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Atmospheric Ammonia Measurements and Implications for Particulate Matter Formation in Urban and Suburban Areas of Texas

by

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ABSTRACT

Atmospheric Ammonia Measurements and Implications for Particulate Matter Formation in Urban and Suburban Areas of Texas

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In order to improve the current understanding of the dynamics of ammonia (NH₃) in the Greater Houston and Dallas-Fort Worth (DFW) areas and to examine the effects of NH₃ on local and regional air quality with respect to particulate matter formation, intensive field investigations were made. A 10.4-µm external cavity quantum cascade laser based-sensor employing conventional photo-acoustic spectroscopy was used to conduct real-time and continuous measurements of atmospheric NH₃ in this work.

Results from the Houston campaign indicate that the mixing ratio of NH₃ ranged from 0.1 to 8.7 ppb with a mean of 2.4±1.2 (1σ) ppb in winter and ranged from 0.2 to 27.1 ppb with a mean of 3.1±2.9 ppb in summer. The larger levels in summer probably are due to higher ambient temperature. A notable morning increase and a mid-day decrease were observed in the diurnal profile of NH₃ mixing ratios. Motor vehicles were found to be major contributors to the elevated levels during morning rush hours in winter. However, changes in vehicular catalytic converter performance and other local or regional emission sources from different wind directions governed the behavior of NH₃ during morning rush hours in summer. There was a large amount of variability, particularly in summer, with several episodes of elevated NH₃ mixing ratios that could be linked to industrial facilities. A considerable discrepancy in NH₃ mixing ratios existed between weekdays and weekends. During the simultaneous high-time-
resolution measurements of gaseous and aerosol species in summer, elevated NH$_3$ levels occurred around mid-day when NH$_4^+$ (0.5 ± 1.0 µg m$^{-3}$) and SO$_4^{2-}$ (4.5 ± 4.3 µg m$^{-3}$) also increased considerably, indicating that NH$_3$ likely influenced aerosol particle mass. NH$_4^+$ mainly existed in the form of (NH$_4$)$_2$SO$_4$ and NH$_4$HSO$_4$; by contrast, the formation of NH$_4$NO$_3$ and NH$_4$Cl was suppressed. Power plant plumes were found to be potential contributors to the enhancements in NH$_3$ at the urban sampling site under favorable meteorological conditions. Increased particle number concentrations were predicted by the SAM-TOMAS model downwind of a large coal-fired power plant when NH$_3$ emissions (based on these measurements) were included, highlighting the potential importance of NH$_3$ with respect to particle number concentration. Measurements also show the role of NH$_3$ in new particle formation in Houston under low-sulfur conditions.

Results from the DFW campaign indicate that the mixing ratio of NH$_3$ ranged from 0.1 to 10.1 ppb, with a mean of 2.7 ± 1.7 ppb. The diurnal profile of NH$_3$ exhibited a daytime increase, likely due to increasing temperatures affecting temperature-dependent sources in the study region. Automobiles might be potential sources of NH$_3$ on Sundays based on the Pearson’s correlation coefficient between NH$_3$ and carbon monoxide, but the relationship did not exist on weekdays and Saturdays, probably due to decreased traffic volume and different traffic composition. According to the results from the EPA PMF 3.0 model, biogenic (primarily vegetation and soil) emissions were major contributors to gas-phase NH$_3$ levels measured at the suburban site during the campaign. In addition, agriculture (especially livestock-related activities) also was expected to be a potentially significant source of NH$_3$ based on the nature of the region. Inorganic aerosol components of submicron particles (PM$_1$) (4.41 ± 2.13 µg m$^{-3}$) were dominated by SO$_4^{2-}$ (1.25 ± 0.66 µg m$^{-3}$), followed by NH$_4^+$ (0.44 ± 0.24 µg m$^{-3}$) and NO$_3^-$.
(0.12 ± 0.11 µg m⁻³). Pearson’s correlation coefficients between NH₄⁺, SO₄²⁻, and NO₃⁻ imply that particulate NH₄⁺ mainly existed as (NH₄)₂SO₄ and that NH₄NO₃ was not formed during most of the study period, likely due to high temperatures (30.15 ± 4.12 °C) over the entire campaign.

Ambient aerosols tended to be nearly neutral. Theoretical calculations of thermodynamic equilibrium were performed to consider the formation of NH₄NO₃ and NH₄Cl. When relative humidity (RH) was lower than deliquescence relative humidity (DRH), the partial pressure products of P_{NH₃}P_{HNO₃} and P_{NH₃}P_{HCl} were smaller than the associated equilibrium constants, indicating the lack of NH₄NO₃ and NH₄Cl formation. When RH was above DRH, higher levels of NO₃⁻ often were observed. A strong relationship between NO₃⁻ and SO₄²⁻ at higher RH suggests that NH₄NO₃ might be formed on the moist surface of pre-existing sulfate aerosols. In the particle mixture, (NH₄)₂SO₄ reduces the equilibrium constant, making the aqueous system a more favorable medium for NH₄NO₃ formation. In addition, measured particle number size distributions showed that an aerosol nucleation and growth event was coincident with humid periods characterized by substantially increased concentrations of particulate NH₄⁺, NO₃⁻, and SO₄²⁻. Excess NH₄⁺ also was found to be correlated closely with NO₃⁻ during this episode when elevated PM₁ levels imply aqueous NH₄NO₃ formation.
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During my PhD journey at Rice University, I received huge help from many people. First and foremost, I would like to acknowledge the great contribution from my advisor, Professor Robert J. Griffin, who continuously provides me with invaluable instruction and essential guidance. His strong support and encouragement are indispensable in shaping and improving this study. I also want to express my gratitude to the committee members, Professor Daniel S. Cohan and Professor Frank K. Tittel. This thesis would not have been possible without their precious and constructive comments.

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<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMoN</td>
<td>Ammonia Monitoring Network</td>
</tr>
<tr>
<td>AM-PAS</td>
<td>amplitude modulated photo-acoustic spectroscopy</td>
</tr>
<tr>
<td>CAFOs</td>
<td>concentrated animal feeding operations</td>
</tr>
<tr>
<td>CAMS</td>
<td>continuous ambient monitoring station</td>
</tr>
<tr>
<td>DFW</td>
<td>Dallas-Fort Worth</td>
</tr>
<tr>
<td>DRH</td>
<td>deliquescence relative humidity</td>
</tr>
<tr>
<td>E-AIM</td>
<td>Extended Aerosol Inorganics Model</td>
</tr>
<tr>
<td>EC-QCL</td>
<td>external cavity quantum cascade laser</td>
</tr>
<tr>
<td>HR-ToF-AMS</td>
<td>High-Resolution Time-of-Flight Aerosol Mass Spectrometer</td>
</tr>
<tr>
<td>HSC</td>
<td>Houston Ship Channel</td>
</tr>
<tr>
<td>HYSPLIT</td>
<td>Hybrid Single-Particle Lagrangian Integrated Trajectory</td>
</tr>
<tr>
<td>IC</td>
<td>ion chromatography</td>
</tr>
<tr>
<td>MC/IC</td>
<td>mist chamber/ion chromatography</td>
</tr>
<tr>
<td>NAAQS</td>
<td>National Ambient Air Quality Standards</td>
</tr>
<tr>
<td>NADP</td>
<td>National Atmospheric Deposition Program</td>
</tr>
<tr>
<td>NEI</td>
<td>National Emissions Inventory</td>
</tr>
<tr>
<td>OH</td>
<td>hydroxyl radical</td>
</tr>
<tr>
<td>PAS</td>
<td>photo-acoustic spectroscopy</td>
</tr>
<tr>
<td>PBL</td>
<td>planetary boundary layer</td>
</tr>
<tr>
<td>PILS</td>
<td>particle-into-liquid-sampler</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>--------------</td>
<td>-----------</td>
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<tr>
<td>PM</td>
<td>particulate matter</td>
</tr>
<tr>
<td>PMF</td>
<td>Positive Matrix Factorization</td>
</tr>
<tr>
<td>ppb</td>
<td>parts per billion</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>ppt</td>
<td>parts per trillion</td>
</tr>
<tr>
<td>SAM</td>
<td>System for Atmospheric Modeling</td>
</tr>
<tr>
<td>SCR</td>
<td>selective catalytic reduction</td>
</tr>
<tr>
<td>SEMS</td>
<td>Scanning Electrical Mobility Spectrometer</td>
</tr>
<tr>
<td>TCEQ</td>
<td>Texas Commission on Environmental Quality</td>
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<td>Texas Air Quality Study</td>
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<td>TwO-Moment Aerosol Sectional</td>
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<td>Toxics Release Inventory</td>
</tr>
<tr>
<td>UH</td>
<td>University of Houston</td>
</tr>
<tr>
<td>USDA</td>
<td>U.S. Department of Agriculture</td>
</tr>
<tr>
<td>U.S. EPA</td>
<td>United States Environmental Protection Agency</td>
</tr>
<tr>
<td>VOC</td>
<td>volatile organic compound</td>
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Chapter 1

Introduction

As the predominant alkaline gas, ammonia (NH$_3$) plays an important role in atmospheric chemistry. It has many anthropogenic (e.g., agricultural crops, mineral fertilizers, and biomass burning) and natural (e.g., animals, oceans, and vegetation) sources in the environment. Livestock remains the largest category in its emission inventory [Clarisse et al., 2009], while in certain areas, industrial and motor vehicle activities can contribute to significant increases in local and/or regional NH$_3$ levels [Kean et al., 2009; Hsieh and Chen, 2010]. Gaseous NH$_3$ is normally present in the atmosphere at trace concentration levels, ranging from parts per trillion (ppt) to parts per billion (ppb). Specifically, ambient mixing ratios of NH$_3$ usually vary between 0.1 and 10 ppb, depending on the proximity to sources [Seinfeld and Pandis, 2006].
1.1. Impact of NH$_3$ on PM formation and environmental implications

From a perspective of environmental concern, NH$_3$ is a precursor of particulate matter (PM), also known as atmospheric aerosol, because it can lead to the production of ammonium salts (e.g., (NH$_4$)$_2$SO$_4$, NH$_4$HSO$_4$, NH$_4$NO$_3$, and NH$_4$Cl) through chemical reactions with sulfuric acid (H$_2$SO$_4$) and nitric acid (HNO$_3$) formed by oxidation of sulfur dioxide (SO$_2$) and nitrogen oxides (NO$_x$), respectively, and with hydrochloric acid (HCl) [Sutton et al., 2008]. Ambient temperature and relative humidity govern the direction and rate of these reversible reactions [Stelson and Seinfeld, 1982a]. Experimental observations have revealed that formation of ammonium salts may lead to homogeneous aerosol nucleation events and can accelerate nanoparticle formation [Kulmala et al., 2002; McMurry et al., 2005; Kirkby et al., 2011]. These secondary inorganic materials typically account for a large portion of fine particle mass [Malm et al., 2004]. In addition, recent studies have shown that excess NH$_3$ can provide sufficient aerosol alkalinity that gaseous nitrous acid will form particulate nitrite [Song et al., 2009].

Particulate ammonium has a longer lifetime than its gaseous counterpart and can be transported far from sources under favorable meteorological conditions, thereby affecting the temporal and spatial distributions of nitrogen (N) participating in the N cycle. The resultant PM alters the Earth’s energy flow via direct effects and modifies the properties of clouds (e.g., lifetime and albedo) via indirect effects by serving as cloud condensation and/or ice nuclei. The largest uncertainties among all radiative forcing components in the global climate models are associated with PM [IPCC, 2007]. Increased levels of atmospheric PM also cause degradation of atmospheric visibility. Additionally, a number of epidemiological studies worldwide have demonstrated a strong correlation between human exposure to PM and increasing rates of
respiratory and cardiovascular illness and other adverse health effects [Dockery, 2001; MacNee and Donaldson, 2003; Pope et al., 2002; Pope and Dockery, 2006].

Despite these implications for ammonia’s negative impacts on air quality, NH$_3$ currently is not regulated under the National Ambient Air Quality Standards (NAAQS) by the United States Environmental Protection Agency (U.S. EPA). Relevant regulatory controls also remain inadequate in other countries, which poses substantial difficulties and rigorous challenges to emission reduction. Moreover, governmental air quality monitoring network sites often do not regularly measure ambient NH$_3$ concentrations. The U.S. EPA has only 25 monitoring sites in nine states estimating NH$_3$ emissions from concentrated animal feeding operations (CAFOs). As a consequence, there are substantial uncertainties in spatial and temporal variations of NH$_3$ due to the lack of ground-based observations. For example, recent studies report considerably higher satellite-retrieved NH$_3$ concentrations north of 30° N compared to model simulations, indicating that NH$_3$ emissions likely are underestimated in the Northern Hemisphere by current inventories [Clarisse et al., 2009].
1.2. Characteristics of major NH$_3$ sources in urban and suburban areas

In the 1980s, three-way catalytic converters were introduced to control traffic emissions in the U.S. Since then, motor vehicles have become significant contributors to elevated NH$_3$ levels in urban areas. When NO$_x$ is over-reduced inside the converters, post-catalyst NH$_3$ is formed. Many studies have observed this phenomenon. In Los Angeles, Fraser and Cass [1998] estimated an average NH$_3$ emission rate of 61 mg per km driven for a vehicle fleet driving under rich air-fuel conditions in a roadway tunnel. In San Francisco, Kean and Harley [2000] reported reductions in NO$_x$ and carbon monoxide (CO) emissions but large increases in NH$_3$ concentrations (with an emission factor of 475 mg per liter of fuel consumed) after catalytic converters were installed widely on automobiles. In Rome, Perrino et al. [2002] found a strong correlation between NH$_3$ and CO, and at traffic sites, NH$_3$ concentrations were five times larger than at background sites. In New York City, Li et al. [2006] conducted NH$_3$ measurements at a school. Many NH$_3$ spikes were observed during rush hour periods. In addition, increased NH$_3$ concentrations on school days compared to non-school days were associated with increased traffic volumes. Light-duty gasoline cars have the largest emission factors of NH$_3$ among all on-road vehicles [Harley, 2009; Kean et al., 2009], but not all motor vehicles emit significant amounts of NH$_3$. For example, heavy-duty diesel trucks have minor contributions to gaseous NH$_3$ levels.

Unlike urban and more developed areas, rural/suburban areas have more agricultural activities as strong NH$_3$ emission sources. This is part of the reason why previous NH$_3$ studies mainly were conducted near dairy operations, animal housing, livestock facilities, slurry lagoons, croplands and forests where higher than average NH$_3$ concentration levels are often observed.
[Aneja et al., 2001; Kawashima and Yonemura, 2001; Pryor et al., 2001; Mount et al., 2002; Ferm et al., 2005; Bajwa et al., 2006; Rumburg et al., 2008]. In the California South Coast Air Basin, Nowak et al. [2012] estimated NH$_3$ emissions from dairy farms to range from 33±16 to 176±88 tons per day using NH$_3$ data from aircraft measurements. Over the San Joaquin Valley (known as a highly polluted agricultural region), Clarisse et al. [2010] reported that average NH$_3$ mixing ratios at an altitude of 700 m above sea level varied between 3 and 10 ppb, with a maximum value of 78 ppb, during daytime based on satellite data. In eastern North Carolina, Wilson and Serre [2007] found elevated NH$_3$ levels up to 80 ppb (with a mean of 13.8 ppb) near hog CAFOs. On the southern High Plains, Todd et al. [2008] observed average NH$_3$ emission rates of 7.42 and 3.33 tons per day in summer and winter, respectively, from a beef cattle feedyard with a population of 44,651 head.

