Measurement of atmospheric ammonia species: development, validation, and field applications of an analytical method

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MEASUREMENT OF ATMOSPHERIC AMMONIA SPECIES: 
DEVELOPMENT, VALIDATION, AND FIELD APPLICATIONS OF 
AN ANALYTICAL METHOD

By

Jian Hou

A Dissertation Submitted to the University at Albany, State University of New York 
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School of Public Health
Department of Environmental Health Sciences

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ABSTRACT

Ammonia is the primary base in the atmosphere. It reacts readily with atmospheric acids such as sulfuric acid (H$_2$SO$_4$), nitric acid (HNO$_3$), and hydrochloric acid (HCl) to form ammonium salts that occur predominantly in the fine aerosol particle (PM2.5) fraction. The ability to measure ammonia species (NH$_x$, the sum of gaseous NH$_3$ and particulate NH$_4^+$) is essential for the investigation of atmospheric behaviors of NH$_x$. In this dissertation work, a highly sensitive technique has been developed for the measurement of atmospheric NH$_x$ species. The method is based on aqueous scrubbing of the atmospheric NH$_3$ and NH$_4^+$ using a Continually-Wetted Frit (CWF) sampler, followed by derivatization of the analyte to form a highly efficient light-absorbing indophenol in an on-line reaction coil, and analysis of the derivative by LOng-Path Absorption Photometry (LOPAP) using a miniaturized optical fiber spectrophotometer with a long-path liquid waveguide capillary cell. The method was first validated by calibrations using aqueous and gas-phase standards. The method possesses a wide linearity range of 0-35 ppbv, a lower detection limit of 30 pptv, a good precision of 3% at 1.5 ppbv level, and a good sample time resolutions of ≤5 min. The method was further validated by inter-comparisons with several independent measurement techniques in the laboratory and in the field. These methods include Particle-Into-Liquid sampler/Ion Chromatography (PILS/IC), Quadropole-Aerosol Mass Spectrometry (Q-AMS) and integrated filter/ion chromatography (STN) for NH$_4^+$, and Tunable Diode Laser Absorption Spectroscopy (TDLAS), Wet Effusive Diffusion Denuder (WEDD), Ion Mobility Spectrometry (IMS), and laser acousto-opticalabsorption (Nitrolux) for NH$_3$. The method was successfully deployed in 4 field measurement intensives: a rural forest...
site in University of Michigan Biological Station in Pellston, MI during the summer of 2003; an urban site on Queens College campus in Queens, NY, during the winter of 2004; a rural site in Pinnacle State Park in Addison, NY, during the summer of 2004; and an urban environment in downtown Albany, NY, during the summer of 2005. Ambient NH$_3$ and NH$_4^+$ were measured continuously for 2–4 weeks in each campaign. The NH$_4^+$ concentrations in aerosol phase were in the range of 0.03-9.4 ppbv (0.02-6.9 µg m$^{-3}$); The NH$_3$ mixing ratios in gaseous phase were in the range of 0.1-22.7 ppbv. Atmospheric behaviors of NH$_x$ species were investigated in these environments, such as the partitioning of ammonia between the gas and the aerosol phases, the diurnal variation patterns, and the impact of metrological parameters on the variation of ammonia species such as wind direction, ambient temperature and precipitation. Back trajectories of air masses were calculated to aid the data interpretation.

Dissertation advisor: Dr. Xianliang Zhou
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CHAPTER 1. INTRODUCTION

Ammonia (NH₃) and its reaction product ammonium (NH₄⁺) are increasingly being recognized as major atmospheric pollutants. This is attributable to their roles in regional scale tropospheric chemistry, to their acute toxic health impacts, and to their effects when deposited into ecosystems (Sutton et al., 1993; Angus et al., 2003; Schlesinger and Cassee, 2003).

NH₃ is the third most abundant nitrogen-containing substance, after N₂ and N₂O, and is the primary basic gas in the atmosphere (Seinfeld and Pandis, 1998). NH₄⁺, mainly combined with nitrate and sulfate, contribute significant portion to fine particle mass (Kean et al., 2000; Anderson et al., 2003). Ammonia species (NHₓ = NH₃ + NH₄⁺), along with amines, are generally categorized as reduced nitrogen in the atmosphere.

1.1 Sources of atmospheric ammonia species

In fact, all NHₓ emission occurs in the form of NH₃, while NH₄⁺ in the atmosphere is originated from reactions of NH₃ (Asman et al., 1998). The ammonia emission inventory has been relatively well established in recent years (Schlesinger and Hartley, 1992; Dentener and Crutzen, 1994; Bouwman et al., 1997; Battye et al., 2003). According to the estimation of Bouwman et al., (1997), the total global NH₃ emission is in the order of 50 Tg N yr⁻¹. The distribution of NH₃ emission is shown in the Figure 1.1. The total emission rate of ammonia for the continent of North American is estimated as 3.6 Tg N yr⁻¹ (Bouwman et al., 1997). Figure 1.2 shows the emission distribution in the United States (US EPA, NEI Database). The contribution of NH₃ emission sources to the
global inventory is shown in Figure 1.3. With the expansion of the population, the NH₃ emission will keep increasing if no further means are applied to control the release of ammonia into the atmosphere.

Figure 1.1 Global NH₃ emission on a 1×1 grid (Bouwman et al., 1997).
**Figure 1.2** NH$_3$ emission distribution in the United States (NEI, 2001).

**Figure 1.3** Contribution of NH$_3$ emission sources to the global inventory. Data (Bouwman et al., 1997; Asman et al., 1998).
1.1.1 Agriculture related emissions

It is well established that the primary source of NH$_3$ emissions into the atmosphere is volatilization from decomposing livestock waste. The second major source is the ammonia losses from agriculture plant canopies, especially following the application of nitrogen-containing fertilizers (Finlayson-Pitts and Pitts, 2000; Sutton et al., 2000).

NH$_4^+$ is formed in the microbial decomposition of urea and uric acid in animal excreta (Anderson et al., 2003).

$$\text{CO(NH}_2\text{)}_2 + 3\text{H}_2\text{O} \rightarrow 2\text{NH}_4^+ + \text{HCO}_3^- + \text{OH}^- \quad (1.1)$$

Equilibrium between NH$_4^+$ and NH$_3$ exists in the aqueous solution:

$$\text{NH}_4^+ + \text{OH}^- \leftrightarrow \text{NH}_3 + \text{H}_2\text{O} \quad (1.2)$$

With increasing temperature and pH, the dissolved NH$_3$ releases into the surrounding air by volatilization.

The nitrogen loss in the application of synthetic nitrogen fertilizer is known as a significant emission source of NH$_3$. It is estimated that the contribution from fertilizer application is as much as 10 ~ 20% of the United States’ national total emission in some existing inventories (Anderson et al., 2003).

1.1.2 Biomass combustion and natural ecosystems

Biomass combustion generally includes forest and savanna fire, agriculture waste burning and combustion of biofuels for energy purposes (Bouwman et al., 1997). It has been confirmed that biomass burning can release significant amounts of NH$_x$. Compared with biomass burning, combustion processes in industrial plant and internal combustion
engines generally emit only a small amount of NH$_3$ (Lee and Dollard, 1994). Nitrogen in plant material is mostly present as amino acids. During combustion processes, nitrogen is transformed into various compounds, including NH$_3$ and other N-containing substances (Andreae, 1991). Concentrations of ammonia species in plume from biomass burning have been measured to be up to 2 orders of magnitude higher than background (Lee and Atkins, 1994). It is estimated biomass combustion contributes 4-15% of the global emission of NH$_3$ (Andreae et al., 1988; LeBel et al., 1988).

Research has shown the natural vegetation/soil can act as either a sink or source of ammonia (Langford and Fehsenfeld, 1992; Husted et al., 2000; Pryor et al., 2001; Sarwar et al., 2005). Many organisms in soil involved in the degradation of organic substances can excrete ammonia directly or some N-containing compounds that easily hydrolyze to NH$_x$ (Bouwman et al., 1997; Rumburg et al., 2004).

\[
\text{Organic matter } \rightarrow \text{ NH}_3 + \text{ CH}_4 + \text{ CO}_2 + \text{ H}_2 + \text{ H}_2\text{S} \tag{1.3}
\]

1.1.3 Ocean emissions

The Ocean has been observed to be a net NH$_3$ emission source in remote marine areas (Quinn et al., 1992; Dentener and Crutzen, 1994; Gibb et al., 1999). It is believed that the ocean origin NH$_3$ released from degradation of organic nitrogen-containing compounds and excretion of zooplankton (Quinn et al., 1996; Norman and Leck, 2005). According to the estimation, oceans account for about 15 ~ 20% of the global NH$_3$ emissions into the atmosphere (Dentener and Crutzen, 1994; Bouwman et al., 1997).
1.1.4 Human direct emissions

Although it is known ammonia is a normal component of exhaled air, the possibility that humans themselves may be a significant ammonia emission source has received little attention (Atkins and Lee, 1993). Direct human ammonia emissions occur mainly from breath, sweat and excretion which are related to the normal metabolic process (Lee and Dollard, 1994; Sutton et al., 2000). The human direct ammonia emission rate has been estimated as 0.21-1.3 kg NH$_3$-N person$^{-1}$ yr$^{-1}$ (Moller and Schieferdecker, 1989; Sutton et al., 1995). Based on this factor, the direct human emissions contribute up to 1~5% of global ammonia emissions.

1.1.5 Transportation emissions

The contribution of on-road vehicles to NH$_3$ emissions was previously considered to be rather small based on early investigations of the exhaust of normal petrol and diesel engines. Generally, there is no significant ammonia production during the combustion of fossil fuel in engines (Sutton et al., 1995; Sutton et al., 2000). However, three-way catalytic converters, which were introduced in 1990s and have been widely used in vehicles, significantly increase emission of NH$_3$ from automobiles. Therefore, ammonia emission from transportation has attracted more attention (Moeckli et al., 1996; Fraser and Cass, 1998). Ammonia emissions from catalytic converter-equipped vehicles have been shown to be significantly higher than vehicles without catalytic converters, especially in the fuel-rich condition that exists when the air/fuel ratio is lower than the stoichiometric value (Tagliaferri et al., 1998). Ammonia can be formed over Pt/Al$_2$O$_3$ in
the absence of O\textsubscript{2} and H\textsubscript{2}O according to the following reaction (Dumpelmann et al., 1995):

\[
\text{CO} + \text{NO} + \frac{3}{2} \text{H}_2 \rightarrow \text{NH}_3 + \text{CO}_2
\] (1.4)

The ammonia emission factor of vehicles has been increased from 1.3 ± 3.5 mg km\textsuperscript{-1} determined in 1981 to about 60 mg km\textsuperscript{-1} determined in 1993 (Perrino et al., 2002). In more recent studies, (Baum et al., 2001) reported a value of 94 ± 8 mg km\textsuperscript{-1}. So, in urban environments, ammonia emission from traffic is an important factor affecting the air quality.

1.1.6 Ammonia emissions from minor sources

Industrial processes, fossil fuel combustion and wild animals also release ammonia into the atmosphere. Their emission factors were estimated as 0.1~0.2 Tg N yr\textsuperscript{-1}. Their contribution to the global NH\textsubscript{3} emission is less than 1% (Bouwman et al., 1997).

1.2 Behaviors of ammonia species in the atmosphere

As the most abundant gaseous alkaline component in the atmosphere, ammonia is responsible for neutralizing a significant portion of acidic substances formed via atmospheric oxidation of sulfur and nitrogen oxides (Finlayson-Pitts and Pitts, 2000; Pryor et al., 2001; Plessow et al., 2005). Ammonia species also play major roles in biogeochemical cycles of nitrogen and long distance pollutants transportation.
1.2.1 Chemistry

Ammonia is far from an inert gas. It plays an important role in the atmospheric chemical processes.

1.2.1.1 Reaction with atmospheric oxidants

NH$_3$ is involved in photochemical reactions in the atmosphere, and is a potential source of NO and N$_2$O (Diau et al., 1990).

\[ \text{NH}_3 + \text{OH} \cdot \rightarrow \text{NH}_2 \cdot + \text{H}_2\text{O} \]  
\[ \text{NH}_2 \cdot + \text{NO}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} \]  
\[ \text{NH}_2 \cdot + \text{O}_3 \rightarrow \text{NH} \cdot, \text{NHO}, \text{NO} \]

At 298 K, the reaction rate \( k_5 = 1.6 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \) (Demore et al., 1992). The atmospheric lifetime of NH$_3$ for \([\text{OH} \cdot] = 10^6 \text{ cm}^{-3}\), is about 72 day.

\[ \tau_{\text{NH}_3} = \frac{1}{k[\text{OH}]} = \frac{1}{1.6 \times 10^{-13} \times 10^6} = 6.25 \times 10^6 \text{ s} \approx 72d \]

Studies (De Pena et al., 1973; Olszyna et al., 1974) show that NH$_3$ can react with ozone to form ammonium nitrate:

\[ 2\text{NH}_3 + 4\text{O}_3 \rightarrow \text{NH}_4\text{NO}_3 + 4\text{O}_2 + \text{H}_2\text{O} \]  
\[ k_8 = 1.24 \times 10^{-6} \text{ cm}^3 \text{ min}^{-1} \]. Considering the low concentrations of OH radicals (1-10×10$^6$ molec cm$^{-3}$) and ozone (Less than 100 ppb) in the troposphere (Seinfeld and Pandis, 1998), the pathways above can be neglected due to the slow reaction rates (Renard et al., 2004).
1.2.1.2 Reactions with atmospheric acids

Neutralizing atmospheric acids is the most important chemical behavior of ammonia. It reacts rapidly with the available acids (mainly sulfuric, nitric, and sometimes hydrochloric acid) to form the corresponding salts in the atmosphere.

\[
\begin{align*}
\text{NH}_3(g) + \text{H}_2\text{SO}_4(l) & \rightarrow \text{NH}_4\text{HSO}_4(s, l) \quad \text{(ammonium bisulfate)} \quad (1.9) \\
\text{NH}_3(g) + \text{NH}_4\text{HSO}_4(l) & \rightarrow (\text{NH}_4)_2\text{SO}_4(s, l) \quad \text{(ammonium sulfate)} \quad (1.10) \\
\text{NH}_3(g) + \text{H}_2\text{O}_3(g) & \leftrightarrow \text{NH}_4\text{NO}_3(s) \quad \text{(ammonium nitrate)} \quad (1.11) \\
\text{NH}_3(g) + \text{HCl}(g) & \leftrightarrow \text{NH}_4\text{Cl}(s) \quad \text{(ammonium chloride)} \quad (1.12)
\end{align*}
\]

NH\textsubscript{3} prefers to convert the most acidic form H\textsubscript{2}SO\textsubscript{4} to its less acidic form NH\textsubscript{4}HSO\textsubscript{4}. If there is enough NH\textsubscript{3} ([NH\textsubscript{3}] > 2 [H\textsubscript{2}SO\textsubscript{4}]) in the system, all acidic species are neutralized into ammonium sulfate. The excess “free ammonia” is then available to react with the other acid vapors.

The reaction of NH\textsubscript{3} and HNO\textsubscript{3} that forms ammonium nitrate is reversible because NH\textsubscript{4}NO\textsubscript{3} can easily evaporate. The direction of reaction (1.11) is contingent upon the relative humidity and temperature of the environment. Low temperatures and high relative humidity support the ammonium nitrate formation. It should also be noted that the prevalence of the reaction is inversely related to the SO\textsubscript{2} concentration, as the emissions of SO\textsubscript{2} are decreased, NO\textsubscript{x} emissions become the dominant pollutants in some areas.

1.2.1.3 Acceleration the oxidation of SO\textsubscript{2}

It was observed that the oxidation of SO\textsubscript{2} by oxygen is significantly accelerated in the presence of ammonia (Junge and Ryan, 1958; Hansen et al., 1991; Benner et al.,
1992). 80% of the SO₂ was oxidized to (NH₄)₂SO₄ in less than 10 min under typical atmospheric conditions, while only 1% of SO₂ was oxidized without the presence of the NH₃ (Junge and Ryan, 1958; Hansen et al., 1991; Benner et al., 1992).

