk. Furthermore, current air quality models assume that inorganic aerosol achieves equilibrium within one model time-step. It is imperative to determine why plume-influenced episodes appear to be in disequilibrium and whether or not this observation is real or simply an artefact of an incomplete ion balance or instrumental bias. Lastly, more research is needed to better constrain
both anthropogenic and natural sources of NH$_3$ throughout the AOSR because this has a direct influence on particle neutralization and N-deposition.

5.6 Contributions

Gregory Wentworth operated the AIM-IC and performed all related data analysis, in addition to the E-AIM calculations. Megan Willis, Alex Lee, and Jonathan Abbatt operated the AMS and provided the AMS data set for input into E-AIM. Shao-Meng Li and Jeff Brook oversaw the FOSSILS campaign and provided the AMS for the field study. This chapter was written by Gregory Wentworth with significant input from Jennifer Murphy.

5.7 References


Martin, S. T., Hung, H.-M., Park, R. J., Jacob, D. J., Spurr, R. J. D., Chance, K. V. and Chin, M.:


Chapter 6
Summary, conclusions and future research

6    Chapter 6

6.1    Summary and conclusions

Over the last three decades our understanding of surface-atmosphere NH$_3$ exchange has greatly improved (Farquhar et al., 1980; Flechard et al., 2013; Sutton et al., 2007). Mechanistic, field-scale models (e.g. Burkhardt et al., 2009; Nemitz et al., 2001) have been developed to describe bi-directional NH$_3$ exchange over a wide variety of land surfaces, although the majority of studies have been in or near agricultural areas (see reviews by Massad et al., 2010; Zhang et al., 2010). Research has focused on agricultural regions for two main reasons: 1) they are the largest global source of atmospheric NH$_3$ (Bouwman et al., 1997; Paulot et al., 2014), and 2) flux measurements used to derive and evaluate field-scale NH$_3$ exchange models are easier when the magnitude of fluxes are large. Bi-directional exchange has begun to be incorporated in larger-scale (regional and global) chemical transport models (CTMs) (Bash et al., 2013; Wen et al., 2014; Wichink Kruit et al., 2012; Zhu et al., 2015). These models generally provide better model-measurement agreement for a variety of NH$_3$-related metrics. For instance, reduced model biases for NH$_x$ deposition and PM$_{2.5}$ concentrations across the United States (Bash et al., 2013), and improvements in modelled NH$_3$ mixing ratios throughout Europe (Wichink Kruit et al., 2012). Although these updated CTMs are significant steps forward, large model biases and uncertainties still remain, especially with regards to spatial/temporal patterns of NH$_3$ bi-directional exchange.

The specific research questions for this thesis were outlined at the end of Section 1.5. The primary goals were to: 1) improve our understanding of NH$_3$ sources and sinks in rural and remote environments (non-fertilized soil in Chapter 2; dew in Chapter 3; seabird guano, Arctic ocean, and melt ponds in Chapter 4; the AOSR in Chapter 5), and 2) provide data sets that can be used to evaluate and improve field-scale models and CTMs. Ultimately, improvements to CTMs, such as including a seabird guano NH$_3$ source or identifying missing NH$_3$ sources in the AOSR, will enhance the predictive power of these models. In turn, this could help inform effective...
policy decisions aimed at alleviating negative effects of NH$_3$ such as increased PM$_{2.5}$ loading (Seinfeld and Pandis, 2006) or deposition to sensitive ecosystems, which can result in soil acidification and/or eutrophication (Bobbink et al., 2010; Krupa, 2003).