Ammonia emissions from natural vegetation also have been found to be important. Lefer et al. [1999] noted that measured NH$_3$ mixing ratios at Harvard Forest were consistently below the canopy compensation point as a function of temperature, suggesting plants might continuously lose NH$_3$ to the atmosphere. Based on the measurements over a forest in the Colorado mountainous area, Langford and Fehsenfeld [1992] concluded that the ecosystem appeared to be a source for atmospheric NH$_3$ when exposed to low ambient NH$_3$ concentrations.

Although NH$_3$ has drawn increasing attention over the last decade, information about measured atmospheric NH$_3$ levels in Texas, especially in major metropolitan areas such as Greater Houston and Dallas-Fort Worth (DFW), is still very scarce. Generally, most relevant NH$_3$ studies described in the literature focus on the characterization of point sources such as CAFOs. On the other hand, Corsi et al. [2000] reported the first estimation of non-point source NH$_3$ emissions in Texas. Measurements of NH$_3$ emissions from pine and oak forests further
improved the non-industrial NH$_3$ emissions inventory in Texas [Corsi et al., 2002; Sarwar, et al., 2005]. However, the comprehensive mapping of NH$_3$ hotspots is impeded by limited field sampling efforts. As a result, the lack of sufficient emission inventory data confounds NH$_3$ source apportionment.
1.3. Measurement techniques for atmospheric NH$_3$

Measurement of NH$_3$ is notoriously difficult because it is readily converted to particulate ammonium and easily adsorbed onto surfaces. Among all sampling protocols, the bulk denuder technique probably has been the most widely used [Hoek et al., 1996; Burkhardt et al., 1998; Matsumoto and Okita, 1998; Erisman et al., 2001; Olszyna et al., 2005; Smith et al., 2007]. Because gas molecules diffuse faster than particles, gaseous NH$_3$ can be stripped from the air stream when passing through an acid coated denuder and further detected with off-line analysis such as ion chromatography (IC) [Ferm, 1979]. Instead of employing denuders, a mist chamber/ion chromatography (MC/IC) relies on a separation/concentration procedure in which water-soluble gases such as NH$_3$ in air are dissolved in pure deionized water [Cofer et al., 1990]. In this collection technique, a filter must be used to remove aerosol particles. Drawbacks of these wet-chemistry approaches include low time resolution and human-induced contamination/errors.

NO$_x$ monitors based on chemiluminescence combined with NH$_3$ converters also have been developed. NH$_3$ levels are estimated as the difference between total reactive nitrogen species (NO$_y$) and NO$_x$. Initially a C-Cu composite was used to oxidize NH$_3$ to NO and reduce NO$_2$ to NO simultaneously [Breitenbach and Shelef, 1973]. Recently, thermal oxidizers have become more popular [McCulloch and Shendrikar, 2000; Hansen et al., 2003]. The major disadvantage/shortcoming of this measurement technique is that the availability of atmospheric amines potentially interferes with NH$_3$ estimations.

In chemical ionization mass spectrometry, NH$_3$ is ionized through ion-molecule reactions using reagent ions such as (C$_2$H$_5$OH)$_n$H$^+$ produced from ethanol with the presence of radioactive
sources. The peaks of resultant \((C_2H_5OH)_nNH_4^+\) are detected by a quadrupole mass analyzer [Fehsenfeld et al., 2002; Nowak et al., 2006, 2007]. Similarly, ion mobility spectrometry measures the ion time-of-flight in an electrical field, while ionized NH\(_3\) molecules are separated by mobility and detected by an electrometer [Myles et al., 2006]. Due to their size, NH\(_3\) instruments using these measurement techniques often require extra space during the field deployment and pose difficulties for transportation.

Laser absorption spectroscopy (e.g., differential optical absorption spectroscopy and cavity ring down spectroscopy) utilizes the natural properties of species of interest in the atmosphere to achieve real-time detection. Different spectroscopic sources including tunable diode lasers and quantum cascade lasers have been used to study the absorption feature of NH\(_3\) [Li et al., 2006; Ellis et al., 2011]. The signal is amplified during multiple passes of the laser beam through the absorption cell and acquired by optical detectors. The multi-pass procedure for assuring the long pathlength using reflecting mirrors increases the complexity of the sampling system and the difficulty of laser alignment during sensor calibration.

In photo-acoustic spectroscopy (PAS), the laser usually is modulated to match the resonance frequency of a photo-acoustic cell. After absorption, excited NH\(_3\) molecules release energy in the form of heat. Periodic temperature changes cause a pressure wave, essentially sound, which can be detected by a microphone [Pogány et al., 2010]. The intensity of sound is proportional to the amount of NH\(_3\) in the sample. The instruments based on PAS are relatively compact and portable. Detailed information about the application of this measurement technique can be found in the following section.
Although the temporal resolution and minimum detection limits of atmospheric NH$_3$ instruments largely have been improved in the past few years, NH$_3$ measurements still are difficult and need special handling and extra attention in the field compared to other trace gases such as CO and ozone (O$_3$). Schwab et al. [2007] pointed out that the instrument time response, as a critical parameter in environmental measurements, was sensitive to sample handling materials and varied among different methods, which posed substantial difficulties for inter-comparison. Researchers, therefore, need to select appropriate sampling protocols from different designs and mechanisms used in NH$_3$ measurement techniques based on specific needs and study environments.
1.4. \textit{NH}_3 \textit{instrument used in this work}

For the purpose of the \textit{NH}_3 environmental study in this work, a widely tunable external cavity quantum cascade laser (EC-QCL), emitting a maximum optical power of 72 mW (Daylight Solutions Inc, Model 21106-MHF-001), is employed as a spectroscopic source. The single mode frequency output of the EC-QCL can be coarsely tuned from 933 to 1006 cm\(^{-1}\) with a minimum step size of 0.01 cm\(^{-1}\). In order to perform high resolution spectroscopy, a sinusoidal voltage, with a maximum amplitude of 100 V, is applied to the EC-QCL piezo element enabling mode hop free tuning within ~1 cm\(^{-1}\). An amplitude modulated photo-acoustic spectroscopy (AM-PAS) technique is employed to monitor atmospheric \textit{NH}_3 at trace concentration levels. The state-of-the-art photo-acoustic detector uses two balanced electret microphones placed in a 9.1-cm differential resonant photo-acoustic cell. The amplitude modulation of the laser beam is performed by a mechanical chopper wheel operating at 1.8 kHz to match the resonance frequency of the photo-acoustic cell at the selected working pressure of 220 Torr. The \textit{NH}_3 sensor architecture is depicted schematically in Figure 1.
In order to improve and obtain a detection limit of single ppb levels required for sensitive atmospheric NH$_3$ measurements, the optical beam is passed through the cell three times. A pyroelectric detector placed after a 10-cm reference cell filled with 0.2% of NH$_3$ at 30 Torr is used to compensate for possible EC-QCL wavelength drift, as well as to monitor its power. The pressure inside the system is kept at 220 Torr while the flow rate is maintained at 175 ml min$^{-1}$. In order to minimize NH$_3$ adsorption onto surfaces and to prevent water vapor condensation in the sensor, the sensor enclosure is heated to 38 °C. All tubing is made of Teflon$^\text{®}$, and a particle filter is placed before the inlet to avoid undesirable contamination. In the present work, the 965.35 cm$^{-1}$ absorption line of NH$_3$ is chosen. This frequency is the optimal selection for the
amplitude modulated PAS technique based on laser power, absorption strength, and minimized water vapor and carbon dioxide interferences. Under ambient conditions, these interferences are negligible compared to the signal from NH$_3$.

For the sensor calibration, a certified mixture of 5 part per million (ppm) of NH$_3$ in nitrogen is used. To determine atmospheric concentration levels of NH$_3$, each acquired sample scan is compared with the 5 ppm NH$_3$ reference scan by implementing a LabView-based general least-square linear fitting algorithm. This procedure yields a fit coefficient value, which generally indicates to what extent each sample scan represents a reference scan. If the coefficient is equal to one, the NH$_3$ mixing ratios for both reference and sample scans are identical. Meanwhile, pure nitrogen is used to obtain related spectral data for the zero line. The accuracy of the NH$_3$ sensor is estimated to be ±6%, combining an uncertainty of ±1% for the algorithm calculation method and an uncertainty of ±5% for the NH$_3$ cylinder used for sensor calibration.

Field tests demonstrate that the time response of the NH$_3$ sensor is on the order of seconds to one minute, which is sufficient to capture plumes during environmental measurements. No NH$_3$ losses are observed according to the detected signals when a standard of 5 ppm NH$_3$ is employed. Large events usually last less than one hour. For example, after putting fingers close to the sensor inlet as a test, NH$_3$ mixing ratios are rapidly elevated to ~30 ppb, which is related to the NH$_3$ generation from human skin. The subsequent decay to the baseline takes ~30 minutes according to a 90% recovery from the peak signal. In addition, the majority of the sampling inlet is heated using autotransformators and is made as short as possible to minimize the sites for NH$_3$ to stick.
To investigate the long-term stability of the NH$_3$ sensor, a set of data was acquired in the laboratory while pure nitrogen was flushed through the photo-acoustic cell. An Allan deviation analysis, defined as the square root of the Allan variance, was performed. A long data-averaging time is beneficial for the improvement of measurement accuracy because some noise sources can be removed by the averaging process. The minimum detection limit of the NH$_3$ sensor used for real-time measurements in the field is 3.4 ppb for a five-second acquisition time. The Allan deviation plot flattens out approximately after 300 s. Therefore, an averaging time of five minutes is the optimal selection in terms of the measurement accuracy. A NH$_3$ concentration level detection limit of ~0.7 ppb is achieved after averaging the data over 300 seconds.
1.5. Recent trend in routine NH$_3$ measurements

In 2007, the National Atmospheric Deposition Program (NADP) initiated the passive Ammonia Monitoring Network (AMoN) which later was approved as an official NADP network in 2010. It is the only U.S. national NH$_3$ monitoring network, including 61 active sites in 35 states by far. Most sites are located in remote areas and agricultural regions. For example, the only site in Texas is set up near Palo Duro Canyon State Park in Randall County. AMoN uses commercial passive samplers (Radiello®) that work on diffusion theory. Gaseous NH$_3$ is stripped from the air stream when passing through a phosphoric acid coated denuder. Absorbed NH$_3$ (as NH$_4^+$) is removed by sonication in deionized water and is further detected by Flow Injection Analysis. Samples are collected and analyzed every two weeks. This low-maintenance method provides an inexpensive and effective way to continue the efforts on ambient measurements of atmospheric NH$_3$ with a reasonable/acceptable time resolution. It also enhances the collaboration and interaction among different governmental agencies, research centers, universities, and interested stakeholders. NADP plans to expand the network by launching more monitoring sites in the future. Preliminary data suggest that atmospheric NH$_3$ concentration levels are continuously increasing, while the levels of other criteria pollutants such as SO$_2$ have decreased in the past few years. This highlights the importance of establishing and operating a national NH$_3$ monitoring network in order to thoroughly evaluate current emission control strategies and properly prepare future mitigation plans. A better understanding of temporal and spatial variations in atmospheric NH$_3$ can bring a series of benefits to modelers, scientists, and policymakers.
Chapter 2

Atmospheric NH$_3$ measurements and implications for PM formation in Houston, TX

2.1. Background

The Toxics Release Inventory (TRI) of the U.S. EPA highlights the importance of NH$_3$ as an air pollutant in urban communities nationwide [U.S. EPA, 2010]. Figure 2.1 (a) presents the total toxics air releases (20.8 million pounds) by species in the Houston-Sugar Land-Baytown metropolitan area according to the TRI in 2010 [U.S. EPA, 2010]. It can be seen that NH$_3$ has the third largest individual magnitude of emissions after ethylene and propylene. Based on the U.S. EPA National Emissions Inventory (NEI) [U.S. EPA, 2008], agricultural and automobile activities are major contributors to gaseous NH$_3$ emissions. Figure 2.1 (b) summarizes the NEI NH$_3$ emissions (10.2 million pounds) by source categories specifically for Harris County, Texas
in 2008 and indicates that on-road gasoline light duty vehicles and fertilizer application account for approximately 56% of the annual NH\textsubscript{3} emissions.
Figure 2.1 (a) Annual total air toxics releases (20.8 million pounds) by species in the Houston-Sugar Land-Baytown metropolitan area [U.S. EPA, 2010]; (b) Annual NH$_3$ emissions (10.2 million pounds) by source categories in Harris County, Texas [U.S. EPA, 2008].

Data regarding NH$_3$ levels for the industrial and urban area of Greater Houston are still very limited. According to a photochemical model, the estimated NH$_3$ mixing ratios for the Houston area are in the range of 1 to 15 ppb [Pavlovic et al., 2006]. The same study suggested NH$_3$-rich conditions over southeast Texas. The only published study on NH$_3$ measurements in Houston reported airborne observations below and above the planetary boundary layer (PBL) using a 14-day data set during the second Texas Air Quality Study (TexAQS II) [Nowak et al., 2010]. In that study, NH$_3$ mixing ratios typically ranged from 0.2 to 3 ppb, but specific plumes with elevated NH$_3$ levels (5 to 80 ppb) were related to point source emissions near the highly industrialized Houston Ship Channel (HSC). The NH$_3$ enhancement was also coincident with a decrease in HNO$_3$ mixing ratios and an increase in particulate nitrate concentrations, indicating that NH$_4$NO$_3$ was formed in these plumes. The paucity of data makes it crucial to improve the current understanding of the dynamics of NH$_3$ in Houston and to further investigate the effects of NH$_3$ on local and regional air quality.
2.2. Methodology

2.2.1. Sampling site

All instruments were deployed in a trailer atop an 18-story (~65 m above ground level) building (North Moody Tower) located on the University of Houston (UH) main campus, which is influenced by many local and regional emission sources such as highways, airports, and industrial facilities from almost all wind directions. The site is considered highly urban without agricultural activities. It is ~2.5 miles southeast of downtown Houston and ~7 miles southwest of the HSC. Detailed information about this sampling site can be found in Lefer and Rappenglück [2010]. Meteorological parameters (e.g., temperature and relative humidity) as well as mixing ratios of some important air pollutants (e.g., CO, O\textsubscript{3}, NO\textsubscript{x}, and SO\textsubscript{2}) are measured regularly by the UH research group at this location [Day et al., 2010; Lefer et al., 2010; Luke et al., 2010]. All data were averaged into 1-hr intervals solely for temporal consistency.