1.2.2 Deposition

Gaseous NH₃ is mainly removed by dry and wet depositions as well as reactions with acidic species to form aerosols (Renard et al., 2004). Aerosol NH₄⁺ is only removed from the atmosphere by dry and wet depositions (Krupa, 2003). Dry deposition is more important in areas close to NH₃ emission sources while wet deposition is dominant in regions with low emissions (Fangmeier et al., 1994).

The dry deposition of NH₃ is controlled by diffusion while the fine particulate NH₄⁺ is controlled by Brownian motion. The dry deposition velocities (νᵈ) are highly variable, and related to many environmental factors such as time of the day, temperature, humidity, receptors, and roughness of the surface. Dew may play an important role in the dry deposition of ammonia species by enhancing surface wetness (Moumen et al., 2004). The typical dry deposition velocities range from 0.3-3 cm s⁻¹ for NH₃. The values are one order of magnitude lower for dry deposition of fine particulate NH₄⁺ (Fangmeier et al., 1994; Krupa, 2003).

The wet removal process of NHₓ by precipitation can be divided into two regimes: in-cloud process and below-cloud process (Walker et al., 2000). The NHₓ is removed by nucleation and diffusion into cloud drops in the in-cloud process, and removed by precipitation such as rain, hail, and snowfall in the below-cloud process. It is commonly believed that the in-cloud removal process is more efficient than below-cloud process due
to the much larger total surface of droplets, and longer contact time with droplets in the clouds (Asman, 1995).

1.2.3 Transport
The residence time of ammonia in the lower atmosphere is expected to be quite short; approximately 0.5 h to 5 d (Dentener and Crutzen, 1994; Seinfeld and Pandis, 1998). In contrast, the ammonium ion, as an aerosol, has a typical lifetime on the order of 5-15 days (Aneja et al., 1998; Anderson et al., 2003). The short lifetime of NH₃ is due to the rapid gas-to-particle conversion of NH₃ to NH₄⁺, and deposition to natural surfaces. In general, gaseous NH₃ may only be transported to short distances from the emission sources due to the efficient scavenging from the atmosphere while aerosol NH₄⁺ can be transported over longer distances.

1.3 NH₃ as pollutants in the atmosphere
1.3.1 Concentrations
The typical NH₃ mixing ratios over continents range between 0.1 and 10 parts per billion by volume (ppbv) (Seinfeld and Pandis, 1998). In remote areas, NH₃ levels can be quite low, less than 50 parts per trillion by volume (pptv), whereas in areas adjacent to sources such as livestock operations, agriculture area, or events like forest fires, the concentrations can be 3 to 4 orders magnitude higher (LeBel et al., 1991; Krupa, 2003). The typical fine particulate ammonium ions concentrations in the ambient air range between 0.5 to 10 μg·m⁻³, with urban areas usually at higher levels than rural (Pratt and
Krupa, 1985; Yamamoto et al., 1995; Schwab et al., 2004). **Table 1.1** summarizes the characteristic field measurement results of ammonia species in various environments.

### 1.3.2 Impact on ecosystems

Ammonia and its salts can adversely affect terrestrial and aquatic ecosystems (Fangmeier et al., 1994; Baum et al., 2001; Krupa, 2003). NH₃ can cause acute damages to vegetation close to the emission sources (Pearson and Stewart, 1993). Dry and wet depositions of ammonia species disturb the balance of soil nutrients (Hornung and Sutton, 1995), leads to soil acidification following nitrification (Makarov and Kiseleva, 1995) and contributes significantly to large-scale nitrogen eutrophication of aquatic ecosystems (Lee et al., 1998; Sutton et al., 1998). High concentrations of nitrogen nutrients in a water body often result in a large production of algae. Oxygen will be consumed in the decomposition of dead algae, leading to oxygen depletion. That will result in a severe reduction in water quality and a detrimental effect on aquatic life.

Plants exchange ammonia with the atmosphere. The canopy acts as an ammonia source when exposed to an environment containing low NH₃ concentrations, but a sink when exposed to air enriched by nearby NH₃ emission sources (Langford and Fehsenfeld, 1992). The compensation points have been measured as less than 1 ppbv in canopies of pine, spruce and aspen, and up to 25 ppbv in wheat plants (Schjoerring et al., 1998). Foliage injuries occur when the foliar uptake rate and capacity of NH₃ are greater than the rate and capacity for in vivo detoxification by the plant (Krupa, 2003).
The NH$_4^+$ deposited into the soil can either be taken by plants and stored as organic R-NH$_2$ forms, or be transformed into NO$_3^-$ by nitrification (Sutton et al., 1993; Krupa, 2003).

\[ \text{NH}_4^+ \rightarrow \text{R-NH}_2 + \text{H}^+ \]  \hspace{1cm} (1.13)

\[ \text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + 2\text{H}^+ \]  \hspace{1cm} (1.14)

Both of the processes result in the release of proton and lead to the soil acidification.

1.3.3 Degradation of atmospheric visibility

In urban areas, the high-level ammonia emissions can lead to a serious problem for air quality control due to the ability of ammonia to transform itself into secondary ammonium aerosols (Fraser and Cass, 1998). The fine particulate matter (PM$_{0.1}$-PM$_1$) suspended in the atmosphere contributes the most to light scattering, and is responsible for a reduction in visibility (Sloane et al., 1991; Barthelmie and Pryor, 1998; Finlayson-Pitts and Pitts, 2000), accounting for the dense haze common to many polluted urban atmosphere.

1.3.4 Human health implications

Generally, no direct health effects have been found in humans exposed to typical environmental concentrations of gaseous ammonia (ATSDR, 2004). However, when exposed to elevated levels of NH$_3$, for example, livestock barns, can induce toxic effects (Gustin et al., 1991). NH$_3$ gas can be absorbed in the upper airways and is able to reach the lungs directly or by absorption onto particulate matters. Short-term exposure can
lower the defending mechanisms of the respiratory tract against microbiological agents. Long-term exposure can lead to respiratory diseases. High levels exposure of ammonia may irritate skin, eyes, throat, and lungs; cause coughing and burns. Lung damage and death may occur after exposure to very high concentrations of ammonia. Ammonia toxicity seems also be enhanced by combination with other chemical, physical or biological factors (Gustin et al., 1991).

The increasing concern regarding ammonia species in recent years is due to the role NH₃ plays in fine particle formation. NH₄⁺ ions are important components of continental tropospheric aerosols (Seinfeld and Pandis, 1998). They comprise a significant portion of the fine particulate mass. About 47% of the PM₂.₅ mass is ammonium sulfate in the eastern United States (Anderson et al., 2003). The scientific community has realized high levels of particulate-based smog could cause dramatic increases in daily mortality since the air pollution disaster in London in 1952 (Bell and Davis, 2001; Davis et al., 2002). Moreover, polluted air could not only cause an immediate increase in deaths and illness rates but also result in longer-term effects. Studies have shown the particulate-based air pollution has a wide range of health impacts, ranging from increased mortality rates in infants, low birth weight, impaired development, and cancer. Studies also indicate the exposure to lower levels of airborne particles result in smaller but nonzero increases on daily mortality (Schwartz, 1994).

The mechanisms by which particles influence human health are far from well understood (Englert, 2004). In-vitro and in-vivo studies in animals and human beings have shown the inhaled particles can lead to inflammatory effects on lung epithelial cells and alveolar macrophages (Fujii et al., 2001; Lundborg et al., 2001). Recent studies have
recognized that ultra fine particles (PM$_{0.1}$, mass median diameter < 0.1 μm) are more toxic than larger particles (PM$_{10}$) when inhaled, suggesting that the ultra fine particles are much easier to be absorbed into tissues and the circulation system. The increased surface/volume ratio may be an important factor (Brown et al., 2001; Brunekreef and Holgate, 2002).

1.4 Determination of atmospheric NH$_x$

The ability to measure ammonia species is essential for the investigation of atmospheric behaviors of NH$_x$, i.e., for monitoring ambient NH$_x$ concentrations and flux determination between ground surfaces and the overlying atmosphere.

Ammonia is well known to be a difficult gas to measure in the field (Sutton et al., 1998). The challenges mainly come from its stickiness, resulting from its adsorption onto any inlet surface. In addition, the human body could be a significant emission source, and the presence of an operator near the instruments/inlets may cause interference on ammonia measurements in the field, especially in the clean low ammonia environments. So, an effective ammonia determination technique should meet two basic requirements: sampling directly from the ambient with a minimum inlet wall surface, and sample handling in a closed system without contacting room air.

Since the bubbler technique was first introduced for collecting ammonia in the air in the 19th century, a wide range of techniques have been developed (Sutton et al., 1993). Methods for the measurement of atmospheric NH$_x$ may be divided into two categories: physicochemical direct methods and chemical indirect methods.
Table 1.1 Summary of typical ambient NH₃ concentrations in various environments.

<table>
<thead>
<tr>
<th>Environments</th>
<th>Site location</th>
<th>Measurement period</th>
<th>Concentrations</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>NH₃, ppbv</td>
<td>NH₄⁺, μg·m⁻³</td>
</tr>
<tr>
<td><strong>Urban</strong></td>
<td>Yokohama, Japan</td>
<td>Jan. 1987-Dec. 1991</td>
<td>2.4 - 11.9</td>
<td>1.5 - 3.1</td>
</tr>
<tr>
<td></td>
<td>Rome, Italy</td>
<td>Spring 2001-Spring 2002</td>
<td>4.1-63.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pittsburgh, PA</td>
<td>Summer, fall 1993</td>
<td>0.01-5.2</td>
<td>0.26-16</td>
</tr>
<tr>
<td></td>
<td>Vinton, VA</td>
<td>Summer, 1995, 1996</td>
<td>0.9-2.7</td>
<td>0.9-8.6</td>
</tr>
<tr>
<td><strong>Agricultural &amp; Livestock</strong></td>
<td>Boulder, Colorado</td>
<td>Summer, 1987</td>
<td>5.5 (Mean)</td>
<td>1.1 (Mean)</td>
</tr>
<tr>
<td></td>
<td>Winter, 1987</td>
<td></td>
<td>4.0 (Mean)</td>
<td>0.7 (Mean)</td>
</tr>
<tr>
<td></td>
<td>Clinton, NC</td>
<td>Oct, 1998- Sept.1999</td>
<td>0.16-46</td>
<td>0.03-10.07</td>
</tr>
<tr>
<td></td>
<td>Eastern NC</td>
<td>Fall, 1997</td>
<td>0.44 -140</td>
<td>0.036-14.58</td>
</tr>
</tbody>
</table>
Table 1.1 (Continued)

<table>
<thead>
<tr>
<th>Environments</th>
<th>Site location</th>
<th>Measurement period</th>
<th>Concentrations</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\text{NH}_3$, ppbv</td>
<td>$\text{NH}_4^+ \mu\text{g}\cdot\text{m}^{-3}$</td>
</tr>
<tr>
<td>Rural</td>
<td>Northeast US</td>
<td>Jan.-Mar. 1984</td>
<td>0-0.5</td>
<td>1.2-2.5</td>
</tr>
<tr>
<td></td>
<td>Lexington, Kentucky</td>
<td>Summer, 1983</td>
<td>0.05-7.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Southern Indiana</td>
<td>Spring, 1998, 1999</td>
<td>0.8-1.6 (Mean)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Winter, 1999, 2000</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Harvard Forest, MA</td>
<td>1991-1996</td>
<td>0.2-0.3</td>
<td>1.35 (Mean)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Look Rock, TN</td>
<td>Summer, 2002</td>
<td>0.7-3.9</td>
<td>1.44-3.78</td>
</tr>
<tr>
<td>Remote</td>
<td>Central Pacific Ocean</td>
<td>May, 1987</td>
<td>0.02-0.08</td>
<td>&lt;0.12</td>
</tr>
<tr>
<td></td>
<td>Niwot Ridge, CO (3517m)</td>
<td>Summer, 1998</td>
<td>0.01-0.09</td>
<td>0.02-0.11</td>
</tr>
</tbody>
</table>
1.4.1 Direct NH₃ determination techniques

Physicochemical direct NH₃ determination techniques were developed in recent years along with the fast advancement in electronic engineering and data processing. The characteristics of these approaches are: fast response, good time resolution and highly automated. Usually these instruments are expensive and need intensive maintenance. Fourier Transform Infra-Red Spectroscopy (FTIRS), Differential Optical Absorption Spectroscopy (DOAS) and Tunable Diode Laser Absorption Spectroscopy (TDLAS) methods are all based on the Beer-Lambert law (Finlayson-Pitts and Pitts, 2000):

\[ A = \ln(I_0/I) = \sigma Nl, \]  

(1.15)

Where \( I_0 \) and \( I \) are the densities of a light beam entering and exiting a sample with length \( l \) (cm). The absorption cross section \( \sigma \) (cm² molecule⁻¹) is the unique spectral feature of the analyte. The specific spectra of NH₃ provide the possibility to determine the concentration in the atmosphere.

DOAS measures photo-absorption in the ammonia \(^1\!A_2 \leftarrow ^1\!A_1\) ultraviolet band progression in the \( v_2 \) bending mode near 220 nm. The whole spectrum is predissociated (NH₃ \( \rightarrow \) NH₂(X\(^2\!B_1\))+H), giving a diffuse spectrum with no rotational structure (Mount et al., 2002). The typical optical paths of DOAS range from tens of meters to kilometers. The sensitivity of DOAS for NH₃ is in the order of 1 ppbv.

FTIR measures the molecular vibration absorption of ammonia in the infrared region. Usually the lines at 1103.4 and 867.9 cm⁻¹ are selected for analysis since they are least interfered with H₂O and CO₂ absorptions. Multiple reflection optical systems and multiple scans are used for extending the optical path and enhancing the sensitivity. An
estimated detection limit of 60 nmol m$^{-3}$ (1.34 ppbv) and 5 min time resolution were reported (Wiebe et al., 1990; Galle et al., 2000).

TDLAS acquires an absorption spectrum of analytes also in the infrared region, then analyzes it by performing an advanced type of sweep integration (Li et al., 2004). The line at 1065.5654 cm$^{-1}$ is chosen for ammonia analysis. A long path length (150 m, by multiple reflection) optical system is used for enhancing sensitivity. A detection limit of 0.1 ppbv and 1 min time resolution were reported (Li et al., 2006).

By now, the most sensitive ammonia detection method reported is Vacuum UV Photo Fragmentation/Laser-Induced Fluorescence (VUVPF/LIF). The detection limit of 5 pptv has been achieved for a 5 min integration period (Schendel et al., 1990). PF/LIF uses a near-vacuum UV laser ($\lambda=193$ nm) to photolyze NH$_3$ via a two-photon process, producing a NH ($b^1 \Sigma^+$) photofragment. A second laser ($\lambda=450$ nm) is then used to excite NH ($b^1 \Sigma^+$) into NH ($c^1 \Pi^+$), the resultant fluorescence ($\lambda=326$ nm) is then observed (Williams et al., 1992).

Photo-Acoustic Spectroscopy (PAS) was reported recently for monitoring the atmospheric ammonia in sub ppbv level (Schilt et al., 2004). The method employs laser-based resonant photoacoustic spectroscopy for the detection of ammonia. NH$_3$ molecules are excited by a CO$_2$ laser, then undergo collisional deactivation, which converts the absorbed energy into periodic local heating at the modulation frequency of the laser. The resulting acoustic waves are detected with a low-noise microphone to quantify NH$_3$. The sensitivity of this method is claimed as 0.1–1 ppbv with a time resolution of 1 min (Kenski et al., ; Schilt et al., 2004).
1.4.2 Chemical indirect NH₃ determination methods

The Chemical indirect ammonia determination methods also can be divided into dry chemical and wet chemical processes. Dry chemical methods generally are based on the oxidation of NH₃ into NOₓ, followed by a monitoring with a chemiluminescence detector. These methods can be automated through controlling the temperature of desorption and oxidation reactions. WO₃, V₂O₅ and Molybdenum Oxide are usually used as oxidants (Langford et al., 1989; Mennen et al., 1996). A 50 pptv detection limit and 30 min of time resolution were reported for these methods (Langford et al., 1989; Williams et al., 1992).