In Chapter 2, simultaneous measurements of water-soluble gases, PM$_{2.5}$ composition, and soil parameters (NH$_4^+$, pH and temperature) at a rural field site were presented. Observations were used to provide the first direct measurements of $\Gamma_{\text{soil}}$ in a non-fertilized grassland. The $\Gamma_{\text{soil}}$ ranged from 35 to 1850 (average = 290) and was significantly below the range of 2,000 to 200,000 suggested by Zhang et al. (2010) for this land type. Wen et al. (2014) used the Zhang et al. (2010) range for $\Gamma_g$ in an updated version of STILT-Chem and found persistent model overestimations of NH$_3$ in grassland and forest sites. The authors attributed this overestimation to uncertainties in $\Gamma_g$. Our $\Gamma_{\text{soil}}$ observations were consistent with the overestimation of $\Gamma_g$ in non-fertilized fields implied by their study. Our results were in better agreement with a $\Gamma_g = 500$ recommended by Massad et al. (2010) for non-fertilized areas. The measured $\Gamma_{\text{soil}}$ from our study were used to calculate $\chi_{\text{soil}}$ and infer soil-atmosphere NH$_3$ fluxes. An average net emission of 2.6 $\pm$ 4.5 ng m$^{-2}$ s$^{-1}$ and average net deposition of 5.8 $\pm$ 3.0 ng m$^{-2}$ s$^{-1}$ were computed for August and September, respectively. Air mass back-trajectories revealed that NH$_3$ was the only atmospheric pollutant that did not exhibit a directional bias, whereas other species (NH$_4^+$, SO$_4^{2-}$, NO$_3^-$, SO$_2$, and HNO$_3$) had enhanced concentrations in air originating from the south. This lack of directional bias for NH$_3$ was surprising given the abundance of agricultural activity south of the site. This implied soil-atmosphere NH$_3$ exchange happens sufficiently fast to modulate near-surface mixing ratios of NH$_3$. Back-of-the-envelope calculations showed that 1) the soil NH$_4^+$ pool is large enough to sustain soil-to-air fluxes, and 2) fluxes are sufficiently large enough to influence near-surface (<10 m) NH$_3$ mixing ratios on relevant timescales.

Evidence presented in Chapter 2 suggested that the morning spike of NH$_3$ is related to dew and/or fog evaporation. This hypothesis was quantitatively explored in Chapter 3. Laboratory studies on synthetic dew revealed that the fraction of NH$_3$ released from drying dew (Frac(NH$_3$)) could be predicted by dew ion balance and pH. Measurements of dew composition at a high altitude remote site in Rocky Mountain National Park (RMNP) had an average Frac(NH$_3$) of 0.94 (i.e. nearly all NH$_4^+$ in the dew is predicted to volatilize as NH$_3$). Dew mass and NH$_3$ mixing ratio were measured at RMNP and showed that dew evaporation and the NH$_3$ increase were coincident. In other words, NH$_3$ mixing ratio would increase as dew evaporated, and then
immediately plateau or decrease once dew had completely disappeared. The NH₃ morning spike was never observed on a morning without dew. Approximate mass balance closure was achieved between NH₃ lost in the nocturnal boundary layer overnight and NH₄⁺ gained in the dew. In addition, at the onset of dew evaporation there was, on average, 1.6 times as much NH₄⁺ in dew than NH₃ in the morning boundary layer. This study yielded several independent lines of evidence that the morning spike of NH₃ is a result of dew evaporation, at least at RMNP. If dew exerts a similar influence on NH₃ across a wide range of sites, then there are significant implications for regional N-deposition calculations, diurnal patterns of NH₃ and surface-atmosphere NH₃ exchange models. Currently, no CTMs include any dew-NH₃ interactions.