2.2.2. Gaseous species measurements

Gas-phase NH\textsubscript{3} was measured using a 10.4-µm external cavity quantum cascade laser-based sensor employing conventional photo-acoustic spectroscopy. The laser sensor was capable of unattended operation with continuous data acquisition for extended periods of time. Remote access enabled the real-time monitoring of the sensor performance. Gas-phase HNO\textsubscript{3} and HCl were measured using a MC/IC system (Dionex, Model CD20-1), where the minimum detection limits of ppt levels were reached for a temporal resolution of 10 minutes with an uncertainty of ±10% [Dibb et al., 2004; Luke et al., 2010].
2.2.3. Aerosol species measurements

Particle chemical composition was measured using a particle-into-liquid-sampler (PILS) (BMI, Model 4002) coupled directly to two IC systems (Dionex, Model 1600) [Lee et al., 2003; Orsini et al., 2003]. Mass concentrations (µg m⁻³) of water-soluble inorganic components including ammonium (NH₄⁺), sodium (Na⁺), potassium (K⁺), calcium (Ca²⁺), magnesium (Mg²⁺), sulfate (SO₄²⁻), nitrate (NO₃⁻), nitrite (NO₂⁻) and chloride (Cl⁻) in fine particle aerosols (with diameters smaller than 1 µm) were determined at 16-min intervals. The detection limit for measured ions is 100 ng m⁻³, and the uncertainty of PILS-IC measurements is ±7% [Sorooshian et al., 2007]. The continuous and real-time monitoring of particle number concentration (# of particles per volume of air) with a temporal resolution of one minute was performed using a condensation particle counter (TSI, Model 3772). Detailed information regarding measurement techniques is provided in Table 2.1.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$</td>
<td>Daylight Solutions External Cavity Quantum Cascade Laser (Photo-acoustic Spectroscopy)</td>
</tr>
<tr>
<td>NO$_x$</td>
<td>Thermo Electron Corp. 42C Trace Level NO-NO$_2$-NO$_3$ Analyzer (Chemiluminescence)</td>
</tr>
<tr>
<td>NO$_y$</td>
<td>Thermo Electron Corp. 42C-Y NO$_x$ Analyzer (Molybdenum Converter)</td>
</tr>
<tr>
<td>CO</td>
<td>Thermo Electron Corp. 48C Trace Level CO Analyzer (Gas Filter Correlation)</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>Thermo Electron Corp. 43C Trace Level SO$_2$ Analyzer (Pulsed Fluorescence)</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>Mist Chamber coupled to Ion Chromatography (Dionex, Model CD20-1)</td>
</tr>
<tr>
<td>HCl</td>
<td>Mist Chamber coupled to Ion Chromatography (Dionex, Model CD20-1)</td>
</tr>
<tr>
<td>Aerosol component</td>
<td>Particle-Into-Liquid-Sampler (BMI, Model 4002) coupled to Ion Chromatography (Dionex, Model 1600)</td>
</tr>
<tr>
<td>Particle number concentration</td>
<td>Condensation Particle Counter (TSI, Model 3772)</td>
</tr>
<tr>
<td>PBL height</td>
<td>Vaisala DigiCORA Tethersonde System</td>
</tr>
<tr>
<td>Temperature</td>
<td>Campbell Scientific HMP45C Platinum Resistance Thermometer</td>
</tr>
<tr>
<td>Relative humidity</td>
<td>Campbell Scientific HMP45C Humicap® 180 Capacitive Relative Humidity Sensor</td>
</tr>
<tr>
<td>Wind speed</td>
<td>Campbell Scientific 05103 R. M. Young Wind Monitor</td>
</tr>
<tr>
<td>Wind direction</td>
<td>Campbell Scientific 05103 R. M. Young Wind Monitor</td>
</tr>
</tbody>
</table>
2.3. Results and Discussion

2.3.1. Gaseous NH\textsubscript{3} measurements

The atmospheric NH\textsubscript{3} measurements were conducted in both winter and summer. Figure 2.2 presents a time series of hourly-averaged NH\textsubscript{3} mixing ratios during two sampling periods (12 February 2010 – 1 March 2010 and 5 August 2010 – 25 September 2010) and indicates a large amount of variability and several episodes of elevated NH\textsubscript{3} levels. The statistics of the two data sets are listed in Table 2.2.

Table 2.2 Statistics of NH\textsubscript{3} data collected during the two sampling periods (< DL indicates numbers below the detection limit) at the North Moody Tower.

<table>
<thead>
<tr>
<th></th>
<th>NH\textsubscript{3} mixing ratio (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Winter</td>
</tr>
<tr>
<td>Mean</td>
<td>2.42</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>1.16</td>
</tr>
<tr>
<td>Maximum</td>
<td>8.72</td>
</tr>
<tr>
<td>Minimum</td>
<td>0.10 (&lt; DL)</td>
</tr>
<tr>
<td>Median</td>
<td>2.21</td>
</tr>
<tr>
<td>10th Percentile</td>
<td>1.16</td>
</tr>
<tr>
<td>25th Percentile</td>
<td>1.59</td>
</tr>
<tr>
<td>75th Percentile</td>
<td>3.17</td>
</tr>
<tr>
<td>90th Percentile</td>
<td>3.80</td>
</tr>
</tbody>
</table>
Figure 2.2 A time series of NH$_3$ mixing ratios measured using an EC-QCL-based sensor atop the North Moody Tower in Houston, TX during the two sampling periods (2010). Notable increases in the NH$_3$ mixing ratio are associated with transport from a coal-fired power plant, a chemical fire on an adjacent highway as a result of a crash of a tanker carrying agricultural chemicals, transport from the heavily industrialized Houston Ship Channel, and transport from the Gulf of Mexico during Hurricane Hermine.
2.3.1.1. Seasonal variation

Mixing ratios of NH\textsubscript{3} were elevated in summer (mean of 3.1±2.9 ppb) compared to winter (mean of 2.4±1.2 ppb), leading to an inference that ambient temperature has a strong effect on NH\textsubscript{3} levels. The average temperatures during the winter and summer sampling periods were 9.5±2.2 °C and 28.7±1.9 °C, respectively. This observation agrees well with previous studies that found that temperature-dependent sources and/or processes affected seasonal variations of NH\textsubscript{3} concentrations [Yamamoto et al., 1995; Lee et al., 1999; Aneja et al., 2000; Robarge et al., 2002; Lin et al., 2006; Ianniello et al., 2010; Saylor et al., 2010]. For example, natural emissions of NH\textsubscript{3} (e.g., vegetation and volatilization of animal waste) increase in strength with increasing temperature. In addition, colder conditions favor particulate ammonium formation while higher temperatures in summer shift the thermodynamic equilibrium towards the gas phase, consequently elevating gaseous NH\textsubscript{3} levels.

2.3.1.2. Diurnal variation

Auxiliary data collected atop the North Moody Tower were incorporated into data analyses to assist in the NH\textsubscript{3} source identification in Houston. For example, primary pollutants such as NO\textsubscript{x} and CO emitted from tailpipes are usually used as indicators of vehicular emissions. Figure 2.3 shows a set of box plots that indicate the diurnal profiles of NH\textsubscript{3} and CO mixing ratios as well as temperature and relative humidity during the two sampling periods. Generally, NH\textsubscript{3} mixing ratios increased in the morning and peaked at 08:00 CST in winter and at 11:00 CST in summer, respectively, while the CO peak also was observed during morning rush hours as a consequence of large vehicular emissions in combination with the lingering effect of a shallow
nocturnal boundary layer. Note that the CO peak appeared two hours later in winter (08:00 CST) than in summer (06:00 CST), which may be attributed to seasonal traffic conditions resulting from different human activity patterns. Then the mixing ratio of NH$_3$ quickly decreased and reached the minimum value around mid-day, suggesting that some removal and/or dilution mechanisms play critical roles at that time. Recurring increases in NH$_3$ were observed in the early afternoon; the bimodal trend was more pronounced in summer compared to winter. A second enhancement in CO mixing ratios can be observed with increasing traffic between 17:00-21:00 CST, followed by a decrease at night due to the absence of sources. The mixing ratio of NH$_3$ remained relatively depleted at night in winter, while a gradually slow increase in NH$_3$ mixing ratios during nighttime in summer was observed. Replicate measurements were conducted in the winter of 2011 (1 February – 10 March) and indicate similar wintertime dynamics of NH$_3$.

In summer, NH$_3$ mixing ratios increased not only after sunrise but also between midnight and 06:00 CST. However, the magnitude was much smaller, and the rate was much slower compared to the sharp morning increase. Small amounts of emissions (from a relatively small number of sources) into a shallow nocturnal boundary layer could lead to the increasing mixing ratios.
NH₃ mixing ratio (ppb)

CO mixing ratio (ppb)

Temperature (°C)

Relative humidity (%)

Hour of day

5 August 2010 - 25 September 2010

(b)
Figure 2.3 Diurnal profiles of NH$_3$ and CO mixing ratios as well as temperature and relative humidity during the two sampling periods at the North Moody Tower. The bottom whisker, box bottom, line inside the box, box top, and top whisker represent the 10th, 25th, 50th, 75th, and 90th percentiles of the data, and the continuous lines represent mean values, respectively. (a) 12 Feb – 1 Mar 2010; (b) 5 Aug – 25 Sep 2010.

2.3.1.3. Correlation between NH$_3$ and vehicular emissions

In order to examine the relationship between NH$_3$ and vehicular emissions, Figure 2.4 summarizes hourly average NH$_3$ and CO data during the two sampling periods. To eliminate potential interferences, the “outlier plumes” leading to elevated NH$_3$ levels from sources other than traffic emissions were removed for Figures 2.4 and 2.5. The mixing ratios of NH$_3$ larger than 95th percentile of the data are considered as the “outlier plumes” for the analysis in this work. The determination of non-traffic sources is based on the analysis of other auxiliary data and meteorological parameters. Detailed descriptions can be found in the following sections. Generally, these plumes occurred during the daytime on weekdays when the sampling site was downwind of specific emission sources. Resultant episodes of high NH$_3$ mixing ratios were very large compared to other periods of the measurements.
As shown in Figure 2.4, winter morning enhancements in NH$_3$ were coincident with enhanced CO, indicating that motor vehicles are likely a major emission source of NH$_3$ in Houston during this period; no such concurrent increases were observed in summer. This phenomenon is further illustrated by the linear regressions given in Figure 2.5 that show Pearson’s correlation coefficients ($r$) of 0.76 between NH$_3$ and CO during morning rush hours (06:00-10:00 CST) in winter and of 0.14 in summer. A temporal gap between the NH$_3$ peak and NO$_x$ and NO$_y$ peaks in the morning further confirms that vehicular emissions were not major sources of NH$_3$ in summer.
Figure 2.5 Scatter plot of NH$_3$ versus CO for rush hours (06:00-10:00 CST) during the two sampling periods in Houston. As discussed in the text, outlier plumes are removed from this analysis in summer.

It is hypothesized that this seasonal difference is related to changes in vehicular catalytic converter performance as a function of ambient temperature. In winter, engines more frequently run under high-load conditions in order to reach and maintain the optimal operating temperature. This potentially induces fuel-rich combustion which favors reducing processes on the catalyst surface. As a result, more NH$_3$ is produced in vehicle exhaust [Shelef and McCabe, 2000; Heck and Farrauto, 2001; Defoort et al., 2004; Heeb et al., 2006]. Additional emission sources of NH$_3$ present in summer also may obscure the correlation between NH$_3$ and CO.
Another explanation for the inconsistent NH\textsubscript{3}-CO relationship between seasons is that air masses transported from different wind directions to the North Moody Tower have distinct characteristics. As shown in Figure 2.6 (a), the wind mainly blew from the SE (William P. Hobby Airport and highways) during morning rush hours in winter, while the wind mainly blew from the NE (HSC) during morning rush hours in summer. It is assumed that air transported from the SE contains more primary combustion species than air transported from the NE despite the highly industrial nature of the HSC. The prevailing wind direction shifted at the sampling site during other time periods of the day.
12 February 2010 - 1 March 2010

5 August 2010 - 25 September 2010

(a)
12 February 2010 - 1 March 2010

5 August 2010 - 25 September 2010

(b)
Morning increases in NH$_3$ mixing ratios were notable throughout the measurement periods. For example, the morning increase in winter appeared to be associated with motor vehicular activities. However, many factors may be responsible for this behavior. It can be seen in Figure 2.3 that there were significant changes in temperature and relative humidity beginning at 06:00 CST, when NH$_3$ mixing ratios also began to increase quickly. It is possible that the evaporation of dew associated with increasing temperature releases NH$_3$ into the atmosphere, especially in summer when the early morning relative humidity was higher compared to winter. Ellis et al. [2011] also pointed out that the natural emissions of NH$_3$ from vegetation and soil through photosynthetic processes might be important contributors to a morning increase.

The dynamics of LIDAR-measured PBL heights were consistent from day to day in summer. The height remained low during nighttime, and the PBL did not break up until 07:00 CST, while NH$_3$ mixing ratios began to increase at 05:00 CST. Therefore, vertical mixing of NH$_3$ from the residual layer is ruled out as a contributing source of NH$_3$ in the morning.

2.3.1.4. Source identification

In order to evaluate the effect of local or regional sources on atmospheric NH$_3$ levels, Figure 2.6 (b) illustrates the dependence of NH$_3$ mixing ratios on wind direction for the duration
of both sampling periods. The wind rose is divided into 16 sectors, and the data correspondingly are grouped into 22.5° intervals. The polar plots present the median mixing ratio in each bin, showing increased NH\textsubscript{3} levels were often associated with the wind blowing from NE or E in the direction of the HSC where numerous petrochemical refineries are densely located. The estimated NH\textsubscript{3} emissions in that area were approximately 0.25 ton per hour during TexAQS II [Mellqvist et al., 2007]. Large NH\textsubscript{3} concentrations near industrial facilities were also noted by some other studies, including that of Hsieh and Chen [2010] who measured NH\textsubscript{3} levels elevated compared to ambient background levels by a factor of 50-150 in three heavily industrialized parks in south Taiwan.

Large weekday-weekend differences in NH\textsubscript{3} and CO mixing ratios were observed throughout the measurements as shown in Figure 2.7. Enhanced NH\textsubscript{3} values on weekdays compared to weekends are probably due to increased industrial activity between Monday and Friday when most of the “outlier plumes” occurred. Brooks et al. [2010] concluded that the HSC is a major emission source of mercury species in Houston, and concentrations measured atop the North Moody Tower were much higher on weekdays than weekends. CO values displayed a similar behavior with the substantially smaller morning rush hour maximum on weekends with decreased traffic volumes. It is also noted that CO mixing ratios between midnight and 04:00 CST were higher on weekends than weekdays in summer. This may be attributed to vehicular emissions related to some late night human activities in warm seasons.
In August, some rapid NH$_3$ increases were found to be synchronous with similar SO$_2$ increases when the wind blew from the SW (as verified by both wind direction and Hybrid Single-Particle Lagrangian Integrated Trajectory (HYPLIT, Draxler and Rolph [2011]) backward trajectory analysis), the direction of the second largest coal-fired electricity generating station (W. A. Parish) in the U.S. After 2004, this power plant employed the selective catalytic reduction (SCR) technique to control NO$_x$ emissions [Peischl et al., 2010]. In SCR, a large amount of NH$_3$ is used as a reducing reagent. Occasional NH$_3$ slips into the atmosphere during SCR processes may contribute to the coincident enhancements in NH$_3$ and SO$_2$ mixing ratios, suggesting the co-emission from a point source. Interestingly, Nowak et al. [2010] did not observe similar spikes of NH$_3$ in the plume from this power plant during the summer of 2006.

In addition, the EPA Positive Matrix Factorization (PMF) 3.0 model was used to conduct source attribution [Paatero and Tapper, 1994; Paatero, 1997]. Results clearly show that in summer, the HSC (62.5%) is the largest source category followed by power plants (35.5%) and automobiles (2%). Because volatile organic compound (VOC) data used in the model were collected at a local ambient air quality monitoring station in the HSC area operated by the Texas Commission on Environmental Quality (TCEQ) instead of at the North Moody Tower due to the current unavailability of data from co-located instruments, these results must be viewed as preliminary.
2.3.1.5. Remarkable events

There is a considerable degree of variability in atmospheric NH$_3$ mixing ratios in the Houston atmosphere. Some unexpected events were observed during summertime measurements, indicating that local or regional sources present in Greater Houston affected the observational results at the North Moody Tower. For example, the laser sensor recorded a significant and lasting increase in NH$_3$ mixing ratios (~21 ppb) on 14 August 2010, when a major accident occurred during the same time period on the Gulf Freeway (Interstate 45) in Houston, only two miles from the sampling site. The elevated concentration levels are assumed to be associated with NH$_3$ generation from a chemical fire resulting from the collision of two 18-wheeled tankers/cargo vehicles, one carrying fertilizer (trimethylammonium) and pesticide (dimethylamine). To our knowledge, this is the first time that an accidental release of NH$_3$ has been detected remotely and in real-time by an optical sensor. Similar observations were reported by Nowak et al. [2010] who found elevated NH$_3$ mixing ratios up to 80 ppb in a plume due to an industrial accident in Baytown, along the HSC.