The wet chemical indirect ammonia measurement methods generally follow these steps: gaseous NH₃ is collected and transferred into aqueous NH₄⁺ then analyzed by a variety of detection techniques. Several continuous sampling and analyzing methods have been developed in recent years, which greatly enhanced the data collection efficiency and eliminated the necessity for the labor-intensive sample treatment.

Aqueous scrubbing is a widely used ammonia sampling method. This technique is based on the high solubility of NH₃ in H₂O and acidic solutions. Impinger (Emmenegger et al., 2004; Shah et al., 2008), bubbler (Sutton et al., 2001; Cassel et al., 2005; Shah et al., 2008), coil sampler (Huang, 2002) and wet denuder techniques (Simon et al., 1991; Pryor et al., 2001) belong in this category. The impinger or bubbler sampling techniques remain useful for the studies with high ammonia concentration environments such as measurement of emission from slurry and fertilizer application, where NH₃ concentrations are much higher than NH₄⁺. Both gaseous NH₃ and aerosol NH₄⁺ are collected during sampling. However, in most instances, the individual concentrations of
gaseous NH₃ or aerosol NH₄⁺ are needed respectively, so it is necessary to find ways to separate them.

Diffusion denuder techniques are widely used for differentiating gas phase and particle phase samples. These techniques are based on the differences in the diffusion properties of gases compared to particles (Finlayson-Pitts and Pitts, 2000). A laminar flow of air is pulled through a tube; the gases strike the wall of the tube a number of times with high diffusivity, while particles will pass through with significantly fewer strikes because of their relatively low diffusivity. If the walls are coated with an acidic substance, the gaseous NH₃ molecules diffuse onto the walls and are removed from the gas flow, while the aerosol passes through to be captured on a subsequent collector.

There are a variety of denuder designs for collecting ammonia species. Annular diffusive denuders (ADD) coated with citric acid or oxalic acid were widely reported (Allegrini et al., 1984; Lewin et al., 1986; Andersen and Hovmand, 1994; Perrino and Gherardi, 1999). Wet Effluent Diffusion Denuder (WEDD) techniques were developed to collect and convert NH₃ to NH₄⁺ since the 1980’s (Dasgupta, 1984; Wyers et al., 1993; Sorensen et al., 2003; Pryor et al., 2004). In this method, the “coating” is a stream of water that continuously flows along the walls of denuder (Finlayson-Pitts and Pitts, 2000). WEDD performs the ammonia analysis both automatically and continuously.

Another main method that has been applied in NHₓ sampling is filter packs. An inert pre-filter separates gaseous and particulate phases of NHₓ; the gas NH₃ that passes through is captured by a subsequent acidic coated filter. This method is widely used because of its simplicity (Harrison and Kitto, 1990; Williams et al., 1992; Andersen and
Hovmand, 1994; Sickles et al., 1999). Interactions between phases may occur in some situations, and can affect the accuracy of this method (Sutton et al., 1993).

There are a variety of detection techniques for aqueous NH$_4^+$.  

Ion Chromatography (IC) analyzes the extracted NH$_4^+$ with an ion exchange cation column, micro-membrane suppressor and conductivity detector. A detection limit of 1 part per billion by mass (ppbm), or 55.6 nM is achieved (Orsini et al., 2003).

Colorimetric method is widely used for detecting aqueous NH$_4^+$. This method is based on the Berthelot’s reaction which transforms NH$_4^+$ into a highly efficient light-absorbing indophenol and monitors at 630~660 nm (Lewis and Mann, 1963; Van Staden and Taljaard, 1997).

An HPLC-fluorescence method is based on the reaction of NH$_4^+$ with o-Phthalaldehyde (OPA) and sulfur-containing reagents to form sulfonatoisoindoles, a group of compounds with high fluorescence sensitivity:

![Chemical Reaction](image)

A very low detection limit of 8 nM can be achieved (Huang, 2002).

1.4.3 NH$_4^+$ aerosol analysis techniques

With low cost and flexible installation options, filter packs and impactors have been widely used for NH$_4^+$ aerosol collections; however the sensitivity and time resolution are relatively poor (Finlayson-Pitts and Pitts, 2000; Huang et al., 2004). There were several
sampling techniques developed recently, such as Particle Into Liquid Sampling (PILS) by Georgia Tech, and Aerosol Mass Spectrometer (AMS) by Aerodyne Research Inc. These techniques make it possible for monitoring NH4⁺ aerosol continuously.

The principle of PILS is to collect ambient particles, which have grown to many times their original size by condensation of water, into a small stream of high purity water with a Steam Jet collector, thereby producing a solution containing the aerosol species sampled at a specific moment in time. The resulting liquid stream is analyzed with an ion chromatograph to quantitatively measure the bulk aerosol ionic components. PILS has advantages in both collection efficiency and time resolution (Zhang et al., 2002; Orsini et al., 2003).

AMS uses an aerodynamic lens to focus the particles into a narrow beam. After being focused, the particles impact on a 500 - 700 °C heater surface under high vacuum, where volatile and semi-volatile particle components evaporate. The vapor is ionized by electron impact, and ions are analyzed with a quadrupole mass spectrometer. Particle size is measured via particle time-of-flight. The AMS is operated in two modes:

1. Continuous mass spectrum mode without size information.
2. Size distribution measurement mode for selected m/z settings of the quadrupole.

Single particles can also be detected and their sizes measured. AMS is uniquely capable of identifying the particle size distribution and chemical composition of single particle (Jayne et al., 2000; Jimenez et al., 2003; Drewnick et al., 2004).

Table 1.2 summarizes the mainly used atmospheric ammonia species measurement techniques.
Table 1.2 Summary of main atmospheric ammonia species measurement techniques.

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Target</th>
<th>MDL</th>
<th>Resolution</th>
<th>Remarks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOAS</td>
<td>NH₃</td>
<td>1 ppbv</td>
<td>1s - 3 min</td>
<td>Good for measurements over open fields;</td>
<td>(Mennen et al., 1996; Mount et al., 2002)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>High noise level.</td>
<td></td>
</tr>
<tr>
<td>FTIR</td>
<td>NH₃</td>
<td>1.3 ppbv</td>
<td>5 min</td>
<td>Useful in high NH₃ level environment.</td>
<td>(Wiebe et al., 1990; Galle et al., 2000)</td>
</tr>
<tr>
<td>TDLAS</td>
<td>NH₃</td>
<td>0.1-0.5 ppbv</td>
<td>1 min</td>
<td>Quick response, high cost and skilled operators needed.</td>
<td>(Pyor et al., 2004; Li et al., 2006)</td>
</tr>
<tr>
<td>PF/LIF</td>
<td>NH₃</td>
<td>~ 5 pptv</td>
<td>5 min</td>
<td>Excellent sensitivity and time resolution, high cost and skilled operators needed.</td>
<td>(Scheidel et al., 1990; Williams et al., 1992)</td>
</tr>
<tr>
<td>PAS</td>
<td>NH₃</td>
<td>0.1-1 ppbv</td>
<td>1 min</td>
<td>Fast response, but CO₂ and H₂O in the atmosphere may affect the result.</td>
<td>(Kenski et al.; Schilt et al., 2004)</td>
</tr>
<tr>
<td>MOADS</td>
<td>NH₃</td>
<td>~ 40 pptv</td>
<td>10 min</td>
<td>High sensitivity, complex of temperature controlling.</td>
<td>(Langford et al., 1989; Williams et al., 1992)</td>
</tr>
<tr>
<td>Techniques</td>
<td>Target</td>
<td>MDL</td>
<td>Resolution</td>
<td>Remarks</td>
<td>Reference</td>
</tr>
<tr>
<td>------------------</td>
<td>--------</td>
<td>-----------</td>
<td>------------</td>
<td>-------------------------------------------------------------------------</td>
<td>--------------------------------</td>
</tr>
<tr>
<td>WEDD</td>
<td>NH₃</td>
<td>~22 pptv</td>
<td>2 min</td>
<td>Good sensitivity and temporal resolution, skilled operators required.</td>
<td>(Dasgupta, 1984; Pryor et al., 2004)</td>
</tr>
<tr>
<td>Adsorbent Tube/GC</td>
<td>NH₃</td>
<td>100 pptv</td>
<td>15 min</td>
<td>Fair sensitivity and time resolution, not applied widely.</td>
<td>(Yamamoto et al., 1994)</td>
</tr>
<tr>
<td>Filter Pack</td>
<td>NH₃</td>
<td>36 pptv</td>
<td>2 hr</td>
<td>Good sensitivity with poor resolution, low cost but intensive labor needed.</td>
<td>(Williams et al., 1992; Ardersen and Hovmand, 1994)</td>
</tr>
<tr>
<td></td>
<td>NH₄⁺</td>
<td>0.04 μg·m⁻³</td>
<td>3 hr</td>
<td>Flexible to install and operate, sample loss on semi-volatile components.</td>
<td></td>
</tr>
<tr>
<td>PILS/IC</td>
<td>NH₄⁺</td>
<td>0.05 μg·m⁻³</td>
<td>4 min</td>
<td>Excellent sensitivity and time resolution, can analyze multiple aerosol ions simultaneously.</td>
<td>(Lee et al., 2003; Orsini et al., 2003)</td>
</tr>
<tr>
<td>AMS</td>
<td>NH₄⁺</td>
<td>&lt;10 min</td>
<td></td>
<td>Obtains both information of aerodynamic size distribution and chemical composition.</td>
<td>(Jeyne et al., 2000; Jimenez et al., 2003; Drewnick et al., 2004)</td>
</tr>
</tbody>
</table>
1.5 **Research objectives**

This dissertation research is focused on an atmospheric ammonia species measurement method development, validation, and field applications. Specific goals include:

1. To develop an efficient measurement technique for atmospheric NH$_3$ and NH$_4^+$, which can provide sufficient sensitivity and minimal sampling time resolution, with simplified deployment and operation.

2. To validate the self-developed NH$_x$ analytical method by certified standard calibrations and inter-comparisons with other major available atmospheric ammonia and ammonium analytical methods in both laboratory and field measurements.

3. To deploy the technique for NH$_x$ field measurements in the lower atmosphere. Apply the method to establish the temporal distributions of ammonia species in both urban and rural environments, and to elucidate their relationships with other physical, chemical, and meteorological parameters.
CHAPTER 2. METHOD DEVELOPMENT

In this dissertation work, a sensitive atmospheric NHx measurement technique is developed. The method is based on aqueous scrubbing of the atmospheric NH3/NH4+ by a glass frit impactor coupled with a gas-liquid separator; followed by derivatization of the analytes to form a highly efficient light-absorbing indophenol in an on-line reaction coil; and analysis of the derivative by a long-path absorption spectrophotometer.

2.1 Sampling

Both gaseous NH3 and aerosol NH4+ are highly soluble species. The intrinsic Henry’s law constant of NH3 is 62 M atm⁻¹ at 25°C (Dasgupta and Dong, 1986). Taking into account its dissociation constant in an aqueous solution of pKa 9.25 (Lide, 1996-1997), the effective Henry’s law coefficient of NH3 in the aqueous solution at pH ≤ 6 is expected to be:

\[
H_{NH_3}^* \approx H_{NH_3} \frac{K_{eq}[H^+]}{K_w} = \frac{62 \text{ M} \cdot \text{atm}^{-1} \times 10^{-(14-9.25)} \times 10^{-6} \text{ M}}{10^{-14} \text{ M}^2} = 1.1 \times 10^5 \text{ M} \cdot \text{atm}^{-1} \quad (2.1)
\]

Therefore, aqueous scrubbing of the gaseous ammonia should be quantitative, and would be a desirable technique for ambient sampling.

The schematic diagram of the sampling system is shown in Figure 2.1. Ambient air is pulled directly into a glass-frit sampler with a vacuum pump (Model DOA-P161-AA, GAST). The sampling flow is generally set at 2.0 L min⁻¹, controlled with a mass flow controller (0–5 L min⁻¹, Model GFC171S, Aalborg or Model 33116-24, Cole-Parmer). The glass-frit sampler (1” OD, 10-20µm porosity disc, Ace Glass) is continuously wetted with deionized water. Gaseous NH3 is scrubbed and dissolved into
the water membrane formed on the surfaces of the porous frit disc, and NH$_4^+$ salts are captured onto the disc and rinsed continuously to dissolve into solution. The solution with the collected ammonia species is removed into a derivatization coil quickly through the gas-liquid separator.

**Figure 2.1** Schematic diagram of wet scrubbing sampling system.
Through a test conducted with two identical sampling systems connected in series, the NH$_x$ collection efficiency is determined to be above 95% at a scrubbing flow rate of 0.24 mL·min$^{-1}$ and air sampling flow rate of 2.0 L·min$^{-1}$ sampling conditions. The un-wetted portion of the inlet is designed to be as short as possible; only 2 centimeters in this case; and thus insures the minimum absorption of NH$_3$ onto the inlet wall surface.

### 2.2 Derivatization

#### 2.2.1 Berthelot’s reaction

The Berthelot’s reaction is selected as the derivatization step because the derivative indophenol is a highly efficient light-absorbing chromophore ($\varepsilon_{\text{max}} > 10^4$ (Krom, 1980)). The generally accepted reaction scheme can be simplified as (Lau et al., 2004):

\begin{align*}
\text{NH}_3 + \text{HOCI} & \rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O} \\
\text{NH}_2\text{Cl} + \text{R} & \rightarrow \text{[Fe(CN)$_5$NO]}^{2-} + \text{HCl} + \text{H}_2\text{O} \\
\text{R} & \rightarrow \text{[Fe(CN)$_5$NO]}^{2-} + \text{OH}^- - \text{HCl} + \text{H}_2\text{O}
\end{align*}

(Where R = H or COO$^-$)

The Berthelot’s reaction is mainly used for NH$_4^+$ determination in water bodies and in food industry applications (Crowther and Evans, 1980; Barnes and Sugden, 1990; Aminot et al., 1997; Wang et al., 2003). The previous studies indicate this reaction is
strongly dependent on the conditions of the reaction medium such as the concentrations of reactants, temperature, and pH (Krom, 1980; Kempers and Kok, 1989; Pai et al., 2001). Moreover, this is a relatively slow reaction. For an un-catalyzed reaction, it could take over an hour to reach equilibrium (Lau et al., 2004). So, it is necessary to re-examine the kinetics of Berthelot’s reaction and find the optimized conditions to make it feasible for measuring the atmospheric NH$_4^+$ species.

2.2.2 Choice of reagents

The essential reagents of Berthelot’s reaction are composed of ammonia, phenolic compounds, chlorine donors and catalysts. A variety of reagents in different combinations have been used for Berthelot’s reaction (Krom, 1980). In this research, sodium hypochlorite (NaClO) was selected as a chlorine donator reagent because it is readily accessible. Sodium salicylate was chosen for a phenolic reagent mainly because it is less toxic and more environmentally friendly. For a catalyst, sodium nitroprusside was selected because it was found to be the most effective amongst various catalysts (Van Staden and Taljaard, 1997).

2.2.3 Kinetics and effect factors of derivatization reaction

Based on literature and laboratory preliminary tests, the derivatization medium containing 80mM salicylate, with 10mM hypochlorite as an oxidizing agent, and 0.1mM nitroprusside as a catalyst, is found to produce sufficient derivative yields and reasonably low interference signals. Further experiments were carried out in this medium to study the effects of pH, retention time and temperature.
2.2.3.1 Effect of pH on indophenol production rates.

The derivatization is an alkaline-catalyzed reaction. Many studies have shown the close control of the reaction medium’s pH is important (Pai et al., 2001; Lewandowska and Falkowska, 2004). In this study, the effect of pH on derivative indophenol production yields was re-examined. The reaction medium’s pH was adjusted by adding different amounts of sodium hydroxide and was measured with a pH meter (Model 440, Corning). In this series of experiments, the reagent medium was maintained at 50 °C, and the retention time was 12 min. The results are shown on Figure 2.2.

![Figure 2.2. The effect of pH on indophenol production rates.](image-url)
The derivative indophenol production yields are found to increase with pH, with a significant jump between pH 12.0 and pH 12.5. That is mainly due to the positive equilibrium shift with the increase of the concentration of OH\(^-\), according to the reaction scheme.

