ATMOSPHERIC CHEMISTRY OF TRACE NITROGENOUS BASES AND ACIDS:
ALKYL AMINES IN THE GAS AND PARTICULATE PHASES AND NITROUS ACID INTERACTIONS WITH THE GROUND SURFACE

by

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Atmospheric chemistry of trace acids and bases: Alkyl amines in the gas and particulate phases and nitrous acid interactions with the ground surface

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ABSTRACT

Accurate measurements of the trace nitrogenous atmospheric species amines (NR₃) and nitrous acid (HONO) are essential to understanding their chemistry and potential influence on new particle formation and oxidation capacity in the atmospheric boundary-layer, respectively.

Ambient Ion Monitor – Ion Chromatography (AIM-IC) methods developed in this work have provided quantitative online observations of atmospheric amines in the gaseous and condensed phases with detection limits of pptv and ng m⁻³ at hourly time resolution. Size-resolved particle observations demonstrated maximum amine mass loadings in 320 – 560 nm particles, and an increase in importance relative to ammonium for the smallest particles measured (56 – 180 nm). In particular, the size-resolved samples analysed in this work indicate that bulk aerosol measurements may not be appropriate for modelling the atmospheric processes that govern the incorporation of amines and ammonia into atmospheric particles.

Measurements of HONO made during the two intensive field campaigns (NACHTT, CalNex) and a lab study provided a new perspective on the interactions of this trace compound with ground surfaces. Integrated atmospheric column measurements of HONO and NO₂ during NACHTT provided clear evidence that the ground surface dominates HONO production and loss at night. Simultaneous measurements of the gas and particle phases made by the AIM-IC system during CalNex demonstrated the potential for reactive uptake of HONO on mineral dust/soil as a nocturnal sink. Similarly, the potential for nitrite salts to react with strong acids, displacing HONO during the day was suggested by this dataset. Lab study results showed that HONO is taken up irreversibly on carbonate salts and real soil extracts. Relative humidity-dependent reactive uptake coefficients were derived. Subsequent release of HONO by displacement reactions with HNO₃ and HCl was also confirmed. Together, these field and lab studies have
produced a new picture of HONO surface interactions by providing i) a more explicit description of a nocturnal sink of HONO that could act as a surface reservoir and ii) a new mechanism for daytime HONO formation that does not require NO₂.
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PREFACE

This thesis is comprised of a series of manuscripts that have been published or are in preparation for submission to be published in peer-reviewed scientific journals. Consequently, repetition of introductory and experimental details was inevitable. All manuscripts were written by Trevor C. VandenBoer with editorial/critical comments provided by J. G. Murphy. The specific contributions of co-authors are detailed below.

CHAPTER ONE – Introduction to chemistry of alkyl amines and nitrous acid in the troposphere: Importance of amines in new particle formation and the role of the ground surface as a sink and source of nitrous acid

Contributions - T. C. VandenBoer prepared and wrote the contents of this chapter. J. G. Murphy provided editorial comments.

CHAPTER TWO - Ion chromatographic separation and quantitation of alkyl methylamines and ethylamines in atmospheric gas and particulate matter using preconcentration and suppressed conductivity detection

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Author List - T. C. VandenBoer, M. Z. Markovic, A. Petroff, M. F. Czar, N. Borduas and J. G. Murphy

Contributions - T. C. VandenBoer and M. Z. Markovic developed the ion chromatographic methods, and collected AIM-IC samples. T. C. VandenBoer collected the MOUDI sample and A. Petroff performed sample analysis and data work up for this sample. M. F. Czar and T. C. VandenBoer developed the framework for the chemically-relevant curve fitting function of partially dissociated bases. N. Borduas developed the method and calibration data for monoethanolamine. T. C. VandenBoer prepared the manuscript under the guidance of J. G. Murphy.

CHAPTER THREE - Size distribution of alkyl amines in continental particulate matter and their online detection in the gas and particle phase

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Author List - T. C. VandenBoer, A. Petroff, M. Z. Markovic, and J. G. Murphy

Contributions - T. C. VandenBoer and A. Petroff collected and analyzed MOUDI samples. A. Petroff designed the MOUDI methodology and data analysis of collected samples. M. Z. Markovic developed ion chromatography methods and collected data by AIM-IC during the online observation period. T. C. VandenBoer performed data analysis for all samples and prepared this manuscript under the guidance of J. G. Murphy.

CHAPTER FOUR - High resolution vertical profiles of trace atmospheric acids from a 300 m tower during Nitrogen, Aerosol Composition and Halogens on a Tall Tower (NACHTT) in Erie, CO: Understanding the ground surface role in nitrous acid (HONO) vertical structure


Contributions - T. C. VandenBoer designed, constructed and conducted inlet experiments, collected and quality controlled data on all trace acids using the NI-PT-CIMS from the BAO tower during the NACHTT campaign, operated the PISA overnight on several nights, and conducted all data analysis discussed below.

J. M. Roberts aided in the design and construction of the inlet and subsequent validation experiments, collected data on all trace acids using the NI-PT-CIMS from the BAO tower during the NACHTT campaign, operated the PISA overnight on several nights, maintained and calibrated the NI-PT-CIMS and provided editorial comments on the chapter contents.

J. G. Murphy aided in the development of the simple box model, data analysis of integrated column HONO in the parameterization of ground surface processes in its production and loss and provided editorial comments on the chapter contents.
C. Warneke aided in the modifications, calibration and maintenance of the NI-PT-CIMS during NACHTT and modified the data analysis software for data reduction and quality control of the field data.

J. A. de Gouw provided critical analysis of data quality and resources for the operation of the NI-PT-CIMS.

N. L. Wagner, C. J. Young, W. P. Dube, J. A. Thornton, T. P. Riedel, A. M. Middlebrook, R. Bahreini, F. Ozturk, C. Brock, and S. S. Brown collected supporting data from the PISA used in the data analysis (NO, NO$_2$, aerosol surface area, aerosol composition) and operated the PISA overnight on remaining nights during NACHTT. In particular, W. P. Dube designed the PISA and maintained its operational capacity, N. L. Wagner provided all data synchronization, PISA meteorology data and PISA control software, and T. P. Riedel aided in the maintenance of the NI-PT-CIMS during the data collection period.

W. Keene, A. Pszenny, and J. Maben collected supporting data with the mist chamber–ion chromatography instrument for the measurement intercomparison of atmospheric acids and carried out ion chromatographic quantitation of acid calibration standards at the BAO tower.

S. Kim made OH measurements used in the box model and daytime HONO source analysis, B. Lerner provided photolysis frequency data, D. Wolfe and E. Williams coordinated site logistics and provided meteorological data for the site.

CHAPTER FIVE - Evidence for a potential nitrous acid (HONO) reservoir at the ground surface: Simultaneous observations of trace acids and PM$_{2.5}$ water-soluble ions in Bakersfield, CA during CalNex 2010

Author List - T. C. VandenBoer, M. Z. Markovic, J. E. Sanders, X. Ren, S. Pusede, E.

Contributions - T. C. VandenBoer collected AIM-IC data during CalNex 2010, performed quality control on AIM-IC HONO/HCl/NH$_3$ dataset, developed box model, performed intercomparison, undertook data analysis and prepared manuscript under the guidance of J. G. Murphy. M. Z. Markovic collected AIM-IC data, performed quality control on AIM-IC HNO$_3$/H$_2$SO$_4$/NH$_3$ dataset, and performed HONO breakthrough experiment under the guidance of J. G. Murphy. J. E. Sanders and X. Ren collected HONO REA data for HONO measurement intercomparison. S. Pusede, E. Browne, collected NO and NO$_2$ data under the guidance of R. C. Cohen for correction of AIM-IC dataset and input into simple HONO box model. R. J. Weber collected meteorological, relative humidity, temperature and photosynthetically active radiation data for use in data analysis and input to simple HONO box model. W. H. Brune collected OH data for input to simple HONO box model. D. A. Day, S. Liu, L. Ahlm, collected PM$_{2.5}$ samples for XRF analysis under the guidance of L. M. Russell.

CHAPTER SIX - A chemical mechanism for the relative humidity dependent reactive uptake and displacement of nitrous acid (HONO) on reactive carbonate and soil substrates: Flow tube experiments at atmospheric pressure


Contributions - T. C. VandenBoer designed and performed experiments with contributions from C. J. Young and R. Talukdar. T. VandenBoer prepared this manuscript under the guidance of J. M. Roberts, S. S. Brown and J. G. Murphy.
Other publications during PhD:


CHAPTER ONE
Introduction to chemistry of alkyl amines and nitrous acid in the troposphere: Importance of amines in new particle formation and the role of the ground surface as a sink and source of nitrous acid
Author Contributions:

T. C. VandenBoer prepared the contents of this chapter and J. G. Murphy provided editorial comments.
Alkyl amines and nitrous acid: Exotic members of the reactive nitrogen family

Atmospheric reactive nitrogen compounds are comprised of reduced (Figure 1-1) and oxidized (e.g. Figure 1-2) nitrogen species. Research on the atmospheric reduced nitrogen family has largely been focused on ammonia (NH₃) (Pinder and Adams, 2007), but the role of other reduced nitrogen compounds (e.g. amines (NR₃) and other N-containing organics) is poorly understood (Ge et al., 2011a; Miyazaki et al., 2010; Facchini et al., 2008). Primary emissions are fairly well constrained for NH₃, while budgets for amine emissions have been estimated based on a few studies (Schade and Crutzen, 1995; Traube et al., 2011), but are by no means well constrained. Ammonia has a long atmospheric lifetime against oxidation, resulting generally in mixing ratios of a few ppbv, up to tens of ppbv near sources. Ammonia is volatile, but also relatively water soluble and a base. As a consequence, ammonia can partition to or react with aqueous and/or acidic particles in the atmosphere (Finlayson-Pitts and Pitts, 2000; Seinfeld and Pandis, 2006).

Figure 1-1. Reactive reduced nitrogen chemistry of amines (NR₃) and ammonia (NH₃).

Amines can have many different functionalities (-R) that alter their properties, but those most abundant in the atmosphere have simple alkyl chains (e.g. methyl, ethyl) in these positions (Ge et al., 2011a). These amines are volatile, more basic than NH₃ (Mackay et al., 2004), and more easily oxidized (Atkinson et al., 1977a, b; Atkinson et al., 1997). Overall, this oxidative reactivity reduces the abundance of amines in the atmosphere, but much smaller amounts of amines may promote similar chemistry to NH₃. In particular, the potential for amines to form molecular
clusters with H$_2$SO$_4$ and, subsequently form new particles, has generated much interest in these compounds (Kirkby et al., 2011; Smith et al., 2010; Zhang et al., 2012). Formation rates, growth rates and chemistry of new particles in the atmosphere are important to understand because they can influence i) the formation of clouds, changing precipitation patterns or the heating and cooling of the atmosphere through interactions with radiation, ii) general visibility by scattering light (i.e. haze) and iii) human health since small particles can be easily respired and interact with tissues in the human body (Zhang et al., 2012; Forster et al., 2007).

In general, the oxidized families have undergone significant investigation for their impact on air quality (e.g. O$_3$ formation), nitrogen deposition (e.g. HNO$_3$) and nitrogen transport to remote locations (e.g. PAN). The fast chemical cycling between NO and NO$_2$ allow them to be grouped together into the NO$_x$ (= NO + NO$_2$) family, while inclusion of the remaining species in Figure 1-2 defines the NO$_y$ family (i.e. total gas phase reactive oxidized nitrogen). With declining NO$_x$ emissions from fossil fuel combustion sources due to emission reduction strategies, the potentially important roles of trace reactive nitrogen species, those present at parts per trillion by volume (pptv) up to a few parts per billion by volume (ppbv), are being realized.

![Diagram of Reactive Nitrogen Oxides](image)

**Figure 1-2.** Reactive nitrogen oxides commonly found in the troposphere. Links with atmospheric oxidants, photolysis, thermal decomposition and heterogeneous chemistry have been indicated.
These trace species include: i) nitrate radical (NO$_3$), which can form organic nitrates by oxidizing volatile organic compounds or organic aerosols at night (Brown et al., 2006; Brown et al., 2007), ii) dinitrogen pentoxide (N$_2$O$_5$), which can react with aerosols to produce particulate nitrate and nitric acid or, in the presence of particulate chloride and water, the photolabile nitryl chloride (ClNO$_2$) (Chang et al., 2011) and iii) nitrous acid (HONO) whose photolysis yields OH radical, the dominant atmospheric oxidant. In particular, HONO as a significant daytime OH radical source has only recently been realized (Young et al., 2012; Volkamer et al., 2010; Kleffmann et al., 2005). That this compound may significantly alter the oxidation capacity of the troposphere at a local or regional level indicates that understanding the chemistry governing the fate of HONO should be important to air quality control strategies (Elshorbany et al., 2012b; Czader et al., 2012).
1.1 Amines as atmospheric bases: Challenges in analytical detection of amines (NR$_3$) and their role in new particle formation

Numerous laboratory studies and theoretical chemical investigations (Kurten et al., 2008; Barsanti et al., 2009; Lloyd et al., 2009; Berndt et al., 2010; Bzdek et al., 2010; Loukonen et al., 2010) have raised questions concerning the role of alkyl amines (NR$_3$) in the formation and growth of new particles in the atmosphere. The formation of new particles has implications for climate change, through direct radiative forcing and the formation of clouds (Forster et al., 2007), and for human health (Burnett et al., 2000). Recent focus on the role of amines in particle formation has been motivated by field observations reporting ubiquitous detection of NR$_3$ in particles less than 100 nm in diameter in urban, rural and marine atmospheres (Facchini et al., 2008; Huang et al., 2009; Muller et al., 2009; Pratt et al., 2009; Smith et al., 2010; Smith et al., 2008; Sorooshian et al., 2008; Tan et al., 2002; Zhao et al., 2011). Current understanding, summarized in Figure 1-1, suggests that NR$_3$ and NH$_3$ enhance particle formation and growth through acid-base chemistry with sulfuric acid (Benson et al., 2011; Berndt et al., 2010; Bzdek et al., 2010; Bzdek et al., 2011; Erupe et al., 2010b; Qiu et al., 2011; Zhao et al., 2011) and potentially organic acids (Zhang et al., 2004; Barsanti et al., 2009). The resulting salts of these reactions are not volatile, causing them to condense on to pre-existing particles (growth) or forming new molecular clusters that can grow by condensation of other low volatility compounds. Alternatively, amines can also contribute to particle growth by reacting with particles consisting of low volatility acids (e.g. H$_2$SO$_4$) to form aminium salts. Ongoing research aims to resolve if this amine chemistry contributes to the discrepancy between predicted and observed new particle formation rates (Bzdek et al., 2010; Bzdek et al., 2011; Berndt et al., 2010; Benson et al., 2011; Erupe et al., 2010b; Zhao et al., 2011; Kirkby et al., 2011), but is analytically challenging due to the trace nature of these compounds in the atmospheric matrix.
Figure 1-3. Scheme of alkyl amine (NR$_3$) emissions, loss processes and particle formation reactions.

1.1.1 Amines and ammonia: Atmospheric emissions and fate of simple nitrogenous bases

Alkyl amines and ammonia are emitted to the gas phase from a wide variety of anthropogenic and natural processes (Ge et al., 2011a). The largest amine sources are thought to be degradation of natural organic matter (Gibb et al., 1999; Mopper and Zika, 1987; Van Neste et al., 1987); animal husbandry and agricultural emissions (Mosier et al., 1973; Rabaud et al., 2003; Schade and Crutzen, 1995; Kuhn et al., 2011; Traube et al., 2011), biomass burning, industrial incineration, and sewage treatment (Finlayson-Pitts and Pitts, 2000; Leach et al., 1999). In particular, the metabolism and decarboxylation of proteins in natural organic matter likely result in direct amine emissions from marine and terrestrial environments. Numerous other sources of amines have been identified, but are important only on local scales (Ge et al., 2011a; Seo et al., 2011). Many quantitative gas phase measurements of NR$_3$ have been made. Ge et al. (2011a) report that 150 amine species have been found in air samples from all studies to date. Overall, the atmospheric importance of these trace base compounds is poorly understood. In particular, there is emerging concern that fugitive emissions of amines or amine-functionalized compounds employed in CO$_2$-capture applications would increase the atmospheric burden of these compounds with little understanding of their likely fate and environmental impact (Veltman et al., 2010; Heydari-Gorji et al., 2011; Vaidhyanathan et al., 2010; Mac Dowell et al., 2011; Lee et al., 2011).
The most common and abundant atmospheric NR₃, after NH₃, are: methylamine (MA), ethylamine (EA), dimethylamine (DMA), diethylamine (DEA), trimethylamine (TMA) and triethylamine (TEA). The greatest direct source of NR₃ has been suggested to be animal husbandry operations, with global emissions estimated at 0.15 TgN annum⁻¹, leading to amine concentrations up to hundreds of ppb near animal housing and waste storage areas (Schade and Crutzen, 1995; Rabaud et al., 2003). Gaseous amine levels in marine and background continental environments are generally on the order of < 1 – 100 ppt (Mopper and Zika, 1987; Gronberg et al., 1992; Gibb et al., 1999; Chang et al., 2003; Akyuz, 2007). Amines are often volatilized concomitantly with NH₃, but typically at mixing ratios 1 - 3 orders of magnitude smaller (Gronberg et al., 1992; Chang et al., 2003; Huang et al., 2009; Veltman et al., 2010). Relative gas phase ratios of NH₃:NR₃ near sources have been measured to range from 100:1 to more than 1000:1, typically with NH₃ mixing ratios on the order of ppbv (µg m⁻³) and NR₃ at pptv (ng m⁻³) (Barsanti et al., 2009; Gibb et al., 1999; Gronberg et al., 1992; Kuhn et al., 2011; Mosier et al., 1973; Schade and Crutzen, 1995). The primary sinks of the simple alkyl amines are thought to be oxidation by OH and wet deposition via rain scavenging.

Lifetimes for NR₃ against oxidation are on the order of a few hours to a day in the presence of atmospherically relevant concentrations of OH, compared to a month for NH₃ (Atkinson et al., 1977a; Atkinson et al., 1977b; Pitts et al., 1978; Atkinson et al., 1997). Oxidation by O₃ can also be an appreciable sink for secondary and tertiary amines (lifetimes of hours to days) in polluted environments (Finlayson-Pitts and Pitts, 2000). Elucidation of the fast oxidation losses for NR₃ indicated that formation of significant quantities of carcinogenic nitrosamines in the atmosphere was not possible and led to a decline in research concerning their role in the atmosphere in the 1970s. In fact, the underlying mechanisms and products of amine oxidation have remained largely unexplored since this initial work (Atkinson et al., 1977a, b; Atkinson et al., 1997). Recently, oxidation rates and mechanisms for monoethanolamine (MEA) have been investigated as this compound is a leading candidate in CO₂-scrubbing technologies, giving better constraints on the oxidation products and pathways of this compound class (Onel et al., 2012; Nielsen et al., 2011; Karl et al., 2012). However, amines, as a class of atmospheric compounds, have been poorly characterized in terms of confirmed oxidation products and mechanisms (Schade and
Crutzen, 1995). The potential importance of amines partitioning from the gas to the particle phase has gained renewed appreciation in the last decade of research due to frequent qualitative identification of amines in atmospheric particulate samples due to innovations in particle mass spectrometry (Angelino et al., 2001; Denkenberger et al., 2007; Pratt et al., 2009; Silva and Prather, 2000; Smith et al., 2010; Smith et al., 2008; Tan et al., 2002; Zhao et al., 2011). The mechanisms and products of condensed phase amine oxidation have not been reported.

1.1.2 Incorporation of amines into atmospheric particles

Gaseous bases can become incorporated into the particulate phase through several processes (R1-R4, Figure 1-1). They can undergo reactive uptake with acidic molecular clusters (Kurten et al., 2008; Loukonen et al., 2010; Bzdek et al., 2010; Bzdek et al., 2011) and secondary inorganic aerosol (Zhao et al., 2011; Facchini et al., 2008; Muller et al., 2009; Wang et al., 2010; Qiu et al., 2011; Forster et al., 2007) or they can undergo oxidation to form less volatile products that condense on existing aerosol (Silva et al., 2008; Angelino et al., 2001; Zahardis et al., 2008). A comprehensive review of the thermodynamic properties of amines that govern their gas-particle partitioning can be found in Ge et al. (2011b). Generally, amines are likely candidates for forming aminium salts with atmospheric acids resulting in the formation of secondary aerosol mass (Pratt et al., 2009). With pKa values ranging from 9.25 - 10.98 (pKaNH3 = 9.25 (Seinfeld and Pandis, 2006)) and similar water solubilities to NH3 (Gibb et al., 1999; Mackay et al., 2004), amines can partition to and neutralize aqueous acidic particles. The partitioning and reactive uptake mechanisms of NH3 in to particles and aqueous solutions have been well explored (Mozurkewich, 1993; Donaldson, 1999; Dinar et al., 2008) and impacts on aerosol properties continue to be investigated (Mmereki et al., 2000; Wang et al., 2010; Qiu and Zhang, 2012; Zarzana et al., 2012). Amines detected in an aqueous particle or as a salt are likely to be protonated since they are strong bases, and will therefore be denoted with an appended H+ in the following discussion. The degree to which amines may be scavenged by aqueous aerosols is dependent on the effective pH of the solution and the pKa of the amine (R1). The degree of protonation will have a buffering effect on isolating amine molecules from exchange back to the gas phase (Pankow, 2003):

\[
\text{NR}_3(g) \rightleftharpoons \text{NR}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{R}_3\text{NH}^+_{(aq)} + \text{OH}^-_{(aq)} \quad (R1)
\]
Second, subsequent reaction with acidic solution components could lead to the formation of insoluble salts:

\[ R_3NH^+(aq) + A^-(aq) \rightarrow R_3NHA(s) \]  
(R2)

Where \( A^- \) is a conjugate base in solution and HA is the parent acid. Third, gas phase acid-base reactions to form an insoluble salt:

\[ NR_3(g) + HA(g) \rightarrow R_3NHA(s) \]  
(R3)

Finally, reactive uptake and displacement of ammonia from pre-existing salts may also occur:

\[ NR_3(g) + (NH_4)_n(A)_m(s) = NH_3(g) + (NH_4)_{n-1}(R_3NH)(A)_m(s) \]  
(R4)

Field data supporting laboratory observations of these processes, however, are limited (Creamean et al., 2011; Junninen et al., 2010; VandenBoer et al., 2011). Modeling and laboratory studies indicate that amines can enter the condensed phase by all the routes proposed above in Reactions 1 - 4 (Mmereki et al., 2000; Murphy et al., 2007; Barsanti et al., 2009; Ge et al., 2011b) and suggest that small chain (C1-C5) alkyl amines may be important for the initiation of particle formation events and growth of nucleating aerosols. Junninen et al. (2010) used an atmospheric pressure interface time-of-flight mass spectrometer to collect ambient atmospheric ions from the gas phase, including molecular clusters where the formation of inorganic aminium salts might be occurring. Preliminary results showed homologous series of alkyl amines and pyridines in their samples in addition to the typical HNO\(_3\) and H\(_2\)SO\(_4\) acids. These results are indicative of gas phase reaction prior to particle formation between the trace constituents, supporting the hypothesis that amines may promote H\(_2\)SO\(_4\) nucleation through the formation of non-volatile salts. Further support for this from laboratory investigations was made by Berndt et al. (2010) in a series of lab experiments comparing the nucleation rate of H\(_2\)SO\(_4\) as a function of relative humidity (RH) and the presence of NH\(_3\) and a surrogate amine, tert-butylamine. The results showed that both basic species had significant and similar promoting effects on the
nucleation rate of H$_2$SO$_4$. The number density of amine was also two orders of magnitude smaller than NH$_3$, showing that given typical near-source atmospheric concentrations of both gases, they may have similar impacts on nucleation rates. Similar observations have been found in several following lab studies (Zollner et al., 2012; Yu et al., 2012; Wang et al., 2010; Kirkby et al., 2011). Alkyl amines, like ammonia, will form salts (R2, R3) with inorganic and organic acid species due to their basic nature (Angelino et al., 2001; Murphy et al., 2007; Barsanti et al., 2009). Finally, laboratory studies have shown that in some instances, alkyl amines can displace ammonium from charged molecular clusters of the inorganic salts to form aminium salts (R4) (Murphy et al., 2007; Lloyd et al., 2009; Bzdek et al., 2010; Qiu and Zhang, 2012; Qiu et al., 2011). However, the importance and prevalence of these exchange reactions are not yet clear. Smog chamber experiments have also shown that the oxidation of amines can lead to the formation of secondary organic aerosol (SOA) or N-containing products that can also form salts with atmospheric acids (Murphy et al., 2007; Nielsen et al., 2011; Karl et al., 2012). The relative importance of these processes for the incorporation of amines in ambient atmospheric fine particulate matter is not yet clear and our understanding is severely limited by a lack of measurements (Zhang et al., 2012).

1.1.3 Quantitative and qualitative measurements of alkyl amines in atmospheric gas and particle phases

Few methodologies are capable of monitoring amines quantitatively in the gas (1 – 1000 pptv) and/or particle (< 1 – 100 ng m$^{-3}$) phase on timescales of an hour or less without significant sample manipulation (Chang et al., 2003). Atmospheric gas and particulate samples typically require long collection periods to reach quantities detectable by GC-MS (Akyuz, 2007; Key et al., 2011), LC-MS (Huang et al., 2009; Key et al., 2011; Rampfl et al., 2008), capillary electrophoresis (Rampfl et al., 2008; Riviello and Harrold, 1993; Fekete et al., 2006; Dabek-Zlotorzynska and Maruszak, 1998) or IC (Facchini et al., 2008; Makela et al., 2001; Muller et al., 2009). Most analytical methodologies entail complex extraction and derivatization procedures to improve detection limits, but also decrease sample throughput capabilities, limit application in continuous monitoring strategies, introduce the possibility of sampling artifacts, reduce analyte recovery, and require dedicated operators and significant operation costs.
Amines have been detected frequently in atmospheric fine and ultrafine particulate matter by a number of online techniques, including: aerosol time-of-flight mass spectrometry (AToF-MS) (Angelino et al., 2001; Pastor et al., 2003; Denkenberger et al., 2007), compact time-of-flight aerosol mass spectrometry (c-ToF-AMS) (Murphy et al., 2007; Sorooshian et al., 2008), atmospheric pressure interface time-of-flight mass spectrometry (API-TOF-MS) (Junninen et al., 2010), thermal desorption chemical ionisation mass spectrometry (TDCIMS) (Smith et al., 2008; Smith et al., 2010), and particle into liquid sampler ion chromatography (PILS-IC) (Murphy et al., 2007; Sorooshian et al., 2008; Sorooshian et al., 2009). The R$_3$NH$^+$ contributed 10 - 47 % of the positive ions in 8-10 nm particles sampled by Smith et al. (2010) indicating that amines may be a significant constituent of newly formed particles. Their frequent presence as detectable fractions of fine mode particles, specifically that which may not be fully neutralized by ammonia, indicates that they may also contribute to condensational growth through reactive uptake (Murphy et al., 2007). A drawback of many mass spectrometric observations is that they cannot provide quantitative mass loadings of specific R$_3$NH$^+$ constituents. For example, AMS response factors for various aminium salts have been reported to range from 5 – 10 times that of ammonium nitrate depending on the composition of the salt, thereby limiting this method to amine identification only (Silva et al., 2008). Similarly, Murphy et al. (2007) showed that the exchange of ammonium by methylaminium in sulphate particles enhanced the collection efficiency by the C-TOF-AMS significantly due to changes in the physical properties of the particles. Simultaneous observations by C-TOF-AMS and PILS-IC by Sorooshian et al. (2008) bridged the gap in producing quantitative amine information in addition to detailed knowledge of particle composition. They found instances of EA and DEA in sub-micrometer particles at mass loadings of 50 – 200 ng m$^{-3}$ (~20 % of the mass loading of NH$_4^+$), indicating that alkyl amines can contribute significantly to the neutralizing capacity of particles less than 1 µm in diameter.

More recently, Huang et al. (2009) described an online derivatization method for the detection of NR$_3$/R$_3$NH$^+$, and reported simultaneous NH$_3$/NH$_4^+$ and MA/MAH$^+$ observations near a small animal farm in New York on the order of 10 ppbv / 5 µg m$^{-3}$ and 100 pptv / 0.1 µg m$^{-3}$, respectively, giving a ratio of 0.01/0.02.

Ion chromatography has recently seen increased use in quantitative online techniques as a sensitive and cost effective tool (Praplan et al., 2012; Li et al., 2009a; Erupe et al., 2010a). Cation
exchange stationary phases using various combinations and proportions of carboxylate, sulphate, phosphate and crown ether functionalities have all been proposed as having amine selectivity (Rey et al., 1998; Rey and Pohl, 1996, 2003; Pohl et al., 1999). However, reported separations of amines from common cations have been restrictive in the exact chemical composition of the separated mixture, potentially omitting coeluting cations. Environmental matrices are expected to be more complex than model solutions and have varying proportions of cationic constituents based on the specific matrix being analyzed. Separation times are also a challenge when time constraints arise from interfacing IC with an automated sampling system to enable near real-time analysis. For example, the PiLS-IC collects samples into an autosampling vial cassette in order to achieve 15 minute time resolution and samples continue to be analyzed long after the online portion of the investigation, increasing the potential for artifact formation during storage (e.g. degradation, chemical reaction, etc.). Therefore, applied identification strategies either need to enhance selectivity of the stationary phase (e.g. changing column temperature or adding organic solvent to the mobile phase) or the detector (e.g. ESI-MS) if issues of separation time or coelution arise.

Fortunately, the gas and particle phases of the atmosphere have been well characterized for many water soluble species, allowing IC methods to easily anticipate the dominant cationic species in both phases, and the relevant range over which separation and detection techniques need to operate. However, online ion chromatography detection methodologies have not yet reported separation and quantitation of the full suite of the most commonly emitted amine compounds listed above, in the presence of the most common cations in atmospheric samples (Chang et al., 2003) and these IC methods often struggle to detect amines at relevant levels in the atmosphere (pptv or ng m$^{-3}$), let alone in both phases (Erupe et al., 2010a; Facchini et al., 2008; Murphy et al., 2007; Sorooshian et al., 2008; Li et al., 2009a; Huang et al., 2009). In addition, the complications in resolving methyl and ethyl amines from each other and the remaining water-soluble cations in atmospheric samples, by ion chromatography, has received limited discussion (Sorooshian et al., 2008; Murphy et al., 2007).
1.1.4 Atmospheric importance of alkyl amines in the formation, growth and properties of new particles

The presence of DMAH$^+$ in nucleation event particles reported by Mäkelä et al. (2001) provided the first indication of a potentially important role that amines might play in particle formation and growth. The presence of DMAH$^+$ was also reported in the 10 nm fraction for particulate collected in the absence of new particle nucleation, but at much lower mass loadings. Further investigations of the size-distribution of particle phase amines have shown the presence of DEAH$^+$ and MAH$^+$ in the 0.01 – 1.0 µm range in marine aerosols, their presence being attributed to biogenic sources metabolizing water-soluble organic carbon (Facchini et al., 2008; Muller et al., 2009; Miyazaki et al., 2010). A number of size-segregated investigations of particle composition in air masses impacted by marine sources have reported a ubiquitous contribution of amines to water-soluble organic nitrogen (WSON) in sub-micron aerosols (Makela et al., 2001; Facchini et al., 2008; Muller et al., 2009; Violaki and Mihalopoulos, 2010). However, their size-dependent composition in continental air masses has not been reported to date, despite the fact that the largest known amine sources are terrestrial (Rabaud et al., 2003; Seo et al., 2011; Ge et al., 2011a).

In general, online and offline observations of R$_3$NH$^+$ have shown them to be only a small fraction of the total reduced nitrogen in particles, but because many amines are stronger bases than ammonia their presence may significantly impact aerosol composition and properties. An increase in effective basicity of aqueous aerosol has been proposed as a way to reduce the free fraction of protons and therefore significantly alter pH values even in the presence of relatively small R$_3$NH$^+$ concentrations (Angelino et al., 2001; Pratt et al., 2009). Simultaneous measurements of amines and other chemical constituents and physical properties of aerosol can help to understand their impact on the pH of aerosols, which can affect particle chemistry, e.g. SOA formation. To improve our understanding of the mechanisms governing amine exchange between the gas and particle phases, online methods to separately observe and quantify individual amines in both phases are required. The applicability of simple thermodynamic equilibrium algorithms to describe gas-particle partitioning also needs to be evaluated by size-resolved measurements of amine mass loadings in the sub-micrometer range to appropriately
determine if size-dependent or bulk aerosol chemistry captures amine incorporation in to particulate matter.

1.1.5 Amine research in this thesis

The Ambient Ion Monitor – Ion Chromatography (AIM-IC) system was originally developed for the detection of major atmospheric constituents capable of partitioning between the gas and particle phases (e.g. HNO$_3$/pNO$_3^-$, NH$_3$/pNH$_4^+$, pSO$_4^{2-}$, etc.). The modifications to the 9000D version of this system, used throughout these works, required a cation selective ion chromatograph instead of a flow injection analysis system for a full suite of cationic constituents to be detected instead of just NH$_3$/NH$_4^+$. During preliminary field sampling (online amine dataset presented in Chapter 3), a number of significant, but unidentified, peaks appeared in our chromatographs for both gas and fine particulate matter (PM$_{2.5}$) measurements. The literature reported common ions separated on this cation selective column, with methods similar to ours (Rey and Pohl, 2003), suggested that alkyl amines were the most likely species to arise in both channels of the AIM-IC instrument due to their volatile nature and previous detection in PM samples by ion chromatography (Sorooshian et al., 2008;Murphy et al., 2007). The work presented in Chapter 2 summarizes the method development that was carried out to confirm that these amines were being detected by the ion chromatograph, what the sensitivity and selectivity of the instrumentation was, whether these limits would allow online atmospheric detection of the alkyl amines in both phases, how reproducible the separation method could be when applied across platforms, and whether other cation selective chromatography columns could provide similar selectivity.

Indeed, we found that this separation and detection scheme were generally more than sufficient to carry out (semi-)quantitative analysis of the most prevalent amines in the atmosphere in both gas and particle phases with the cation selective columns at our disposal. This allowed us to revisit the first dataset collected in Toronto, Canada in the summer of 2009 (Chapter 3) to investigate the partitioning of these trace atmospheric bases in light of their emerging significance as ubiquitous components of ultrafine particles (< 100 nm in diameter) (Smith et al., 2008;Barsanti et al., 2009). The accumulation of amines in particulate matter and their gas-particle partitioning are not well understood and our dataset allowed a first comparison between
the results of lab experiments (Murphy et al., 2007) and modeling of these processes (Barsanti et al., 2009). These first field observations also motivated the analysis of size-resolved particulate matter samples collected using the Micro-Orifice Uniform-Deposit Impactor (MOUDI) for alkyl amines from several locations throughout Ontario, Canada. Similar instrumentation in marine environments showed that amines were present throughout the fine mode (< 2.5 µm) suggesting that they might be important in the formation of new particles (Muller et al., 2009; Facchini et al., 2008). However, no previous work had aimed to detect the size-distributions of amines in continentally derived particulate matter. Our results showed that amines were present ubiquitously in sub-micron particles. Furthermore, size-resolved sampling with ion chromatographic analysis allowed us to determine that amines increased in significance in particulate matter, relative to ammonium, as a function of decreasing size. Finally, we deployed the AIM-IC and MOUDI in Egbert, ON during the fall of 2010 and found that amines were ubiquitous in both phases at this site, but at the lower limit of anticipated atmospheric concentrations, which was confirmed by the MOUDI sample. These observations allowed us to highlight the sensitivity of this instrumentation toward detecting these compounds in the atmosphere under challenging environmental conditions and was therefore included in the analytical report presented in Chapter 2.
1.2 Atmospheric chemistry of nitrous acid (HONO)

Traditionally, observations of tropospheric HONO are made from in situ or remote sensing instruments located at the surface, where HONO is observed to accumulate at night and decline quickly during the day. The underlying chemistry of these diurnal trends in HONO has undergone significant investigation since the first measurements made by Perner and Platt (1980; 1979) with a long path differential absorption spectrometer over 30 years ago and this chemistry is discussed in detail in the following sections. Overall, the major pathways for HONO formation and loss in the gas phase are largely known, while direct emissions from combustion processes are thought to be minor. However, there are two significant gaps remaining in the understanding of the most important HONO sources and sinks (Figure 1-4).

At night, HONO is often observed to reach a pseudo stationary state that is postulated to arise from dry deposition of HONO accumulated in the gas phase back to the surface (Harrison and Peak, 1997; Harrison and Kitto, 1994; Stutz et al., 2002; Stutz et al., 2004; Sorgel et al., 2011a; Su et al., 2008b; Su et al., 2008a). The unknown in this case is the fate of the surface deposited HONO, which has not been explicitly explored. Lab investigations of HONO uptake into aqueous films and pH controlled liquids have demonstrated reversibility and some irreversibility in these reactions (Hirokawa et al., 2008; He et al., 2006). Irreversible loss was postulated to arise when reactive impurities were present at the surfaces investigated. Conversely, lab studies investigating the heterogeneous formation of HONO from NO$_2$ reacting on wet surfaces state that HONO formed on a surface does not remain adsorbed and partitions immediately to the gas phase (Miller et al., 2009; Kamboures et al., 2008; Finlayson-Pitts et al., 2003; Finlayson-Pitts, 2009). Uptake of HONO in to atmospheric aqueous solutions, such as dew and fog water, has been well documented from field observations to be a diffusion limited equilibrium process (Rubio et al., 2009; Rubio et al., 2008; Sorgel et al., 2011b). Aqueous partitioning has also been suggested to understand the rapid formation of the pseudostationary state in a marine atmosphere (Wojtal et al., 2011). Therefore, it seems likely that HONO can partition to aqueous reservoirs located at the ground surface under atmospherically relevant conditions and that this loss mechanism can potentially be enhanced if reactive sinks are also present. However, investigations of atmosphere-surface exchange mechanisms of HONO have only recently been
postulated (Su et al., 2011). Such a dynamic coupling of the atmosphere and surface with a HONO reservoir could lead to the release of HONO from the surface during the day. Daytime HONO observations have indicated that a significant HONO source at the ground surface must exist in order to explain observed mixing ratios of HONO greater than the photostationary state expected from known gas phase reactions (Section 1.2.1). Many recent lab studies have revealed photoenhanced heterogeneous mechanisms for NO₂ conversion to HONO on a wide variety of substrates (Section 1.2.2). However, the major mechanism in the production of HONO during the day remains largely unknown. A recent report by Sorgel et al. (2011a) has calculated that known mechanisms utilizing NO₂ as a HONO precursor are only capable of explaining up to 30 % of the required unknown daytime source at a rural field site. More frequently, the formation of HONO from precursors other than NO₂ have been proposed to constrain the required daytime production of HONO from photolysis of HNO₃ (Zhou et al., 2011) and partitioning of soil nitrite (Su et al., 2011). These new mechanisms are not well understood for their potential importance to the daytime production of HONO, although they have been suggested to account for the entire daytime source, due to a lack of field observations and lab investigations under natural conditions. Figure 1-5 describes the general fate of HONO in the troposphere for the most important and well characterized reactions.

Figure 1-4. Scheme of current understanding of HONO atmospheric processes. The sink of HONO at night and the source of HONO during the day required to reconcile observations are both not well understood.
These two issues must be resolved in order to accurately understand the sources and sinks of HONO in the atmosphere. Improvement in understanding the fate of HONO deposited to the surface at night has the potential to reveal whether a reservoir can be formed at the ground surface that can contribute to the missing production of HONO during the day. Furthermore, a more complete understanding of these processes will allow atmospheric models to appropriately include HONO chemistry in the production of OH. The photolysis of HONO has been shown as an important source of OH throughout the day at a number of field locations in the summer (Elshorbany et al., 2009; Elshorbany et al., 2012a; Alicke et al., 2002; Volkamer et al., 2010). This source of OH is expected to become more important in a winter atmosphere when production of O(1D) from O3 photolysis is minimized. Nitrous acid as an OH source is not routinely considered in atmospheric models and has only recently been suggested to have a significant impact on a global scale, demanding that understanding of HONO chemistry be improved to properly predict atmospheric oxidation capacity (Li et al., 2011; Ensberg et al., 2010; Elshorbany et al., 2012b).

Figure 1-5. Scheme of known diurnal HONO emissions, formation and loss processes. Photolysis and photoenhanced heterogeneous NO2 conversion are indicated by yellow arrows.
1.2.1 Gas phase reactions

The dominant gas phase reactions in the production and loss of nitrous acid have been well-characterized through field and lab investigations over the past 20 years. The photolysis of HONO (R1, $j_{\text{HONO}} \approx 1$ to $4 \times 10^{-3} \text{ s}^{-1}$) is a significant source of OH radicals early in the morning (Platt et al., 1980; Perner and Platt, 1979) and the dominant fate of HONO during the day. Meanwhile, loss of HONO with OH is a minor gas phase process during the day (R2, $k_2 = 5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$), since the effective rate ($k_2[\text{OH}] \approx 5 \times 10^{-6} \text{ s}^{-1}$) is small compared to that of photolysis. The importance of nitrous acid photolysis as a significant source of OH throughout the day has recently been revisited using field measurements in many environments (Elshorbany et al., 2012a; Kleffmann et al., 2005; Su et al., 2008b; Young et al., 2012; Li et al., 2010a). More recently, HONO has been proposed as the dominant OH source under atmospheric conditions when the generation of O(1D) from the photolysis of O$_3$ (R3) is limited, particularly during winter months (Elshorbany et al., 2012b).

\[
\text{HONO}_{(g)} + h\nu (\lambda < 400 \text{ nm}) \rightarrow \text{NO}_{(g)} + \text{OH}_{(g)} \quad (R1)
\]

\[
\text{HONO}_{(g)} + \text{OH}_{(g)} \rightarrow \text{H}_2\text{O}_{(g)} + \text{NO}_2(g) \quad (R2)
\]

\[
\text{O}_3(g) + h\nu \rightarrow \text{O}(^1\text{D})_{(g)} + \text{O}_2(g) \quad (R3)
\]

Improvements in the analytical certainty of field instrument measurements has generated a consensus that HONO is present throughout the day at mixing ratios on the order of tens to hundreds of pptv when the photostationary minimum is reached (Kleffmann and Wiesen, 2008; Kleffmann et al., 2006; Broske et al., 2003; Stutz et al., 2010; Stutz et al., 2002), implying a strong surface source (up to 2 ppbv hr$^{-1}$) that is largely unknown (Amoroso et al., 2008; Elshorbany et al., 2012a; Elshorbany et al., 2009; Sorgel et al., 2011a; Li et al., 2012). Gas phase HONO formation and loss mechanisms have generally been found to be too slow to account for HONO formed at night or during the day. The termolecular reaction of OH and NO (R4) is the major gas phase source of HONO during the day ($k_3 \approx 8 \times 10^{-12} \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1}$), while R5 contributes negligibly at atmospherically relevant concentrations (Chan et al., 1976). These reactions are not fast enough to account for the formation rate of HONO at night.
\[ \text{OH} \text{(g)} + \text{NO} \text{(g)} + M \rightarrow \text{HONO} \text{(g)} + M \]  \hspace{1cm} (R4)

\[ \text{NO} \text{(g)} + \text{NO}_2 \text{(g)} + \text{H}_2\text{O} \text{(g)} \rightarrow 2 \text{HONO} \text{(g)} \]  \hspace{1cm} (R5)

Recently, a gas phase mechanism between photoexcited NO\textsubscript{2} and water vapour (R6) was proposed to account for a significant fraction of the unknown daytime HONO source (Carr et al., 2009; Li et al., 2008, 2009b). However, this has since been shown to be a two photon excitation process and therefore negligible under atmospheric conditions (Amedro et al., 2011; Wu and Chen, 2012). Similarly, photolysis of ortho-nitrophenols has been shown to yield HONO efficiently, but atmospheric concentrations of these compounds are small and anticipated to be significant only under specific conditions (e.g. power plant plumes or heavily polluted urban zones) (Bejan et al., 2006). In most cases, this HONO source is also not expected to be significant (Wong et al., 2012).

\[ \text{NO}_2^* \text{(g)} + \text{H}_2\text{O} \text{(g)} \rightarrow \text{OH} \text{(g)} + \text{HONO} \text{(g)} \]  \hspace{1cm} (R6)

Heterogeneous HONO formation mechanisms have since been utilized to understand the production rate of HONO at night and during the day using NO\textsubscript{2} as a precursor.

1.2.2 Heterogeneous reactions

The only acknowledged process for formation of HONO at night occurs by the reaction of NO\textsubscript{2} on wet surfaces (R7), although the exact mechanism relevant to the atmosphere remains uncertain because formation of the intermediate N\textsubscript{2}O\textsubscript{4} in the proposed mechanism is limited and the rate of HONO formation is linearly proportional to NO\textsubscript{2} (Barney and Finlayson-Pitts, 2000; Finlayson-Pitts, 2009; Finlayson-Pitts et al., 2003; Kamboures et al., 2008; Miller et al., 2009). In any case, lab studies have shown reactions of NO\textsubscript{2} to form HONO from heterogeneous conversion coefficients of \( \gamma = 1 \times 10^{-6} \) to \( 1 \times 10^{-5} \) on a variety of substrates, and these overall conversion rates have been successfully incorporated into models of nighttime formation (Broske et al., 2003; Kleffmann et al., 1998; Kurtenbach et al., 2001; Wong et al., 2011).
2 \text{NO}_2(g) + \text{H}_2\text{O}_{(ads)} \rightarrow \text{HONO}_{(g)} + \text{HNO}_3(ads) \quad \text{(R7)}

However, when this mechanism is constrained by observations of \text{NO}_2 in a model it produces more HONO in the nocturnal atmosphere than is observed, suggesting that HONO undergoes significant losses at night. The sink is assumed to be heterogeneous because the gas phase sinks (R1 and R5) are not active in the dark. The fate of HONO lost to surfaces at night is not known. Generally, models utilize a dry deposition rate to remove HONO from the nocturnal boundary layer to the surface assuming that the process is terminal and HONO has been irreversibly lost (Sorgel et al., 2011a; Wong et al., 2011).

To reconcile the daytime HONO source strength, lab studies have proposed several daytime HONO formation mechanisms by reaction of \text{NO}_2 with a variety of solid substrates (e.g. R8 and R9 for hydrocarbons). These substrates reduce \text{NO}_2 to HONO via proton transfer and are photocatalytic. Substrates that have exhibited such reactivity are: i) humic acid (Stemmler et al., 2007; Stemmler et al., 2006; Bartels-Rausch et al., 2010), ii) organic films (George et al., 2005; Broske et al., 2003; Brigante et al., 2008; Ammar et al., 2010), iii) soot (Monge et al., 2010; Khalizov et al., 2010; Gerecke et al., 1998; Aubin and Abbatt, 2007; Ammann et al., 1998) and iv) TiO$_2$ (Langridge et al., 2009; Bedjanian and El Zein, 2012; Ndour et al., 2008; Ndour et al., 2009).

\[ [\text{R-H}] + \text{hv} \rightarrow [\text{R-H}]^* \quad \text{(R8)} \]

\[ \text{NO}_2 + [\text{R-H}]^* \rightarrow \text{HONO} + [\text{R}'] \quad \text{(R9)} \]

These HONO formation mechanisms are consistent with observations that qualitatively suggest a relationship between the strength of the daytime HONO source and the product of \text{NO}_2 with OH or surface irradiance (Li et al., 2012; Ren et al., 2011; Wong et al., 2012), but in situ observations suggest that the current range of \text{NO}_2 heterogeneous reactions can only account for a small fraction of the required HONO production (Wong et al., 2012; Wong and Stutz, 2010; Wong et al., 2011). An upper estimate of the humic acid conversion of \text{NO}_2 to HONO by Sorgel et al. (2011a) was found to be capable of explaining 30\% of the unknown daytime source when
parameterizing the findings of Stemmler et al. (2006). To date, mechanisms of daytime HONO formation not utilizing NO$_2$ as a precursor have been infrequently reported. However, this may be the case and instead a HONO reservoir at the surface may be formed, from which, HONO deposited at night can be emitted during the day. The potential significance of such a reservoir has been previously explored for a marine environment (Wojtal et al., 2011).

Alternative hypotheses for sources that may produce daytime HONO heterogeneously, without requiring NO$_2$, are the photolysis of nitrate and HNO$_3$ on surfaces (Zhou et al., 2011; Handley et al., 2007), and partitioning from nitrite (NO$_2^-$) rich soils as their water content is reduced (Su et al., 2011). The potential importance of the nitrate photolysis mechanism, particularly for leaf surfaces, has not yet been resolved since yields and photolysis rates remain unpublished (Zhou et al., 2011). Some circumstantial evidence has been found from field data that this process may be active in the real atmosphere, but the mechanism remains poorly constrained (Zhou et al., 2011; Li et al., 2012). The other HONO formation process that has been proposed by Su et al. (2011) suggests that soil nitrite partitioning from soil pore water in a dynamic equilibrium with the overlying atmosphere (R6 and R7) can account for the daytime HONO source, similar to the mechanism reported for observed HONO pseudo-stationary states over water in a nocturnal atmosphere (Wojtal et al., 2011). The authors have proposed that soil nitrite produced by microbial activity is the HONO source in this system (Su et al., 2011).

\[
\text{H}_3\text{O}^+ (\text{aq}) + \text{NO}_2^- (\text{aq}) \rightleftharpoons \text{HONO} (\text{aq}) + \text{H}_2\text{O} (\text{l}) \quad \text{(R6)}
\]

\[
\text{HONO} (\text{aq}) \rightleftharpoons \text{HONO} (\text{g}) \quad \text{(R7)}
\]

While the mechanism presented seems feasible, the underpinning experimental evidence of Su et al. (2011) is questionable due to their direct modification of the sample with reactants known to produce HONO when combined, and failure to present experimental positive and negative controls justifying this modification. This highlights the need for significant work on improving the general state of knowledge for i) the fate of nocturnally deposited HONO at the surface and ii) soil nitrite abundance and fate. The relative importance of these two reservoirs is uncertain, with no independently reproduced confirmations of the mechanisms and/or their associated...
kinetics to date. Elucidation of the atmospheric relevance for each heterogeneous source process clearly requires further study before obtaining broad acceptance.

1.2.3 Particulate nitrite: a new framework for thinking about sources and sinks of HONO

Nitrous acid is a weak acid, with a pKa near 3.5, and a Henry’s Law constant that is highly pH dependent, ranging from 39 M atm$^{-1}$ from pH = 2 – 3 (Park and Lee, 1988) to 3x10$^6$ at pH 7-8 (Hirokawa et al., 2008). As such, it is not expected that any significant amount of HONO would be taken up on to aqueous secondary aerosols, such as (NH$_4$)$_2$SO$_4$ (Becker et al., 1998). Secondary aerosols of mixed inorganic and organic matter, in general, present the dominant fraction of the total aerosol surface area for kinetically limited reactive gas uptake. The pH of these aerosols - for fully neutralized NH$_4^+$-NO$_3^-$-SO$_4^{2-}$ aerosols – is between 3 and 5, which inhibits the accommodation of HONO even under aqueous solution conditions (Kleffmann et al., 1998; Becker et al., 1998). However, larger aerosols, such as fog (Rubio et al., 2008; Rubio et al., 2009; Sorgel et al., 2011b; He et al., 2006), and solutions of higher pH (Hirokawa et al., 2008) have been consistently shown to accommodate significant amounts of HONO. Observations of particulate nitrite have been reported, but the mechanism of nitrite accumulation in these samples has not been determined (Acker et al., 2005; Song et al., 2009; Simon and Dasgupta, 1995; Lammel and Cape, 1996; Chang et al., 2008). Preliminary investigations into the fate of HONO in contact with surface substrates and water suggest that the presence of mineral cations and dust (e.g. CaCO$_3$) may control the accumulation of nitrite in the condensed phase (Li et al., 2010b; He et al., 2006). Whether this accumulation is reversible (R6, R7) or not depends on whether the substrate is reactive (R8). Specific investigation of the reactivity of HONO with mineral carbonates (R8) has been limited by the ability to make very fast (~0.1 – 1 Hz) and accurate HONO measurements, as well as a stable source of HONO. While it seems likely that this reaction will occur on atmospheric dust and surface soils, it has not yet been reported in the literature.

\[
\text{HONO}_\text{(g)} + \text{NaHCO}_3\text{(s)} \rightarrow \text{NaNO}_2\text{(s)} + \text{H}_2\text{O}_\text{(g)} + \text{CO}_2\text{(g)} \quad \text{(R8)}
\]

Therefore, this would imply that basic coarse mode particles and/or the ground surface may be a dominant sink for HONO at night, particularly under humid conditions. This could have a
significant impact on HONO chemistry globally since mineral dust accounts for 36 % of global aerosol emissions (5900 Tg yr$^{-1}$) (Forster et al., 2007) and soil pore water is ubiquitous. While the ground surface is highly variable in composition (e.g. buildings, vegetation and open soil), it is well known that dust arising from erosion of soil and concrete contains carbonates that impart a basic nature to lofted aerosols, resulting in high reactivity with gaseous acids (Cwiertny et al., 2008; Gibson et al., 2006; Hatch and Grassian, 2008). Numerous lab studies and field observations have confirmed that HNO$_3$, HCl, HCOOH and CH$_3$COOH are all reactive with mineral dust, namely those enriched in carbonates (Preszler Prince et al., 2007; Preszler Prince et al., 2008; Al-Hosney et al., 2005; Vlasenko et al., 2009; Vlasenko et al., 2006; Sullivan et al., 2007a; Sullivan et al., 2007b; Sullivan et al., 2009; Ooki and Uematsu, 2005).