Another episode of elevated NH$_3$ levels (~22 ppb) occurred on 7 September 2010, which might be related to the transport of emissions from the Gulf of Mexico during Hurricane Hermine. The storm led to strong wind (~20 miles per hour) blowing from the SE, and HYSPLIT backward trajectories showed that before arriving at the North Moody Tower, air masses passed by some industry in the Texas City area, approximately 40 miles SE of downtown Houston. The fast air movement decreased the probability of physical and chemical losses in the plumes prior to their arrival in Houston. Some previous studies have shown increased concentrations of halogen containing compounds in the atmosphere associated with emissions
from the ocean during storm/hurricane activities [Varner et al., 2008]. Enhanced emissions from the Gulf cannot be eliminated in this case.

The third notable event occurred on 17 September 2010 when the sampling site was downwind of the HSC in the morning. The NH$_3$ levels were elevated to ~27 ppb while no concurrent enhancements in mixing ratios of other air pollutants were observed. However, specific NH$_3$ sources in that heavily industrialized area cannot be identified on the basis of the data presented here.

### 2.3.2. Effect of NH$_3$ on particle mass concentrations

The simultaneous measurements of trace gases and particle chemical composition were carried out from 5 August 2010 to 9 August 2010. Although a five-day dataset is relatively limited, the total number of data points is large due to the highly time-resolved nature of the measurements and therefore can provide insight into air pollution episodes in an urban area potentially affected by power plant plumes.

Figure 2.8 presents a time series of hourly-averaged mixing ratios of gaseous NH$_3$ (3.0 ± 2.5 ppb (overall average ± one standard deviation)), HNO$_3$ (287.4 ± 291.6 ppt), HCl (221.3 ± 260.7 ppt), and CO (109.8 ± 22.4 ppb) and concentrations of particulate NH$_4^+$ (0.5 ± 1.0 µg m$^{-3}$), SO$_4^{2-}$ (4.5 ± 4.3 µg m$^{-3}$), NO$_3^-$ (0.3 ± 0.2 µg m$^{-3}$), and Cl$^-$ (0.2 ± 0.1 µg m$^{-3}$) along with meteorological parameters. NH$_3$ levels were elevated around mid-day, when NH$_4^+$ and SO$_4^{2-}$ also dramatically increased compared to other time periods of the measurements. This suggests that NH$_3$ played an important role in PM mass formation and that gas-particle conversion
occurred when NH$_3$ was available, though SO$_4^{2-}$ partitions to the aerosol phase regardless of NH$_3$ level. However, NO$_3^-$ and Cl$^-$ concentrations did not change significantly throughout the study period.
During these peaks, the wind mainly blew from the southwest in the direction of the second largest coal-fired power plant (W. A. Parish) in the U.S. (also verified by HYSPLIT modeling [Draxler and Rolph, 2011]). The average wind speed was about 10 miles per hour when these mid-day spikes occurred, leading to an inference that the electricity generating station, which is approximately 23 miles (37 km) away from the sampling site, may be a source of NH$_3$ in Houston during this period. The SCR technique was installed to control NO$_x$ emissions from Parish after 2004 [Peischl et al., 2010].

During the five days of measurements, concurrent decreases in HNO$_3$ and HCl and concurrent increases in NO$_3^-$ and Cl$^-$ were not observed when NH$_3$ levels were elevated around mid-day, indicating that NH$_4$NO$_3$ and NH$_4$Cl were not formed in significant amounts. This hypothesis is confirmed by the very low saturation ratios ($<<1$) illustrated in Figure 2.9. The saturation ratio is the partial pressure product ($P_{\text{NH}_4 \text{NO}_3}$ or $P_{\text{NH}_4 \text{Cl}}$, in units of ppb$^2$) divided by the equilibrium constant ($K_{\text{NH}_4 \text{NO}_3}$ or $K_{\text{NH}_4 \text{Cl}}$, in units of ppb$^2$) that can be calculated using empirical equations [Pio and Harrison, 1987; Seinfeld and Pandis, 2006] based on the reversible formation of NH$_4$NO$_3$ and NH$_4$Cl (eqs 1 and 2).

\[ \text{NH}_3(g) + \text{HNO}_3(g) \leftrightarrow \text{NH}_4\text{NO}_3(s \text{ or } aq) \quad (1) \]

\[ \text{NH}_3(g) + \text{HCl}(g) \leftrightarrow \text{NH}_4\text{Cl}(s \text{ or } aq) \quad (2) \]
Figure 2.9 Time series of the saturation ratios of NH$_4$NO$_3$ and NH$_4$Cl.

\[ S = \frac{P_{NH_3} P_{HNO_3}}{K_{NH_4NO_3}} \text{ or } \frac{P_{NH_3} P_{HCl}}{K_{NH_4Cl}} \]

where \( S \) is saturation ratio; \( P \) is partial pressure (in units of ppb); \( K \) is equilibrium constant (in units of ppb$^2$).

\[ K=\exp[84.6-24220/T-6.1\ln(T/298)] \] for NH$_4$NO$_3$

\[ K=\exp[2.2358\ln T-2.13204*10^{-4}T^{-1}+65.437516-8.167*10^{-3}T+4.64383*10^{-7}T^{-2}-1.10475*10^{-10}T^{-3}] \]

for NH$_4$Cl

where \( T \) is temperature in Kelvin.
Particulate NH$_4$NO$_3$ and NH$_4$Cl condense when the saturation ratio is larger than one, and they evaporate when the saturation ratio is smaller than one. This is in contrast to the study of Nowak et al. [2010] during TexAQS II who observed NH$_4$NO$_3$ formation in HSC plumes with elevated NH$_3$ levels ranging from 5 to 80 ppb, likely due to the shift in the thermodynamic equilibrium towards the aerosol phase caused by very high NH$_3$ mixing ratios. Because the time scales to achieve thermodynamic equilibrium for NH$_4$NO$_3$ and NH$_4$Cl usually are on the order of minutes under ambient conditions [Wexler and Seinfeld, 1992; Meng and Seinfeld, 1996], the time since emission likely can be eliminated as the reason for the lack of NH$_4$NO$_3$ and NH$_4$Cl formation in the present work. However, high temperatures (30.1 ± 2.3 °C) likely do inhibit the formation of NH$_4$NO$_3$ and NH$_4$Cl because volatilization increases with temperature; by contrast, sulfate is considered essentially non-volatile [Bassett and Seinfeld, 1984]. The Extended Aerosol Inorganics Model (E-AIM) also was employed, and it yielded similar results for the calculation of thermodynamic equilibrium/gas-particle partitioning using measurement data from this work [Clegg et al., 1998].

Comparable results have been reported previously by some urban-scale studies in other parts of the world. For example, in Barcelona, Pandolfi et al. [2012] conducted simultaneous measurements of gaseous NH$_3$ and aerosol species during summertime. It was found that the coefficients of determination between NH$_4^+$ and SO$_4^{2-}$ and NO$_3^-$ were 0.80 and 0.03, respectively, suggesting that NH$_4$NO$_3$ was not formed probably due to relatively high temperatures. In Central Taiwan, Lin et al., [2006] characterized NH$_3$, HNO$_3$, NH$_4^+$, and NO$_3^-$, and attributed lower NO$_3^-$ concentrations in summer to the higher volatility levels of particulate NH$_4$NO$_3$. In Beijing, Meng et al. [2011] observed the decreased correlation between NH$_4^+$ and NO$_3^-$ in summer compared to other seasons and noted that most of NH$_4^+$ in PM$_{2.5}$ is present as
(NH₄)₂SO₄ during summertime. These findings support the hypothesis above for the lack of NH₄NO₃ in this work.

Table 2.3 summarizes the Pearson’s correlation coefficients (r) between cations and anions during the measurement period, indicating that particulate (NH₄)₂SO₄, NaNO₃, NaCl, Mg(NO₃)₂, and MgCl₂ might be formed based on the corresponding r values (> 0.80). This could partially result from the different origin of air masses. For example, the concentrations of Na⁺, Mg²⁺, and Cl⁻ increased concurrently when southerly winds off the Gulf of Mexico were prevalent, indicating that air masses transported from the marine environment possibly affected the sampling site during those periods. Additionally, the slope (0.77) of the regression line between [NH₄⁺] and [SO₄²⁻] implies that (NH₄)₂SO₄ and NH₄HSO₄ might have co-existed.
Table 2.3 Pearson's correlation coefficients (r) between cations and anions during the measurement period.

<table>
<thead>
<tr>
<th></th>
<th>SO\textsubscript{4}^{2-}</th>
<th>NO\textsubscript{3}^-</th>
<th>Cl\textsuperscript{-}</th>
<th>NO\textsubscript{2}^-</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH\textsubscript{4}\textsuperscript{+}</td>
<td>0.98</td>
<td>0.49</td>
<td>0.40</td>
<td>0.02</td>
</tr>
<tr>
<td>Na\textsuperscript{+}</td>
<td>0.58</td>
<td>0.90</td>
<td>0.94</td>
<td>0.28</td>
</tr>
<tr>
<td>Ca\textsuperscript{2+}</td>
<td>0.05</td>
<td>0.07</td>
<td>0.04</td>
<td>0.20</td>
</tr>
<tr>
<td>Mg\textsuperscript{2+}</td>
<td>0.41</td>
<td>0.81</td>
<td>0.91</td>
<td>0.07</td>
</tr>
<tr>
<td>K\textsuperscript{+}</td>
<td>0.41</td>
<td>0.36</td>
<td>0.15</td>
<td>0.38</td>
</tr>
</tbody>
</table>

A regression between molar concentrations of cations and anions yields a strongly linear relationship (Figure 2.10, \( R^2 = 0.96; p < 0.0001; \) slope = 1.53), suggesting that ambient aerosols were likely acidic as a result of incomplete neutralization. However, the average value of the molar concentration ratio of gaseous NH\textsubscript{3} to total NH\textsubscript{3} (the sum of NH\textsubscript{3} and NH\textsubscript{4}\textsuperscript{+}), also known as the gas fraction (\( \sigma = 0.86 \pm 0.17 \)), suggests that NH\textsubscript{3} remained predominantly in the gas phase rather than the aerosol phase, as shown in Figure 2.11, although sampled aerosols were ammonium-lean.
Figure 2.10 Linear relationship between measured cations and anions.
Figure 2.11 Time series of gas fractions for NH₃, HNO₃ and HCl and of the ratio of NH₃ to the sum of HNO₃ and HCl.
It is unlikely that aerosols are high in acid content when gaseous NH$_3$ is prevalent in the atmosphere. There may be cations from material less likely to volatilize present in aerosols not measured with the PILS-IC. One, though not the only possible, hypothesis is that amines contribute to the cationic composition of PM. Amines widely exist in the atmosphere from a variety of sources, and they are subject to physical and chemical processes such as gas-particle partitioning [Ge et al., 2011a; Ge et al., 2011b]. It has been reported that aminium can displace NH$_4^+$ in ammonium salts [Bzdek et al., 2010; Smith et al., 2010]. In addition, the availability of amines enhances sulfuric acid-water (H$_2$SO$_4$-H$_2$O) nucleation [Kurtén et al., 2008; Loukonen et al., 2010], which may partially account for relatively high SO$_4^{2-}$ levels (up to 33.7 µg m$^{-3}$) observed during the measurements. If we assume that ambient aerosols are neutral and attribute all missing cations to aminium, the estimated required mixing ratio of gaseous amines is approximately 55 ppb following the example in Ge et al. [2011b]. While this is a very large value, observed atmospheric amine mixing ratios range from ppt to hundreds of ppb levels; even parts per million (ppm) levels were found in power plant regions [Shao and Stangeland, 2009]. Some existing plants in the U.S. use amine-based solvent to capture post-combustion carbon dioxide [Rubin and Rao, 2002]. However, to our knowledge, Parish currently uses only NH$_3$ tank farms instead of amine technology. Given the strong linear relationship between measured anions and cations (Figure 2.10), the aminium concentrations would be correlated strongly with NH$_4^+$ if present.

It is also noted that the mean gas fractions for HNO$_3$ ($\sigma = 0.71 \pm 0.14$) and HCl ($\sigma = 0.72 \pm 0.24$) were larger than 0.5, as shown in Figure 2.11, indicating they existed mainly in the gas phase. This observation may be attributed to the warm conditions during the measurements, which favor volatilization of NH$_4$NO$_3$ and NH$_4$Cl. In addition, Figure 2.11 displays the molar
concentration ratio of NH$_3$ to the sum of HNO$_3$ and HCl (11.3 ± 9.5) over the entire course of sampling, indicating that NH$_3$ was much more abundant than HNO$_3$ and HCl.

### 2.3.3. Effect of NH$_3$ on particle number concentrations

Nucleation of new particles frequently is observed in many locations throughout the world, even in the polluted atmosphere (e.g., Pittsburgh, St. Louis, Mexico City, Beijing, and the Po Valley) where the condensation sink is expected to be significant [Stanier et al., 2004; Hamed et al., 2007; Qian et al., 2007; Smith et al., 2008; Yue et al., 2010]. Aerosol nucleation and growth processes in coal-fired power plant plumes have been found to be great contributors to particle number concentrations near source regions [Brock et al., 2002]. In Rochester, New York, Wang et al. [2011] observed largely decreased particle number concentrations (over a size range of 10-500 nm) attributable to the shutdown of a nearby large coal-fired power plant. Stevens et al. [2012] incorporated the TOMAS aerosol microphysics module [Adams and Seinfeld, 2002; Pierce and Adams, 2009] into the SAM Large-Eddy Simulation/Cloud Resolving model [Khairoutdinov and Randall, 2003] (SAM-TOMAS) and simulated significant nucleation and growth in the plume of two power plants (including the Parish plant), in agreement with aircraft measurements. Using the SAM-TOMAS to simulate the changes in NO$_x$ and SO$_2$ emissions, Lonsdale et al. [2012] found enhanced particle nucleation and growth in the Parish plume as a result of the implementation of power plant emissions-control technologies (due to stronger NO$_x$ controls than SO$_2$ controls). In the present work we also used this model to investigate how the excess NH$_3$ observed at an urban sampling site (presumably from the Parish power plant) may affect the nucleation and growth of particles in the plume. The model
simulates the aerosol size distribution using 15 size bins segregated by dry mass per particle covering a size range from 3 nm to 10 µm and microphysical processes including coagulation, H₂SO₄ condensation, and nucleation [Stevens et al., 2012]. Modeled H₂SO₄ vapor formation depends on SO₂ and hydroxyl radical (OH) concentrations, and the OH concentrations in turn depend on the amount of sunlight and the NOₓ concentrations.

Ammonia is considered to be a potentially important participant in aerosol nucleation and formation [Kulmala et al., 2000; Birmili et al., 2003; Kirkby et al., 2011]. In order to evaluate the effects of NH₃ on particle number concentrations along the trajectory of power plant plumes, we hypothesize that elevated NH₃ levels originated from NH₃ slips at Parish, and we add NH₃ emissions from the plant to the SAM-TOMAS simulations, although relevant data from simultaneous measurements of particle number concentrations are not available as direct evidence for the 2010 campaign. Two ternary (H₂SO₄-H₂O-NH₃) nucleation schemes, Merikanto et al. [2006] and Napari et al. [2002] (which is scaled by a factor of 10⁻⁵ to better agree with observations [Westervelt et al., 2012]), are tested in SAM-TOMAS.