2.2.3.2 Effect of temperature on indophenol production rates.

The Berthelot’s reaction is relatively slow under ambient temperature conditions (25 °C). To accelerate the reaction to achieve a better time resolution, the effect of temperature on indophenol production rates was conducted in a laboratory. The alkalinity of the reaction medium was maintained at pH 12.4. The reaction coil was placed in a water bath with a temperature controller (Model 9106, Polyscience). The retention time of the reactants in the temperature-controlled zone was maintained at 12 min. The results are shown on Figure 2.3.

Empirically, the derivatization reaction is very sensitive with temperature. The indophenol production rate initially increases with the temperature, and reaches its maximum at 45–55 °C. This is mainly because the elevated temperature accelerates the reaction rate, while the signal drop is due to the decomposition of indophenol under overheated conditions. The decrease of ammonia’s solubility in the reaction medium at elevated temperatures also accounts for the lower response.
2.2.3.3 Detailed kinetics of derivatization reaction

For further understanding the derivatization reaction and optimizing the operation conditions in field measurements, the kinetics of the Berthelot’s reaction was studied. The retention times of the reactants’ mixture were controlled by adjusting the volume of the reaction coil. With the temperature of the reagent medium kept at 50 °C, and the pH maintained at 12.4, the effect of the derivatization reaction time on production yields is illustrated in Figure 2.4.

**Figure 2.3** The effect of temperature on indophenol production rate.

![Graph showing the effect of temperature on indophenol production rate](image-url)
Figure 2.4 The effect of derivatization reaction time on indophenol production yields.

The indophenol production increases with the retention time through the reaction coil, especially in the first 10 min. The derivatization reaction approaches equilibrium at ~20 min. The pseudo-first order rate constant can be obtained through the logarithmic curve fit of the response peak height and the reaction time (Figure 2.5), which is calculated to be 0.26 min⁻¹.
2.2.3 Optimization of reaction conditions

Considering the characteristics of atmospheric ammonia species determination, to make the method practical for the field real time NH$_x$ measurements, the operation parameters of the derivatization reaction need to be optimized. The typical HN$_3$ mixing ratios are 0.1-10 ppbv, NH$_4^+$ aerosol concentrations are 0.5 -10 $\mu$g·m$^{-3}$ in the atmosphere, while the concentrations of NH$_x$ could be much lower in some remote areas. Therefore, the proposed NH$_4^+$ measurement method should be sensitive enough for the field atmospheric studying applications. Moreover, for system automation and continuous
operation, the derivatization should be completed in a time frame as short as possible to minimize the response time delay. Furthermore, the selected operation conditions should keep the derivative production rate relatively stable to make sure there is no significant response change occurring during the sample measurements.

The pH 12.4 was selected as the operating alkalinity of derivatization reaction. Although a further increase in alkalinity may still enhance the indophenol production rate, but the margin is very limited (only about 10%). Additionally, an excessive basic reaction medium may damage the detection unit (capillary cell), which is made of fused silica.

The volume of the derivatization coil was fixed at 6.2 ml. With the total reactants’ mixture flow rate sustained at 0.55 ml min⁻¹, the retention time was 11.3 min. These parameters can ensure the reaction achieves about 90% of the maximum derivative yield, and at the same time, preserves a relatively short response time delay.

The derivatization temperature was selected to be 50 °C, the optimum temperature to acquire the maximum production yield of the derivative.

2.3 Detection system

The colorimetric method based on Berthelot’s reaction is a classic NH₄⁺ determination technique due to its simplicity and high selectivity. According to the Beer-Lambert’s law (Formula 1.15), the absorbance is proportional to the length of the optical path in the solution. Thus, increasing the optical path length of the sample cell is the most common and simplistic way to enhance the sensitivity of the colorimetric method (Zhang et al., 2001). The typical optical path of commonly used quartz cuvettes or flow
cells, ranges from 0.5 cm to 5 cm, and has a limited potential to extend due to the design of the colorimetric detectors, and the limit of the volume of the samples. The idea of fluid-filled light waveguide capillary tubing has been proposed since the 1980’s (Lei et al., 1983; Dasgupta, 1984). With the invention of a fluorocarbon material (Teflon AF-2400), which has a refractive index (1.29) less than water (1.33), the long-path waveguide capillary cell technique began being utilized in spectrophotometric analysis (D'Sa et al., 1999; Zhang et al., 2001). The source light is guided into a Liquid Waveguide Capillary Cell (LWCC) with a fiber optic cable, and the beam is totally reflected at the liquid-wall interface inside the capillary cell. The beam is then guided into a photometer or a spectrometer for detection. The optical length of a waveguide capillary cell can be extended up to 200 cm, while the sample volume can be reduced to a sub-milliliter level. Absorbance signals are significantly enhanced by 2 orders of magnitude compared to regular colorimetric apparatus due to the extended optical path length.

In this study, the detection system is composed of a liquid waveguide capillary cell (100 cm, 200 μL, World Precision Instruments, Inc), a low-drift tungsten light source (FO-6000, World Precision Instruments, Inc), which provides a complete VIS spectrum (380 – 1700 nm); and a miniature fiber optic spectrometer (USB2000, Ocean Optics). A computer is used to perform spectrometer control and data acquisition with OOIBase32 operating software (Ocean Optics). The schematic diagram of a long-path absorption photometer detection system is shown in Figure 2.6.
Figure 2.6 Schematic diagram of a long-path absorption photometer detection system.

The absorption spectrum of derivatization product was determined as shown in Figure 2.7. The indophenol produced in reaction mainly absorbs wavelengths between 525-800 nm with $\lambda_{\text{max}} = 660$ nm. As a result, 660 nm was selected as the detection wavelength, and 810 nm as the reference wavelength due to the significant difference in absorbance at these two wavelengths.

Figure 2.7 The UV-Vis spectrum of indophenol in UV/VIS
Figure 2.8 Schematic diagram of an automatic measurement system for NH₃/NH₄⁺
2.4 System assembly and automation

To efficiently collect continuous atmospheric NH$_x$ concentration data, the individual function modules of sample collection, derivatization and detection were assembled together into an analytical system. A simplified diagram in Figure 2.8 illustrates the assembly of the atmospheric NH$_x$ measurement system. Sampling and on-line derivatization were realized by using a peristaltic pump (IPC, Ismatec) to continuously deliver the scrubbing solution through the samplers, and thoroughly combine it with the derivatization reagents in temperature controlled reaction coils. After remaining in the coils for designed optimal time interval, the derivatized fluids were then loaded into sample loops (200 μL) and injected by an electrically actuated auto-injection valve (10-port, VICI) into a liquid waveguide capillary cell for analysis. There are two separate channels in the system to measure total NH$_x$ and NH$_4^+$ simultaneously. With an acidic-coated (1% citric acid) annular diffusive denuder (30×150 mm, URG), which was connected upstream of a sampler, the gaseous NH$_3$ and aerosol NH$_4^+$ were differentiated. The injection valve, which was controlled by a PC, alternately injected the analytes of each channel every 2 minutes.

The reaction coils were embedded into an aluminum block (Dimensions: 100×60×100 mm), which was regulated by a temperature controlling system (LOVE CONTROLS). To lower the measurement blank, an ion exchange column packed with polystyrene divinylbenzen sulfonic acid resin (AG50W-X8, 20-50 mesh, Bio-Rad) was connected on-line to remove residual NH$_4^+$ in the scrubbing deionized water.
2.5 Concentration calculations

Concentrations of an analyte I in gaseous and aerosol phases could be calculated:

\[ P_i^{\text{gaseous}} = R \, T \, (C_{1i} \, F_{1i} \, / \, F_{1g} \, - \, C_{2i} \, F_{2i} \, / \, F_{2g}) \quad \text{(pptv)} \quad (2.5) \]

\[ P_i^{\text{aerosol}} = C_{2i} \, F_{2i} \, R \, T \, / \, F_{2g} \quad \text{(pptv)} \quad (2.6) \]

Where \( C_{1i} \) and \( C_{2i} \) are the concentrations of analyte in scrubbing solution (nM) in channel 1 and 2; \( F_{i} \) is the flow rate of the scrubbing solution (mL min\(^{-1}\)), and \( F_{g} \) is the flow rate of the air sampling (L min\(^{-1}\)), \( R \) is the gas constant, and \( T \) is the absolute temperature used for mass flow controller calibration (273 K).

2.6 Reagents and materials

The reagents and materials used for the study are listed in the Table 2.1.
Table 2.1 Specifications of the chemicals used in this research

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Molecular Formula</th>
<th>Grade (Purity)</th>
<th>Producer</th>
<th>Use / Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium salicylate</td>
<td>HOC₆H₄COONa</td>
<td>99+%</td>
<td>Aldrich/Fisher</td>
<td>Derivatization reagent</td>
</tr>
<tr>
<td>Sodium hypochlorite</td>
<td>NaClO</td>
<td>Reagent grade</td>
<td>Aldrich</td>
<td>Derivatization reagent/</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Available chlorine ≥4 %</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>NH₄NO₃</td>
<td>99+%</td>
<td>Sigma-Aldrich</td>
<td>Lab experiments</td>
</tr>
<tr>
<td>Ammonium sulfate</td>
<td>(NH₄)₂SO₄</td>
<td>99+%</td>
<td>Sigma-Aldrich</td>
<td>Lab experiments</td>
</tr>
<tr>
<td>Sodium nitroprusside</td>
<td>Na₅[Fe(CN)₅NO]·2H₂O</td>
<td>99.99+%</td>
<td>Aldrich</td>
<td>Derivatization catalyst</td>
</tr>
<tr>
<td>Ammonium chloride</td>
<td>NH₄Cl</td>
<td>99.99+%</td>
<td>Aldrich</td>
<td>Calibration reagent</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>NaCl</td>
<td>99.99+%</td>
<td>Aldrich</td>
<td>Derivatization reagent</td>
</tr>
<tr>
<td>Citric acid</td>
<td>HOC(COOH)(CH₂COOH)₂</td>
<td>99.5+%</td>
<td>Sigma-Aldrich</td>
<td>Denuder coating</td>
</tr>
<tr>
<td>AG 50W-X8 Resin</td>
<td>Polystyrene divinylbenzen sulfonic acid</td>
<td>20-50 mesh</td>
<td>Bio-Rad</td>
<td>D.I. H₂O Purification</td>
</tr>
<tr>
<td>Ammonia</td>
<td>NH₃</td>
<td>Certified/</td>
<td>Matheson</td>
<td>Calibration gas</td>
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<tr>
<td></td>
<td></td>
<td>10 ppm in N₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deionized water</td>
<td>D.I. H₂O</td>
<td>≥ 18.0 MΩ</td>
<td>Millipore Mili-Q</td>
<td>Scrubbing solution</td>
</tr>
</tbody>
</table>
CHAPTER 3. METHOD VALIDATION

Method validation is a necessary process to demonstrate the validity, quality, and reliability of a newly developed analytical technique. Method validation is a process used to confirm that the analytical procedure employed for a specific measurement is suitable for its intended use (LabCompliance, 2009), and is an integral part of any good analytical practice.

Generally, an analytical method validation includes the following steps (LabCompliance, 2009):

1. Accuracy
2. Precision
3. Specificity/selectivity
4. Limit of detection
5. Linearity and range
6. Ruggedness
7. Robustness

In this study, all of above aspects of this newly developed atmospheric NH$_3$/NH$_4^+$ measurement method were examined. The validation procedure includes:

2. Calibration with blended gaseous standards.
3. Inter-comparisons with other major available atmospheric ammonia and ammonium analytical methods in both laboratory and field measurements.
3.1 Calibration

For this wet-scrubbing/colorimetric analytical method, the ideal calibration is to use a series of certified gas-phase standards. Since trace (ppb/sub-ppb) levels of gaseous NH$_3$ standards are not commercially available, a permeation device (Luo et al., 1995) and a blender with elevated (ppm level or higher) gaseous standards (Schwab et al., 2007) are alternately used to verify the performance of the ammonia analytical instrument for both gaseous NH$_3$ and aerosol NH$_4^+$ measurements.

3.1.1 Aqueous standard calibration

For field measurement practices, neither a permeation device nor a blending system is convenient for regular calibration of the ammonia species measurement instrument. As an alternative, an aqueous standard calibration was developed for this study. Based on the formula of E2.5 and E2.6 presented in Chapter 2, if the fluctuations of the sample collection efficiency, the aqueous scrubbing flows, and air sampling flows are controllable and negligible; the WS/LOPAP can be calibrated with a series of NH$_4^+$ standard solutions. The results obtained from laboratory calibration using gas-phase standards, and inter-comparisons with other measurement techniques (to be discussed below), validated the aqueous standard calibration procedure.

The freshly prepared 10.0 mM NH$_4$Cl solution was diluted into 50 μM, then was further diluted into 0.1, 0.25, 1.0, 2.5 and 10.0 μM. The standards were introduced into the sampling and measurement system and the response signals (peak areas) were then recorded. A linear calibration curve was obtained for the concentration range (Figure
3.1), corresponding to a concentration up to 35 ppbv in the air. Low concentrations of aqueous standards, from 0.05 to 0.5 μM, were routinely used for calibration in the field.

![Figure 3.1 The calibration with aqueous NH$_4^+$ standards](image)

3.1.2 Gaseous standard calibration

As a portion of method inter-comparison experiments for NH$_3$ measurement, gaseous standard calibrations for this NH$_3$ measurement system were conducted in a laboratory at the Atmospheric Sciences Research Center (ASRC), University at Albany, New York.

The gaseous standards were prepared using dilutions of a certified ammonia standard source with zero air in a specially designed manifold (Schwab et al., 2007). The
certified ammonia standard (3.55 ppmv NH₃ in N₂, aluminum high-pressure cylinder) was purchased from Scott-Marrin (Riverside, CA). The manifold, which was heated at 40 °C to reduce the ammonia adsorption effect, was made of glass tube with 25 mm I.D. and 4 m length. Five mass flow controllers strictly regulated the gas flows and were calibrated before and after the study period. An oil-free compressor was used to produce compressed air. Zero-air was generated by passing compressed air through a membrane dryer, and then through a zero-air generator (Thermo Electron, Model 111). The certified standard ammonia source was diluted with zero-air to 5 ppbv, standing for 5 hours, 10 ppbv for 5 hours and 20 ppbv for 14 hours respectively. All seven NH₃ measurement systems collected standard samples simultaneously. A piece of 6’ × ¼” PFA tubing was used to pull air from the manifold into 2 samplers of the WS/LOPAP system. The measurement results from WS/LOPAP are presented in Figure 3.2. The regression curve of calibration is shown in Figure 3.3.
Figure 3.2 The gaseous standard calibration results of WS/LOPAP
The measured NH₃ concentrations by WS/LOPAP agreed well with the target values as prepared from the certified ammonia standard. After testing the concentration range of 0-20 ppbv, the response of NH₃ was determined to be linear (R² = 0.99). There was a positive intercept of 0.45 ppbv, most likely due to the NH₃ residue in the “zero-air” generated by filtration system. There were delays in instrument responses, suggesting a relatively slow NH₃ adsorption/desorption process on the wall surfaces of the manifold and the sample inlets of the LOPAP (to be discussed below). The results obtained by WS/LOPAP agreed well with those measured by other ammonia analytical techniques (Schwab et al., 2007).

![Figure 3.3 The calibration with gaseous NH₃ standards](image-url)
3.2 Detection limit and precision

In analytical chemistry, the lowest quantity of an analyte that can be distinguished from the absence of that substance is defined as the detection limit. In some environments, the ambient NH$_x$ concentrations are quite low. In some remote areas, NH$_3$ concentrations can be less than 50 pptv (LeBel et al., 1991; Krupa, 2003). Obviously, a successful atmospheric NH$_x$ measurement method must be sensitive enough to fulfill the field monitoring requirements.