In particular, single particle mass spectrometry has observed mineral dust chemistry with reactive acids at high time resolution. However, this measurement technique is limited to qualitative measurements and cannot exclusively identify nitrite since the ion is a major by-product of the laser ablation processing of nitrate (Sullivan et al., 2007a; Sullivan et al., 2007b). Long duration filter and size-resolved particle sampling methods have found that HONO mixing ratios are enhanced in dust storms (Saliba and Chamseddine, 2012; Wang et al., 2003) and attributed this to efficient conversion of NO$_2$ to HONO despite little evidence for this from lab studies on mineral dust not containing irradiated TiO$_2$ (Ndour et al., 2008; Goodman et al., 1999; Bedjanian and El Zein, 2012; Angelini et al., 2007). These sample collection methods are also prone to carrying out additional chemistry as a result of prolonged collection times that is not representative of the collected composition, particularly chain acid displacement reactions on dust with HNO$_3$ (Ooki and Uematsu, 2005; Saliba and Chamseddine, 2012). Nitrate and nitrite are usually not speciated from these filter samples due to oxidative conditions of the extraction methods (Ooki and Uematsu, 2005) and have limited the ability to develop further insight in to the importance that mineral dust might have in the production and loss of HONO in the atmosphere. To improve the state of knowledge on the interaction of mineral dust, NO$_2$ and HONO, simultaneous real-time observations of gaseous and particle phase composition would be ideal.
1.2.4 HONO chemistry explored in this thesis

During the CalNex 2010 field campaign, the Ambient Ion Monitor – Ion Chromatography system was deployed in Bakersfield, California to investigate the influence that inorganic gas-particle partitioning chemistry had on local air quality. Unexpectedly, we observed both gaseous HONO and particulate nitrite in nearly all the samples collected during this campaign (Chapter 5). Another instrument specifically designed to measure HONO, the relaxed eddy accumulation (REA) system (Ren et al., 2011), was used to intercompare HONO measurements to better understand if the particulate nitrite measurements were believable. We had previously established, from lab work performed during my MSc, that NO$_2$ produced correctable interferences in the gas channel of the AIM-IC, but not the particle channel. The intercomparison and subsequent lab characterization of HONO scrubbing efficiency under a simulated atmosphere further confirmed that our particulate nitrite measurements were real and that the magnitude of the measurement was greater than any previously published interferences for wet chemical systems (Kleffmann and Wiesen, 2008; Broske et al., 2003). Subsequent data analysis suggested that nitrite accumulation was enhanced when HONO and dust tracers (Ca$^{2+}$ and Na$^{+}$) also increased in the atmosphere. Therefore, we concluded that dust components, such as carbonates, might be reactive towards HONO and that similar chemistry might be occurring on the ground surface at night, forming a reservoir of nitrite. The formation of a reservoir of HONO via the nitrite ion as a salt or in solution had not yet been discussed in the community as a potential daytime source of HONO, despite a wide call for further mechanistic understanding of the otherwise uncharacterized daytime HONO source(s) (Kleffmann et al., 2005; Sorgel et al., 2011a; Zhou et al., 2011; Su et al., 2008b; Kleffmann, 2007; Elshorbany et al., 2009). Further circumstantial evidence from our CalNex dataset suggested that daytime mixing ratios of HONO were enhanced when the strong acids HNO$_3$ and HCl were likely depositing to the surface, leading to our hypothesis that HONO deposited into a surface reservoir at night could be displaced by HNO$_3$ and HCl the following day.

In addition, we observed reproducible vertical gradients in HONO measurements between the AIM-IC (4 m above ground level) and REA (13.5 m above ground level) systems throughout CalNex, but did not have sufficient vertical resolution to determine their significance. Vertically resolved measurements are only just emerging in the literature and are at odds as to whether
vertical gradients of HONO were real and what relative importance the ground and/or aerosol surfaces played in the nocturnal formation of HONO (Wong et al., 2012; Villena et al., 2011; Vogel et al., 2003; Kleffmann et al., 2003; Zhang et al., 2009). Previous studies had encountered many limitations in resolving these questions. The Nitrogen, Aerosol Composition and Halogens on a Tall Tower (NACHTT) field campaign, at the Boulder Atmospheric Observatory (BAO) in Erie, Colorado during the winter of 2011 provided the ideal opportunity to probe this chemistry (Chapter 4). The site provided a 300 m tall tower with an electric carriage capable of full vertical profile (0 m to 300 m and back to 0 m) collection every ten minutes, while outfitted with all instrumentation required to constrain the HONO chemical system. Specifically, the state-of-the-science Negative-Ion Proton-Transfer Chemical Ionisation Mass Spectrometer (NI-PT-CIMS), which I operated, provided continuous 0.1 Hz measurements of HONO at parts per trillion by volume detection limits without any detectable interferences from a novel inlet design. These measurements showed good temporal intercomparison with a fixed height measurement by a Mist Chamber Ion Chromatgraphy (MC-IC) system, with some inlet losses in the MC-IC. Vertical gradients in HONO were observed on nights when a nocturnal boundary layer formed. The full column measurements made on these nights allowed a critical assessment that ground surface chemistry dominates over aerosols in the nocturnal production of HONO. Furthermore, deposition of HONO to the surface at night was the only way to account for the observed pseudo stationary states, again indicating that the fate of HONO on the ground surface is poorly understood if a reservoir is being formed. The construction of a simple box model, constrained by our field observations, led to the discovery that surface deposited HONO could be a significant source of HONO during the day if the pool was labile in some way.

The subsequently collected lab data presented in Chapter 6 was carried out to determine if the dust/ground surface chemistry, particularly that of carbonates, with HONO suggested from these two field experiments was actually possible under atmospherically relevant conditions. It also sought to determine if the acid displacement mechanism of HONO from nitrite salts by HNO₃ and HCl was a feasible daytime source of HONO. The proxy substrates and real soil extracts from CalNex and NACHTT showed reactive uptake of HONO which was enhanced by increasing relative humidity over the surfaces. Subsequent exposure of these reactive substrates
to HNO$_3$ and HCl confirmed that acid displacement yielding HONO is likely to occur in the real atmosphere during the day and may contribute to the unknown daytime source.
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CHAPTER TWO

Ion chromatographic separation and quantitation of alkyl methylamines and ethylamines in atmospheric gas and particulate matter using preconcentration and suppressed conductivity detection

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Author Contributions:

T. C. VandenBoer and M. Z. Markovic developed the ion chromatographic methods, and collected AIM-IC samples. T. C. VandenBoer collected the MOUDI sample and A. Petroff performed sample analysis and data work up for this sample. M. F. Czar and T. C. VandenBoer developed the framework for the chemically-relevant curve fitting function of partially dissociated bases. N. Borduas developed the method and calibration data for monoethanolamine. T. C. VandenBoer prepared the manuscript under the guidance of J. G. Murphy.
Abstract

Two methods based on ion chromatography (IC) were developed for the detection of methyl and ethyl alkyl amines (methylamine (MA), ethylamine (EA), dimethylamine (DMA), diethylamine (DEA), trimethylamine (TMA) and triethylamine (TEA)) and NH$_3$/NH$_4^+$ in online atmospheric gas-particle and size-resolved particulate samples. The two IC methods were developed to analyze samples collected with an Ambient Ion Monitor (AIM), an online gas-particle collection system, or with a Micro Orifice Uniform Deposit Impactor (MOUDI) for size-resolved particle samples. These methods enable selective and (semi-) quantitative detection of alkyl amines at ambient atmospheric concentrations (pptv and pg m$^{-3}$) in samples where significant interferences can be expected from Na$^+$ and NH$_4^+$, for example marine and rural air masses. Sample pre-concentration using a trace cation column enabled instrumental detection limits on the order of pmol (sub-ng) levels per sample, an improvement of up to $10^2$ over current IC methods. Separation was achieved using a methanesulfonic acid gradient elution on Dionex CS12A and CS17 columns. The relative standard deviations in retention times during 3 week continuous (hourly) sampling campaigns ranged from 0.1 – 0.5 % and 0.2 - 5 % for the CS12A and CS17 across a wide dynamic range of atmospheric concentrations. Resolution of inorganic and organic cations is limited to 25 minutes for online samples. Mass-dependent coelution of NH$_4^+$/MA/EA occurred on the CS12A column and DEA/TMA coeluted on both columns. Calibrations of ammonium show a non-linear response across the entire calibration range while all other analytes exhibit high linearity ($R^2 = 0.984 - 0.999$), except for EA and TEA on the CS12A ($R^2 = 0.960$ and 0.941, respectively). Both methods have high analytical accuracy for the nitrogenous bases ranging from 9.5 – 20 % for NH$_3$ and < 5 – 15 % for the amines. Hourly observations of amines at Egbert, ON in October 2010 showed gaseous DMA and TMA + DEA at 1 – 10 pptv in air, while particulate DMA and TMA + DEA were present at 0.5 – 4 ng m$^{-3}$. A size-resolved particulate sample collected over 23 hours was found to contain DMA, TMA + DEA and EA at 1.78, 8.15 and 0.03 ng m$^{-3}$ mass loadings, with the amine mass enhanced in particle sizes between 100 – 1000 nm. These results highlight a need for very sensitive and selective detection of methyl and ethyl amines in addition to NH$_3$ in continuous online monitoring strategies.
2.1 Introduction

Numerous laboratory studies and theoretical chemical investigations (Kurten et al., 2008; Barsanti et al., 2009; Lloyd et al., 2009; Berndt et al., 2010; Bzdek et al., 2010; Loukonen et al., 2010) have raised questions concerning the role of alkyl amines (NR$_3$) in the formation and growth of new particles in the atmosphere. The formation of new particles has implications for climate change, through direct radiative forcing and cloud formation (Forster et al., 2007), and for human health (Burnett et al., 2000). The recent focus on the role of amines in particle formation was motivated by field observations reporting ubiquitous detection of NR$_3$ in particles less than 100 nm in diameter in urban, rural and marine atmospheres (Facchini et al., 2008; Huang et al., 2009; Muller et al., 2009; Smith et al., 2010; Smith et al., 2008; Sorooshian et al., 2008; Zhao et al., 2011). Current understanding suggests that NR$_3$ and NH$_3$ enhance particle formation and growth through acid-base chemistry with sulfuric acid (Benson et al., 2011; Berndt et al., 2010; Bzdek et al., 2010; Bzdek et al., 2011; Erupe et al., 2010b; Qiu et al., 2011; Zhao et al., 2011) and potentially organic acids (Zhang et al., 2004; Barsanti et al., 2009). Ongoing research aims to resolve if this amine chemistry contributes to the discrepancy between predicted and observed new particle formation rates (Bzdek et al., 2010; Bzdek et al., 2011; Berndt et al., 2010; Benson et al., 2011; Erupe et al., 2010b; Zhao et al., 2011), but the research is analytically challenging due to the trace nature of the atmospheric matrix.

NR$_3$ and NH$_3$ are emitted to the gas phase from a wide variety of anthropogenic and natural processes (Ge et al., 2011). The largest sources are thought to be degradation of natural organic matter (Gibb et al., 1999; Mopper and Zika, 1987; Van Neste et al., 1987), animal husbandry and agricultural emissions (Mosier et al., 1973; Rabaud et al., 2003; Schade and Crutzen, 1995; Kuhn et al., 2011; Traube et al., 2011), biomass burning, industrial incineration, and sewage treatment (Finlayson-Pitts and Pitts, 2000; Leach et al., 1999). Numerous other sources have been identified, but are important only on local scales (Ge et al., 2011; Seo et al., 2011). Of emerging concern are fugitive emissions of amines or amine-functionalized compounds employed in CO$_2$-capture applications (e.g. monoethanolamine (MEA)) that would increase the atmospheric burden of these compounds (Veltman et al., 2010; Heydari-Gorji et al., 2011; Vaidhyanathan et al., 2010; Mac Dowell et al., 2011; Lee et al., 2011). The most common and abundant atmospheric NR$_3$ are: methylamine (MA), ethylamine (EA), dimethylamine (DMA), diethylamine (DEA),
trimethylamine (TMA) and triethylamine (TEA). Many quantitative measurements of these and other NR$_3$ have been made. Ge et al. (Ge et al., 2011) report a total of 150 amine species that have been found in air samples from all studies to date. Relative gas phase ratios of NH$_3$:NR$_3$ near sources can range from 100:1 to more than 1000:1, typically with NH$_3$ mixing ratios on the order of ppbv (µg m$^{-3}$) and NR$_3$ at pptv (ng m$^{-3}$) (Barsanti et al., 2009; Gibb et al., 1999; Gronberg et al., 1992; Kuhn et al., 2011; Mosier et al., 1973; Schade and Crutzen, 1995). Recently, qualitative identification of amines has been common in atmospheric particulate samples due to innovations in particle mass spectrometry (Silva and Prather, 2000; Angelino et al., 2001; Tan et al., 2002; Denkenberger et al., 2007; Smith et al., 2008; Pratt et al., 2009; Smith et al., 2010; Rehbein et al., 2011; Zhao et al., 2011). The gaseous bases can enter the particulate phase as salts (denoted R$_3$NH$^+$) by several processes. They can undergo reactive uptake with acidic molecular clusters (Kurten et al., 2008; Loukonen et al., 2010; Bzdek et al., 2010; Bzdek et al., 2011) and secondary inorganic aerosol (Zhao et al., 2011; Facchini et al., 2008; Muller et al., 2009; Wang et al., 2010; Qiu et al., 2011; Forster et al., 2007) or they can undergo oxidation to form less volatile products that condense on to existing aerosol (Silva et al., 2008; Angelino et al., 2001; Zahardis et al., 2008). Field data supporting laboratory observations of these processes, however, are limited (Creamean et al., 2011; Junninen et al., 2010; Markovic et al., 2012). Furthermore, few methodologies are capable of monitoring amines quantitatively in the gas and/or particle phase on timescales of an hour or less without significant sample manipulation (Chang et al., 2003). Atmospheric gas and particulate samples typically require long collection periods to reach quantities detectable by GC-MS (Akyuz, 2007; Key et al., 2011), LC-MS (Huang et al., 2009; Key et al., 2011; Rampfl et al., 2008), capillary electrophoresis (Rampfl et al., 2008; Riviello and Harrold, 1993; Fekete et al., 2006; Dabek-Zlotorzynska and Maruszak, 1998) or IC (Facchini et al., 2008; Makela et al., 2001; Muller et al., 2009). Most analytical methodologies entail complex extraction and derivatization procedures to improve detection limits, but also decrease sample throughput capabilities, limit application in continuous monitoring strategies, introduce the possibility of sampling artifacts, reduce analyte recovery, and require dedicated operators and significant operation costs. IC separations have recently seen increased use in quantitative online techniques. However, online detection methodologies using IC have not yet reported separation and detection of the full suite of the most commonly emitted amine compounds listed above (Chang et al., 2003) and often struggle to detect them at relevant levels.
in the atmosphere, let alone in both phases (Erupe et al., 2010a; Facchini et al., 2008; Murphy et al., 2007; Sorooshian et al., 2008; Li et al., 2009). In addition, the complications in resolving methyl and ethyl amines from each other and the remaining water-soluble cations in atmospheric samples, have received limited discussion. In this work, we describe the application of ion chromatography to the offline analysis of size-resolved particle samples (Section 2.2.4.2) and the online analysis of simultaneous hourly gas and particle samples using the Ambient Ion Monitor Ion Chromatograph, AIM-IC, (Section 2.2.4.3).

2.2 Experimental

2.2.1 Materials and Chemicals

HPLC grade aqueous and stock solutions of MA (40 % w/w), DMA (40 % w/w), TMA (45 % w/w), EA (71 % w/w), DEA (>99.5 % w/w), TEA (100 %), MEtA (> 99.99 %) were purchased from Sigma-Aldrich (Oakville, ON). Ethanol (95 %) was purchased from Commercial Alcohols (Brampton, ON) and ultrapure deionised water (18.2 MΩ) was produced in house with a Barnstead™ Easypure® RoDi system (VWR, Mississauga, ON). Premixed analytical standards for inorganic cations (Li⁺, Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺) and eluent generator cartridges of MSA were purchased from Dionex Corporation (Sunnyvale, CA). Standard solutions were prepared by serial dilution in deionised water and stored at 4 °C. Calibration ranges for each cation are as follows: Li⁺ (8 – 800 ng), Na⁺ (32 – 3200 ng), NH₄⁺ (64 – 6400 ng), K⁺ (32 – 3200 ng), Mg²⁺ (32 – 3200 ng), Ca²⁺ (160 – 16000 ng), methyl and ethyl amines (0.8 – 800 ng), MEtA (5 – 1000 ng).

2.2.2 Instrumentation

2.2.2.1 Ion Chromatograph

Separation of the inorganic cations and alkyl amines listed in Section 2.2.1 was accomplished using a Dionex ICS-2000 system. The IC houses a dual piston pump fitted with a pressure transducer and pulse dampener. High purity eluent is generated from 18.2 MΩ deionised water passing through a degassing unit, followed by a reagent-free eluent generation system, and a constantly regenerated trap column before acquiring the sample and entering the separation columns. A trace cation concentrator column (TCC-ULP1, 5 mm x 23 mm i.d.) was used to
preconcentrate standards and samples loaded by autosampler (Dionex AS40, 6.6 mL aqueous sample, injection rate: 1 mL min\(^{-1}\)) prior to analysis, except in the case of the AIM-IC samples where 5 mL aqueous samples were collected and injected at 1 mL min\(^{-1}\) via an onboard 5 mL syringe pump (Markovic et al., 2012). Two separate methods have been developed for the separation of the cations of interest using the Dionex CS17 (250 mm x 4 mm i.d.) and CS12A (250 mm x 4 mm i.d.) cation exchange columns fitted with a CG17 (50 mm x 4 mm i.d.) or CG12A (50 mm x 4 mm i.d.) guard column by gradient elution with methanesulfonic acid (MSA). The effluent from the analytical column passes through a CSRS® 300 suppressor operating in recycle mode prior to entering the heated digital conductivity detector. Analyte peaks are visualized and integrated using the Chromeleon® v6.8 software package with the following parameters set: locked baseline, 0.001 µS min peak area threshold, and 1 x 10\(^{-4}\) µS sensitivity.

2.2.3. CS17 and CS12A Chromatography

Development of the chromatography programs discussed here was based on the step-wise gradient methods recommended by Rey and Pohl (Rey and Pohl, 1996, 2003) for both columns (published in the Dionex hardware manuals) since they have shown good selectivity for some alkyl and aromatic amines. The CS12A column is standard hardware on the AIM-IC monitoring systems, while the CS17 was chosen for amine selectivity (Rey and Pohl, 2003). The better separation of Na\(^+\) and NH\(_4^+\) reported for this column is of particular analytical utility when collecting atmospheric particulate samples in coastal regions where significant loadings of sea salt can be expected. The Na\(^+\)-NH\(_4^+\) resolution and moderate amine selectivity are the basis for exploring the ability of this stationary phase to also resolve alkyl amines as opposed to the CS15 which has been more specifically developed for separation of Na\(^+\)-NH\(_4^+\) at extreme mass ratios (Rey et al., 1998; Pohl et al., 1999).

Subsets of the alkyl amines were successfully resolved from NH\(_4^+\) on the CS12A and CS17 columns (Rey and Pohl, 1996, 2003) and from the same inorganic cations of interest here. However, the potential for coelution between methylamines and ethylamines was not explored. For continuous online atmospheric sampling it is essential to resolve these alkyl amines as they are emitted in greatest quantity to the atmosphere (Ge et al., 2011) and, therefore, are most likely to be detected and quantified erroneously by ion chromatography and conductivity detection if
coelution occurs (Murphy et al., 2007; Sorooshian et al., 2008). We explored variations of the published step-wise programs, modifying them to linearly ramped gradient elution programs covering wider ranges of MSA eluent strengths and flow rates. Eluent strengths ranging from 0.25 – 12 mM were investigated on the CS17 column and 1 – 80 mM on the CS12A column, with flow rates from 0.6 – 1 mL min⁻¹ and 1 – 1.2 mL min⁻¹ respectively (Figure 2-1). A comprehensive list of the trial conditions can be found in Appendix A (Tables 2-S1 and 2-S2). The separation run time was limited by the AIM-IC interface, which requires sample resolution in 25 minutes or less when performing online analysis of gas and particulate matter samples on an hourly basis, to allow at least 5 minutes of column equilibration at initial conditions before the next run. To evaluate the impact of this constraint, some separations were performed under more moderate eluent concentration gradients and elution times of 40 and 60 minutes to yield higher selectivity and resolution for all analytes. However, no significant improvements were found when operating exploring resolution within these limitations (Figure 2-1).

The analytical performance of the optimized separations were then determined on each column and is reported in Section 2.3.1. For the CS17 column, the optimized separation (Figure 2-1A, Trial 1) ran a linear MSA gradient the first 11.55 min from 2-8 mM, then increased linearly again to 10 mM over the next 4.45 min and equilibrated back to 2 mM for 9 min at an eluent flow rate of 1.0 mL min⁻¹. Column and detector temperatures were maintained at 30 °C and the suppressor current at 30 mA. For the CS12A column, higher eluent strengths were used due to higher capacity of the stationary phase (Figure 2-1B, Trial 8). Over the first 12 min the MSA concentration was ramped linearly from 5-10 mM and then from 10-80 mM over the next 10 min and allowed to equilibrate back to 5 mM according to an exponential decrease in MSA (time constant = 0.5 min) over the final 3 min of the 25 min run at a flow rate of 1.2 mL min⁻¹. Column and detector temperatures were maintained at 30 °C and the suppressor current at 110 mA. On both columns, 5 minutes of equilibration were performed before the next sample injection.
Figure 2-1. Method development results for the resolution of atmospherically relevant alkyl amines and inorganic cations by cation exchange chromatography via A) gradient elutions on Dionex CS17 analytical column and B) gradient elutions on a Dionex CS12A. The specific conditions of each separation can be found in Appendix A in Tables 2-S1 and 2-S2. The elution programs in A) use lower linear concentration gradients in trials 1 – 3, an isocratic elution at 6 mM MSA in Trial 4, decreasing flow rates with stronger concentration gradients in trials 5 – 8 and a model step-wise gradient in trial 9, based on (Rey and Pohl, 2003). The gradient in trial 1 was the best achieved (Section 2.2.3). The elution programs in B) use progressively lower starting concentration in trials 1 – 6 (20 – 1 mM MSA), increased slightly for trials 7 (3mM) and 8 (5mM) and increased flow rates (1.0 – 1.2 mL min⁻¹) in trials 5 and 6 to reach the optimum separation in trial 8 (Section 2.2.3)
2.2.4 Field Observations of Gaseous and Particulate Amines

2.2.4.1 Egbert, ON - Site Description

The AIM-IC system was deployed from 15 October to 2 November 2010 in Egbert, ON (44°13’50.44”N, 79°46’58.21”W) at the Environment Canada Centre for Atmospheric Research Experiments (CARE). Egbert is an agricultural and semi-forested location 80 km north of Toronto, ON. Our instrumentation sampling site was located on an open ridge 125 m from a rural road with air masses originating alternately between northern and southern Ontario, at times including air from Michigan and the northeastern United States. Ambient temperatures during this collection period had a range of -1 – 18 °C. Analytical instrumentation was housed in a trailer and connected to a sampling interface on a tower 20 m away.

2.2.4.2 Micro Orifice Uniform Deposit Impactor (MOUDI)

The general methodology for MOUDI filter preparation has been described previously (VandenBoer et al., 2011). Briefly, the MOUDI operates at a flow rate of 30 L min\(^{-1}\) with 10 stages with 50 % cut-off points at particle aerodynamic diameters of: 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.1, and 0.056 μm. In this deployment, particle collection by impaction used an aluminum foil substrate. A back filter made of quartz fibre was used to collect particles less that 0.056 μm in the air sample at the exit of the MOUDI sampler. However, the back filters were prone to sampling artifacts by adsorption of gases, a problem previously reported (Hanson et al., 2011). Therefore they are not included in the data analysis and discussion. The MOUDI sample was collected for 23 h from 1 – 2 November 2010, the foils were transferred to individual sealed petri dishes and extracted within 24 hours. Foil substrates were extracted by room temperature sonication in deionized water, filtered and analyzed by ion chromatography using the CS17 method. Field blanks were collected by transporting filters to and from the sampling site to determine method detection limits. Extraction efficiencies for this method are known to be quantitative for water-soluble compounds (Kouvarakis et al., 2002).

2.2.4.3 Ambient Ion Monitor Ion Chromatograph (AIM-IC)

The AIM-IC consists of an AIM 9000D air sampler (URG Corp., Chapel Hill, NC) and two ICS-2000 ion chromatography systems (Dionex, Sunnyvale, CA). A newly developed sampling platform for the AIM-IC was deployed during this campaign compared to previous reports (Ellis
et al., 2011; VandenBoer et al., 2011). The particle impactor, parallel-plate wet denuder, and particle supersaturation chamber assembly were housed in a separately mountable aluminum box connected to the syringe pumps of the AIM 9000D air sampler by 20 m of PFA lines (0.16 cm o.d., 0.076 cm i.d., Upchurch Scientific, Oak Harbor, WA). The particle impactor allows only atmospheric particles with aerodynamic diameters less than 2.5 microns (PM$_{2.5}$) to be sampled by the system. To prevent freezing, the liquid lines were accompanied by a heated line and sheathed in 3 cm commercial pipe insulation while the aluminum box was insulated and outfitted with a ceramic heater. Extensive details of this inlet design and the operation of the AIM-IC can be found in Markovic et al. (Markovic et al., 2012). The inlet assembly was mounted on a 3 m tower for continuous sampling of particulate and gaseous acids and bases. Offline calibrations were carried out during the campaign by injecting aqueous standards to the IC system to track the response of the concentrator columns. Instrument backgrounds and detection limits were determined by carrying out in-field, online measurements of zero grade air (AI 0.0 UZ-T, Praxair Inc., Mississauga, ON) over a 24 hour period.

2.3 Results and Discussion

2.3.1 General Characteristics of Separation Methodologies

The separation time was limited to 25 min on both analytical columns in order to successfully make hourly online observations of gas and particle composition (i.e. 30 min per sample per phase). The MSA gradient programming achieved good resolution and reproducibility in that time (Tables 2-1 and 2-2). Method sensitivity, linearity, and accuracy were determined from calibrations (n = 6) performed with standard solutions (n ≥ 5). Accuracy was determined by relative error between the calibration slopes for each analyte (Skoog et al., 1998). It was also found that the relative error within individual slope determinations was insignificant in comparison to the average relative error between calibration slopes. All of the analytes show linear responses over the calibration range except for NH$_4^+$. The reproducibility of retention times and peak areas demonstrates very high stability of the separation methods even when running the IC systems continuously over hundreds of samples. Relative standard deviations in retention times were generally less than 2 %, consistent with previously established IC separations (Chang et al., 2003; Erupe et al., 2010a; Li et al., 2009). The cation NH$_4^+$ has a non-
linear response across the calibration range and is best quantified by fitting the calibration points with Equation 1.

\[ y = (-A) + \sqrt{A^2 + Bx} \]

Where \( y \) is the conductivity detector response, \( x \) is the total concentration of weak acid or base and its conjugate, and \( A \) and \( B \) are the fitting coefficients. This fit was determined as the most representative way to describe the response of the conductivity detector to \( \text{NH}_4^+ \) based on the chemistry occurring in the suppressor outflow (see Appendix A for derivation and modeled chemistry).

Our calibration approach evaluates the offset in the \( \text{NH}_4^+ \) calibration by analysis of at least three deionized water blanks (same volume as the samples) to offset the calibration signals. Therefore, the blank point lies at the origin for all calibrations. Across the calibrated mass loading range the fit passes more reliably near the origin according to Equation 1, which is the ideal response in this range.

Detection limits for all analytes were calculated as the mole, mixing ratio or mass loading equivalents of three times the standard deviation in the background signal at the retention time of the amine in consideration (MacDougall and Crummett, 1980). For offline applications, the detection limits were determined from sequential injections of deionised water or method blanks, while online detection limits were determined from sampling air free of gaseous and particulate water soluble analytes (Tables 2-1 and 2-2). The \( \text{R}_3\text{NH}^+ \) detection limits, ng or sub-ng, were comparable to those found for \( \text{Li}^+ \) and \( \text{Ca}^{2+} \), an order of magnitude or more greater in sensitivity than the other inorganic analytes. In online samples, only a lower limit of quantitation can be determined since ionic analyte is lost if the preconcentration column capacity is exceeded (i.e. there is at least the quantity reported, possibly more). Saturation and breakthrough effects during preconcentration occur in samples with high ionic strength (\( \mu \text{g mL}^{-1} \)) or large volumes (> 10 mL), respectively (Markovic et al., 2012). Saturation and excessive volume conditions were avoided in offline samples by dilution whenever possible and 5 mL samples are routinely collected by the AIM-IC. Furthermore, the capacity of the concentrating columns declines after 1200 – 1400 injections. As the concentrating columns age they experience a decline in ion
retention, reducing instrument sensitivity and increasing the limits of detection by a factor of two or more (see discussion in Section 2.3.3).

The two methodologies developed were based on interferences potentially encountered in the real atmosphere, particularly in particulate samples. The CS12A method was developed for use in environments where high loadings of Na$^+$ are expected (e.g. coastal regions) since this column performs well in separation of Na$^+$ from NH$_4^+$. The CS17 method was developed for use under all other atmospheric conditions and focuses on the resolution of NR$_3$/R$_3$NH$^+$. Note that K$^+$ is infrequently detected in PM$_{2.5}$ samples and arises from specific point sources (Section 2.3.1.2). Overall, the methods presented here are the first to comprehensively address the application of ion chromatography to the full suite of NR$_3$/R$_3$NH$^+$ expected to be present in atmospheric samples. These amines are thought to be emitted in the greatest quantity to the atmosphere (Ge et al., 2011) and therefore unambiguous identification by interfacing this method with mass spectrometry, or other efficient analytical means, is critical. This has been indicated in a number of other studies (Murphy et al., 2007; Zhao et al., 2011), but has not been overcome here. On either column, the separation of TMA and DEA cannot yet be accomplished in less than 25 minutes. However, the sensitivities afforded by sample preconcentration of the ions, followed by suppressed conductivity detection, improves instrument detection limits by up to two orders of magnitude over previous ion chromatographic methods (Murphy et al., 2007; Sorooshian et al., 2008; Sellegrini et al., 2005; Erupe et al., 2010a) and makes IC competitive with methods that require derivatization and/or mass selective detection (Akyuz, 2007; Fekete et al., 2006; Huang et al., 2009; Key et al., 2011).
Table 2-1. Separation characteristics of CS12A column according to methodology in S.2.2.3. Retention time statistics - retention time (\(t_r\)), standard deviation in retention (\(\sigma_t\)), relative standard deviation (\(%\ RSD\ t_r\)) and baseline peak width (\(w\)) - are reported from online (\(n > 800\)) and offline sampling. Resolution of all compounds was determined between the specified cation and the one previous. Resolution between amines considers only the presence of amines in a chromatographic sample. Sensitivity, precision and linearity were determined from the instrument response across standard solutions of 0.0005 – 0.1 µg for amines and 0.005 to 3 µg for the other cation analytes (\(n = 6\)). Sensitivities reported for NH\(_4\)\(^+\) are determined from the A term of Equation 1 (see Appendix A). Volumes of injected samples are omitted due to the sample preconcentration columns utilized. Limits of detection were determined from three times the standard deviation in: replicate blank injections for the IC (\(n = 12\)), calibration blanks or zero air sample analysis for the AIM-IC system in both the gas (ppt) and particle (ng m\(^-3\)) components (\(n = 8\)), and in replicate method blank extracts for 24 hour samples by MOUDI (pg m\(^-3\)) (\(n = 3\)). Detection limits are not reported for the AIM-IC mineral cations in the gas channel since they are not gaseous components of the atmosphere.

<table>
<thead>
<tr>
<th>#</th>
<th>Cation</th>
<th>(t_r) (min)(^\dagger)</th>
<th>(\sigma_t) (min)</th>
<th>%RSD (t_r)</th>
<th>(w) (min)</th>
<th>Resolution</th>
<th>Sensitivity (µS min mol(^{-1}))</th>
<th>Accuracy (%)</th>
<th>Linear (R^2)</th>
<th>IC Only (mol)</th>
<th>AIM-IC (ppt)</th>
<th>MOUDI (ng m(^-3))</th>
<th>MOUDI (pg m(^-3))</th>
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<tr>
<td>1</td>
<td>Li(^+)</td>
<td>6.64</td>
<td>0.03</td>
<td>1.00</td>
<td>0.45</td>
<td>-</td>
<td>-</td>
<td>2.00E+08</td>
<td>0.5</td>
<td>0.999</td>
<td>1.50E-12</td>
<td>-</td>
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<td>-</td>
<td>2</td>
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<td>1.44</td>
<td>0.53</td>
<td>1.0</td>
<td>-</td>
<td>1.04E+08</td>
<td>9.5</td>
<td>-</td>
<td>1.32E-09</td>
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<td>130</td>
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<td>1.26</td>
<td>0.20</td>
<td>0.2</td>
<td>-</td>
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<td>-</td>
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<td>0.8</td>
<td>0.8</td>
<td>5.40E+08</td>
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<td>0.999</td>
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<td>1.5</td>
<td>0.47</td>
<td>0.9</td>
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<td>8.06E+07</td>
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<td>11</td>
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<td>0.16</td>
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<td>0.998</td>
<td>7.39E-13</td>
<td>-</td>
<td>0.16</td>
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\(^\dagger\) = Retention times collected for this statistical analysis were performed after several hundred analytical runs on the CS12A shown in Figure 2-1. Deterioration of the analytical column during these analyses has resulted in the earlier retention times reported in this table, while maintaining the depicted separations.
Table 2-2. Separation characteristics of CS17 column according to methodology in S.2.2.3. Retention time statistics - retention time ($t_r$), standard deviation in retention ($\sigma_{t}$), relative standard deviation (% RSD $t$) and baseline peak width (w) - are reported from online (n > 800) and offline sampling. Resolution of all compounds was determined between the specified cation and the one previous. Resolution between amines considers only the presence of amines in a chromatographic sample. Sensitivity, precision and linearity were determined from the instrument response across standard solutions of 0.0005 – 0.1 µg for amines and 0.005 to 3 µg for the other cation analytes (n = 6). Sensitivities reported for NH$_4^+$ are determined from the A term of Equation 1 (see Appendix A). Volumes of injected samples are omitted due to the sample preconcentration columns utilized. Limits of detection were determined from three times the standard deviation in: replicate blank injections for the IC (n = 12), calibration blanks or zero air sample analysis for the AIM (n = 3). Detection limits are not reported for the AIM-IC mineral cations in the gas channel since they are not gaseous components of the atmosphere.

<table>
<thead>
<tr>
<th>#</th>
<th>Cation</th>
<th>$t_r$ (min)$^\dagger$</th>
<th>$\sigma_{t}$ (min)</th>
<th>%RSD $t$</th>
<th>Width (min)</th>
<th>Resolution</th>
<th>Sensitivity</th>
<th>Accuracy</th>
<th>Linear</th>
<th>IC Only</th>
<th>AIM-IC</th>
<th>MOUDI</th>
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<td>Li$^+$</td>
<td>8.65</td>
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<td>2</td>
<td>0.77</td>
<td>-</td>
<td>-</td>
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<td>0.998</td>
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<td>0.8</td>
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<td>1.25</td>
<td>-</td>
<td>-</td>
<td>3.67E+07</td>
<td>1.4</td>
<td>0.996</td>
<td>8.17E-11</td>
<td>-</td>
</tr>
</tbody>
</table>

$^\dagger$ = Retention times collected for this statistical analysis were performed after several thousand analytical runs on the CS17 shown in Figure 2-2. Deterioration of the analytical column during these analyses has resulted in much earlier retention times reported in this table, while separation efficiency has been maintained.

$^+$ = Preliminary assessment of monoethanolamine resolution and sensitivity by the CS17 optimized elution method, statistics given in the caption are not applicable to this compound.


2.3.1.1 CS12A Separation, Sensitivity and Limits of Detection

This analytical method was developed for environments with high mass loadings of analyte compounds, particularly Na⁺ and NH₃/NH₄⁺. The CS12A column has a higher density of exchange sites compared to the CS17, providing more stability in retention time and peak shape for potentially high levels of interfering species. In coastal or polluted agricultural areas, with sample masses of NH₃/NH₄⁺ above 2 µg and masses of Na⁺ above 1.5 µg, these properties are essential for accurate quantitation of NH₃/NH₄⁺. Figure 2-2 displays the best separation of the full suite of methyl and ethyl amines and inorganic cations using the CS12A method. Resolution, sensitivity and detection limit characteristics of the separation are listed in Table 2-1. The resolution of Na⁺ and NH₄⁺ is substantially better on the CS17 column than on the CS12A (1.2 versus 1.0) due to narrower peak widths in the low concentration range. As the mass loadings of Na⁺ and NH₄⁺ increase, the peaks eluting from the CS12A column retain their Gaussian shape due to the higher capacity of this column. It can therefore be used more accurately than the lower capacity CS17 to quantify these compounds at high mass loadings in coastal and rural environments. The smaller relative standard deviation of the retention times for the CS12A compared to the CS17 in Na⁺ (0.98 % vs 3 %) and NH₄⁺ (1.44 % vs 5 %) exemplify this difference.

However, the CS12A method performs in a less than ideal fashion for the resolution of the alkyl amines. MA and EA coelute (they can only be partially resolved from NH₄⁺, but not from each other) and the coelution is mass loading dependent (Figure 2-2). DMA shows valley-to-valley resolution (R = 0.8). DEA and TMA coelute, but are nearly baseline resolved from K⁺ (R = 0.9) and completely resolved from Mg²⁺ (R = 5.4). TEA is baseline resolved (R = 2.2) from Ca²⁺. Previous reports of alkyl amine identification and separation by IC methods have omitted the contribution of inorganic cations in their separation optimization. In this study, an emphasis was placed on the separation of the alkyl amines with relevant constituents of atmospheric particulate matter like NH₄⁺ and K⁺. The incorporation of the wide range of matrix constituents found in atmospheric samples into the developed methods reflects the real atmosphere more accurately (Chang et al., 2003; Erupe et al., 2010a; Li et al., 2009). Furthermore, selecting for only the methyl or ethyl amine families would overlook potential interferences due to coeluting species from both substituent groups (Ge et al., 2011). The CS12A method is semi-quantitative if only
methyl or ethyl amine groups exist in a given sample of mixed composition depending on the relative loading of $\text{NH}_4^+$. Improvement in the selectivity of the CS12A column between $\text{NH}_4^+/\text{MA}/\text{EA}$ may be possible by increasing the column temperature and analyte mass transfer, as shown by Rey and Pohl (1996), or using columns with smaller diameters (e.g. 2 mm i.d. or capillary columns) to limit band broadening by diffusion, which will give narrower and better resolved peaks. While these options were not specifically investigated in this study, they will be explored in our future use of the CS12A stationary phase for the analysis of atmospheric samples.

**Figure 2-2.** Resolution of most abundant water-soluble aerosol cation constituents using the Dionex CS12A cation exchange column. Eluent: MSA, linear gradients from 5 - 10 mM over 12 min, 10 - 80 mM over 10 min, 10 – 5 mM by exponential decrease (time constant = 30 s) over 3 min and 5 min of column equilibration. Eluent flow: 1.2 mL min$^{-1}$. Detection: suppressed conductivity. Suppressor: recycle mode, 110 mA. Column and detector temperatures: 30 °C. Inorganic cations (low standard - dashed trace/high standard – dash-dotted trace), methyl and ethyl amines (black solid trace) separations are shown separately. 1 – lithium (8/160 ng), 2 – sodium (32/640 ng), 3 – ammonium (64/1280 ng), 4 – methylamine (160 ng), 5 – potassium (32/640 ng), 6 – ethylamine (160 ng), 7 – dimethylamine (160 ng), 8 – trimethylamine (160 ng), 9 – diethylamine (160 ng), 10 – triethylamine (160 ng), 11 – magnesium (32/640 ng), 12 – calcium (160/3200 ng). Background contamination of sodium, ammonium, potassium, magnesium and calcium in the deionised water used to prepare the amine standards is the source of the small peaks observed in the amine traces.
The CS12A sensitivities range from $8 \times 10^7$ to $5 \times 10^8$ µS min mol$^{-1}$ including NH$_4^+$, which has a non-linear detection response due to the partial ionization of NH$_3$/NH$_4^+$ in the detector (Section 2.3.1, Equation 1). Less reproducibility is observed in repeat calibrations for NH$_4^+$, giving it an accuracy of 9.5%. The CS17 method has better sensitivity than the CS12A towards MA, EA and TEA by a factor of 1.5 to 3.5, and less sensitivity towards DEA and TMA by a factor of 0.6 and 0.7, respectively. Compounds other than NH$_4^+$ show very good calibration reproducibility and quantitative determinations are accurate to within 5%. This calibration consistency includes MA, DMA, TMA and TEA. However, EA and DEA show more retention time variability at 12% and 14%. EA and DEA also show reduced calibration linearity (0.960 and 0.941), potentially due to reduced dissociation if the higher concentration standards are near the non-linear region after suppression (see Appendix A). We expect the increased variability is arising due to random error when pipetting the low viscosity/high volatility stock solutions for the NR$_3$. The errors with the CS17 column are 10% and 3.5% and R$^2$ linear least-squares regression fit values of 0.995 and 0.996, respectively. The use of solid salts or dispensing pure/aqueous standards by mass to prepare calibration standards for NR$_3$ is expected to significantly improve accuracy.

The CS12A AIM-IC detection limits for NR$_3$ are at the sub-pptv and pg m$^{-3}$ levels, which are well below the anticipated atmospheric concentrations of these compounds in source regions. However, lack of selectivity complicates speciated quantitative detection. MA and EA always coelute with each other and with NH$_4^+$ at high loadings (Figure 2-2). Coelution of TMA and DEA could not be avoided. This coelution could result in a non-detection of the analytes, or require calculations of a combined mass loading analysis of coeluting compounds (see Section 2.3.2). Therefore, the requirements for sensitivity versus selectivity in sample analysis must be considered before employing this methodology. The CS17 method addresses many of the drawbacks of the CS12A, at the expense of a decrease in sensitivity and utility in samples with high Na$^+$ and/or NH$_4^+$ mass loadings.

2.3.1.2 CS17 Separation, Sensitivity and Limits of Detection

The best separation of the full suite of NR$_3$ and inorganic cations most frequently encountered in ambient particulate matter was achieved using the CS17 method (Figure 2-3). Comparison of the separations on the CS17 to the CS12A methodology in Figure 2-2 shows that, unless extenuating circumstances are encountered (e.g. high loadings of NH$_4^+$ and/or Na$^+$), this method has much
better selectivity between the methyl and ethyl amines and the remaining mineral cations. Unfortunately, the issue of TMA+DEA coelution persists on this column. The retention times of single standards of TMA and DEA are observably different (15.05 min and 15.07 min), but not significant in terms of resolution. The CS17 method is ideal for gaseous atmospheric sampling focused on NR₃, since K⁺ is not found in the gas phase. It is also infrequently encountered in atmospheric particulate samples, thereby increasing the reliability of the MA, EA, and DMA quantification. However, K⁺ is known to be present in particulate matter in air masses influenced by biomass burning (Amici et al., 2011), fireworks (Chang et al., 2011), or mineral dust (Flament et al., 2011) up to several µg m⁻³. In such instances, quantitation of MA and EA may be compromised if mass loadings of K⁺ are high enough to affect peak resolution.

Figure 2-3. Resolution of most abundant water-soluble aerosol cation constituents using the Dionex CS17 cation exchange column. Eluent: MSA, linear gradients from 2 – 8 mM over 11.55 min, 8 – 10 mM over 4.45 min, 10 – 2 mM over 9 min and 5 min of column equilibration. Eluent flow: 1.0 mL min⁻¹. Detection: suppressed conductivity. Suppressor: recycle mode, 30 mA. Column and detector temperatures: 30 °C. Inorganic cations (short dashed trace), methyl amines (black trace) and ethyl amines (long dashed trace) separations are shown separately. Peaks: 1 – lithium (1 ng), 2 – sodium (40 ng), 3 – ammonium (80 ng), 4 – methylamine (100 ng), 5 – potassium (40 ng), 6 – ethylamine (100 ng), 7 – dimethylamine (100 ng), 8 – trimethylamine (100 ng), 9 – diethylamine (100 µg), 10 – triethylamine (100 µg), 11 – magnesium (40 ng), 12 – calcium (200 ng). Background contamination of sodium, ammonium, potassium, magnesium and calcium in the deionised water used to prepare the amine standards is the source of the small peaks observed in the amine traces. Note that the retention time axis starts at 10 minutes.
The resolution, sensitivity and detection limit characteristics of the CS17 method are listed in Table 2-2. The ability to partially resolve and quantify MA, EA and NH$_4^+$ is the most noticeable improvement offered by this column (Figure 2-3). Also, DMA, TMA+DEA and TEA are more resolved from each other and the mineral cations. The exchange capacity of the CS17 is smaller than that of the CS12A and the comparison of retention variability was assessed under similar atmospheric analyte mass loadings. The retention time variabilities for the mineral cations increased by a factor of 2 – 4, except Ca$^{2+}$, and are a manifestation of the wide range of mass loadings on the lower capacity column. In contrast, the improvement in the selectivity of the alkyl amines reduces the variability in their retention times by a factor of 5 – 7.5, except for MA which only improves by a factor of 1.5. The detection limits of the CS17 method, while higher than the CS12A by about an order of magnitude are still at the pptv and ng m$^{-3}$ levels. These detection limits are still well within the range of anticipated atmospheric concentrations, even far from emission sources. The exception to this loss of sensitivity is the detection of TEA, which is improved on the CS17 by about an order of magnitude and still retains full baseline resolution. A preliminary investigation of the CS17 method to resolve monoethanolamine (MEtA), a proposed agent for industrial CO$_2$ capture, showed that the protonated base coelutes with K$^+$. It also exhibits the lowest sensitivity of all amines tested to date by a factor of 30 (Table 2-2) since it is the weakest organic base in this suite of analytes. Due to the poor selectivity of the CS12A, a comparison was not made for MEtA. Finally, this method shows high accuracy of quantitation for all the cationic species investigated, with less than 15 % error except for NH$_4^+$ which was 20 %. Clearly, targeted online analysis of atmospheric amines is best accomplished with the CS17 column.

2.3.2 Reconciliation of Quantitation Error in Coeluting Compounds

Our chemical analysis of online IC samples may sacrifice selectivity to meet the time constraints of the sampling timeframe of the AIM-IC (vide supra). Coelution prevents identification of the NR$_3$ species present and their relative contributions to the observed peak area. Prior investigations of alkyl amines by IC have acknowledged this problem and addressed it in several ways: not quantifying the amines, reporting measurements only for species which do not coelute, or neglecting to determine if coelution is a problem for environmental samples. The first two approaches sacrifice the data entirely, while the latter could lead to inaccuracies in the
quantitative analyses of real samples by IC. However, if the instrument sensitivity for the interferents is thoroughly characterized, a lower limit estimation of the total amount of coeluting analytes can be made by assuming that the observed signal is derived from the analyte with the highest instrumental sensitivity. We refer to the error in this calculation as *underestimation uncertainty* in the subsequent discussion. For example, both methods have a higher sensitivity for DEA over TMA. Calculating the moles of the analytes detected as though they are just DEA provides a lower limit on the summed quantity of both analytes. This conservative approach avoids an overestimation bias, provides constraints on chemical analyses and is useful in overcoming the current method separation limitations. Using this approach, the underestimation uncertainty on the quantitative analysis for TMA+DEA mass by CS17 methodology is up to 20 % and 12 % in the CS12A method. This error is in addition to the analytical errors listed in Tables 2-1 and 2-2. For the CS12A coelution of MA and EA, the response would be calculated as though the peak is only MA, giving an underestimation error of up to 56 %. Clearly, separation of these compounds would be a more ideal approach in improving analytical accuracy, but may not be an option when undertaking long-term online monitoring at sites heavily influenced by NH$_3$/NH$_4^+$ and Na$^+$.

### 2.3.3 AIM-IC and MOUDI Field Observations – Egbert, ON

The deployment of the AIM-IC in Egbert, ON utilized the CS17 methodology for real-time monitoring of NH$_3$/NH$_4^+$ and NR$_3$/R$_3$H$^+$. A more comprehensive discussion of these observations is available in the Appendix A. The observations made during this campaign showed little variation in the number and concentrations of amines detected. DMA was detected consistently with gaseous mixing ratios ($\pm 1 \sigma$) between 1 - 10 pptv (mean = 6.5±2.1 pptv) and particulate mass loadings (mean = 0.1±0.2 ng m$^{-3}$) at or below the 0.5 ng m$^{-3}$ campaign detection limits. TMA+DEA were near the 1 pptv gaseous detection limit and frequently below the 1.2 ng m$^{-3}$ (mean = 1±0.6 ng m$^{-3}$) particulate detection limit. The TMA+DEA measurement error shows that the conservative lower limit approach places the data very close to the detection limits. Clearly, further measurements are required to better understand the spatial and temporal variations observed for NR$_3$ species. The observations of NH$_3$ (Figure 2-4) show mixing ratios ranging from a background of about 0.5 ppb up to 4 ppb (mean = 1.21±0.72 ppbv), with several large plumes influencing the ground site during the campaign. These plumes are also coincident with
increases in the observed mass loadings of NH$_4^+$, which ranged from the detection limit (0.017 µg m$^{-3}$) to 3 µg m$^{-3}$. The temperatures during the observation period (-1 – 18 °C) are expected to reduce the total emission rates of NH$_3$ and NR$_3$ if they are being emitted via volatilization. However, a temporal correlation between NH$_3$ and NR$_3$ would be expected if they were co-emitted from the same source (Hanson et al., 2011), but this was not observed by linear regression ($R^2 = 0.0003$). Thus, the observed DMA and TMA+DEA may be emitted separately from NH$_3$ in this region and partially explain the low variability in mixing ratios for the NR$_3$. The detection limits shown in Figures 2-4 and 2-5 were much lower for the CS17 during this campaign due to clean backgrounds in the AIM-IC system compared to the values listed from multiple assessments of offline injections and online zero air sampling listed in Table 2-2 (see Section 2.2.4.3 for details).

**Figure 2-4.** Gaseous mixing ratios of ambient alkyl amines (left axis) and NH$_3$ (right axis) collected at Egbert, ON in October 2010. The absolute mixing ratios of TMA + DMA were very low and have been multiplied by a factor of 10. Solid lines represent the ambient measurements and the dashed lines the limits of detection.
Figure 2-5. Particulate mass loadings of ambient alkyl amines (left axis) and NH$_4^+$ (right axis) collected at Egbert, ON in October 2010. Solid lines represent the ambient measurements and the dashed lines the limits of detection.

The distribution of amines in the size-segregated MOUDI aerosol sample showed EA was detected in significant diameter-weighted mass in the 0.056 – 0.1 and 0.32 – 0.56 µm size bins at 0.032 and 0.082 ng m$^{-3}$, respectively. DMA was detected on all but two stages and showed a bimodal distribution between the accumulation and coarse mode, with nearly equal mass loadings in each, consistent with previous size-resolved observations in marine and continental environments (Facchini et al., 2008; Makela et al., 2001; Muller et al., 2009; VandenBoer et al., 2011). TMA+DEA were detected in every size fraction, averaging around 3.5 ng m$^{-3}$ between 0.054 – 2.5 µm and showing more variability in the coarse mode. The integrated mass of all amines up to 2.5 µm was 2.38 ng m$^{-3}$. If this total mass of amines was distributed evenly over the entire 23 hr sampling period, the particulate loadings would be near or below the detection limits of the AIM-IC (2.5 - 3.5 ng m$^{-3}$), which samples only PM$_{2.5}$, and is consistent with the mass loadings below or near the detection limit at the end of the online observation period (Figure 2-6). Results of modeling and laboratory studies, which use NH$_3$/NR$_3$ from 100 – 400, indicate that the overall competition to neutralize acidic aerosol strongly favours NH$_4^+$ over R$_3$NH$^+$ (Murphy et al., 2007; Barsanti et al., 2009; Bzdek et al., 2011). The detection of DMA and TMA+DEA in both online and MOUDI samples suggests that the periodic observations of these compounds in the ambient particulate matter is real, although the mass loadings cannot be directly compared
since the observation periods did not overlap. The particle/gas ratio (±1σ) of TMA+DEA was 0.54±0.39, on average, compared to 0.01±0.04 for DMA. TMA+DEA shows both higher mass loadings in the MOUDI samples and higher particle/gas ratios in the AIM-IC data, compared to DMA. This is consistent with other observations made with this method (VandenBoer et al., 2011) and suggests either a greater preference for the particle phase for TMA+DEA or possibly a rapid condensed phase loss mechanism for DMA.

**Figure 2-6.** Mass distribution of particulate alkyl amine loadings at Egbert, ON from a 23-hr MOUDI sample. Alkyl amine mass enhancement was observed in the ultrafine (< 0.1µm), fine (0.1 – 1 µm) and coarse (1 – 100 µm) particle populations. Nodes of zero mass near 0.1 and 2.5 µm are typically seen in atmospheric aerosol.
2.4 Conclusions

Two methods have been developed that use simple online sample preconcentration and conductivity suppression prior to detection to improve selectivity and detection limits of NR$_3$/R$_3$NH$^+$. Detection limits of these methodologies have improved over traditional methods by up to 2 orders of magnitude in hourly samples, reaching pptv and ng m$^{-3}$ levels, the known range of amines found in atmospheric samples (Ge et al., 2011). The CS17 methodology showed the best selectivity for the suite of NR$_3$/R$_3$NH$^+$ investigated, although increasing column temperature or decreasing bore size may improve both methods and will be explored in future investigations.