Chapter 4 presented results from a 5 week ship-based field study throughout the Canadian Arctic Archipelago and Baffin Bay. Concentrations of NH₃ ranged from 30 to 650 ng m⁻³ with the highest values in Lancaster Sound and Nares Strait. Measurements of [NH₄] in the ocean surface layer and sea ice melt ponds were used to compute median χ values of 0.8 ng m⁻³ and 2 ng m⁻³, respectively. The χ values were several orders of magnitude lower than ambient NH₃ indicating the open ocean and melt ponds are net sinks of NH₃. To our knowledge, this was the first study to report NH₃ concentrations in the Canadian Arctic as well as the first that explored melt pond-air exchange of NH₃. Levels of NH₃ were sufficient to neutralize nss-SO₄²⁻ produced from DMS oxidation, in contrast to previous GEOS-Chem simulations (Breider et al., 2014). This model-measurement disparity implied a missing source(s) of NH₃ in the emission inventories included in a widely used CTM. GEOS-Chem simulations and FLEXPART-WRF retroplumes were used to identify decomposing seabird guano as the primary contributor of NH₃ to the summertime Arctic boundary layer. Wildfires in the Northwest Territories were also a source of NH₃ to the central Canadian Arctic. GEOS-Chem simulations were performed both with and without seabird NH₃ emissions to interrogate the effects of seabirds on atmospheric chemistry and climate forcing. Without guano emissions, GEOS-Chem underpredicted NH₃ mixing ratios and extent of nss-SO₄²⁻ neutralization throughout the study region. Seabird NH₃ emissions are responsible for nitrogen deposition on the order of ~2-10 mg N m⁻² in areas up to several hundred kilometers away from large colonies.

This work laid the foundation for a manuscript investigating the impacts of seabird NH₃ on the cloud-albedo effect (Croft et al., 2016). GEOS-Chem-TOMAS was used to simulate the influence of seabird NH₃ on new particle formation (NPF). A simulation without seabird NH₃
was unable to reproduce N10 particle (particles >10 nm in diameter) bursts observed at Alert, Nunavut during the summer of 2011. Including seabird NH₃ reduced the mean fractional model-measurements bias of N10 at Alert from -0.86 to -0.47. Adding seabird NH₃ emissions also increased cloud droplet number concentration (CDNC) by >10% in most (64%) of the Arctic relative to the simulation without seabird NH₃. The RRTMG model calculated a mean aerosol indirect effect of -0.5 W m⁻² over the summertime Arctic Ocean due to seabird NH₃, while regions near the largest colonies exceeded a cooling of 1 W m⁻². This study identified a novel contribution of seabird NH₃ to NPF and CDNC in the pristine summertime Arctic boundary layer which results in a substantial regional cooling effect in an area extremely sensitive to climate change.

Chapter 5 presented AIM-IC observations from a six-week intensive study in the Athabasca Oil Sands Region (AOSR). Measurements from the primary ground site were divided into two regimes: plume influenced and non-plume influenced (background) periods. Concentrations of SO₂ and SO₄²⁻ were substantially elevated during plume influenced periods, along with comparably modest increases in NH₃, NH₄⁺, HNO₃ and NO₃⁻. NH₃ during background periods exhibited a unimodal diurnal trend reaching a maximum of ~1 ppbv around midday. Shephard et al. (2015) reported a maximum background NH₃ mixing ratio of 0.2 ppbv (average <0.05 ppbv) throughout the AOSR in GEM-MACH simulations. This discrepancy is likely related to lack of bi-directional exchange in GEM-MACH and/or an underestimation of natural NH₃ sources. Aerosol during plume times were acidic (1.56 < pH < 2.81 when gas-particle partitioning was allowed) and appeared to be in disequilibrium as inferred by a discrepancy in predicted versus measured NH₃ mixing ratios. Possible explanations for the apparent disequilibrium in the NH₃-
NH₄⁺-HNO₃-NO₃⁻-SO₄²⁻-H₂O system include: i) thick hydrophobic organic coatings, ii) insufficient NH₃/PM₂.₅ mixing time, and/or iii) exclusion of base cations from the ion balance.

The work in this thesis has improved our understanding of unrecognized or underrepresented sources (seabird guano, dew evaporation, non-fertilized soil) and sinks (dew accumulation, Arctic ocean, melt ponds, non-fertilized soil) of NH₃ in a variety of rural (southwestern Ontario, AOSR) and remote (RMNP, Arctic Ocean) environments. This thesis has provided an important improvement to CTMs by updating the NH₃ emissions inventory in GEOS-Chem to yield much better model-measurement agreement for summertime Arctic NH₃. It has also laid the
groundwork for further model development (e.g. better representation of $\Gamma_{\text{soil}}$, incorporation of dew-NH$_3$ interactions, missing NH$_3$ source(s) in the AOSR).