To determine the lower detection limit of the method, an NH$_x$-scrubbed air sample with the NH$_x$ concentration close to blank (~ 0 ppbv) was introduced into the measurement system and measured 10 times under typical measurement conditions (i.e., at a scrubbing flow rate of 0.24 mL·min$^{-1}$, an air sampling flow rate of 2.0 L·min$^{-1}$, and 1.5 min sampling resolution). A detection limit of method (LOD) of 30 pptv was estimated based on three times of standard deviation (3$\sigma$) of the signals. The analytical precision, which is defined as relative standard deviation, was determined by replica sampling ($n = 10$) of ambient samples, which is ±3.0% at $C_{NH_x} \sim 1.5$ ppbv level.

3.3 Linear dynamic range

Linear dynamic range (LDR) is an important factor to evaluate an analytical method. Analytical methods are usually expected to have a LDR of at least two orders of magnitude (Mitra, 2003)

The ambient levels of ammonia species vary significantly in different environments. The typical ranges of NH$_x$ concentrations are from 50 pptv to more than
10 ppbv. Therefore, an NH₃/NH₄⁺ analytical technique with a wide linearity range is essential to simplify the sample preparation procedure and ensure the effectiveness of the analytical data in various environments.

Based on the calibration data presented in 3.1, NH₄⁺ calibration is linear up to a concentration of 10 μM. Under the typical measurement conditions, the linearity range of the method is 30 pptv ~ 35 ppbv, indicating the linear dynamic range of WS/LOPAP as over 3 orders of magnitude. Furthermore, with adjusting the sampling parameters (scrubbing flow rate and air sampling flow rate, see E2.5-2.6), the linearity range for the method can be extended to up to 100 ppbv. Considering the typical NHₓ levels in ambient air range between 0.1~10 ppbv (Seinfeld and Pandis, 1998), the linearity range of this analytical system can ensure full coverage of atmospheric NHₓ measurements in virtually all environments.

### 3.4 Time response and resolution

Time response and resolution are key features for evaluating the performance of a real-time atmospheric compounds monitoring instrument. Rapid response and fine resolution can provide accurate and detailed concentration information especially in some special “events”. **Figure 3.4** shows a calibration signal trace using an aqueous NH₄Cl standard solution for the measurement system. T90 response time, which is defined as the time it takes a detector to reach 90% of its response to a concentration change, was equal to only one or two injection cycles (~6 min).
Adsorption of ammonia on the air sample inlet wall surface has been a great challenge in the atmospheric ammonia measurement, due to its stickiness toward surfaces. The degraded time resolution, caused by the gaseous NH₃ adsorption-desorption on manifold and inlet wall surface, can be found in Figure 3.2. During the step calibration experiment with gaseous standards, the readings from instrument changed gradually instead of a sharp transition, with the T90 response time increased to ~40 min.

To evaluate the time resolutions of the ammonia determination methods during the inter-comparison experiments, two artificial spikes with elevated concentrations (~40 ppbv) were intentionally generated by a blending system to simulate the “atmospheric events”. The results of WS/LOPAP are shown in Figure 3.5. The first spike was based
on zero-air while the second was based on 5 ppbv of NH₃ background. Both spikes were 40 ppbv, lasting for 1 hour. The LOPAP captured both of the spikes quantitatively, as suggested by the similar areas under the measurement trace and the predicted concentration trace. However, the measured concentrations did not reach the targeted values within one hour after the spikes began, and then did not return to the baseline about one hour after spikes were removed; mostly due to the response retardation by NH₃ adsorption and desorption on manifold and inlet wall surface. In the field studies, the samplers were usually installed at the desirable sampling location and height, with a minimal length of the sampling inlet tubing, as short as 2 cm, to minimize the inlet wall surface effect.

![Figure 3.5](image.png)

**Figure 3.5** The response of LOPAP for NH₃ measurement
3.5 Selectivity and interferences

The atmosphere is a mixture of various gases, suspended solids, and liquids that surround the Earth. The selectivity and specificity are important characteristics of atmospheric analytical methods, especially in connection with validation procedures. A successful analytical technique should be able to determine the particular analytes in real samples (mixtures or matrices) without interferences by other components.

Potential interfering factors have been considered and evaluated in this study, including atmospheric reactive species that may react with NH$_3$ during sampling, with the reagent during derivatization, and amino compounds that may interfere with derivatization reaction. O$_3$ and H$_2$O$_2$ are the most abundant atmospheric oxidant. Their potential interference effect on a similar ammonia measurement method, based on aqueous scrubbing followed by OPA derivatization and HPLC/fluorescence detection, had been studied in detail and found to be negligible (Huang, 2002). HCHO, which may consume NH$_3$ through a nucleophilic reaction mechanism, has also been found to be insignificant under similar sampling conditions. Two more atmospheric species were investigated: NO$_2$ and SO$_2$ during the inter-comparison experiments. 110 ppbv SO$_2$ and 60 ppbv NO$_2$ spikes (30 min durations for each) were added into the air stream, respectively, and there was no significant interference occurred in either case.

Organic amino compounds, such as alkyl amines and amino acids, may cause interference on ammonia measurement method based on OPA-derivatization methods (Huang, 2002). However, the Berthelot method is specific for ammonia species; there will not be any other compounds to form into the indophenol during the derivatization process. According to the derivatizing mechanism described in Chapter 2, all three
bonds of nitrogen atom have been occupied to form the indophenol chromophore. Therefore, organic amino compounds, with an alkyl group attached to the nitrogen atom, are unable to form the indophenol derivatives and will not cause any interference with the inorganic NHx detection based on this derivatization reaction.

The indophenol derivative is detected by measuring its light absorbance in a 100 cm long liquid waveguide capillary cell at the wavelength of 660 nm (Figure 2.6). An ambient air sample was introduced into the LOPAP after pass through a citric acid-coated filter to remove the NH3. The response was equivalent to the signal of the blank generated by D.I. H2O. This result indicates that there are few atmospheric species capable of absorbing light at the wavelength to cause any significant interference. However, air bubbles and insoluble particles may block/disturb the optical beam, and could lead to an error in NHx determination. Air bubbles can be mostly removed with a T-shape debubbler assembled prior to the liquid waveguide capillary cell detector. The effectiveness of the debubbler was confirmed by field applications. Most of the insoluble dust is blocked by the glass frit of the sampler described in Figure 2.1. So in this LOPAP system, the interferences are technically minimized to guarantee the accurate determination of the ambient ammonia species.

3.6 Accuracy and reliability

The proximity between the true concentration and the mean test results of the analyte is defined as accuracy of an analytical method. Accuracy is determined by replicate analysis of samples containing a known amount of the analyte. Certified standards are generally used for calibration and accuracy determination. Sometimes the
true value of the sample is unknown or difficult to obtain. In these cases, inter-
comparison with other proven analytical techniques is an alternative way to evaluate the
accuracy and reliability of a newly developed method.

3.6.1 Validation with certified standards

Calibration with certified gaseous standards has been discussed in section
3.1(Figure 3.2 and 3.3). The results from the WS/LOPAP agreed well with target values
blended from a certified gaseous standard. There was only a ~ -3.2% bias (Slope = 0.97)
compared with the expected concentrations. The possible breakthrough of the NH₃
during sampling may account for this underestimation. As discussed in Chapter 2, the
sample collection efficiency of ammonia by the glass-fit sampler was determined to be
above 95% with controlled sampling condition.

3.6.2 Laboratory intercomparison of NH₃ methods

The comprehensive inter-comparison experiments of five atmospheric NH₃
measurement instruments were conducted from September 14-28, 2005 in Atmospheric
Science Research Center, University at Albany. The details of the experiment setups
and results have been described elsewhere (Schwab et al., 2008). Five methods were
involved in the inter-comparisons, including the tunable diode laser absorption
spectrometer (TDLAS) of ASRC (Li et al., 2004; Li et al., 2006), the wet effusive
diffusion denuder (WEDD) of Indiana University (Pryor et al., 2004), the ion mobility
spectrometer (IMS) purchased from Particle Measuring System (Myles et al., 2006;
Schwab et al., 2007), the Nitrolux laser acousto-optical absorption analyzer manufactured
from Pranalytica, Inc. (Schwab et al., 2007) and this newly developed WS/LOPAP technique from School of Public Health, University at Albany (SUNY-SPH). Key results related to the LOPAP are summarized in Figures 3.6 and 3.7.
Figure 3.6 The inter-comparison results of five NH₃ measurement methods in a laboratory setting. The log of operations of the manifold is presented in Table 3.1.
Figure 3.7 Scatter plots for 15-min NH₃ comparison of TDLAS, WEDD, Nitrolux and IMS with LOPAP in a laboratory setting.
Table 3.1 The operation log of the sample manifold for inter-comparison of five NH$_3$ measurement methods

<table>
<thead>
<tr>
<th>Date</th>
<th>Time</th>
<th>Operations</th>
<th>Target [NH$_3$]</th>
</tr>
</thead>
<tbody>
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<td>15:50</td>
<td>“Zero Air”</td>
<td>0</td>
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<td>9/14/2005</td>
<td>17:00</td>
<td>Synthetic Standard</td>
<td>20</td>
</tr>
<tr>
<td>9/15/2005</td>
<td>8:00</td>
<td>“Zero Air”</td>
<td>0</td>
</tr>
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<td>Synthetic Standard</td>
<td>20</td>
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<tr>
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<td>Ambient Air</td>
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<td>17:00</td>
<td>“Zero Air”</td>
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</tr>
<tr>
<td>9/16/2005</td>
<td>8:00</td>
<td>Ambient Air</td>
<td>N/A</td>
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<td>16:00</td>
<td>Ambient Air</td>
<td>N/A</td>
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<td>N/A</td>
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<td>0</td>
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<td>10</td>
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<tr>
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<td>40</td>
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<td>9/26/2005</td>
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<td>9/27/2005</td>
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</tr>
<tr>
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<td>10</td>
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<tr>
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</table>
The LOPAP instrument performed very well during the experimental period. All proposed targets of the experiments were achieved:

✧ Under the stable calibration concentrations, the LOPAP agreed with the expected value within 10% bias.

✧ During the spike tests, the LOPAP caught every spike accurately, with reasonable response time.

✧ The overall results of the LOPAP agreed with TDLAS (R²=0.90) and IMS (R²=0.96) very well. These three instruments performed the best during the inter-comparison experiments.

✧ The LOPAP showed its robustness during the 15 days of continuous testing. Except for scheduled calibration and maintenance, the LOPAP monitored the samples constantly during the entire experimental testing period without interruption.

The inter-comparison of the ambient air sample is shown in Figure 3.8. During the 64-hour measurement, the results showed excellent agreement between the LOPAP and the IMS, the LOPAP and the TDLAS, in both concentration values and timing of events.
Figure 3.8 A 64-hour measurement of NH₃ in ambient air with IMS, TDLAS, WEDD, Nitrolux and LOPAP in Albany, NY.
3.6.3 Field intercomparison of aerosol NH$_4^+$ methods

Four aerosol NH$_4^+$ measurement techniques have been intercompared during two intensive field campaigns, including the particle-into-liquid sampler – ion chromatography (PILS-IC) of Georgia Tech (Orsini et al., 2003), quadropole-aerosol mass spectrometer (Q-AMS) of ASRC (Alfarra et al., 2004), EPA’s speciation trends network (STN) filter method from ASRC (Schwab et al., 2004), and the wet scrubbing long-path absorption photometer (LOPAP) from SUNY-SPH. The details of sites, experimental setups, and results were described in literature (Bae et al., 2007).

During the winter of 2004, PILS-IC, Q-AMS and LOPAP were deployed for real-time ammonium aerosol measurements as a part of the campaign of PM2.5 Technology Assessment and Characterization Study-New York (PMTACS-NY). Because of the unusual cold weather during the campaign, LOPAP system was set up in a trailer with a 1.5-m PFA inlet (heated at 50°C to reduce surface adsorption) extended 2.7 m above ground. The inlets were 12 m and 15 m for PILS-IC and Q-AMS, respectively, in the next trailer. The results of aerosol NH$_4^+$ measurements by PILS-IC, Q-AMS and LOPAP were presented in Figure 3.8. The LOPAP data agreed well with PILS-IC and Q-AMS during the majority of the time. It caught every major “event”, as the peer instruments did. However, the measured NH$_4^+$ concentrations during major events were lower by the LOPAP than by PILS-IC and Q-AMS. The discrepancies in the measured NH$_4^+$ concentrations may in part due to the difference in sampling heights/location of the measurement systems, and in part due to wall loss/decomposition of NH$_4$NO$_3$ on the heated inlet of our system.
Figure 3.8 Hourly averaged inter-comparison of particulate NH$_4^+$ measured with PILS-IC, Q-AMS and LOPAP in Queens College, NY from January 14 to February 7 in 2004. This plot is cited from literature (Bae et al., 2007).
During the summer of 2004, PILS-IC, Q-AMS, STN filter and LOPAP were deployed for NH$_4^+$ measurements as a part of PMTACS-NY field campaign in Pinnacle State Park site, New York from July 18 to August 8 in 2004. This time all system inlets were set up at five meters above ground. The glass-frit coils of LOPAP were installed at the sampling location and thus a minimum short inlet (2 cm) was used. The inter-comparison results of PILS-IC, Q-AMS and STN filter with LOPAP are presented in Figure 3.9 and 3.10. The data from LOPAP consistently agreed very well with other two real-time instruments: PILS-IC ($R^2 = 0.89$) and Q-AMS ($R^2 = 0.82$). The daily average agreed well with the results from the STN filter method ($R^2 = 0.99$). The LOPAP system was working properly and continuously, recording every detail of the “events”.
Figure 3.9 Inter-comparison of particulate NH$_4^+$ measured with PILS-IC, Q-AMS, Filter and LOPAP in Pinnacle State Park, NY from July 18 to August 8 in 2004.
Figure 3.10 Scatter plots for particulate NH$_4^+$ comparison of PILS-IC, Q-AMS, and Filter with LOPAP in Pinnacle State Park, NY.
3.7 Summary

We have confirmed all the criteria for evaluating the validity of a newly developed analytical method for the measurement of atmospheric ammonia and ammonium based on Berthelot’s reaction with long path absorption photometer detection. It has been demonstrated to be a highly-sensitive method for both gaseous NH$_3$ and aerosol-phase NH$_4^+$ with a lower detection of 30 pptv, and T90 response time of <5 min. No significant interferences were found from reactive atmospheric species such as O$_3$, H$_2$O$_2$, HCHO, NO$_2$ and SO$_2$ and from organic amino compounds. Calibration using certified gas-phase standards and intercomparisons with other established methods validated this measurement technique. Long inlets have been found to prolong response time in NH$_3$ measurement due to its stickiness, and cause potential loss of NH$_4^+$ by NH$_4$NO$_3$ decomposition on surface. To obtain the best data quality, the shortest possible inlets should be used in the field.
CHAPTER 4. FIELD MEASUREMENT APPLICATIONS

Atmospheric chemistry, as the name implies, involves study of the chemistry of the Earth’s atmosphere. The research activities mainly include field measurement campaigns, laboratory studies, modeling, and instrument development. Field observations are essential to our understanding of the chemical behaviors of the atmosphere. They provide first-hand information of the chemical compositions and their changes over time. The field application is also a unique way to evaluate the validity of a newly developed analytical method.

To investigate the ammonia species temporal variations in different environments, elucidate their relationships with other physical, chemical and meteorological parameters, and to further understand the atmospheric behaviors of NH₃ and their potential impact on the ecosystems, intensive field studies were conducted in four representative environments from the Summer 2003 to the Summer 2005. These field campaigns included:

1. Summer rural forest environment in University of Michigan Biological Station (UMBS) in Pellston, MI in 2003.
2. Winter urban site on Queen College campus, Queens, NY in 2004.

The information summary of ammonia species measurement sites for CWF/LOPAP field applications is listed in **Table 4.1**. The locations of the
measurements’ sites are shown on the map (Figure 4.1). Results from each field study will be presented and discussed in one of the following 4 sections.