Overall, the field data presented show that the use of the AIM-IC and MOUDI systems (via the CS17 analytical method) allow for a comprehensive analytical approach to the quantitation of the full suite of methyl and ethyl amines in an agricultural environment where ambient concentrations are at the pptv/ng m$^{-3}$ levels. In order to enhance selectivity and sensitivity of the AIM-IC system, refitting the hardware to accommodate a variable sampling time chipset followed by collecting and resolving all cationic species over longer periods could be undertaken. Such hardware has only recently become available. Alternatively, as analytical columns increase in selectivity (e.g. capillary IC columns) for the resolution of NR$_3$, shorter collection times could be employed in regions with higher mixing ratios of NR$_3$ to probe atmospheric partitioning thermodynamics more explicitly. Integration of mass-selective detection could improve both factors, with the trade-off of increased instrumentation and operation costs.
2.5 Acknowledgements

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CHAPTER THREE

Size distribution of alkyl amines in continental particulate matter and their online detection in the gas and particle phase

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Author Contributions:

T. C. VandenBoer and A. Petroff collected and analyzed MOUDI samples. A. Petroff designed the MOUDI methodology and data analysis of collected samples. M. Z. Markovic developed ion chromatography methods and collected data by AIM-IC during the online observation period. T. C. VandenBoer performed data analysis for all samples and prepared this manuscript under the guidance of J. G. Murphy.
Abstract
An ion chromatographic method is described for the quantification of the simple alkyl amines: methylamine (MA), dimethylamine (DMA), trimethylamine (TMA), ethylamine (EA), diethylamine (DEA) and triethylamine (TEA), in the ambient atmosphere. Limits of detection (3σ) are in the tens of pmol range for all of these amines, and good resolution is achieved for all compounds except for TMA and DEA. The technique was applied to the analysis of time-integrated samples collected using a micro-orifice uniform deposition impactor (MOUDI) with ten stages for size resolution of particles with aerodynamic diameters between 56 nm and 18 μm. In eight samples from urban and rural continental airmasses, the mass loading of amines consistently maximized on the stage corresponding to particles with aerodynamic diameters between 320 and 560 nm. The molar ratio of amines to ammonium (R₃NH⁺/NH₄⁺) in fine aerosol ranged between 0.005 and 0.2, and maximized for the smallest particle sizes. The size-dependence of the R₃NH⁺/NH₄⁺ ratio indicates differences in the relative importance of the processes leading to the incorporation of amines and ammonia into secondary particles. The technique was also used to make simultaneous hourly online measurements of amines in the gas phase and in fine particulate matter using an Ambient Ion Monitor Ion Chromatograph (AIM-IC). During a ten day campaign in downtown Toronto, DMA, TMA + DEA, and TEA were observed to range from below detection limit to 2.7 ppt in the gas phase. In the particle phase, MAH⁺ and TMAH⁺ + DEAH⁺ were observed to range from below detection limit up to 15 ng m⁻³. The presence of detectable levels of amines in the particle phase corresponded to periods with higher relative humidity and higher mass loadings of nitrate. While the hourly measurements made using the AIM-IC provide data that can be used to evaluate the application of gas-particle partitioning models to amines, the strong size-dependence of the R₃NH⁺/NH₄⁺ ratio indicates that using bulk measurements may not be appropriate.
3.1 Introduction

Recent ambient measurements of amines in the gas and particle phase have prompted research into their role in the formation and growth of atmospheric particulate matter. Amine emissions have been detected from animal husbandry operations (Mosier et al., 1973; Schade and Crutzen, 1995), decomposition of organic matter on land and in the oceans (Van Neste et al., 1987; Gibb et al., 1999; Miyazaki et al., 2010; Sorooshian et al., 2009), and from biomass burning and the incineration of waste (Finlayson-Pitts and Pitts, 2000; Chang et al., 2003). In the future, increased emissions may arise from the proposed use of amines as CO\textsubscript{2} scrubbing agents in industrial applications (Veltman et al., 2010). Ge et al. (2011b) provide a detailed review of all known amine emissions and sinks in the atmosphere. The amines emitted in the greatest quantity to the atmosphere are thought to be the simple alkyl amines: methylamine (MA), dimethylamine (DMA), trimethylamine (TMA), ethylamine (EA), diethylamine (DEA) and triethylamine (TEA). Collectively, these alkyl amines will be referred to as NR\textsubscript{3} throughout the discussion that follows. The greatest direct source of NR\textsubscript{3} has been suggested to be animal husbandry operations, with global emissions estimated at 0.15 TgN a\textsuperscript{-1}, leading to amine concentrations up to hundreds of ppb near animal housing and waste storage areas (Schade and Crutzen, 1995; Rabaud et al., 2003). Gaseous amine levels in marine and background continental environments are generally on the order of < 1 – 100 ppt (Mopper and Zika, 1987; Gronberg et al., 1992; Gibb et al., 1999; Chang et al., 2003; Akyuz, 2007). Amines are often present concomitantly with NH\textsubscript{3}, typically at mixing ratios 1 - 3 orders of magnitude smaller (Gronberg et al., 1992; Chang et al., 2003; Huang et al., 2009; Veltman et al., 2010). The primary sinks of the simple alkyl amines are thought to be oxidation by OH and wet deposition via rain scavenging. Lifetimes for NR\textsubscript{3} against oxidation are on the order of a few hours to a day in the presence of atmospherically relevant concentrations of OH, compared to a month for NH\textsubscript{3} (Atkinson et al., 1977b; Atkinson et al., 1977a; Pitts et al., 1978; Atkinson et al., 1997). Oxidation by O\textsubscript{3} can also be an appreciable sink for secondary and tertiary amines (lifetimes of hours to days) in a polluted environment (Finlayson-Pitts and Pitts, 2000). Elucidation of the fast loss mechanisms for NR\textsubscript{3} led to a decline in research concerning their role in the formation of nitrosamines in the 1970s, however, their importance in the particle phase has gained renewed appreciation in the last decade of research.
There are several different scenarios in which amines might become associated with atmospheric aerosols. A comprehensive review of the thermodynamic properties of amines that govern their gas-particle partitioning can be found in Ge et al. (2011a). Amines are likely candidates for forming aminium salts with atmospheric acids resulting in the formation of secondary aerosol mass (Pratt et al., 2009). With pKa values ranging from 9.25 - 10.98 (pKaNH₃ = 9.25 (Seinfeld and Pandis, 2006)) and similar water solubilities to NH₃ (Gibb et al., 1999; Mackay et al., 2004), amines can partition to and neutralize aqueous acidic particles. The partitioning and reactive uptake mechanisms of NH₃ in to particles and aqueous solutions have been well explored (Mozurkewich, 1993; Donaldson, 1999; Dinar et al., 2008) and impacts on aerosol properties continue to be investigated. Amines detected in an aqueous particle or as a salt are likely to be protonated since they are strong bases, and will therefore be denoted with an appended H⁺ in the following discussion. The degree to which amines may be scavenged by aqueous aerosols is likely dependent on the effective pH of the solution and the pKa of the amine (R1). The degree of protonation will have a buffering effect on isolating amine molecules from exchange back to the gas phase (Pankow, 2003):

\[
\text{NR}_3(\text{g}) \rightleftharpoons \text{NR}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{R}_3\text{NH}_3^+(\text{aq}) + \text{OH}^-\text{(aq)} \quad (R1)
\]

Second, subsequent reaction with acidic solution components could lead to the formation of insoluble salts:

\[
\text{R}_3\text{NH}_3^+(\text{aq}) + \text{A}^-\text{(aq)} \rightarrow \text{R}_3\text{NHA}_3(\text{s}) \quad (R2)
\]

Where A⁻ is a conjugate base in solution and HA is the parent acid. Third, gas phase acid-base reactions to form an insoluble salt:

\[
\text{NR}_3(\text{g}) + \text{HA}(\text{g}) \rightarrow \text{R}_3\text{NHA}_3(\text{s}) \quad (R3)
\]

Finally, reactive uptake and displacement of ammonia from pre-existing salts may also occur:

\[
\text{NR}_3(\text{g}) + (\text{NH}_4)_n(\text{A})_m(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + (\text{NH}_4)_{n-1}(\text{R}_3\text{NH})(\text{A})_m(\text{s}) \quad (R4)
\]
Modeling and laboratory studies indicate that amines can enter the condensed phase by all the routes proposed above in Reactions 1 - 4 (Mmereki et al., 2000; Murphy et al., 2007; Barsanti et al., 2009; Ge et al., 2011a) and suggest that small chain (C1-C3) alkyl amines may be important for the initiation of particle formation events and growth of nucleating aerosols. Junninen et al. (2010) used an atmospheric pressure interface time-of-flight mass spectrometer to collect ambient atmospheric ions from the gas phase, including molecular clusters where the formation of inorganic aminium salts might be occurring. Preliminary results showed homologous series of alkyl amines and pyridines in their samples in addition to the typical HNO3 and H2SO4 acids. These results are indicative of gas phase reaction prior to particle formation between the trace constituents, supporting the hypothesis that amines may promote H2SO4 nucleation through the formation of non-volatile salts. Further support for this from laboratory investigations was made by Berndt et al. (2010) in a series of lab experiments comparing the nucleation rate of H2SO4 as a function of relative humidity (RH) and the presence of NH3 and a surrogate amine, tert-butylamine. The results showed that both basic species had significant and similar promoting effects on the nucleation rate of H2SO4. However, the number density of amine was also two orders of magnitude smaller than NH3, showing that given typical near-source atmospheric concentrations of both gases, they may have similar impacts on nucleation rates. Alkyl amines, like ammonia, will form salts (R2, R3) with inorganic and organic acidic species due to their basic nature (Angelino et al., 2001; Murphy et al., 2007; Barsanti et al., 2009). Laboratory studies have shown that in some instances, alkyl amines can displace ammonium from inorganic salts to form aminium salts (R4) (Murphy et al., 2007; Lloyd et al., 2009; Bzdek et al., 2010). Smog chamber experiments have also shown that the oxidation of amines can lead to the formation of secondary organic aerosol (SOA) or basic products that can also form salts with atmospheric acids (Murphy et al., 2007). The relative importance of these processes for the incorporation of amines in ambient fine particulate matter is not yet clear.

Amines have been detected frequently in atmospheric fine and ultrafine particulate matter by a number of online techniques, including: aerosol time-of-flight mass spectrometry (AToF-MS) (Angelino et al., 2001; Pastor et al., 2003; Denkenberger et al., 2007), compact time-of-flight aerosol mass spectrometry (C-ToF-AMS) (Murphy et al., 2007; Sorooshian et al., 2008), atmospheric pressure interface time-of-flight mass spectrometry (APi-TOF-MS) (Junninen et al.,
thermal desorption chemical ionisation mass spectrometry (TDCIMS) (Smith et al., 2008; Smith et al., 2010), and particle into liquid sampler ion chromatography (PILS-IC) (Murphy et al., 2007; Sorooshian et al., 2008; Sorooshian et al., 2009). The $\text{R}_3\text{NH}^+$ contribution of 10 - 47 % of the positive ions in 8-10 nm particles sampled by Smith et al. (2010) indicates that amines may be a significant constituent of newly formed particles. Their frequent presence as detectable fractions of fine mode particles, specifically that which may not be fully neutralized by ammonia, indicates that they may also contribute to condensational growth through reactive uptake (Murphy et al., 2007). A drawback of many mass spectrometric observations is that they cannot provide quantitative mass loadings of specific $\text{R}_3\text{NH}^+$ constituents. For example, AMS response factors for various aminium salts have been reported to range from 5 – 10 times that of ammonium nitrate depending on the composition of the salt, thereby limiting this method to amine identification only (Silva et al., 2008). Similarly, Murphy et al. (2007) showed that the exchange of ammonium for methylaminium in sulphate particles enhanced the collection efficiency by the C-TOF-AMS significantly due to changes in the physical properties of the particles. Simultaneous observations by C-TOF-AMS and PILS-IC by Sorooshian et al. (2008) bridged the gap in producing quantitative amine information in addition to detailed knowledge of particle composition. They found instances of EA and DEA in sub-micrometer particles at mass loadings of 50 – 200 ng m$^{-3}$ (~20 % of the mass loading of $\text{NH}_4^+$), indicating that alkyl amines can contribute significantly to the neutralizing capacity of particles less than 1 µm in diameter. More recently, Huang et al. (2009) described an online derivatization method for the detection of NR$_3$/R$_3$NH$^+$, and reported simultaneous NH$_3$/NH$_4^+$ and MA/MAH$^+$ observations near a small animal farm in New York on the order of 10 ppb and 100 ppt, respectively.

The presence of DMAH$^+$ in nucleation event particles reported by Mäkelä et al. (2001) provided the first indication of a potentially important role that amines might play in particle formation and growth. The presence of DMAH$^+$ was also reported in the 10 nm fraction for non-event particulate collected, but at much lower mass loadings. Further investigations of the size-distribution of particle phase amines have shown the presence of DEAH$^+$ and MAH$^+$ in the 0.01 – 1.0 µm range in marine aerosols, their presence being attributed to biogenic sources metabolizing the labile fraction of water-soluble organic carbon (Facchini et al., 2008; Muller et al., 2009; Miyazaki et al., 2010). A number of size-segregated investigations of the composition
of particles impacted by marine sources have recently reported a ubiquitous contribution of amines to the detectable fraction of the sub-micrometer aerosol water-soluble organic nitrogen (WSON) (Makela et al., 2001; Facchini et al., 2008; Muller et al., 2009; Violaki and Mihalopoulos, 2010). However, their size-dependent composition in continental air masses has not been reported to date, despite the fact that most known amine sources are terrestrial. In general, online and offline observations of $R_3NH^+$ have shown them to be only a small fraction of the total reduced nitrogen in particles, but because many amines are stronger bases than ammonia their presence may significantly impact aerosol composition and properties. An increase in effective basicity of aqueous aerosol has been proposed as a way to reduce the free fraction of protons and therefore significantly alter pH values even in the presence of relatively small $R_3NH^+$ concentrations (Angelino et al., 2001; Pratt et al., 2009). Simultaneous measurements of amines and other chemical constituents and physical properties of aerosol can help to understand their impact on the pH of aerosols, which can affect particle chemistry, e.g. SOA formation. To improve our understanding of the mechanisms governing amine exchange between the gas and particle phases, online methods to separately observe and quantify individual amines in both phases with high time resolution are required. The applicability of simple thermodynamic equilibrium algorithms to describe gas-particle partitioning also needs to be evaluated by size-resolved measurements of amine mass loadings in the sub-micrometer range.

We present observations of the simple alkyl amines: MA, DMA, TMA, EA, DEA and TEA quantitatively measured using ion chromatography. This method was used for the analysis of size-resolved micro-orifice uniform deposit impactor (MOUDI) samples using a protocol described in Section 3.2.1. In Section 3.2.2, we describe the method developed to resolve and detect this suite of alkyl amines at pmol levels using ion chromatography. We also employed the technique for simultaneous hourly gas and particle phase measurements using continuous online sampling with an Ambient Ion Monitor - Ion Chromatography (AIM-IC) system (Section 3.2.3). In Section 3.3 we discuss the observations made using these methods including the size-resolved water-soluble composition of particulate matter in urban and rural locations in south-western Ontario (Section 3.3.1) and gas and PM$_{2.5}$ observations from Toronto, Canada in July of 2009 (Section 3.3.2).
3.2 Methods

3.2.1 MOUDI Filter Preparation and Field Operation

To ensure particle collection filters were free of residual organic compounds and salts prior to use in particle collection, the following pretreatment methodology was used to ensure their removal. The filters (47 mm, 0.1 mm thickness, 5 – 6 µm pore size, PTFE, Savillex, MN) were soaked for 24 h in ethanol with intermittent shaking, rinsed thoroughly with 100 mL of deionised water, placed in a drying rack and dried for 12 h. The filters were then transferred to clean petri dishes (50 mm, Pall Canada Ltd, Ville St. Laurent, QC) and stored in a light shielded container for 24 h to equilibrate. The filters were mounted on the collection stages of the MOUDI (Model 110, MSP, MN) (Marple et al., 1986) for online sampling just prior to collection.

The MOUDI was used to collect size-resolved aerosol samples in urban and rural environments in Ontario periodically from July 2009 – May 2010. Specifically, these locations were: on the roof of the Physical Geography Building of the University of Toronto (43° 39' 37.60" N, 79° 23' 47.42" W), on top of a 3 m shed in Dorset (45° 14' 14.96" N, 78° 53' 47.33" W) and an open grass field in Lambton Shores (43° 9' 43.41" N, 81° 56' 4.33" W), under a rain shelter that allowed for free ventilation. The sampling interval varied between 20 and 46 hours according to the level of particulate matter reported in real time by the Ontario Ministry of the Environment (http://www.airqualityontario.com/history/summary.cfm). The MOUDI was operated at a flow rate of 30 L min⁻¹ with 10 stages at the following 50 % cut-off points for the particle aerodynamic diameters: 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.1, and 0.056 µm. Due to pump limitations, no back filters were used to collect particles less that 0.056 µm. No denuders were used upstream of the MOUDI in order to limit possible size-dependent particle losses on the denuder walls. These losses can occur both in Aitken mode particles (< 0.1 µm) by Brownian diffusion (Ye et al., 1991) and in the coarse mode particles (> 2.5 µm) by impaction (Spurny, 1999). Filter extracts were obtained by room temperature sonication in 10 mL of deionized water for 1 h, filtration through a 0.45 µm PTFE membrane (Pall Ion Chromatography Acrodisc®, VWR International, Mississauga, ON) and dilution to a final volume of 15 mL with deionised water. While extraction efficiencies were not explicitly determined in this study, the method is known to be nearly quantitative for water soluble compounds (Kouvarakis et al., 2002). Extracts were then analyzed by ion chromatography using one or both of the methods described below.
Field blanks were collected by transporting filters to and from the sampling site and subjecting them to the same extraction and analysis procedures. The application of ion chromatography to offline MOUDI samples had method detection limits of sub-ng m\(^{-3}\) for the particulate samples collected.

### 3.2.2 Ion Chromatography (IC)

Chromatographic resolution of anions and cations was performed using two Dionex ICS-2000 systems operating with reagent-free eluent and suppressed conductivity detection. Anions were separated using a gradient elution method on an AS19 hydroxide-selective anion exchange column fitted with a trace anion concentrator column (TAC-ULP1), guard column and an ASRS\(^{®}\) 300 conductivity suppressor using KOH as an eluent. A linear gradient from 1-20 mM was employed over the first 12 min, with a linear increase to 85 mM over the next 6 min and then equilibrated back to 1 mM for the final 7 min of the total 25 min run time at a flow rate of 1 mL min\(^{-1}\). Two separate methods have been developed for the separation of cations using the Dionex CS17 and CS12A cation exchange columns fitted with a trace cation concentrator column (TCC-ULP1), CG17 or CG12A guard column and a CSRS\(^{®}\) 300 suppressor by gradient elution with methanesulfonic acid (MSA). For the CS17, a linear gradient was used at an eluent flow rate of 1.0 mL min\(^{-1}\) from 2-8 mM over the first 11.55 min, increased to 10 mM over the next 4.45 min and then equilibrated back to 2 mM for 9 min prior to the next run. For the CS12A column, higher eluent strengths were used due to the increased capacity of the column for ion exchange. Over the first 12 min the MSA concentration was ramped linearly from 5-10 mM and then from 10-80 mM over the next 10 min and allowed to equilibrate back to 5 mM over the final 3 min of the 25 min run at a flow rate of 1.2 mL min\(^{-1}\). Column temperatures, in all cases, were maintained at 30 °C.

All chemicals used were reagent ACS or HPLC grade. Stock solutions of MA (40 % w/w), DMA (40 % w/w), TMA (45 % w/w), EA (71 % w/w), DEA (> 99.5 % w/w), TEA (100 %), formic acid (1 mg/mL), acetic acid (1 mg/mL) and oxalic acids (1 mg/mL) were purchased from Sigma-Aldrich (St. Louis, MO). Ethanol (95 %) was purchased from Commercial Alcohols (Brampton, ON) and deionised water (18.2 MΩ) was produced in house with a Barnstead™ Easypure\(^{®}\) RoDi system (VWR, Mississauga, ON). Premixed analytical standards for inorganic anions (F\(^{-}\), Cl\(^{-}\),
NO$_2^-$, Br$^-$, NO$_3^-$, SO$_4^{2-}$, PO$_4^{3-}$) and cations (Li$^+$, Na$^+$, NH$_4^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$) and eluent generator cartridges of KOH and MSA were supplied by Dionex Corporation (Sunnyvale, CA).

3.2.3. Ion Chromatography for Resolution of Amines and Inorganic Cations in Atmospheric Samples

Previous investigations of aliphatic amines have used ion chromatography for the detection and quantification of amines in atmospheric samples (Murphy et al., 2007; Chang et al., 2003; Facchini et al., 2008; Sorooshian et al., 2008; Sorooshian et al., 2009; Erupe et al., 2010), but none has reported the full range of species measured in this study. The design of commercial columns has been focused on the separation of inorganic cations, limiting their ability to fully resolve them from protonated organics, such as alkyl amines, especially where their solvated properties are similar. Over the last decade their use in the separation of a number of amines has been demonstrated (Chang et al., 2003; Murphy et al., 2007; Erupe et al., 2010). The amine resolution achieved using the methodology we have developed on the Dionex CS17 column using preconcentration is shown in Fig. 3-1. TMA and DEA are not resolved and, henceforth, will be referred to as TMA + DEA / TMAH$^+$ + DEAH$^+$, a complication that has been reported previously for Dionex columns (Murphy et al., 2007). Under conditions of higher concentration, poor separation of Na$^+$ and NH$_4^+$ and poor peak shapes become problematic for retrieving accurate peak area integrations, particularly in offline sample analysis.

![Figure 3-1](image)

**Figure 3-1.** Sample CS17 chromatogram of particles collected on the 440 ± 120 nm MOUDI stage at Dorset, ON. Peaks are: 1 - sodium, 2 - ammonium, 3 - potassium, 4 - dimethylamine, 5 - trimethlyamine and diethylamine, 6 - triethylamine, 7 - magnesium, 8 - calcium.
For analysis of online and offline samples from environments impacted by high loadings of water-soluble cations, a method using a Dionex CS12A column was developed. Figure 3-2 shows the increased resolution between Na$^+$ and NH$_4^+$, but persistent coelution of TMA and DEA. Coelution of MA and EA with NH$_4^+$ in the CS12A method occurred at relative concentration ratios 5 times lower than in our CS17 methodology, making it more prone to NH$_4^+$ interfering in R$_3$NH$^+$ detection.

**Figure 3-2.** Chromatograms of particles collected on the 780 ± 200 nm MOUDI stage at Lambton Shores, ON separated on (A) CS12A and (B) CS17 columns. Compounds are: 1 - sodium, 2 - ammonium, 3 - potassium, 4 - dimethylamine, 5 - trimethylamine and diethylamine, 6 - magnesium, 7 - calcium.
The ability to resolve and quantify amines in an atmospheric sample, therefore, depends not only on the absolute amount of amine present, but on the relative amounts of amine and ammonia. In an ideal situation, the sampling period will be sufficiently long to collect enough amine to exceed the detection limit, but short enough that NH$_4^+$ will not coelute. Instrument and method detection limits for ion chromatography analysis were calculated as an absolute number of moles using the slope and three times the standard deviation in the area of the background conductivity observed in sequential blank samples or field blanks at the elution time of the analyte of interest (MacDougall and Crummett, 1980). Positive instrument response for target analytes at these concentrations was confirmed by offline injection of aqueous standards. The instrument detection limits for the alkyl amines were < 50 pmol and NH$_4^+$ ~ 1 nmol. Detection limits for all other inorganic analytes are < 500 pmol.

For offline samples, such as the MOUDI samples collected in this study, dilution and reanalysis to improve separation and quantitation of amines and inorganics was utilized to overcome coelution in samples with high concentrations of ammonium. However, this is not an effective strategy for online sample analysis. Since NH$_3$/NH$_4^+$ arise from similar sources as NR$_3$/R$_3$NH$^+$ (Van Neste et al., 1987; Schade and Crutzen, 1995), separation of these species is an issue that must be addressed. For online observations, the best approach was the CS17 methodology described above. Note that the retention times of analytes here are at later values than those shown in Figure 2.3 (Chapter 2) since these analyses were performed using a different CS17 column installed on a different ICS-2000. A change in total volume from different plumbing schemes and column capacity between CS17 columns are likely responsible for these differences.

### 3.2.4 Online Detection by URG-AIM

The operational principles of the AIM-IC 9000D (URG, Chapel Hill, NC) system have been previously described (Ellis et al., 2011). Briefly, the AIM-IC system employs two online ion chromatography systems for the simultaneous detection of cations and anions from gas and particle samples concentrated from a continuous flow of ambient air. In our system, the air sample is pulled at 3.0 L min$^{-1}$ through a minimum inlet length constructed of Teflon-coated aluminum and fitted with an impactor assembly to select particles with an aerodynamic diameter of less than 2.5 µm. Gases are stripped from the air stream by passing through a liquid parallel
plate denuder with continuously replenished solvent flowing across the surface. The particles in the air flow are constrained into a supersaturated steam condensation coil and cyclone assembly and grown hygroscopically for collection as an aqueous solution. The sample flows containing the soluble gas and particle analytes are separated into equal aliquots for anion and cation chromatographic analyses every hour following 60 minutes of ambient sampling.

The AIM-IC was deployed utilizing the CS17 columns and operated according to the separation methodology described in Section 3.2.2 to monitor ambient air in downtown Toronto, ON at the University of Toronto’s St. George Campus from 26 June – 3 July 2009. Hourly detection of MA, DMA, TMA, EA, DEA and TEA at the ppt and ng m\(^{-3}\) levels was achieved with the AIM-IC system methodology. Quantities were determined from offline injections of known aqueous standards of the analytes of interest across the relevant range of observed atmospheric concentrations. Background levels of all compounds detected by the AIM-IC were determined by overflowing the inlet with high purity zero air and subtracting the average peak area acquired over 8 h from the peaks observed while sampling ambient air. If background peaks were not observed for a particular species, the 5 lowest points of the time series were taken as blank values, the average of which was subtracted from the ambient dataset. Simultaneous gas phase NH\(_3\) measurements were made using a quantum cascade tunable infrared diode laser absorption spectrometer (QC-TILDAS) system (Aerodyne, USA) (Ellis et al., 2010).

### 3.3 Results and Discussion

#### 3.3.1 Size-Resolved Particulate Amines

Eight samples were collected using the MOUDI under the conditions listed in Table 3-1. The fine aerosol fraction (PM\(_{1.8}\)) collected by the MOUDI is determined by summing the six lowest MOUDI size bins. The total water soluble mass was determined from the sum of the species quantified by ion chromatography. The fraction of amines in the total mass of soluble PM\(_{1.8}\) (% \(m_{\text{sal}}\)) ranges from < 1 % to 9.1 % across our observations. The amine mass fraction in PM\(_{2.5}\) (% \(m_{\text{tot}}\)) was calculated by dividing PM\(_{1.8}\) amines by the total mass loading of PM\(_{2.5}\) obtained from the nearest Ontario Ministry of Environment air quality monitoring station for the period of observation. The sum of the particulate alkyl amines was never more than 1 % of the PM\(_{2.5}\) aerosol mass loadings. PM\(_{1.8}\) mass loadings of all the amines, denoted as R\(_3\)NH\(^+\), and NH\(_4^+\) are
shown in Table 3-1. While the R₃NH⁺ mass loadings only span one order of magnitude among the samples, the mass loading of NH₄⁺ varies by a factor of 60. The final column includes the molar ratio of the sum of amines to ammonium (R₃NH⁺/NH₄⁺) in PM₁₈, the variability of which depends more on the mass loading of NH₄⁺ than that of R₃NH⁺.

The presence of amines was detected throughout the fine mode (0.056 – 1.8 µm) in all cases for DMAH⁺ and TMAH⁺+DEAH⁺. The presence of TEAH⁺ was found in 5 samples and MAH⁺ near the instrument LOD in the sample collected at Dorset, ON. In all cases the mass loadings or moles of TMAH⁺+DEAH⁺ were calculated assuming everything was DEA⁺. DEA has a larger Henry’s law constant and pKa value, indicating that it would be more likely to partition to an aqueous particle than TMA under conditions of similar gas phase mixing ratios (Ge et al., 2011a). Furthermore, the dissociation constants (K_p) calculated by Murphy et al. (2007) for the formation of aminium nitrate salts from gas phase precursors (R3) were at least three orders of magnitude lower for DEA than TMA. DEA showed higher analytical sensitivity under the CS17 method described in Section 3.2.2 and has a lower molecular mass than TMA. Therefore, the values we have calculated and report here are the lower estimate for the sum of these species. The true values could be up to 23 % greater for mass and moles if an appreciable fraction of the sample is actually TMA.
Table 3-1. MOUDI size-resolved particulate matter sample collection and analysis information. Eight samples were collected over the course of a year using either a rotating or fixed set of MOUDI stages. Mass loadings of PM$_{1.8}$ amines in the particulate MOUDI samples are reported and then calculated as a function of measureable water soluble mass ($m_{\text{sol}}$), total mass ($m_{\text{tot}}$), as well as relative to PM$_{1.8}$ NH$_4^+$.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Location</th>
<th>Start Date mm/dd/yyyy</th>
<th>Sample Time (h)</th>
<th>Amines Detected</th>
<th>R$_3$NH$^+$ (ng m$^{-3}$)</th>
<th>$m_{\text{sol}}$ (%)</th>
<th>$m_{\text{tot}}$ (%)</th>
<th>NH$_4^+$ (ng m$^{-3}$)</th>
<th>R$_3$NH$^+$ NH$_4^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^\uparrow$</td>
<td>Toronto, ON</td>
<td>07/21/2009</td>
<td>24</td>
<td>DMA, TMA+DEA</td>
<td>16</td>
<td>0.78</td>
<td>0.31</td>
<td>470</td>
<td>0.014</td>
</tr>
<tr>
<td>2$^\uparrow$</td>
<td>Toronto, ON$^*$</td>
<td>08/07/2009</td>
<td>22</td>
<td>DMA, TMA+DEA, TEA</td>
<td>55</td>
<td>9.10</td>
<td>0.98</td>
<td>90</td>
<td>0.11</td>
</tr>
<tr>
<td>3$^\uparrow$</td>
<td>Toronto, ON$^*$</td>
<td>08/07/2009</td>
<td>22</td>
<td>DMA, TMA+DEA, TEA</td>
<td>35</td>
<td>7.52</td>
<td>0.68</td>
<td>90</td>
<td>0.17</td>
</tr>
<tr>
<td>4$^\uparrow$</td>
<td>Dorset, ON</td>
<td>08/14/2009</td>
<td>46</td>
<td>MA, DMA, TMA+DEA, TEA</td>
<td>42</td>
<td>7.98</td>
<td>0.71</td>
<td>120</td>
<td>0.14</td>
</tr>
<tr>
<td>5$^\uparrow$</td>
<td>Toronto, ON</td>
<td>08/16/2009</td>
<td>24.25</td>
<td>DMA, TMA+DEA, TEA</td>
<td>81</td>
<td>0.42</td>
<td>0.24</td>
<td>5210</td>
<td>0.0045</td>
</tr>
<tr>
<td>6$^{\beta}$</td>
<td>Toronto, ON</td>
<td>03/16/2010</td>
<td>29</td>
<td>DMA, TMA+DEA, TEA</td>
<td>35</td>
<td>0.88</td>
<td></td>
<td>740</td>
<td>0.011</td>
</tr>
<tr>
<td>7$^{\beta}$</td>
<td>Lambton Shores, ON</td>
<td>04/09/2010</td>
<td>24.25</td>
<td>DMA, TMA+DEA</td>
<td>19</td>
<td>0.48</td>
<td>0.74</td>
<td>790</td>
<td>0.0065</td>
</tr>
<tr>
<td>8$^{\beta}$</td>
<td>Lambton Shores, ON</td>
<td>04/10/2010</td>
<td>24</td>
<td>DMA, TMA+DEA</td>
<td>33</td>
<td>0.58</td>
<td>0.45</td>
<td>1320</td>
<td>0.0067</td>
</tr>
</tbody>
</table>

$^\uparrow$ = Indicates CS17 separation method
$^{\beta}$ = Indicates CS12A separation method
$^*$ = Samples collected simultaneously using fixed and rotating MOUDI setups. Differences in amine mass represent actual sampling variability for the MOUDI in atmospheric samples.
### 3.3.1.1 Aerosol Composition of Water-soluble Ionic Species

Figure 3-3 shows the composition of water-soluble particulate species, as a function of particle size at three different sampling sites. In all cases, the dominant cation at particle diameters less than 1.8 µm was NH$_4^+$, which nearly balanced the major anionic components of SO$_4^{2-}$, NO$_3^-$, formic, acetic and oxalic acids. Thus, the sub-micrometer aerosol we sampled were neutralized or nearly neutral, with respect to ion balance, in all cases. In some cases, amines were found to have important contributions to the total mass of the fine mode. Panel A displays a sample collected at Dorset, Ontario, a rural forest site, on 14 August 2009 with the air mass originating over south-western Ontario. Amines contribute about 5 % of the total water-soluble cation fraction in the accumulation mode aerosol from 0.056 - 1.8 µm. This sample was also particularly enhanced in formic, acetic and oxalic acids in addition to the dominant SO$_4^{2-}$ anion. The sample composition displayed in Panel B was collected from the roof of the Physical Geography Building at University of Toronto, a dense urban location, on 7 August 2009. The aerosol is neutralized in terms of NH$_4^+$-NO$_3^-$-SO$_4^{2-}$ throughout the accumulation mode, with < 5 % of the water-soluble cation fraction being contributed by amines. Ca$^{2+}$ and NO$_3^-$ dominate the coarse mode, likely as CaCO$_3$ with some Ca(NO$_3$)$_2$ from processing of lofted particles. The relative composition of this sample is typical for samples collected in downtown Toronto, although the magnitude of mass in the sample can vary considerably, particularly in the accumulation mode. The sample displayed in Panel C was collected from Lambton Shores, Ontario, a rural location, on 10 April 2010. The contribution of amines was insignificant to the aerosol neutrality, despite NO$_3^-$ representing about 30 % of the anion water-soluble fraction at the peak of the accumulation mode.

Ion chromatography cannot measure H$^+$ in solution, but it is assumed to balance most of the remaining negative ions in the PM$_{1.8}$. No significant unidentified peaks were observed in the cation or anion chromatographs. The dominant cation at particle diameters greater than 1.8 µm was Ca$^{2+}$, which is not balanced by a quantifiable anionic species. The most likely constituent that balances the observed Ca$^{2+}$ is HCO$_3^{-}$/CO$_3^{2-}$, which cannot be quantitatively detected by the sample handling and ion chromatographic methods used in this study. Ca(HCO$_3$)$_2$ and CaCO$_3$ are known to be major components of concrete and arise from surface erosion in urban environments. This is likely responsible for the large Ca$^{2+}$ signal seen in Panel B of Figure 3-3.
Figure 3-3. Mole equivalent distribution of major water-soluble ions in MOUDI samples. (A) Sample 4 collected in Dorset, (B) Sample 3 collected in Toronto (C) Sample 8 collected in Lambton Shores.
In Panels B and C, coarse mode nitrate was also observed. It has been well-documented that coarse mode nitrate can be formed by acid displacement reactions between HNO$_3$ and Ca(HCO$_3$)$_2$ and CaCO$_3$ to form Ca(NO$_3$)$_2$ (Goodman et al., 2000; Hanisch and Crowley, 2001; Bauer et al., 2004; Vlasenko et al., 2006; Liu et al., 2008), which further supports the presence of unmeasured carbonate in our samples. Despite being a small fraction of the total cation composition and the total aerosol mass, the alkyl amines measured may influence the effective pH of aqueous aerosols by several units (Pankow, 2003; Pratt et al., 2009), especially where they represent more than 1% of the water-soluble aerosol mass. Stronger basic properties compared to NH$_4^+$ make the amines better at limiting the H$^+$ freely available in solution, even when present in molar quantities more than an order of magnitude smaller than NH$_4^+$.  

### 3.3.1.2 Size-dependence of Alkyl Amine Mass

Size distributions of amines by mass in samples collected at Dorset, Toronto and Lambton Shores, ON are shown in the panels of Fig. 3-4. The size dependence of the alkyl amines shows that their mass maximizes most often in the accumulation mode. The amines detected in our samples maximized in the 320 - 560 nm size range in 7 of 8 samples. Often, only tens of ng m$^{-3}$ were observed in the size bin with the largest contributions from TMAH$^+$ + DEAH$^+$ and DMAH$^+$. The maximum mass loading of each amine detected in our samples and the size bin in which it maximized is given in Table 3-2. TEAH$^+$, when present, showed the most variability in the distribution of the mass throughout the aerosol populations we collected. In Sample 6 (collected in Toronto) the abundance of TEAH$^+$ was 14 ng m$^{-3}$, the highest we encountered in this sample set, and was found to maximize in the 3.2 – 5.6 µm size range.

The variety of amines detected changed based on sampling location and time of year. This could be due to changes in the source region of the air mass sampled, regional temperature and relative humidity, and seasonality as amine emissions are expected to increase with temperature and biological activity (Schade and Crutzen, 1995; Muller et al., 2009; Pratt et al., 2009). Figure 3-4A illustrates Sample 4 from Dorset, ON, which had the widest array of amines present in any sample collected. The sampled air mass originated over a region of south-western Ontario with a high density of agricultural activity, including animal husbandry, a likely source region for the primary emission of alkyl amines to the atmosphere.
Figure 3-4. Amine mass distributions as a function of particle diameter for (A) Sample 4 collected in Dorset, (B) Sample 3 collected in Toronto (C) Sample 8 collected in Lambton Shores, and (D) Sample 1 collected in Toronto.
Two samples, one displayed in Fig. 3-4C, were collected in this source region at Lambton Shores to investigate particulate amines in proximity to presumed sources. During the collection period, air originated over Michigan and the northern Great Lakes region of Ontario. Whether the amines we observed in Fig. 3-4C had partitioned from local emissions or were pre-existing components of transported aerosol is not possible to determine from these samples. The collected sample had 19 ng m$^{-3}$ of TMAH$^+$ + DEAH$^+$ in the 320 - 560 nm size bin, the highest detected mass of a single amine species in our samples. While the absolute mass loadings of amines seem comparable, or higher, in the downwind Dorset sample compared to the source region sample, it should be kept in mind that these samples were collected in the summer and spring, respectively. The seasonality of amine emissions and partitioning has been related to primary productivity (Muller et al., 2009; Sorooshian et al., 2009; Miyazaki et al., 2010) and local meteorology (Pratt et al., 2009). Online observations of both gas and PM$_{2.5}$ ionic, water-soluble composition could yield more information in identifying source regions and thermodynamic factors that govern the partitioning of amines.

**Table 3-2.** The maximum mass loading (ng m$^{-3}$) on a single stage, for each amine species quantified in the MOUDI sample. The median diameter (nm) of the size bin where each species maximizes is given in parentheses when it is not the 320-560 nm size bin. No amines were consistently detected in all size bins from 0.056 to 18 µm, so a range was not reported as the lower value would always be below the limit of detection. ND indicates the species was not detected on any stage of the MOUDI.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>MMA</th>
<th>DMA</th>
<th>TMA+DEA</th>
<th>TEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ND</td>
<td>4</td>
<td>3</td>
<td>ND</td>
</tr>
<tr>
<td>2</td>
<td>ND</td>
<td>5</td>
<td>11</td>
<td>1.3</td>
</tr>
<tr>
<td>3</td>
<td>ND</td>
<td>3</td>
<td>7</td>
<td>0.3</td>
</tr>
<tr>
<td>4</td>
<td>0.05</td>
<td>6</td>
<td>5</td>
<td>0.4</td>
</tr>
<tr>
<td>5</td>
<td>ND</td>
<td>10</td>
<td>19</td>
<td>2 (780)</td>
</tr>
<tr>
<td>6</td>
<td>ND</td>
<td>2 (100)</td>
<td>10</td>
<td>14 (4400)</td>
</tr>
<tr>
<td>7</td>
<td>ND</td>
<td>0.8</td>
<td>5 (780)</td>
<td>ND</td>
</tr>
<tr>
<td>8</td>
<td>ND</td>
<td>0.4 (1400)</td>
<td>9</td>
<td>ND</td>
</tr>
</tbody>
</table>
Figure 3-4B from Toronto, ON shows an atypical amine mass loading compared to our other MOUDI samples collected in Toronto. Sample 3 was collected simultaneously with Sample 2 using two different particle collection strategies (fixed and rotating impaction plates, Tables 3-1 and 3-2). The total amine mass collected was smaller in Sample 3 than in Sample 2, indicating that variability in atmospheric samples of these compounds could be significant despite quantitative IC accuracy being high (see error bars in Fig. 3-4B). The sampled air for these samples originated over central Ontario and Georgian Bay with similar amine loadings to those collected at the other two locations. Figure 3-4D shows a more typical size-dependence of the mass loading of individual amines in our urban samples. In general, the observations from Fig. 3-3 and Fig. 3-4 show that even in instances where very large quantities of NH$_4^+$ were present throughout the fine mode, the presence of DMAH$^+$ and TMAH$^+$ + DEAH$^+$ was observed. These observations are consistent with previous quantitative observations of alkyl amines in fine particulate samples (Sorooshian et al., 2008; Sorooshian et al., 2009). Our measurements show the size-resolved distributions throughout the sampled aerosol populations are also consistent with previous observations in marine atmospheres (Makela et al., 2001; Facchini et al., 2008; Muller et al., 2009; Violaki and Mihalopoulos, 2010; Miyazaki et al., 2010) with the maximum mass loadings seen in the accumulation mode, specifically from 320 – 560 nm. Our observations are, to the best of our knowledge, the first to show the size-dependence of particulate alkyl amines mass concentrations in continental air masses.

3.3.1.3 Size-dependence of R$_3$NH$^+$/NH$_4^+$

The dominance of NH$_4^+$ throughout the accumulation mode is most likely due to the ambient concentrations of NH$_3$ being significantly higher than gas phase amines at our sampling sites (Section 3.3.2 provides evidence in Toronto). Typical NH$_3$ measurements in south-western Ontario are on the order of a few ppb (Ellis et al., 2011). While alkyl amines are not routinely measured, they are expected to range from several ppb close to sources to ppt levels in the background atmosphere due to their short lifetime against OH ($\tau \sim$ 1 day). A higher ambient concentration of NH$_3$ would allow its uptake to dominate the neutralization of the aerosol as growth by condensation occurs and the ratio of surface area to volume becomes more limited for reactive uptake. Theoretical calculations by Kurten et al. (2008) and Loukonen et al. (2010) have shown that small cluster formation of aminium salts with inorganic acids is thermodynamically
favoured over ammonium salts. At smaller particle sizes (e.g. clusters – 10 nm), amines may be able to successfully out-compete NH$_3$ due to thermodynamics of the system as shown experimentally (Murphy et al., 2007; Bzdek et al., 2010; Lloyd et al., 2009). As particles grow by condensation and reactive uptake, competition with NH$_3$ for transport to the surface becomes dominant and the influence of relative concentrations supersedes the thermodynamic considerations.

To examine the size-dependence of the relative importance of amines versus ammonia, the molar ratio of the sum of amines to ammonium (R$_3$NH$^+$/NH$_4^+$) detected in each sample was compared in Fig. 3-5. The error bars represent the uncertainty calculated based on the propagation of errors for the measured ammonium and only those amines that were detected in the sample. In most cases the observed ratio is well-constrained because the amounts of all the considered analytes are above the instrument detection limits. Small quantities of all the analytes in the coarse mode produced larger uncertainties in those ratios. In all MOUDI samples, the molar ratio R$_3$NH$^+/NH_4^+$ showed one maximum below 200 nm and decreased as the particle size increased up to about 1 µm; the ratio then increased again in the coarse mode. All samples show this behaviour regardless of the absolute values of the R$_3$NH$^+/NH_4^+$ fraction. In the fine mode, maxima for an individual size bin ranged from ratios of 0.02 to 0.37, with the largest fraction being observed in a sample from Dorset, ON (Fig. 3-5A). A similar enhancement in R$_3$NH$^+/NH_4^+$ in excess of 0.30 was seen in Toronto (Fig. 3-5B) from an air mass also originating from south-western Ontario. However, most samples from the Toronto region typically show ratios below 0.04 (Fig. 3-5D). The samples collected at Lambton Shores (e.g. Fig. 3-5C), were in closer proximity to agriculturally active regions, but did not have ratios of R$_3$NH$^+/NH_4^+$ greater than 0.05 despite having the highest absolute amine mass loading of all the samples collected. The average molar ratio for PM$_{1.8}$ in each sample is given in the final column on Table 3-1.

These observations of amine composition in conjunction with other ionic aqueous species can help to inform models of particle formation and thermodynamic partitioning and predictions of aerosol properties, such as pH and hygroscopicity. The observations in Fig. 3-5 demonstrate that there is a strong size-dependence to the fine aerosol composition, especially with reference to the R$_3$NH$^+/NH_4^+$ ratio.
Figure 3-5. Ratio of the sum of all particulate amines (R$_3$NH$^+$) measured to the total ammonium (moles/moles) as a function of particle diameter for (A) Sample 4 collected in Dorset, (B) Sample 3 collected in Toronto (C) Sample 8 collected in Lambton Shores, and (D) Sample 1 collected in Toronto.
In general, the amines contribute more importantly, in a relative sense, to the reduced nitrogen composition of particles with diameters < 200 nm. Possible explanations include the higher thermodynamic stability of aminium salt clusters, or the preferential reactive uptake of amines by ultrafine particles with higher surface area-to-volume ratios. Alternately, particulate amines may be more susceptible to condensed phase reactions than ammonium, leading to their preferential degradation as particles age and grow.

In the future, a back filter can be included to collect the smallest particles which may provide more information on nucleation mode particles. The maxima in the coarse mode are highly uncertain, but do appear to be higher than the accumulation mode particles. From Fig. 3-3 and Fig. 3-4, it is evident that the coarse mode represents a population of particles with very different composition than the fine particles, and with lower absolute amounts of amines. The coarse mode amines may result from primary biogenic emissions, similar to enhanced marine coarse mode organic nitrogen seen by Miyazaki et al. (2010) in highly biologically influenced aerosols, or reactive uptake on aqueous coarse mode aerosol that has been significantly aged by secondary acidification with HNO$_3$. In either case, the ammonium signal in these coarse mode samples was near or below our instrument detection limits, enhancing the observed ratio when any amines are above their detection limits.

3.3.2 Online Detection of Amines in the Gas Phase and PM$_{2.5}$

The utility of the information provided by the MOUDI data is limited by the long integration time necessary for collection and the absence of simultaneous gas phase measurements. To address these limitations, continuous online collection and analysis of gas and particle phase analytes was performed with the AIM-IC from 26 June – 6 July 2009. This time period was characterized by cool and humid conditions, with rain events occurring from 09:00 – 14:00 and at 21:00 on 28 June, from 14:00 - 16:00 and 20:00 - 22:00 on 29 June, at 04:00 and 20:00 on 30 June, and at 22:00 on 1 July (all times are Eastern Daylight Savings). The north-westerly flow at the start and end of the campaign was interrupted by a period of south-westerly flow between 28 June and 1 July, and stagnant air early on 2 July. Amines were detected in both the gas and particle phases throughout the campaign. Figure 3-6 shows that amines in the gas phase (Panel A) were almost always at or near the instrument detection limits. Mixing ratios of DMA, and
TMA + DEA (displayed as DEA) ranged from below the detection limit to 2.7 ppt for both sets of compounds. While observations of TEA are reported, the measured values were consistently below the detection limit. Amine emission sources in the Toronto area and their collective emission rates are not well-known, although particulate amines have been previously detected during new particle formation events (Tan et al., 2002). The variability in mixing ratio is not consistent across all species or with NH₃, indicating different sources may exist for each. If local amine sources are limited, the observed abundances of a few ppt may be due to dilution and/or reaction with OH ($\tau \sim 1$ day) prior to arriving at our sampling location.

Simultaneous observations of NH₃ (Fig. 3-6A) showed mixing ratios ranging from 1 – 18 ppb. Therefore, the relative ratios of NR₃/NH₃ in the gas phase range from 1.6 to 20 x $10^{-3}$ over the course of our observations. According to the modelling studies by Murphy et al. (2007) and Barsanti et al. (2009), at this range of gaseous ratios, alkyl amines would seldom out-compete ammonia in bulk partitioning to the particle phase. Our particle observations showed only periodic amine mass loadings in PM$_{2.5}$ above our online method detection limits. Figure 3-6 shows the sum of TMAH$^+$ + DEAH$^+$ observed in the particle phase (DEAH$^+$, Panel B) at mass loadings in the range of below detection limit to 16 ng m$^{-3}$. The sporadic nature of the MAH$^+$ observations results from the difficulty in resolving this peak in the presence of much higher amounts of NH$_4^+$. On two occasions, the increase in TMAH$^+$ + DEAH$^+$ coincided with mass loadings of PM$_{2.5}$ NO$_3^-$ greater than 1 ug m$^{-3}$, suggestive of the formation of aminium nitrate salts. However, early on June 30 TMAH$^+$ + DEAH$^+$ was not detected when NO$_3^-$ was high and early on 1 July, it was observed despite NO$_3^-$ being lower than 0.1 µg m$^{-3}$. Therefore, an increased presence of NO$_3^-$ in fine particulate matter does not appear to govern the presence and concentration of TMAH$^+$ + DEAH$^+$. In Sorooshian et al. (2008), high amine mass loadings were measured by PILS-IC at the same time as positive values of excess nitrate, defined as the nitrate left over after sulfate and nitrate have been neutralized by the available ammonium, as measured by C-ToF-AMS. Values of excess nitrate inferred from the AIM-IC were zero within the uncertainty of the calculation, and this uncertainty is much larger than the mass loading of the observed amines. In our observations, it is more likely that the presence of nitrate in the particle phase is indicative of either high relative humidity or high nitric acid, both of which would be conducive to the partitioning of amines to the particle phase.
Figure 3-6. Online AIM-IC observations of amines and dominant inorganic constituents in (A) the gas phase and (B) PM$_{2.5}$. In each panel, the left axis applies to amines, and the right axis to inorganic constituents. Detection limits for amines are depicted using dashed lines. Note: Black traces in both panels represent TMA + DEA, calculated as DEA equivalents. In some cases, increases in particulate amine loadings coincided with a decrease of amines in the gas phase, but mass balance was not observed (e.g. formation of 7.7 ng m$^{-3}$ (2.54 pptv equivalent) of TMAH$^+$ + DEAH$^+$ on July 1 and a coincident decrease in 0.85 pptv of TMA + DEA). This may be indicative of a sudden change in the total (gas + particle) amines during the
time period or a slow time response to changing amine concentrations in our gas channel because of adsorption in our inlet. Such small amounts of amines partitioning to the particle phase make it challenging to use our online observations to determine if R$_3$NH$^+$ is displacing NH$_4^+$ from particles because changes in the abundance of NH$_4^+$ smaller than 100 ng m$^{-3}$ are below our measurement precision for that species.

While the online sampling campaign did not coincide with the collection dates of the Toronto MOUDI samples, some consistency may be expected between the R$_3$NH$^+/NH_4^+$ observed in both sets of samples. Based on the final column in Table 3-1, the molar ratio for PM$_{1.8}$ in MOUDI samples ranged from $\sim$10$^{-3}$ to 10$^{-1}$. Because the online AIM-IC method has higher detection limits than the time-integrated MOUDI samples, at an NH$_4^+$ mass loading of 0.5 µg m$^{-3}$, representative of the online sampling campaign, the lowest ratio we could quantitatively measure in hourly samples is > 10$^{-2}$. In the MOUDI samples with similar PM$_{1.8}$ mass loadings of NH$_4^+$, the R$_3$NH$^+/NH_4^+$ ratio was always less than 1.5 x 10$^{-2}$. Based on the observed gas phase NR$_3/NH_3$ ratios of 1.6 to 20 x 10$^{-3}$ (quantifiable because of high NH$_3$), a R$_3$NH$^+/NH_4^+$ ratio in PM$_{2.5}$ of > 10$^{-2}$ would only be expected if amines are able to significantly outcompete ammonia based on thermodynamic considerations. Barsanti et al. (2009) and Murphy et al., (2007) suggested that the formation of stronger aminium salts with organic acids or nitric acid could favour partitioning of amines to the particle phase. Particulate organic acids, such as oxalic acid, were not above the AIM-IC detection limits (0.1 µg m$^{-3}$) during any of the online observation period. Because of the high humidity conditions during much of the campaign, the aerosol were likely aqueous, in which case partitioning according to R1 may be most relevant. For example, the effective Henry’s law constant for DEA (after accounting for protonation) is an order of magnitude higher than NH$_3$, which would result in a stronger preference for partitioning to aqueous aerosol (Ge et al., 2011a). Observation periods spanning a wider range of atmospheric conditions would be valuable to assess the relative importance of meteorological conditions and chemical composition in dictating the gas-particle partitioning of atmospheric amines.
3.4 Conclusions
These measurements contribute to the small, but expanding, collection of ambient observations of atmospheric amines (Angelino et al., 2001; Makela et al., 2001; Tan et al., 2002; Denkenberger et al., 2007; Facchini et al., 2008; Sorooshian et al., 2008; Muller et al., 2009; Sorooshian et al., 2009; Smith et al., 2010; Violaki and Mihalopoulos, 2010; Ge et al., 2011b). An advantage of the ion chromatography analysis described here is that the calibration protocol provides measurements (mass loadings or mixing ratios) with a high degree of precision for trace quantities (ng m\(^{-3}\) or ppt). The sensitivity of the IC technique is a factor of 5 - 10 higher for the individual amines measured compared to ammonia, which contributes to the low instrument detection limits for the amines. Nevertheless, because in atmospheric samples ammonia/ammonium can be present in concentrations several orders of magnitude higher than the amines, it can impede the detection of some amines (e.g. methylamine and ethylamine) by this method. An ongoing issue with IC measurements of amines is the inability to resolve DEA and TMA. Because one, or both, of these amines appear to be among the most significant of the simple alkyl amines in atmospheric samples, and because their \(K_H\) and pKa values are quite different, it is highly desirable to achieve individual quantitative measurements.

Our MOUDI observations in one urban and two rural environments demonstrate consistent trends with respect to size-dependence: an absolute maximum of amine mass loading in 320 – 560 nm particles, and an increase in importance relative to ammonium for the smallest (56 – 180 nm) particles measured. The importance relative to ammonium in the coarse mode is less meaningful because ammonium was often below our detection limits, despite the presence of detectable levels of amines. In PM\(_{1.8}\) measurements, calculated by summing the six lowest MOUDI size bins, amines contributed tens of ng m\(^{-3}\) and constituted between 0.3 and 10 % of the water soluble particulate mass loading. To the best of our knowledge, the AIM-IC data represent the first simultaneous observations of gas and particle phase amine species with accompanying water-soluble ionic speciation in PM\(_{2.5}\) at hourly time resolution. Through online sampling in an urban environment, we observed instances of amines increasing in the particle phase at times with elevated PM\(_{2.5}\) nitrate. The mass loading of amines in PM\(_{2.5}\) never exceeded 20 ng m\(^{-3}\) during the online sampling period, a value too low to cause observable changes to the abundance of NH\(_4^+\) or NO\(_3^-\). Observations made using this technique can provide data which is
valuable in the evaluation of models designed to predict the contribution of amines to particle nucleation, or to bulk particle composition based on thermodynamic partitioning. However the size dependence of the $\text{R}_3\text{NH}^+/\text{NH}_4^+$ ratio consistently seen in the MOUDI samples shows that an assumption that each size fraction of the fine aerosol population has the same relative composition as the bulk is not appropriate.

### 3.5 Acknowledgements

The AIM-IC was purchased with support from the Canada Foundation for Innovation and the Ontario Research Fund. The authors would like to thank: L. Oliver, V. Oldham and L. Yin for their contributions to method development, instrument operation and MOUDI sampling, and R. Ellis for ammonia measurements. Financial support for T. VandenBoer was provided through an Alexander Graham Bell Canada Graduate Scholarship from the Natural Sciences and Engineering Research Council of Canada (NSERC).
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CHAPTER FOUR

High resolution vertical profiles of trace atmospheric acids from a 300 m tower during Nitrogen, Aerosol Composition and Halogens on a Tall Tower (NACHTT) in Erie, CO: Understanding the ground surface role in nitrous acid (HONO) vertical structure

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Note: This chapter consists of two sections of material.