Figure 2.12 shows twelve simulations from SAM-TOMAS under various environmental conditions. It shows the number of new particles in the plume normalized by the SO₂ emitted as a function of the distance downwind from the plant. Both schemes were run with 900 ppt and 0 ppt NH₃ background mixing ratios. In addition, three different NH₃ emission scenarios (high: 0.012 kg/s; medium: 0.007 kg/s; low: 0.0012 kg/s) were employed and tested based on the calculated range of NH₃ emission factors (82,500 to 825,000 lb/yr) from Parish based on vendor-estimated slip values (1 to 10 ppm) [Electric Power Research Institute, 2009]. In all simulations, the number of new particles reaches a maximum near 10 km downwind; beyond this point, concentrations decrease because coagulation rates exceed nucleation rates. It can be seen that
NH$_3$ emissions are very important for new particle formation, especially in the simulations in which background NH$_3$ mixing ratios are low (i.e., the green and red lines show a large variation in nucleation between simulations with different NH$_3$ emission rates). When background NH$_3$ mixing ratios were larger, the simulated effect of NH$_3$ emissions on nucleation was more saturated and the predicted differences between NH$_3$ emission scenarios were smaller. Specifically, the fractional increases in particle concentrations between the low and high NH$_3$ emission simulations at 50 km downwind were 1.1 for Merikanto’s nucleation scheme with 900 ppt NH$_3$ background mixing ratio, 2.0 for Merikanto’s nucleation scheme with 0 ppt NH$_3$ background mixing ratio, 1.2 for Napari’s nucleation scheme with 900 ppt NH$_3$ background mixing ratio, and 2.5 for Napari’s nucleation scheme with 0 ppt NH$_3$ background mixing ratio, respectively. Larger NH$_3$ emissions accelerate aerosol nucleation in the simulations, as the system exhibits a high sensitivity to the amount of NH$_3$ slip, which emphasizes the significance of future NH$_3$ measurements in areas near power plants that utilize SCR. In addition, although Houston is currently in compliance with the mass-based PM$_{2.5}$ standards, efforts to characterize particle number concentration and size distribution synchronously with measurements of gaseous and particulate species are needed to better understand NH$_3$ impacts on both particle mass and number concentrations.
Figure 2.12 The modeled number of particles formed by nucleation in the Parish plume per SO$_2$ mass emitted as a function of the distance downwind from the Parish plant.
In order to further examine the link between atmospheric NH$_3$ and particle number concentration, simultaneous measurements of these two variables were conducted from 19 July 2012 to 21 August 2012 atop the North Moody Tower. Concurrent and significant increases in NH$_3$ mixing ratios and particle number concentrations were observed during some periods (an example of the episode on 11 August 2012 is shown in Figure 2.13), although SO$_2$ levels were relatively and consistently low likely due to the lack of air masses transported from the power plant region. However, this underscores the importance of NH$_3$ as a potential precursor of aerosol particles, even in a sulfur-poor atmosphere.

Figure 2.13 Hourly variations in particle number concentration, NH$_3$, and SO$_2$ on 11 August 2012.
Chapter 3

Atmospheric NH$_3$ measurements and implications for PM formation near Fort Worth, TX

3.1. Background

The U.S. EPA TRI highlights the importance of NH$_3$ as an air pollutant in urban communities nationwide [U.S. EPA, 2010]. Figure 3.1 (a) presents the total air releases (2.4 million pounds) by species in the DFW metropolitan area according to the TRI in 2010 [U.S. EPA, 2010]. It can be seen that NH$_3$ has the largest individual magnitude of emissions compared to other air wastes. According to the U.S. EPA NEI, agricultural and automobile activities are major contributors to gaseous NH$_3$ emissions. Figure 3.1 (b) summarizes the NEI NH$_3$ emissions (642.6 million pounds) by source categories specifically for all of Texas in 2008 and indicates that livestock waste and fertilizer application account for approximately 90% of the annual NH$_3$ emissions [U.S. EPA, 2008].
(a) Pie chart showing the following percentages:
- Ammonia: 27%
- n-Butyl alcohol: 7%
- 1,2,4-Trimethylbenzene: 7%
- Sulfuric acid: 7%
- Toluene: 6%
- Other: 46%

(b) Pie chart showing the following sources:
- Livestock waste: 62.9%
- Fertilizer application: 20.8%
- On-road gasoline light duty vehicles: 3.0%
- Prescribed fires: 2.4%
- Wildfires: 1.4%
- Electric generation: 1.1%
- Others: 2.4%
Measured atmospheric NH$_3$ levels in the DFW area remain ambiguous, and pertinent information is very scarce in the previous studies, even comprehensive field campaigns such as the TexAQS. The only published literature regarding ambient NH$_3$ sampling in the DFW area calculated the NH$_3$ emission factor from oak forests at Cooper Lake State Park in Delta County and predicted that domestic sources (e.g., dogs, cats, and humans) are predominant contributors to non-industrial NH$_3$ emissions in Dallas County (41%) and Tarrant County (45%) of the DFW area [Sarwar et al., 2005]. The NEI, by contrast, estimates that on-road gasoline light duty vehicles have the largest contribution among all source categories of NH$_3$ in Dallas County (52%) and Tarrant County (46%) [U.S. EPA, 2008]. This prominent discrepancy underscores the paucity of sufficient experimental data.

The DFW area, with a population of 6.4 million people, has experienced rapid economic growth. Nevertheless, air pollution problems threaten sustainable development [Grodach, 2011]. Therefore, relevant field investigations of the dynamics of gaseous NH$_3$ in this particular region are highly valuable and provide new insights into local and regional air quality, especially the impact of NH$_3$ on PM formation.
3.2. Methodology

3.2.1. Sampling site

A one-month campaign was conducted at the Eagle Mountain Lake continuous ambient monitoring station (CAMS 75) operated by TCEQ at 32°59’16”N and 97°28’37”W in TC. It is ~17 miles northwest of downtown Fort Worth and ~42 miles northwest of downtown Dallas. The CAMS is equipped with an automated gas chromatograph, O$_3$ and NO$_x$ analyzers, and meteorological instrumentation. Real-time monitoring has been active since 6 June 2000. The Texas National Guard manages the land, which is flat, has an elevation of 226 m above sea level, and is surrounded by shrubs, grasses, and trees.

NH$_3$ was measured as a complement to a summer project that focused primarily on the examination of O$_3$ formation mechanisms in the DFW area. All instruments except the MC/IC system were deployed in a climate-controlled trailer at ground level. The NH$_3$ sensor had an inlet height of ~2.5 m above the surface. This site is expected to be influenced by urban (e.g., regional transport from the city center), industrial (e.g., natural gas operations), and biogenic (e.g., vegetation) sources. The U.S. Department of Agriculture (USDA) Texas livestock inventory estimated 15,000 cattle in Tarrant County in 2011, and 57.8% of county land was classified as pasture in the 2007 Census of Agriculture [USDA, 2007, 2011]. Cows sometimes were observed near the site during the measurements. Figure 3.2 shows the sampling location as well as the nearby point sources of NH$_3$ specified in the U.S. EPA NEI and TRI. Point sources are associated with food manufacturing, chemical production, and electricity generation/distribution.
Figure 3.2 The location of the sampling site (black star, ~17 miles northwest of downtown Fort Worth) and six point sources (black dots) of NH$_3$ specified in the EPA NEI and TRI (point source 1: chemical production; 2: chemical production; 3: food manufacturing; 4: food manufacturing; 5: electricity station; 6: chemical production). The map includes the entire Tarrant County.

3.2.2. Gaseous species measurements

In this work, atmospheric NH$_3$ measurements were performed using the same optical technique that was employed previously during the Houston field campaign. The high sensitivity and selectivity allows effective capture of the fast-changing behaviors of NH$_3$. The sensor box and inlet were heated to ~38 °C, and a 1.7 m length of 13 mm (outside diameter) PTFE Teflon® tubing was used as the sampling line to minimize NH$_3$ adsorption. Auxiliary data of other important trace gases (e.g., CO, SO$_2$, NO$_x$, NO$_y$, HNO$_3$, soluble chloride (presumably HCl), and VOCs also were collected simultaneously. Detailed information about measurement techniques can be found in Table 3.1.
Table 3.1 Measurement techniques for gaseous species, planetary boundary layer (PBL) dynamics, and meteorological parameters.

<table>
<thead>
<tr>
<th>Species/parameter</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$</td>
<td>Daylight Solutions External Cavity Quantum Cascade Laser (Photo-acoustic Spectroscopy)</td>
</tr>
<tr>
<td>CO</td>
<td>Thermo Electron Corp. 48C Trace Level CO Analyzer (Gas Filter Correlation)</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>Thermo Electron Corp. 43C Trace Level SO$_2$ Analyzer (Pulsed Fluorescence)</td>
</tr>
<tr>
<td>NO$_x$</td>
<td>Thermo Electron Corp. 42C Trace Level NO-NO$_2$-NO$_x$ Analyzer (Chemiluminescence)</td>
</tr>
<tr>
<td>NO$_y$</td>
<td>Thermo Electron Corp. 42C-Y NO$_y$ Analyzer (Molybdenum Converter)</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>Mist Chamber coupled to Ion Chromatography (Dionex, Model CD20-1)</td>
</tr>
<tr>
<td>HCl</td>
<td>Mist Chamber coupled to Ion Chromatography (Dionex, Model CD20-1)</td>
</tr>
<tr>
<td>VOCs</td>
<td>IONICON Analytik Proton Transfer Reaction Mass Spectrometer and TCEQ Automated Gas Chromatograph</td>
</tr>
<tr>
<td>PBL height</td>
<td>Vaisala Ceilometer CL31 with updated firmware to work with Vaisala Boundary Layer View software</td>
</tr>
<tr>
<td>Temperature</td>
<td>Campbell Scientific HMP45C Platinum Resistance Thermometer</td>
</tr>
<tr>
<td>Wind speed</td>
<td>Campbell Scientific 05103 R. M. Young Wind Monitor</td>
</tr>
<tr>
<td>Wind direction</td>
<td>Campbell Scientific 05103 R. M. Young Wind Monitor</td>
</tr>
</tbody>
</table>
3.2.3. Aerosol species measurements

Mass concentration and chemical composition (e.g., \( \text{NH}_4^+ \), \( \text{SO}_4^{2-} \), and \( \text{NO}_3^- \)) of submicron particles (PM\(_1\)) were measured using an Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) at 15-minute intervals. In addition, particle number-based size distributions were monitored using a Scanning Electrical Mobility Spectrometer (SEMS) (BMI, Model 2002).

3.3. Results and Discussion

3.3.1. Gaseous \( \text{NH}_3 \) measurements

3.3.1.1. \( \text{NH}_3 \) mixing ratio profile

A time series of hourly-averaged \( \text{NH}_3 \) data over the entire campaign (30 May 2011 – 30 June 2011) is given in Figure 3.3. The gaps in the time series indicate sensor calibration and system resetting. The mixing ratios of \( \text{NH}_3 \) showed a large amount of variability, ranging from 0.1 to 10.1 ppb with a mean of 2.7 ± 1.7 ppb, comparable to the results observed at some other suburban sites [Ellis et al., 2011]. The statistics of the datasets for \( \text{NH}_3 \) as well as other measured gaseous species are listed in Table 3.2. Since no comparison can be made at this time due to the lack of \( \text{NH}_3 \) information in the DFW area in the literature, long-term continuous \( \text{NH}_3 \) monitoring in the future is necessary to explore inter-annual variation and seasonality of \( \text{NH}_3 \). The prominent variability on the hourly time scale also emphasizes the significance of the use of
high time-resolution instruments to measure NH₃, which is considerably affected by physical and chemical processes in the atmosphere.
Figure 3.3 Time series of mixing ratios of NH$_3$, SO$_2$, CO, HNO$_3$, HCl, NO$_x$, and NO$_y$ measured at the Eagle Mountain Lake site in the early summer of 2011.

Table 3.2 Statistics of gaseous species data collected during the measurement period (< DL indicates numbers below the detection limit).

<table>
<thead>
<tr>
<th></th>
<th>NH$_3$ (ppb)</th>
<th>CO (ppb)</th>
<th>NO$_x$ (ppb)</th>
<th>NO$_y$ (ppb)</th>
<th>SO$_2$ (ppb)</th>
<th>HNO$_3$ (ppt)</th>
<th>HCl (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>2.7</td>
<td>137.1</td>
<td>3.5</td>
<td>5.8</td>
<td>0.4</td>
<td>533.2</td>
<td>350.5</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>1.7</td>
<td>42.4</td>
<td>4.2</td>
<td>4.6</td>
<td>0.5</td>
<td>519.0</td>
<td>277.1</td>
</tr>
<tr>
<td>Maximum</td>
<td>10.1</td>
<td>359.7</td>
<td>28.5</td>
<td>31.6</td>
<td>6.8</td>
<td>5039.3</td>
<td>1883.6</td>
</tr>
<tr>
<td>Minimum</td>
<td>0.1 (&lt; DL)</td>
<td>75.9</td>
<td>0.5</td>
<td>1.1</td>
<td>0.01 (&lt; DL)</td>
<td>44.5</td>
<td>23.8</td>
</tr>
<tr>
<td>Median</td>
<td>2.4</td>
<td>127.5</td>
<td>1.9</td>
<td>4.3</td>
<td>0.3</td>
<td>376.8</td>
<td>283.8</td>
</tr>
<tr>
<td>10th Percentile</td>
<td>0.7</td>
<td>93.8</td>
<td>0.7</td>
<td>2.3</td>
<td>0.1</td>
<td>125.2</td>
<td>92.4</td>
</tr>
<tr>
<td>25th Percentile</td>
<td>1.5</td>
<td>106.2</td>
<td>1.0</td>
<td>3.0</td>
<td>0.2</td>
<td>210.4</td>
<td>153.0</td>
</tr>
<tr>
<td>75th Percentile</td>
<td>3.6</td>
<td>153.1</td>
<td>4.3</td>
<td>6.7</td>
<td>0.4</td>
<td>648.6</td>
<td>470.8</td>
</tr>
<tr>
<td>90th Percentile</td>
<td>5.1</td>
<td>197.9</td>
<td>8.5</td>
<td>11.3</td>
<td>0.8</td>
<td>1104.3</td>
<td>676.5</td>
</tr>
</tbody>
</table>
Moreover, NH₃ mixing ratios exhibited a near-log-normal distribution, illustrated in Figure 3.4 as a histogram. It is also noted that approximately 90% of observational values were between 0.7 and 7.5 ppb as shown in the inset of Figure 3.4, a cumulative probability distribution of NH₃ mixing ratios. NH₃ levels were relatively larger during the first week (4.3 ± 2.1 ppb) compared to other periods of the measurements (2.2 ± 1.4 ppb). This phenomenon was probably related to weaker air movement resulting from lower wind speed. Similarly, relatively higher levels of CO (173.0 ± 48.6 ppb) and NOₓ (5.4 ± 5.9 ppb) were observed during the first week compared to other periods of the measurements (125.6 ± 32.3 ppb and 2.9 ± 3.1 ppb, respectively), suggesting that stronger local fuel combustion sources might have influenced the site and contributed to the elevated mixing ratios of these air pollutants during the first week. Further discussion can be found in Section 3.3.1.4.
3.3.1.2. Diurnal variation

Figure 3.5 presents the diurnal profiles of NH$_3$ mixing ratios and ambient temperatures (the bottom whisker, box bottom, line inside the box, box top, and top whisker represent the 10th, 25th, 50th, 75th, and 90th percentiles of the data, and the continuous solid lines represent mean values, respectively). In general, NH$_3$ increased in the morning starting from 05:00 CST and peaked in the early afternoon between 14:00-15:00 CST, after which the levels decreased and remained relatively low during nighttime, presumably due to the decrease of sources. The
daytime behavior of NH$_3$ was likely associated with increasing temperatures (30.2 ± 4.2 °C) affecting temperature-dependent sources such as volatilization of animal waste and vegetation/soil through photosynthetic processes [Krupa, 2003; Mukhtar et al., 2009; Bash et al., 2010; Riddick et al., 2012]. This phenomenon is further illustrated by a strongly linear relationship (r=0.99) between bin-averaged NH$_3$ and temperature (12:00-16:00 CST) as shown in Figure 3.6. The dataset is grouped into 2°C intervals [bin: 30-32°C (n=6), 32-34°C (n=21), 34-36°C (n=55), 36-38°C (n=34), 38-40°C (n=9)] and the solid dots represent mean values of NH$_3$ and temperature in each bin.
Figure 3.5 Diurnal profiles of NH$_3$ mixing ratio and ambient temperature during the measurement period.
The dynamics of LIDAR-measured PBL heights were consistent from day to day over the entire campaign. The height remained low (~500 m) during nighttime, and the PBL did not break up until 07:00 CST, while NH$_3$ mixing ratios began to increase at 05:00 CST. Therefore, downward vertical mixing of NH$_3$ from the residual layer is ruled out as a contributing source of NH$_3$ in the morning.