Table 4.1. Information summary of ammonia species measurement sites

<table>
<thead>
<tr>
<th>Site</th>
<th>UMBS$^1$</th>
<th>QUEENS$^2$</th>
<th>PSP$^2$</th>
<th>Albany</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latitude</td>
<td>45.50°N</td>
<td>40.74°N</td>
<td>42.09°N</td>
<td>42.70°N</td>
</tr>
<tr>
<td>Longitude</td>
<td>84.70°W</td>
<td>73.82°W</td>
<td>77.21°W</td>
<td>73.80°W</td>
</tr>
<tr>
<td>Elevation above MSL</td>
<td>238 m</td>
<td>25 m</td>
<td>505 m</td>
<td>86 m</td>
</tr>
<tr>
<td>Sampling elevation</td>
<td>29 m</td>
<td>2.7 m</td>
<td>5 m</td>
<td>5 m</td>
</tr>
<tr>
<td>Classification</td>
<td>Rural</td>
<td>Rural</td>
<td>Urban</td>
<td>Urban</td>
</tr>
<tr>
<td>Characteristics</td>
<td>Forest</td>
<td>Residential/ Forest/ Residential/</td>
<td>Commercial Golf course Commercial</td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>2003 summer</td>
<td>2004 winter</td>
<td>2004 summer</td>
<td>2005 summer</td>
</tr>
</tbody>
</table>

Notes: 1. Information is from Carroll et al, 2001.
4.1 Measurement of ambient NH$_x$ over a forest area in Northern Michigan

4.1.1 Site descriptions

The measurements were conducted in the University of Michigan Biological Station, which is located in the northern tip of the Michigan Lower Peninsula (45° 30’ N, 84° 47’ W, elevation 238 m, A.S.L.). This region is largely characterized as forest and woodlands, lakes, small towns, villages and farms. The area is featured as “mixed” or “transition” forest, with northern hardwood, mixed aspen, pine and oak (Carroll et al., 2001). The ammonia emission is estimated at a relatively low density (0-0.86 ton·mi$^{-2}$, NEI 1999 data) in this region, make it an ideal site to study the natural interactions between the atmosphere and the forested ground surfaces.
Figure 4.2. The NH₃ measurement site in Michigan forest (from Google Earth). The symbol ⊕ indicates the location of PROPHET site in the UMBS.

The CWF/LOPAP system was set up on the PROPHET tower, which is located in a forest area about 3.5 km west of the UMBS campus. The location is showed on the map (Figure 4.2). The 31 m tall measurement tower was built initially for the Program for Research on Oxidants: Photochemistry, Emissions, and Transport. To investigate the temporal variations of the ammonia species above the canopy level (average ~21 m in 2003), the CWF/LOPAP was installed at 29 m level. There were two inlets to collect the air samples in parallel, one with a citric acid coated denuder for particulate ammonium (NH₄⁺), while the other without a denuder for total ammonia species (NH₃). There were
two pieces of 2’ L × 1/4”-OD× 1/8”-ID PFA tubing connected to the samplers to deliver the air samples. The measurement system settings are shown in Figure 4.3.

**Figure 4.3.** Instrument set-up for NHₙ measurements in UMBS. Position of the instrument on the PROPHET tower is presented on left panel. Sampling system is illustrated on right panel.

4.1.2 Summary of the measurement results

This is the very first time the CWF/LOPAP system was utilized for measurements of ammonia species. Overall, the maiden work had been accomplished pretty well. 97%
of the data captured by the channel for total ammonia species was valid; while 88% was captured by ammonium aerosol channel due to a 1.5-day’s failure during a severe thunder storm. Typically, during the two-week monitoring period, both gaseous NH$_3$ and aerosol NH$_4^+$ mixing ratios were measured to be below 1 ppbv. In general, the aerosol ammonium was dominant and the gaseous ammonia was at relatively low level. The summary of the measurement results is presented in Table 4.2. The CWF/LOPAP system caught a major “event” that appeared in July 26, 2003, which lasted about 30 hours with a peak concentration of 4.5 ppbv. The origin of this polluted plume will be discussed below. The measured time series of ammonia species mixing ratios is presented in Figure 4.4.

Table 4.2. Statistics of the results of NH$_x$ measurement in Michigan forest.

<table>
<thead>
<tr>
<th>Target species</th>
<th>NH$_x$</th>
<th>NH$_4^+$</th>
<th>NH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monitoring Periods</td>
<td>7/17/03, 18:00 – 7/31/03, 21:00</td>
<td>4 min</td>
<td></td>
</tr>
<tr>
<td>Data Frequency</td>
<td>0.04 – 4.47</td>
<td>0.04 – 2.18</td>
<td>≤ 0.03 – 0.94</td>
</tr>
<tr>
<td>Data captured</td>
<td>97%</td>
<td>88%</td>
<td>87%</td>
</tr>
<tr>
<td>Median, ppbv</td>
<td>0.84</td>
<td>0.51</td>
<td>0.27</td>
</tr>
<tr>
<td>Mean, ppbv</td>
<td>0.99</td>
<td>0.55</td>
<td>0.30</td>
</tr>
</tbody>
</table>
Figure 4.4. Time series of ammonia species concentrations in UMBS-2003 measurement.
4.1.3 Back trajectory analysis

To investigate the sources of the polluted air mass with elevated NH$_x$ detected by LOPAP in July 26, 2009, a Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model was employed to trace the origin of the plume. HYSPLIT, which was developed by National Oceanic and Atmospheric Administration (NOAA), is a model for computing simple air parcel trajectories to complex dispersion and deposition simulations (ARL, 2009). It is an effective tool for the back trajectory analysis of air masses in atmospheric chemistry research. The computing results of the back trajectory are presented in Figure 4.5. 72-hour trajectories were calculated with the HYSPLIT model for the air masses monitored in July 26, which represents a “dirty” plume (NH$_x$ levels up to 4.5 ppb), and in July 29, which represents a “clean” air parcel (NH$_x$ levels below 0.5 ppbv).

![Figure 4.5. Back trajectory analysis for the origins of the air masses in UMBS](image-url)
Panel A in the Figure 4.5 indicates the air mass containing elevated concentrations of ammonia species came from northern Indiana which is characterized an agriculture intensive area with relatively heavy ammonia emissions (1.7-4.5+ ton·mi⁻², NEI 1999 data). Before reaching the measurement site, this air parcel had been moving relatively close to the ground surface (lower than 100 m), which could thus effectively pick up the freshly emitted ammonia species from the sources. The panel B shows the air mass with the low level NHₓ in July 29 originated from north Ontario of Canada. It started at ~500 m altitude and passed through Lake Superior and Lake Michigan before arriving at the measurement site. All the regions this air parcel had been traveling through are characterized as relatively clean areas. The ammonia emission distribution information of the adjacent regions is shown in Figure 4.6.

![Image](image.png)

**Figure 4.6.** The ammonia emission distribution in adjacent areas of the UMBS

(Source: US EPA Office of Air and Radiation, NEI Database)
4.1.4 Diurnal pattern and correlation with temperature

The concentrations of the total ammonia species presented an interesting diurnal pattern during the measurement duration. On a 24-hr scale, the total NH$_x$ concentrations showed a maximum at afternoon (~ 4:00 p.m.) and a minimum during nighttime (11:00 p.m. - 6:00 a.m.). Figure 4.7 shows the NH$_x$ level had been correlated to the environmental temperature during the most time of the measurement period. The only exception is in July 26 - 27; the ammonia species didn’t follow the temperature pattern because the exotic polluted air parcel masked its inward trend.

Figure 4.7. The time series of ammonia species concentrations and ambient temperature.

(Temperature data source: [www.wunderground.com](http://www.wunderground.com); Pellston, MI, Airport)
To investigate the relation between the ambient temperature and the concentration of the ammonia species, further statistical studies were made based on the measurement results. To avoid the interference from the externally introduced pollutions especially in July 27-28, the results from the first week’s measurements (July 18-25, 2003) were picked for the statistical analysis. The typical diurnal patterns of the total ammonia species, gaseous ammonia and aerosol ammonium are shown in Figure 4.8.

On average, the ambient temperature started to rise after sunrise, at around 6:00, due to surface heating, reach a relatively broad maximum plateau from 12:00 to 18:00. The mixing ratio of aerosol NH$_4^+$ showed similar variation pattern, starting to increase around 8:30, and reached a relatively broad maximum concentration plateau from 13:00 to 18:00. NH$_4^+$ was lowest in ~6:00, while the temperature is bottomed. The NH$_4^+$ diurnal fluctuation range was 0.32 – 0.65 ppbv. Compared with NH$_3$, the diurnal pattern of NH$_4^+$ is more similar to the temperature. The NH$_x$ mixing ratio followed the diurnal pattern of NH$_4^+$, with a range of 0.5 – 1.1 ppbv. On the other hand, NH$_3$ mixing ratios exhibited a different diurnal variation pattern from those of ambient temperature, NH$_4^+$ and NH$_x$, with a maximum of ~0.4 ppbv at 12:00 and a minimum of 0.25 ppbv at 21:00.
Figure 4.8. The diurnal patterns of ammonia species at PROPHET site (NH₃, NH₄⁺ and NH₃ data are hourly averaged from the measurement results during July 18-25, 2003; Temperature data are hourly-mean in the same duration from www.wunderground.com; Pellston, MI, Airport.)

With one-dimensional linear regression processing, the temperature dependences of the mean concentrations of NH₃, NH₄⁺ and NH₃ measured from July 18-25, 2003 were presented in Figure 4.9. The results indicate NH₄⁺ and total NHₓ were significantly correlated with ambient temperature, with a R² of 0.87 and 0.85, respectively. No significant correlation existed between NH₃ and ambient temperature (R² = 0.05).
Figure 4.9. The temperature dependence of the mean concentrations of ammonia species measured at the PROPHET site over the forest canopy during July 18-25, 2003.
4.2 Measurement of ambient NH$_x$ in New York City urban environment

4.2.1 Site descriptions

The PM2.5 Technology Assessment and Characterization Study-New York (PMTACS-NY) is one of several U.S. EPA "Supersites" field campaigns intended to provide enhanced measurement data on chemical and physical composition PM and its associated precursors (http://www.asrc.cestm.albany.edu/pmtacsny/; Drewnick et al., 2004). As a part of PMTACS-NY-2004 Winter Intensive campaign, the NH$_x$ measurement was conducted at Queens College (40.74 °N, 73.82 °W; altitude, ~25 m A.S.L.), which is located between the Flushing and Forest Hills neighborhoods in the borough of Queens.

Figure 4.10 The NH$_x$ measurement site in Queens College, NY (source: maps.google.com).
The site location is illustrated in Figure 4.10. It is about 750 m south of the Long Island expressway (I-495) and about 1 km east of the Van Wyck expressway (I-678), which are two high-traffic highways in the New York City metropolitan area (Drewnick et al, 2004). The site is adjoined to the east by a roughly one square kilometer cemetery. Flushing Meadow Corona Park and Kissena Park (both large urban parks) are each less than 2 km from the site.

The inlets set-up of the CWF/LOPA measurement system is shown in Figure 4.11. The sampling system was initially placed on the roof of the trailer at five meters above the ground. However, due to the unusually cold weather conditions (T = -17.1−5.6 °C) during the campaign, the samplers were then moved into the trailer to prevent the scrubbing solution from freezing. The sample inlets were left outside of the trailer, about 0.35 m from the window, and 2.7 m above the ground.

Figure 4.11. The sampling setting for NH₃ measurements in Queens College
There were two inlets to collect the air samples in parallel; one with a citric acid-coated denuder for particulate ammonium (NH$_4^+$), while the other without a denuder for total ammonia species (NH$_x$). There were two pieces of 5’ L × 1/4”-OD × 1/8”-ID PFA tubing connected to the samplers to deliver the air samples. The inlets were heated with a heating tape to reduce the adsorption on the wall surfaces.

4.2.2 Summary of the measurement results

The CWF/LOPAP collected three weeks of data continuously from January 14 to February 3, 2004. During the measurement duration, 87% of the data captured by the channel for total ammonia species was valid, while 84% of the data captured by ammonium aerosol channel was also valid. In general, the gaseous ammonia was dominant compared to the aerosol ammonium. The summary of the measurement results is presented in Table 4.3. The measured time series of ammonia species mixing ratios is presented in Figure 4.12.

Table 4.3. Statistics of the results of NH$_x$ measurement in Queens College

<table>
<thead>
<tr>
<th>Target species</th>
<th>NH$_x$</th>
<th>NH$_4^+$</th>
<th>NH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampling Duration</td>
<td>1/14/04, 18:30 – 2/03/04, 6:30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Data Frequency</td>
<td>3 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Data Range, ppbv</td>
<td>0.13 – 22.47</td>
<td>≤ 0.03 – 3.93</td>
<td>≤ 0.1 – 21.0</td>
</tr>
<tr>
<td>Mean, ppbv</td>
<td>2.23</td>
<td>0.76</td>
<td>1.49</td>
</tr>
<tr>
<td>Median, ppbv</td>
<td>1.48</td>
<td>0.63</td>
<td>0.79</td>
</tr>
<tr>
<td>Data captured</td>
<td>87%</td>
<td>84%</td>
<td>81%</td>
</tr>
</tbody>
</table>
Figure 4.12. Time series of ammonia species concentrations in PMTACS-NY-Queens College-2004.
The NH$_3$ levels spread over a broad range of $\leq 0.1$ - 22 ppbv, with a mean of 1.49 ppbv. The median mixing ratio over the campaign was 0.79 ppbv, which agrees with the result of 0.8 ppbv measured with tunable diode laser absorption spectrometer (Li et al., 2006). The inlet of the TDLAS was located ~ 3 m south from the inlets of the LOPAP and at the same height from the ground (~2.7 m). Overall, the ammonia concentration trend was relatively smooth during the first half of the campaign (before January 24, 2004), and then became increasingly erratic after. Compared to the gaseous NH$_3$, the trend of aerosol NH$_4^+$ was steadier with fewer spikes. Typically, the ammonium levels were in the range of 0-2 ppbv, with a median of 0.63 ppbv and a mean of 0.76 ppbv.

### 4.2.3 Diurnal patterns

The measured results of gaseous NH$_3$ and aerosol NH$_4^+$ collected over a three-week period were averaged hourly. Their diurnal patterns are shown in Figure 4.13. On a 24-hour scale, both NH$_3$ and NH$_4^+$ presented twin-peak patterns. Daily measurements of gaseous NH$_3$ fluctuated over a much broader range (0.71-2.46 ppbv) compared to aerosol NH$_4^+$, whose range was between 0.61 to 0.99 ppbv. The mixing ratio of NH$_3$ started increasing around 6:00 a.m. It reached the first peak value at 9:00 a.m., then started falling until ~2:00 p.m., when it reached its daytime low. The NH$_3$ level began increasing again at approximately 2:00 p.m. and reached its second summit, the highest value of the day, at 6:00 p.m. The level then steadily declined to its daily low-point at around 5:00 a.m.
The \( \text{NH}_4^+ \) concentration reached the two peaks at 10:00 a.m. and 6:00 p.m., and the daily low appeared at around the mid-night (12:00 – 1:00 a.m.). Based on correlation coefficients of \( R^2_{\text{NH}_4/T} = 0.41 \) and \( R^2_{\text{NH}_4^+/T} = 0.01 \), neither the ammonia nor the ammonium measured at Queens College site indicated clear temperature dependence.

**Figure 4.13.** The diurnal patterns of ammonia species in PMTACS-NY-Queens College-2004. Temperature, \( \text{NH}_4^+ \) and \( \text{NH}_3 \) data were averaged hourly from the measurement results recorded during January 14-February 3, 2004.
4.2.4 Distribution with wind direction

The ammonia species diurnal patterns described above (Figure 4.13) suggests a significant correlation between NH$_x$ level and traffic intensity. The measurement site is adjacent to two major highways (I678 and I495). To further understand the major source of the ammonia in urban areas, it is necessary to investigate the contribution of on-road vehicles to the total ammonia emissions. For this reason, the wind impact is considered. The gaseous NH$_3$ mixing ratios plotted by wind direction in this field campaign is shown in Figure 4.14. It presented southern direction minimums and northwest direction maximums.