The first is the instrument inlet design and intercomparison during the field campaign as part of measurement validations between platforms. This data is not currently slated for publication outside of the HONO characterizations.

The second section focuses on HONO vertical profiles as part of the NACHTT objectives towards understanding the vertical structure of nitrogen oxides in the nocturnal boundary layer and is in preparation for:

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Author Contributions

T. C. VandenBoer designed, constructed and conducted inlet experiments, collected and quality controlled data on all trace acids using the NI-PT-CIMS from the BAO tower during the NACHTT campaign, operated the PISA overnight on several nights, and conducted all data analysis discussed below.

J. M. Roberts aided in the design and construction of the inlet and subsequent validation experiments, collected data on all trace acids using the NI-PT-CIMS from the BAO tower during the NACHTT campaign, operated the PISA overnight on several nights, maintained and calibrated the NI-PT-CIMS and provided editorial comments on the chapter contents.

J. G. Murphy aided in the development of the simple box model, data analysis of integrated column HONO in the parameterization of ground surface processes in its production and loss and provided editorial comments on the chapter contents.

C. Warneke aided in the modifications, calibration and maintenance of the NI-PT-CIMS during NACHTT and modified the data analysis software for data reduction and quality control of the field data.

J. A. de Gouw provided critical analysis of data quality and resources for the operation of the NI-PT-CIMS.

N. L. Wagner, C. J. Young, W. P. Dube, J. A. Thornton, T. P. Riedel, A. M. Middlebrook, R. Bahreini, F. Ozturk, C. Brock, and S. S. Brown collected supporting data from the PISA used in the data analysis (NO, NO2, aerosol surface area, aerosol composition) and operated the PISA overnight on remaining nights during NACHTT. In particular, W. P. Dube designed the PISA and maintained its operational capacity, N. L. Wagner provided all data synchronization, PISA meteorology data and PISA control software, and T. P. Riedel aided in the maintenance of the NI-PT-CIMS during the data collection period.

W. Keene, A. Pszenny, and J. Maben collected supporting data with the mist chamber – ion chromatography instrument for the measurement intercomparison of atmospheric acids and carried out ion chromatographic quantitation of acid calibration standards at the BAO tower.

S. Kim made OH measurements used in the box model and daytime HONO source analysis, B. Lerner provided photolysis frequency data, D. Wolfe and E. Williams coordinated site logistics and provided meteorological data for the site.
Abstract
Continuous vertical profiles of trace atmospheric acids were made during the Nitrogen, Aerosol Composition and Halogens on a Tall Tower (NACHTT) field campaign in Erie, CO using a Negative-Ion Proton-Transfer chemical ionisation mass spectrometer (NI-PT-CIMS). Measurements were made from 17 February to 14 March 2011 using a mobile carriage mounted on a 300 m open-framed tower. A novel inlet for the NI-PT-CIMS was deployed during this campaign for the collection of atmospheric acids and underwent an intercomparison with a stationary mist-chamber ion chromatography system sampling through a 20 m inlet during a period of near-continuous profiling. The novel inlet was capable of 0.1 Hz measurements, automated background/interference/calibration collection, and led to detection limits on the order of a few parts per trillion by volume (pptv). Intercomparison results show that the NI-PT-CIMS was capable of making high accuracy nitrous acid (HONO) measurements, while the remaining acids underwent significant inlet losses in the mist-chamber system. The intercomparison also indicated a particle nitrate interference in the CIMS resulting from particle volatilization in the heated inlet.

High resolution vertical profiles of HONO, averaged to 2 hour time steps, revealed i) the ground surface is the dominant nighttime surface on which HONO is formed from the heterogeneous reaction of nitrogen dioxide (NO₂) with water, ii) significant quantities of HONO are expected to be deposited to the ground surface at night, and iii) the unknown daytime source of HONO is comparable to the potential ground HONO reservoir. Total column observations of HONO and NO₂ allowed direct evaluation of the ground uptake coefficients for these species at night as a function of relative humidity (γNO₂, surf = 2 x 10^{-6} to 1.6 x 10^{-5} and γHONO, surf = 2 x 10^{-5} to 2 x 10^{-4}). Both parameters are consistent with laboratory and model values, although it is possible that the HONO uptake values are limited by aerodynamic transport to the surface. These constraints are the first field observation-derived NO₂ and HONO uptake values using nocturnal integrated column observations and time rate of change of each species separately.

Daytime vertical concentration gradients indicated the ground surface as the location of the unknown HONO source required to explain observed mixing ratios based on known sources and sinks. A simple box model utilizing observational constraints on the HONO chemical system
shows that the daytime source may be more dynamic than previously proposed and that it is likely a combination of mechanisms. Alternative mechanisms of bidirectional flux and acid displacement of HONO from a ground reservoir generated at night are discussed in accounting for the production of daytime HONO.
4.1 Introduction

In the past decade, as the next generation of analytical instrumentation, capable of fast measurements and sensitive at pptv mixing ratios, have been deployed in the field, our understanding of the potential atmospheric importance of nitrous acid has undergone a dramatic revolution. The night time production of HONO (R1) was first measured in polluted regions as the mixing ratios were often in excess of 5 ppbv (Perner and Platt, 1979; Platt et al., 1980). In some locations these high mixing ratios of HONO formed at night can still be observed (Li et al., 2011; Li et al., 2010; Villena et al., 2011). Subsequent photolysis of HONO (R2) was assumed to be complete when mixing ratios fell below the instrumental detection limits, near 200 pptv.

\[
2 \text{NO}_2(g) + \text{H}_2\text{O}_{\text{ads}} \rightarrow \text{HONO}_g + \text{HNO}_3(\text{ads}) \quad (R1)
\]

\[
\text{HONO}_g + \text{hv} (\lambda < 400 \text{ nm}) \rightarrow \text{NO}_g + \text{OH}_g \quad (R2)
\]

However, daytime measurements in polluted regions observed HONO above the detection limits - not as a result of interferences - called in to question whether there was (an) uncharacterized source(s) of HONO during the day. The Long Path Absorption Photometer (LOPAP) and similar derivatization instruments (Kleffmann and Wiesen, 2008; Kleffmann et al., 2006; Heland et al., 2001; Zhang et al., 2009), the Differential Optical Absorption Spectrometer (DOAS) (Wong et al., 2012; Stutz et al., 2010; Stutz et al., 2002) and Negative-Ion Proton-Transfer Chemical Ionisation Mass Spectrometer (NI-PT-CIMS) (Roberts et al., 2010) have all recently reported detection limits lower than 10 pptv for time-resolved measurements of 10 minutes or faster. These state-of-the-science instruments confirmed the presence of highly variable photostationary HONO mixing ratios ranging from 10 to 1000 pptv during midday (Zhou et al., 2011; Wong et al., 2012; Su et al., 2008b; Sorgel et al., 2011a; Kleffmann et al., 2005; Elshorbany et al., 2009; Elshorbany et al., 2012; Acker et al., 2006). In some remote regions, the diurnal trend has been found to be inverted, with lowest mixing ratios at night and highest during the day (Zhou et al., 2011; Ren et al., 2010; Honrath et al., 2002; Beine et al., 2008). In either case, these daytime observations have generated a new appreciation for the potential of HONO to be produced during the day and to be a significant contributor to the total OH production, generating up to 50% of the observed daytime OH in rural locations (Kleffmann et al., 2005; Elshorbany et al.,...
2012; Alicke et al., 2003) and up to 30% in urban zones (Young et al., 2012; Volkamer et al., 2010). The required production rate of HONO from the unknown source has been found to range from a few hundred pptv per hour to over a ppbv per hour, depending on the location. These values are in addition to the gas phase source from reaction of OH and nitrogen monoxide (R3) and from the heterogeneous surface reaction of nitrogen dioxide (R1).

\[ \text{NO}_2(g) + \text{OH}(g) + M \rightarrow \text{HONO}_2(g) + M \]  \hspace{1cm} (R3)

Laboratory studies have elucidated several alternative reaction pathways for the formation of daytime HONO using NO\textsubscript{2} and photo-excited substrates (e.g. R4), such as soot (Monge et al., 2010; Khalizov et al., 2010; Gerecke et al., 1998; Aubin and Abbatt, 2007; Ammann et al., 1998), TiO\textsubscript{2} (Langridge et al., 2009; Bedjanian and El Zein, 2012; Ndour et al., 2008; Ndour et al., 2009), humic acid (Stemmler et al., 2007; Stemmler et al., 2006; Bartels-Rausch et al., 2010), and solid organic films (Brigante et al., 2008; Gutzwiller et al., 2002; George et al., 2005).

\[ \text{NO}_2(g) + [\text{R-H}]^* \rightarrow \text{HONO}_2(g) + [\text{R}'] \]  \hspace{1cm} (R4)

\[ \text{HONO}_2(g) + \text{OH}(g) \rightarrow \text{NO}_2(g) + \text{H}_2\text{O}(g) \]  \hspace{1cm} (R5)

Minor contributors to the fate of HONO during the day occurs by reaction with OH (R5), and photolysis of ortho-nitrophenols, which has also been shown to yield HONO, although direct measurements of their impact in urban atmospheres are yet to be made (Bejan et al., 2006). Similarly, photolysis of surface adsorbed nitric acid has been suggested as a HONO source, but remains poorly constrained (Zhou et al., 2011; Li et al., 2012; Ziemba et al., 2010). Reaction of electronically excited NO\textsubscript{2} with water vapour (Li et al., 2008) was also proposed as a major formation pathway for daytime HONO, but has since been shown to be a two photon process (Amedro et al., 2011) and of little relevance to the atmosphere (Wong et al., 2012; Sorgel et al., 2011a; Ensberg et al., 2010; Czader et al., 2012). Extrapolation of photochemical mechanisms to field data has shown that they cannot fully account for the formation rates of HONO required to match the observations (Sorgel et al., 2011a). Therefore, there still exist(s) (an) unknown daytime source(s) of HONO to the atmosphere which generate(s) most of the observed HONO.
Whether this occurs in the gas phase, on lofted aerosols, or on the ground surface remains an article of open debate.

The relative importance of aerosol and ground surfaces in the production of nighttime HONO via R1 has become the focus of a few studies which have investigated the vertical distribution of HONO in the atmosphere to unequivocally allocate the ground surface as the most important HONO source (Lammel and Perner, 1988; Lammel and Cape, 1996; Kleffmann et al., 2003; Su et al., 2008a; Wong et al., 2011; Zhang et al., 2009). However, datasets capable of resolving the relative importance of ground and aerosol surfaces in night and daytime production have often been challenged by the lack of collocated measurements of hydroxyl radical, nitrogen oxides, aerosol surface area, and aerosol chemical composition. Other limitations have been the inability to collect continuous vertical profile measurements of HONO, and the availability of cost-effective infrastructure (e.g. tall towers, buildings or aircraft). Vertical gradients in nighttime HONO have been reported in a number of environments, suggesting that the ground surface is the major source of HONO, but these data appear infrequently in the literature (Wong et al., 2011; Stutz et al., 2002; Villena et al., 2011; Harrison et al., 1996; Harrison and Kitto, 1994).

In most cases, the HONO gradients have had limited measurement frequency and limited vertical resolution between the surface, and/or nocturnal boundary layer and/or residual layer of the previous day’s convective boundary layer. These limitations have been due to: i) the capacity of the available infrastructure to conduct vertical profiling and ii) the ability of instrumentation to quickly and accurately measure HONO mixing ratios along with other key measurements (e.g. NO₂, NO, aerosol surface area) to elucidate the underlying conditions of its heterogeneous formation. In early studies, gradient measurements were made using time integrated annular denuder samples near the surface. The results of these measurements led to the first atmospheric observation that suggested that nighttime HONO production occurs by reaction of NO₂ on the ground surface (Harrison and Kitto, 1994; Harrison and Peak, 1997). This has subsequently been confirmed by other flux measurements (Stutz et al., 2002; Ren et al., 2011), although the magnitude of the observed surface flux may be dependent on the sampling height if the ground surface is the dominant source. That is, surface flux may be underestimated if significant loss of HONO due to photolysis has taken place during transport from the surface to the measurement.
height. The potential for a sampling height bias in field measurements of nighttime HONO has only recently come to be appreciated based on vertically resolved measurements indicating enhanced HONO mixing ratios at the ground surface.

In a semi-rural environment in Germany, Kleffmann et al. (2003) used a long path absorption photometer (LOPAP) on a tall tower to measure HONO at 30 m intervals over 4 profiles (i.e. transects from the surface to the top of the tower) up to 190 m. While they observed vertical gradients, they were required to remain stationary for 20 min periods at each interval to prevent local production of HONO from NO\textsubscript{2} emitted by the generator that moved the elevator and to acquire time averaged measurements on the order of minutes. In an urban atmosphere, a long path differential optical absorption spectroscopy (LP-DOAS) instrument used retroreflectors placed on buildings of different heights to make half-hourly measurements of HONO vertical gradients between 20 and 300 m (Wong et al., 2012). Finally, an aircraft-mounted LOPAP was used to measure 7 vertical profiles of HONO above a boreal forest through the atmospheric boundary layer and lower troposphere in the early morning and evenings (Zhang et al., 2009). In some cases, vertical profiles have suggested that the ground surface dominates over aerosol surfaces as a source of HONO at night. However, limited datasets with continuous profiles suffering from poor vertical and temporal resolution limit the conclusions which can be reached on the atmospheric parameters governing the observed amounts of HONO in the nocturnal atmosphere.

An interesting feature of these few vertical gradient observations is that the production of HONO in NO\textsubscript{X}-rich regions reaches a pseudo-steady state near the surface, implying an unknown sink of HONO at night which is generally assumed to be irreversible deposition to the earth surface (Wong et al., 2011; Sorgel et al., 2011a). The degree of HONO loss back to the ground surface has been proposed to be a function of nocturnal boundary layer height and stability (Geyer and Stutz, 2004; Wong and Stutz, 2010; Wong et al., 2011). Only recently has this loss process been considered as potentially reversible from observations made over water bodies in a polluted marine boundary layer (Wojtal et al., 2011) or if significant amounts of water are available as a reservoir at the surface, such as soil water (Su et al., 2011).
Here the first highly-continuous dataset of HONO vertical profiles with a negative-ion proton-transfer CIMS (NI-PT-CIMS) are presented. The data were collected from 0 – 250 m above ground level (agl), with collocated meteorology, nitrogen oxide, ozone, aerosol surface area and composition data. In addition, in situ measurements of OH, and meteorology were made during the Nitrogen, Aerosol Composition and Halogens on a Tall Tower (NACHTT) campaign. In this chapter we discuss i) the utility of the NI-PT-CIMS to the fast measurement of trace atmospheric acids via a fully characterized novel inlet design, ii) an intercomparison of fixed-height trace acid measurements with a Mist Chamber – Ion Chromatography (MC-IC) system, iii) issues with relying on the HONO to NO\textsubscript{2} ratio as an indicator for HONO production in a winter atmosphere, iv) nighttime heterogeneous HONO formation on aerosols and the ground via vertical gradients, v) daytime vertical gradients in HONO and the magnitude of the daytime source and vi) parameterization of HONO sources and sinks with a simple box model to describe the potential fate of surface deposited HONO towards the unknown daytime source.

4.2 Methods

4.2.1 Site Description and Instrumentation

The NACHTT field campaign was located at the Boulder Atmospheric Observatory (BAO) in Erie, CO (40° 03’ 00” N, 105° 00’, 14” W). Instrumentation was deployed from all site platforms from 17 February – 14 March 2011. The main sampling platform was a 300 m triangular open tubular-frame tower. The tower was outfitted with an electric internal elevator through the center of the structure and an externally mounted instrument carriage (the Portable Instrument Shelter with Amenities, PISA) powered by electric motors mounted on rails attached to the side tower. The PISA was capable of reaching an altitude of 250 – 275 m. Round-trip vertical transects were completed approximately every 10 minutes when performing continuous profiles. During high wind events (> 12 m s\textsuperscript{-1}) the carriage was kept stationary at or below 20 m agl to prevent structural damage to the tower. The PISA housed a large suite of instrumentation, including: a meteorology station, GPS and analog height instrumentation, an ultra-high sensitivity aerosol spectrometer (UHSAS), aerosol mass spectrometer (AMS), two chemical ionisation mass spectrometers for ClNO\textsubscript{2}/N\textsubscript{2}O\textsubscript{5}/Cl\textsubscript{2} (UW-CIMS), using CH\textsubscript{3}I reagent ion, from University of Washington (Riedel et al., 2012) and for HCl/HONO/HNCO/HCOOH/HNO\textsubscript{3} (NI-PT-CIMS), using CH\textsubscript{3}COO\textsuperscript{-} reagent ion, from NOAA (Veres et al., 2008;Roberts et al., 2010;Veres et al.,
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2011), and a cavity ring-down spectrometer (ARNOLD) for NO/NO₂/O₃/NO₃/N₂O₅ (Wagner et al., 2011). Measurements were made between 0.1 – 1 Hz by each instrument when collecting data.

An externally mounted platform for fixed height measurements, accessible by the internal elevator, was installed at 20 m agl on the 300 m tower. Micro-orifice uniform deposit impactor (MOUDI) samplers collected size-resolved aerosol ionic and elemental composition, mist chamber ion chromatography (MC-IC) sampled gas phase NH₃, inorganic and organic acids via a high volume (> 1000 CFM) PVC inlet located at 20 m agl (Keene et al., 2004; Keene et al., 2007).

On a separate 20 m scaffolding tower, less than 20 m south of the 300 m tower, measurements of OH and H₂SO₄ were made by another CIMS (Eisele and Tanner, 1991; Tanner et al., 1997; Petaja et al., 2009), photolysis rates were measured by a filter radiometer, and additional meteorological measurements were made.

4.2.2 Negative-Ion Proton-Transfer Mass Spectrometer (NI-PT-CIMS)

Measurements of inorganic and organic trace acids were made by a NI-PT-CIMS. Briefly, the NI-PT-CIMS detects acids as their negative ions by proton transfer reaction with an acetate ion. Acetate ions are generated by passing approximately 3 ppm of gaseous acetic anhydride in dry nitrogen in a 2 SLPM flow through a ²¹⁰Po source and into a reaction flow tube pumped down to a pressure of 25 Torr. Atmospheric samples are drawn simultaneously through a critical orifice into the flow tube at a flow of approximately 880 sccm. Acids and polyalcohols with lower pKa values than acetic acid undergo quantitative proton transfer with these ions at 25 Torr in the reaction flow tube (Veres et al., 2008). This ionisation scheme for gaseous compounds has been shown to be both selective and sensitive to a wide variety of atmospheric acids (Veres et al., 2008; Veres et al., 2010; Roberts et al., 2010; Veres et al., 2011). The ions are then transferred through a critical orifice to a collision dissociation chamber to decluster at 3.1x10⁻¹ Torr and focused through an ion lens stack to the quadrupole (< 1x10⁻⁵ Torr) for detection. Absolute stability in the ion reaction rates and cluster formation was controlled during NACHTT by the addition of a flow tube pressure controller (MKS, Model 649A, 100 Torr, Andover, MA) to the
roughing pump vacuum line that bled in ambient air when necessary to maintain a reaction flow tube pressure of 25 Torr.

During the NACHTT field campaign the NI-PT-CIMS measured HCl, isocyanic acid (HNCO), formic acid (HCOOH), HONO, HNO₃, acrylic acid (C₃H₄O₂), propionic acid (C₃H₆O₂), and HBr at m/z 35, 42, 45, 46, 62, 71, 73, and 80 respectively. In addition, the acetate reagent ion and reagent ion dimers were monitored at m/z 59 and 119 for subsequent normalization and quality assurance in the data analysis procedure. Ion signals were collected using one second dwell periods on each ion, resulting in a 0.1 Hz measurement rate. Dry nitrogen gas for the ion source was supplied to the instrument via a Pressurized Liquid Nitrogen (PLiN) system on board the carriage that was refilled every 18 – 24 hours.

4.2.3 NI-PT-CIMS Inlet Design

Particular emphasis was made on fast time response and high accuracy measurements of HCl, HNCO and HONO during this campaign as they were central to the campaign investigation of halogen partitioning and reactive nitrogen compounds. In order to meet these demands, a custom designed sampling inlet was devised that was capable of interfacing with the NI-PT-CIMS, performing online background measurements and calibration checks, while maintaining rapid transmission of the target compounds and minimizing potential interferences (Figure 4-1).

**Figure 4-1.** Schematic representation of custom inlet for NI-PT-CIMS. Atmospheric samples were drawn directly to the NI-PT-CIMS for analysis through (1) a three-way PFA-coated solenoid valve or directed through (2) an annular denuder coated with Na₂CO₃ to reactivity remove acids for backgrounds by acid displacement. Online HCOOH calibrations were controlled using (3) another three-way PFA-coated solenoid valve through which the output from a HCOOH permeation device was constantly flowing. Online calibrations were introduced in to background flows coming from the annular denuder.
The entire length of the inlet was thermally controlled with a NiCr resistive wire heater, K-type thermocouple and digital temperature controller to optimize the transmission of gases through the inlet. In particular, transmission of HNO₃ and HCl, which have strong surface adsorption characteristics, were optimized for detection. The inlet assembly was insulated to reduce the magnitude of temperature fluctuations experienced by the sample flow. The inlet was constructed using 1/8” PFA tubing with a tee fitting on the end to minimize the total number of particles sampled by the instrument. The atmospheric sample was then directed in to another tee fitting where the gas was forced to make a 180° turn before entering the sampling or background channel. The sampling channel pulls the atmospheric sample through solenoid valve 1 in to the CIMS and the background channel pulls the atmospheric sample through the annular denuder before also passing through solenoid valve 1 and entering the CIMS (Figure 4-1). The sample was directed in to the CIMS for detection of trace acids or in to the background channel by altering the state of solenoid valve 1 (Figure 4-1). The total volume of the tubing in both channels was made near-equal (5.23 cm³) to achieve identical residence times of atmospheric samples in each channel. In the background channel, the sample enters an annular denuder (Model URG-2000-30x150-3CSS, URG, Chapel Hill, NC) coated with Na₂CO₃ according to EPA Compendium Method IO-4.2 (Information, 1999) where strong acids are removed by reactive uptake on the carbonate substrate, displacing CO₂ and H₂O. Unreactive components continue to the reaction flow tube and allow quantification of any interferences and/or determining background counts for each target acid. Quantifying interference signals cannot always be accomplished using an inlet overflow of nitrogen or ultrapure air. Therefore, this is a significant improvement to analytical specificity of the NI-PT-CIMS for the acids quantified during NACHTT. Finally, online calibrations were performed by adding the output of a formic acid permeation device to the acid scrubbed flow in the background channel by modulating a second solenoid valve (Figure 4-1). By introducing the calibration gas in to an acid-scrubbed atmospheric sample, instrument sensitivity changes due to relative humidity, hardware modifications and unknown atmospheric components can be captured on-the-fly during field missions. An online calibration of all the acid species is ideal, but was not possible for this study. Inlet temperature-dependent sample transmission, background channel acid removal efficiency, and flow tube acid desorption during background tests were performed on this system for the analysis and correction of NACHTT field data.
4.2.4 NI-PT-CIMS Calibrations

Primary calibration standards of HCl, HONO, HNO$_3$, HNCO and HCOOH were generated using permeation devices, standard gas cylinders, and capillary diffusion cells. For each calibration performed on the NI-PT-CIMS, ion counts were collected at 1 Hz, with one or more supporting measurements of the calibration gas made by instruments operating according to alternative chemical principles, similar to those reported in Roberts et al. (2010) and Veres et al. (2008). Permeation devices (VICI Metronics, Poulsbo, WA) were used to produce HCl, HNO$_3$ and HCOOH at the temperatures listed in Table 4-1. Each device was housed in an insulated and temperature-controlled PFA cell outfitted with a Tylan® mass flow controller (MFC) with a range between 1 – 50 sccm to continuously transport the calibration gas to the NI-PT-CIMS dilution flow setup or to waste in a flow of ultrapure zero air or dry nitrogen. In all cases, the calibration gases never passed through the stainless steel mass flow controllers in order to avoid adsorptive or decompositional losses of the calibration gases in a potentially inconsistent fashion. This approach also prevented reactive degradation of seals in the MFCs. The calibration gas flows were mixed in to dilution flows before entering the NI-PT-CIMS inlet with any excess flow being vented to a waste line. The emission rate of the HCl permeation tube was confirmed by a standard cylinder of 10.1 ppmv HCl certified by the manufacturer (Spectra Gases, Stewartsville, NJ) outfitted with a dry and conditioned 10 sccm mass flow controller. The HCl cylinder was also used to confirm permeation rates and calibration factors in the field. The emission rate of the HNO$_3$ permeation tube was determined by UV absorption spectroscopy according to the method of Nueman et al. (2003) in-house before and after the campaign, and by ion chromatographic determination of NO$_3^-$ collected in to sequential bubblers in the field.

The calibration source of HONO was adapted from that of Roberts et al. (2010) to use an HCl permeation device as the HCl source instead of the 10.1 ppmv cylinder of HCl. This allowed sub-ppbv calibration mixing ratios of HONO to be generated. Briefly, HONO is generated by acid displacement with HCl on humidified NaNO$_2$ in a salt bed packed around glass beads. The NaNO$_2$ reaction bed was also insulated to limit temperature fluctuations from affecting the displacement efficiency and partitioning of HONO between the aqueous and gas phase. The HONO source output was confirmed in-lab by catalytic conversion of HONO to NO on a
molybdenum converter, followed by O₃ chemiluminescent detection (Roberts et al., 2010) and cavity ring-down detection of trace (< 0.5 %) nitrogen oxides (NO + NO₂) (Wagner et al., 2011). In the field, the HONO source output was determined by sequential bubbler collection and ion chromatographic detection of the NO₂⁻ ion. Calibration in the sub-ppbv range found an improvement over previously reported sensitivities and detection limits for the NI-PT-CIMS (Roberts et al., 2010).

Table 4-1. Certified primary standard acid permeation device emission rates for the NI-PT-CIMS.

<table>
<thead>
<tr>
<th>Acid Species†</th>
<th>Temperature (°C)</th>
<th>Rate (ng min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>55</td>
<td>10.20</td>
</tr>
<tr>
<td>HNO₃</td>
<td>40</td>
<td>17.67</td>
</tr>
<tr>
<td>HCOOH</td>
<td>30</td>
<td>33.66</td>
</tr>
</tbody>
</table>

† - HNCO and HONO were not generated by permeation device

The HNCO thermal decomposition/diffusion source was constructed in-lab post-campaign according to the method of Roberts et al. (2010) and references therein. Simply, solid cyanuric acid was placed in to a capillary diffusion cell and heated to 225 °C to liberate gaseous HNCO. The gas then diffused through the capillary, was collected in to nitrogen carrier gas and was sequentially diluted for calibrations. The total output was quantified by FTIR immediately before and after calibrating the NI-PT-CIMS, since a continual decline in HNCO output was observed as the diffusion cell and tubing walls were presumably condensing HNCO back to the cyanuric acid trimer (visible as a white precipitate). Therefore, this process occurring during calibration is the major source of uncertainty in the measurement of this compound.

Finally, HCOOH was generated using a permeation device. The emission rate was quantified by complete catalytic oxidation of HCOOH to CO₂ on a platinum catalyst, followed by non-dispersive infrared spectroscopic quantitation of CO₂ on the Mobile Organic Carbon Calibration System (MOCCS) (Veres et al., 2010). The formic acid permeation source was used to continuously track the online sensitivity of the NI-PT-CIMS by recording ion counts for 10
minutes on a bi-hourly basis. The field data for all acid species were normalized to sensitivity changes in HCOOH accordingly. Isotopic interference (1.1 %) between H\textsuperscript{13}COOH and HONO was also determined and corrected from calibration data. Additionally, several field calibrations of HCl, HONO, and HNO\textsubscript{3} were performed to assess any coincident sensitivity changes in the detection of the inorganic acids.

4.2.5 NI-PT-CIMS Inlet Characterization

During these tests, measurements of each acid anion (Section 4.3.1) were made at 1 Hz (a faster timescale than the 0.1 Hz used in the field) to optimize measurement quality and instrument response of the NI-PT-CIMS. Temperature-dependent inlet transmission of trace acids was characterized using a method similar to Veres et al. (2008) and Roberts et al. (2010) by modulating moderate mixing ratios, on the order of 1 ppb, with dry nitrogen gas as a blank to characterize the response time in reaching maximum signal or minimum background ion counts. Temperatures between 30 – 60 °C were tested for HCl, HONO, HNO\textsubscript{3} and HNCO, to optimize their response time to be near or better than the 0.1 Hz measurement time intervals. Response time was determined by fitting the decays (or inverted transmission responses when going from nitrogen to acid of interest) with an exponential of the following form and determining the decay constant, k:

\[
A = A_0 e^{-kt}
\]  

\text{(E1)}

Where, A is the observed normalized counts for the acid ion, \(A_0\) is the maximum normalized ion counts, and t is the measurement time in seconds from the switch between acid and dry nitrogen.

Acid removal efficiency of the Na\textsubscript{2}CO\textsubscript{3} annular denuder in the background channel was determined by switching between the sampling channel and background channel at constant acid concentration. Scrubbing efficiency was assessed by comparing the ion counts in the background channel to background signals measured in the presence of dry nitrogen. Breakthrough signals were recorded over several concentrations (pptv – ppbv) for HCl, HNO\textsubscript{3}, HONO, HNCO and
HCOOH to quantify artifact background signal due to inadequate reactive scrubbing of these compounds.

Reaction flow tube acid desorption can be quantified as the sum of the flow tube volume exchange rate and the chemical desorption rate by measuring the decay rates of compounds with strong surface adsorption characteristics (e.g. NH₃, HNO₃ and HCl) during the course of an instrument background measurement (Ellis et al., 2010). The desorption time constants of several minutes, found in this study, were much longer than the less than one second exchange rate of the flow tube volume. Hence, the single decay constant approach of E1 was used as opposed to a double exponential, such as that used in Ellis et al. (2010). Known mixing ratios of an acid, at mixing ratios of several ppbv, were added to the NI-PT-CIMS sampling inlet for about 1 hour before simultaneously switching to the blank channel and overflowing the inlet with dry nitrogen. This timing scheme is roughly equivalent to the rate of background ion counts collected under field conditions. The subsequent desorption features were then monitored for 10 minutes, the typical duration of a background ion count in the field, to quantify the rate of desorption and concentration-dependent effect on background ion counts for HCl and HNO₃, so that corrections could be made to field data affected by this phenomenon.

4.2.6 Intercomparison with Mist Chamber-Ion Chromatograph (MC-IC)

An intercomparison between the MC-IC and NI-PT-CIMS was made for HONO, HCl, HNO₃ and HCOOH. Data were intercompared by averaging data collected within 10 m to either side of the fixed height MC-IC (20 m agl) as the carriage passed by, giving NI-PT-CIMS data above and below the fixed height MC-IC from 11 – 14 March 2011. Under continuous vertical profiling conditions, the NI-PT-CIMS passed any fixed height every 5 minutes. However, NI-PT-CIMS data were seldom fully continuous over a 2 hour sampling period due to the frequency of collecting background signals, and online calibrations. Therefore, a minimum intercomparison condition of the NI-PT-CIMS passing the fixed height every 10 minutes was set to achieve the best compromise between the number of compared measurements between instruments and the data averaged per MC-IC measurement compared.
4.2.7 Vertical Profile Analysis

Previous studies on vertical structure have not been able to explore HONO heterogeneous production both near the surface and aloft continuously throughout several days and nights due to either limitations in the ability of aircraft to regularly sample close to the surface (Zhang et al., 2009), the sparse number of vertical levels of DOAS measurements (Wong et al., 2011; Wong et al., 2012) or the creation of artifact HONO from NO\textsubscript{2} emitted by a mobile platform when changing altitude (Kleffmann et al., 2003). The emission-free and continuously mobile PISA transporting the NI-PT-CIMS and supporting instruments, therefore, provided a unique opportunity to explore the vertical distributions of HONO. The vertical structure of HONO, relative humidity, NO\textsubscript{2}, aerosol surface area and aerosol composition were explored to contrast the production rate of HONO on lofted aerosols and at the surface at night. Vertical profile data were retained for wind conditions less than 6 m s\textsuperscript{-1} and periods of near-continuous collection of vertical measurements to avoid biases in observations from prolonged sampling under stationary conditions or synoptic scale weather perturbations.

The presence of nocturnal thermal inversions at the surface were determined according to the method of Brown et al. (2007) using potential temperature and ozone measurements. Under such conditions the integrated column rate of change in HONO was used to constrain both surface production and loss of HONO (Sections 4.2.7.3 and 4.3.6). Note that the term thermal inversion is used interchangeably with nocturnal boundary layer (NBL) henceforth. On nine occasions thermal inversions were found (18-19, 19-20, 21-22, 27-28 Feb, 28 Feb – 1 March, 1-2, 2-3, 4-5 and 7-8 March) and vertical mixing from the surface was expected to be confined to the surface or nocturnal boundary layer. The utility of using the HONO to NO\textsubscript{2} ratio for winter observations of HONO production was assessed and an alternative NO\textsubscript{q} family (NO\textsubscript{q} = NO\textsubscript{2} + NO\textsubscript{3} + 2*N\textsubscript{2}O\textsubscript{5}) was considered for HONO production in atmospheres where nocturnal production of NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} are also significant.

4.2.7.1 Relative Importance of Aerosol and Ground Surface in Nocturnal HONO Production

To evaluate the relative importance of HONO production on aerosol and the ground surface, vertical profile data was binned in 10 m intervals from the surface to 250 m agl and the
production of HONO in 2 h intervals within these air masses investigated. The relative importance of nocturnal heterogeneous production on each surface was evaluated using the best available model constraints on the reactive uptake coefficient of HONO and NO₂ from Wong et al. (2011), lab studies on NO₂ uptake and conversion (Kurtenbach et al., 2001; Kleffmann et al., 1998; Broske et al., 2003) and NO₂ deposition velocity to a surface representative of bare soil and grass (Spicer et al., 1989). The yield of the reaction assumed equimolar disproportionation of 2 NO₂ molecules to form HONO and HNO₃, immediately releasing HONO, according to the currently accepted hydrolysis mechanism of the N₂O₄ intermediate (Finlayson-Pitts et al., 2003; Finlayson-Pitts, 2009). Aerosol reactive uptake of NO₂ was assumed to occur on all available surface area, regardless of chemical composition, using the reactive uptake approximation of Brown et al. (2006), modified to account for the equimolar disproportionation (E2).

\[
P_{(\text{HONO})} = \frac{1}{2} y_{\text{NO}_2} A \sqrt{\frac{3RT}{M}} [\text{NO}_2] \tag{E2}
\]

Where \( \gamma \) is the uptake coefficient (10⁻⁶ - 10⁻⁵; (Wong et al., 2011)), and \( A \) is the measured aerosol surface area (\( \mu \text{m}^2 \text{ cm}^{-3} \)). The gas constant (\( R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \)), temperature (\( T, \text{ K} \)), and molecular mass of NO₂ (\( M, \text{ kg mol}^{-1} \)) are used to calculate its molecular speed. The calculated conversion rate of NO₂ on aerosol surfaces was compared with observed variability in HONO mixing ratios for 2 hour intervals in the residual layer (i.e. above the NBL) to assess the threshold where HONO in excess of the variability between the profiles could be observed.

### 4.2.7.2 Observationally Constrained Ground Surface Uptake Parameters for NO₂ and HONO

Nocturnal surface production of HONO was parameterized under the assumption that production of HONO on aerosols was insignificant compared to the ground surface, which several other studies of HONO vertical structure have suggested (Zhang et al., 2009; Wong et al., 2011; Villena et al., 2011). Using integrated, 2 hour average, NBL column (up to 250 m) densities of HONO, it was possible to evaluate the time rate of change of HONO in the column as a function of HONO and NO₂ in contact with the surface. Contributions of transport, diffusion and reactive uptake to the observed reactive uptake values were calculated for HONO and NO₂ to the surface using a
simple resistance parameterization, such as that presented in E3 from Huff and Abbatt (2002), to interpret the applicability of the observations to a broader application in modelling these processes.

\[ v_d = \left( \frac{1}{\frac{1}{R_A} + \frac{1}{R_B} + \frac{1}{R_C}} \right) \]  

(E3)

Where, \( v_d \) is the deposition velocity (cm s\(^{-1}\)), \( R_A \) is the aerodynamic transport resistance (E4), \( R_B \) is the molecular diffusion resistance (E5) and \( R_C \) is the reactive loss resistance (E6). Each term can be calculated as follows:

\[ R_A = \left( \frac{1}{\mu k^2} \right) \left[ \ln \left( \frac{z}{z_0} \right) \right]^2 \]  

(E4)

\[ R_B = \frac{z_0}{D} \]  

(E5)

\[ R_C = \frac{4}{\gamma C} \]  

(E6)

Where \( \mu \) is the wind speed (0.1 – 6 m s\(^{-1}\)), \( k \) is a proportionality constant (0.4), \( z \) is the surface layer depth from observations (15 m), \( z_0 \) is the roughness length of the surface (4 x 10\(^{-3}\) m), \( D \) is the molecular diffusivity of HONO (7.2 x 10\(^{-5}\) m\(^2\) s\(^{-1}\) at 622 torr (Hirokawa et al., 2008)), \( \gamma \) is the reactive uptake coefficient and \( C \) is the mean molecular speed (~ 366 m s\(^{-1}\) for HONO).

These processes are a consistent feature of vertically resolved models run by Wong et al. (2010;2011) where the transport of NO\(_2\) and HONO to the surface must be calculated to compare to measurements instead of being constrained by direct observations of surface production and loss of these gases which are used in the model deployed here (vide infra). The vertical profiles collected during NACHTT provide continuous observations from the surface to 250 m, allowing the integrated column concentrations of HONO to be determined. Therefore, at night, the change in integrated HONO throughout the column was parameterized as a function of NO\(_2\) and HONO.
concentrations at the ground surface, which can be approximated using the mean molecular speed \( C \) of the respective gases in (E7).

\[
\frac{d\text{HONO}_{\text{column}}}{dt} = \frac{1}{8} \gamma_{\text{NO}_2, \text{ground}} C_{\text{NO}_2}[\text{NO}_2]_{\text{ground}} - \frac{1}{4} \gamma_{\text{HONO}, \text{ground}} C_{\text{HONO}}[\text{HONO}]_{\text{ground}}
\]

(E7)

Where \( \text{HONO}_{\text{column}} \) is the integrated column density of HONO throughout the observed atmospheric column (molec cm\(^{-2}\)). The calculated uptake coefficients of NO\(_2\) and HONO allow the contributions of each term in E3 to be more thoroughly explored, but are limited in identifying when transport limitations, such as the aerodynamic resistance in E4, may be significant in limiting the uptake of HONO at the ground surface. The second term in E7 determines the net exchange of HONO from field observations and does not assume irreversible loss to the surface. The ground uptake coefficient of NO\(_2\) at the surface was calculated from 18:00 – 24:00 MST when HONO mixing ratios (and the second term of (E7)) were small. These uptake coefficient values were used to calculate the subsequent uptake coefficient of HONO at the surface as its mixing ratios increased from 00:00 – 06:00. Conversion of NO\(_2\) has been suggested to depend on relative humidity (Stutz et al., 2004), and presumably uptake of HONO is as well. Nitrous acid uptake should also exhibit a pH-dependence due to its weak acidic nature (Hirokawa et al., 2008; Becker et al., 1998). Therefore, relative humidity-dependent relationships were explored for both processes and weighted linear parameterization of the ground uptake coefficients were developed (Section 4.3.6). Suitability of the field-derived measures were compared to lab results for this surface chemistry and the surface production of HONO via NO\(_2\) with both production and loss terms in (E5) were used in the simple box model. These parameterizations are more representative of nocturnal production and loss of HONO than the traditional NO\(_2\) conversion frequencies (0.1 to 2 % (Sorgel et al., 2011a; Su et al., 2008b)) used when the vertical structure and column change in HONO and NO\(_2\) concentrations are not measured.
4.2.7.3 Simple Box Model for HONO

A simple box model was created to separate the contributions of individual mechanisms in the diurnal production and loss of HONO (E9). Rates for i) the temperature and pressure-dependent reaction of OH + NO (k₃) and ii) the temperature-dependent reaction of OH + HONO (k₅) were calculated from data tabulated in Sander et al. (2011), using observed [M], temperature and pressure. The HONO photolysis rate (was calculated as a combination of j₉NO₂ and j₉O₃. This method of calculating j₉HONO was developed from measurements of j₉HONO, j₉NO₂ and j₉O₃ made during CalNex 2010 combining j₉NO₂ and j₉O₃ in an iterative linear algorithm to yield the coefficients in E8 (R² > 0.999) (Young et al., 2012).

\[ j_{HONO} = (j_{NO2} \times 0.19308) + (j_{O3} \times 2.54024) \]  
(E8)

Surface processes were carried out in a dynamic boundary layer with a fixed height of 150 m at night, which grew monotonically from 06:00 – 13:00 MST to a 1000 m mixed layer from 13:00 – 18:00 MST and collapsed back to 150 m from 18:00 – 20:00 MST. Reaction of NO₂ and HONO on the ground surface represented by E7 were used to explore the sensitivity of the unknown daytime HONO source and total surface deposited HONO. A literature deposition velocity of NO₂ to the surface, vₑ, of 0.02 cm s⁻¹ (Spicer et al., 1989) was used in place of \( \frac{1}{8} V_{NO_2,ground} \times C_{NO_2} \) to contrast the HONO production parameter (E10) to the data attained from full column measurements of NO₂ and HONO.

\[
\frac{d[HONO]}{dt} = P(HONO)_{unk} + k₃[OH][NO] + \frac{1}{8} V_{NO_2,ground} C_{NO_2} [NO_2]_{ground} \\
- \frac{1}{4} \frac{V_{HONO,ground} C_{HONO}}{h} [HONO]_{ground} - k₅[HONO][OH] - j_{HONO}[HONO] \\
(E9)
\]

\[ P_{(HONO)} = \frac{1}{2} \frac{V_{dep,NO_2}}{h} [NO_2] \]  
(E10)

It was further assumed that horizontal and vertical advection were minor particularly in the NBL due to the local to regional scale production of HONO under the low wind conditions selected...
and that the well mixed daytime boundary layer was not significantly influenced by direct HONO emissions from local sources. Chemical production of HONO in the model was initialized at 18:00 MST using the observational constraints shown in Figure 4-2.

Figure 4-2. Box model input values of measured constraints for diurnal modeling of HONO chemical behaviour and quantifying the missing HONO source/sink.

4.2.7.4 Magnitude of the Unknown Daytime HONO Source

The pseudo steady state in HONO observed late in the day (i.e. \( \frac{d\text{HONO}}{dt} = 0 \)) was used to infer the presence of an unknown HONO daytime source. The strength of the daytime source was calculated using E9. To run the model through daytime hours the HONO photolysis rate (\( j_{\text{HONO}} \)), [OH], [M] and [NO], temperature and pressure were required as described above. Production of HONO from the termolecular gas-phase reaction of NO with OH (R3) and loss of HONO by reaction with OH (R5) were determined using T, P and [M] to solve for the rate coefficients (Sander et al., 2011). The model was run using observational constraints and the same approximated dynamic daytime boundary layer height described in 4.2.7.3 (\textit{vide supra}). The magnitude of known contributions to the daytime production of HONO were compared to the
unknown source calculated from the observations and initialized using the observed values at 18 h (Figure 4-2). Continuous surface measurements of OH at 10 m agl were limited to 17 – 27 February and the input values were limited to those observed over this period. The sensitivity of the daytime source from a continuous surface production and deposition of HONO via the nighttime heterogeneous mechanisms was determined using E9. Finally, we investigated the potential importance of a HONO reservoir at the surface if HONO deposited to the surface were available as a source the following day by integrating the surface deposited HONO and unknown source terms.
4.3 Results and Discussion

4.3.1 Calibrations and Inlet Characterization

Calibrations of each inorganic gas have been previously reported by Roberts et al. (2010) for measurements made with a different inlet design. The addition of a heated inlet, optimized for the transmission of inorganic acid gases and with minimized volume required extensive characterization before being deployed for NACHTT. Calibrations displayed in Figure 4-3 show responses similar to that previously reported (Roberts et al., 2010), with high linearity (Table 4-2). However, in this investigation the dynamic ranges for calibration were significantly more relevant to typical mixing ratios of these inorganic acids in the atmosphere, ranging from hundreds of pptv to several ppbv, as opposed to several tens of ppbv. Therefore, there is increased certainty in the abilities of NI-PT-CIMS to successfully sample and ionize these gases without negative interferences resulting in their loss at atmospherically relevant mixing ratios.

<table>
<thead>
<tr>
<th>Acid Species</th>
<th>Sensitivity (counts pptv(^{-1}))</th>
<th>Detection Limits (pptv)</th>
<th>Accuracy (%)</th>
<th>Linearity (R(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl (35)</td>
<td>1.98 (0.09)</td>
<td>70</td>
<td>15</td>
<td>0.999</td>
</tr>
<tr>
<td>HNCO (42)</td>
<td>9.18 (0.21)</td>
<td>20</td>
<td>15</td>
<td>0.997</td>
</tr>
<tr>
<td>HCOOH (45)</td>
<td>4.40 (0.12)</td>
<td>20</td>
<td>15</td>
<td>0.998</td>
</tr>
<tr>
<td>HONO (46)</td>
<td>10.35 (1.76)</td>
<td>3.8</td>
<td>15</td>
<td>0.999</td>
</tr>
<tr>
<td>HNO(_3) (62)</td>
<td>5.00 (0.35)</td>
<td>27</td>
<td>15</td>
<td>0.980</td>
</tr>
</tbody>
</table>

Several calibrations for each standard gas, run by independent methods/instruments, gave complimentary results for NI-PT-CIMS sensitivity before, during and after the campaign. This is reflected in the high precision of the sensitivity values for the inorganic acids which were evaluated over all calibrations, ranging from 1.1 – 7 % for HONO and HNO\(_3\), respectively. The overall accuracy of the instrument (Table 4-3) is largely due to the uncertainty in the secondary method of quantitation for the primary calibration standard (e.g. ion chromatography ionic solution calibrations, absorption cross-sections in FTIR). The sensitivity for the formic acid...
permeation device was determined after the campaign when the permeation emission rate was determined (Table 4-1). A linear calibration was obtained prior to the campaign with $R^2 > 0.999$ using relative concentrations normalized to the highest standard mixing ratio.

![Figure 4-3](image_url)

**Figure 4-3.** Typical calibration curves for each acidic gas species during the NACHTT campaign. Error bars represent 1 σ in both ion counts and calibration gas concentrations. Larger error bars at higher mixing ratios is a function of lower dilution flows, where variability in the output of the calibration source causes greater variability. Lines represent a linear least-squares regression fit to the data. Sensitivities (slopes) and correlation coefficients are listed in Table 4-2.

This formic acid calibration was subsequently normalized to the calibrated standard concentration, along with the online calibrations carried out throughout the NACHTT campaign (Figure 4-4) This normalization enabled changes in the instrument sensitivity towards organic acids to be tracked when it was online. A dramatic shift in HCOOH sensitivity from a factor of 2 to 1.4 after the acetic anhydride reservoir was refilled in the field was found, but no change in
sensitivity towards the inorganic acid sensitivities was observed in calibrations performed within 24 hours of the reservoir refill. The explanation for a change only in the HCOOH sensitivity remains unclear. The formic acid mixing ratios were calculated accounting for the change in instrument sensitivity recorded in real time. The numerous calibrations for HCl, HNO$_3$ and HONO carried out in the field did not show any significant variability. Hence, a static calibration factor for these compounds was applied to calculate the measured mixing ratios of these gases throughout the campaign.

**Figure 4-4.** Formic acid observations from NACHTT according to end of campaign calibration (green trace) and corrected formic acid mixing ratios according to sensitivity changes from online HCOOH calibrations (black trace). The red trace shows the real-time changes in instrument sensitivity towards HCOOH defined by smoothed fit to the online calibrations recorded every other hour, normalized to the calibrated HCOOH sensitivity.

Inlet transmission efficiency for HCl and HONO was initially optimized as these compounds were the most desired in the NACHTT framework of halogen activation and the heterogeneous chemistry of nitrogen oxides. The sampling frequency of the NI-PT-CIMS was 0.1 Hz, so transmission efficiencies less than 10 s were optimal in this study. Nitrous acid was found to be transmitted within this limitation at all temperatures, while HCl showed variable transmission times up to 60 °C, at which the 10 s transmission was achieved in all trials (Figure 4-5). Subsequent measures of HNCO and HCOOH transmission efficiencies were solely evaluated at 60 °C to confirm less than 10 s transmissions. Finally, the transmission of HNO$_3$ was evaluated
at 60 °C and found to be on the order of 40 s to reach the maximum signal. While this is a significant improvement over the previously reported transmission time of > 8 min by Roberts et al. (2010), it indicated that vertical resolution for this compound would be a running 4 point average for HNO₃ at a 0.1 Hz measurement rate. An operating inlet temperature of 60 °C was chosen for field sampling because reduced transmission times and greater variability were observed for HNO₃ at 70 and 80 °C. The transmission times for all acids in the heated inlet design reported in Table 4-3 were at least a factor of 4 better than those previously reported for this instrument (Roberts et al., 2010).

Breakthrough investigations showed minor transmission of HNCO and HONO through the annular denuder in the blank channel at 0.1 and 0.5 % of the calibration gas mixing ratio ranges reported in Table 4-3. The other acids tested showed no breakthrough. These values held even when using a denuder that had operated in the field for several weeks. Since no significant issues were found with collection efficiencies of trace acids in the annular denuder, the background corrections for these acids are thought to be the best possible for automated backgrounds carried out by the inlet.

![Figure 4-5](image.png)

**Figure 4-5.** Temperature dependence of gaseous acid transmission through novel inlet design presented in Figure 4-1. Error bars indicate 2 σ collected over n = 5 trials conducted at each temperature.

However, desorption of HCl and HNO₃ produced positive artifact signals for these species during the on-the-fly backgrounds conducted during the NACHTT field campaign. These acids show strong surface adsorption characteristics, particularly with metals such as the stainless steel
flow tube of the NI-PT-CIMS and has been a noted issue (Roberts et al., 2010). Lab trials conducted using the standard reaction flow tube pressure of 25 Torr found that these acids displayed significant ion count signals during backgrounds. The magnitude of the signal was dependent on the mixing ratio of acid sampled prior to the start of a background measurement, with decay time constants on the order of 2 minutes. The final signal in all lab trials with these two acids was always on the order of a few hundred pptv after the 10 minute duration of a field background, considerably higher than was observed in the backgrounds collected during NACHTT. Since the primary standards were not capable of replicating the normally small concentrations of these acids seen during the field campaign, these tests served as proof of a positive interference due to physical desorption. They did not provide the ability to apply a fully characterized correction of this phenomenon.

Table 4-3. Summary of results from laboratory inlet characterisation tests performed.

<table>
<thead>
<tr>
<th>Acid Species (m/z)</th>
<th>Breakthrough (%)</th>
<th>60 °C Inlet Response Time (s)</th>
<th>Bkg Desorption Correction</th>
<th>Concentration Range (pptv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl (35)</td>
<td>0</td>
<td>5</td>
<td>Yes</td>
<td>1 000 – 25 000</td>
</tr>
<tr>
<td>HNCO (42)</td>
<td>0.3</td>
<td>0.1</td>
<td>No</td>
<td>4 000 – 8 000</td>
</tr>
<tr>
<td>HCOOH (45)</td>
<td>0</td>
<td>0.7</td>
<td>No</td>
<td>2 500</td>
</tr>
<tr>
<td>HONO (46)</td>
<td>0.5</td>
<td>0.6</td>
<td>No</td>
<td>600 – 7 000</td>
</tr>
<tr>
<td>HNO₃ (62)</td>
<td>0</td>
<td>44</td>
<td>Yes</td>
<td>900 – 10 000</td>
</tr>
</tbody>
</table>

Instead, the desorption of HCl and HNO₃ during NI-PT-CIMS backgrounds was corrected for manually throughout the dataset by removing the automatic subtraction of background counts from the data analysis software (IgorPro, Version 6.22A, Wavemetrics, Lake Oswego, OR) was disabled and manual assessment of the lower limit of the recorded background data was done instead. Therefore, a lower limit for concentrations of HCl and HNO₃ during NACHTT were reported with average offsets of 270 and 200 pptv, respectively. This may be an over correction to the true values of HCl and HNO₃, but it is a more accurate approach than subtracting the significantly higher positive artifact corrections and is likely within 100 ppt of the true values for these species. Improvement in the overall accuracy of the NI-PT-CIMS when measuring these
acids requires a reaction flow tube operating at significantly lower pressures to reduce surface adsorption. Alternatively, a full characterization of the concentration-dependent adsorption-desorption properties of HCl and HNO₃ at mixing ratios from 0 – 5000 pptv, representative of the atmospheric mixing ratios observed for these gases would also suffice.

4.3.2 Intercomparison with fixed height MC-IC measurements
During NACHTT, tropospheric trace acids HONO, HCl and HNO₃ measured by the MC-IC system showed consistently lower mixing ratios than those averaged over the NI-PT-CIMS pass-bys throughout the campaign (Figure 4-6). The consistent bias is likely due to losses on the large diameter inlet system used by the MC-IC to draw air samples from 20 m agl to the sampling apparatus located on the ground. Measurements of HCOOH, on the other hand, were comparable with the MC-IC, but the MC-IC often measured higher mixing ratios.

![Graph](image)

**Figure 4-6.** Time series of data points which met the statistical parameters for intercomparison between the MC-IC (open circles, grey line) and NI-PT-CIMS (filled black circles and line) measurements of HCOOH, HONO, HCl and HNO₃, descending from the top respectively.

Also, potential issues occurring in the NI-PT-CIMS due to particle volatilization may have created bias. As shown in the previous section, extensive characterization experiments were required to transmit and scrub gases efficiently by using small inlet volumes and heated lines when acids have strong surface adsorption properties.
Sampling bias through inlet losses are particularly obvious in the intercomparison of HCl measurements, where the NI-PT-CIMS measured 4 times more of this gas than the MC-IC system, particularly at night (Figure 4-7). Unfortunately, each instrument had significant periods where HCl was not detected due to infrequent passes by the NI-PT-CIMS, measurements below the detection limit of the MC-IC, or instrument maintenance. In particular, periods where the MC-IC detected maxima in HCl mixing ratios occurred mid-day when the carriage was on the ground for maintenance and calibrations. Frequently, the NI-PT-CIMS was not making measurements during that period because the PLiN was being refilled with liquid nitrogen. The best continuous coverage and temporal correlation between HCl measurements occurred from 26 February – 02 March, with the NI-PT-CIMS measuring significantly higher concentrations (Figure 4-6).