Figure 3.7 summarizes the hourly-averaged data for NH$_3$, CO, SO$_2$, NO$_x$, HNO$_3$, and HCl, displaying distinctive characteristics and dynamics among species. As good indicators of
vehicular emissions, CO and NO\textsubscript{x} had similar trends, with levels that increased in the early morning (04:00-05:00 CST), reached maximum values at 06:00 CST, and dropped quickly and dramatically until second peaks occurred in the late afternoon (18:00-21:00 CST). The increases were a result of enhanced traffic volume during rush hour together with the lingering effect of a shallow nocturnal boundary layer (morning) or a developing nocturnal boundary layer (evening). However, none of these spikes were exactly coincident with temporal patterns of NH\textsubscript{3}. Motor vehicles were unlikely to have been major sources of NH\textsubscript{3} during the measurement periods, despite the fact that three-way catalytic converters have been found to be significant producers of NH\textsubscript{3} \cite{Shelef and McCabe, 2000; Heck and Farrauto, 2001; Kašpar et al., 2003; Heeb et al., 2006}. In the rural/suburban area of the present work, heavy-duty diesel trucks, which have minor contributions to NH\textsubscript{3} but emit tremendous amounts of NO\textsubscript{x}, account for a large fraction of traffic composition, as opposed to light-duty gasoline cars, which have the largest emission factors of NH\textsubscript{3} among all on-road vehicles \cite{Harley, 2009; Kean et al., 2009}. This is a likely explanation for these observations. Additionally, a cargo/freight rail near the site was not considered as a NH\textsubscript{3} source according to the NEI.
Sulfur dioxide mixing ratios did not change significantly during the daytime, but they became elevated at night, indicating that PBL dynamics played a vital role. Based on this profile, SO₂ likely was emitted from sources different than those of NH₃.

The changes in HNO₃ and HCl levels tracked one another closely. For both acidic trace gases, morning enhancements and mid-day peaks were observed. Nitric acid is primarily formed by oxidation of NOₓ in the atmosphere, and strong solar radiation facilitates photochemical processes. In this work, total photosynthetically available radiation (W m⁻²) reached maximum values at 12:00 CST. Hydrochloric acid is mainly produced by biomass burning/coal
combustion and the salt metathesis reaction between HNO$_3$ and sodium chloride. In addition, NH$_3$ was more abundant than HNO$_3$ and HCl. The average ratio of NH$_3$ to the summation of HNO$_3$ and HCl (calculated in units of $\mu$mol m$^{-3}$) during the measurements was $4.1 \pm 4.0$. Larger ratios (>10) sometimes were observed when higher NH$_3$ levels and significantly lower HNO$_3$ and HCl levels were present in the early morning (06:00-07:00 CST) as shown in Figure 3.8. Some removal mechanisms and/or processes other than gas-phase chemistry may govern the concentration levels of these acidic gases.

![Figure 3.8](image-url)  

**Figure 3.8** A time series of the molar concentration ratio of NH$_3$ to the sum of HNO$_3$ and HCl.
Remarkable differences in behavior exist between rural/suburban- and urban-scale NH$_3$ measurements. For example, at a near-downtown Houston site, a sharp decrease in NH$_3$ was observed around mid-day when the ratio of NO$_x$ to NO$_y$, as an indicator of the photochemical age of air masses or plumes, also reached the minimum value. By contrast, no such phenomenon occurred in the present work in which NH$_3$ mixing ratios continuously increased through the early afternoon (14:00-15:00 CST). Although HNO$_3$ and HCl peaked at mid-day, increased emissions from temperature-dependent sources under the most intense sunlight at noon might significantly replenish NH$_3$ and outweigh any loss mechanisms.

### 3.3.1.3. Weekday-weekend and daytime-nighttime behaviors

As will be shown in the next section, the winds uniformly emanated from the southeast sector throughout the campaign, offering little variability in source regions. In this section we consider variability arising from weekday-weekend and daytime-nighttime differences. Here, daytime and nighttime are consistently defined as periods of 06:00-19:00 CST and 19:00-06:00 CST, respectively. Table 3.3 summarizes the Pearson’s correlation coefficients between NH$_3$ and other traces gases during different time periods. The coefficient between NH$_3$ and CO was significantly larger on Sundays (0.61) than on weekdays (0.08) and Saturdays (0.10), but there was no statistically meaningful difference between daytime and nighttime. There was a significant increase in traffic volume due to human activities on Sundays because of a large church very close to the site. It is known that gasoline engines emit ~10 times more CO compared to diesel engines [Fairbanks, 1997]. Also as discussed above, gasoline-powered cars have much larger emission rates of NH$_3$ than other vehicles. The combined effects were likely
responsible for the observation, suggesting that automobiles might be contributing NH$_3$ on Sundays when the maximal mixing ratio of CO also occurred.

**Table 3.3 Pearson's correlation coefficients (r) between NH$_3$ and other air pollutants during different measurement periods.**

<table>
<thead>
<tr>
<th></th>
<th>Weekday</th>
<th>Saturday</th>
<th>Sunday</th>
<th>Daytime</th>
<th>Nighttime</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$ vs. CO</td>
<td>0.08</td>
<td>0.10</td>
<td>0.61</td>
<td>0.32</td>
<td>0.41</td>
</tr>
<tr>
<td>NH$_3$ vs. NO$_x$</td>
<td>0.10</td>
<td>0.09</td>
<td>0.42</td>
<td>0.10</td>
<td>0.26</td>
</tr>
<tr>
<td>NH$_3$ vs. NO$_y$</td>
<td>0.09</td>
<td>0.08</td>
<td>0.56</td>
<td>0.20</td>
<td>0.26</td>
</tr>
<tr>
<td>NH$_3$ vs. NO$_z$</td>
<td>0.02</td>
<td>0.12</td>
<td>0.62</td>
<td>0.09</td>
<td>0.11</td>
</tr>
<tr>
<td>NH$_3$ vs. SO$_2$</td>
<td>0.06</td>
<td>0.03</td>
<td>0.20</td>
<td>0.12</td>
<td>0.10</td>
</tr>
<tr>
<td>NH$_3$ vs. HNO$_3$</td>
<td>0.05</td>
<td>0.11</td>
<td>0.67</td>
<td>0.11</td>
<td>0.12</td>
</tr>
<tr>
<td>NH$_3$ vs. HCl</td>
<td>0.47</td>
<td>0.36</td>
<td>0.20</td>
<td>0.18</td>
<td>0.08</td>
</tr>
</tbody>
</table>

The weak relationships between NH$_3$ and SO$_2$ were consistent during all periods, while the correlation coefficients between NH$_3$ and NO$_x$, NO$_y$, NO$_z$ (=NO$_y$-NO$_x$), and HNO$_3$ displayed a similar trend for that of NH$_3$ versus CO, indicating stronger relationships on Sundays. This is probably due to the co-emission of NH$_3$ and NO$_x$ from motor vehicles and subsequent rapid oxidation of NO$_x$ via photochemical processes. The relationship between NH$_3$ and HCl was slightly stronger on weekdays than weekends, though the reason for this remains unclear. HNO$_3$ and HCl have similar diurnal variations as shown in Figure 3.7, but the correlation coefficient
between the two species is only 0.09 using the entire dataset. It is also noted that the good relationship between HNO$_3$ and HCl was observed within nearly any given day, but it is not the case after combining several different days. The contribution from different source regions was eliminated as a plausible reason for this phenomenon because the wind direction was relatively consistent during the measurement period. The algorithm used in the regression analysis can not solve the HNO$_3$-HCl puzzle and can not explain the large discrepancy between NH$_3$-HNO$_3$ and NH$_3$-HCl correlations.

### 3.3.1.4. Source attribution

During the one-month campaign, the wind mainly blew from the southeast sector at the site, illustrated by Figure 3.9. Because of this relative consistency, almost no information about the dependence of NH$_3$ on wind direction can be drawn. There are six specific point sources of NH$_3$ in the study region listed in the NEI and TRI. Most of the time, the site was downwind of these sources. As shown in Figure 3.2, they are in the range of ~13 to ~22 miles southeast of the site. Given an average wind speed of 12 miles per hour, emissions events at those facilities could possibly affect measured NH$_3$ mixing ratios at the site within one to two hours.
Besides industry, agriculture, especially livestock-related activities, is an additional potential contributor to NH$_3$. A review paper reported average emission factors of NH$_3$ for dairy farms (59 g milk cow$^{-1}$ day$^{-1}$) and beef feedlots (119 g beef cow$^{-1}$ day$^{-1}$) using data from forty relevant studies in North America and Europe [Hristov et al., 2011]. Based on the cattle population in Tarrant County, the estimated emissions of NH$_3$ from cows are about 1.3 tons day$^{-1}$. 

Figure 3.9 Wind direction distributions over the entire campaign.
However, the tracks from animals (not only cattle but also deer and other wildlife) near the site could not be documented. Hence, it is hard to pinpoint the accurate source location and to evaluate quantitatively these effects with respect to observed values.

Natural emissions of NH$_3$ from vegetation and soil have been found to be important, and they often increase as ambient temperatures increase [Robarge et al., 2002; Sutton et al., 2009]. Forests emit NH$_3$ more strongly than grassland and shrub land [Battye et al., 2003]. Simultaneous measurements of NH$_3$ fluxes in the future are desirable to better understand the NH$_3$ exchange between plants, soil, and atmosphere and to better quantify the related contributions from biogenic sources. Based on the emission factors in the literature and geographic/geological information in Tarrant County, the estimated emissions of NH$_3$ from soils and vegetation are about 0.15 ton day$^{-1}$ [Texas Parks & Wildlife Department, 1984; Bureau of Economic Geology, 2000; Battye et al., 2003].

Air masses rarely were transported from the south-southwest (occurrence frequency = 2.3%) so infrequently passed over Eagle Mountain Lake (~0.5 mile from the site). It is known that NH$_3$ has a relatively large Henry’s law constant. Thus, the occasional plumes coming in that direction over the water body were associated with smaller NH$_3$ levels. There are likely fewer animals (especially cows) and less vegetation along the lake area than in the pastures close to the site. In addition, fewer industrial activities in the southwest region might cause relatively lower NH$_3$ levels. Specifically, the mean NH$_3$ mixing ratio was 2.0 ppb (a decrease of ~26% compared to the campaign-average value of 2.7 ppb) when the wind blew from that sector.

The EPA PMF 3.0 model was used to conduct source attribution in which NH$_3$ and ancillary data for other gaseous species (e.g., VOCs including ~40 compounds) were employed
as inputs [Paatero and Tapper, 1994; Paatero, 1997]. In addition to a concentration file, an uncertainty file associated with the collected samples/data was used, which can be derived based on the user guide. PMF requires the user to have a general understanding of the dataset (e.g., potential sources influencing the study region) and to choose the number of source categories or factors. It also allows the user to examine the initial assumption for factors according to the base run results and make the relevant model reconstruction if needed. In this work, a four-factor solution was found including biogenic (isoprene/monoterpene), natural gas/industry (ethane/ethylene/propane/propylene), heavy duty motor vehicle (n-decane), and light duty motor vehicle (o-xylene/toluene) sources. These were identified using dominant or key species accordingly, while other measured trace gases and VOCs were also fed into the model. The simulation results explicitly show that biogenic (74.1%) is the largest source category of NH$_3$, followed by light duty vehicles (12.1%), natural gas/industry (9.4%), and heavy duty vehicles (4.4%). As unique chemical signatures of biogenic emissions, isoprene and monoterpene as well as the non-indicator NH$_3$, were predominantly apportioned to this particular factor resolved by PMF. A preliminary analysis for the biogenic sector implies that livestock might account for approximately 66.4% of total NH$_3$ emissions in the present work, assuming that biogenic source category mainly consists of soil, plants, and animals (especially cows). This upper bound estimate is calculated by multiplying the entire contribution from the biogenic source category (74.1%) by the estimated proportion of cows in biogenic emissions derived from previously estimated emission rates of cows (1.3 tons day$^{-1}$) and soils and vegetation (0.15 tons day$^{-1}$). Future work with updated species categorization and additional exploration of sources in the area is needed to improve the constraints in the model. In addition, long-term datasets are required in
PMF to investigate the aggregate contributions (e.g., yearly and seasonal contributions) from different factors.

PMF also was used to examine the observation of higher NH$_3$ levels during the first week of the campaign only. The simulation results clearly show that the relative contributions from industry increase from 9.4% to 18.9% using the dataset only covering that period. This prominent change is likely due to the enhanced tracers of industry. For example, elevated levels of ethane (9.48 ± 9.22 ppb), ethylene (0.27 ± 0.21 ppb), propane (3.47 ± 3.40 ppb), and propylene (0.15 ± 0.09 ppb) were measured during the first week compared to other periods of the measurements (4.76 ± 4.32 ppb, 0.15 ± 0.09 ppb, 1.96 ± 1.75 ppb, and 0.09 ± 0.04 ppb, respectively). This suggests that local industrial activities have potentially significant influences on atmospheric NH$_3$ mixing ratios in the study region. Improved NH$_3$ emission inventories with better documentation and monitoring of anthropogenic sources (especially industry) are also needed.

3.3.2. Effect of NH$_3$ on PM formation

The gas-particle partitioning and salt formation of NH$_3$ has been investigated recently in some urban and suburban areas throughout the world. In the South Coast Air Basin of California, Nowak et al. [2012] concluded based on aircraft measurements that NH$_3$ emitted from dairy facilities and automobiles lead to thermodynamically favorable conditions for NH$_4$NO$_3$ formation. In the Great Lakes region, Stanier et al. [2012] noted that wintertime air pollution episodes were characterized by large contributions of NH$_4$NO$_3$ to PM under low temperature, high relative humidity, and air mass stagnation conditions that facilitated NH$_3$ and HNO$_3$
contribution to aerosols. In Ontario, Ellis et al. [2011] observed that NH$_3$ was efficiently converted to particulate NH$_4^+$ in the presence of high levels of SO$_4^{2-}$, which subsequently triggered NH$_3$ release from the surface due to bi-directional flux. In Beijing, Meng et al. [2011] reported that NH$_3$ was closely correlated with NH$_4^+$, that NH$_4^+$ primarily existed as (NH$_4$)$_2$SO$_4$ in summer, and that both (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ were major forms of particulate NH$_4^+$ in winter. In Shanghai, Du et al. [2010] found that NH$_4$NO$_3$ and NH$_4$Cl were present in sampled PM$_{2.5}$ ($d_p < 2.5$ µm) and PM$_{10}$ ($d_p < 10$ µm), indicating that NH$_3$ is a vital precursor of aerosol particles in the polluted atmosphere. In Barcelona, Pandolfi et al. [2012] attributed the low gas fraction of NH$_3$, defined as the molar concentration ratio of gaseous NH$_3$ to total NH$_3$ (the sum of NH$_3$ and NH$_4^+$), to dramatic secondary formation of sulfate, suggesting that the evolution of NH$_3$ concentrations is subject considerably to gas-particle partitioning.