6.2 Future Work

6.2.1 Modifying the AIM-IC for Relaxed Eddy Accumulation

One of the biggest advantages of the AIM-IC is its ability to simultaneously measure both gases and PM$_{2.5}$. With significant modifications the AIM-IC could be adapted to simultaneously measure fluxes of gases and PM$_{2.5}$ using the relaxed eddy accumulation (REA) technique. The optimized set-up would use a 3-D sonic anemometer to control a three-way solenoid valve to conditionally sample updrafts and downdrafts into two separate streams. An additional PM$_{2.5}$ impactor, parallel plate wet denuder and particle supersaturation chamber would have to be installed in the sampling inlet box to collect the additional stream. Hardware changes (e.g. another sample syringe assembly, deionized water syringe assembly) in addition to substantial software changes would be required for the AIM 9000D. The latter would necessitate collaboration with URG Corp. since the software and device drivers that control the AIM 9000D are proprietary and cannot be accessed or altered by the user. One alternative would be to construct an analogous instrument from scratch to separate and collect gases/PM$_{2.5}$. Another alternative is to collect and analyze only one AIM channel (i.e. gas or particle), which would alleviate the need for extensive software modifications.

A validation study would be necessary for a custom-built (or modified) REA system. An alternative method of flux measurement (e.g. eddy covariance using the QC-TILDAS) will be required to evaluate the REA system for NH$_3$ and other gases of interest. For instance, Hensen et al. (2009) performed an inter-comparison of four custom-built REA systems to measure NH$_3$ fluxes. The authors compared fluxes from each system to fluxes estimated by the aerodynamic gradient method (AGM) and found the REA systems had a persistent underestimation (ranging from 48-71%) and a flux offset of 10s to 100s of ng m$^{-2}$ s$^{-1}$ relative to the AGM results. Two of these systems have subsequently been used to measure ambient NH$_3$ fluxes (Hansen et al., 2013, 2015; Sutton et al., 2009).

Additional studies would be required to evaluate the REA system for other species. Nemitz et al. (2004) performed a study to compare fluxes of NH$_3$, HCl, SO$_2$, HNO$_3$ and HONO from several
different on-line instruments using AGM. One of these multi-analyte instruments could be co-located with the proposed REA system for evaluation of its ability to measure gas fluxes. It would be much more challenging to validate the system for PM$_{2.5}$ fluxes, especially for speciation as opposed to total PM$_{2.5}$ mass. There have been several studies to use wet-chemical techniques (ion chromatography and/or flow injection analysis) to measure simultaneous fluxes of water-soluble gases and aerosols using AGM (Rumsey and Walker, 2016; Thomas et al., 2009; Wolff et al., 2010). All three studies highlight the importance of instrument precision for measuring fluxes with AGM. Even higher precision is required for REA due to the small concentration differences in updraft and downdraft channels. Before attempting to construct an AIM-IC REA system, calculations should be performed to verify that the AIM-IC has the precision necessary for REA measurements.