During this period refractory chloride detected by the AMS PM_{1.0} measurement was observed at night. When fine mode aerosol chloride was present, the mass loadings were equivalent to 0.01 to 0.04 % of the difference between the HCl measurements. As discussed previously (Section 4.3.1), the data collected by the NI-PT-CIMS is more likely to underestimate the amount of HCl in the atmosphere based on the correction strategy employed for desorption during backgrounds, possibly meaning there is an even greater discrepancy. Therefore, it seems likely that the MC-IC inlet suffered significant losses of HCl. This is difficult to confirm given the paucity of comparable points and the lack of inlet characterization of HCl transmission for the MC-IC.
Figure 4-7. Intercomparison of MC-IC and NI-PT-CIMS HCl measurements (± 1σ) from 19 February – 02 March. Correlation between datasets was determined using an orthogonal least distance fit to the data to account for the error in each measurement.

In contrast, MC-IC inlet transmission of HONO, an acid species which does not exhibit strong surface adsorption properties, appears to be reasonable, resulting in a good comparison between instruments by least-square analysis (R² = 0.87). The NI-PT-CIMS measures about 40% more than the MC-IC throughout the campaign, with less difference at the lowest observed concentrations (10 - 15 %). These observations support the hypothesis that the MC-IC was losing acids on the walls of the 20 m inlet, regardless of the high flow rate employed. Again the MC-IC measures less HONO than the NI-PT-CIMS on all occasions. The temporal correlation and continuity of data – due to maximum HONO concentrations at night when both instruments were online – offers a better perspective on inlet loss that the other acids. To ensure that the difference was not driven by a gradient in HONO around the fixed height platform, binned measurements were recalculated by measurements made i) 4 m to either side of the platform and ii) only 8 m above. Neither approach changed the slope of the best fit intercomparison line by more than 5 %. Therefore, it can be concluded that inlet or sampling losses are responsible for the difference in these measurements and that HONO is measured accurately by the NI-PT-CIMS.
Figure 4-8. Intercomparison of MC-IC and NI-PT-CIMS HONO measurements (± 1σ) from 19 February – 02 March. Correlation between datasets was determined using an orthogonal least distance fit to the data to account for the error in each measurement.

In comparing HCOOH, the greatest driver of uncertainty was the MC-IC 500 pptv detection limit and the associated 225 pptv uncertainty (Figure 4-9). This significantly limited the ability to draw firm conclusions on the abilities of either instrument. In general, the MC-IC appears to be measuring more HCOOH than the NI-PT-CIMS in context of the 1σ error bars in Figure 4-9. However, 2σ error (i.e. the 95% confidence interval) would generally encompass the 1:1 line and exceed the quantity of HCOOH measured above the detection limit of the MC-IC. Meanwhile, the NI-PT-CIMS has undergone rigorous evaluation to certify its ability to detect and accurately quantify HCOOH here and in previous work (Veres et al., 2008; Veres et al., 2010; Veres et al., 2011), in addition to the continuous online calibrations conducted throughout NACHTT. The HCOOH observed by the NI-PT-CIMS throughout the NACHTT campaign was often below the MC-IC detection limits, suggesting that the MC-IC may be prone to an artifact or calibration issue in quantifying this organic acid.
Finally, measurements of HNO$_3$ were compared. Of particular interest for the NI-PT-CIMS measurement was whether an interference existed from the transmission of volatile fine mode (< 1 µm) NH$_4$NO$_3$ in to the inlet. The extent of repartitioning of the NH$_4$NO$_3$ aerosol when suddenly heated in the inlet was uncertain prior to sampling in the field. Thermodynamic partitioning favours the formation of NH$_4$NO$_3$ from precursor gases under the cold, higher relative humidity, conditions of the wintertime atmosphere. The construction of the inlet was designed to exclude as many particles as possible, but fine mode aerosols were likely efficient at remaining constrained in the sample flow of the NI-PT-CIMS. Subsequently, aerosols heated to 60 ºC from ambient temperatures of -10 - 25 ºC would have dried and repartitioned the condensed phase NH$_4$NO$_3$ to gaseous NH$_3$ and HNO$_3$.

The rate of NH$_4$NO$_3$ repartitioning as a function of aerosol water content and inlet transit time was not characterized before the campaign. Instead, the field data was examined to determine the potential for and extent of this interference. The MC-IC HNO$_3$ observations – despite their likely low mixing ratios – and the aerosol mass spectrometer particle nitrate (pNO$_3^-$) measurements were used in this assessment (Figure 4-10). Panel A shows a dramatic interference in the NI-PT-
CIMS measurement of HNO₃ at high mass loadings of PM₁₀ volatile pNO₃⁻ (> 4 µg m⁻³) creating an artifact of more than 1 ppbv in HNO₃. There are also indications that the MC-IC measured more HNO₃ than the NI-PT-CIMS on a number of occasions, particularly from 26 February – 4 March. Panel B illustrates that this occurred when relative humidity was less than 30 % and under low mass loadings of pNO₃⁻. As mentioned in the previous section, the offset correction in the HNO₃ measurement of the NI-PT-CIMS could account for up to 200 pptv of error in the difference and the MC-IC quantitative error is 45 pptv, giving a total potential error of 245 pptv. However, some observations in excess of this error suggest a negative artifact in the NI-PT-CIMS or a positive artifact in the MC-IC at low relative humidity. Under conditions of low relative humidity, it is expected that the NI-PT-CIMS would transmit HNO₃ more effectively since there would be less water-driven adsorption to the inlet surface. However, we do not have a measure of compounds such as NH₃ from the carriage, but the MC-IC NH₃ measurement indicates a wide range NH₃ (1.4 – 15 ppbv) at these low relative humidities. Therefore, if the inlet was being coated with ammonia, it could have been causing inlet losses, but we do not see a correlative trend with atmospheric mixing ratios.
Figure 4-10. Interference of NH$_4$NO$_3$ on the NI-PT-CIMS measurement of A) HNO$_3$ during NACHTT and B) the relative humidity dependence of the difference between the NI-PT-CIMS and MC-IC HNO$_3$ as function of pNO$_3^-$ mass loadings. The colour scale in A ends at 4 µg m$^{-3}$, but mass loadings up to 16 µg m$^{-3}$ are depicted using the same shade.

Alternatively, heating of the MC-IC inlet could volatilize any adsorbed HNO$_3$ during the day, when relative humidity is low. This is a likely fate for HNO$_3$ in this inlet since we observed similar issues in HCl and HONO, which did not have high particulate loadings (i.e. potential for particulate positive interference). Furthermore, the large diurnal cycles in relative humidity (5 – 92 %) and temperature (-10 – 20 °C) that would have affected the 20 m inlet could have easily driven a difference of a few hundred pptv (Figure 4-10B) if condensation losses at night accumulated HNO$_3$ on the MC-IC inlet and repartitioned under favorable conditions. Overall, we observed the greatest interference in the NI-PT-CIMS HNO$_3$ measurements at RH > 30 % and pNO$_3^-$ > 1 µg m$^{-3}$. Unfortunately, too few data points were collected using the 2 hour comparison interval to derive a robust correction for the interference from the difference in HNO$_3$. 
observations at the 20 m sampling height (Figure 4-10B). These data suggest that any inlet for the NI-PT-CIMS can quantify this interference by generating known quantities of NH$_4$NO$_3$ under variable conditions of RH. Alternatively, a comprehensive particle exclusion apparatus, such as a virtual impactor or automated filter changing system, could improve HNO$_3$ measurements in the presence of significant mass loadings of volatile pNO$_3^-$ (e.g. 1 µg m$^{-3}$, fully volatilized, generates 0.388 ppbv of HNO$_3$). The NACHTT field campaign was the first field dataset where such an evaluation was possible and presents a clear limitation in the use of the NI-PT-CIMS to make measurements of HNO$_3$ or other acids that may form significant quantities of semi-volatile salts relative to their gas phase mixing ratios by volatilizing in a heated inlet.
4.3.3 Nitrous Acid (HONO): General Observations

Figure 4-11 shows the full measurement dataset for the physical and chemical components of the HONO formation system. There were four different weather regimes throughout the campaign. From 18-25 February there was a cold, moist period. Temperatures cycled between -10 – 10 °C with relative humidities between 30 – 90% diurnally. This was followed by a warm moist period from 26 February – 3 March, with daytime maximum temperatures nearing 20 °C and rarely cooling below 0 °C at night. Conditions similar to those of the first period occurred from 4-9 March, with a freezing fog event on the night of 4-5 March before starting to warm again for the end of the campaign. The background concentration of O₃ at this site is on the order of 50 ppb (Figure 4-12).

![Figure 4-11](image_url)

**Figure 4-11.** Continuous vertically resolved field observations used in the analysis of HONO nighttime formation during NACHTT filtered to remove wind speeds greater than 6 m s⁻¹ and periods of stationary measurements. Daytime OH measurements were made only for the first 10 days of the campaign.

At night, the development of the nocturnal boundary layer can be observed by the depletion of ozone via reactions with NOₓ emissions at the surface. Combining the depletion of O₃ with inversions in the potential temperature from the surface at night allowed the presence and depth
of the nocturnal boundary layer to be assessed (Figure 4-12) according to the method previously published for this site by Brown et al. (2007). Identification of the height at which measurements of potential temperature and ozone show small changes with subsequent increases in height were manually determined to assign the location of the NBL.

**Figure 4-12.** Binned evolution of a nocturnal boundary layer in 2 hour intervals after sunset until the next morning on 27 – 28 February, except 00:00 – 02:00. Small rate of change in both potential temperature and O$_3$ concentration aloft indicate the approximate location of the nocturnal boundary layer. Note that O$_3$ increases throughout the night as new air is transported to the site in the residual layer, returning the background concentration of O$_3$ to near 50 ppbv.

At night, HONO was found to accumulate in greatest quantities near the surface, building up to mixing ratios greater than 1 ppb on five nights (19, 20, 28 February and 4, 8 March), and roughly 500 pptv on the remaining nights of observations (Figure 4-11). Vertical stratification was variable between nights. On some nights, the NBL formed from a stable surface layer like that shown in Figure 4-12, while on others the NBL was fully developed within two hours after
sunset. This NBL variability can be observed in Figure 4-13 by the height of HONO vertical transport on a night-to-night basis. The presence of stable boundary conditions has been suggested as a key parameter in the accumulation and stratification of HONO at night in models (Geyer and Stutz, 2004; Wong et al., 2011; Vogel et al., 2003) and in field observations of HONO vertical profiles (Kleffmann et al., 2003; Wong et al., 2011; Zhang et al., 2009). Higher HONO mixing ratios in surface layers indicates that the ground surface dominates the surface area responsible for heterogeneous production of HONO from NO$_2$ at the BAO tower. However, mixing ratios of HONO up to several hundred pptv were also found to accumulate in the residual layer on a number of nights (e.g. 22-23 and 27-28 February). In-column HONO production on aerosol surfaces may, therefore, also have generated a non-negligible quantity of HONO at night (S.4.3.5). Nights when stable layers of air were formed at the surface generally occurred with low wind speeds (< 6 m s$^{-1}$) meaning HONO production was regional in scale (Figure 4-15). Several high wind events on 19, 23, 26, 28 February and 3 March, due to synoptic scale storms from the Pacific coast, significantly inhibited the accumulation of HONO. Transport of air masses with small amounts of precursor NO$_2$ and high dilution of the local atmosphere resulted in little HONO production. Due to the dilution effect on the observable chemistry, these high wind events were excluded from the nighttime analysis of HONO formation.
Figure 4-13. Curtain plot of HONO vertical mixing ratios measured by the NI-PT-CIMS during NACHTT. Note that the colour scale ends at 800 pptv of HONO to optimize contrast in the vertical gradients of HONO observed even though mixing ratios up to 2 ppbv were observed during the campaign. Mixing ratios of HONO in excess of 800 pptv are white data points.

Photolytic loss of HONO throughout the column during the day, specifically near the surface in the early morning, has an observable impact on the early morning and total production of OH radicals in the wintertime atmosphere of Erie (Saewung Kim, personal communication; Figure 4-14), an observation expected under low actinic flux conditions, but not reported to date.
Figure 4-14. Net OH production throughout the mixed surface layer from HONO production and loss processes during NACHTT. Sources of OH are positive ($j_{\text{HONO}}[\text{HONO}]$), sinks are negative (OH + NO and OH + HONO) and contributions are stacked for each. Overlaid are the net OH production (black) and the observed OH concentrations (red) over the period of 19 – 25 February.

Average photostationary mixing ratios of ~100±80 pptv HONO were seen during the day (12:00 – 16:00 MST) throughout the campaign. Vertical profiles during the day showed HONO enhanced near the surface, indicative of a daytime surface source postulated by the results of other field observations (Stutz et al., 2002; Qin et al., 2009; Zhou et al., 2011; Sorgel et al., 2011a; Li et al., 2012), and supported by conversion of NO$_2$ to HONO on photoexcited substrates in lab studies (Gerecke et al., 1998; George et al., 2005; Brigante et al., 2008; Ndour et al., 2008; Ndour et al., 2009; Bartels-Rausch et al., 2010; Ammar et al., 2010; Stemmler et al., 2006). However, the lab-derived mechanisms for HONO production at the ground surface are not well-constrained by field observations due to the difficulty in quantifying their separate contributions. The potential HONO production from these sources has largely been considered inadequate in accounting for daytime HONO production rates in polluted regions ranging from several hundred
pptv per hour to 2 ppbv hr\(^{-1}\) (Kleffmann et al., 2005; Kleffmann, 2007; Su et al., 2008b; Qin et al., 2009; Sorgel et al., 2011a; Wong et al., 2012). The exception to this comes from Sorgel et al. (2011a), where humic acid at the surface was estimated to account for up to 30% of the daytime source. The magnitude and temporal trend of the daytime HONO source at the BAO tower are explored in detail in S.4.3.8.

![Windrose plot of HONO observations](image)

**Figure 4-15.** Windrose plot of HONO observations with 0° as north. Rings around the origin denote increasing windspeeds in 4 m s\(^{-1}\) intervals up to 16 m s\(^{-1}\). HONO mixing ratios have been sorted from highest to lowest to depict the local to regional nature of HONO formation at night.

### 4.3.4 Nighttime HONO vertical profile structure

#### 4.3.4.1 HONO, NO\(_2\), and the nocturnal boundary layer

During NACHTT vertical profiles were observed during nights when stable surface and nocturnal boundary layers (NBLs) formed (Figure 4-16). The height of the mixing ratio gradient in HONO was found to increase with the depth of the observed boundary layer (Figure 4-16), and higher mixing ratios of NO\(_2\) (Figure 4-17). The upper panel in Figure 4-16 depicts an example of the evolution of a HONO vertical profile with increasing nocturnal boundary layer (NBL) height collected on 27 - 28 February.
Figure 4-16. Example of evolution of HONO vertical profiles from 18:00 – 06:00 in 2 hour bins (excluding 00-02 hr due to instrument maintenance) on 27-28 February. Each time bin shows the average vertical structure of HONO from 18 - 20 hr (green), 20 - 22 hr (gold), 22 - 00 hr (purple), 02-04 hr (black), 04 - 06 hr (blue). The height of the thermal inversion layer was not constant throughout the night and is denoted in each bin by the shaded yellow bar. In the bottom set of panels, vertical profiles of relative humidity and NO\textsubscript{2} (increased by a factor of 10) also show vertical structure in the nocturnal boundary layer.

As the boundary layer grows through the night, the gradient in HONO increases approaching the surface by a small amount in the first two hours, then the mixing ratio of HONO increases at the surface by 100, 500, 750, and 850 pptv in each subsequent two hour interval. During this same
period, the mixing ratio of NO\textsubscript{2} at the surface increases from 7 to 16 ppbv. The bottom series of panels in Figure 4-16 shows that the stable NBL is also confining emissions of NO\textsubscript{2} to the surface, enhancing HONO formation. Relative humidity throughout the night decreases from 80 to 35% when moving from the surface to above the NBL, but remains near 80% at the surface throughout the night. The accumulation of HONO near the surface plateaus near 1000 pptv from 02 – 06 hr. There are two competing processes that can lead to this observation: i) a decrease in the HONO production rate due to limited transport and conversion of NO\textsubscript{2} at the surface (R1), and/or ii) loss of HONO to the surface by dry deposition. Both terms are limited by diffusion of the molecules to the surface and their reaction probabilities. Assuming that ground surface production dominates observed HONO formation, the integrated column amount of HONO can be described in terms of the surface processes in E7 since the remaining terms in E9 are only significant during the day.

The observations in Figure 4-16 are consistent with the description of HONO production and dry deposition rates having reached a pseudo steady state during the last 4 hours of the night. This is also consistent with observations in several other studies over land (Kleffmann et al., 2003; Stutz et al., 2004; Wong et al., 2011) and the ocean (Wojtal et al., 2011). In Figure 4-16, it is clear that the mixing ratios of HONO are increasing faster than those of NO\textsubscript{2} at the surface throughout the night, thereby increasing the value of the second term in the column rate change from (E7) relative to the production term. Similar profiles were observed on 9 other nights in the campaign, although there is considerable variation in the vertical structure due to: i) the presence and depth of surface and NBLs, ii) the amount of NO\textsubscript{2} and iii) the relative humidity at the surface. These vertical profiles are presented in the supporting information (Figure S1a, b) while the HONO to NO\textsubscript{2} correlations for all nights are shown in Figure 4-17.
Figure 4-17. Correlation plots of HONO to NO$_2$ for nights identified with nocturnal inversions and significant HONO production. All data points collected in each time bin are shown to highlight the dynamic progression of HONO production. Evolution of the average HONO/NO$_2$ is show by linear least-squares regression analysis of 2 hr bins of all data points collected from 0 – 250 m on these nights (18-20 hr, green; 20-22 hr, gold; 22-00 hr, purple; 02-04 hr, black; 04-06 hr, blue). Note the different HONO and NO$_2$ scales for Feb 18-19, 19-20, and 27-28. Least-squares linear regression slopes and correlation coefficients are presented in Table 4-4.

The linear least-squares regression correlations of HONO to NO$_2$ in Figure 4-17 are generally better than $R^2 = 0.8$, particularly from 22 - 06 h (Table 4-4). Such high correlation between HONO and NO$_2$ throughout the nocturnal boundary layer and highest absolute HONO concentrations at the surface suggest that HONO observed throughout the depth of our
measurements is dominantly derived from surface conversion of NO$_2$ on the ground followed by vertical transport throughout the column.

Table 4-4. Orthogonal least-squares linear regression slopes and correlation coefficients of HONO to NO$_2$ throughout nights identified with thermal inversions in 2 h intervals.

<table>
<thead>
<tr>
<th>Night</th>
<th>Time Period (h, MST)</th>
<th>NBL Height (m)</th>
<th>HONO-NO$_2$ Correlation Slope (%)</th>
<th>R$^2$</th>
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<tr>
<td>18 - 19 Feb</td>
<td>18 - 20</td>
<td>105</td>
<td>1.7</td>
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</tr>
<tr>
<td></td>
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</tr>
<tr>
<td></td>
<td>00 - 02</td>
<td>95</td>
<td>4.9</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>02 - 04</td>
<td>135</td>
<td>3.6</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>04 - 06</td>
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<td>3.2</td>
<td>0.89</td>
</tr>
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<td>0.08</td>
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</tr>
<tr>
<td></td>
<td>00 - 02</td>
<td>125</td>
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<td>0.78</td>
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<tr>
<td></td>
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<td></td>
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<td>205</td>
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<td>0.61</td>
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<td>0.07</td>
</tr>
<tr>
<td>1-2 Mar</td>
<td>18 - 20</td>
<td>45</td>
<td>1.1</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
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<td>2.8</td>
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<tr>
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</tr>
<tr>
<td></td>
<td>00 - 02</td>
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<td>3.7</td>
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</tr>
<tr>
<td></td>
<td>02 - 04</td>
<td>215</td>
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<td>0.71</td>
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<td>215</td>
<td>35</td>
<td>55</td>
<td>65</td>
</tr>
<tr>
<td>4-5 Mar</td>
<td>18 - 20</td>
<td>18 - 20</td>
<td>20 - 22</td>
<td>22 - 24</td>
</tr>
<tr>
<td></td>
<td>145</td>
<td>145</td>
<td>145</td>
<td>145</td>
</tr>
<tr>
<td>8-9 Mar</td>
<td>18 - 20</td>
<td>20 - 22</td>
<td>22 - 24</td>
<td>00 - 02</td>
</tr>
<tr>
<td></td>
<td>75</td>
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<td>75</td>
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</table>

We have made an approximation of the observability of aerosol-produced HONO using a scenario favoring conversion of 5-15 ppbv of NO$_2$ over a period of 2 hours with an available aerosol surface area of 100 $\mu$m$^2$ cm$^{-3}$, approximately the campaign average surface area. From these initial conditions an average increase of at least 30 pptv in the column mixing ratio of HONO would be necessary to exceed the profile-to-profile observation variability. A mixing ratio of 5 ppbv of NO$_2$ would require an uptake coefficient of at least $2 \times 10^{-4}$ to generate this quantity of HONO. Even at 15 ppb of NO$_2$, the uptake coefficient would need to be $5.5 \times 10^{-5}$ to generate observable HONO production and such high mixing ratios were seldom observed aloft (Figure 4-11). These NO$_2$ uptake coefficient values are a factor of 5 – 20 greater than those observed in lab studies on relevant surfaces (Kleffmann et al., 1998; Kurtenbach et al., 2001). Therefore, this suggests that even if NO$_2$ was being converted to HONO on aerosol surfaces, the absolute amount produced in an interval of 2 hours would barely be observable given the sensitivity of current instrumentation ($\sim$ 4 pptv for the NI-PT-CIMS) and realistic variability expected between vertical profile measurements ($\sim$ 50 pptv; Figure 4-16). In conclusion, the
HONO observed throughout the atmospheric column could only be derived from production on the ground surface and subsequent vertical transport.

Ground surface-dominated production is supported by observations of the ratio HONO/NO$_q$ throughout the campaign. These were generally uniform throughout the column. However, the use of this ratio may not be the best parameterization for understanding HONO chemistry at the surface, particularly when extensive vertical information is available and competitive sinks for NO$_2$ exist at night.

**4.3.4.2 Identifying wintertime HONO production on ground and aerosol surface: Is HONO/NO$_q$ appropriate?**

Generally, the production of HONO at night is identified by an increase in its ratio to the amount of NO$_2$ (i.e. HONO/NO$_2$), since the abundance of HONO has been shown to be highly correlated to NO$_2$. High correlations between HONO and NO$_2$ were found on all nights during NACHTT with identifiable NBLs (Figure 4-17). It is clear that the ratio of HONO to NO$_2$ increases throughout the night on most occasions, eventually reaching a pseudo steady state around midnight, and that the absolute amount of HONO produced depends on the available NO$_2$ since it is a surface dominated process (*vide supra*). What then can the HONO/NO$_2$ ratio tell us about HONO production in an air mass, is it applicable to the wintertime atmosphere, and does it have utility that direct observations of the vertical time rate of change in HONO do not?

Interpretation of the ratio of HONO to NO$_2$ generally relies on the assumption that the major sink of NO$_2$ at night is reaction to produce HONO, that most of the HONO produced is derived from NO$_2$, and that $\frac{dHONO}{dNO_2}$ is first order. The NACHTT campaign was carried out during February and March, with nighttime temperatures frequently below 0 °C. Under these conditions, competitive reactions for the loss of NO$_2$ to form NO$_3$ (R6) and N$_2$O$_5$ (R7) becomes significant and the thermal equilibrium of R7 favours N$_2$O$_5$, particularly aloft where fresh NO emissions cannot interrupt its formation via R8:

$$\text{NO}_2(g) + \text{O}_3(g) \rightarrow \text{NO}_3(g) + \text{O}_2(g)$$

(R6)
\[ \text{NO}_3(g) + \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_5(g) \]  
(R7)

\[ \text{NO}_3(g) + \text{NO}(g) \rightarrow 2 \text{NO}_2(g) \]  
(R8)

Therefore the HONO/NO\textsubscript{2} ratio can increase significantly, even in the absence of HONO production due to other NO\textsubscript{2} losses. From the NACHTT dataset the nighttime HONO/NO\textsubscript{2} ratios would be significantly overestimated, by up to a factor of two, if these sinks were not accounted for (Figure 4-18). To develop a more robust assessment in using this ratio in assigning HONO production during NACHTT we summed these sinks with NO\textsubscript{2} in to a family denoted as NO\textsubscript{q}, where:

\[ \text{NO}_q = \text{NO}_2 + \text{NO}_3 + (2*\text{N}_2\text{O}_5) \]  
(E11)

While this cannot account for the potentially fast sinks of NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} to VOC reactions and aerosol uptake, respectively, it is a more thorough representation of the NO\textsubscript{2} reservoir in a winter nighttime atmosphere. This has not been considered in other studies, where HONO/NO\textsubscript{2} ratios as high as 30 % have been reported (Yu et al., 2009).

![Figure 4-18. Potential bias in the ratio of HONO to NO\textsubscript{2} during NACHTT when assessing HONO production when sinks of NO\textsubscript{2} to form NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} are non-negligible. The sum of NO\textsubscript{2} and its measurable sinks are termed NO\textsubscript{q}.](image)
Two different observations have been made with respect to vertical gradients in the HONO/NO$_2$ ratio, which can provide context for interpreting the observations made during NACHTT. Kleffmann et al. (2003) observed the ratio to increase from 1 to 3% below 100 m as their instrument elevator approached the ground. Wong et al. (2011) observed a nearly uniform ratio up to 300 m agl on all nights, except one, during TRAMP in Houston, TX. In Houston the HONO/NO$_2$ generally increased after sunset and reached a relatively constant value from midnight to sunrise. Similar observations were made by Stutz et al. (2002) in gradient HONO measurements from 1 – 5 m agl, and Villena et al. (2011) from 9 – 60 m agl (assuming 1 story = 3 m). While the transferability of these more shallow measurements throughout the NBL is not a straightforward comparison to make, they are the best available. Kleffmann et al. (2003) took the enhanced HONO/NO$_2$ ratio near the surface to indicate that production of HONO was enhanced at the surface. However, a single profile required 4 hours to complete (18 – 24 hr) and Wong et al. (2011) and Villena et al. (2011) have shown that HONO/NO$_2$ increases hourly in column profiles after sunset. Therefore, the relative production rates of HONO at the surface relative to that aloft have been poorly characterized to date by limited investigation of HONO vertical structure.

During NACHTT, HONO/NO$_q$ profiles were measured on a 10 - 15 minute timescale when performing continuous vertical profiles over the full 250 m height of the tower. To develop a more general understanding of the evolution of HONO/NO$_q$, 2 hr interval averages were calculated from near-continuous profiling throughout several nights (Figure 4-19). These high resolution observations are the most complete picture of the vertical evolution of HONO production from field observations to date. We observed HONO/NO$_q$ ratios throughout the atmospheric column that increased throughout the early night, reaching a constant ratio near midnight. Ratios aloft were generally the same (within the observed variability between profiles) as those observed at the surface, through the NBL, and in to the residual layer. Ratios observed throughout the profiles on 27 - 28 Feb in Figure 4-19 showed stepwise increases of this ratio over each interval with values of 2, 4, 5, 6 and 6.5%. We observed this increasing trend in the presence of a shallow boundary layer on 3-4 March and a constant boundary layer with significant aerosol formation on 4-5 March (Figure 4-19). Figure 4-17 shows that uniform ratios
are likely the case throughout the campaign, since linear fits with correlations generally greater than 0.8 define any 2 hour period of observations on nights with NBLs.

The consistent HONO/NO$_q$ ratio has two mechanistic explanations i) vertical transport of air from the NBL in to the residual layer or ii) formation of HONO from conversion of NO$_2$ on aerosols is accomplishing similar conversion efficiency from the smaller precursor concentrations and available surface area in the residual layer. As discussed in Section 4.3.4.1, an observable increase in HONO from aerosol conversion of NO$_2$ is unlikely. As NO$_2$ concentrations decrease to less than 5 ppb aloft, the uptake coefficient would have to be much larger than values reported in the literature (Kleffmann et al., 1998; Broske et al., 2003; Kurtenbach et al., 2001) in order to explain our observations. Therefore, the most reasonable explanation for observing consistent ratios of HONO/NO$_2$ or HONO/NO$_q$ throughout a vertical profile of the atmosphere is simply due to HONO formation being dominated by the ground surface, followed by vertical transport, even when it is very limited (e.g. large error bars above the NBL due to small mixing ratios of all species).

Outlying points from this consistent HONO/NO$_q$ trend occur on 27-28 Feb and 3-4 March from 22-24 h showing a significantly enhanced ratio of HONO/NO$_q$ of 9% and 25% at 5 m above the surface. Such an enhancement near the ground surface would generally make the conclusion that HONO production at night is, in fact, dominated by conversion on the ground. However, this interpretation may be misleading since the absolute change in HONO mixing ratio is not considered and competing losses for NO$_2$ may be significant. Figure 4-17 shows that NO$_2$ concentrations at the surface were significant on these two nights (10 – 20 ppbv) and Figure 4-16 shows the enhancement of NO$_2$ and HONO in this near-surface layer during the same time period. However, the NO$_2$ in the surface layer (5 m agl) from 22-24 h does not continue to increase in the bin closest to the surface, while HONO has continued to be produced at the surface by roughly 250 pptv hr$^{-1}$. Therefore, these high ratio values are possibly a product of increased losses of NO$_2$ in the winter atmosphere (R6, R7) and may be misleading. Values of HONO/NO$_2$ near or in excess of 10%, have been reported for measurements made within 5 m of the ground surface before (Sorgel et al., 2011b; Yu et al., 2009), but are otherwise not generally observed.
Figure 4-19. HONO/NOq ratios (±1σ) from three nights of the NACHTT campaign with clear NBLs throughout the night. Panels moving from left to right indicate 2 h time steps from the onset of night to just before sunrise the next day (18-20 h, green; 20-22 h, gold; 22-24 h, purple; 00-02 h, red; 02-04 h, black; 04-06 h, blue). Nocturnal boundary layer height is shaded in yellow and aerosol surface areas are shown in solid grey.
Alternatively, in the two cases of HONO/NO\textsubscript{q} > 9\% during NACHTT, it is possible that a stable surface layer was present in addition to the NBL, further stratifying the nocturnal atmosphere. If the ground surface is the dominant source of HONO, then an enhanced ratio of HONO/NO\textsubscript{q} could be expected from a surface layer within the NBL as the steady state would be more quickly approached due to both reactant and product accumulating in this layer (E7). When this layer is perturbed, efficient vertical mixing with the rest of the column masks this enhanced ratio. A more informative approach requires absolute measurements of HONO and NO\textsubscript{2} at the surface and does not rely on assumptions when identifying production and loss of HONO.

Surface production and deposition of HONO may also generate a reservoir at the surface, such that ratios as high as 10\% might also result if HONO is released from the surface when the overlying air is depleted in NO\textsubscript{2} and HONO (R9, R10). Such a dynamic process has been proposed for both soil (Su et al., 2011) and ocean (Wojtal et al., 2011) surfaces where HONO mixing ratios in the atmosphere are determined by partitioning processes in an aqueous medium. In this scenario, the HONO/NO\textsubscript{2} ratio will increase, but the production of HONO should not be attributed to NO\textsubscript{2}. Simultaneous measurements of nitrite in either reservoir and near-surface HONO mixing ratios have yet to be made to confirm the validity of these hypotheses and will be a challenging task for future investigations.

\begin{align*}
\text{NO}_2(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) &\rightleftharpoons \text{HONO}(\text{aq}) + \text{H}_2\text{O}(l) \\
\text{HONO}(\text{aq}) &\rightleftharpoons \text{HONO}(g)
\end{align*}

An additional opportunity for misinterpretation of the HONO/NO\textsubscript{2} or HONO/NO\textsubscript{q} ratios is presented in a case study here. On 4-5 March an enhancement in the HONO/NO\textsubscript{q} ratio was observed to correlate with aerosol surface area in the NBL from 02 – 06 hr (Figures 4-19 and 4-20). The conversion of NO\textsubscript{2} to HONO on aerosol surfaces is generally ascribed as being negligible in the absolute production of nighttime HONO (Kleffmann et al., 2003; Wong et al., 2011). The value of the reactive uptake coefficient for NO\textsubscript{2} on a number of surfaces has been roughly constrained by lab and modeling studies at \( \gamma = 10^{-6} \) to \( 10^{-5} \) (Harrison et al., 1996; Kleffmann et al., 1998; Kurtenbach et al., 2001). The wide range of values indicates that
surface composition and the amount of available water significantly affect the heterogeneous conversion and release of HONO. Field observations that definitively identify HONO formation on atmospheric aerosols are limited and uncertain due to both ground and aerosol heterogeneous processes forming HONO in the NBL (Lammel and Perner, 1988; Reisinger, 2000; Broske et al., 2003; Su et al., 2008a; Finlayson-Pitts, 2009). Previous correlations between HONO/NO$_2$ and aerosol surface area have produced mixed results with Kleffmann et al. (2003) observing no correlation and Reisinger et al. (2000) and Su et al. (2008a) observing significant correlations. In the last study, black carbon was the primary component of the observed aerosol suggested to be responsible for this relationship, although this has been shown to quickly deactivate under dark conditions (Ammann et al., 1998; Gerecke et al., 1998; Aubin and Abbatt, 2007; Khalizov et al., 2010; Monge et al., 2010). Reisinger et al. (2000) observed a correlation with aerosol surface area, but did not have information on either aerosol composition or NBL height to provide conclusive evidence of aerosol surface production.
During NACHTT, a measure of black carbon mass loadings was not available, but NH$_4^+$-NO$_3^-$-SO$_4^{2-}$ composition was available from the AMS in addition to N$_2$O$_5$ via cavity ring-down. During the night of 4-5 March there was misting precipitation followed by near saturated humidities from 00 – 06 hrs (Appendix B, Figure 4-S1b). This resulted in > 100 $\mu$m$^2$ cm$^{-3}$ surface area of deliquesced NH$_4^+$-NO$_3^-$-SO$_4^{2-}$ aerosol throughout the 145 m NBL. In Figure 4-20, the aqueous nature of the aerosol can be inferred via increasing mass loadings of NO$_3^-$ with increasing humidity in excess of 10 $\mu$g m$^{-3}$. Two processes can lead to such observations: i) increased partitioning of HNO$_3$ and ii) increased reactive uptake of N$_2$O$_5$ to the aqueous phase (Bertram...)

**Figure 4-20.** Correlations between HONO/NO$_q$ and aerosol surface area on 4-5 March from 02-04 (black line, slope = 7.41x10$^{-5}$) and 04-06 hr (blue line, slope = 1.43x10$^{-4}$) as a function of relative humidity (top) and mass loading of particulate matter NO$_3^-$ in aerosols less than 1 $\mu$m in diameter (bottom).
and Thornton, 2009). Figure 4-21 shows a maximum of 1 ppbv N\textsubscript{2}O\textsubscript{5} near the top of the boundary layer, decreasing rapidly as the aerosol surface area increases from 100 to 350 \textmu m\textsuperscript{2} cm\textsuperscript{-3}. The reduced N\textsubscript{2}O\textsubscript{5} mixing ratios approaching the surface are most likely due to efficient uptake of N\textsubscript{2}O\textsubscript{5} on the aqueous aerosol and ground surface water, with the possibility that the loss of N\textsubscript{2}O\textsubscript{5} in this layer is occurring nearly as fast as it is formed. The accumulation of nitrate in the aerosol supports the N\textsubscript{2}O\textsubscript{5} loss hypothesis since it is a direct product and HNO\textsubscript{3} mixing ratios are too small to produce the observed mass loadings of pNO\textsubscript{3}\textsuperscript{-} by partitioning. Therefore the correlation of enhanced HONO/NO\textsubscript{2} or HONO/NOq ratio and aerosol surface area is misleading in suggesting HONO formation because the change in the ratio is due to a fast indirect sink of NO\textsubscript{2}. Inspecting the HONO measurements directly shows that there is a net loss of HONO in this same period (650 pptv to 450 pptv).

**Figure 4-21.** Average vertical profiles of N\textsubscript{2}O\textsubscript{5} on 4-5 March (00-02 hr, red; 02-04 hr, black; 04-06 hr, blue) with aerosol surface area (solid line, grey) in the nocturnal boundary layer (yellow). The mixing ratio of N\textsubscript{2}O\textsubscript{5} is likely depleted by efficient reactive uptake on to aqueous aerosols within the boundary layer.

Since the AMS and UHSAS size cut-offs are both near 1 \mu m, there could be even more surface area available when including 2.5 \mu m diameter aerosols during a titration of N\textsubscript{2}O\textsubscript{5}. The emphasizes that under some conditions, even the quantity NO\textsubscript{q} is not a conserved tracer of NO\textsubscript{2}.

To conclude, it is again stressed that increased caution in the reliance on the HONO/NO\textsubscript{2} ratio must be taken when assigning HONO production in the atmosphere, in particular, when making
measurements under conditions that support significant NO₃ and N₂O₅ formation, and conversion of gas phase NOₓ to aerosol nitrate. When possible, absolute measurements of HONO production and loss should be used. These provide the additional benefit of identifying alternative HONO precursors other than NO₂, but require vertically resolved measurements to account for vertical structure. Finally, unless conversion of NO₂ on aerosols can be shown to have an uptake coefficient an order of magnitude larger than current studies suggest, production from this mechanism should be viewed as negligible and measurements of the production or loss of HONO be addressed directly by the known chemistry of this compound.

4.3.5 Ground surface HONO production at night: Observation-based parameterization of the pseudo steady state

From all the nights with an observable NBL, two relationships between HONO production and loss were explored according to the proposed dependencies of the nighttime production and loss in (E7). In this analysis the total column refers to the integrated value from the surface to 250 m above the surface.

If the production of HONO at night is indeed dominated by reactions at the ground surface, the integrated column concentration of HONO is expected to show i) proportionality to both the amount of HONO observed at the surface and ii) the amount of NO₂ at the surface. Assuming that all of the HONO produced at the surface remains in the lowest 250 m (if not confined to the NBL) observed rates of change in the total column HONO can then be used to investigate the ground source and sink without complications related to vertical gradients. Prior to midnight, the time rate of change is dominated by the production term, but as HONO accumulates the loss term also becomes significant. Figure 4-22 shows that the integrated column of HONO is strongly related to the amount of HONO observed at the surface, corroborating that the observed enhancement of HONO near the surface is indicative of the ground surface as the location where HONO is dominantly formed.
Figure 4-22. Orthogonal linear least-squares correlation between 2 hr average total column HONO and HONO measured from the surface to 10 m agl at the BAO tower for the 9 nights with identifiable NBLs indicating surface formation as the dominant source of nighttime HONO.

The change in column HONO concentration shows two regimes in the relationship with the amount of NO$_2$ observed at the surface. Between sunset and midnight (18:00 – 24:00), the column HONO concentration increases at a rate that can be approximately equated to the surface production from NO$_2$. Figure 4-23 displays the relationship between observed HONO column increases and the NO$_2$ mixing ratio at the lowest measurement height. The data are coloured by relative humidity, which seems to explain most of the scatter in the relationship. Conversion of NO$_2$ to HONO according to (R1) requires adsorbed water at a surface for the reaction to proceed and suggests that the relative humidity threshold for enhanced conversion at the BAO tower is 60%. Such relative humidity dependence of HONO formation has been suggested by numerous lab studies (Ramazan et al., 2006; Miller et al., 2009; Finlayson-Pitts et al., 2003; Finlayson-Pitts, 2009), but has received little attention in analysis from field studies. The dependence on HONO formation as a function of relative humidity from field data has only been addressed by Stutz et al. (2004) and has only recently been revisited by Wojtal et al. (2011). In their investigation of several field datasets, Stutz et al. (2004) found an increased likelihood of a higher ratio of HONO to NO$_2$ at high relative humidities. In particular, the data explored by Stutz et al. (2004)
suggested that HONO production was often enhanced at relative humidities above 60%. However, a clear relationship between the observed accumulated HONO and relative humidity was not elucidated, a property that has been parameterized below (Figure 4-23).

Figure 4-23. Surface relative humidity dependence for reaction of NO$_2$ on the ground in the production of HONO throughout the observed atmospheric column at BAO tower for the 9 nights with identifiable NBLs from 18 – 24 h. HONO$_{\text{column}}$ values were integrated from the surface to the NBL and NO$_2$$_{\text{surface}}$ concentrations were averaged from the surface to 10 m agl. Lines on graph indicate the effective $\gamma_{\text{NO}_2, \text{ground}}$ from i) orthogonal linear least-squares analysis (solid black, 8.0x10$^{-6}$), ii) double the best fit (short dash, 1.6.0x10$^{-5}$), iii) value derived from NO$_2$ 0.02 cm s$^{-1}$ deposition velocity of Spicer et al. (1989) (solid red, 2.0x10$^{-6}$) and iv) half of best fit (long dash, 4.0x10$^{-6}$)

Nights with NBLs were used to isolate a field-specific uptake of NO$_2$ at the surface ($\gamma_{\text{NO}_2, \text{ground}}$) for the total column production of HONO during the NACHTT campaign during the early evening hours (18:00 – 24:00) when the deposition term for HONO in E7 is expected to be small. Mixing ratios of HONO were typically below 250 pptv during these hours. The ground uptake coefficient for NO$_2$ was found from the best linear fit to the data in Figure 4-23 ($\gamma_{\text{NO}_2, \text{ground}} = 8*\text{slope}/C_{\text{NO}_2}$) as 8.0x10$^{-6}$. The average value calculated from all individual data points was 8.0(±1)x10$^{-6}$ and not significantly different from the value found by the linear fit. These values are within the range of reactive uptake coefficients of NO$_2$ on aerosols (1x10$^{-6}$ to 1x10$^{-5}$) determined by several lab studies (Kurtenbach et al., 2001; Kleffmann et al., 1998; Broske et al., 2003). The variability in observed values displayed in Figure 4-23 suggests that the reaction
efficiency of NO\textsubscript{2} increases with relative humidity at the surface (i.e. water surface coverage), a known dependence of the NO\textsubscript{2} heterogeneous conversion from lab studies (Miller et al., 2009; Finlayson-Pitts et al., 2003; Finlayson-Pitts, 2009; Barney and Finlayson-Pitts, 2000). Our field data suggest that a simple relative humidity dependence for the production of column HONO at this site can be parameterized by applying a factor of RH/50, to $\gamma_{\text{NO}_2, \text{ground}} = 8.0 \times 10^{-6}$ (E12).

As the night progresses, the deposition of HONO becomes an increasing important term in the HONO time rate of change equation. To estimate the deposition rate of HONO to the surface, E7 can be rearranged to solve for the sink term. The difference between the calculated column production rate and the observed column rate of change for two hour intervals between 0:00 and 06:00 is plotted against the observed HONO in Figure 4-24. The relative humidity dependent parameterization of $\gamma_{\text{NO}_2, \text{ground}}$ was used to calculate HONO production. This approach yielded $\gamma_{\text{HONO, ground}}$ uptake values of i) $8.7 \times 10^{-5}$ from fitting the data with a linear least-squares regression, and ii) $7.3(\pm1) \times 10^{-5}$ averaged from all data points. These values are roughly an order of magnitude larger than $\gamma_{\text{NO}_2, \text{ground}}$ and consistent with the relative magnitudes for these terms employed in models of nocturnal production and deposition (Wong et al., 2011). Furthermore, the data in Figure 4-24 suggest that there may be a relative humidity dependence to the uptake of HONO on to the ground surface that can be parameterized by a factor of RH/20 (E12).

\[
\frac{d[HONO]_{\text{column}}}{dt} = \frac{1}{8} \gamma_{\text{NO}_2, \text{ground}} \frac{RH}{50} [NO_2]_{\text{ground}} C_{\text{NO}_2} - \frac{1}{4} \gamma_{\text{HONO, ground}} \frac{RH}{20} [HONO]_{\text{ground}} C_{\text{HONO}}
\]

(E12)

Partitioning of HONO to simulated dew has been shown in a flow tube study by He et al. (2006). The uptake is also pH dependent and has been observed or suggested in a several investigations (Hirokawa et al., 2008; Longfellow et al., 1998; Kleffmann et al., 1998; He et al., 2006). Therefore, parameterization of the HONO surface deposition will likely change between environments depending on the dominant characteristics of the surface on which NO\textsubscript{2} reacts to form HONO and the subsequent capacity of the surface to also act as a HONO sink. The BAO tower was surrounded by tilled earth, with a local pH of 7.7 in a nearby field (n = 1). Urban or forested areas will have buildings, paved and plant surfaces that are expected to change the
deposition efficiency of HONO. The RH-dependent values of $\gamma_{\text{NO}_2, \text{ground}}$ and $\gamma_{\text{HONO, ground}}$ were added to our simple box model as the best approximation of surface processes governing total column HONO for this location (Section 4.3.8). To the best of our knowledge these are the first field-derived surface parameters of nocturnal HONO production from NO$_2$ and surface deposition of HONO.

![Figure 4-24](image)

**Figure 4-24.** Production of HONO from the reaction of NO$_2$ on the ground surface in excess of the observed change in column HONO as a function of the average HONO observed at the surface between 00 – 06 h. The slope of the orthogonal linear least-squares analysis is the product of $\gamma_{\text{HONO, ground}}$ and the mean molecular speed of HONO (c$_{\text{HONO}}$). The values displayed for each line are the effective $\gamma_{\text{HONO, ground}}$ for i) linear fit to observed data (solid black, 3.2x10$^{-5}$), ii) average calculated value (dash-double dot, 2.3x10$^{-5}$), iii) upper limit of observed data (dotted, 5x10$^{-5}$) iv) best fit when $\gamma_{\text{NO}_2, \text{ground}}$ used from Spicer et al. (1989) (solid red, 1.8x10$^{-5}$) and v) lower limit of observed data (dashed, 1.0x10$^{-5}$).

To determine the likely factors controlling the surface conversion observations of NO$_2$ and HONO, a simple resistance model accounting for transport, diffusion and reactive loss, operating in series at the surface, was used to evaluate the potential broad scale applicability of the values calculated. Assuming that the upper limit to the observed HONO reactive uptake was limited
equally by molecular diffusion and aerodynamic transport (E3), a value for the local surface roughness length of $4 \times 10^{-3}$ m and a surface layer height of 15 m could be approximated since the data was filtered for wind speeds less than 6 m s$^{-1}$. These values clearly delimit the range of HONO uptake coefficients seen during NACHTT (Figure 4-25) and suggest that the HONO surface uptake values from $2 \times 10^{-5}$ to $2 \times 10^{-4}$ are likely limited by a combination of transport and diffusion to the ground surface if the real uptake values are greater than $2 \times 10^{-4}$, but if they are closer to $2 \times 10^{-5}$, then the system is limited by reaction probability at the surface, except at wind speeds less than 2 m s$^{-1}$. Therefore, a combination of the process was likely observed during NACHTT.

On the other hand, the range of NO$_2$ uptake coefficients indicates that the rate of surface reaction was limited only by the reactive uptake process. The broad scale applicability of these field-derived terms for surface conversion of NO$_2$ should therefore be possible, while those found for HONO are not yet clear. To enable models to better predict the extent of HONO deposition and the variability of these nocturnal processes, more observations from various environments are required. The consistency between our findings, lab investigations of NO$_2$ conversion on wet surfaces, and the values of these parameters in models suggest that these values are within an appropriate order of magnitude.
Figure 4-25. Estimated contributions of resistance parameters to the observable ground surface processes for the HONO and NO₂ uptake values derived from NACHTT integrated column observations. Shaded regions define the borders of the reactive uptake resistance ($R_C$), the observed upper and lower limit uptake values for HONO converted to a range of $R_c$ values is shown in red. The aerodynamic transport resistance ($R_A$, black line) and diffusion resistance ($R_B$, green line) were calculated using data limitations and E5 and E6.

4.3.6 Daytime HONO: A ground surface source

Daytime HONO was not specifically targeted during the NACHTT campaign, since the focus was on nighttime chemistry. The instrument carriage was often shut down for several hours during the day for instrument maintenance, resulting in only 6 days with near-continuous vertical profiles from 06 – 18 hr. Throughout the day, HONO was observed above the 3.8 pptv detection limits of the NI-PT-CIMS throughout the 250 m profiles, reaching average daytime minimum mixing ratios of 80 pptv at the surface and 35 pptv aloft. Figure 4-26 shows the characteristic diurnal cycle as HONO formed from the previous night undergoes photolysis throughout the column during the early morning hours, mixes throughout the boundary layer around 10 h and
continues to decrease throughout the column for the duration of the day, eventually reaching a pseudo photostationary state throughout the atmospheric boundary layer between 14-18 h.

**Figure 4.26.** Average vertical profiles of daytime HONO during NACHTT at 10 m intervals, starting at 5 m agl. Each trace represents a 2 h average of vertical HONO measurements (06-08 h, green; 08-10 h, gold; 10-12 h, purple; 12-14 h, red; 14-16 h, black; 16-18 h, blue).

Vertical structure in HONO was observed on all days with HONO mixing ratios increasing as the surface was approached, most notably within 20 m of the ground. This strongly suggests that daytime production of HONO is occurring at the ground surface and being mixed throughout the daytime boundary layer. Recently, vertical profiles of HONO in Houston, TX during the day have provided evidence towards these assertions that the ground surface is the HONO source (Wong et al., 2012). Confirmation of the daytime source and determining the magnitude of daytime HONO production at the BAO tower was accomplished using a simple box model at the ground surface, throughout a representative mixed layer and constrained by the measured NO, NO₂, and OH (Figure 4.2).

**4.3.7 Modeling HONO Diurnal Chemistry: Magnitude of the Daytime Surface Source and Nighttime Deposition**

The existence of a daytime HONO source was inferred at this site via photostationary mixing ratios at the surface in excess of the calculated HONO mixing ratio throughout most of the
daytime hours (Figure 4-27). Previously, the dark ground conversion of NO$_2$ has been ruled out as the missing daytime source of HONO (Su et al., 2008b; Kleffmann et al., 2005; Kleffmann, 2007; Zhou et al., 2011; Vogel et al., 2003; Sorgel et al., 2011a; Li et al., 2011; Li et al., 2010; Aumont et al., 2003; Wong et al., 2012). While our nighttime analysis indicates an RH dependence to R1, it does not seem reasonable to conclude that this source cannot persist during the day. The rural location of the BAO tower is surrounded by tilled farm land. Soil matrices have been well characterized to have a persistent surface water layer under atmospherically relevant conditions of temperature and relative humidity (Conklin, 2005). The analysis of nighttime conversion in Section 4.3.6 suggests that this production continues under all conditions of relative humidity, albeit suppressed at relative humidities below 60%. The overall sensitivity of predicted HONO mixing ratios in a 1 km mixed boundary layer due to inclusion/exclusion of heterogeneous conversion of NO$_2$ throughout was negligible. However, the mechanism does contribute to the production of daytime HONO and should be accounted for when determining the magnitude of the daytime HONO source discussed below. It may be particularly important in explaining vertical gradients. Therefore, the ground surface conversion of NO$_2$ is included in all analyses of the daytime HONO source. This avoids overestimation of the missing daytime HONO source strength.

The description of the model was provided in Section 4.2.7.3. The red trace in Figure 4-27 shows the output of the parameterization where only nocturnal production of HONO at the surface is considered. The predicted mixing ratio grows throughout the night, in contrast to observations, that roughly plateau after midnight. Clearly, there must be a significant HONO sink in the nocturnal boundary layer (i.e. deposition to the ground) in order to understand the observations.
Figure 4-27. Observed HONO atmospheric concentrations (left axis, black line, ±1σ) and the calculated HONO photolysis rate (right axis, filled yellow) from 19 – 25 February during NACHTT from 0 – 20 m agl. Modeled HONO production throughout the mixed boundary layer is determined from observational constraints according to (E8) with field-derived surface exchange parameters for the NO$_2$ heterogeneous reaction (R1) without (red line) and with (blue line) depositional loss of HONO included in the calculation of boundary layer HONO concentrations and at 20 m agl with depositional HONO loss (green line). The blue trace describes the calculated boundary layer HONO concentrations when the RH-dependent parameters derived from the column HONO and NO$_2$ observations, on 9 nights with NBLs (Section 4.3.6), are implemented in to the model. The dataset to which the parameters are applied contains two of the nights from which they were derived and four others. The model was tested for sensitivity towards the relative humidity parameterization developed, but this was found to affect the calculated HONO concentrations minimally (i.e. width of blue trace). This negligible influence is not surprising given the small diurnal variation in relative humidities, 30 – 60 % on average, for this period (Figure 4-2). The underestimate of the HONO concentration output by the model when using a 150 m nocturnal boundary layer compared to the observations made at 20 m are expected due to the increase in HONO concentration as the surface is
approached. The average HONO concentration from the surface to 150 m determined in the model, therefore, should be smaller than the observations.

The implementation of the two surface parameters for NO$_2$ and HONO into a model run with a surface layer depth of 20 m agl (Figure 4-27; green trace) largely captures the nighttime HONO production and subsequent daytime chemistry, within 30% of measured values, when starting from the photostationary minimum at 16 h. This supports the observations and assertions that HONO nocturnal chemistry is dominated by the ground surface. The lower calculated concentrations throughout the night may indicate that the parameterization of the source and sink terms are not exact. The relative humidity weighting in (E12) was applied in a linear fashion based on a best representation of the data from this study. However, the conversion of NO$_2$ (Stutz et al., 2004) and uptake of HONO on wet surfaces may not be described so simply as done in this work. The influences of surface composition and relative humidity on HONO surface uptake have not undergone rigorous constraint for atmospherically relevant surfaces and require controlled lab investigations to improve the understanding of its fate. Overall, the accuracy in this parameterization to within 30% of measured values, given the lack of advection terms in the box model, is a significant accomplishment.