Figure. 4.14. NH$_3$ concentrations distribution with wind direction. Distance from the origin indicates the mixing ratios of ammonia in ppbv. Wind direction was recorded as degrees clockwise from true north.
4.3 Measurement of ambient NH\textsubscript{x} in Pinnacle State Park

4.3.1 Site descriptions

Pinnacle State Park is located in Addison, NY, a rural area in the New York/Pennsylvania Twin Tiers Region (42.09°N, 77.21°W; 515 m elevation). It is a rural site operated by ASRC located in the “transport corridor” between the industrial Midwest and the eastern seaboard (NASTRO, 2009; Schwab \textit{et al} 2004). The measurement site is located in an open clearing on Orr Hill, which is ~ 12 m below and about 100 m east of the highest hill in the park. The closest trees are ~ 50 meters away and the surrounding areas include a 50 acre pond, pastures, undeveloped state forest lands and a 9-hole golf course (NARSTO, 2009; Dutkiewicz \textit{et al.}, 2004). The detailed site location is illustrated the map below (\textbf{Figure 4.15}).

\textbf{Figure 4.15.} The NH\textsubscript{x} measurement site in Pinnacle State Park, NY (source: maps.google.com).
The village of Addison (population ~ 1,800) is 4 km to the northwest and the town of Corning (population ~ 12,000) is 15 km to the northeast of the site. It is an ideal site to study the long distance transportation of the atmospheric pollutants from the Midwest to the Northeastern region of the U.S.

The CWF/LOPAP instrumentation was housed in a 10’ × 8’ camping tent, which was neighbored closely to a trailer for housing other equipments. About 2 meters south to the trailer, there was an Ekto shelter, with a 10-meter meteorological tower installed at the site. Two sample inlets (with and without a citric acid-coated denuder) were installed on the roof of the trailer, about 5 meters from the ground. The detailed set up is presented in Figure 4.16.

![Sampling Set Up](image)

Figure 4.16. The sampling set up for NH$_x$ measurements in Pinnacle State Park.
4.3.2 Summary of the measurement results

The CWF-LOPAP collected about four weeks of effective data continuously from July 13 to August 8, 2004. During the measurement duration, 93% of the data captured by the channel for total ammonia species was valid, while 90% of the data captured by ammonium aerosol channel was also valid. In general, the aerosol NH$_4^+$ (mean of 1.3 ppbv) was dominant and the gaseous NH$_3$ (mean of 0.55 ppb) was at relative low level. The summary of the measurement results is presented in Table 4.4. The time series of ammonia species mixing ratios is presented in Figure 4.17. The aerosol NH$_4^+$ concentration spread from below the detection limit of 30 pptv to 9.4 ppbv, and the mixing ratios of NH$_3$ spread from ≤ 30 pptv to 5.27 ppbv. Several polluted air-mass events were captured and the origin will be discussed below.

Table 4.4. Statistics of the results of NH$_x$ measurement in Pinnacle State Park.

<table>
<thead>
<tr>
<th>Target species</th>
<th>NH$_x$</th>
<th>NH$_4^+$</th>
<th>NH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monitoring Periods</td>
<td>7/13/2004, 12:00 – 8/8/2004, 12:00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Data Frequency</td>
<td>3 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Data Range, ppbv</td>
<td>≤ 0.03 – 9.65</td>
<td>≤ 0.03 – 9.40</td>
<td>≤ 0.03 – 5.27</td>
</tr>
<tr>
<td>Median, ppbv</td>
<td>1.39</td>
<td>0.79</td>
<td>0.47</td>
</tr>
<tr>
<td>Mean, ppbv</td>
<td>1.84</td>
<td>1.30</td>
<td>0.55</td>
</tr>
<tr>
<td>Data captured</td>
<td>93%</td>
<td>90%</td>
<td>86%</td>
</tr>
</tbody>
</table>
Figure 4.17 Time series of ammonia species concentrations in PSP-2004.
4.3.3 Back trajectory analysis

72-hour trajectories were calculated with the HYSPLIT model for the typical air masses monitored. The computing results are presented in Figure 4.18.

Figure 4.18 Back trajectory analysis for the origins of the air masses in PSP.
Four typical episodes were investigated for their possible origins. They are: low NH$_x$ level quiet periods at July 24, 8:00 p.m. (panel A) and at August 3, 11:00 p.m. (panel B); elevated NH$_x$ level periods at July 22, 8:00 a.m. (panel C) and at July 30, 9:00 a.m. (panel D). Both panel A and B in the Figure 4.18 indicate the “clean” air masses originated from Northern Canada, then passed through the Lake Ontario and western New York. All regions the air parcels traveled are less populated areas with relatively low ammonia emissions. Panel C shows the air mass came from southern Ohio, passed thorough northern West Virginia and from south to north Pennsylvania. Panel D shows the itinerary of the air mass was mainly inside the Pennsylvania and hovered around the Philadelphia adjacent area. Those regions are either populated or industrialized areas with relatively heavy ammonia emissions (0.86-4.5+ ton·mi$^{-2}$, NEI 1999 data, Figure 4.6).

4.3.4 Diurnal patterns

The measured results of gaseous NH$_3$ and aerosol NH$_4^+$ collected over a four-week period were averaged hourly. Their diurnal patterns are shown in Figure 4.19. On a 24-hour period, NH$_4^+$ presented a single-peak pattern, while NH$_3$ showed a relatively flat concentration trend. Daily measurements of aerosol NH$_4^+$ fluctuated over a much broader range (0.54-1.35 ppbv) compared to gaseous NH$_3$, whose range was between 0.37 to 0.67 ppbv. The NH$_4^+$ concentration started increasing around 10:00 a.m. It reached the peak value at 2:00 p.m., and then started falling to the daily low during the nighttime. The mean temperature also showed a diurnal pattern with a minimum in the early morning before sunrise and a maximum in the early afternoon. However, the shapes of the diurnal pattern of NH$_4^+$ concentration and temperature were quite different:
the daytime maximum of NH$_4^+$ was narrow and pointy, while that of temperature was broad and round.

**Figure 4.19.** The diurnal patterns of ammonia species in PSP -2004. Temperature, NH$_4^+$ and NH$_3$ data were averaged hourly from the measurement results recorded during July 13-August 9, 2004.
4.4 Measurement of ambient NH₃ in Empire State Plaza, Albany, NY

4.4.1 Site descriptions

The last field application of CWF/LOPAP was conducted at the Empire State Plaza (42°39' N, 73°46' W; altitude, ~60 m A.S.L.), which is located in Downtown area of Albany City, New York (Figure 4.20), and is at the southeastern corner of the Capital District metropolitan area. It is about 1 mile south of the interstate highway I-90 and about 500 m west of the local highway 787, which are two high-traffic roads in the area during the rush hours.

The sampling devices and measurement system of ammonia species and NOₓ were placed in a large courtyard that serves as the air intake for the entire Plaza. The courtyard is roughly a cube with 30m in length, width and height. About 15,300 m³ min⁻¹ air is drawn through the area, resulting 1.8 min residence time in the courtyard.

Figure 4.20. The NH₃ measurement site in ESP, Albany, NY (source: maps.google.com)
The CWF/LOPAP instrumentation was installed in a rack of 19” L × 19” W × 65” H. The samplers (one with a citric acid-coated denuder, one without a denuder) were put at 2.2 m above the ground. Sampling inlet (a 9-ft ¼”-OD PFA tubing) for NOₓ analyzer was put next to the NHₓ inlets with same height. The detailed set up is shown in Figure 4.21.

Figure 4.21 The instruments set-up for NHₓ measurements in ESP, Albany, NY.
4.4.2 Summary of the measurement results

The CWF/LOPAP collected about four weeks of effective data continuously from June 20 to July 18, 2005. During the measurement duration, 93.5% of the data captured by the channel for total ammonia species was valid, while 93.2% of the data captured by ammonium aerosol channel was also valid. The summary of the measurement results is presented in Table 4.5. The measured time series of NH$_4^+$, NH$_3$, NH$_x$ and NO$_x$ mixing ratios, ambient temperature and relative humidity is presented in Figure 4.22.

Table 4.5. Statistics of the results of NH$_x$ measurement in ESP, Albany, NY

<table>
<thead>
<tr>
<th>Species</th>
<th>NH$_x$</th>
<th>NH$_4^+$</th>
<th>NH$_3$</th>
<th>NO</th>
<th>NO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monitoring period</td>
<td></td>
<td>6/20/2005-7/18/2005</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Data frequency</td>
<td></td>
<td>3 min</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mixing Ratios, ppbv</td>
<td>0.53 - 15.6</td>
<td>≤0.03 - 9.38</td>
<td>≤0.1 - 10.9</td>
<td>≤0.05 - 106.7</td>
<td>0.53-51.69</td>
</tr>
<tr>
<td>Mean, ppbv</td>
<td>3.89</td>
<td>2.07</td>
<td>1.83</td>
<td>3.44</td>
<td>9.39</td>
</tr>
<tr>
<td>Median, ppbv</td>
<td>3.39</td>
<td>1.53</td>
<td>1.63</td>
<td>1.66</td>
<td>7.81</td>
</tr>
<tr>
<td>Data captured</td>
<td>93.5%</td>
<td>93.2%</td>
<td>93%</td>
<td>99.7%</td>
<td>99.7%</td>
</tr>
</tbody>
</table>
Figure 4.22 Time series of ammonia species and NOx concentrations, ambient temperature and relative humidity in ESP, Albany, NY.
The aerosol ammonium concentration spread from below the detection limit to 9.4 ppbv, with a mean of 2.07 ppbv and a median of 1.53 ppbv. The mixing ratios of ammonia spread from 0.1 ppbv to 10.9 ppbv, with a mean of 1.83 ppbv, median of 1.63 ppbv. Several polluted air-mass events were captured and the origin will be discussed below.

4.4.3 Back trajectory analysis

48-hour trajectories were calculated with the HYSPLIT model for the typical air masses monitored. The computing results are presented in Figure 4.23. During the clean “background” periods, the air masses were usually fast-moving and came from low NH3-emission regions such as northern Canada (Panel A, 7/7/05) or from the Atlantic ocean (Panel B, 6/29/05). There were a few “episodes” with high levels of NHx during the measurement period. The aerosol ammonium concentrations were notably higher (above 5 ppbv) in days of June 25-27, 30, July 1, 5 and 14. The air masses either originated and/or passed through the industrial and farming areas in the Midwest (Panel C, 6/25/05-6/27/05) or a densely populated and industrial mid Atlantic region (Panel A, 7/6/05). The air parcel with elevated NH3 (above 10 ppb) of July 16 (Panel D) came from southeast. However the aerosol NH4+ level (2-3 ppbv) was relatively low, suggesting that the elevated NH3 mainly came from the emission sources nearby. Indeed, the back trajectory result indicates that the air mass originated from New York City metropolitan area and lingered in the neighborhood of Albany-capital region over ~24 hr.
Figure 4.23  Back trajectory analysis for the origins of the air masses in monitored in ESP, Albany, NY
Figure 4.24 The diurnal patterns of ammonia species in ESP, Albany, NY. NH$_4^+$ and NH$_3$ concentrations were averaged hourly from the measurement results recorded during June 20 to July 18, 2005.
4.4.4 Diurnal patterns

The measured results of gaseous NH$_3$ and aerosol NH$_4^+$ collected over a four-week period were averaged hourly. Their diurnal patterns are shown in Figure 4.24. On a 24-hour scale, both NH$_4^+$ and NH$_3$ presented a weak double-peak pattern, indicating the contribution of local emission from traffic source to the ambient NH$_x$.

4.4.5 Wet scavenging of ammonia species

There were six major precipitation processes during measurement period: June 22, 29 and July 1, 5, 7, 14. The sharply drops of NH$_3$ and NH$_4^+$ concentrations were observed in all of the heavy rain periods. The results indicated wet scavenging is one of the major sinks of the atmospheric ammonia species.

4.5 Discussion

4.5.1 Forest as an NH$_x$ source in rural environments

The similar diurnal variation patterns of NH$_x$ and ambient temperature, observed at the PROPHET site (Figure 4.8) and at a lesser degree at the PSP site (Figure 4.19), may be due to the local NH$_3$ emission from the canopy surface. Indeed, natural forests have been found to exchange ammonia with atmosphere: the canopy acts as an ammonia source when exposed to environment containing low NH$_3$ concentrations, but a sink when exposed to air enriched by nearby NH$_3$ emission sources (Langford and Fehsenfeld, 1992; Schjoerring et al., 1998). The concentration gradient between the sub-stomatal cavities of leaves and the atmosphere will lead to an ammonia flux (Schjoerring et al., 1998):
\[ F_{NH_3} = g_{NH_3} \cdot (\chi_s - \chi_a) \]  

where the \( F_{NH_3} \) represents the ammonia flux; \( g_{NH_3} \) is the conductance to diffusion of NH\(_3\) through the stomata and the boundary layer surrounding the leaf; \( \chi_s \) stands for the NH\(_3\) concentration in the air of the sub-stomatal cavities; \( \chi_a \) is the NH\(_3\) concentration in the ambient atmosphere.

The direction of the ammonia flux is decided by the relative \( NH_3 \) concentrations of the internal and external air of the leaves. When \( F_{NH_3} \) is zero, it means the ammonia uptake rate of the plant is equal to the rate of ammonia released by the plant. At this point, equilibrium has been reached. The \( NH_3 \) concentration at this time is defined as compensation point (Schjoerring et al., 1998).

The ammonia compensation points of the vegetation have been measured in several studies. It was reported that they are typically within 0.5–20 ppbv (Schjorring and Husted, 1997). Langford and Fehsenfeld (1992) also reported a forest-averaged compensation point was 0.8 parts per billion by volume at 20 °C in the Colorado Mountains. Over the forest canopy at the UMBS site, the mean \( NH_3 \) mixing ratio was 0.3 ppbv and the diurnal fluctuation range of the \( NH_3 \) was 0.25 – 0.42 ppb. So, during the most of the time, the ambient \( NH_3 \) level was lower than the compensation point, the forest should be acting as a net source of the ammonia. At the PSP site, the mean \( NH_3 \) mixing ration was 0.55 ppbv, and a diurnal fluctuation range from 0.37 to 0.67 ppbv. The surrounding forest canopy could also be an \( NH_x \) source during majority of the time.

According to the Henry’s law:

\[ p = k_{ij}c \]  

(4.2)
where $p$ represents the partial pressure; $c$ is the concentration of the solute; $k_H$ is the Henry's law constant, which is dependent on the temperature:

$$k_H(T) = k_H(T^\theta) \cdot \exp\left[-C\left(\frac{1}{T} - \frac{1}{T^\theta}\right)\right]$$  \hspace{1cm} (4.3)$$

where $T$ is the environmental temperature; $T^\theta$ refers to the standard temperature (298 K); $C$ is a constant. The NH$_3$ partial pressure in the air of the sub-stomatal cavities ($\chi_s$) increases with temperature increasing. Since the ambient gas-phase NH$_3$ remained relatively constants (Figures 4.8 and 4.19), the increase in NH$_3$ the partial pressure in the air of the sub-stomatal cavities would lead to an increase of the ammonia flux from vegetation to the atmosphere (E4.1).

At both the PROPHET and PSP sites, the atmosphere is relatively acidic (NADP, Dutkiewicz et al., 2004). For example, according to the historical records of ion concentrations in precipitation at the UMBS in July of 2003 from the National Atmospheric Deposition Program (NADP) contained 0.17 mg·L$^{-1}$ NH$_4^+$, 0.67 mg·L$^{-1}$ NO$_3^-$ and 0.75 mg·L$^{-1}$ SO$_4^{2-}$. Because the acidic H$_2$SO$_4$ and HSO$_4^-$ in the ambient aerosols were far from fully neutralized, they reacted with the freshly released ammonia and transformed gaseous NH$_3$ in to the particulate NH$_4^+$ (E1.9, E1.10). As the combined results of the increased NH$_3$ flux and fast neutralization with acidic aerosols, the concentration of the particulate ammonium presented a temperature dependent pattern at the PROPHET site ($R^2 = 0.88$) and at the PSP site ($R^2 = 0.31$). The gaseous NH$_3$ mixing ratios didn’t show a dependence on the ambient temperature, with a $R^2$ of 0.046 and 0.10. At PROPHET and PSP sites, respectively, implying the nitric acid didn’t get involved in
the NH\textsubscript{3} neutralization through the pathway of E 1.11. The unneutralized sulfate aerosols (H\textsubscript{2}SO\textsubscript{4} and HSO\textsubscript{4}\textsuperscript{-}) dominated the ammonia neutralization process.