As the 3-way solenoid valve rapidly switches, the flow rate in a given REA channel will transition between 3.0 L min$^{-1}$ and 0 L min$^{-1}$. This transition must happen instantaneously since a transient flow rate will compromise measurement reliability. For instance, the PM$_{2.5}$ impactor must have flow between 2.8 to 3.2 L min$^{-1}$ to work properly (URG Corp., 2014). Outside this flow range the 2.5 µm size cut is no longer valid and the impactor will either remove an unpredictable fraction of particles smaller than 2.5 µm or fail to remove an unpredictable fraction of coarse particles. In principle, the upstream and downstream channel could share an impactor such that the flow through the impactor is continuously ~3 L min$^{-1}$. However, this could introduce sample carryover if NH$_3$ sorbs/desorbs from the impactor walls on timescales longer than the transition between updrafts/downdrafts. This is not an issue with the AIM-IC under normal operating conditions because there is only one sample collection channel. Furthermore, the collection efficiency of the parallel plate wet denuder has only been evaluated at 3.0 L min$^{-1}$ (Hsu and Clair, 2015; Markovic et al., 2012). If the AIM-IC operates at a significantly higher flow then the denuder will have a lower collection efficiency for gases. At lower flows it may collect an unpredictable fraction of particles. Knowledge of the precise flow rate is important since it is used to calculate mixing ratios and mass loadings. If the transition between 0 and 3 L min$^{-1}$ in each REA channel is not instantaneous then the total volume of air sampled will be uncertain and dependent on the rate at which the REA system switches between updrafts and downdrafts.
One last inherent issue with optimizing the AIM-IC for REA is the large inlet box (~20 x 40 x 76 cm). Large sampling inlets distort flow and compromise flux measurements. The size of the inlet box cannot be significantly reduced since it would have to house two denuders, two particle collection chambers, and two impactors. For comparison, the four REA systems reported by Hensen et al. (2009) only required denuders and had inlets in close proximity to the sonic anemometer with the denuders ranging in length from 12.5 to 30 cm and width of ~3 cm. One of these systems had a short piece of tubing (3.2 cm in length, 0.32 cm in diameter) close to the sonic anemometer to minimize flow distortion. An inlet box for the modified AIM-IC would need to be reduced in size or placed sufficiently far away from the sonic anemometer to allow for proper REA measurements.

Although modifying the AIM-IC to measure REA fluxes is ambitious and has significant technical challenges, it could provide extremely unique and valuable data sets once it is properly validated. Simultaneous flux measurements of gases and PM$_{2.5}$ would yield a more complete picture of pollutant deposition to ecosystems, particularly for inorganic nitrogen. Furthermore, it could be used to assess NH$_3$ flux divergence caused by gas-particle partitioning which has proved to be an elusive issue for the NH$_3$ flux community.

6.2.2 Dew-Air exchange studies

Chapter 3 detailed one of the first attempts to quantify the influence of dew on NH$_3$ mixing ratios. Unlike previous efforts that only estimated dew amount (Bash et al., 2010; Burkhardt et al., 2009), our study continuously monitored dew accumulation/evaporation with a custom-built dewmeter (Price and Clark, 2014). Future studies examining surface-air NH$_3$ exchange should use similar methodology (i.e. dewmeter and dew collector) to quantify dew-air NH$_3$ exchange. The dewmeter and dew collector are inexpensive and simple to operate so little time and effort would be required to incorporate them in upcoming field studies.

Although dew at Rocky Mountain National Park (RMNP) had a high fraction of NH$_3$ released during evaporation (average Frac(NH$_3$) = 0.94), this may not be the case in all environments. For instance, urban environments with significant HNO$_3$ and SO$_2$ could yield dew with a greater abundance of NO$_3^-$ and SO$_4^{2-}$ relative to NH$_4^+$ plus other cations resulting in a low or zero Frac(NH$_3$). A first step could be to perform a literature review of dew composition studies (e.g. Lekouch et al., 2010; Polkowska et al., 2008; Wagner et al., 1992; Yadav and Kumar, 2014) and
calculate the average Frac(NH$_3$) for each study to examine if there is a dependence of Frac(NH$_3$) on land type. One might be able to ascertain a spatial dependency (i.e. low values in urban areas and high values in agricultural regions). It is important to note that most dew composition studies typically report only major inorganic anions (SO$_4^{2-}$, NO$_3^-$, Cl$^-$) and cations (NH$_4^+$, Mg$^{2+}$, Ca$^{2+}$, Na$^+$, K$^+$) and exclude organic acids and carbonate/bicarbonate. This could result in an overestimation of Frac(NH$_3$) calculated from literature values and would have to be taken into consideration.