From 09:00 – 17:00 the model under predicts the photostationary minimum in HONO, with a brief period of equality from 10:00 – 11:00. The discrepancy between these values is indicative of a daytime surface source of HONO at the BAO tower site. This dataset has a complete set of gas phase constraints and parameterized surface processes which can be used to determine the magnitude of the source from E9. Figure 4-28 depicts the outputs of the model HONO sources and sinks from the balance of NO + OH (R3), photolysis (R2), HONO + OH (R5), and heterogeneous surface production and loss. The individual contributions of each source and sink in the model are displayed in the bottom panel. The conversion of NO$_2$ on the ground surface is the most important source of HONO throughout the night, while production of HONO from gas phase chemistry between OH and NO during the day dominates and was particularly significant when plumes of fresh NO$_x$ emissions were intercepted at this site. The loss of HONO by photolysis is the dominant sink of HONO during the day, with minor contributions to surface deposition in the morning and negligible loss to OH. The discrepancy between these daytime
sources and sinks indicates that an additional (missing) source of HONO must be active to produce the observed atmospheric concentration of HONO. The modeled period of near-continuous observations from 19 – 25 Feb in Figure 4-2 (observations input) and Figure 4-27 (model output) shows that the arrival of local NO\textsubscript{x} plumes between 09-12 in the morning significantly increases the predicted HONO production. This NO chemistry results in a significant reduction in the unknown source strength of HONO to balance the model with the observed HONO mixing ratios. This potentially indicates that the daytime HONO source strength at the surface depends on the HONO concentration in the overlying atmosphere.

![Figure 4-28](image)

**Figure 4-28.** Separated contributions of the P(HONO)\textsubscript{unknown} in the simple box model throughout the mixed layer. Relative and overall magnitude are shown by stacking sources (positive) and sinks (negative). The model run calculated the missing source using observational constraints on NO\textsubscript{2} ground conversion and HONO reactive loss from vertical profiles during NACHTT. The calculated missing source/sink of HONO is overlaid (green line).

The magnitude of this source for the period 19 – 25 February using averaged 10 minute resolution measurements from 0 – 20 m is overlaid as a green line in Figure 4-28. The unknown source of HONO is highest in the morning (4x10\textsuperscript{6} molec cm\textsuperscript{-3}s\textsuperscript{-1}, 600 pptv hr\textsuperscript{-1}) and declines throughout the day to about 1x10\textsuperscript{6} molec cm\textsuperscript{-3}s\textsuperscript{-1} (165 pptv hr\textsuperscript{-1}). The daytime source in Erie is consistent with the range of strong daytime HONO surface sources determined at other field
locations, with source strengths ranging from 100 – 1000 pptv hr\(^{-1}\) (Kleffmann et al., 2005; Kleffmann, 2007; Amoroso et al., 2008; Su et al., 2008b; Elshorbany et al., 2009; Qin et al., 2009; Sorgel et al., 2011a; Elshorbany et al., 2012). As mentioned earlier, this period of the campaign often intercepted NO\(_x\) plumes from the nearby interstate between 09:00 – 12:00, reducing the clarity of the daytime source at this time. That a continuous source was not observed during this period suggests that the system may be more dynamic than previously considered. It has been previously shown by Wong et al. (2012) that P\(_{HONO}\) normalized to NO\(_2\) correlates strongly to the total surface irradiance. In this case, if photochemical mechanisms were the dominant source of the unknown HONO they would be expected to be enhanced in the presence of additional NO and NO\(_2\), not suppressed. However, the magnitude of the daytime HONO source is similar to that observed in summertime campaigns and exhibits a similar trend in absolute P\(_{HONO}\) (Wong et al., 2012). Therefore, the daytime HONO source at the BAO tower may arise from alternative mechanisms, such as reservoirs of HONO generated at the ground surface or in the soil throughout the night. The fate of surface deposited HONO at night has not been extensively explored.

The NO\(_2\)-as-a-HONO-precursor perspective has been common to all elucidated daytime HONO heterogeneous formation mechanisms on photoexcited surfaces, such as humic acid (Stemmler et al., 2007; Stemmler et al., 2006; Bartels-Rausch et al., 2010), soot (Monge et al., 2010; Khalizov et al., 2010; Gerecke et al., 1998; Aubin and Abbatt, 2007; Ammann et al., 1998), organic films (Gutzwiller et al., 2002; George et al., 2005; Broske et al., 2003; Brigante et al., 2008) and TiO\(_2\) in mineral dust (Langridge et al., 2009; Bedjanian and El Zein, 2012; Wang et al., 2003; Ndour et al., 2008). The observations of Wong et al. (2012) show that this mechanism is likely active during the day, but its significance may be small compared to other processes by mass. A recent study by Sorgel et al. (2011a) has suggested that the largest contributing photocatalytic mechanism is humic acid conversion of NO\(_2\), approximated at 30 % of the daytime source for a semi-urban location in Spain. Furthermore, NO\(_2\) and surface irradiance are expected to show an anticorrelation as NO\(_2\) is diluted and lost during the day, which may build a falsely consistent correlation between P\(_{HONO}/NO_2\) and surface irradiance if P\(_{HONO}/NO_2\) is nearly constant throughout the day, as was observed at the BAO tower, and as was observed in Houston (Wong et al., 2012). Therefore, again, we stress that such a ratio approach may be misleading in
understanding daytime HONO unless conversion of NO$_2$ is the only HONO source. Clearly, investigations on alternative HONO sources not requiring NO$_2$ need to be considered and contrasted to existing mechanisms to elucidate the relative importance of NO$_2$ as a precursor and HONO reservoirs.

Daytime mechanisms to date largely neglect the potential for HONO emission from reservoirs or reactions that do not involve NO$_2$. Recently, soil nitrite has been proposed as a potential daytime source of HONO via a dynamic equilibrium regulated by soil water content, pH, and overlying composition of the atmosphere (Su et al., 2011), similar to a traditional NH$_4^+$/NH$_3$ compensation point. Also, the photolysis of HNO$_3$ at the surface has been postulated as a potential source of HONO at the surface (Ziemba et al., 2010; Zhou et al., 2011; Zhou et al., 2003). Both soil nitrite and surface HNO$_3$ represent potential reservoirs for daytime HONO. Therefore, there is no requirement for considering NO$_2$ in the release of HONO from such reservoirs. The data presented in Figure 4-28 and Figure 4-29 show that a significant amount of HONO is expected to be deposited to the surface during the night, possibly forming a reservoir. The relative magnitude of the integrated loss of HONO to the surface and the integrated HONO source strength were therefore explored further. This was done by testing the sensitivity of the model reservoir to the range of $\gamma_{\text{HONO, ground}}$ values found from the integrated HONO column measurements (Section 4.3.6).
Figure 4-29. Temporal loss rates of HONO by ground uptake parameterized by four approaches from lines in Figures 4-23 and 4-24: i) best fit of least squares correlation (dark purple), ii) relative humidity depended ground uptake parameterization (E8), iii) average ground uptake and iv) literature comparison of NO$_2$ deposition velocity from Spicer et al. (1989). Traces are overlaid on each other. Integrated daily loss of HONO (Lost) and the integrated unknown source of HONO (Unk Source) under each set of parameterizations is provided.

Total HONO produced during daytime by the unknown source during NACHTT ranged from 5.9 to 6.6x10$^{10}$ molec cm$^{-3}$day$^{-1}$ for the period of 19 – 25 Feb. The modeled nighttime depositional losses of HONO showed much more variability from the surface parameterization, ranging from 1.5x10$^{10}$ to 1.5x10$^{11}$ molec cm$^{-3}$day$^{-1}$. The uncertainty in the calculated $\gamma_{\text{HONO, ground}}$ does not depend strongly on the assumptions made about $\gamma_{\text{NO}_2, \text{ground}}$. Even when using the literature reported value of $v_{\text{dep, NO}_2} = 0.02$ cm s$^{-1}$ ($\gamma_{\text{NO}_2, \text{ground}} = 2.0x10^{-6}$ (Spicer et al., 1989)), $\gamma_{\text{HONO, ground}}$ still falls within the range predicted (Figure 4-24; red line). The parameterization of $\gamma_{\text{HONO, ground}}$, therefore, is likely accurate within a factor of two and well represented by the average or literature derived deposition parameters. In Figure 4-29, the influence of the $\gamma_{\text{HONO, ground}}$ values on the magnitude of the total HONO deposited to the ground surface is presented. In three out of four cases the HONO deposited to the ground was sufficient (93, 112, and 250 % of the integrated daytime source calculated) to explain the daytime source. Using the absolute lower limits for NO$_2$ conversion and HONO deposition 25 % of the total daytime source can be
deposited to the surface. Therefore, if the HONO deposited to the ground is emitted/displaced the following day, it can account for 25 to \(>100\,\%\) of the HONO required to understand the photostationary mixing ratios observed. Loss of HONO to the ground surface at night has frequently been necessary to reconcile observations of a pseudo steady state in nighttime production (Wojtal et al., 2011; Su et al., 2008a; Wong et al., 2011; Stutz et al., 2002; Stutz et al., 2004; Ren et al., 2011; Ren et al., 2010). However, the fate of this deposited HONO (i.e., mechanisms for being reemitted to the atmosphere) has not been carefully considered, but further investigation is beyond the scope of the available measurements from the NACHTT campaign.

In conclusion, if a HONO reservoir is formed by HONO deposition to the ground at night and is capable of being re-emitted to the atmosphere as HONO the following day, then surface emissions from this reservoir could account for at least 25\% or completely reconcile the required quantities of unknown daytime HONO at this location. While it is expected that the values of the individual terms governing HONO production and loss will change from location to location, expanding on our understanding of the underlying properties governing these exchange parameters, and making more measurements of these values in a variety of environments will greatly aid in improving the ability of models to predict the production and loss of HONO in the nocturnal boundary layer, during the day and the subsequent impact of the OH radicals released to the atmosphere.
4.4 Conclusions and Atmospheric Implications

Continuous vertical profiles of trace atmospheric acids were made during the Nitrogen, Aerosol Composition and Halogens on a Tall Tower (NACHTT) field campaign in Erie, CO using a Negative-Ion Proton-Transfer chemical ionisation mass spectrometer (NI-PT-CIMS). The new inlet for the NI-PT-CIMS deployed during this campaign showed good intercomparison for HONO measurements with a stationary mist-chamber ion chromatography (MC-IC) system sampling through a 20 m inlet during periods of near-continuous profiling. The NI-PT-CIMS measured more HONO than the MC-IC at all times (Slope = 1.4), but temporal correlation was good ($R^2 = 0.87$) indicating that inlet losses were likely responsible for the measurement discrepancy. Intercomparison of the remaining acids indicated significant inlet losses of acids in the MC-IC system and a particle nitrate interference in the CIMS inlet. Overall, the new inlet was most suited to making 0.1 Hz HONO measurements, with automated background/interference/calibration collection, and detection limits on the order of a few parts per trillion by volume (pptv). These measurements were central to the NACHTT objectives concerning nocturnal formation and fate of nitrogen oxides.

High resolution vertical profiles of HONO, averaged to 2 hour time steps, revealed i) the ground surface as the dominant nighttime surface on which this photolabile species is formed from the heterogeneous reaction of nitrogen dioxide ($NO_2$) with water, ii) significant quantities of HONO are expected to be deposited to the ground surface at night, and iii) the unknown daytime source of HONO is comparable to the potential ground HONO reservoir. Total column observations of HONO and $NO_2$ allowed direct evaluation of the ground uptake coefficients for these species at night as a function of relative humidity ($\gamma_{NO_2, \text{surf}} = 2 \times 10^{-6}$ to $1.6 \times 10^{-5}$ and $\gamma_{HONO, \text{surf}} = 2 \times 10^{-5}$ to $2 \times 10^{-4}$). Both parameters are consistent with laboratory and model values, although it is possible that the HONO uptake values observed experienced limitation by aerodynamic transport to the surface. These constraints are the first field observation-derived $NO_2$ and HONO uptake values using nocturnal integrated column observations and time rate of change of each species separately.

Daytime vertical concentration gradients indicated the ground surface as the location of the unknown HONO source with a magnitude of 165 – 600 pptv h$^{-1}$ required to explain observed
mixing ratios based on known sources and sinks, similar to observations made at many other locations and environments (Zhou et al., 2011; Su et al., 2008b; Sorgel et al., 2011a; Kleffmann et al., 2005; Kleffmann, 2007; Elshorbany et al., 2009; Elshorbany et al., 2012; Wong et al., 2012). A simple box model utilizing observational constraints on the HONO chemical system shows that the daytime source may be more dynamic than previously proposed and that a combination of several significant mechanisms is the most probable resolution to understanding this source (e.g., photocatalytic conversion of NO₂, acid displacement of surface deposited HONO, and partitioning of nitrite from soil pore water). Alternative mechanisms of bidirectional flux and acid displacement of HONO from a ground reservoir generated at night were found to potentially account for the production of daytime HONO. The quantity of surface deposited HONO determined with the simple box model showed that, under reasonable constraints, the integrated amount of HONO deposited to the surface at night was 93 – 250 % of the integrated unknown daytime HONO source. Under worst case constraints, the integrated deposited HONO in the model was 25 % of the unknown daytime HONO source. Overall, these results suggest that if nocturnally deposited HONO can form a reservoir, which can be accessed the following day, then a significant fraction of the daytime HONO source at the BAO tower may be explained for the NACHTT observation period. However, the relative magnitude of the deposition process is expected to be variable based on: i) location since ground surfaces are highly variable in composition, which will change the uptake of HONO, and ii) time of year since temperature, relative humidity, other meteorological parameters and chemical composition of the atmosphere will all have seasonal changes. Expansion of future field measurements to more explicitly address the potential for bidirectional flux of HONO from soil pore water nitrite and the production of nitrite salts that can undergo acid displacement at the surface will significantly improve the ability of models to capture this chemistry. Furthermore, increased focus on the fundamental properties of reactive uptake and pH-dependent partitioning of HONO in to solutions should be undertaken in laboratory investigations.
4.5 References


CHAPTER FIVE

Evidence for a potential nitrous acid (HONO) reservoir at the ground surface: Simultaneous observations of trace acids and PM$_{2.5}$ water-soluble ions in Bakersfield, CA during CalNex 2010

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Mineral dust reactive uptake of HONO data will be used in conjunction with Chapter 6 results and is in preparation for: Geophysical Research Letters

Intercomparison, daytime source, and modeling in preparation for: Journal of Geophysical Research – Atmospheres – CalNex 2010 Special Issue

Author Contributions:

T. C. VandenBoer collected AIM-IC data during CalNex 2010, performed quality control on AIM-IC dataset and prepared manuscript under the guidance of J. G. Murphy. M. Z. Markovic collected AIM-IC data, performed quality control on AIM-IC dataset, and performed HONO breakthrough experiment under the guidance of J. G. Murphy. J. E. Sanders and X. Ren collected HONO REA data for HONO measurement intercomparison. S. Pusede, E. Browne, collected NO and NO₂ data under the guidance of R. C. Cohen for correction of AIM-IC dataset and input into simple HONO box model. R. J. Weber collected meteorological, relative humidity, temperature and photosynthetically active radiation data for use in data analysis and input to simple HONO box model. W. H. Brune collected OH data for input to simple HONO box model. D. A. Day, S. Liu, L. Ahlm, collected PM₂.₅ samples for XRF analysis under the guidance of L. M. Russell.
Abstract

Measurements of HONO and particulate nitrite were made with an Ambient Ion Monitor – Ion Chromatography (AIM-IC) instrument during CalNex 2010 in Bakersfield, CA. Observations of gas and PM2.5 water soluble composition showed accumulation of both species at night, followed by loss the next day. Intercomparison with a relaxed eddy accumulation system for HONO measurements demonstrated excellent agreement with the AIM-IC gas phase measurement and the particulate nitrite observations validated as not arising from significant known interferences for wet chemical sampling platforms. The particulate matter composition measurements by AIM-IC suggest that accumulation of nitrite into particulate matter is enhanced in the presence of the mineral cations Na\(^+\) and Ca\(^{2+}\). A potential mechanism to explain these observations is that HONO is undergoing reactive uptake on to carbonate minerals (i.e. on dust and the ground surface). Such chemistry has the potential to act as a HONO reservoir the following day.

The AIM-IC HONO measurements were parameterized in a simple box model to calculate the ground surface daytime HONO source strength. This was found to be on the order of 1.27 ppb hr\(^{-1}\), consistent with the range reported from many other locations. Measurements of gas phase HNO\(_3\) and HCl indicate that these acids might lead to the displacement of HONO from mineral surfaces such as reacted carbonate salts. Observations from Bakersfield show that HCl displacement is occurring when mixing ratios of HNO\(_3\) are elevated, suggesting that the HONO displacement mechanism likely follows a similar trend, but the reservoir appears to be NO\(_2^-\) limited by the amount HONO deposited to the surface at night. If all deposited HONO is reemitted the following day, up to 30 % of the daytime source may be accounted for from the results of a simple box model for this chemistry. This estimate is strongly dependent on the estimated height of the boundary layer and our assumption that HONO is well-mixed throughout the boundary layer. The observations of HONO and NO\(_2^-\) in Bakersfield, during CalNex, suggest a new source of HONO to the atmosphere that has not previously been reported from field observations or laboratory studies. Extension of currently accepted acid displacement reactions to those proposed to contribute to the unknown source of daytime HONO should therefore be sound, but the relative contribution of all surface sources remains to be resolved.
5.1. Introduction

Understanding of the importance of the photolabile trace gas nitrous acid (HONO) in the atmosphere has continuously evolved over the past fifteen years. The photolysis of HONO (R1) has been traditionally viewed as a dominant source of OH radicals early in the morning, and has recently become appreciated as a significant source of OH throughout the day (Alicke et al., 2002; Kleffmann et al., 2005; Elshorbany et al., 2009; Volkamer et al., 2010; Elshorbany et al., 2012). In some instances, HONO has been shown to be a comparable OH source to the reaction of O(1D) with water vapour (R2) in summer months in the shallow mixed layer in Los Angeles, USA (Young et al., 2012), Mexico City, Mexico (Li et al., 2010a; Volkamer et al., 2010) and Santiago, Chile (Elshorbany et al., 2009). Improvements in the analytical accuracy and precision of field instrument measurements has generated a consensus that HONO is present throughout the day at mixing ratios on the order of tens to hundreds of pptv when the photostationary minimum is reached, implying a strong source (up to 2 ppbv hr⁻¹) that is unknown (Amoroso et al., 2008; Elshorbany et al., 2009; Sorgel et al., 2011a; Elshorbany et al., 2012; Li et al., 2012b).

\[
\text{HONO}_{(g)} + \text{hv} (\lambda < 400 \text{ nm}) \rightarrow \text{NO}_{(g)} + \text{OH}_{(g)} \quad \text{(R1)}
\]

\[
\text{O}^{(1}\text{D})_{(g)} + \text{H}_{2}\text{O}_{(g)} \rightarrow 2 \text{OH}_{(g)} \quad \text{(R2)}
\]

Laboratory studies have identified several HONO formation mechanisms by reaction of NO₂ with irradiated solid substrates, such as humic acid (Stemmler et al., 2006; Stemmler et al., 2007; Bartels-Rausch et al., 2010), organic films (Broske et al., 2003; George et al., 2005; Brigante et al., 2008; Ammar et al., 2010), soot (Ammann et al., 1998; Gerecke et al., 1998; Aubin and Abbatt, 2007; Khalizov et al., 2010; Monge et al., 2010) and TiO₂ (Ndour et al., 2008; Langridge et al., 2009; Ndour et al., 2009; Bedjanian and El Zein, 2012), which yield HONO as a primary product. These HONO formation mechanisms are consistent with observations that suggest a relationship between the strength of the daytime HONO source and the product of [NO₂] and [OH] or [NO₂] and surface irradiance (Ren et al., 2011; Li et al., 2012b; Wong et al., 2012). However, field observations suggest that the NO₂ heterogeneous reactions described above can only account for a fraction of the required HONO production (Wong and Stutz, 2010; Sorgel et al., 2011a; Wong et al., 2011; Wong et al., 2012). Other reactions that have been hypothesized to
produce HONO include the reaction of photoexcited NO₂ with water vapour (Li et al., 2008), the photolysis of nitrate and HNO₃ on surfaces (Handley et al., 2007; Zhou et al., 2011), and partitioning from nitrite (NO₂⁻) rich soils as their water content is reduced (Su et al., 2011). The photoexcited NO₂ reaction has since been shown to be negligible in the ambient atmosphere, since it is the product of a two photon excitation mechanism (Amedro et al., 2011; Wu and Chen, 2012). The relative contributions of the other hypothesized sources remain uncertain and calls for additional field observations in a variety of environments.

The most widely acknowledged pathway for formation of HONO at night occurs by the reaction of NO₂ on wet surfaces (R3), although the exact mechanism relevant to the atmosphere remains uncertain in comparison to that derived from lab investigations (Barney and Finlayson-Pitts, 2000; Finlayson-Pitts et al., 2003; Kamboures et al., 2008; Finlayson-Pitts, 2009; Miller et al., 2009).

\[ 2 \text{NO}_2(g) + \text{H}_2\text{O}_{(ads)} \rightarrow \text{HONO}_{(g)} + \text{HNO}_3(ads) \]  \hspace{1cm} (R3)

The concentration of HONO at night often reaches a steady state between production, vertical mixing, and a dry deposition sink of HONO, which is described by irreversible deposition/uptake to ground and aerosol surfaces in models (Wong et al., 2011; Czader et al., 2012). However the fate of HONO lost to surfaces is poorly understood. The ground surface has been suggested as the primary source of nighttime HONO from vertically resolved data (Kleffmann et al., 2003; Vogel et al., 2003; Zhang et al., 2009; Villena et al., 2011; Wong et al., 2011), but HONO production on such surfaces has received limited investigation.

Nitrous acid is a weak acid, with a pKa near 3.5, and an effective Henry’s Law constant that is highly pH dependent, ranging from 39 M atm⁻¹ from pH = 2 – 3 (Park and Lee, 1988) to 3x10⁶ at pH 7-8 (Hirokawa et al., 2008). These properties suggest that generation of a HONO reservoir could occur by uptake of HONO into solutions in contact with the atmosphere, such as secondary aerosols, fog droplets and surface water according to Reactions 4 and 5. It has been shown that insignificant amounts of HONO will be taken up on to aqueous secondary aerosols, such as (NH₄)₂SO₄ (Becker et al., 1998). These aerosols, in general, are less than 2.5 μm in diameter and
present the dominant fraction of the total aerosol surface area for reactive gas uptake. Secondary atmospheric aerosols have a maximum pH near 5 (for neutralized NH$_4^+$-NO$_3^-$-SO$_4^{2-}$ aerosols) and a maximum liquid water content below 100 µg m$^{-3}$, which strongly inhibits accommodation of HONO. However, larger aerosols, such as fog (He et al., 2006; Rubio et al., 2008; Rubio et al., 2009; Sorgel et al., 2011b), and solutions of higher pH (Hirokawa et al., 2008) have been consistently shown to accommodate significant amounts of HONO. This implies that alkaline coarse mode particles and/or the ground surface may be a sink for HONO at night, particularly under high humidity conditions. While the ground surface is highly variable in composition (e.g. buildings, vegetation and open soil), it is well known that dust arising from the erosion of soil and concrete contains carbonates, which are reactive with gaseous acids (Gibson et al., 2006; Cwiertny et al., 2008; Hatch and Grassian, 2008). Numerous lab studies and field observations have confirmed that HNO$_3$, HCl, HCOOH and CH$_3$COOH are reactive with carbonate-containing mineral dust (Al-Hosney et al., 2005; Vlasenko et al., 2006; Preszler Prince et al., 2007; Sullivan et al., 2007a; Sullivan et al., 2007b; Preszler Prince et al., 2008; Sullivan et al., 2009; Vlasenko et al., 2009). Based on these studies, it seems likely that reactive uptake of HONO onto atmospheric dust and surface soils will occur. Therefore, we suggest a new mechanism for loss of HONO, which forms a reservoir of nitrite by reactive uptake with carbonate salts (R6).

\[
\begin{align*}
\text{H}_3\text{O}^+_{(aq)} + \text{NO}_2^-_{(aq)} & \rightleftharpoons \text{HONO}_{(aq)} + \text{H}_2\text{O}_{(l)} & \text{(R4)} \\
\text{HONO}_{(aq)} & \rightleftharpoons \text{HONO}_{(g)} & \text{(R5)} \\
\text{HONO}_{(g)} + \text{NaHCO}_3(s) & \rightarrow \text{NaNO}_2(s) + \text{H}_2\text{O}_{(g)} + \text{CO}_2(g) & \text{(R6)}
\end{align*}
\]

It is therefore conceivable that HONO retained at the surface as nitrite during the night may present a reservoir for HONO during the day. In this chapter we show i) the results of an instrument intercomparison of HONO measurements during CalNex 2010, ii) validation of in situ measurements of particulate nitrite (NO$_2^-$), iii) field observations supporting the hypothesis of reactive uptake of HONO on to mineral dust and iv) a mechanism for generating a HONO reservoir on dust and soil that can act as both a nighttime sink and a daytime source of HONO.
5.2. Field Observations During CalNex 2010 – Bakersfield, CA

5.2.1. Site Description
The California at the Nexus of Air Quality and Climate (CalNex) intensive field campaign was carried out from May – July 2010 from multiple platforms, including a ground supersite at the southern end of the San Joaquin Valley at the Kern County Cooperative Extension in Bakersfield, California (35° 20’ 46.46” N, 118° 57’ 55.54” W, 116 m asl). The location was influenced by prevailing winds down the valley (NW) during the day, transporting local air from the Bakersfield city centre and highways, as well as regional emissions from intensive agriculture and industrial processes. Air flow at night was often stagnant or returning downslope at lower speeds from the Tehachapi mountains (SE). The field site was outfitted with an 18 m scaffolding tower and several ground containers from which atmospheric and meteorological measurements were made.

5.2.2. HONO, Particulate Nitrite and Supporting Measurements
During this campaign a modified Ambient Ion Monitor – Ion Chromatography (AIM-IC) system (URG, Chapel Hill, NC) was used for the collection of an extensive suite of water-soluble compounds in both gas and particulate phases. A detailed description of this inlet design and the performance characteristics of the AIM-IC system can be found in Markovic et al. (2012). Briefly, particle size selection was carried out using a PM$_{2.5}$ inertial impactor (URG, Chapel Hill, NC) on the 3 L min$^{-1}$ sample flow. The sample was then carried through a parallel-plate wet denuder where HONO and other water-soluble gases were quantitatively scrubbed into deionised water containing 5mM H$_2$O$_2$. The remaining water-soluble particles were hygroscopically grown in the particle supersaturation chamber and collected as an aqueous solution in a cyclone assembly. The aqueous sample aliquots from both channels were transported to the ion chromatography systems housed inside a ground container for one hour semi-continuous online analysis of the gas (e.g. NH$_3$, HNO$_3$, HCl, HONO, HCOOH, CH$_3$COOH) and particulate phases (e.g. NH$_4^+$, Ca$^{2+}$, Na$^+$, Cl$^-$, NO$_2^-$, NO$_3^-$, SO$_4^{2-}$, HCOO$^-$, CH$_3$COO$^-$). The PM$_{2.5}$ particle impactor, parallel-plate wet denuder and particle supersaturation chamber were placed in a mobile casing that was mounted at 4 m on the tower. This minimized inlet surface area for adsorptive loss of gases and prevented sampling bias of gas-particle chemical partitioning by collecting analytes at ambient temperature and relative humidity.
Coincident HONO measurements were made during this campaign by a Relaxed Eddy Accumulation (REA) system, utilizing coil scrubbers, azo-dye derivitization and absorption detection, which was located at 13.5 m agl. A detailed description of this system can be found in Ren et al. (2011) along with an analysis of HONO fluxes observed at this field site throughout the AIM-IC observation period. This allowed for the first intercomparison between an established HONO measurement technique and the AIM-IC observations at a field location. Intercomparison was made from 03 – 23 June when background corrections and calibrations in both instruments had been recently assessed and HONO measurements had the greatest accuracy.

Measurements of NO₂ at 4 m were made by thermal dissociation laser-induced fluorescence (Day et al., 2002), and NO at 4 m by a commercial chemiluminescence instrument. OH was measured at 13.5 m by laser-induced fluorescence (Faloona et al., 2004). Supporting measurements of PM₂.₅ mineral dust components, and mass loading estimates, were made by x-ray fluorescence on 24-hour integrated filter samples collected from a ground container roof, with cyclone-based size selection, near the base of the tower at approximately 2 m height.

The HONO photolysis rate (j_{HONO}) was calculated using the Tropospheric Ultraviolet and Visible (TUV) radiation model (http://cprm.acd.ucar.edu/Models/TUV/Interactive_TUV/). NOₓ and OH measurements were used to estimate HONO production rates and conversion efficiencies when calculating the unknown daytime HONO source strength.

5.3 Results and Discussion

5.3.1 AIM-IC Collection Efficiency of HONO

The NO₂ measurements were used to correct for known interferences due to the heterogeneous reaction of NO₂ with water in the AIM-IC gas channel measurements of the NO₂⁻ and NO₃⁻ ions. The corrections corresponded to approximately 0.1 % of the HNO₃ measurements and 0.2 % of the HONO measurements. The particle nitrite channel was not corrected for any artefacts related to atmospheric NO₂. Some interferences cannot be accounted for easily in wet chemical systems, for example NO₂ reacting with diesel exhaust components (Gutzwiller et al., 2002; Kleffmann and Wiesen, 2008). However, previous characterization studies suggest this to
be much less than 10 % of measured HONO (Kanda and Taira, 1990; Vecera and Dasgupta, 1991; Chang et al., 2008), the minimum particle nitrite to HONO ratio observed by the AIM-IC (Section 5.3.3). The intercomparison in Section 5.3.2 also does not suggest that we suffer from significant uncharacterized interferences.

During the campaign, mixing ratios of atmospheric ammonia averaged 22 ppb, in great excess over the gas phase acidity. This situation improved the collection efficiency of HONO in the denuder by increasing the pH of the aqueous solution. We quantified the maximum breakthrough of HONO to the particle channel, under a simulated atmosphere containing 4 - 8 ppb of NH₃, as 4% in the presence of this lower limit of NH₃ observed during this field campaign and corrected the dataset accordingly. That is, HONO values were corrected by dividing by 0.96 and particulate nitrite values were corrected by subtracting 4% of the simultaneous HONO measurement. It is possible that other atmospheric gases collected as acid anions (e.g. HCl, HNO₃) in the wet parallel-plate denuder could lower the effective pH of the solution and reduce the collection efficiency of HONO. Since it was most often the case that NH₃ was in excess of the total acids in the denuder solution, the pH of the denuder solution was calculated using the campaign average NH₃ (22 ppb), and maximum HNO₃ (1.6 ppb) and HCl (0.8 ppb) as a worst case scenario for HONO collection. With this composition, the denuder solution was calculated to have a pH of 8.94. The Henry’s Law coefficient for HONO is $>10^4$ M atm$^{-1}$ above pH 6 (Park and Lee, 1988; Hirokawa et al., 2008). Furthermore, HNO₃ and HCl had much lower mixing ratios at night, when HONO concentrations were highest. Therefore, in the absence of strong acids and with considerable dissolved NH₃, a denuder solution of pH 8.5 or greater would have favored quantitative collection of HONO. Therefore, while some fraction of our particulate nitrite signal may be derived from inefficient scrubbing of HONO, it is not expected to exceed the 4 % correction applied to the data from the post-campaign breakthrough characterization. Therefore, the nitrite observed in the particle channel at Bakersfield is attributed to atmospheric particulate nitrite. This is further supported by the HONO measurement of the AIM-IC showing nearly 1:1 agreement with the HONO measured by the REA system deployed at the site.
5.3.2 HONO Measurement Intercomparison between AIM-IC and REA

To validate measurements made by the AIM-IC, an intercomparison with the REA gaseous HONO measurements was undertaken. Figure 5-1A depicts the comparison of hourly HONO measurements, which show very good agreement with the REA HONO measurement (Least Orthogonal Distance Fit; Slope = 0.957; Linear Regression $R^2 = 0.86$). The colour scale applied to the data points in Figure 5-1A shows that most of the deviation between the two measurements occurs between 07:00 – 12:00 (PDT) when the nocturnal boundary layer is breaking up. This difference may be driven by an enhanced vertical gradient in HONO at this time. The AIM-IC inlet is closer to the ground and measures higher HONO. This would be consistent with a daytime source located at the ground surface (Kleffmann et al., 2005; Su et al., 2008; Elshorbany et al., 2009; Sorgel et al., 2011a; Wong et al., 2012). HONO could also be released from the surface in response to chemical and physical changes at the same time as the boundary layer breakup (e.g. release from stomata, evaporation of dew) (Warneke et al., 2002; He et al., 2006; Schimang et al., 2006; Rubio et al., 2008). Consistency between HONO measurements throughout the night indicates that there is little vertical stratification of HONO between 4 and 13.5 m of the nocturnal boundary layer on a one hour sampling timescale. Overall, the agreement seen between these two instruments is comparable to other successful HONO measurement intercomparisons between a new technique and an established sampling method (Kleffmann et al., 2006). Therefore, the HONO measurements made by the AIM-IC in Bakersfield during CalNex are considered reliable.

Particle nitrite measurements, other than in fog and dew, have been seldom reported (Lammel and Perner, 1988; Lammel and Cape, 1996; He et al., 2006; Rubio et al., 2008; Rubio et al., 2009; Song et al., 2009). This has resulted in a paucity of information regarding the presence of particle nitrite ($\text{NO}_2^-$) in urban and rural environments. Furthermore, validation of such measurements with coincident HONO measurements has not been made. We can explore the possibility that our particle nitrite measurements are a result of breakthrough from the gas channel denuder, by comparing our measurements to the REA system. Comparing the total nitrite (HONO + particle $\text{NO}_2^-$) measured by the AIM-IC to the HONO measured by the REA system in Figure 5-1B shows that there is an increased slope of about 20 % between the two measurements when particulate nitrite is included in the comparison.
Figure 5-1. Panel A - Comparison of HONO measured during CalNex by REA (13.5 m) and AIM-IC (4 m) from the Bakersfield sampling tower between 03 – 23 June 2010. Points coloured by the local hour of day indicate that most deviation from the dotted black 1:1 line occur between 07 – 12 h where the AIM-IC measures higher mixing ratios. Panel B – Comparison of AIM-IC total nitrite and REA HONO coloured by mass loading of NO$_2^-$ in AIM-IC water-soluble PM$_{2.5}$ measurement. The colour scale includes mass loadings of NO$_2^-$ up to 0.38 ppb. The red solid line in both figures represents a least orthogonal fit difference. The black dotted line is the 1:1 line.

The colour scale shows that the difference between HONO measured by the REA and the AIM-IC is often smaller than the mixing ratio equivalents of NO$_2^-$ (Figure 5-1A). In fact, some points where the AIM-IC measures elevated mixing ratio equivalents of NO$_2^-$ are also periods where it
measures more HONO than the REA instrument. This is expected if the ground surface is dominating conversion of NO\textsubscript{2} to HONO at night, as vertical gradients have been observed to develop at the surface and decrease with altitude (Kleffmann et al., 2003; Vogel et al., 2003; Zhang et al., 2009; Villena et al., 2011; Wong et al., 2011; Wong et al., 2012). To the extent that the AIM-IC and REA were measuring air containing comparable levels of HONO, Figure 5-1B further suggests that the particle nitrite measurements from the AIM-IC are not the result of HONO breakthrough from the gas channel.

Finally, Figure 5-1B also suggests that the REA system may sample particulate nitrite and identify it as HONO (i.e. points lying between the line of best fit and the 1:1 line). The dual channel correction for interferences in the scrubbing coils of the REA system assumes than any interferences are effectively transmitted to the second channel to produce similar artifact signals. However, such an approach may not be effective if there is a particle size-dependence to the collection of aerosols. Interferences from particle collection using the scrubbing coil apparatus have shown transmission of sub-micron aerosol through both channels with less than 1% being captured (Kleffmann et al., 2006; Kleffmann and Wiesen, 2008). However, a rigorous assessment of the collection efficiency of super-micron aerosol, in particular those between 1 – 2.5 μm diameter, has not yet been made, but is expected to be an issue when present (Kleffmann and Wiesen, 2008). Large aerosols (> 1 μm) have been reported to not transmit as effectively through the first scrubbing channel in some systems (Huang et al., 2002), with a greater fraction of the total number being collected by inertial collision with the scrubbing solution as particle size increases. Observed interferences in field observations have been reported during fog events where partitioned HONO was credited with producing an artifact signal in a system similar to the REA (Sorgel et al., 2011b). Other supermicron aerosol containing soluble nitrite may produce an interference in HONO systems that do not remove or account for particles in their sampling strategy.

5.3.3 Measurements of HONO and Particulate Nitrite in Bakersfield, CA

Hourly measurements of gas phase HONO in Bakersfield showed typical diurnal trends. The average night time maximum HONO mixing ratio was 0.7 ppb, ranging from 0.2 to 1.37 ppb, while daytime values reached an average minimum of 0.08 ppb, ranging from 0.03 – 0.13 ppb.
(Figure 5-2). The typical diurnal cycle shown in Figure 5.2 can be explained by photolysis during the day (R1) and accumulation overnight, most likely resulting from the heterogeneous reaction of NO$_2$ on wet surfaces (R3). Night time accumulation of HONO, on average, shows two regimes, with fast accumulation of ~0.1 ppb hr$^{-1}$ from 19:30 to 22:30 PDT followed by slower accumulation of ~0.04 ppb hr$^{-1}$ from 22:30 until sunrise (near 05:30 PDT). The observed decrease in the accumulation rate starting around 22:30 PDT suggests that HONO sinks became more important throughout the night. The main loss of HONO at night is thought to be dry deposition to the surface (Wong et al., 2011; Czader et al., 2012). The fate of HONO lost by dry deposition is uncertain. Higher values of water-soluble nitrite (NO$_2^-$) measured in the PM$_{2.5}$ channel of the AIM-IC were coincident with the accumulation of HONO during the nighttime in Bakersfield, suggesting that particles might be a sink of HONO at night.

Figure 5-2. Observations of HONO (orange) and PM$_{2.5}$ nitrite (red) by the AIM-IC during CalNex. Interruptions in the data indicate periods when calibrations and backgrounds were performed. Vertical grid lines represent midnight of each day and are spaced at one day intervals. The black line of the upper trace displays the ratio of particulate nitrite to HONO with maxima typical in the late afternoon.
Nitrite observed during this study showed mass loadings ranging from below the detection limits of the instrument (1 ng m$^{-3}$) to 0.73 µg m$^{-3}$, with a campaign average of 0.15 µg m$^{-3}$, equivalent to 0.078 ppb of HONO. Depletion of NO$_2^-$ was observed throughout the day and the mass loading reached its minimum (0.043 µg m$^{-3}$ on average) at 18:30 PDT, corresponding with the time of minimum observed gas-phase HONO (Figure 5-3).

![Figure 5-3](image)

**Figure 5-3.** Diurnal averages in hourly measured HONO and NO$_2^-$ (as ppb) from all AIM-IC measurements. Error bars represent one standard deviation.

### 5.3.4 Role of Mineral Cations in Formation of Particulate Nitrite

Accumulation of nitrite in particulate matter (0.04 µg m$^{-3}$ h$^{-1}$ = 0.02 ppb h$^{-1}$) occurred at the same time as accumulation of HONO in the gas phase. The average ratio of nitrite to HONO was 0.25 (Range: 0.06 – 0.54) throughout the campaign (Figure 5-2), often maximizing in the late afternoon when HONO and NO$_2^-$ were minimized. Figure 5-4 shows that the absolute mass loading of NO$_2^-$ generally scales according to the measured amount of gas phase HONO. The heterogeneous production mechanism for HONO from NO$_2$ occurs in the presence of water (R3). Thus, some atmospheric surfaces may not release HONO, but instead retain the nitrite on the surface if the substrate is reactive or the surface solution has a basic nature (Hirokawa et al.,...)
Most lab investigations of the HONO production mechanism from NO\textsubscript{2} on surfaces generate highly acidic surface media on which HONO cannot be retained (Finlayson-Pitts et al., 2003; Finlayson-Pitts, 2009; Miller et al., 2009). These systems may not be representative of many surfaces in contact with the real atmosphere, such as secondary aerosol, the ground, buildings or vegetation. HONO release could be inhibited on real surfaces when NO\textsubscript{2} reacts on them or they could take up HONO from the gas phase, while acidic surfaces would promote HONO release. Several possible pathways were therefore explored to explain how HONO might enter the condensed phase.

**Figure 5-4.** Enhancement of NO\textsubscript{2}\textsuperscript{-} in particles in the presence of high HONO mixing ratios. Nitrite measurements are coloured by the observed mixing ratio of HONO. The colour scale for HONO mixing ratio has an upper limit of 0.8 ppb. All measurements greater than this value appear as yellow points. The solid black line is the mean NO\textsubscript{2}\textsuperscript{-} mass loading from all measurements. The hashed region between the black dotted lines represents the 2 \( \sigma \) deviation of the observations from the mean.

Using HONO as a precursor, nitrite might be formed by i) partitioning to aqueous aerosol according to the product of its Henry’s Law coefficient and acid dissociation constant (R4, R5);
ii) forming the semi-volatile salt NH$_4$NO$_2$; and iii) reacting with other aerosol salts composed of weaker acid anions that can be displaced (R6).

Thermodynamic partitioning to aqueous aerosol was investigated using the Extended Aerosol Inorganics Model (E-AIM) online at [http://www.aim.env.uea.ac.uk/aim/aim.php](http://www.aim.env.uea.ac.uk/aim/aim.php) using the typical mixing ratio of HONO and mass loadings of NH$_4^+$, NO$_3^-$ and SO$_4^{2-}$ observed by the AIM-IC. Thermodynamic data for the partitioning of HONO into solution were used to define it as a unique chemical compound in a Model II run in comprehensive mode for gas phase constraints on aerosol pH (Clegg et al., 1992; Clegg et al., 1998; Wexler and Clegg, 2002). The HONO Henry’s Law partitioning coefficient was defined as 49 M atm$^{-1}$ (Park and Lee, 1988; Becker et al., 1998), the acid dissociation constant as 3.25 M (Lide, 2005), and the enthalpy change of dissociation as -40.58 kJ mol$^{-1}$ (Park and Lee, 1988). Partitioning conditions used measured AIM-IC concentration inputs favourable to moderate aerosol water content and pH to investigate the potential for HONO to partition to the condensed phase. Measured gas-phase mixing ratios of HONO (1.12 ppb), aerosol NH$_4^+$-NO$_3^-$-SO$_4^{2-}$ composition (1.16 - 1.5 - 1.0 µg m$^{-3}$) with pH constrained by observations of HNO$_3$ (0.11 ppb) and NH$_3$ (40 ppb) were used for this investigation. Night time relative humidities ranged from 40 – 80 % during the campaign. The E-AIM Model II was run at 70 % relative humidity and 293 K from observations made simultaneously with the atmospheric composition, allowing formation of solids and/or solutions to occur. This resulted in an aqueous aerosol pH of approximately 5 and a liquid water content of 3.5 µg m$^{-3}$. Even under these favourable conditions, no significant formation of aqueous HONO and/or nitrite by equilibrium partitioning was found to be possible. The maximum ratio of particle nitrite to gas-phase HONO was found to be 5x10$^{-5}$, much lower than the ratios observed. It was possible at 99 % RH, using the same aerosol and gaseous atmospheric composition to partition 33 % of the HONO to the aqueous aerosol phase (pH = 6.3, LWC = 133 µg m$^{-3}$). This increased partitioning fraction is expected for high liquid water loadings with neutral pH since field observations of dew and fog water nitrite (Rubio et al., 2008; Rubio et al., 2009) and flow tube uptake of HONO on to neutral solutions (He et al., 2006; Hirokawa et al., 2008) show it to be an efficient process. However, such high relative humidity conditions were not encountered during this campaign and therefore cannot help explain the observed mass loadings of particulate nitrite. Therefore, partitioning of HONO to aqueous secondary inorganic
aerosols can be excluded as a significant contributor to the observed accumulation of particulate NO$_2^–$ in Bakersfield.

The very high concentrations of NH$_3$ at this location (avg = 19.7 ppbv) suggested that NH$_4$NO$_2$ might form at night as a semivolatile salt. Since the E-AIM model does not include the formation of salts such as NH$_4$NO$_2$, and the solid formation constant ($K_p$) has not been determined for atmospheric conditions, the potential for salt formation was determined by calculating the number of moles of free ammonium measured ($\text{NH}_4^+_{(\text{excess})}$, E2) in the aerosol. The potential for salt formation was assessed by correlation of $\text{NH}_4^+_{(\text{excess})}$ with observed NO$_2^–$ accumulation. The free ammonium was calculated by difference from measured SO$_4^{2–}$ and NO$_3^–$ in the PM$_{2.5}$.

$$\text{moles NH}_4^+(\text{excess}) = \text{moles NH}_4^+(\text{total}) - (2 \times \text{moles SO}_4^{2–}) - \text{moles NO}_3^– \quad \text{(E1)}$$

It should be noted that it is possible that some of the NO$_3^–$ measured by the AIM-IC is due to reactive uptake of HNO$_3$ on CaCO$_3$ mineral dust in the PM$_{2.5}$ aerosol fraction. The AIM-IC cannot explicitly distinguish the amounts of each salt and it has been assumed for this analysis that the secondary inorganic NO$_3^–$ is in significant excess of that arising from processed mineral dust. This was corroborated by similar mass loading observations of PM$_{1.0}$ nitrate from a high-resolution aerosol mass spectrometer (HR-AMS) (data not shown). The excess NH$_4^+$ calculated using (E2) shows no correlation with particle NO$_2^–$ accumulation ($R^2 = 0.03$). Therefore, it is unlikely that formation of NH$_4$NO$_2$ was responsible for the observed NO$_2^–$.

The analysis above shows that partitioning of HONO to aqueous secondary inorganic aerosol and formation of NH$_4$NO$_2$ are not significant contributing mechanisms to the nitrite observations. Enhanced NO$_2^–$ at higher HONO mixing ratios, therefore, suggests that HONO is undergoing reactive uptake to the particulate phase.

Figure 5-5 shows that for a given amount of HONO, particulate NO$_2^–$ may be enhanced when high mole equivalence loadings of each Ca$^{2+}$ and Na$^+$ were measured. This relationship is suggestive of reactive uptake of HONO on to aerosols containing these mineral cations. In mineral/soil dust, these cations are commonly found as carbonates, particularly in arid regions.
(Orlov, 1992; Tan, 1993). Furthermore, liming is often used in agricultural regions to control acidity and Ca\(^{2+}\) content of soils, which adds CaCO\(_3\) directly to surface soils. Bakersfield is an agriculturally intensive area, utilising extensive irrigation and with much exposed soil that could lead to the formation and lofting of these soil components into the atmosphere. In the immediate vicinity of the Bakersfield tower, soils have been characterized with a neutral to mildly basic pH (7.0 – 7.5) and to have 4.5 – 6.0 g kg\(^{-1}\) of water-soluble Ca\(^{2+}\) and 0.7 – 1.1 g kg\(^{-1}\) Na\(^+\) (Karlik, 2011), some of which are present as CaCO\(_3\), CaMg(CO\(_3\))\(_2\), NaHCO\(_3\) and Na\(_2\)CO\(_3\) salts. One carbonate fraction of mineral dust, namely CaCO\(_3\), has been shown by lab and field observations to have fast and efficient reactivity with the strong acids HNO\(_3\) (Vlasenko et al., 2006; Sullivan et al., 2007a; Vlasenko et al., 2009), and HCl (Sullivan et al., 2007b), as well as the weak organic acids HCOOH (formic acid) and CH\(_3\)COOH (acetic acid) (Al-Hosney et al., 2005; Preszler Prince et al., 2007; Preszler Prince et al., 2008).
Nitrous acid is a stronger acid than either HCOOH or CH\textsubscript{3}COOH and similar reactive uptake chemistry could be expected between HONO and carbonate salts (R6), but this has not previously been investigated. Based on thermodynamic calculations, the formation of nitrite salts from reaction of HONO with carbonates likely occurs at atmospherically relevant conditions, but is not necessarily spontaneous unless corrected for specific conditions of temperature and gaseous partial pressures (see Table 5-1). Our data show that the total amount of nitrite observed
never exceeded the total amount of water-soluble Ca$^{2+}$ and Na$^+$, suggesting that nitrite salts of these minerals might be the end products of the reaction. The carbonates CaCO$_3$, NaHCO$_3$ and Na$_2$CO$_3$ are not very hygroscopic (Meng et al., 1995; Martin, 2000) and the AIM-IC may not sample particles made primarily of these salts with high efficiency in the particle supersaturation chamber. Thus, the measured Ca$^{2+}$ and Na$^+$ in Bakersfield may not represent the total mass of the two ions in the sampled PM$_{2.5}$, but just the most hygroscopic salts. The AIM-IC does not quantitatively measure CO$_3^{2-}$, impeding a definitive identification of these salts in the Bakersfield dataset. The products of the reactive uptake of HONO (i.e. Ca(NO$_2$)$_2$ and NaNO$_2$) however, are more water soluble and are expected to be quantitatively measured by the AIM-IC. Therefore, the AIM-IC measurements may be biased towards processed mineral dust, although measured Ca$^{2+}$ mass loadings were in significant excess of measured NO$_2^-$ mass loadings. Furthermore, most of the dust mass is expected to lie in particle sizes greater than PM$_{2.5}$, which the AIM-IC does not measure. This limits the extent of the possible conclusions that can be drawn from our mass measurements regarding total nitrite loadings and the uptake of HONO on to these aerosols.

**Table 5-1.** Calculated standard Gibb’s free energy values for carbonate reaction systems (Lide, 2005).

<table>
<thead>
<tr>
<th>Reaction System</th>
<th>$\Delta G_{\text{reaction}}$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HONO$(_g)$ + NaHCO$_3$(s) $\rightarrow$ NaNO$_2$(s) + H$<em>2$O$</em>(g)$ + CO$_2$(g)</td>
<td>-10.2</td>
</tr>
<tr>
<td>2 HONO$(_g)$ + Na$_2$CO$_3$(s) $\rightarrow$ 2 NaNO$_2$(s) + H$<em>2$O$</em>(g)$ + CO$_2$(g)</td>
<td>-55.4</td>
</tr>
<tr>
<td>2 HONO$(_g)$ + Na$_2$SO$_4$(s) $\rightarrow$ 2 NaNO$_2$(s) + H$_2$SO$_4$(l)</td>
<td>103</td>
</tr>
<tr>
<td>HCl$(_g)$ + NaNO$_2$(s) $\rightarrow$ NaCl$(s)$ + HONO$(_g)$</td>
<td>-50.2</td>
</tr>
<tr>
<td>HNO$_3$(g) + NaNO$_2$(s) $\rightarrow$ NaNO$_3$(s) + HONO$_2$(g)</td>
<td>-54.9</td>
</tr>
</tbody>
</table>

Assuming HONO is undergoing reactive uptake on lofted dust, the observed plateau in the average NO$_2^-$ mass loading starting at 00:00 in Figure 5-4 has two potential explanations. The first is that reactive aerosol emission and deposition rates are at steady-state. The second is that the pool of reactive substrate in lofted dust (e.g. carbonate) has been reacted to completion and no further nitrite can accumulate. The first case is most consistent with the data presented in Figures 5-4 and 5-5 because they show that more NO$_2^-$ is present at higher mixing ratios of HONO. This would suggest that the amount of reactive sink is not limiting NO$_2^-$, but that the steady-state aerosol flux is limiting the amount of NO$_2^-$ that stays aloft. Recent investigations of vertical gradients and size distribution of dust emissions have shown that under stagnant meteorological conditions, standing dust populations exist with a significant mode and mass
loading in the PM$_{2.5}$ size fraction (Chkhetiani et al., 2011; Kok, 2011). Although the magnitudes of such dust phenomena are likely to be variable between locations due to physical differences in the source material (Kok, 2011), the arid conditions in Bakersfield during CalNex would have been conducive to the production of a standing dust aerosol population. The ubiquitous presence of mineral dust in the fine mode aerosol, measured by x-ray fluorescence, supports this assertion (Figure 5-6). Every 24-hour sample showed significant quantities of Si, Fe, Al and Ca, indicative of lofted surface dust (Orlov, 1992; Tan, 1993). Therefore, under the stagnant and low wind conditions, typical of nights in Bakersfield, it is proposed that steady-state dust emissions from the surface were a reactive sink for HONO, which was observed by the AIM-IC as PM$_{2.5}$ NO$_2^-$. Given that: i) the AIM-IC NO$_2^-$ measurements are enhanced in the presence of mineral cations, and ii) the previous work on reactive uptake of acids on carbonate salts; we hypothesize that the formation of particulate NO$_2^-$ in Bakersfield arises from the reaction of carbonate minerals with HONO. This could occur both on the ground surface and on lofted particles.

**Figure 5-6.** Daily PM$_{2.5}$ mineral distribution as detected by XRF analysis of filter samples. Bar height represents the relative total amount of the major detectable components between days. Each bar is coloured according the relative fraction in each sample that the measured elements contributed.
5.3.5 Significance of Nocturnally Deposited HONO to the Unknown Daytime Source

In Figure 5-3, it is clear that neither HONO nor nitrite is completely depleted throughout the course of the day in Bakersfield, both reaching their minima between 16:00 – 19:00 PDT each day. Given the short lifetime of HONO against photolysis (< 1h at low solar zenith angles) the gas phase production rate is not sufficient to explain afternoon mixing ratios greater than ~10 ppt. The higher levels observed in many environments have generally been taken to indicate the presence of a strong daytime source of HONO. We suggest that the reactive uptake of HONO on mineral dust or soil during the night may form a nitrite reservoir that can contribute to the production of HONO during the day.