However, the evaluation of the impact of NH$_3$ on local and regional air quality with respect to PM formation in the DFW area is far from complete. In this work conducted near Fort Worth, the mixing ratios of NH$_3$ and primary acidic trace gases were fully examined, the mass concentrations of aerosol components such as NH$_4^+$ in PM$_1$ were systematically explored, and the size distributions of fine particles were simultaneously determined, consequently improving the present understanding of the gas-particle partitioning of NH$_3$ in the study region.

### 3.3.2.1. Temporal and diurnal variations of aerosol species

Figure 3.10 shows time series of hourly-averaged HR-ToF-AMS data along with meteorological parameters during the aerosol measurements (9 June 2011 – 30 June 2011). The statistics of the dataset for inorganic aerosol components are listed in Table 3.4. Their mass
concentrations displayed a large amount of variability. Sulfate (overall average ± one standard deviation, 1.25 ± 0.66 µg m\(^{-3}\)) accounted for 28% of total PM\(_1\) mass, which ranged from 1.32 to 14.70 µg m\(^{-3}\) with a mean of 4.41 ± 2.31 µg m\(^{-3}\). The highest pollution level occurred around midnight on 23 June, when the largest spike of SO\(_4^{2-}\) was observed under low wind speed conditions. Ammonium (0.44 ± 0.24 µg m\(^{-3}\)) tracked closely with SO\(_4^{2-}\), indicating that NH\(_4^+\) was likely formed through the neutralization of H\(_2\)SO\(_4\) by NH\(_3\). Nitrate (0.12 ± 0.11 µg m\(^{-3}\)) did not change significantly, except during periods when gas-phase HNO\(_3\) also was substantially available, suggesting that NO\(_3^-\) might be formed primarily through gas-particle conversion. In addition, as important environmental variables for PM formation, temperature (30.15 ± 4.12 °C) and RH (47.17±16.84 %) were continuously recorded, and their effects are discussed in detail in the following sections. Wind mainly blew from southeast and south-southeast (70%) throughout the measurements, and wind speed (8.18 ± 1.37 m s\(^{-1}\)) reached up to 12.51 m s\(^{-1}\) in the middle of the campaign.
Figure 3.10 Time series of hourly-averaged HR-ToF-AMS data along with meteorological parameters during the study period (9 June 2011 – 30 June 2011).
Table 3.4 Statistics of inorganic aerosol components in PM1 (μg m$^{-3}$) collected during the measurement period.

<table>
<thead>
<tr>
<th></th>
<th>SO$_4^{2-}$</th>
<th>NO$_3^-$</th>
<th>NH$_4^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>1.25</td>
<td>0.12</td>
<td>0.44</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.66</td>
<td>0.11</td>
<td>0.24</td>
</tr>
<tr>
<td>Maximum</td>
<td>5.84</td>
<td>0.84</td>
<td>2.03</td>
</tr>
<tr>
<td>Minimum</td>
<td>0.20</td>
<td>0.03</td>
<td>0.06</td>
</tr>
<tr>
<td>Median</td>
<td>1.09</td>
<td>0.09</td>
<td>0.39</td>
</tr>
<tr>
<td>10th Percentile</td>
<td>0.62</td>
<td>0.06</td>
<td>0.21</td>
</tr>
<tr>
<td>25th Percentile</td>
<td>0.81</td>
<td>0.07</td>
<td>0.27</td>
</tr>
<tr>
<td>75th Percentile</td>
<td>1.57</td>
<td>0.13</td>
<td>0.56</td>
</tr>
<tr>
<td>90th Percentile</td>
<td>2.09</td>
<td>0.19</td>
<td>0.74</td>
</tr>
</tbody>
</table>

Figures 3.11 (a), (b), and (c) illustrate the diurnal profiles of inorganic aerosol species in PM$_1$ based on the HR-ToF-AMS data. The bottom whisker, box bottom, line inside the box, box top, and top whisker represent the 10th, 25th, 50th, 75th, and 90th percentiles of the data, respectively, and the continuous solid lines represent mean values, respectively. In general, it can be seen that NH$_4^+$ increased in the morning and evening, with a greater magnitude in the enhancement during the later period. The behavior of SO$_4^{2-}$ was very similar to NH$_4^+$, indicating the probable presence of (NH$_4$)$_2$SO$_4$ and/or NH$_4$HSO$_4$. Nitrate began to decrease at 05:00 CST and remained relatively low during daytime but was elevated in the evening and tended to be relatively constant during nighttime. LIDAR-measured PBL height (not shown here) started to
increase at 07:00 CST and reached the maximum value (2000 m) around 17:00 CST, after which it rapidly decreased and remained as low as 500 m at night. It is likely that the dynamics of PBL affected the trend of aerosol species in the evening when their concentration levels rose in a developing nocturnal PBL.
3.3.2.2. Ammonium salt formation

Figure 3.12 presents scatter plots of [NH$_4^+$] versus [NO$_3^-$], [SO$_4^{2-}$] (to prevent overlap in the figure, 2[SO$_4^{2-}$] is not adopted here), and [NO$_3^-$] + 2[SO$_4^{2-}$] (all in units of µmol m$^{-3}$). The regression yields a strongly linear relationship between NH$_4^+$ and SO$_4^{2-}$ with a Pearson’s correlation coefficient (r) of 0.98, and the slope (0.52) of the regression line implies that NH$_4^+$ mainly existed as (NH$_4$)$_2$SO$_4$. This is further confirmed by a mean equivalent ratio (i.e. [NH$_4^+$]/2[SO$_4^{2-}$]) of 0.94. By contrast, no such good relationship exists between NH$_4^+$ and NO$_3^-$ (r=0.41). In addition, the near-unit slope (1.09) of the regression line between [NH$_4^+$] and [NO$_3^-$] + 2[SO$_4^{2-}$] suggests that ambient aerosols were nearly neutral.
Figure 3.12 Scatter plots of $[\text{NH}_4^+]$ versus $[\text{NO}_3^-]$, $[\text{SO}_4^{2-}]$, and $[\text{NO}_3^-] + 2[\text{SO}_4^{2-}]$ (in units of $\mu$mol m$^{-3}$) during sampling periods.

In order to investigate the formation of NH$_4$NO$_3$ and NH$_4$Cl, theoretical calculations of thermodynamic equilibrium for the chemical reactions between NH$_3$ and HNO$_3$ or HCl were performed. When ambient RH is lower than deliquescence relative humidity (DRH), NH$_4$NO$_3$ and NH$_4$Cl are solids at equilibrium, and the equilibrium constants can be estimated empirically [Stelson and Seinfeld, 1982a; Pio and Harrison, 1987].
\[
K_{\text{NH}_4\text{NO}_3} = \exp[84.6 - 24220/T - 6.1\ln(T/298)]
\]  

\[
K_{\text{NH}_4\text{Cl}} = \exp[2.2358\ln T - 2.13204 \times 10^{4} T^{-1} + 65.437516 - 8.167 \times 10^{-3} T + 4.64383 \times 10^{-7} T^2 - 1.10475 \times 10^{-10} T^3]
\]  

where \(K_i\) is the equilibrium constant for salt \(i\) and \(T\) is temperature in Kelvin.

The DRH for \(\text{NH}_4\text{NO}_3\) and \(\text{NH}_4\text{Cl}\) can be determined as follows [Pio and Harrison, 1987; Seinfeld and Pandis, 2006]

\[
(\text{DRH})_{\text{NH}_4\text{NO}_3} = \exp[1.6954 + 723.7/T]
\]

\[
(\text{DRH})_{\text{NH}_4\text{Cl}} = 137.13 - 0.2T
\]

When ambient RH is higher than DRH, \(\text{NH}_4\text{NO}_3\) and \(\text{NH}_4\text{Cl}\) take water up and exist in the aqueous phase. In this work, RH is below DRH during the majority of the measurement period. Figure 3.13 (a) presents the theoretically calculated equilibrium constant for solid \(\text{NH}_4\text{NO}_3\) (solid line) based on equation (3) and partial pressure product \(P_{\text{NH}_3}P_{\text{HNO}_3}\) as a function of ambient temperature under RH<DRH conditions. On the \(x\) axis, \(1000/T\) values vary between 3.20 and 3.36 K\(^{-1}\), corresponding to a range of 24.47 to 39.35 °C. The equilibrium constant is very sensitive to the ambient temperature, changing over two orders of magnitude. It is noted that the \(P_{\text{NH}_3}P_{\text{HNO}_3}\) calculated using measured mixing ratios of \(\text{NH}_3\) and \(\text{HNO}_3\) is always smaller than \(K_{\text{NH}_4\text{NO}_3}\). Therefore, the thermodynamic condition is not favorable for \(\text{NH}_4\text{NO}_3\) formation, and solid \(\text{NH}_4\text{NO}_3\) is not expected to be formed. During those periods, measured \(\text{NO}_3^-\) concentrations remained relatively low and did not change significantly.
\[ \text{[NH}_3\text{][HNO}_3\text{]} \text{ (ppb)} \]

\[ \text{[NH}_3\text{][HCl}\text{]} \text{ (ppb)} \]

\[ K_{\text{NH}_4\text{NO}_3} \]

\[ K_{\text{NH}_4\text{Cl}} \]

1000/T (K\text{ }^{-1})
Figure 3.13 Theoretically calculated equilibrium constant (solid line) as a function of ambient temperature under RH<DRH conditions for (a) solid NH₄NO₃ based on $K_{\text{NH4NO3}}=\exp[84.6-24220/T-6.1\ln(T/298)]$ and partial pressure product $P_{\text{NH3PNO3}}$ (black dots); and (b) solid NH₄Cl based on $K_{\text{NH4Cl}}=\exp[2.2358\ln T-2.13204*10^4 T^{-1}+65.437516-8.167*10^{-3} T+4.64383*10^{-7} T^2-1.10475*10^{-10} T^3]$ and partial pressure product $P_{\text{NH3PHCl}}$ (black dots).

By contrast, when RH is above DRH, increased levels of NO₃⁻ were often observed. The equilibrium value of $[\text{NH}_3][\text{HNO}_3]$ over a solution decreases swiftly with RH [Seinfeld and Pandis, 2006]. Hence, the dissolution of NH₃ and HNO₃ in the deliquescent aerosols might be one of the likely explanations for this phenomenon. Figure 3.14 illustrates that NO₃⁻ concentrations were relatively elevated at high RH and that there was a poor overall relationship ($r=0.32$) between NO₃⁻ and SO₄²⁻ during the entire study period, probably influenced by the frequent absence of NH₄NO₃ formation due to high temperatures and inadequate NH₃ and/or HNO₃ in the gas phase. However, it is known that $K_{\text{NH4NO3}}$ decreases as aerosols deliquesce and the ionic strength of NH₄NO₃ decreases [Stelson, 1982]. As a consequence, the abundance of NH₃ and HNO₃ in the atmosphere required for NH₄NO₃ formation decreases. The new equilibrium constant $K_{\text{NH4NO3}}^*$ can be derived by multiplying $K_{\text{NH4NO3}}$ by the NH₄NO₃ ionic strength fraction (Y) which is expressed by $Y=[\text{NH}_4\text{NO}_3]/([\text{NH}_4\text{NO}_3]+3[(\text{NH}_4)_2\text{SO}_4])$ [Stelson and Seinfeld, 1982b]. In the NH₄⁺/NO₃⁻/SO₄²⁻ mixture, additional (NH₄)₂SO₄ reduces the equilibrium constant, makes the aqueous system a more favorable medium for NH₄NO₃ formation, and shifts the thermodynamic equilibrium toward the aerosol phase.
Figure 3.14 Scatter plot of [NO$_3^-$] versus [SO$_4^{2-}$] (in units of μg m$^{-3}$) color-coded by RH over the entire campaign.

For example, during a high RH (75.24 ± 10.63 %) period between the evening of 22 June and the morning of 23 June, RH was well above DRH. Nitrate reached the maximum value (0.84 μg m$^{-3}$) over the entire campaign, and the mean value during this time was 0.64 μg m$^{-3}$ (~5 times larger than the campaign-average value of 0.12 μg m$^{-3}$). The Pearson’s correlation coefficient between NO$_3^-$ and SO$_4^{2-}$ during this period was 0.55 (an increase of ~70% compared to the campaign-wide r value of 0.32), indicating that NH$_4$NO$_3$ might be formed on the moist surface of pre-existing sulfate aerosols. Additionally, regression yields a good relationship between NO$_3^-$ and particle surface area concentration measured by SEMS (r=0.71), indicating potential nitrate formation through heterogeneous conversion on particle surfaces. Similarly,
during another high RH (72.66 ± 6.56 %) period between the evening of 23 June and the morning of 24 June, NO$_3^-$ increased to 0.54 µg m$^{-3}$ and was strongly correlated with SO$_4^{2-}$ (r=0.93). This further demonstrates that co-existence of SO$_4^{2-}$ in the deliquescent aerosols favors aqueous NH$_4$NO$_3$ formation.

In Shanghai, Pathak et al. [2009] attributed high NO$_3^-$ levels to the nighttime heterogeneous hydrolysis of dinitrogen pentoxide on the surface of SO$_4^{2-}$ aerosols in an NH$_3$-deficient atmosphere. In Beijing, Ianniello et al. [2011] observed a strong relationship between NO$_3^-$ and SO$_4^{2-}$ (r=0.89) at high RH and estimated an average Y value of 0.2 with elevated NO$_3^-$ concentrations during summertime. In Guangzhou, Hu et al. [2008] found that when RH is above DRH, $P_{NH_3P_{HNO_3}}$ is larger than the calculated $K_{NH_4NO_3}^*$ and suggested that NH$_4$NO$_3$ formation is possible. All these studies interpreted the observations as nitrate being produced on the wet surface of pre-existing sulfate aerosols, underscoring the conclusion that the same process is important in this study area.