Work should be done to optimize the dewmeter for different canopies. Price and Clark (2014) developed the dewmeter to represent short grass/turf. The field site at RMNP consists primarily of grass and short vegetation, but other sites, such as cropland and forests, are unlikely to be sufficiently represented by artificial turf on the dewmeter to allow for quantification of ambient dew. One potential solution is to use leaf area index (LAI) to relate dewmeter results to the actual canopy. In other words, the measured mass of dew could be multiplied by the ratio of the canopy LAI to the dewmeter (artificial turf) LAI. However, it would need to be verified that: 1) dew accumulates/evaporates uniformly from the ground to top of the canopy, and 2) the emissivity of the turf sufficiently mimics the emissivity of the canopy. Another solution would be to replace the artificial turf on the dew meter with material representative of the canopy. For instance, in a pine forest the tray could be covered with small branches of pine needles. The results would still have to be normalized to LAI, and it would be difficult to secure the “miniature canopy” on top of the tray to prevent pieces of it from blowing away.

Consideration must also be given to how sensitive dew composition is to existing salts or sorbed species on vegetative surfaces. Studies have shown that deliquesced particles are persistent on leaf surfaces although the accumulation and composition of these salts are difficult to quantify (Burkhardt and Hunsche, 2013; Burkhardt, 2010). These deliquesced particles have the ability to be taken up by both the stomata and cuticle (Burkhardt, 2010). The fate of particles on leaf surfaces during dew formation and evaporation are unknown, but presumably they are dissolved into dew. Since the dew collector is rinsed with deionized prior to deployment, it will not measure the contribution of existing surface species to dew composition. Furthermore, the dew collector will not account for changes in dew composition due to uptake or release of species through stomata. The phyllosphere (habitats on above ground portions of plants) could also contain microbes that cycle nitrogen and act as either a source or sink of NH$_4^+$. The phyllosphere
supports diverse microbial communities consisting primarily of bacteria, with culturable bacteria counts ranging from $10^2$ to $10^{12}$ cells per gram of leaf (Inacio et al., 2002; Whipps et al., 2008). Although the phyllosphere has been the focus of numerous microbiology studies (e.g. see reviews by Heaton and Jones, 2008; Muller and Ruppel, 2014), its influence on dew composition and dew-atmosphere interactions remains unexplored.

Chapter 3 also highlighted several species (acetic acid, formic acid, HONO, HNO$_3$) with large effective Henry’s law constants ($K_{H^{\text{eff}}} > 10^5 \text{ M atm}^{-1}$) that could have dew act as a large nighttime sink and morning source. Subsequent studies should quantitatively examine these species in both the dew-phase and gas-phase. Additional laboratory studies would be needed to verify that the ion balance method for calculating Frac(X) (where X is the analyte) can be used for each analyte.

Ultimately dew should be included in field-scale models of NH$_3$ bi-directional exchange. Sufficient field measurements of dew composition and accumulation will likely be required to accurately parameterize dew as its own surface pool with an associated Γ and resistance(s). Incorporation of dew into a resistance model (e.g. Fig 1.2) should be relatively straightforward although its optimization and validation would likely be more challenging. If the observations from RMNP are representative of the importance of dew across many environments, then the inclusion of dew in models will greatly improve their ability to represent the frequently observed morning spike of NH$_3$.

Perhaps the most significant implication of dew is its ability to act as a temporary NH$_3$ reservoir. Currently, N-deposition estimates assume all deposited NH$_3$ remains at or below the surface and is counted towards total N input to the ecosystem. The results presented in Chapter 3 challenge that assumption. N-deposition estimates are critical since they inform scientists and policymakers on whether the critical N load has been exceeded for a given ecosystem (e.g. Fisher et al., 2007; Matejko et al., 2009). Furthermore, current chemical transport models (CTMs) and earth system models (ESMs) do not allow for emission of NH$_3$ from evaporating dew (Zaehle et al., 2014; Zhao et al., 2015). This could have implications for air quality, N deposition and biogeochemical cycles in these models. For instance, Zaehle et al. (2014) found a strong connection between nitrogen availability and terrestrial carbon uptake in nine different coupled carbon cycle-climate models. Further work is needed to ascertain to what extent NH$_3$ release from dew affects total N-
deposition. An important aspect that must also be considered is whether NH₃ deposited prior to dew formation is incorporated into dew. In other words, dew could also be important for volatilizing what was deposited the previous day. Since N-deposition is typically small at night, the volatilization of NH₃ from existing surface NH₃ could be more significant than release of NH₃ incorporated into dew overnight via dissolution.