4.5.2 Motor vehicle emission as a major NH\textsubscript{x} source in urban environment

The distinct “twin-peak” diurnal variation pattern of NH\textsubscript{x}, observed at the Queens College site in New York City, and at a lesser degree in Downtown Albany, can be attributed to the NH\textsubscript{3} emission from the motor vehicle emissions in the densely populated urban areas.

The ammonia emission from transportation has recently attracted some attention, although the motor vehicles are not recognized to be a significant global source of ammonia (Kean et al., 2009). Ammonia emissions from catalytic converter-equipped vehicles have been shown to be significantly higher than vehicles without catalytic converters, especially in the fuel-rich condition that the air/fuel ratio is lower than the stoichiometric value (Tagliaferri et al., 1998). The formation of NH\textsubscript{3} is widely accepted through the follow reaction (Dumpelmann et al., 1995):

\[
\text{CO} + \text{NO} + \frac{3}{2} \text{H}_2 \rightarrow \text{NH}_3 + \text{CO}_2
\]

The “twin-peak” diurnal pattern of the NH\textsubscript{3} mixing ratios agreed with the pattern of the local traffic intensity, which shows two high volumes during the morning and late afternoon commuting maxima, in both NYC and Albany areas. In addition, the data statistics showed that the mean NH\textsubscript{3} level during the weekday (1.23 ppbv) was higher than the level during weekend (1.02 ppbv) at the Queen College site, consistent with the fact that there were higher traffic volumes in the major highways in the vicinity of the site during the weekdays than weekend.
The local traffic on the college campus also accounted for the spiky features in the NH$_3$ time series at the Queen’s College site (Figure 4.12). There were fewer moving vehicles around the campus during the first week of measurement due to school winter break; the observed NH$_3$ concentrations were relatively smooth. The traffic resumed to normal after the date of January 24, 2004, resulting ammonia concentration spikes.

Wind direction clearly affects the ammonia concentration levels. Figure 4.14 shows that, at the Queen’s College site, NH$_3$ levels are higher when air masses came from north and west. It agrees to the fact that the measurement site was located 750 m south of the long Island Expressway and 1 km east of the Van Wyck Expressway, which are two of the busiest highways in the New York City.

![Figure 4.14](image)

**Figure. 4.25.** Diurnal covariations of mean black carbon (BC), Carbon Monoxide (CO), Non-methane Hydrocarbon (NMHC) and NOx concentrations at Queens College site for January 12 through February 5, 2004 (Demerjian, 2005).
In addition, carbon monoxide (CO) concentration showed a similar twin-peak
diurnal variation pattern (Figure 4.25) to that of NH$_3$ (Figure 4.13). Similarity of diurnal
variation patterns of CO and NH$_3$ suggests that they came from the common sources. CO
is known to be produced in motor vehicle exhaust and is used as an indicator to estimate
the efficiency of the three-way catalytic converter (Kean et al., 2009; Zavala et al., 2009).
It implies that the on-road vehicles made the primary contribution of the ambient NH$_3$
emissions.

In Downtown Albany, the NH$_x$ “twin-peak” diurnal variation pattern was not as
distinct as that in New York City, probably reflecting the fact that Albany is a much
small city (population ~100,000 in the City of Albany, and 850,000 in the NYS Capital
Region) compared to New York City (population 8,000,000)
(http://en.wikipedia.org/wiki/Capital_District) and much lower volume of motor vehicle
traffic. In addition, the sampling site was located at the southeastern corner of the NYS
Capital Region, and when air mass arrived from the south and east directions, the
contribution from the local urban NH$_x$ sources would be missed.

4.5.3 Comparison of NHx levels in different environments

The NH$_x$ levels are highly dependent on the location of the measurement site and
the origins and the traveling paths of the air masses, as shown in the back trajectory
calculations (Figures 4.5, 4.18, 4.23). Figure 4.6 shows the ammonia emission
distribution in Northeastern U.S. The PROPHET site is located in the “very low
emission density” region (<0.86 ton·mi$^{-2}$); the NH$_x$ levels were thus low, with mean of ~1
ppbv. The occasional south flow from urban centers (Chicago and Detroit) and farming regions may bring some high NH$_x$ air masses to the site (Figures 4.5 and 4.6).

Pinnacle State Park is a site located in a typical rural environment. This area is characterized as a “relatively low emission density” region (0.86-1.7 ton·mi$^{-2}$, NEI 1999; Figure 4.6). Due to the low population density, human activities are not considered the primary source of ammonia emissions. The local ammonia emissions should be relatively small and should mainly come from the natural sources. Indeed, there were several days with very low levels of both NH$_4^+$ and NH$_3$ (July 15-16, 24-25, August 6-7, Figure 4.17), implying that there were not many active emission sources nearby. However, the site is located in the “transport corridor” between the industrial Midwest and the eastern seaboard; the temporal distributions of ambient ammonia species are thus heavily influenced by the origins of the air masses arriving at the site: low NH$_x$ levels (NH$x < 1$ ppbv) in the air masses from “clean” regions such as north Canada and high NH$_x$ levels (NH$_x$ up to 8 ppbv) in the air masses from source regions such as Midwest agricultural areas (Figures 4.6 and 4.18).

New York City metropolitan area is characterized as a “high emission density” region (>4.5 ton·mi$^{-2}$, NEI 1999 data in Figure 4.6). So the human activities are considered as the primary contribution of the ammonia emissions. As discussed in the Section 4.5.2, several lines of evidences have indicated that motor vehicle emission seemed to the major local sources. The mean NH$_x$ level was 2.2 ppbv; the short-term spikes due to local traffic emission could be up to ~22 ppbv.

Albany is a small urban area within a “relatively low emission density” region (0.86-1.7 ton·mi$^{-2}$, NEI 1999; Figure 4.6). The NH$_x$ levels varied from the background
values of sub ppbv to ~10 ppbv when air masses coming from NH$_3$ source regions or when local contribution become favorable in stagnant period.

### 4.5.4 [NH$_4^+$]/[NH$_3$] ratios

NH$_4^+$ ions are important components of continental tropospheric secondary aerosols (Seinfeld and Pandis, 1998). Combined with sulfate or nitrate, ammonium comprises a significant portion of the fine particulate mass (Anderson et al., 2003). NH$_3$ prefers to convert the most acidic form H$_2$SO$_4$ to its less acidic form NH$_4$HSO$_4$. If there is enough NH$_3$ ([NH$_3$] > 2 [H$_2$SO$_4$]) in the system, all acidic species are neutralized into ammonium sulfate. And the excess “free ammonia” is available to react with the other acid vapors (Seinfeld and Pandis, 1998).

The atmospheric at both rural sites at PROPHET and at PSP are acidic with SO$_4^{2-}$ as the major anion. During most of the measurement period, the aerosol NH$_4^+$ was dominant NH$_x$ species, with a mean [NH$_4^+$]:[NH$_3$] ratio of 1.8 at the PROPHET site and 2.4 at the PSP site. The observation of high [NH$_4^+$]:[NH$_3$] ratio at the PSP site is consistent with the fact that the site is located downwind of the industrial Midwest. The high SO$_2$ emission from power plants in the upwind region results in high sulfate content in the aerosols at this site (Dutkiewicz et al., 2004). Once emitted into the atmosphere, gaseous NH$_3$ would therefore be taken up by the acidic aerosols efficiently to form stable NH$_4$HSO$_4$ and (NH$_4$)$_2$SO$_4$ salt (Seinfeld and Pandis, 2007).

The Queen’s College site was located in a source region. During the whole measurement period, the relative levels of aerosol ammonium and gaseous ammonia were: [NH$_4^+$]:[NH$_3$] = 0.51: 1. The domination of NH$_3$ is consistent with the argument that
there were active emission sources nearby. It could also be due to low concentrations of acidic species in the ambient air.

**Figure 4.26.** The correlations of hourly averaged $\text{NH}_4^+$ and $\text{SO}_4^{2-}+\text{NO}_3^-$ concentrations measured at Queens College site for January 14 through February 3, 2004. The particulate $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ measured with Quadropole Aerosol Mass Spectrometer (Q-AMS). Data of sulfate and nitrate came from (Demerjian, 2006).

The correlation between $\text{NH}_4^+$ and the sum of $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ is reasonably good ($R = 0.74$, **Figure 4.26**). However, the slope of 1.35 indicates that not all the aerosol acids had been converted into their corresponding salts, even though gaseous ammonia was in excess amounts. $\text{HNO}_3$ was also measured during this campaign; the mean concentration was 0.32 ppbv (He et al., 2006). Under the average condition of the
measurement period, the product of $[\text{NH}_3] \times [\text{HNO}_3] = 0.32 \text{ ppbv} \times 1.49 \text{ ppbv} = 0.48 \text{ ppbv}^2$, several times greater than the literature value of Ksp, $<0.1$ at $-2 \degree \text{C}$ of thermodynamic equilibrium constant of Reaction (E1.11). The deviation from thermodynamic equilibrium is likely to be due to the dynamic factors, i.e., the NH$_3$ uptake was low that the NH$_3$ emission rate at this source region, which also explains why not all the aerosol acids had been converted into their corresponding salts, even though gaseous ammonia was in excess amounts.

The mean $[\text{NH}_4^+]:[\text{NH}_3]$ ratio in Downtown Albany was 1.1, between those of the New York City site and the rural sites, with no clear dominant NH$_x$ species. Significant $[\text{NH}_4^+]:[\text{NH}_3]$ ratio variation, from 0.2 to over 4 (Figure 4.22), was a result of various air masses of different origins and travel paths (Figure 4.23), as well as varying degrees of local NH$_3$ contribution.
CHAPTER 5. SUMMARY AND FUTURE RESEARCH

In this research, a highly sensitive measurement technique has been developed for gaseous ammonia (NH₃) and particulate ammonium (NH₄⁺) species in the atmosphere. The method is based on aqueous scrubbing of the NH₃ and NH₄⁺ using a continuously wetted frit (CWF) sampler, followed by derivatization of the analyte to form a highly efficient light-absorbing indophenol in an on-line reaction coil, and analysis of the derivative by long-path photometry (LOPAP) using a miniaturized optical fiber spectrophotometer with a long-path flow cell.

The design of the continuously wetted glass frit sampler with minimum air inlet has overcome the inlet surface adsorption due to the stickiness of the target species, which is one of major difficulties to measure trace level ammonia. With using a citric acidic-coated denuder, aerosol ammonium has been differentiated from gaseous ammonia. Through re-examination the kinetics of the classic Berthelot’s reaction, the derivatization conditions have been optimized, resulting in a higher derivative yield and thus higher detection sensitivity, and a shorter derivatization time and thus a better sample time resolution. The utilization of long-path absorption photometric detection has greatly enhanced the sensitivity of the method, by up to a factor of 100 compared to the conventional photometric method, making this instrument one of the most sensitive techniques for atmospheric NH₃ determination.

In order to confirm the reliability of this newly developed analytical technique, the method was validated with calibrations as well as inter-comparisons with other independent analytical methods in both laboratory settings and field measurements. A
wide linearity range of 0-35ppbv, lower detection limit of 30 pptv, response time of T90 <5 min, good precision, and accuracy were demonstrated with aqueous NH$_4^+$ standard calibration and gaseous NH$_3$ standard calibration. Experiments of artificial interferants introduction have proven this method is highly selective and specific for ammonia species. The NH$_4^+$ measurement method was inter-compared with a particle-into-liquid sampler/ion chromatograph (PILS/IC), a quadropole- aerosol mass spectrometer (Q-AMS) and an integrated filter method in two field campaigns including PMTACS-NY 2004 Winter Intensive and PSP-NY 2004 Summer Intensive. The NH$_3$ measurement method was inter-compared with a tunable diode laser absorption spectrometer, a wet effusive diffusion denuder/ion chromatograph (WEDD/IC), an ion mobility spectrometer (IMS), and a chemiluminescence method (Nitrolux) in a laboratory setting. Very good agreement has been achieved in all inter-comparisons when sampling inlets were co-located.

The technique developed in this study has been deployed for field investigations in four measurement campaigns from the Summer 2003 to the Summer 2005. The measurement sites included urban areas in New York City and in Downtown Albany, and rural areas in a Michigan forest and Pinnacle State Park in Addison, New York. The temporal distribution of gaseous NH$_3$ and aerosol NH$_4^+$ had been measured. Back trajectories of typical event air masses were calculated; typical diurnal patterns in different environments were explained; and the impact of metrological parameters on the variation of ammonia species such as wind direction, ambient temperature and precipitation were discussed. The major results and findings from these field measurements can be summarized below:
In urban sites, especially highly populated metropolitan areas, on-road vehicles should be considered as one of the major sources of ammonia to the atmosphere. The significant contribution of NH$_x$ from auto emission to the urban atmosphere were suggested by the following observations in New York City: a typical twin-peak ammonia diurnal pattern coincided with the morning and evening traffic rush hours; correlation of high ammonia period with wind directions from major highways; and agreement of temporal distributions of NH$_3$ and traffic exhaust indicators (CO and elemental carbon).

In rural sites, especially areas with relatively low ambient NH$_3$, natural vegetation could be a net source of ammonia for the overlying atmosphere. The NH$_x$ diurnal pattern and the good correlation between NH$_x$ concentration and ambient temperature observed in Michigan forest implies that the natural vegetation may assume the role of the net source in a region where there is a deficiency of significant anthropogenic ammonia emission sources, and where the unneutralized acidic aerosols depress the ammonia concentration below the compensation point.

NH$_3$ mainly came from the local sources due to its shorter lifetime while NH$_4^+$ may come from neutralization of the local emitted NH$_3$ combined with aged aerosol from air mass migrations. The relative distribution of ammonium and ammonia can be considered as one of the characteristics of the atmospheric environment. Among these four field measurements, the mean ratios of [NH$_3$]/[NH$_4^+$] in urban areas are greater than the ratios measured in the rural sites. Certainly, the important role of atmospheric acidic species played should be counted.
and further investigated. Combined with SO$_4^{2-}$ and NO$_3^-$, the information of aerosol NH$_4^+$ may help to trace the origination of the polluted air masses.

Although this newly developed method was fully validated and successfully deployed in the field campaigns, there is still some work needed to consummate this technique. Moreover, many issues related to the atmospheric ammonia species are far from well-understood and waiting for researchers to explore.

The time resolution and T90 response time of the current method are 3 and 5 minutes, respectively, which may be acceptable for most of the atmospheric applications. However, if the technique is to be utilized in some specific studies, such as vertical NH$_x$ profile measured on an aircraft, flux measurement, and testing of single engine exhaust, they may not be short enough. Improvements may be achieved by: (1) Removing measuring the derivatized sample directly continuously using a two channel system with one dedicated for the blank control; (2) Shortening the delivery path or increasing the flow rate can improve the response; and (3) using another ammonium derivatization method with rapid reaction rate. A successful improvement has recently been applied in the HONO determination, reducing the sampling resolution from 3 min to ~10 seconds and the T90 response time from ~3 min to < 1 min.

The current data processing is a little time and labor consuming. This makes the instrument not quite user friendly. So the data acquisition and processing software needs to be further improved to achieve the goal so that the CWF-LOPAP may become an on-line real-time ammonia species monitor.

Through analysis the results from those four field measurement campaigns, we have found some new facts and phenomena. Some hypothesis has been generated but
still need to be confirmed by further field studies. For example, the inter-transformation of gaseous NH$_3$ and aerosol NH$_4^+$ in the atmosphere under various metrological conditions is interesting. However, we need simultaneous measurements of a whole suite of parameters, such as aerosol phase cations and anions and gas-phase HNO$_3$, to understand the atmospheric secondary aerosol formation mechanism. In addition, in order to fully understand the behaviors of atmospheric NH$_x$, long term investigations, such as year-round field monitoring, may be needed; this low-cost, robust instrument is definitely one of the candidates for the task.
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