Measured particle number size distributions, given in Figure 3.15, display a growth in particle size between the evening of 23 June and the morning of 24 June, implying that NH$_3$ participated in an aerosol nucleation and growth event as a result of the formation of aqueous NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$ during that humid period. Meanwhile, both NH$_4^+$ and SO$_4^{2-}$ reached their maximum values (2.03 µg m$^{-3}$ and 5.84 µg m$^{-3}$, respectively) over the entire campaign, and the mean event values were 1.42 µg m$^{-3}$ (~three times larger than the campaign-average value of 0.44 µg m$^{-3}$ for NH$_4^+$) and 3.99 µg m$^{-3}$ (~three times larger than the campaign-average value of 1.25 µg m$^{-3}$ for SO$_4^{2-}$), respectively. Highly efficient gas-particle conversion contributed significantly to this specific pollution episode characterized by the highest PM$_1$ level observed in this work. Figure 3.16 shows a large increase in the size-resolved particle number concentration
during the event compared to the campaign-average size distribution. It can be seen that smaller particles ($d_p < 250$ nm) were major contributors to the episode. The ternary plot of NH$_4^+$, NO$_3^-$, and SO$_4^{2-}$ indicates the higher relative NO$_3^-$ fraction at higher RH given in Figure 3.17 (percentage of concentrations in $\mu$eq m$^{-3}$). The proportion of NO$_3^-$ in the inorganic components of PM$_1$ increased up to 21% compared with the campaign-average value of 4% probably due to aqueous NH$_4$NO$_3$ formation.
Figure 3.15 Contour plot of particle number size distribution between 23 and 25 June.
Figure 3.16 Size-resolved particle number concentration during the entire campaign and during the aerosol nucleation and growth event.
Figure 3.17 Ternary plot of $\text{NH}_4^+$, $\text{NO}_3^-$, and $\text{SO}_4^{2-}$ during the campaign.
Figure 3.13 (b) shows the theoretically calculated equilibrium constant for solid NH₄Cl (solid line) based on equation (4) and the partial pressure product $P_{NH_3}P_{HCl}$ as a function of ambient temperature under RH<DRH conditions. It can be seen that $P_{NH_3}P_{HCl}$ calculated using measured mixing ratios of NH₃ and HCl is always smaller than $K_{NH_4Cl}$. Therefore, the thermodynamic conditions are not favorable for NH₄Cl formation, and solid NH₄Cl is not expected to be formed at equilibrium, as with NH₄NO₃. Nevertheless, detailed investigations about the formation of solid and/or aqueous NH₄Cl are impeded by the unavailability of particulate Cl⁻ data because Cl⁻ levels were at or near the detection levels of the HR-ToF-AMS and other high time-resolution instrumentation.

In the present work, the average gas fraction of NH₃ ($=NH_3/(NH_3+NH_4^+)$) is 0.74 ± 0.18, indicating that NH₃ remained predominantly in the gas phase rather than the aerosol phase. Additionally, the HNO₃ gas fraction ($=HNO_3/(HNO_3+NO_3^-)$), with a mean of 0.86 ± 0.10, reflects the lack of nitrate aerosol formation during most of the study period. High temperatures (30.15 ± 4.12 °C) favored the evaporation of volatile ammonium salts (e.g., NH₄NO₃ and NH₄Cl) and shifted the thermodynamic equilibrium toward the gas phase. Similar observations have been reported by other studies. Robarge et al. [2002] estimated an average gas fraction higher than 0.8 for NH₃ in summer at an agricultural site in the Coastal Plain region of North Carolina. Saylor et al. [2010] found much greater NH₃ levels compared to NH₄⁺ in PM$_{2.5}$ in a rural area near Atlanta, leading to a mean NH₃ gas fraction of 0.89. Baek and Aneja [2004] measured ammonium-poor (1.64 ± 1.26 µg m$^{-3}$) aerosols in eastern North Carolina, while NH₃ (17.89 ± 15.03 µg m$^{-3}$) was abundant in the gas phase.

Ammonia preferentially reacts with H₂SO₄ in the atmosphere, and if extra NH₃ is available after the neutralization process, HNO₃ and HCl will further react with it. Here, excess
NH$_4^+$ is defined as [NH$_4^+$]-2[SO$_4^{2-}$] (in units of µmol m$^{-3}$). Figure 3.18 is an example of the relationship between excess NH$_4^+$ and NO$_3^-$ during the event described previously. The slope (0.84) of the regression line and a Pearson’s correlation coefficient of 0.94 suggest that NH$_4$NO$_3$ was formed. Analogously, Du et al. [2010] observed that the slope of the regression function between non-sulfate NH$_4^+$ and NO$_3^-$ was 0.88 in the early summer at an urban site in Shanghai. The slope was further improved to 0.98 when Cl$^-$ was included in the calculation. Thus, sufficient availability of NH$_3$ in the gas phase is indispensable for the complete neutralization of H$_2$SO$_4$ and for an environmental condition favoring HNO$_3$ partitioning into the aerosol phase.
Figure 3.18 Scatter plot of excess [NH$_4^+$] versus [NO$_3^-$] during the aerosol nucleation and growth event.
Chapter 4

Conclusions

4.1. Major findings

4.1.1. Houston field campaign

Real-time and continuous measurements of atmospheric NH$_3$ were conducted atop the North Moody Tower during two sampling periods in 2010. NH$_3$ mixing ratios ranged from 0.1 to 8.7 ppb with a mean of 2.4±1.2 ppb in winter and ranged from 0.2 to 27.1 ppb with a mean of 3.1±2.9 ppb in summer. The results showed apparent seasonal variations, with elevated levels in summer compared to winter. Vehicular emissions were found to be major contributors to the morning rise in the diurnal profile of NH$_3$ mixing ratios in winter. There was no correlation between NH$_3$ and primary combustion pollutants such as CO, NO$_x$, and NO$_y$ during morning rush hours in summer, which might be attributed to changes in catalytic converter performance as a function of ambient temperature and influences by some other local or regional sources of NH$_3$. There was a large amount of variability in atmospheric NH$_3$ mixing ratios observed at our
sampling site, particularly in summer. Notable spikes were associated with transport from a coal-fired power plant, a chemical fire on an adjacent highway as a result of the crash of a tanker carrying agricultural chemicals, transport from the heavily industrialized HSC, transport from the Gulf of Mexico during Hurricane Hermine, and other potential ambient sources. The large weekday-weekend differences in NH$_3$ mixing ratios are likely due to more industrial activities between Monday and Friday, presumably in the HSC area, which has been shown to be a predominant emission source of NH$_3$. Unfortunately, source attribution is confounded by factors such as boundary layer dynamics, meteorology, and the lack of sufficient emission inventory data.

In addition, simultaneous measurements of gaseous and aerosol species were made in early August of 2010. Elevated NH$_3$ levels were synchronous with enhancements in NH$_4^+$ and SO$_4^{2-}$ around mid-day, indicating the contribution of atmospheric NH$_3$ to particle mass concentrations. NH$_4^+$ existed in the form of (NH$_4$)$_2$SO$_4$ and NH$_4$HSO$_4$; however, the formation of NH$_4$NO$_3$ and NH$_4$Cl was not observed during the study period likely due to high ambient temperatures. Increased particle number concentrations were predicted by the SAM-TOMAS model downwind of a large coal-fired power plant when NH$_3$ emissions based on these measurements were included; observations indicate that NH$_3$ could be important in determining particle number concentrations, even without the presence of large amounts of sulfur. This study shows the significant effects of NH$_3$ on PM formation in the polluted Houston atmosphere, suggesting the importance and necessity of long-term or routine monitoring of aerosol precursors in the future.
4.1.2. DFW field campaign

Atmospheric NH\textsubscript{3} measurements were made northwest of Fort Worth in the early summer of 2011. Ammonia mixing ratios showed a large amount of variability, ranging from 0.1 to 10.1 ppb with a mean of 2.7 ± 1.7 ppb. A daytime increase was observed in the diurnal profile of NH\textsubscript{3}, likely due to increasing temperatures affecting temperature-dependent sources (e.g., volatilization of animal waste and vegetation). A moderate correlation (r = 0.61) between NH\textsubscript{3} and CO was found on Sundays, indicating that motor vehicles might be potential sources of NH\textsubscript{3} during those periods, but there was no relationship on weekdays and Saturdays as a consequence of lower traffic volume and different traffic composition. The correlation coefficients between NH\textsubscript{3} and other air pollutants did not change significantly during daytime versus nighttime. Biogenic and agricultural emissions appear to be major contributors to gaseous NH\textsubscript{3} levels measured at the suburban site in this study. However, detailed source identification was impeded by many factors, such as the lack of relevant NH\textsubscript{3} data in the literature and the paucity of sufficient emission inventory data. Extended measurements in the future are needed to fully examine the seasonality of NH\textsubscript{3} and to further investigate the influence of local and regional sources on NH\textsubscript{3} levels in the DFW area.

In addition, comprehensive aerosol measurements were made using a HR-ToF-AMS and a SEMS simultaneously. Mass concentrations of aerosol species in sampled PM\textsubscript{1} showed a large amount of variability: SO\textsubscript{4}\textsuperscript{2-} (1.25 ± 0.66 µg m\textsuperscript{-3}), NH\textsubscript{4}\textsuperscript{+} (0.44 ± 0.24 µg m\textsuperscript{-3}), and NO\textsubscript{3}\textsuperscript{-} (0.12 ± 0.11 µg m\textsuperscript{-3}). PM\textsubscript{1} levels ranged from 1.32 to 14.70 µg m\textsuperscript{-3}, with a mean of 4.41 ± 2.13 µg m\textsuperscript{-3}. Pearson’s correlation coefficients between NH\textsubscript{4}\textsuperscript{+}, SO\textsubscript{4}\textsuperscript{2-}, and NO\textsubscript{3}\textsuperscript{-} suggest that particulate NH\textsubscript{4}\textsuperscript{+} mainly existed as (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} and that NH\textsubscript{4}NO\textsubscript{3} was not formed during most of the study period,
likely due to high temperatures (30.15 ± 4.12 °C) over the entire campaign. Ambient aerosols were nearly neutral.

In order to investigate the formation of NH$_4$NO$_3$ and NH$_4$Cl, theoretical calculations of thermodynamic equilibrium were performed. When RH<DRH, the partial pressure products of P$_{NH3}P_{HNO3}$ and P$_{NH3}P_{HCl}$ were always smaller the estimated equilibrium constants K$_{NH4NO3}$ and K$_{NH4Cl}$, indicating the absence of NH$_4$NO$_3$ and NH$_4$Cl formation. When RH>DRH, however, relatively increased levels of NO$_3^-$ often were observed. The strong relationships between NO$_3^-$ and SO$_4^{2-}$ and surface area at high RH imply that NH$_4$NO$_3$ might be formed on the moist surface of pre-existing sulfate aerosols. The co-existence of SO$_4^{2-}$ in the wet particles lowers the equilibrium constant, providing a thermodynamically favorable condition for aqueous NH$_4$NO$_3$ formation. In addition, measured particle number size distributions clearly showed the occurrence of an aerosol nucleation and growth event synchronous with ammonium salt formation during some humid periods characterized by increased concentrations of particulate NH$_4^+$ and NO$_3^-$. Excess NH$_4^+$ also was found to be closely correlated with NO$_3^-$ during this event when PM$_1$ levels were significantly elevated. Extensive simultaneous measurements of gaseous and aerosol species in the future are desirable to better evaluate the effect of NH$_3$ on local and regional air quality with respect to PM formation in the DFW area, especially in winter, as NH$_4$NO$_3$ and NH$_4$Cl formation is much more favorable under cold conditions.
4.2. Recommendations for future work (from a Chinese perspective)

This work provides valuable insights to the impacts of ammonia on air quality and fills the relevant data gap. It also emphasizes the importance of making continuous efforts to measure atmospheric NH$_3$ in urban and suburban areas (e.g., populated regions with significant industrial activities and sensitive environments vulnerable to changes in nutrient cycling). As the most abundant alkaline trace gas, NH$_3$ has drawn increasing attention in the aerosol community over the past few decades. However, there still are substantial uncertainties in temporal and spatial variations of NH$_3$ levels across the globe as a consequence of only limited ground-based observations, satellite measurements, and large-scale modeling efforts. With the rapid economic expansion and population growth in many countries, global atmospheric NH$_3$ levels are expected to increase in the future largely due to enhanced anthropogenic emissions. A good network for routine NH$_3$ monitoring worldwide is necessary, and more intergovernmental collaboration should be encouraged in order to promote this environmental initiative internationally.

Developing countries must take greater responsibility for the mitigation of NH$_3$ and PM. For example, China has aggravated air pollution problems that threaten future sustainable development. Megacities such as Beijing and Shanghai experience ambient PM concentrations that frequently exceed the NAAQS set by the U.S. EPA. There are no such existing regulations for PM$_{2.5}$ in China. Nevertheless, the central government of China is determined to mitigate air pollution. During the 7th National Environmental Protection Conference (December 2011), the State Council of the People’s Republic of China distributed the 12th (2011-2015) Five-Year Plan for Environmental Protection, which was prepared by the Ministry of Environmental Protection and the Chinese Academy for Environmental Planning. In this document, a timeline for PM
pollution control was set. Nationwide PM$_{2.5}$ standards (based on the World Health Organization recommendations) are expected to be launched by the end of 2016, which will pose significant challenges given the present environmental situation and emission scenarios in China. Shanghai, with a population of 25 million people, has taken early action by establishing a real-time PM$_{2.5}$ monitoring network system consisting of ten regular measurement sites across the city. Pertinent information is available online and has been accessible to the public since late June 2012.

China is likely the largest emitter of NH$_3$ in the world. Higher than global average NH$_3$ concentrations is often observed in many urban and suburban areas in the country. The estimated NH$_3$ emissions were 13.6 Tg in 2000, with fertilizer application accounting for approximately half. Wang et al. [2013] used this value in a chemical transport model (GEOS-Chem) to investigate the sensitivity of sulfate-nitrate-ammonium aerosols over China to changes in NH$_3$ emissions from 2000 to 2015. They found that if NH$_3$ emissions remain the same from 2006 to 2015 and emissions of SO$_2$ and NO$_x$ are changed by -16% and +16%, respectively, during this period, PM levels would decrease over South China and the Sichuan Basin. By contrast, if NH$_3$ emissions are enhanced by 16% from 2006 to 2015 based on the annual growth rate between 2000 and 2006, the efforts to reduce SO$_2$ emissions would prove fruitless because of the resulting significantly elevated nitrate aerosol concentrations (increase in over 40%).

These results clearly show that NH$_3$ will play a critical role in the possible mitigation and prevention of PM in China. However, the government of China does not regulate NH$_3$ emissions currently. Preliminary field studies measuring atmospheric NH$_3$ have been performed in some regions, but comprehensive mapping of NH$_3$ hotspots in China is still far from complete. Unresolved uncertainties in NH$_3$ emissions significantly affect the ability to implement national
control strategies for airborne PM, making future air pollution mitigation and public health protection in China ambiguous and emphasizing the need for related NH\textsubscript{3} research.

Agriculture is a predominant contributor to gaseous NH\textsubscript{3} in China, but other sources also may be important. Since the introduction of three-way catalytic converters, motor vehicles have become significant NH\textsubscript{3} sources. Vehicle ownership in China is likely to increase quickly in the next few years. With stricter standards for vehicular emissions, more automobiles are required to be equipped with converters. Therefore, traffic-related NH\textsubscript{3} emissions potentially will contribute a larger relative proportion to Chinese NH\textsubscript{3} emission inventories. The contribution from biomass burning also is worth re-evaluating. Crop stubble burn-off by farmers occurs widely in China, sometimes without control on the intensity and affected area. Although some local authorities have banned burning of crop stalks/residues, regulatory enforcement needs to be strengthened.

Future air quality policies in China should be focused not only on decreasing SO\textsubscript{2} and NO\textsubscript{x} emissions but also on curbing release of other important PM precursors, including NH\textsubscript{3}. Improved understanding of atmospheric NH\textsubscript{3} in China and its subsequent control will lead to a cleaner atmosphere for future generations.

Similarly, regulating NH\textsubscript{3} emissions could be a promising strategy for reducing PM in the U.S. Pinder and Adams [2007] demonstrated that NH\textsubscript{3} control technologies are very cost-effective compared to those for cutting SO\textsubscript{2} and NO\textsubscript{x} emissions to achieve the same reduction in inorganic PM concentrations in the Eastern U.S. and that the NH\textsubscript{3} saving potential is larger in winter. The federal government should consider adopting appropriate NH\textsubscript{3} control strategies when making future regulatory plans for PM reduction.
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Appendix A

PUBLICATIONS RELATED TO THE RESEARCH DESCRIBED IN THIS THESIS


Appendix B

PRESENTATIONS RELATED TO THE RESEARCH DESCRIBED IN THIS THESIS