On the other hand, if the effect of NH₃ release from dew on total N-deposition is small (i.e. <5%), then the impacts of excluding of dew-NH₃ interactions from CTMs and ESMs is likely negligible for assessing N-deposition. Addressing these issues would require extensive field measurements of a wide range of N-compounds and dew across many different ecosystems.

6.2.3 Arctic NH₃ Measurements

To our knowledge, published measurements of surface-layer NH₃ in the High Arctic are limited to Chapter 4 (published as Wentworth et al., 2016) and two previous studies (Giamarelou et al., 2016; Johnson et al., 2008). Johnson et al. (2008) made ship-based NH₃ measurements and observed concentrations between 25-275 ng m⁻³ at latitudes up to 81.5º N in the North Sea. This range is consistent with Giamarelou et al. (2016) who reported the long-term (since 1989) average of NH₃ at Ny-Ålesund, Svalbard is 200 ng m⁻³. Chapter 4 also shows similar NH₃ concentrations throughout the Canadian Arctic Archipelago and provides several lines of evidence that seabird colonies are the major source of summertime Arctic NH₃. Emissions from these colonies have large uncertainties and have not been optimized for Arctic seabird species (Riddick et al., 2012).

Since NH₃ from these colonies likely has significant implications for climate (via aerosol indirect effect from increased new particle formation and cloud droplet number concentrations) and N-deposition it is imperative to better understand the spatial and temporal trends of NH₃ throughout the summertime Arctic. Several long-term monitoring sites are present throughout the Arctic (e.g. Alert, Nunavut; Barrow, Alaska; Station Nord, Greenland; Eureka, Nunavut) that are already measuring atmospheric constituents such as greenhouse gases and PM₂.₅ composition. A simple denuder/filter pack system could be added to each site to provide daily or weekly measurements of NH₃, SO₂, HNO₃ and PM₂.₅ composition. The denuder/filter pack systems are easy to operate (Koutrakis et al., 1988) and commercially available (e.g. URG 3000C, URG Corp.). Benedict et al. (2013) reported detection limits of 130 ng m⁻³ for NH₃, 91 ng m⁻³ for SO₂,
and 11 ng m\(^{-3}\) for HNO\(_3\) when the denuder/filter pack system was operated for 24 hours at sites throughout Colorado. Therefore a sampling period of 1 week would likely be necessary to ensure all Arctic-based samples would be above detection limit for NH\(_3\).

To achieve a larger spatial extent of measurements, a passive NH\(_3\) monitoring network could be established throughout the Canadian Arctic, similar to the Ammonia Monitoring Network (AMoN) in the United States (NADP, 2014). Passive NH\(_3\) samplers could be deployed from April to October to capture the full breeding season of Arctic seabird species. Two dozen sites could be set up within several kilometers of existing communities and the deployment/collection of passive samplers could be done by locals after some training. Results from both the intensive and passive monitoring sites would help evaluate and improve the ability of CTMs to model NH\(_3\), and likely allow for better constraints on the magnitude of seabird NH\(_3\) emissions throughout the Arctic. It would also provide more insight on the spatial patterns of N-deposition across the Arctic. Annual trends in NH\(_3\) could be linked to annual seabird population estimates, which would improve our understanding on how industrialization and climate change may affect Arctic seabird NH\(_3\) emissions in the near future.