The presence of the unknown daytime HONO source was inferred from the pseudo steady state observed in the afternoon (i.e. \( \frac{d[HONO]}{dt} = 0 \)) that was greater than predicted from known gas phase sources. The magnitude of the unknown source was estimated from measured constraints on the abundance of HONO observed during the day via i) reaction of OH and NO, ii) surface heterogeneous production via NO\(_2\) and H\(_2\)O on aerosols and the ground, iii) photolysis iv) reaction of HONO with OH and v) deposition of HONO to the ground. Assuming mass balance for HONO, we determined the magnitude of the unknown daytime HONO source (P(HONO)\(_{unk}\)) in Bakersfield.

\[
\frac{d[HONO]}{dt} = P(HONO)_{unk} + k[OH][NO] + \frac{1}{2} \gamma c A \frac{1}{4} [NO_2] + \frac{1}{8} \gamma_{NO_2,ground} \frac{C_{RH}}{50} [NO_2] \\
- j_{HONO}[HONO] - \frac{1}{4} \gamma_{HONO,ground} \frac{C_{RH}}{20} [HONO]
\]

\( (E1) \)

Such that,

\[
P(HONO)_{unk} = - \frac{d[HONO]}{dt} - k[OH][NO] - \frac{1}{2} \gamma c A \frac{1}{4} [NO_2] - \frac{1}{8} \gamma_{NO_2,ground} \frac{C_{RH}}{50} [NO_2] \\
+ j_{HONO}[HONO] + \frac{1}{4} \gamma_{HONO,ground} \frac{C_{RH}}{20} [HONO]
\]

\( (E2) \)
Where, \( j_{\text{HONO}} \) is the photolysis rate (s\(^{-1}\)), \( \gamma \) is the uptake coefficient of NO\(_2\) on aerosols, and \( \gamma_{\text{NO}_2,\text{ground}} \) is the ground reaction probability of NO\(_2\). \( \gamma_{\text{HONO},\text{ground}} \) is the ground reaction probability of HONO, \( c \) is the mean molecular speed of NO\(_2\) or HONO, \( A \) is the available aerosol surface area (um\(^2\) cm\(^{-3}\)), and \( h \) is the height (m) of the mixed boundary layer. Typical values for the uptake coefficient of NO\(_2\) on aerosol surfaces range from \( 1 \times 10^{-6} \) – \( 1 \times 10^{-5} \) (Kleffmann et al., 1998; Broske et al., 2003; Wong et al., 2011), while the uptake of NO\(_2\) on the ground surface is ascribed similar values. The ground surface area is treated as a flat surface for reaction and deposition in this model. The total area of the ground is much larger than that which can be provided by aerosols in the boundary layer, making the heterogeneous conversion of NO\(_2\) on aerosols negligible. Therefore it was not included in the model runs described in Figure 5-7. We assume that even under RH conditions as low as 30% observed during the day in Bakersfield that there is enough water to allow the heterogeneous conversion of NO\(_2\) to take place, using ground reaction probabilities of \( \gamma_{\text{NO}_2,\text{ground}} = 8.0 \times 10^{-6} \) and \( \gamma_{\text{HONO},\text{ground}} = 8.7 \times 10^{-5} \) derived from the work presented in Chapter 4.

The model inputs were generated from campaign diurnally averaged measurements, initialized at 18:30 PDT and run through the course of 24 hours. Each chemical species and physical parameter used in the model is shown in Figure 5-7A. The height of the boundary layer is an estimate based on the measurements of Bianco et al. (2011) throughout the Central Valley. In contrast to the NACHTT dataset analyzed in Chapter 4, we do not have vertical profile measurements at Bakersfield and are forced to assume that all constituents are well-mixed through the boundary layer. The model, again, calculates \( E2 \) using measured concentrations of each species as a function of time (Figure 5-7C), but also calculates an estimate of HONO concentrations based on known chemical mechanisms using the HONO calculated from the previous time step (black line, Figure 5-7B). HONO and NO\(_2\) are highly correlated throughout the course of a day, which is expected for measurements within 15 m of the surface because of the dominant role of the ground surface in HONO production at night. Figure 5-7B shows the average HONO observations (brown) and model output (black). The smaller magnitude of HONO in the model output is expected since it is run with the assumption that the boundary layer is well mixed. A vertical gradient in HONO as the surface is approached is becoming a better described phenomenon as more datasets are collected, particularly those with high
resolution (Chapter 4). Vertical gradients between the REA (13.5 m) and AIM-IC (4 m) measurement heights were observed on several mornings from 06:00 – 12:00. Therefore, the average HONO number density in the 200 m nocturnal boundary layer should be smaller than the HONO measured within 15 m of the surface, as well as throughout the day.

During the day there is the anticipated discrepancy between the mechanisms operating in the model and the measured HONO concentrations, implying an unknown daytime HONO source. Given the close proximity of the AIM-IC to the surface, the strength of the daytime HONO source can be well constrained using E2 and the observations in Figure 5-7A. The daytime HONO source is strongest in the morning, maximizing near 10:30 PDT at about 1.27 ppb hr⁻¹, and decreasing in the afternoon (Figure 5-7C). In other field observations, the photolysis of NO₃⁻ (Zhou et al., 2003; Handley et al., 2007; Schuttlefield et al., 2008; Zhou et al., 2011), photocatalytic conversion of NO₂ on humic and organic surfaces (Stemmler et al., 2006; Stemmler et al., 2007; Bartels-Rausch et al., 2010), or a link between measured NO₂ and surface irradiance (Wong et al., 2012) are suggested as likely pathways to HONO daytime production. At most, 30 % of the daytime HONO source has been accounted for by these processes for a semi-urban location in Spain, dominated by the conversion of NO₂ on photoexcited humic acids (Sorgel et al., 2011a). We have found an observable reservoir in particle nitrite, from which HONO can be re-generated from throughout the day. It is likely that the AIM-IC particle nitrite measurement indicates that the soil composition at the ground surface is also enriched in nitrite. Release of nitrite from these reservoirs does not require NO₂ to generate HONO, counter to previously published daytime HONO sources. Figure 5-7C shows that the net removal of HONO to the surface (light purple) has the potential to generate a reservoir (7.0x10¹⁰ molec cm⁻³ day⁻¹) sufficient to account for 30 % of the integrated daytime unknown HONO source (2.4x10¹¹ molec cm⁻³ day⁻¹). However, mechanisms for recovering deposited HONO depend on its fate. The AIM-IC observations show that reactive uptake on mineral dust aerosol containing Na⁺ and Ca²⁺ is non-negligible at this location. Simultaneous observation of several other atmospheric acids by the AIM-IC allows the potential for an acid displacement mechanism to be investigated in Bakersfield.
Figure 5-7. Panel A – Model inputs of species concentrations and physical parameters required to model diurnal HONO production and loss, as well as the unknown daytime HONO source for the entire CalNex Bakersfield campaign. Panel B – Modeled diurnal HONO (black) and measured HONO (orange, ±1σ) with TUV calculated $j_{\text{HONO}}[\text{HONO}]$ (yellow). Panel C – Individual sources (positive values) and sinks (negative values) to the modeled HONO output stacked with the magnitude of the unknown daytime source overlaid (green line).
This was the first field dataset we collected that led us to propose a link between the known loss of HONO at night and a reservoir for recovery of HONO during the day (the second is presented in Chapter 4). Confirmation of the reactive uptake mechanism for HONO on mineral dust under controlled conditions will be described in Chapter 6. The efficiency of acid displacement reactions under atmospherically relevant conditions with the hypothesized NaNO2 and Ca(NO2)2 observed are also not known. Based on thermodynamic data, acid displacement reactions of NaNO2 with HNO3 and HCl will be spontaneous under atmospheric conditions (Table 5-1). Furthermore, acid displacement reactions can generate stable concentrations of HONO for lab investigations using NaNO2 and an acid, such as H2SO4, HCl and oxalic acid (Braman and de la Cantera, 1986; Taira and Kanda, 1990; Febo et al., 1995; Roberts et al., 2010). The acid displacement mechanism is expected to extend to reactions involving Ca(NO2)2 despite the free energy of formation for this solid being unavailable, since chloride and nitrate salts are generally more stable than nitrite salts of the same mineral cation.

The ground surface has been implicated as the major source of daytime HONO for many field observations, including those in rural locations where mineral dust is expected to be ubiquitous (Vogel et al., 2003; Kleffmann et al., 2005; Acker et al., 2006; Kleffmann, 2007; Amoroso et al., 2008; Elshorbany et al., 2009; Li et al., 2010a; Li et al., 2011; Sorgel et al., 2011a; Elshorbany et al., 2012; Li et al., 2012b). If the suspended particulate observed in Bakersfield is representative of minerals available at the ground surface, then the presence of particulate nitrite suggests that the ground surface can be a HONO source when HNO3 and HCl are reacted with nitrite salts. Figure 5-8 suggests that an acid displacement mechanism could be active throughout the day, peaking in the late afternoon with HCl and HNO3. Acid displacement can be inferred from the HCl, as a product, observed in lockstep with production of HNO3 since displacement of HCl from chloride-containing aerosols is well documented (Keene et al., 1999; Dasgupta et al., 2007). Displaced HCl also has the potential become a reactant displacing weaker acids (Sullivan et al., 2007b). Reactive uptake of HNO3 on CaCO3 has been thoroughly investigated, resulting in the accumulation of NO3- and emission of CO2 on/from mineral dust (Gibson et al., 2006; Vlasenko et al., 2006; Sullivan et al., 2007a; Hatch and Grassian, 2008; Vlasenko et al., 2009; Li et al., 2012a).
The unknown HONO source in Bakersfield maximizes near 10:00 PDT, when the production of HNO₃ and HCl are just beginning (Figure 5-8). To investigate if these acids may influence the magnitude of observable HONO during the day, the hourly HONO measurements were weighted by the observed mixing ratios of HCl and HNO₃ separately. Figure 5-8 shows that when higher mixing ratios of HCl and HNO₃ were present throughout the day, the mixing ratio of HONO at the same time was also elevated. This suggests that at higher concentrations, the strong acids HCl and HNO₃ are increasingly deposited to the surface, potentially displacing HONO. These observations suggest that acid displacement of nitrite at the surface leads to emissions of HONO. Whether or not this is displacement of nitrite salts or soil pore water nitrite cannot be determined from this dataset, but it is likely that the daytime surface HONO source is a combination of mechanisms (Section 5.3.6).

The AIM-IC nitrite measurements suggest that the lofted dust reservoir is never entirely depleted of nitrite, but without a real-time characterization of the nitrite available on the ground, the absolute magnitude of this potential source is difficult to estimate. This could mean that the surface reservoir from nighttime deposition may be depleted over the course of the day and that yet more mechanisms of HONO production at the ground surface are active. It is also possible that not all deposited HONO can be reemitted to the atmosphere or that it undergoes degradation to other nitrogen oxides. The fate of HONO deposited to ground surfaces is completely unknown and warrants significant future research to determine its potential significance towards the maximum 30% contribution to the total required daytime source.
Figure 5-8. CalNex Bakersfield diurnal plot of all hourly HONO measurements weighted by the concentration of the strong acids HCl and HNO₃ measured by AIM-IC. Highest hourly daytime HONO mixing ratios (07:00 – 19:00 PDT, shaded yellow) correspond to days with elevated mixing ratios of HCl and HNO₃.
### 5.3.6 A Framework for Particulate and/or Soil Nitrite as a Potential HONO Reservoir

As discussed previously, nitrous acid taken up on the ground and/or soil surface could occur in two ways: i) as a dynamic partitioning process governed the effective Henry’s law coefficient (He et al., 2006; Hirokawa et al., 2008) or ii) via reactive uptake on to carbonate salts, which may be enhanced further in the presence of surface water as suggested by He et al. (2006).

In the first mechanism, HONO dynamically partitions to the aqueous phase as NO$_2^-$. It can then return to the gas phase reversibly according to the equilibria in (R4) and (R5). Simulated dew and fog water have shown that this chemistry can be efficient in scavenging HONO (He et al., 2006; Rubio et al., 2008; Rubio et al., 2009; Sorgel et al., 2011b). Partitioning to water-coated surfaces was shown in flow tube investigations by He et al. (2006) to be an important process in reversible HONO sequestration that might be enhanced, and potentially irreversible, in the presence of mineral cations if found on building and plant surfaces. Increasing solution pH was shown to enhance the partitioning of HONO between the gas and aqueous phase in wet wall flow tube work by Hirokawa et al. (2008). By extension, the nitrite ion may form a stable salt (e.g. NaNO$_2$ or CaNO$_2$) by reacting with carbonates and displacing H$_2$CO$_3$/H$_2$O/CO$_2$.

As discussed in the previous section, our data indicate that soil and lofted dust could be a reactive sink for HONO if mineral carbonates are present. Being able to predict or model the formation process and presence of carbonate salts in soils and lofted mineral dust is important for understanding the larger scale significance of this chemistry. This will allow HONO and other atmospheric acid lifetimes to be better constrained, which has been indicated by the many studies of calcite and dust reactivity with HNO$_3$, HCl, acetic and formic acids (Al-Hosney et al., 2005; Ooki and Uematsu, 2005; Gibson et al., 2006; Vlasenko et al., 2006; Preszler Prince et al., 2007; Sullivan et al., 2007a; Sullivan et al., 2007b; Liu et al., 2008; Preszler Prince et al., 2008; Vlasenko et al., 2009; Saliba and Chamseddine, 2012). Formation of these carbonate salts in surface soils is determined by two processes. The first is soil pore water near the surface being enhanced in dissolved CO$_2$-HCO$_3^-$-H$_2$CO$_3$ due to microbial and plant root respiration (Orlov, 1992). The second is evaporative water loss at the surface, which leads to the precipitation of mineral carbonate salts, generally calcium or sodium, in a process termed sodification (Orlov, 1992; Tan, 1993). In arid regions this is a common phenomenon, enhanced when land is irrigated,
allowing carbonates to accumulate at soil surfaces. In other environments sodification can occur in any soil experiencing faster evaporative loss of water at the surface compared to gravitational migration to deeper soil (e.g. formation of soil *concretions* or *crust* indicates CaCO₃ precipitate).

A soil solution that would favor precipitation of mineral carbonates upon drying out at the surface, would also be a reactive sink for HONO according to (R4) and (R5). Aqueous solutions with neutral to basic pH values of 6 – 9 could enhance the effective Henry’s Law coefficient (i.e. the product of the acid dissociation constant and the Henry’s Law partitioning coefficient, $K_{R4} \cdot K_{R5}$) of HONO to values greater than $10^4$ M atm$^{-1}$ (Park and Lee, 1988; He et al., 2006; Hirokawa et al., 2008). Furthermore, the reaction free energies between HONO and carbonate salts indicate spontaneous reaction under standard conditions (Table 5-1). Naturally, the observations made suggesting these processes are occurring on lofted dust particles can be easily translated to soils, although the relative amounts of water will become significantly larger.

Investigations into dynamic partitioning processes in soil are limited to a single study that does not identify this mechanistic framework, instead favouring of a simple partitioning description. A nitrite-containing soil solution mechanism, where overlying atmospheric HONO is in equilibrium with aqueous nitrite in soil pore water, was recently proposed by Su et al. (2011). The authors proposed that evaporation of soil pore water in nitrite-containing soils leads to HONO emissions. However, the experimental conditions utilized modified soil through addition of combination of NaNO$_2$, H$_2$O and HCl which is the same reactant combination used in HONO calibration sources (Febo et al., 1995; Roberts et al., 2010). The total quantities of reactants added are not reported by the authors, but the nitrite content of the soil is increased by a factor of ten by weight and enough HCl solution is added to change the soil pH by a full unit. The addition of a strong acid solution will displace HONO from solution regardless of the presence of the solid soil substrate. Use of 100 g of soil modified in this way would provide a more than sufficient quantity of nitrite to account for the time-integrated HONO observed in the > 40 h experiment. A value for comparison in soils without additives was not presented by Su et al. (2011) as a control in their experiment for the effect of added HCl on HONO emission rate, nor was a well-justified reason for taking this approach made by the authors. Thus, the mechanism inadvertently explored in this study was one of acid displacement between HCl and NaNO$_2$ to form HONO.
and the more stable NaCl salt (or its aqueous ions), not partitioning of NO$_2$ and HONO between soil pore water and the gas phase.

The potential for this mechanism to be valid still exists, but requires more thorough investigation. Therefore, in light of the Bakersfield particle nitrite observations, it is proposed that the particle nitrite that was observed could be a new source of daytime HONO via acid displacement reactions occurring on the suspended solids or in surface soil solutions. Conversely, it is also possible that partitioning of HONO was contributing to the observed daytime gradients, fluxes and unknown source between 07 – 12 h (Figures 5-1) by being released from evaporating dew, plant stomatal release and potentially throughout the day as soil pore water evaporates. However, the necessary measurements to isolate these processes are not available for this field study. Future investigations attempting to resolve the underlying mechanisms of daytime HONO production would significantly benefit from fully characterized soil composition and continuous surface and soil water measurements.

In contrast, the acid displacement mechanism that could generate daytime HONO requires soil or solution nitrite derived from reactive uptake of HONO on to carbonate salts or by bacterial processing of soil N-components (e.g. NH$_4^+$ and NO$_3^-$). These nitrite salts will emit HONO if HCl or HNO$_3$ are dry deposited on to, or partition to, the nitrite reservoirs. If the nitrite was accommodated in to the soil by forming salts with mineral cations, such as Na$^+$ or Ca$^{2+}$, it can be displaced through proton exchange with these acids and formation of more stable salts. An alternative scenario could be that the NO$_2^-$ in solution is present by partitioning of HONO, where the uptake of stronger acids or evaporative loss of water could shift the solution pH and enhance the rate of HONO release.

In Bakersfield, the HONO observed during the daytime never went to zero, indicating that a daytime source on the order of 1.27 ppb hr$^{-1}$ would need to be active to maintain the observed steady state. We observed a depletion of particle nitrite throughout the day (one the order of 0.01 ppb hr$^{-1}$), which may indicate that uptake of stronger acids on to these particles is producing HONO. Low daytime relative humidities (~ 20 %) suggest that emission of HONO from soil pore water was likely minimal, particularly in the late afternoon, when the photostationary
HONO minimum was observed. Quantified unknown daytime HONO sources have been most recently been correlated to [OH]*[NO2] (Ren et al., 2011), total surface irradiance*NO2 (Wong et al., 2011) and the previous daily maximum in HNO3 (Li et al., 2012b). The former mechanism using humic acid as the photoexcited substrate has been approximated to contribute up to 30 % of the total source by Sorgel et al. (2011a) during the DOMINO campaign in semi-urban Spain, implying that the daytime source is a combination of that mechanism with others that had not yet been identified. Given the variety of environments in which daytime HONO has been observed at mixing ratios of > 100 pptv, and the number of potential surface reactions for the heterogeneous conversion of NO2, it is likely that various combinations of the known production mechanisms are occurring in a site specific fashion.

With respect to acid displacement, two sets of limiting conditions can be considered to develop the framework of the mechanism further. The first is an excess of displacing acid, such as acid displacement of HCl from sea salt by reactive uptake of HNO3 in coastal regions (Dasgupta et al., 2007), which has been extended to observations of lofted dust (Sullivan et al., 2007a;Sullivan et al., 2009). Secondly, the particulate and/or surface reservoir could be limiting with respect to the displacing acid and potentially be depleted. The work of Su et al. (2011) suggests that soil nitrite is highly abundant in soils globally, but does not disclose whether these are bulk evaluations or samples likely to be in full interactive exchange with the atmosphere. The observations here suggest that the HONO source decreases over the course of the day, but whether this is depletion of the reservoir is unclear. The estimate of HONO deposition to form nitrite salts from our model gives a maximum contribution of acid displacement to the daytime HONO source as 30 %. Therefore, the importance of nitrite limitation in the acid displacement mechanism is currently uncertain.

Without normalizing to NO2, it is possible to identify when each mechanism is active and how they compare to the modeled unknown HONO source strength (Figure 5-9). Data from the REA system indicate that the largest upward flux of HONO is observed at this site in the morning between 05:00 - 11:00 PDT. The upward flux begins sooner than the production of HONO from photocatalytic conversion of NO2 on the ground and when there is not a need for an unknown source in the model. Therefore, during this period the production of HONO by heterogeneous
conversion on the ground and subsequent mixing through the BL is likely responsible for the flux observation. The photocatalytic HONO source is represented by the product of NO$_2$ and photosynthetically active radiation, which maximizes earlier in the day (06:00 – 10:00 PDT) than the modeled daytime source (09:00 – 12:00). The unknown source, therefore, likely also includes other HONO sources active at the ground surface throughout the day. The relative importance of each contributor cannot be assessed by this dataset since little is known about their production efficiency. The overlay of HNO$_3$ in Figure 5-9 and data shown in Figure 5-8 suggests that acid displacement is contributing to HONO production during the middle of the day and into the evening (10:00 – 17:00). Visually, the combination of the photocatalytic source and acid displacement strength via HNO$_3$, could result in the shape of the unknown daytime HONO source. Without more information on the efficiencies, magnitude or relevance of these mechanisms, we can only speculate about the relative contributions at this time. Another source of HONO that was not possible to quantify here is partitioning of soil pore water nitrite as the surface temperature increases, water evaporates and HONO is released to the overlying atmosphere (Su et al., 2011). Combined together, these mechanisms could result in a daytime HONO source of the form observed in Bakersfield. Future work aiming to separate and quantify the contributions of each of the mechanisms for a variety of locations will greatly improve our understanding of the daytime HONO source, how to predict its strength and the influence of photolytic OH from HONO will have on the atmospheric oxidation capacity.
Figure 5-9. Diurnal averages of HONO flux (red) (adapted from Ren et al. (Ren et al., 2011)), NO$_2^*$-photosynthetically-active radiation (black), HNO$_3$ (blue) and the modeled unknown daytime source of HONO (green).

5.4 Conclusions/Atmospheric Relevance

Measurements of HONO and particulate nitrite were made with an AIM-IC instrument, showing accumulation of both species at night, followed by loss the next day. Intercomparison with a relaxed eddy accumulation system that measures HONO indicates excellent agreement with the AIM-IC. The agreement in the gas phase signals from the two systems indicates that the AIM-IC particulate nitrite observations are real and not likely the result of artifacts or inefficient collection in the gas channel.

These HONO measurements, in the context with supporting measurements, were parameterized in a simple box model to calculate the ground surface daytime HONO source strength to be on the order of 1.27 ppb hr$^{-1}$. The particulate matter composition measurements by AIM-IC show
that accumulation of nitrite into particulate matter is enhanced in the presence of the mineral cations Na$^+$ and Ca$^{2+}$, suggesting that reactive uptake on to carbonate minerals was occurring on dust and potentially the ground surface. Such chemistry has the potential to act as a HONO reservoir the following day.

Measurements of gas phase HNO$_3$ and HCl indicate that these acids can lead to the displacement of HONO from mineral surfaces. The observations of HONO and NO$_2^-$ in Bakersfield, during CalNex, suggest a new source of HONO to the atmosphere that has not previously been reported from field observations or laboratory studies. This mechanism would be consistent with the proposal in our framework that observed daytime HONO production is most likely a combination of several mechanisms with i) correlation to the product of NO$_2$ and surface irradiance or OH, ii) partitioning of soil pore water nitrite to the atmosphere and iii) photochemical production of HNO$_3$ followed by HONO displacement. Observations from Bakersfield show that HCl displacement is occurring when mixing ratios of HNO$_3$ are elevated, suggesting that the HONO displacement mechanism likely follows a similar trend, but the reservoir appears to be NO$_2^-$ limited by the amount HONO deposited to the surface at night. If all deposited HONO is reemitted the following day, up to 30 % of the daytime source may be accounted for from the results of a simple box model for this chemistry. This estimate is strongly dependent on the estimated height of the boundary layer and our assumption that HONO is well-mixed throughout the boundary layer. Depletion of the NO$_2^-$ reservoir in PM$_{2.5}$ (Figure 5-8) and on surfaces throughout the day via acid displacement could partially explain the decrease in the modeled unknown HONO source strength in the late afternoon. Extension of currently accepted acid displacement reactions to those proposed to contribute to the unknown source of daytime HONO should therefore be sound, but the relative contribution of all surface sources remains to be resolved.
5.5 References


Wexler, A. S., and Clegg, S. L.: Atmospheric aerosol models for systems including the ions H<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup> and H<sub>2</sub>O., J Geophys Res, 107, 14, 2002.


CHAPTER SIX

A chemical mechanism for the relative humidity dependent reactive uptake and displacement of nitrous acid (HONO) on reactive carbonate and soil substrates: Flow tube experiments at atmospheric pressure

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T. C. VandenBoer designed and performed experiments with contributions from C. J. Young and R. Talukdar. T. VandenBoer prepared this manuscript under the guidance of J. M. Roberts, S. S. Brown and J. G. Murphy.
Abstract
Two new mechanisms in the atmospheric chemistry of HONO have been determined. The first shows reactive uptake of HONO on to carbonate salts by forming nitrite salts. This observation confirms the hypothesis from field observations made in Bakersfield, CA during CalNex suggesting HONO is taken up reactively on soil dust to form mineral nitrites. Furthermore, real soil extracts have also shown reactive uptake towards HONO. Therefore, the presence of carbonates in soils and dust particles is expected to act as a reactive sink for HONO in the real atmosphere.

Flow tube experiments found reactive uptake coefficients for HONO at 298 K and 830 mbar to range from $5 \times 10^{-6}$ – $1.6 \times 10^{-5}$, but were substrate dependent. The associated uncertainty in these measurements is 12 - 20 %. Diffusion limitation, reversible partitioning of HONO and decomposition to NO or NO$_2$ were not found to be significant in any of these experiments. These values of the HONO reactive uptake coefficient are near the lower limit of values derived from 250 m atmospheric column observations made during NACHTT, suggesting that other processes may also be important to consider in the fate of surface deposited HONO at night. Increasing relative humidity above all reactive substrates demonstrated an enhanced uptake of HONO.

Nitrite salts formed by reactive uptake of HONO were also found to undergo subsequent displacement by both HCl and HNO$_3$. Such a HONO emission mechanism is likely contributing to the formation of daytime HONO in the real atmosphere and has not been considered when attempting to account for sources and sinks during the day.
6.1. Introduction

Daytime HONO photolysis has the potential to contribute >10% of the total daily OH production in local atmospheres (Elshorbany et al., 2009; Elshorbany et al., 2012; Acker et al., 2006; Volkamer et al., 2010). Release of OH early in the day when other sources are not active can lead to enhanced ozone, increased radical production and formation of secondary pollutants (e.g. SOA, OVOCs). The formation and fate of nitrous acid (HONO) in the troposphere has two significant issues that need to be addressed. The first is the fate of HONO deposited to the ground surface at night. Atmospheric concentrations of HONO near the ground are often observed to reach a pseudo steady state at night, on the timescale of a few hours, suggesting that vertical mixing and deposition to the surface both contribute to the observations (Wojtal et al., 2011; Wong et al., 2011). However, deposition is alternately viewed as a reversible or irreversible process depending on the environment where the observations are made or the constraints on the model that is run. Furthermore, the mechanism of HONO loss to the surface is not known, although constraints on pH-dependent partitioning to liquids has been explored (Hirokawa et al., 2008; He et al., 2006). Surfaces on which HONO may be taken up reactively have not yet been characterized. Of particular interest is the potential formation of a HONO reservoir on the ground from nighttime deposition capable of releasing HONO back to the atmosphere the following day.

The second significant issue is a poorly constrained unknown daytime source of HONO required to explain observed mixing ratios in many environments (Zhou et al., 2011; Wong et al., 2012; Su et al., 2008; Sorgel et al., 2011; Kleffmann et al., 2005; Elshorbany et al., 2012; Acker et al., 2006). Several heterogeneous NO2-dependent conversion mechanisms have recently been uncovered in laboratory investigations, which are photocatalytic in the production of HONO on irradiated humic acid (Stemmler et al., 2007; Stemmler et al., 2006; Bartels-Rausch et al., 2010), TiO2 (Langridge et al., 2009; Bedjanian and El Zein, 2012), soot (Monge et al., 2010; Khalizov et al., 2010; Gerecke et al., 1998; Aubin and Abbatt, 2007; Ammann et al., 1998), and solid organic surfaces (Ziemba et al., 2010; George et al., 2005; Broske et al., 2003; Brigante et al., 2008). However, the potential contribution from these sources to the required daytime production rate of HONO has not been characterized from field observations and direct confirmation of this mechanism remains a significant challenge for future field measurements. Surface mechanisms
not dependent on NO\textsubscript{2} that have been suggested to account for daytime HONO production are i) HNO\textsubscript{3} surface photolysis (Zhou et al., 2011; Zhou et al., 2003) and reversible partitioning of nitrite from all available surface water in to the overlying atmosphere (Su et al., 2011). In either case, there have again been no supporting field observations to conclude that the mechanisms proposed are active and contributing a significant proportion to the unknown daytime HONO source. Clearly there may be other sources active in the production of daytime HONO. Therefore, there is a clear need and opportunity to better understand the mechanisms underlying the sinks and sources of HONO in the atmosphere as instrumentation capable of making fast HONO measurements at part per trillion by volume (pptv) concentrations becomes more readily available.

In previous field observations from NACHTT and CalNex, it was found that the nighttime ground deposition of HONO in a simple box model could account 25 to > 100 % of the total unknown daytime HONO source if the deposition created a reservoir from which HONO could be recovered the following day (Chapters 4). The deposition of HONO to the ground was parameterised by integrated column measurements of HONO and NO\textsubscript{2} over several nights during the NACHTT field campaign. Another recent study has shown that surface deposition can be utilized to understand HONO pseudo steady states quickly established at night over water bodies (Wojtal et al., 2011). Furthermore, hourly measurements of the gas and particle phases during the CalNex field campaign in Bakersfield, CA showed accumulation of nitrite in particles when mixing ratios of HONO and mass loadings of the mineral dust tracers Na\textsuperscript{+} and Ca\textsuperscript{2+} in PM\textsubscript{2.5} were highest (Chapter 5). These observations suggested a potential reactive uptake mechanism for HONO at night on to soils and lofted dust. This is consistent with the pseudo steady state observed in Bakersfield and provides a more general context for understanding nighttime HONO at other continental locations. However, mechanistic confirmation that HONO can react on mineral dust to create nitrite salts has not been previously explored and the fate of HONO deposited in such a way is not known. Investigations have been made for other acids, both stronger and weaker than HONO (e.g. HNO\textsubscript{3}, HCOOH, CH\textsubscript{3}COOH), which show that carbonates are highly reactive components of mineral dust towards atmospheric acids (Preszler Prince et al., 2008; Preszler Prince et al., 2007; Liu et al., 2008; Hatch and Grassian, 2008; Cwiertny et al., 2008; Al-Hosney et al., 2005; Sullivan et al., 2009; Sullivan et al., 2007b; Vlasenko et al., 2006; Vlasenko et al., 2009). The carbonate fraction of mineral dust
(MCO$_3$) takes up these acids (HA) readily, releasing CO$_2$ and H$_2$O according to the following general mechanism:

\[
\text{MCO}_3(s) + 2 \text{HA}(g) \rightarrow \text{MA}_2(s) + \text{CO}_2(g) + \text{H}_2\text{O}(g)
\]  
 (R1)

or

\[
\text{MHCO}_3(s) + \text{HA}(g) \rightarrow \text{MA}(s) + \text{CO}_2(g) + \text{H}_2\text{O}(g)
\]  
 (R2)

A HONO reservoir formed by reaction with soils, presumably by forming nitrite salts, could potentially regenerate gaseous HONO during the day by undergoing acid displacement reactions with both HCl and HNO$_3$. For example,

\[
\text{NaNO}_2(s) + \text{HNO}_3(g) \rightarrow \text{NaNO}_3(s) + \text{H}_2\text{O}(g) + \text{CO}_2(g)
\]  
 (R3)

The photochemical production of gas phase HNO$_3$ followed by R3 offers a realistic daytime pathway for the production of gas phase HONO. Acid displacement is commonly used in the generation of HONO for laboratory calibration sources (Vecera and Dasgupta, 1991; Taira and Kanda, 1990; Febo et al., 1995; Braman and de la Cantera, 1986) and should be spontaneous under atmospheric conditions (Table 6-1), but to our knowledge its importance to the chemistry in the ambient atmosphere has not been previously considered.

**Table 6-1.** Calculated standard and atmospherically relevant estimations of Gibb’s free energy values for the reaction systems investigated in flow tube experiments at 0 % relative humidity from tables in (Lide, 2005). Estimates made by using atmospherically relevant mixing ratios of reactant and product gases and $\Delta G_{\text{reaction}} = \Delta G^o_{\text{reaction}} + RT \ln Q$ at 298 K.

<table>
<thead>
<tr>
<th>Reaction System</th>
<th>$\Delta G^o_{\text{reaction}}$ (kJ mol$^{-1}$)</th>
<th>$\Delta G_{\text{reaction}}$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HONO$_3$(g) + NaHCO$_3$(s) → NaNO$_2$(s) + H$_2$O(g) + CO$_2$(g)</td>
<td>-10.2</td>
<td>-27.3</td>
</tr>
<tr>
<td>2 HONO$_3$(g) + Na$_2$CO$_3$(s) → 2 NaNO$_2$(s) + H$_2$O(g) + CO$_2$(g)</td>
<td>-55.4</td>
<td>-72.5</td>
</tr>
<tr>
<td>2 HONO$_3$(g) + Na$_2$SO$_4$(s) → 2 NaNO$_2$(s) + H$_2$SO$_4$(l)</td>
<td>103</td>
<td>85.8</td>
</tr>
<tr>
<td>HONO$_3$(g) + NaNO$_2$(s) → HONO$_3$(g) + NaNO$_2$(s)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HCl(g) + NaNO$_2$(s) → NaCl(s) + HONO$_3$(g)</td>
<td>-50.2</td>
<td>-67.3</td>
</tr>
<tr>
<td>HNO$_3$(g) + NaNO$_2$(s) → NaNO$_3$(s) + HONO$_3$(g)</td>
<td>-54.9</td>
<td>-72.0</td>
</tr>
<tr>
<td>HCl(g) + Ca(NO$_2$)$_2$(s) → CaCl$_2$(s) + 2 HONO$_3$(g)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HNO$_3$(g) + Ca(NO$_2$)$_2$(s) → Ca(NO$_3$)$_2$(s) + 2 HONO$_3$(g)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
This study builds on the field observations that suggest that HONO is taken up reactively on soils, carbonates in particular. Investigations of the reactive uptake of HONO on to substrates representative of these surfaces/minerals is presented. We show that i) HONO is reactive with carbonate salts and soil extracts in flow tube experiments, ii) HONO does not decompose to NOx species on these surfaces, and iii) the first heterogeneous uptake coefficients for HONO on these salts as a function of relative humidity are derived. The reacted substrates are also shown to be capable of releasing HONO by simple acid displacement with both HCl and HNO3 under dry conditions. The potential atmospheric implications of these observations are discussed.

6.2 Heterogeneous Reactive Uptake Flow Tube Experiments

6.2.1 Instrumentation, Reactive Gas Sources, and Calibrations

Two state-of-the-science instruments for the detection of nitrogen oxide species were used to probe the fate of HONO with high time resolution (~ 1 Hz), sensitivity and accuracy. A Negative-Ion Proton-Transfer Chemical-Ionisation Mass Spectrometer (NI-PT-CIMS) was used to detect the gas phase acids HCl, HONO and HNO3. A detailed description of this design and testing of this instrument can be found in Veres et al. (2008) and Roberts et al.(2010). Briefly, acetic anhydride gas is passed through a 210Po source to generate acetate ions that undergo the proton exchange chemistry in (R4) with stronger acids (i.e. pK_a(HA) < pK_a(CH3COOH), where HA is the acid analyte). Atmospheric acids are collected in a sample flow of approximately 840 sccm through a critical orifice and inlet assembly.

\[
\text{CH}_3\text{COO}^- + \text{HA} \rightarrow \text{CH}_3\text{COOH} + \text{A}^- \quad (\text{R4})
\]

This enables highly selective and sensitive mass-selective detection of gas-phase acids at atmospherically relevant mixing ratios, on the order of pptv.

A custom inlet was constructed for the flow tube experiments to allow for rapid online background ion count measurements (Figure 6-1). Using 3-way solenoid valves, the sample flow was either pulled straight in to the flow tube or through an annular denuder (Model URG-2000-30x150-3CSS, URG, Chapel Hill, NC) coated with Na2CO3 (according to EPA Compendium Method IO-4.2). The denuder quantitatively removes gas phase acids from the sample flow without altering the relative humidity of the sample, thereby providing on-the-fly backgrounds.
The acid-stripped flow was then directed in to the ion flow tube to collect background spectra. The data were collected by successive counting (0.05 s at each mass) of the ions for: Cl⁻ (m/z 35), NO₂⁻ (m/z 46), and NO₃⁻ (m/z 62) and 0.5 s for CH₃COO⁻ (m/z 59), yielding a data collection rate of approximately 1 Hz.

A diode-based laser (405 nm) cavity ring-down system was used to measure mixing ratios of NO and NO₂, as well as record physical parameters of flow tube relative humidity, temperature and pressure. A comprehensive description of this instrument can be found in Wagner et al. (2011). Detection limits of NO and NO₂ were 150 and 100 pptv at 0.1 Hz measurement rate and a total sample flow rate of 1200 sccm. In these experiments, a modified inlet for automated backgrounds every 10 minutes was constructed to allow the introduction of nitrogen gas in to the ring-down cavities.

![Figure 6-1. Schematic of flow tube and instrumentation setup for reactive uptake of HONO and subsequent acid displacement reactions. The dotted line in the flow tube marks the ‘initial position’ for the reactive gas injector. Dry or humidified N₂ provided the sheath flow in to which reactive gases were mixed. Circles are 3-way solenoid valves used for online background collection for the Negative-Ion Proton-Transfer Chemical Ionisation Mass Spectrometer (NI-PT-CIMS) and Cavity Ring-Down Spectroscopy (CRDS) instruments. Dashed lines on the valves indicate alternate flow paths for backgrounds. The overflow is marked as P atm and the temperature, pressure and relative humidity probes by T-P-%RH.](image-url)

Calibrations of the NI-PT-CIMS were carried out using a method similar to that described in Roberts et al. (2010) for HONO and HNO₃. In this study, two HCl permeation sources were used (VICI Metronics, Poulsbo, WA) that had emission rates of 15 ng min⁻¹ at 40 °C (certified by the
manufacturer) and 10.2 ng min\(^{-1}\) at 55 °C (confirmed by collection of HCl in to aqueous solution with a bubbler followed by ion chromatographic analysis and intercomparison with a high pressure standard (10.1 ± 5 % ppm, Spectra Gases, Stewartsville, NJ)). The 10.2 ng min\(^{-1}\) device was used exclusively in the HONO generation system and the 15 ng min\(^{-1}\) device for acid displacement experiments, and to calibrate the NI-PT-CIMS. A permeation device was also used to produce known quantities of HNO\(_3\) for calibration (VICI Metronics, Poulsbo, WA). The emission rate was quantified by UV absorption spectroscopy according to the method of Neuman et al. (2003), and collection in to aqueous solution followed by ion chromatographic analysis, as 17.67 ng min\(^{-1}\) at 40 °C.

Gaseous nitrous acid was produced by combining a 7.2 sccm output flow from the dedicated HCl permeation device, with a 15 sccm flow of 45 - 55 % RH humidified air from a bubbler. The humidified HCl was passed through a packed ½” (O.D.) PFA tubing containing NaNO\(_2\) salt interspersed with 1.5 mm glass beads. The HCl underwent quantitative exchange for HONO as described in Roberts et al. (2010). By finely tuning the temperature of the HCl permeation device (i.e. the HCl emission rate), NO\(_x\) impurities due to the self-reaction of ppmv HONO levels (R5) and nitrous acidium ion with nitrite (R6, R7) were avoided.

\[
\begin{align*}
H_2ONO^+(aq) + NO_2^-(aq) &\rightarrow N_2O_3(g) \rightarrow NO(g) + NO_2(g) \quad (R5) \\
2 \text{HONO}_{(g,surf)} &\rightarrow NO(g) + NO_2(g) + H_2O(g) \quad (R6) \\
H_3O^+(aq) + HONO_{(aq)} &\rightleftharpoons H_2ONO^+_{(aq)} + H_2O_{(l)} \quad (R7)
\end{align*}
\]

The presence of water and low HCl levels in the salt bed also enhanced the release of HONO relative to the production of nitrogen oxides (via R3) during the reactive exchange process. Such problems have been previously reported in the development of these reactive exchange systems (Febo et al., 1995; Schiller et al., 2001). The HONO source output was determined to be 375 (±23) ppbv by catalytic conversion to NO\(_x\) followed by O\(_3\) chemiluminescence with a conversion efficiency of > 95 % (Roberts et al., 2010). The source output was diluted to concentrations between 0.5 and 5.0 ppbv for calibration analysis. The CRDS did not detect any consistent NO\(_x\)
impurities in the HONO source output. Sensitivity of the NI-PT-CIMS towards HONO was 9.6 counts per pptv and calibrations showed high linearity ($R^2 = 0.994$) between 0 and 10 ppbv. The calibrations performed by dilution in N$_2$ with the HNO$_3$ and HCl permeation devices had sensitivities of 5 and 2 counts per pptv, respectively, across a range of 0.5 – 25 ppbv ($R^2_{HNO3} = 0.991$, $R^2_{HCl} = 0.997$). The 1 Hz detection limits, taken as two times the noise in the background ion counts, for HCl, HONO, HNO$_3$ were determined to be 100, 14, and 44 pptv, respectively, during these experiments.

### 6.2.2 Flow Tube System Design

A vacuum sheathed 20 cm Pyrex flow tube (I.D. 2.5 cm) outfitted with a moveable glass injector was used throughout these experiments. The flow tube was operated under conditions of ambient temperature and pressure for all experiments to simulate the reaction of HONO with the tested substrates under real atmospheric conditions. A sheath flow of nitrogen gas was passed through the flow tube during all experiments at rates of 1200-2500 sccm to vary the concentration or residence time of the reactant gases. This also maintained constant overflow of the instrumentation inlets during sampling (Figure 6-1, $P_{atm}$).

Known quantities of HONO, HCl and HNO$_3$ were introduced into the flow tube using two interchangeable pyrex injectors. Relative humidity was controlled by splitting part of the N$_2$ sheath flow through a 15 L water bubbler and recombining it with dry N$_2$ before entering the flow tube. All flows in the flow tube system were regulated using mass flow controllers (Alicat 0-5 SLPM; ±0.8% of reading + 0.2% full scale). Temperature and relative humidity (Vaisala HMP 110, ±1.7 % of measurement) were measured in the flow tube overflow while pressure was measured inside the flow tube using a precision pressure transducer (Honeywell Model: PPT0015AXN5VA-B). Prior to use, the entire assembly was cleaned via sonication for 30 minutes in MicroClean solution, rinsed with acetone and sonicated again for 30 minutes in deionised water. Cleanliness was confirmed by passing HONO through the flow tube at 0 % RH and modulating the injector to expose the inner surface. Observing a fast and small reversible adsorption of HONO on the surface and its immediate transmission through the flow tube were used to confirm that no reactive sinks for HONO were present as surface impurities. When investigating the influence of reactive substrates, coated Pyrex boats (~44 cm$^2$ or 35 % of total
flow tube surface area 124 cm$^2$) were placed in the flow tube in this same region and the injector distance was used to control the exposure of these surfaces to HONO, HCl and HNO$_3$ under different conditions of relative humidity.

**6.2.3 HONO Reactive Uptake**

A variety of solid substrates were utilized to investigate the competing effects of surface composition, water content and reactive acid-base chemistry on the reactive uptake of HONO. Table 6-2 summarizes the substrates used in this study and the experimental conditions they were tested under. Clean Pyrex boats were used to characterize: i) the effect of the boat on the conduction of HONO through the flow tube; ii) the cleanliness of the flow tube; and iii) the backgrounds for the system prior to experiments. Sodium carbonate and bicarbonate salts were used as reactive substrates representative of the carbonate fractions in real soils. Sodium sulphate was used as a negative control on reactive uptake, since the free energy of the formation of sodium nitrite by reactive uptake of HONO is not favored (Table 6-1). Sodium sulphate also served as a neutral substrate (pH ≈ 6) in the relative humidity experiments where the influence of surface water on the partitioning of HONO was investigated. Sodium nitrite was used as a negative control in the HONO reactive uptake experiments and a positive control in the acid displacement experiments. Solid substrates were prepared on 16 cm long Pyrex boats by pipetting known quantities of 1 mM salt solutions (Na$_2$CO$_3$, NaHCO$_3$, NaNO$_2$, Na$_2$SO$_4$; > 98 % purity; ACS Reagent Grade) in to the boats, followed by dilution and mixing with deionised water to coat the entire surface area. The solutions were dried at 80 °C to form solid coatings on the surface. The extent of coverage achieved was confirmed visually.

Soil samples were collected from the Boulder Atmospheric Observatory tower site in Erie, CO (BAO) and the Kern County Cooperative Extension in Bakersfield, CA (BFL). These soil samples were used to determine if soils may act as a sink for HONO via reactive uptake and a source of HONO via acid displacement with HCl and HNO$_3$. Soil substrates for these experiments were prepared by thoroughly mixing 1 kg samples collected from the surface soil layer at both sites (within the top 5 cm of bare soil) and combining a subsample of the soil in deionised water to create a 50 mg L$^{-1}$ suspension. The suspension was then shaken vigorously for several minutes, sonicated for 1 hour, and left over night to allow low solubility salts to
equilibrate in solution. Soil samples were thoroughly mixed to ensure an even suspension of fine solids before removing aliquots when preparing dry substrate coatings on the Pyrex boats. No separation of organic content or solids was made before preparing boats for investigation of the soil reactivities.

**Table 6-2.** Summary of experiments performed The influence of liquid water and the surface solution chemical composition were investigated for enhancement or inhibition of HONO reactive uptake. Mixing ratios of HONO, HCl and HNO₃ are given for their respective experiments, along the relative humidity values tested for each substrate. Temperature and pressures were generally constant during experiments at 24.7(±0.3) °C and 833(±7) mbar.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>HONO Uptake (0 % RH)</th>
<th>Relative Humidity Effects on HONO Uptake</th>
<th>Acid Displacement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrex</td>
<td>3 ppbv</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>3 ppbv</td>
<td>4 ppbv, 0/30/50/80/95</td>
<td>HCl: 20 ppbv, HNO₃: 60 ppbv</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>3 ppbv</td>
<td>4 ppbv, 0/30/50/80/92</td>
<td>HCl: 20 ppbv, HNO₃: 60 ppbv</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>3 ppbv</td>
<td>1 ppbv, 0/30/50/80/87</td>
<td>-</td>
</tr>
<tr>
<td>NaNO₂</td>
<td>3 ppbv</td>
<td>-</td>
<td>HCl: 20 ppbv, HNO₃: 60 ppbv</td>
</tr>
<tr>
<td>BAO Soil</td>
<td>3 ppbv</td>
<td>2 ppbv, 0/30/50/84/92</td>
<td>-</td>
</tr>
<tr>
<td>BFL Soil</td>
<td>3 ppbv</td>
<td>3 ppbv, 0/30/50/80/95</td>
<td>-</td>
</tr>
</tbody>
</table>

Boats coated with dry substrates were placed in the flow tube and the water content altered by modifying the relative humidity of the N₂ sheath flow. Experiments investigating the reactive uptake of HONO on to salts at 0 % relative humidity were conducted by purging the flow tube with dry N₂ for at least 1 hour beforehand to ensure as much surface water was removed as possible. The position of the moveable injector was used to expose the entire surface area of substrate to HONO (i.e. injector at 16 cm). Experiment times ranged from 5 – 30 min. The surface areas of the exposed substrates in all experiments were assumed to be equal to the geometric surface area of the exposed substrate. The extent of reactive uptake was monitored by observing the change in HONO mixing ratio with the NI-PT-CIMS as a function of substrate surface area available for reaction.
The residence time \( t \) spent in contact with the substrate surface was calculated by

\[
t = \frac{A_r d}{V_f}
\]  

(E1)

Where \( A_r \) is the total surface area (cm\(^2\)) available for HONO exchange in the flow tube (changed by < 1 % with boat inserted), \( d \) is the injector distance (cm) from its initial location in the flow tube, and \( V_f \) is the volumetric flow rate (cm\(^3\) s\(^{-1}\)) of gases through the flow tube.

The uptake rate was determined using:

\[
C_t = C_0 e^{-km t}
\]  

(E2)

Such that,

\[
\ln \left( \frac{C_0}{C_t} \right) = km t
\]  

(E3)

Where \( C_o \) is the observed number density of HONO (molec cm\(^{-3}\)) with the injector fully inserted, \( C_t \) is the number density observed with the injector at a distance, \( d \) (cm), and \( k_m \) is the calculated uptake rate coefficient (s\(^{-1}\)). Since our experiments were carried out at atmospheric pressure, the calculated uptake coefficient required correction for potential diffusion limitations:

\[
\frac{1}{k_c} = \frac{1}{k_m} - \frac{1}{k_D}
\]  

(E4)

Where \( k_D \) is the diffusion rate of HONO to the surface in the flow tube (0.74 s\(^{-1}\), (Hirokawa et al., 2008)), and \( k_c \) is the corrected rate coefficient (s\(^{-1}\)).

The value of \( k_D \) was determined for this flow tube setup using:

\[
k_D = \frac{3.6 D_{N_2}}{r^2}
\]  

(E5)
The corrected rate coefficient was then used to determine the effective uptake coefficient ($\gamma$) of HONO on to a given substrate:

$$\gamma = \frac{2r k_c}{\omega A_f}$$  \hspace{1cm} (E6)

Where $r$ is the radius of the flow tube reactor (cm) and $A_f$ is the fractional geometric area of the flow tube coated with substrate on the Pyrex boats. The mean molecular speed ($\omega$, cm s$^{-1}$) of HONO ($M = 0.047$ kg mol$^{-1}$) was determined by:

$$\omega = \sqrt{\frac{8RT}{\pi M}}$$  \hspace{1cm} (E7)

To account for differences in the observed reactive uptake of HONO due to variable substrate surface reactivity, the influence of physically adsorbed water at crystal edges, and differences in coating thickness, three boats were separately prepared and tested under identical experimental conditions for each substrate. Reproducibility of results for individual boats was determined by performing a minimum of three reactive uptake experiments on the same boat. Since good reproducibility in reactive uptake of HONO was seen between boats under dry conditions, multiple boats were not investigated in the variable relative humidity experiments in the interest of conserving time and resources. Relative humidity is used throughout this work as a proxy term for the quantity of surface adsorbed water in the flow tube setup.

Salts were equilibrated at the relative humidity of interest for 10 minutes prior to measuring HONO uptake on the surface. Reactive uptake kinetics were determined in these experiments by increasing the exposed reactive surface area in 2 cm intervals, collecting data for 5 min at each interval. To perform nitrogen mass balance, and to derive a mechanism for the fate of lost HONO, NO and NO$_2$ were monitored by the CRDS and HNO$_3$ by the NI-PT-CIMS. These species are thought to be the most likely N-containing products to result from decomposition or branching reactions.
6.2.4 Acid Displacement of Nitrite Salts

Substrates that exhibited the ability to take up HONO irreversibly were subsequently exposed to the strong acids HCl and HNO₃ to determine if HONO could be displaced to the gas phase from the nitrite salt reaction products expected to exist at the surface. Reactive substrates of Na₂CO₃ and NaHCO₃ were mounted in the flow tube were allowed to react for up to 16 hours with HONO at 80 % RH to form an approximate 10 % mole fraction of nitrite to carbonate. Following this, HNO₃ or HCl was added to the flow tube under dry conditions as a proof of concept for acid displacement of HONO. Further substrate investigations of acid displacement were modified by direct addition of NaNO₂ to minimize experimental time and achieve displacement HONO concentrations above the NI-PT-CIMS detection limits (Sec. 6.3.7.). Assuming that the irreversible uptake observed in the previous experiments was due to reaction with carbonate salts to form nitrite salts, the addition of sodium nitrite as a proxy for the reaction product is reasonable. The reaction thermodynamics for these systems, whether calcium or sodium is the mineral cation, favors the formation of the nitrate and chloride salts and the displacement of HONO. Therefore, the sodium nitrite addition was utilized to probe the displacement reaction using both HCl and HNO₃ with the substrates listed in Table 6-2. The displacement efficiency of HONO from each substrate was determined by using the moveable injector to modify the substrate surface area available for reaction.

6.3 Results and Discussion

6.3.1 HONO Reactive Uptake on Dry Salts and Soil Extracts: Proof of Concept

Preliminary investigations of this reaction system were targeted to determine: i) whether the hypothesized reactive mechanism (R1 or R2) was active; and ii) if results between substrates were reproducible. Reversible adsorption and desorption were seen in all runs (4 s spikes, e.g. Figures 6-2 and 6-3) as HONO interacted with the uncoated flow tube surface. Fast adsorption was observed as the injector was retracted to expose the flow tube substrate to HONO and desorption when the injector was returned to its initial position. In the presence of a reactive substrate, such as NaHCO₃, HONO lost to the surface was not recovered after the injector was returned to its initial position, suggesting the loss was irreversible. Figures 6-2 and 6-3 show general results for the reactive soil proxy, NaHCO₃, which exhibited reproducible HONO uptake (mean ± 2 %) under dry conditions for multiple prepared salt coatings (Figure 6-2).
Figure 6-2. Triplicate analysis of HONO reactive uptake on three separate pyrex boats coated with NaHCO$_3$ at 0 % relative humidity and 830 mbar. Absolute HONO number densities have been normalized to the average of the initial conditions. Sharp decrease indicates retraction of the injector to expose the full boat surface to HONO and the sharp increase in each trace indicates returning the injector to its initial location via adsorption and desorption on the uncoated components of the flow tube.
Figure 6-3 shows that the HONO lost (~250 ppt s\(^{-1}\)) was undergoing a reaction at the surface and not significantly decomposing to NO and NO\(_2\) (both < 100 ppt s\(^{-1}\)). No significant NO\(_x\) emissions were seen throughout the reactive uptake studies. HNO\(_3\) (not shown) was also not observed. Most of the uncertainty in the reactive uptake observations was derived from the HONO source stability and instrumental noise when making the 1 Hz measurements necessary to resolve fast adsorption and desorption features in the flow tube.

**Figure 6-3.** Mixing ratios of NO, and NO\(_2\) measured during \(n = 3\) HONO reactive uptake trials on NaHCO\(_3\) at 0 % RH. Data gaps are due to collection of backgrounds between trials. Solid lines indicate data averaged to 10 s, with error bars of one standard deviation. Upper bar indicates when the injector was retracted to expose the surface to HONO and returned to its starting position.

Adsorption and desorption were found to be fast processes (~5 s, sharp peaks in Figure 6-2) and difficult to resolve from reactive uptake at longer timescales (e.g. 10 s, Figure 6-3). Data was collected at 1 Hz to avoid incorrect identification of the adsorption and desorption processes as a
strong initial reactive uptake to the surface. The HONO source stability was variable throughout these investigations and could change its output by ± 200 pptv on timescales of 30 minutes and ± 300 pptv on timescales of hours. Therefore, the uptake observations made are subject to these uncertainties and should be viewed as semi-quantitative first estimates of HONO reactive uptake kinetic parameters.

We tested several substrates under dry conditions to form a clear picture of the fate of HONO in contact with these surfaces. The statistical average of all results from replicate analyses of three separately investigated boats for each substrate, except the BAO soil extract, are displayed in Figure 6-4 with the HONO concentration normalized to the initial conditions. It should be noted that the approach in this experimental setup does not address changes in the measured uptake as a function of the mass of substrate coated on to the boat surface. Changes in the substrate mass on the boat may increase the observed uptake if the geometric surface area is an inappropriate description of the actual surface area involved in the observed uptake. Such an investigation was outside the scope of this study and may not be relevant if the substrate surface area does not need to consider accessing internal structure of the substrate. The goal of this work was to determine if the proposed mechanisms occur under atmospheric conditions and the kinetics discussed below should be viewed in the context of this work only considering geometric surface area. However, further refinements of the kinetics of this chemical system are encouraged in future work to improve the understanding of these systems in the real atmosphere.