6.2.4 Improvements to bi-directional NH\(_3\) exchange in CTMs

Significant work has gone into representing NH\(_3\) bi-directional exchange in regional (Bash et al., 2013; Wichink Kruit et al., 2012) and global (Zhu et al., 2015) CTMs. Parameterizations necessary for updating these CTMs were developed using data from numerous field-scale studies aimed at understanding the fundamental processes of surface-atmosphere exchange (Massad et al., 2010; Zhang et al., 2010). These field studies are typically done in areas of high N-input with large NH\(_3\) fluxes (i.e. agricultural areas), therefore measurements of \(\Gamma\) in rural and remote environments are underrepresented and have larger uncertainties. More field measurements of \(\Gamma\) and NH\(_3\) are needed in these locations, particularly over the open ocean. Paulot et al. (2015) provided the most rigorous estimate for global oceanic NH\(_3\) emissions to date (~2.5 Tg N yr\(^{-1}\)) and found their estimate to be lower than previously reported estimates (7-23 Tg N yr\(^{-1}\)), highlighting the large uncertainty for this significant global source and the need for additional sea-air NH\(_3\) flux studies.

Results presented in Chapter 5 highlighted the underestimation of background NH\(_3\) mixing ratios by GEM-MACH throughout the AOSR. GEM-MACH should be updated to include bi-
directional NH$_3$ exchange and re-evaluated with NH$_3$ measurements (Shephard et al., 2015). Model-measurement comparison should also be performed during plume-influenced periods to assess model performance for NH$_3$, NH$_4^+$, SO$_2$, SO$_4^{2-}$, HNO$_3$ and NO$_3^-$. The incorporation of dew into CTMs might help improve the representation of diurnal patterns of surface-layer NH$_3$ and yield better model-measurement agreement for NH$_3$ mixing ratios. Observations shown in Chapter 3 suggested that the deposition of NH$_3$ during the night is limited by high aerodynamic and quasi-laminar resistances (i.e. the presence of dew does not enhance NH$_3$ deposition). If this result is consistent across land types, then incorporating the release of NH$_3$ from dew in CTMs could be relatively straightforward. NH$_3$ deposited while dew is present could be tracked and then this amount could be released over a ~2 hour period after sunrise. This approach would not require any substantial changes to the deposition scheme, although determining an appropriate metric to trigger dew formation in the CTMs could be challenging.

6.3 Final thoughts

My work has yielded valuable data sets that have provided significant insight into processes governing NH$_3$ mixing ratios in rural and remote environments. Since NH$_3$ measurements in these regions are rare, they are prone to large uncertainties with respect to NH$_3$ mixing ratios in regional and global CTMs. We have determined that in rural southwestern Ontario, bi-directional NH$_3$ exchange in a non-fertilized field is sufficient to prevent any directional dependence in NH$_3$ mixing ratios that would be expected at a site that lies on a sharp spatial gradient in NH$_3$ emissions. Measurements at a remote mountain site in Colorado revealed that an often observed morning spike of NH$_3$ is likely from dew evaporation. This underappreciated nighttime reservoir and morning source of NH$_3$ is not currently in CTMs despite its potential to influence diurnal NH$_3$ patterns.

We also presented strong evidence that decomposing seabird guano is a significant source of NH$_3$ throughout the summertime Arctic. This source was previously missing from a common NH$_3$ emissions inventory used in CTMs (Bouwman et al., 1997). GEOS-Chem simulations with and without seabird emissions showed there is a large impact on atmospheric composition, N-deposition and climate forcing. Lastly, measurements in the Athabasca Oil Sands Region suggested both anthropogenic and natural sources of NH$_3$, the latter of which is severely underestimated by GEM-MACH, a regional CTM.
My thesis has helped to improve our understanding of the sources, sinks and impacts of NH$_3$ in rural and remote environments. This work has improved NH$_3$ emission inventories for the Arctic and lays the foundation for subsequent studies to explore new avenues of surface-atmosphere exchange research (i.e. dew-air studies). Despite these advancements, significant research efforts are still needed to improve model-measurement agreement for NH$_3$ mixing ratios and N-deposition, as well as our overall mechanistic understanding of NH$_3$ bi-directional exchange.

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