The dry uptake of HONO on the BAO extract was determined by incremental increase in the residence time of HONO in the flow tube (i.e. incremental increase in exposed substrate surface area) in a single run. Pyrex and Na$_2$SO$_4$ both showed small losses compared to the initial conditions ($\gamma = 2 \pm 2 \times 10^{-6}$), which is due to trace quantities of reactive salts present on the flow tube surfaces after cleaning. These uptake values represent the lower limit of observable reactive uptake in this system (Table 6-3). Limited irreversible uptake of HONO was seen on NaNO$_2$ with $\gamma = 3.3 \pm 2 \times 10^{-6}$. It is unclear what caused this observation in our system, but it is possible that the sodium nitrite salt contains trace impurities that are reactive with HONO, albeit less so than all the other substrates tested. In comparison, the calculated reactive uptake of HONO on to the carbonate salts NaHCO$_3$ and Na$_2$CO$_3$ is larger by a factor of two to four ($\gamma = 7.8 \pm 1 \times 10^{-6}$ and $5.8 \pm 1 \times 10^{-6}$ respectively), while the soil extracts showed more variability. The Bakersfield
(BFL) soil extract showed some reactive uptake of HONO with $\gamma = 5 \pm 1.4 \times 10^{-6}$, while the Erie (BAO) soil extract showed the highest reactive uptake of all the substrates investigated under dry conditions at $\gamma = 1.3 \pm 0.2 \times 10^{-5}$.

The uncertainty in the HONO source output on the observed uptake rate of HONO is depicted in Figure 6-5 for the BAO soil sample as a function of HONO residence time in the flow tube. The overall increasing uptake of HONO on to the substrate as the reactive surface area increases (i.e. residence time) is further confirmation of the reactive uptake mechanism. Deviations in the uptake linearity can arise from a number of physical properties of the salt coating and HONO delivery system, such as coating thickness and surface area, number of crystal edges where HONO and water may strongly adsorb, and turbulent flow altering the transport of HONO to the surface. The scatter of markers and the best fit line for the BAO soil extract in Figure 6-5 also illustrates that a more representative uptake coefficient can be derived in this fashion for each substrate, rather than using only the measure of uptake on a fully exposed surface (e.g. 0 and 1.8 s residence time points only). Uptake on dry substrates here was only determined by the fully exposed surface approach and should be viewed as having greater uncertainty than the remaining results which all utilize the incremental increase in exposed surface area to determine the uptake coefficient. The corrected rate coefficient value determined using E4 was 1 - 10 % larger than measured values, resulting in additional error up to 10 % in the calculated uptake coefficient from diffusion limitation in these experiments. In comparison to the error found in the linear fits of the data (12 – 20 %), this uncertainty seems to be appropriately captured in the reported uptake coefficients. Clearly, if there was a diffusion limitation in this system, it would not be possible to identify changes in the HONO uptake value between different substrates or under changing conditions of relative humidity (Figure 4-25). This is not the case here (Table 6-3).
Figure 6-4. Reactive uptake of HONO observations at 0 % RH on all substrates investigated between the initial injector position and full exposure of the salt/soil coated boat in the flow tube. Shaded region for A - Pyrex (n=5), B - NaHCO₃ (n=9), C - Na₂SO₄ (n=6), D - Na₂CO₃ (n=9), E - NaNO₂ (n=9), and F - BFL (n=9) represent one standard deviation in the measurements. Calculated uptake coefficients for each substrate are given in Table 6-3.

Overall, these investigations found that HONO undergoes reactive uptake on to carbonate substrates and soil extracts. This is consistent with the expectations derived from the calculated free energy of reaction and previously observed reactive uptake of weak acids (Al-Hosney et al.,
2005; Preszler Prince et al., 2008) and strong acids (Sullivan et al., 2009; Sullivan et al., 2007b; Vlasenko et al., 2006) on to carbonate salts. While it would be ideal to have measured the reaction product CO$_2$ to strengthen these assertions, the measurement was not possible to make with our experimental setup. However, surface reactivity can be implied from the following: i) surface saturation is not seen over periods in excess of 24 hours of HONO exposure, ii) HONO signal was only found to return to its initial value after the total amount of HONO lost exceeded the reactive capacity of the coated substrate, iii) equilibrium between the surface or an aqueous film and the overlying gas phase would be established on timescales of the experiments shown in Figures 6-4, iv) uptake on to flow tube surfaces was seen to be fast and reversible (Figures 6-2 and 6-4), and v) if uptake was occurring in to available surface water, saturation would be seen within minutes and reversible emission would have been observed after returning the injector to its initial position.

The magnitude of the reactive uptake was similar for both carbonate salts investigated here, while the BFL soil extract was less reactive and the BAO soil extract was more reactive. The soil extracts are a mixture of salts, organics and insoluble particles and presumably contain some fraction of carbonate minerals in their matrix due to the presence of water soluble Ca$^{2+}$ and Mg$^{2+}$, which are commonly found as calcite (CaCO$_3$) and dolomite (CaMg(CO$_3$)$_2$) in real soils (Tan, 1993; Orlov, 1992; Conklin, 2005). In all cases, there was no observable production of nitrogen oxides (e.g. Figure 6-3), indicating that reactive HONO uptake on to these soils was occurring. The most likely mechanisms for the NaHCO$_3$ and Na$_2$CO$_3$ observations are proposed to be:

$$\text{HONO}_g + \text{NaHCO}_3(s) \rightarrow \text{NaNO}_2(s) + \text{H}_2\text{O}_g + \text{CO}_2(g) \quad (R6)$$

$$\text{HONO}_g + \text{Na}_2\text{CO}_3(s) \rightarrow \text{Na(NO}_2)_2(s) + \text{NaHCO}_3(s) \quad (R7)$$

In real soils, these reactions are expected to take place in the presence of water, which may be located either in the soil interstices from precipitation or at the soil-atmosphere interface as a function of atmospheric relative humidity. The influence of relative humidity on HONO uptake with reactive substrates was explored to improve our understanding of the atmospheric
interactions of HONO on ground and dust aerosol surfaces as suggested by field observations (Chapters 4 and 5).

![Graph](image)

**Figure 6-5.** Uptake of HONO on the BAO soil extract determined by change in signal as a function of residence time of HONO over the substrate (i.e. surface area). Note the potential variability in the calculated uptake from incremental loss of HONO as a function of residence time and the dominant error driven by variability in the HONO source output (black squares, ±1σ). The uptake coefficient was calculated using a linear least-squares regression fit ($R^2 = 0.7$) of the rates determined over each residence time (red line).

### 6.3.2 Influence of Relative Humidity on HONO Reactive Uptake

In general, the uptake of HONO was found to increase with relative humidity for the reactive substrates (Figure 6-6). As the relative humidity increased, equivalent surface areas were found to take up increasing amounts of HONO. In some cases, observable HONO uptake was not seen at low relative humidities and small exposure times (e.g. 0 - 2 s for 0 and 30 % RH, Figure 6-6), but was observable at higher surface areas exposed to HONO (e.g. > 2s, Figure 6-6). For equal areas at higher relative humidities uptake increased, indicating that the surface reactivity was enhanced in the presence of water. The best fit linear least-squares regression slope to these data
for all substrates were used to calculate the reactive uptake coefficient using (E5) and are shown in Figure 6-7 and summarized with the dry uptake results in Table 6-3.

**Figure 6-6.** Increasing reactive uptake of HONO on to Na$_2$CO$_3$ with increasing relative humidity. Solid lines represent linear least-squares regressions passing through the origin for clarity in the trend of the slopes.

Water is expected to enhance HONO uptake by increased adsorption, air-water partitioning (i.e. Henry’s Law coefficient) and reactive loss via the acid displacement reactions (Vlasenko et al., 2006; Liu et al., 2008). The solubility of HONO in solution is known to be pH dependent due to its weakly acidic nature, ranging from 40 to 1x10$^6$ M atm$^{-1}$ between pH 3 – 8 (Hirokawa et al., 2008). The carbonate salts, as reactive soil mineral proxies, are expected adsorb water to crystal edges and surfaces with increasing humidity, but not to deliquesce since the deliquescence relative humidities of the sodium carbonates are greater than 90 % RH (Meng et al., 1995). The HONO uptake of both salts was found to be affected by relative humidity. The uptake onto NaHCO$_3$ increased with increasing RH, reaching maximum uptake coefficients of 1.1 - 1.2 x 10$^{-5}$ at RH > 50 %. The uptake on Na$_2$CO$_3$ also increased with increasing RH, with significant enhancement at 80 and 95 % RH, reaching uptake coefficient values greater than 1.2 x 10$^{-5}$.

Insignificant quantities of reversible HONO release, in comparison to total HONO lost reactively, were observed on humidified surfaces with RH > 80 %, suggesting the presence of surface water films on the reactor walls and substrate were less important than the sink of the
reactive substrate. Uptake near the detection limit of this system was observed on the salt coatings of Na$_2$SO$_4$ over all relative humidities. The investigation of Na$_2$SO$_4$ provided a controlled surface solution near 6.5, if identical to bulk saturated solutions, as opposed to the acidic nature of a bare pyrex surface. Sodium sulphate is also the most hygroscopic salt we investigated, meaning that any surface water influence on HONO loss via partitioning should be particularly enhanced over this salt. Therefore, since the observed loss was near the detectable limits of the employed apparatus, partitioning into water films appears to be minimal in comparison to reactive loss. The calculated reactive uptake coefficients for Na$_2$SO$_4$, thus, denote the lower limit of detectable reactive uptake in this flow tube system to lie between 1.1 - 2.7 x 10$^{-6}$. All carbonate salts and soil extract uptake coefficients were calculated to be greater than that of Na$_2$SO$_4$ under all tested relative humidities, demonstrating that the observed sink of HONO is being influenced by reaction and not partitioning.

The soils investigated were found to exhibit an alkaline nature in the presence of water. The BAO soil had a pH of 7.67 and the BFL soil a pH of 7.51 in 1:1 mass ratios of soil and deionised water. The soils exhibited similar relative humidity dependences on the calculated uptake coefficients. In each there is a general trend of increasing uptake with increasing relative humidity. The BAO soil shows the highest uptake coefficients as a function of relative humidity, ranging from 1.3 - 1.6 x 10$^{-5}$. This value is consistent with the lower limit of the ground uptake coefficient range we derived from field observations at this site (Chapter 4). In contrast, BFL soil showed variability in reactivity between two separately prepared samples under dry conditions, that did not persist at RH ≥ 30 % where the uptake coefficients were within a factor of 2 of one-another, ranging from 0.5 – 1 x 10$^{-5}$. These results suggest that there are other, more reactive, soil components (e.g. CaCO$_3$, CaMg(CO$_3$)$_2$) that may increase the uptake of HONO to the surface at the BAO and BFL field sites. This experimental setup also did not explore surfaces with high porosities in contact with the gas phase, as would be the case for real soils, instead using coatings that were assumed to have a surface area equal to the geometric surface area they covered. Additionally, while high relative humidities were explored, the surface hydration generated in the flow tube is not expected to reflect the chemical and physical properties of soil pore water, which may enable further capacity and efficiency for HONO uptake.
These results demonstrate that reactive sink strength for HONO at the ground surface or on lofted dust aerosols increases with relative humidity and that the process is not reversible under atmospherically relevant conditions. Therefore, a reservoir of HONO can be generated at night by reactive uptake on to the ground surface. This reservoir may be accessible the following day through reaction of the nitrite salt products and stronger acids (i.e. HNO₃ and HCl) produced and deposited to the surface during the day, liberating HONO that can contribute to its daytime production.
Figure 6-7. Calculated reactive uptake coefficients for HONO on substrates mounted in the flow tube reactor at 298 K and 830 mbar as a function of relative humidity. Error bars are ±1σ of the linear regression fit (Figure 6-5).
Table 6-3. Summary of sustained reactive uptake coefficients for HONO on surfaces, salts and soil extracts under dry and variable relative humidities.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>0</th>
<th>30</th>
<th>50</th>
<th>80</th>
<th>90-95</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrex</td>
<td>$2.7 \times 10^{-6}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>$2.1 \times 10^{-6}$</td>
<td>$&lt; 1 \times 10^{-6}$</td>
<td>$&lt; 1 \times 10^{-6}$</td>
<td>$1.1 \times 10^{-6}$</td>
<td>$2 \times 10^{-6}$</td>
</tr>
<tr>
<td>NaNO$_2$</td>
<td>$3.3 \times 10^{-6}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>$7.6-8.1 \times 10^{-6}$</td>
<td>$1.0 \times 10^{-5}$</td>
<td>$1.1 \times 10^{-5}$</td>
<td>$1.1 \times 10^{-5}$</td>
<td>$1.1 \times 10^{-5}$</td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>$5.8 \times 10^{-6}$</td>
<td>$5.0 \times 10^{-6}$</td>
<td>$6.4 \times 10^{-6}$</td>
<td>$1.4 \times 10^{-5}$</td>
<td>$1.4 \times 10^{-5}$</td>
</tr>
<tr>
<td>BAO Soil</td>
<td>$1.3 \times 10^{-5}$</td>
<td>$1.4 \times 10^{-5}$</td>
<td>$1.5 \times 10^{-5}$</td>
<td>$1.6 \times 10^{-5}$</td>
<td>$1.4 \times 10^{-5}$</td>
</tr>
<tr>
<td>BFL Soil</td>
<td>$0.5 - 1.6 \times 10^{-5}$</td>
<td>$5.5 - 6.8 \times 10^{-6}$</td>
<td>$4.7 - 7.8 \times 10^{-6}$</td>
<td>$0.8 - 1.1 \times 10^{-5}$</td>
<td>$0.8 - 1.0 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

6.3.3 Reactive Uptake of HONO Followed by Acid Displacement with HCl and HNO$_3$

The final component of the HONO-surface chemical system explored in these experiments was determining if reactive substrates, on to which HONO was found to be taken up irreversibly, could be sources of HONO. In particular, a mechanism applicable towards the unknown daytime HONO source - via acid displacement of nitrite salts with nitric and hydrochloric acids - was conducted on the reactive salt substrates. Efficient acid reactions of HCl and HNO$_3$ on mineral dust and calcite aerosols have been recently shown in a number of field and laboratory studies (Sullivan et al., 2009; Sullivan et al., 2007b; Sullivan et al., 2007a; Vlasenko et al., 2006; Vlasenko et al., 2009; Ooki and Uematsu, 2005; Hatch and Grassian, 2008; Cwiertny et al., 2008). Furthermore, the photochemical production of HNO$_3$ and displacement of HCl from sea salt aerosols in coastal regions is a well-known phenomenon (Dasgupta et al., 2007; Keene et al., 1999) and would be expected to be active for all aerosol acids with pK$_a$ values between that of HCl and H$_2$CO$_3$.

Figure 6-8 shows the gas phase acid mixing ratios in an experiment in which NaHCO$_3$ was exposed to HONO at 80 % RH over 16 hours, followed by removal of the HONO source and addition of a source of HCl under dry conditions (Figure 6-8A). Figure 6-8B shows the second displacement reaction in more detail. The displacement mechanism was confirmed by
modulating the substrate exposure to HCl. In the absence of HCl exposure, an immediate
decrease in measured HONO mixing ratios from 0.8 ppbv to 0.15 ppbv was observed. The
continued emission of HONO from the surface when not exposed to HCl may be explained by
desorption of HCl from the uncoated flow tube surface and subsequent deposition to the coated
surface. Alternatively, the displacement and emission of HONO from the surface is subject to
some kinetic limitations, resulting in the persistent emission of HONO as equilibrium is
approached. In all cases of HCl displacement, no NO\textsubscript{x} emissions above the instrument detection
limits were observed, while a small amount of HNO\textsubscript{3} was observed as an impurity in the HCl
permeation source (Figures 6-8 and 6-9). Since the objective of these investigations was to
confirm the potential mechanism of HONO acid displacement, the explicit reason for the
continuing emission of HONO in the absence of acid exposure was not explored further.

This experiment was repeated with Na\textsubscript{2}CO\textsubscript{3} as the substrate over a similar time period and using
HCl as the displacement acid (Figure 6-9). The displacement of HONO from the reacted
substrate in this case was found to be 30 pptv, much lower than the observed 0.8 ppbv on the
reacted NaHCO\textsubscript{3}. The reacted ratios of NO\textsubscript{2}⁻:Na\textsuperscript{+} were similar in each case, at 4.5 \% for Na\textsubscript{2}CO\textsubscript{3}
and 2 \% for NaHCO\textsubscript{3}. Therefore, the displacement efficiency of nitrite from various salts may be
linked to the chemical structure of the salt on which the displacement is taking place. In the case
of NaHCO\textsubscript{3} reacting with HONO, the primary product is expected to be NaNO\textsubscript{2}, while the
reaction product of Na\textsubscript{2}CO\textsubscript{3} is likely a more complex mixture of products, such as
Na\textsubscript{2}(NO\textsubscript{2})(HCO\textsubscript{3}) and NaNO\textsubscript{2} (see R6-R8). In either case, it was found that HONO can be
displaced from the nitrite salt product of these reacted substrates.
Figure 6-8. Reactive uptake of HONO on to NaHCO₃ over 16 hours at 80 % RH (top), followed by acid displacement of HONO with HCl at 0 % RH (bottom). A - Three HONO (red, left axis) uptake trials preceded the long duration uptake (14:00 – 18:00). The HONO source was turned off at 10:05 and the relative humidity lowered to 0 % prior to addition of HCl (green, right axis; HNO₃ impurity, blue, left axis) at 10:30 and displacement of HONO from the entire surface. The surface exposure was turned off at 11:35 and resumed at 12:10. B – Magnified region of upper panel for the period when the HCl was deposited to the NaHCO₃ reacted with HONO.
To illustrate the HONO displacement mechanism for HCl and HNO$_3$, explicit control over the form and mass fraction of the reactive precursor was undertaken by adding NaNO$_2$ to the reactive salt coating such that the NO$_2^-$:Na$^+$ ratio was 0.4, instead of reacting the carbonate salt prior to the displacement. Therefore, the acid displacement reactions found here are consistent with those commonly used in HONO generation sources, (Vecera and Dasgupta, 1991; Taira and Kanda, 1990; Febo et al., 1995; Braman and de la Cantera, 1986; Roberts et al., 2010).
Figure 6-10. Displacement of HONO by HCl at 0 % RH from A) NaNO₂, b) NaNO₂ in NaHCO₃ (NO₂⁻:Na⁺ = 0.4) and C) NaNO₂ in Na₂CO₃ (NO₂⁻:Na⁺ = 0.4)

Direct confirmation of the ability of HNO₃ to displace HONO was undertaken after determining that NO, NO₂ and HNO₃ were not generated as significant products in the displacement reactions. Nitric acid is the dominant photochemical acid produced during the day in the real atmosphere and the dominant acid deposited to the surface to drive this HONO production
mechanism. Displacement of HONO from NaNO$_2$ by HNO$_3$ was observed on all substrates (Figure 6-11), with displacement rates similar to those observed for HCl.

For both HCl and HNO$_3$, the major losses of the acids were dominated by surface adsorption processes (data not shown), and so deposition of the acids to the substrates may not have been directly related to the fractional coating of the flow tube. The resulting HONO displacements observed for each acid were similar for each substrate, but a quantitative relationship could not be deduced. The displacement rate of HONO from NaNO$_2$ was smaller than that observed from the NaNO$_2$ + Na$_2$CO$_3$ coating, suggesting that uniform deposition of the strong acids to all surfaces was not occurring. It is unclear what is causing the difference between substrate HONO emissions and unfortunately precludes the ability to determine an acid displacement efficiency for these reactions. Future work aimed at resolving this should utilize a uniformly coated tube insert in place of pyrex boat inserts used here so that observed losses may be attributed directly to uptake on to the surface area of the exposed substrate matrix. Overall, it can be concluded that acid displacement reactions producing HONO from nitrite salts are likely to take place during the day under real atmospheric conditions from the dry deposition of strong acids to the ground surface where nitrite salts are likely to be found; in particular, derived from the reactive uptake of HONO on to mineral salts at night via the following reactions described for the reaction product NaNO$_2$ in these experiments:

$$\text{NaNO}_2(s) + \text{HCl(g)} \rightarrow \text{NaCl(s)} + \text{HONO(g)}$$ \hspace{1cm} (R9)

$$\text{NaNO}_2(s) + \text{HNO}_3(g) \rightarrow \text{NaNO}_3(s) + \text{HONO(g)}$$ \hspace{1cm} (R10)
Figure 6-11. Displacement of HONO by HNO₃ at 0 % RH from A) NaNO₂, B) NaNO₂ in NaHCO₃ (NO₂⁻:Na⁺ = 0.4) and C) NaNO₂ in Na₂CO₃ (NO₂⁻:Na⁺ = 0.4)
6.4 Conclusions and Atmospheric Implications

Two new mechanisms in the atmospheric chemistry of HONO have been determined. The first showed that reactive uptake of HONO on to carbonate salts can generate a nighttime sink for HONO on the ground surface by forming nitrite salts. This observation confirms the hypothesis from field observations made in Bakersfield, CA during CalNex suggesting HONO is taken up reactively on soil dust to form nitrite, with sodium carbonates in particular. This HONO reactivity is expected to also extend to other soil minerals containing carbonate, such as CaCO$_3$ and CaMg(CO$_3$)$_2$, but these compounds were not explored in this study. Furthermore, real soil extracts have also shown reactive uptake towards HONO. Therefore, the presence of carbonates in soils and dust particles is expected to act as a reactive sink for HONO in the real atmosphere.

The results from these flow tube experiments have also provided the first kinetic constraints on the reactive uptake coefficient of HONO at 298 K and 830 mbar. Values of the HONO reactive uptake coefficient were found to be substrate dependent and ranged from 5x10$^{-6}$ – 1.6x10$^{-5}$. The associated uncertainty in these measurements is 12 - 20 %. These values of the HONO reactive uptake coefficient are near the lower limit of values derived from 250 m atmospheric column observations made during NACHTT, suggesting that other processes may also be important to consider in the fate of surface deposited HONO at night. In particular, other reactive substrates and uptake of HONO in to dew water or soil pore water are poorly constrained. Increasing relative humidity above all reactive substrates demonstrated an enhanced uptake of HONO. Diffusion limitation, reversible partitioning of HONO and decomposition to NO or NO$_2$ were not found to be significant in any of these experiments.

The second mechanism showed that once nitrite salts were formed by reactive uptake of HONO, subsequent displacement by both HCl and HNO$_3$ were observed to readily occur. This HONO emission mechanism is likely contributing to the formation of daytime HONO in the real atmosphere and is not considered when attempting to account for sources and sinks during the day. If all HONO deposited to the surface at night formed nitrite salts and underwent displacement the following day, this mechanism may account for 30 – 100 % of the missing daytime HONO source, depending on location and atmospheric conditions. However, the fraction of nocturnally deposited HONO that forms nitrite salts and subsequent displacement...
efficiency is not yet clear. Further field observations of soil composition, water content and a comprehensive suite of gas phase measurements are necessary to better understand the potential importance these new mechanisms might play in the real atmosphere.
6.5 References


CHAPTER SEVEN

CONCLUSIONS AND FUTURE DIRECTIONS

7.1 Conclusions on the atmospheric chemistry of trace nitrogenous bases and acids

The work presented in this thesis has shown that sensitive and selective instrumentation for the detection of trace nitrogenous atmospheric compounds is essential to understanding their chemistry and potential importance in a larger, more general, context, specifically amines in new particle formation and HONO in tropospheric oxidation capacity.

7.1.1 Alkyl amines in the gas and particulate phases

Alkyl amines have been shown to be ubiquitous components of the gas and particle phases using online sampling in a variety of continental locations (urban, rural, forested) (VandenBoer et al., 2011; VandenBoer et al., 2012), similar to the limited number of measurements made in marine-influenced air masses (Makela et al., 2001; Muller et al., 2009; Facchini et al., 2008) and qualitative observations from a wide variety of environments (Murphy et al., 2007; Tan et al., 2002; Silva et al., 2008; Pratt et al., 2009; Denkenberger et al., 2007; Creamean et al., 2011; Angelino et al., 2001). Our MOUDI observations in one urban and two rural environments demonstrate consistent trends with respect to size-dependence: an absolute maximum of amine mass loading in 320 – 560 nm particles, and an increase in importance relative to ammonium for the smallest (56 – 180 nm) particles measured. The importance relative to ammonium in the coarse mode is less meaningful because ammonium was often below our detection limits, despite the presence of detectable levels of amines. Size-resolved compositional analysis showed that the aminium ions dimethylaminium, diethylaminium and trimethylaminium are particularly enhanced relative to ammonium, the dominant base by mass, in very small particles, which suggests that these compounds play a more significant role in the formation and growth of the smallest particles in the atmosphere. In PM$_{1.8}$ measurements, calculated by summing the six lowest MOUDI size bins, amines contributed tens of ng m$^{-3}$ and constituted between 0.3 and 10 % of the water soluble particulate mass loading. In particular, the size-resolved samples analysed in these studies indicate that use of bulk aerosol measurements may not be appropriate for
modelling the processes that govern the incorporation of amines and ammonia into atmospheric particles (Ge et al., 2011; VandenBoer et al., 2011).

Furthermore, the IC methods developed in this work have provided quantitative online observations, via the AIM-IC, of atmospheric amines partitioning between phases with detection limits for parts per trillion by volume (pptv) mixing ratios and nanograms per cubic mass loadings at hourly time resolution. To the best of our knowledge, the AIM-IC data represent the first simultaneous observations of gas and particle phase amine species with accompanying water-soluble ionic speciation in PM$_{2.5}$ at hourly time resolution. Through online sampling in an urban environment, we observed instances of amines increasing in the particle phase at times with elevated PM$_{2.5}$ nitrate. The mass loading of amines in PM$_{2.5}$ never exceeded 20 ng m$^{-3}$ during the online sampling period, a value too low to cause observable changes to the abundance of NH$_4^+$ or NO$_3^-$. Since aerosol formation and growth processes are not currently well understood (Zhang et al., 2012), the emerging role of amines from controlled lab studies suggests that our online gas-particle and size resolved particulate measurements will contribute significantly towards a more thorough understanding of atmospheric new particle formation processes (Kirkby et al., 2011) by providing contextual constraints when translating lab results to real atmospheric processes.

7.1.2 Nitrous acid interactions with the ground surface

The measurements made of nitrous acid during the two intensive field campaigns (Chapters 4 and 5) and in the flow tube lab study (Chapter 6) have likewise provided a new perspective on the interactions of this trace compound with ground surfaces and the larger scale implications this may have in the surface boundary layer. The observations from NACHTT showed that nitrous acid production in the nocturnal boundary layer of a wintertime atmosphere should not be assigned using the HONO/NO$_2$ ratio due to the increased magnitude of other NO$_2$ sinks. Integrated column rate of change measurements of both HONO and NO$_2$ over two hour timescales provided clear evidence that the ground surface dominates conversion of NO$_2$ to HONO at night and that the pseudo steady state observed in HONO is due to deposition back to the ground surface. The range of surface uptake coefficient parameters of $\gamma_{NO_2,\text{surf}} = 2 \times 10^{-6}$ to $1.6 \times 10^{-5}$ and $\gamma_{HONO,\text{surf}} = 2 \times 10^{-5}$ to $2 \times 10^{-4}$ are the first derived from field measurements and
they also indicated uptake variability may be driven by changes in relative humidity (i.e. water content at the surface).

Observations from the CalNex dataset suggested reactive uptake of HONO on mineral dust/soil components as a possible nocturnal sink at the surface from simultaneous measurements of the gas and particle phases made by the AIM-IC system. Similarly, the potential for nitrite salts to react with strong acids, displacing HONO during the day was also suggested by this dataset, because the highest daytime HONO concentrations were observed on the days when the strong acids HNO₃ and HCl were highest in concentration. Together, these field observations provide significant new insight on the HONO chemical system, in which a surface reservoir of HONO is generated at the ground surface at night by deposition/partitioning/reactive uptake, which can then release HONO the following day.

The particular case of reactive uptake and acid displacement was explored in our flow tube lab study, showing that HONO is taken up irreversibly on to sodium carbonate salts and real soil extracts, presumably forming nitrite salts like those observed during CalNex. The efficiency of reactive uptake ($\gamma_{\text{HONO, surf}} = 5 \times 10^{-6} – 1.6 \times 10^{-5}$) was also found to be enhanced with increasing relative humidity, consistent with the NACHTT nocturnal HONO surface uptake observations, although the magnitude of uptake coefficients were smaller in the lab observations. Therefore, we can conclude that such reactions are likely contributing to the surface loss of HONO at night, but that its significance is variable depending on the chemical composition of local surfaces.

Substrates that exhibited irreversible uptake of HONO could also release HONO through acid displacement reactions with HNO₃ and HCl, consistent with the observations of higher daytime HONO mixing ratios when the concentrations of these acids were elevated during CalNex. Together, these studies have produced a new picture of HONO surface interactions that have not been previously explored (Figure 7-1) and may fill the knowledge gaps in its chemistry by providing i) a more explicit sink of HONO at night that could act as a reservoir and ii) a new mechanism for daytime HONO formation that does not require NO₂.

Finally, a simple box model was used to explore the relative magnitudes of the nighttime HONO reservoir at the surface and the daytime unknown HONO sources at each field site using observational constraints to run the model. Daytime vertical concentration gradients observed
during NACHTT indicated the ground surface as the location of the unknown HONO source with a magnitude of 165 to 600 pptv h\(^{-1}\) required to explain observed mixing ratios based on known sources and sinks, similar to observations made at many other locations and environments (Zhou et al., 2011; Su et al., 2008; Sorgel et al., 2011; Kleffmann et al., 2005; Kleffmann, 2007; Elshorbany et al., 2009; Elshorbany et al., 2012a; Wong et al., 2012). Similarly, an unknown daytime HONO source was observed during CalNex which was calculated to have a maximum source strength of 1.27 ppb hr\(^{-1}\), significantly higher than observed during NACHTT.

**Figure 7-1.** Emerging role of ground surface chemistry in chemical fate of atmospheric HONO. Present at the surface are the aqueous nitrite ion (NO\(_2\)\(^-\)(aq)) and nitrite salts (XNO\(_2\)(s)), where X\(^+\) would be the salt cation.

For CalNex, the model calculations of the integrated HONO deposited to the surface were 30 % of the integrated missing daytime source, a significant contribution if all HONO deposited to the surface at night can be released the following day. The NACHTT dataset allowed a more intensive and relevant exploration of these surface processes through the use of the field-derived uptake coefficients at this site. In this case, the integrated HONO deposited to the ground was nearly equal or greater than (93 – 250 %) the calculated unknown daytime source, except when
using the absolute lower limits of the surface parameters (25%). Perhaps this difference is due to reduced contributions of photoenhanced conversion at the ground surface. The daytime source at NACHTT also suggested that the surface production and release of HONO may be more dynamic than previously proposed and that a combination of several significant mechanisms is the most probable resolution to understanding this source (e.g. photocatalytic conversion of NO$_2$ (Stemmler et al., 2006; Ndour et al., 2008), acid displacement of surface deposited HONO (this work), nitrate photolysis (Handley et al., 2007; Shuttlefield et al., 2008; Zhou et al., 2011; Zhou et al., 2003) and partitioning of nitrite from soil pore water (Wojtal et al., 2011; Su et al., 2011)). In any case, these results indicate that nocturnally deposited HONO may represent a significant fraction of the total unknown HONO source observed on the following day and that more research on the fate of HONO at the surface should be carried out. The relative importance of the acid displacement mechanism in governing the release of HONO from the surface reservoir is not yet clear and is likely occurring in parallel with other processes (vide supra).

However, the relative magnitude of the deposition process is expected to be variable based on: i) location since ground surfaces are highly variable in composition, which will change the uptake of HONO, and ii) time of year since temperature, relative humidity, other meteorological parameters and chemical composition of the atmosphere will all have seasonal changes. In conclusion, HONO is gaining appreciation as a dominant radical source during the winter when other photolytic OH sources are not active (Elshorbany et al., 2012b; Czader et al., 2012) and has been recognized as a significant source in the summer as well (Kleffmann et al., 2005; Elshorbany et al., 2012a; Young et al., 2012; Volkamer et al., 2010). Therefore, understanding HONO-surface interactions should be a major focus of future investigations in field, lab and modelling studies, as its impact on the oxidation capacity of the atmosphere may be more significant than previously considered, with far reaching impacts on air quality and atmospheric chemistry.
7.2 Future Directions

7.2.1 Alkyl amines in the gas and particulate phases

Instrumentation capable of making quantitative observations of alkyl amines in the atmosphere simultaneously in both the gas and particle phases should be common, but in fact, is quite rare. Few separation and detection methods provide selectivity towards this entire class of compounds like the AIM-IC system. Therefore, this technique should be used to collect more datasets in a variety of environments, particularly those near known sources where concentrations will be larger. This will provide more certainty in assessing the potential influence that amines may have on particle composition, in particular, whether they might displace observable amounts of ammonium under favourable atmospheric conditions as suggested by many lab studies (Lloyd et al., 2009; Bzdek et al., 2010; Bzdek et al., 2011; Berndt et al., 2010; Yu et al., 2012; Kirkby et al., 2011) and modelling results (Loukonen et al., 2010; Kurten et al., 2008). Such chemistry has been suggested to significantly change the physical properties of the aerosols, and therefore their overall atmospheric and climatic impact (Zhang et al., 2012; Wang et al., 2010; Qiu and Zhang, 2012; Qiu et al., 2011). Simultaneous measurements of ambient aerosol physical and optical properties along with amine composition would be valuable. Furthermore, too few studies have been performed to constrain emission inventories of these compounds (Schade and Crutzen, 1995; Kuhn et al., 2011; Traube et al., 2011), whether they are co-emitted with ammonia from sources or if their release to the atmosphere is governed by other physicochemical or biological processes is unclear (Pratt et al., 2009; Muller et al., 2009; Hanson et al., 2011). Overall, the alkyl amines are understudied in their influence on atmospheric chemical process given their potential for influencing atmospheric particle formation and physical properties.

7.2.2 Nitrous acid interactions with the ground surface

The research presented here demonstrates the potential importance of new mechanisms of HONO formation, which should be further explored to elucidate its importance to HONO atmospheric chemistry. In particular, studies should examine further reactive substrates, such as common calcium salts found in soils (e.g. CaCO$_3$ and CaMg(CO$_3$)$_2$), and determine yields for HONO displacement by strong acids. Partitioning of HONO to aqueous solutions on environmental surfaces should also be examined in more detail. The role of pH and solution
ionic strength on HONO uptake is uncertain and requires further study. These investigations will allow for expansion of field measurements to more explicitly address the potential for bidirectional flux of HONO from soil pore water nitrite and the production of nitrite salts that can undergo acid displacement at the surface, significantly improving the ability of models to capture this chemistry.

Observed daytime HONO production is most likely a combination of several mechanisms with i) correlation to the product of NO$_2$ and surface irradiance or OH, ii) partitioning of soil pore water nitrite to the atmosphere and iii) photochemical production of HNO$_3$ followed by HONO displacement. Future work should explore the relative contributions of each of these processes.

Furthermore, improved modeling of the HONO system from NACHTT would ideally be undertaken using a 1D model similar to that used by the research group of Jochen Stutz (Geyer and Stutz, 2004; Wong et al., 2011; Wong and Stutz, 2010; Wong et al., 2012). This would enable a much more thorough assessment of meteorological parameters and aid in accounting for the relative contributions between transport, diffusion and reversible/irreversible reaction of HONO at the ground surface.
7.3 References


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Appendix A

2. S.1. Conditions tested for resolution of cations by ion chromatography

Table 2-S1. Trials and specific chromatographic conditions employed in method optimization for the CS17 cation exchange column based on the work of Rey (2003) shown in Trial 9 of this work using a stepped gradient elution method. Suppressor conductivity was modified according the maximum eluent concentration for each trial. Column and detector temperatures were maintained at 30 °C for all trials.

<table>
<thead>
<tr>
<th>Trial #</th>
<th>Flow (mL min⁻¹)</th>
<th>Gradient Transition Type</th>
<th>Program - MSA Eluent</th>
<th>Retention Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Li⁺ Na⁺ NH₄⁺ K⁺ MMA MEA DMA TMA DEA TEA Mg²⁺ Ca²⁺</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>Linear</td>
<td>0 - 11.6 min: 2 - 8 mM 11.6 - 16 min: 8 - 10 mM 16 - 22 min: 10 - 2 mM 22 - 27 min: 2 mM</td>
<td>6.9 7.4 7.8 8.5 8 8.3 9.1 10.2 10.2 13.7 16 16.7</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>Linear</td>
<td>0 - 16 min: 0.5 - 10 mM 16 - 22 min: 10 - 0.5 mM 22 - 27 min: 0.5 mM</td>
<td>8.6 9.2 9.6 10.3 9.6 10.1 10.8 12 12 15.3 17.6 18.2</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>Linear</td>
<td>0 - 15 min: 0.25 - 5 mM 15 - 18 min: 5 - 10 mM 18 - 22 min: 10 - 0.25 mM 22 - 27 min: 0.25 mM</td>
<td>11 11.9 12.5 13.4 12.5 13.1 14.1 15.6 15.6 20 23.7 &gt;25</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>Isocratic</td>
<td>6 mM</td>
<td>4.8 5.2 5.5 6.1 5.5 5.9 6.6 7.5 7.9 9.6 14.8 16.3</td>
</tr>
<tr>
<td>5</td>
<td>0.85</td>
<td>Linear</td>
<td>0 - 15 min: 0.25 - 5 mM 15 - 18 min: 5 - 10 mM 18 - 22 min: 10-0.25 mM 22 - 27 min: 0.25 mM</td>
<td>12.1 13 13.7 14.7 13.7 14.4 15.4 17.1 17.1 21.2 &gt;40 &gt;40</td>
</tr>
<tr>
<td>Line</td>
<td>Step</td>
<td>Value</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>------</td>
<td>-------</td>
<td>-------------</td>
<td></td>
</tr>
</tbody>
</table>
| 6    | 0.85 | Linear | 0 - 15 min: 0.25 - 2 mM  
15 - 18 min: 2 - 10 mM  
18 - 28 min: 10 mM  
28 - 30 min: 10-0.25 mM  
30 - 35 min: 0.25 mM | 17.2 18.6 19.2 20 19.3 19.7 20.3 20.3 20.3 24 25.2 25.8 |
| 7    | 0.85 | Linear | 0 - 15 min: 0.25 - 2 mM  
15 - 20 min: 2 mM  
20 - 30 min: 2 - 8 mM  
30 - 35 min: 8 mM  
35 - 38 min: 8 - 0.25 mM  
38 - 45 min: 0.25 mM | 17.3 18.8 19.9 21.8 19.9 21.3 23.3 25.9 25.9 31.2 36.5 37.6 |
| 8    | 0.6  | Linear | n/a  
23 24.7 n/a 26.2 26.2 27.9 30.2 30.2 35.8 >60 >60 |
| 9    | 0.85 | Step-wise | n/a  
12 13 15 14.4 14.2 15.2 16 16 18.5 19.1 19.7 |
Table 2-S2. Trials and specific chromatographic conditions employed in method optimization for the CS12A cation exchange column based on the work of Rey and Pohl (1996). Suppressor conductivity was modified according to the maximum eluent concentration for each trial. Column and detector temperatures were maintained at 30 °C for all trials.

<table>
<thead>
<tr>
<th>Trial #</th>
<th>Flow (mL min⁻¹)</th>
<th>Gradient Transition Type</th>
<th>Program - MSA Eluent</th>
<th>Retention Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Program - MSA Eluent</td>
<td>Li⁺</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>Linear</td>
<td>0 - 20 min: 20 - 40 mM</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20 - 25 min: 40 - 20 mM</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>25 - 30 min: 20 mM</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>Linear</td>
<td>0 - 20 min: 10 - 40 mM</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20 - 25 min: 40 - 10 mM</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>25 - 30 min: 10 mM</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>Linear</td>
<td>0 - 12.2 min: 5 - 40 mM</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12.2 - 20 min: 40 - 65 mM</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20 - 25 min: 65 - 5 mM</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>25 - 30 min: 5 mM</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>Linear</td>
<td>0 - 12.1 min: 1 - 25 mM</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12.1 - 20 min: 25 - 65 mM</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20 - 25 min: 65 - 1 mM</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>25 - 30 min: 1 mM</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.1</td>
<td>Linear-Exponential</td>
<td>0 - 12.1 min: 1 - 15 mM</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12.1 - 20 min: 15 - 65 mM</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20 - 25 min: 65 - 1 mM</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>25 - 30 min: 1 mM</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1.2</td>
<td>Linear-Exponential</td>
<td>0 - 12.1 min: 1 - 10 mM</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12.1 - 20 min: 10 - 80 mM</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20 - 25 min: 80 - 1 mM</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>25 - 30 min: 1 mM</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>Linear-Exponential</td>
<td>0 - 12.1 min: 3 - 10 mM</td>
<td>12.1 - 22 min: 10 - 80 mM</td>
</tr>
<tr>
<td>---</td>
<td>-----</td>
<td>------------------</td>
<td>---------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>7</td>
<td>1.2</td>
<td>Linear-Exponential</td>
<td>0 - 12.1 min: 5 - 10 mM</td>
<td>12.1 - 22 min: 10 - 80 mM</td>
</tr>
</tbody>
</table>
2.S.2 Derivation of a non-linear fit in weak acid and base calibrations

In the case of weakly basic or acidic species, we have found significant deviations from linearity across relevant concentration ranges. In these cases, the non-linear response is driven by the relative increase in the charged species of the weak acid-base conjugate pair (Figure 2-S1) as a function of the total amount of the weak species preconcentrated present in a fixed volume within the detector. Similar detection strategies use second order polynomial fits to NH$_4^+$ standard conductivities when developing a calibration curve (Rahmat Ullah et al., 2006). However, the polynomial fails to describe the ionized fraction of analyte at higher mass loadings caused by a smaller fraction of the weak acid or weak base dissociating in the suppressed eluent outflow (i.e. NH$_4^+/\text{NH}_3$ from the $\text{NH}_3(aq) \rightleftharpoons \text{NH}_4^+(aq)$ equilibrium). That is, the second order polynomial does not allow minor extrapolations above the calibration range unless its vertex is located at the origin. Furthermore, the polynomial fit typically returns y-intercept values that are not representative of the true offsets for NH$_4^+$, resulting in erroneously calculated mass loadings near the detection limits. The dissociation of NH$_3$ (R1) is used as an example in the following derivation, but parallel approaches are valid for any weak acid or base.

$$\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)$$

(R1)

At equilibrium, the amount of the charged species in equilibrium is given as a function of its dissociation constant ($K_a$, for acids; $K_b$, for bases) in the, ideally, pure water exiting the conductivity suppressor, containing only the separated analyte.

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

But, $[\text{NH}_4^+] \approx [\text{OH}^-]$ such that:

$$K_b = \frac{[\text{NH}_4^+]^2}{[\text{NH}_3]}$$
If the sum of the weak base, NH$_3$, and its conjugate acid, NH$_4^+$, is defined as TN, then a rearrangement of the above equation yields:


Therefore, the $[NH_4^+]$ is the solution to the quadratic equation giving positive values only (i.e. set $\pm$ as $+$):

$$[NH_4^+] = \left(-\frac{K_b}{2}\right) + \sqrt{\frac{K_b^2}{4} + K_b[TN]}$$

The conductivity detector response is directly proportional to $[NH_4^+]$ in solution, such that the response is a scalar multiple ($v$) of this function (Figure 2-S1). The variable $K_b$ is allowed to reflect this scaling by reassigning the terms with variables A and B, where

$$A = \frac{K_b}{2}$$

$$B = K_b$$

And

$$v[NH_4^+] = v\left[-A + \sqrt{A^2 + B[TN]}\right]$$

The application of the scalar detector response throughout the equation is not the same for each term. To represent this, the scaled variables A and B are denoted $A'$ and $B'$. The fit to describe a general calibration of a weak acid or base is therefore weighted by the scalar. To avoid issues with over-parametrization, we have found that fitting the curve through the origin performs well for calibration purposes, without the loss of precision. The functional form for the calibration curve is thus:

Equation 1

$$y = (-A') + \sqrt{A'^2 + B'x}$$
Where \( y \) is the conductivity detector response, \( x \) is the total concentration of weak acid or base and its conjugate in the detector, and \( A' \) and \( B' \) are the fitting coefficients. Therefore, a fit function for Equation 1 was developed using the data analysis and coding software Igor Pro (Version 6.22A, Wavemetrics Inc., Lake Oswego, OR). The robustness of the fit was evaluated by the chi-squared value. Typical chi-squared values for the fit are on the order of 0.01, indicating that it is indeed a robust representation of the data. This fit also allows a direct determination of the detector sensitivity to any weak acid or base.

Figure 2-S1. A - Theoretical non-linearity expected in weak base dissociation of \( \text{NH}_4^+ \) (squares, red line) and DMAH\(^+\) (triangles, black line) in pure water detected by conductivity at calibration concentrations employed in this study. Fits were derived with dissociation function for \( \text{NH}_4^+ \) \( (K_b = 1.59 \times 10^{-5}, \text{red line}) \), while limited deviation from linearity occurs for DMAH\(^+\) \( (K_b = 5.89 \times 10^{-4}, \text{black line}) \) in this concentration range. B - Derived fit function applied to real \( \text{NH}_4^+ \) calibration data \( (n = 2) \).
2.5.3. Observed quantities and potential atmospheric implications

An expansion on the atmospheric significance of the measurements reported in the published manuscript is presented here to provide context on the importance of the ability to selectively and accurately quantify the methyl and ethyl amine families:

The deployment of the AIM-IC in Egbert, ON utilized the CS17 methodology for real-time monitoring of NH$_3$/NH$_4^+$ and NR$_3$/R$_3$H$^+$. The observations made during this campaign showed little variation in the number and concentrations of amines detected. DMA was detected consistently with gaseous mixing ratios (±1σ) between 1 - 10 pptv (mean = 6.5±2.1 pptv) and particulate mass loadings (mean = 0.1±0.2 ng m$^{-3}$) at or below the 0.5 ng m$^{-3}$ campaign detection limits. TMA+DEA were near the 1 pptv gaseous detection limit and frequently below the 1.2 ng m$^{-3}$ (mean = 1±0.6 ng m$^{-3}$) particulate detection limit. No clear diurnal or temporal trends were observed in either species, consistent with many previous observations (Chang et al., 2003; Huang et al., 2009; VandenBoer et al., 2011), but not all (Sellegri et al., 2005; Hanson et al., 2011). Longer term monitoring studies suggest that the greatest NR$_3$/R$_3$NH$^+$ variability is seen on a seasonal timescale (Pratt et al., 2009; Seo et al., 2011; Muller et al., 2009). Clearly, further measurements are required to better understand the spatial and temporal variations observed for NR$_3$ species. The TMA+DEA measurement error shows that the conservative lower limit approach places the data very close to the detection limits. Based on current emission inventories it would be expected that the signal comes from TMA since the Egbert region has a high density of animal husbandry facilities (Kuhn et al., 2011; Mosier et al., 1973; Schade and Crutzen, 1995; Traube et al., 2011). However, DEA cannot be entirely discounted since significant concentrations (up to 230 µg m$^{-3}$) have been sporadically detected from similar sources (Rabaud et al., 2003). The observations of NH$_3$ (Figure 2-3) show mixing ratios ranging from a background of about 0.5 ppb up to 4 ppb (mean = 1.21±0.72 ppbv), with several large plumes influencing the ground site during the campaign. These are also coincident with increases in the observed mass loadings of NH$_4^+$, which ranged from the detection limit (0.017 µg m$^{-3}$) to 3 µg m$^{-3}$. The temperatures during the observation period (Range: -1 – 18 °C) are expected to reduce the total emission rates of NH$_3$ and NR$_3$ if they are being emitted via volatilization. However, a temporal correlation between NH$_3$ and NR$_3$ would be expected if they were co-emitted from the same source (Hanson et al., 2011), but this was not observed by linear regression ($R^2 = 0.0003$).
Thus, the observed DMA and TMA+DEA may be emitted separately from NH$_3$ in this region and partially explain the low variability in mixing ratios for the NR$_3$. Recent work suggests that NR$_3$/NH$_3$ emission ratios from agricultural operations are variable between livestock species (2 - 7 %), waste (< 0.01 %), and feed stocks (0.2 – 0.4 %) (Kuhn et al., 2011). Therefore, a correlation between NH$_3$ and NR$_3$ as measured in animal housing (0.3 – 1 %) (Mosier et al., 1973;Schade and Crutzen, 1995) should not necessarily be expected to persist in the ambient atmosphere. The AIM-IC observations of NH$_3$/NR$_3$ range from 100 – 400, which is consistent with the range reported in a recent detailed analysis of these emission ratios from livestock operations (Li et al., 2009;Traube et al., 2011), although a definitive source cannot be identified. Since the campaign was carried out in the autumn, the rate of degradation of the amines with atmospheric oxidants is expected to be slower than during the summer and allows transport of more NR$_3$ farther from the emission source (Atkinson et al., 1997;Atkinson et al., 1977a, b;Finlayson-Pitts and Pitts, 2000). The detection limits shown in Figures 2-3 and 2-4 were much lower for the CS17 during this campaign due to very clean backgrounds in the AIM-IC system compared to the values listed from multiple assessments of offline injections and online zero air sampling listed in Table 2-2 (see Section 2.2.4.3 for details).

The distribution of amines in the size-segregated MOUDI aerosol sample showed EA was detected in significant diameter-weighted mass in the 0.056 – 0.1 and 0.32 – 0.56 µm size bins at 0.032 and 0.082 ng m$^{-3}$, respectively. DMA was detected on all but 2 stages and showed a bimodal distribution between the accumulation and coarse mode, with nearly equal mass loadings in each, consistent with previous size-resolved observations in marine and continental environments (Facchini et al., 2008;Makela et al., 2001;Muller et al., 2009;VandenBoer et al., 2011). TMA+DEA was detected in every size fraction, averaging around 3.5 ng m$^{-3}$ between 0.054 – 2.5 µm and showing more variability in the coarse mode. The integrated mass of all amines up to 2.5 µm was 2.38 ng m$^{-3}$. If this was present evenly over the entire 23 hr sampling period, the particulate loadings would be near or below the detection limits of the AIM-IC (2.5 - 3.5 ng m$^{-3}$), which samples only PM$_{2.5}$, and is consistent with the mass loadings below or near the detection limit at the end of the online observation period (Figure 2-4). Results of modeling and laboratory studies, which use NH$_3$/NR$_3$ from 100 – 400, indicate that the competition to neutralize acidic aerosol strongly favours NH$_4^+$ over R$_3$NH$^+$ (Murphy et al., 2007;Barsanti et al., 2009;Bzdek et al., 2011). The detection of DMA and TMA+DEA in both online and MOUDI
samples suggests that the periodic observations of these compounds in the ambient particulate matter is real, although the mass loadings cannot be directly compared since the observation periods do not overlap. The particle/gas ratio (±1σ) of TMA+DEA was 0.54±0.39, on average, compared to 0.01±0.04 for DMA. TMA+DEA shows both higher mass loadings in the MOUDI samples and higher particle/gas ratios in the AIM-IC data, compared to DMA. This is consistent with other observations made with this method (VandenBoer et al., 2011) and suggests either a greater preference for the particle phase for TMA+DEA (Ge et al., 2011) or possibly a rapid condensed phase loss mechanism for DMA (Zahardis et al., 2008). Preferential partitioning of amines and displacement of NH$_4^+$ has been previously observed in cluster uptake studies (Bzdek et al., 2010; Lloyd et al., 2009), but the thermodynamics of real systems are still not well constrained (Ge et al., 2011). The source(s) of the coarse mode amines are still not clear. These may be directly emitted from biogenic sources (e.g. pollen, plant debris, etc.) or accumulated by uptake from the gas phase.

2.4 References


Atkinson, R., Perry, R. A., and Pitts, J. N., Jr.: Rate constants for the reactions of the OH radical with (CH$_3$)$_2$NH, (CH$_3$)$_3$N, and C$_2$H$_5$NH$_2$ over the temperature range 298-426K, J Chem Phys, 68, 1850-1853, 1977b.


VandenBoer, T. C., Petroff, A., Markovic, M. Z., and Murphy, J. G.: Size distribution of alkyl amines in continental particulate matter and their online detection in the gas and particle phase, Atmos Chem Phys, 11, 4319-4332, 10.5194/acp-11-4319-2011, 2011.

Figure 4-S1a. Vertical profiles of HONO (solid lines, solid circles), NO₂ (solid red line, stars) and RH (solid blue line, solid triangles) on all nights when identifiable nocturnal
boundary layers were observed over at least 4 consecutive hours during the night. Vertical profiles shown are 2 hr averages of 4 – 6 continuous vertical profile measurements (18 – 20 hr, green; 20 – 22 hr, gold; 22 – 24 hr, purple; 00 – 02 hr, red; 02 – 04 hr, black; 04 – 06 hr, blue). Error bars indicate 1σ in the HONO measurements. Boundary layer heights are represented by shaded yellow regions.
Figure 4-S1b. Vertical profiles of HONO (solid lines, solid circles), NO$_2$ (solid red line, stars) and RH (solid blue line, solid triangles) on all nights when identifiable nocturnal boundary layers were observed over at least 4 consecutive hours during the night. Vertical profiles shown are 2 hr averages of 4 – 6 continuous vertical profile measurements (18 – 20 hr, green; 20 – 22 hr, gold; 22 – 24 hr, purple; 00 – 02 hr, red; 02 – 04 hr, black; 04 – 06 hr, blue). Error bars indicate 1σ in the HONO measurements. Boundary layer heights are represented by shaded yellow regions.
Appendix C

The Bakersfield dataset also shows that accumulation of nitrite is enhanced more by the availability of the mineral cations, as opposed to correlation with conditions of high relative humidity ($R^2 = 0.01$) (Figure S5-1). Previous studies have shown enhanced uptake of acids as relative humidity increases (Al-Hosney et al., 2005; Vlasenko et al., 2006; Preszler Prince et al., 2008). Unfortunately, statistical limitations of concurrently measured NO$_2^-$, HONO, and RH in this dataset ($n = 239$) prevented the elucidation of any further enhanced uptake of HONO under conditions of high humidity and mineral cation loading.

**Figure S5-1.** The ratio of nitrite to HONO between 19 – 07 h is enhanced as relative humidity and the total amount of mineral cations present in the particulate phase increase. The mineral cations Ca$^{2+}$, Na$^+$ and K$^+$, measured by the AIM-IC, are derived from water soluble salts, such as carbonates, which are a reactive sink for HONO at night.