Distributions and sources of HONO in the rural troposphere

Ning Zhang
University at Albany, State University of New York, zning78@gmail.com

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DISTRIBUTIONS AND SOURCES OF HONO
IN THE RURAL TROPOSPHERE

by

Ning Zhang

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ABSTRACT

Nitrous acid (HONO) is an important precursor of hydroxyl radical and plays an important role in the terrestrial boundary layer photochemistry. However, there are still many unknowns regarding HONO chemistry such as formation mechanisms and distributions in the troposphere, especially in rural and remote environments. In this research, we presented the first vertical concentration profiles of HONO in the troposphere, measured on a small aircraft platform. The HONO mixing ratios ranged from 4 to 17 pptv in the free troposphere and from 8 to 74 pptv in the rural boundary layer. The HONO distribution patterns were strongly correlated to the air column stability at the surface, suggesting that ground surfaces was a major source of HONO in the boundary layer. Photolysis of HNO₃/nitrate on and in aerosol particles is likely to be the major in situ HONO source, sustaining the large fraction of the observed HONO levels over water bodies and in the free troposphere. A technique based on relaxed eddy accumulation was developed for direct measurement of vertical HONO flux. Mean HONO flux at 10 m above a forest canopy is 0.37×10⁻⁶ moles m⁻² hr⁻¹, accounting for ~60% of the observed daytime HONO concentrations (~70 pptv). Photolysis of HNO₃ deposited on canopy surface is likely to be the major mechanism responsible for the observed daytime HONO flux. Laboratory photochemical experiments indicated that organics enhance surface HNO₃ photolysis by up to ~10 times compared to pure HNO₃ condition, with HONO as the major product and NO₂ as the minor product at 50% RH. A mechanism is proposed for HONO formation from surface HNO₃/nitrate photolysis, involving NO₂⁺ as the primary product, followed by abstraction of H atoms from organic
compounds and/or water on surfaces. Derived HNO$_3$ photolysis rate constants on surfaces and in aerosols well explained field observations in aircraft measurement and flux measurement and confirmed that photolysis of aerosol nitrate and HNO$_3$/nitrate on surfaces is a major daytime HONO source and an important re-NO$_x$-ification pathway in the troposphere.

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CHAPTER 1. INTRODUCTION

Nitrous acid (HONO) is an important atmospheric trace gas. Although it makes up only a small fraction of the total amount of oxidized nitrogen species ($\text{NO}_y = \text{NO} + \text{NO}_2 + \text{HONO} + \text{HNO}_3 + \text{organic nitrates} + \text{particulate nitrate}$) present in the atmosphere, HONO is of great atmospheric interest. As a reservoir for both $\text{HO}_x$ and $\text{NO}_x$ ($= \text{NO} + \text{NO}_2$), HONO disassociates by photolysis to regenerate OH and NO (R1-1):

$$\text{HONO} + hv \rightarrow \text{OH} + \text{NO}. \quad (\text{R1-1})$$

OH is the primary oxidant in the atmosphere responsible for the degradation of most of air pollutants and toxins. It’s estimated that HONO accounts for up to 80% of OH production during early morning hours [Elshorbany et al., 2009; Ren et al., 2006; Vogel et al., 2003] and contributes to 20-60% of the total OH production daily [Acker et al., 2006b; Alicke et al., 2002; 2003; Kleffmann et al., 2005; Villena et al., 2011; Zhou et al., 2002a; 2007].

Despite this importance, HONO was one of the least investigated in NO$_y$ species in the troposphere until about twenty years ago, mainly due to the lack of reliable measurement techniques. The first unambiguous identification of atmospheric HONO can be traced back to that made by Perner and Platt [1979]. Using differential optical absorption spectroscopy (DOAS), they observed up to 0.8 ppbv of HONO before sunrise in the moderately polluted air above Julich, Germany. In the past three decades, there have been an increasing number of studies into the chemistry of HONO with the availability of more sensitive measurement techniques (Figure 1.1). However, as most field studies were made in urban environments, there are still many unknowns regarding
HONO chemistry such as formation mechanisms and distributions in the troposphere, especially in rural and remote environments.

**Figure 1.1** Peer-reviewed papers related to HONO studies published in the year of 1979-2011 (A). Top-ten countries in HONO studies ranking based on published papers (B).

Sources: Databases of Web of Science and SciFinder.
1.1 Field observations of HONO in urban vs. rural environment

Tropospheric HONO concentrations vary greatly depending on the extent of pollution. The concentration ranges from a few parts per trillion (pptv) in remote regions where NO\textsubscript{x} is in the lower tens of pptv concentrations [Beine et al., 2002b; Honrath et al., 2002; Zhou et al., 2001], to several tens of pptv in the rural regions where NO\textsubscript{x} is at sub or lower parts per billion (ppbv) concentrations [Acker et al., 2004; 2006b; He, 2006; Zhang et al., 2009; Zhou et al., 2002a; 2007], to over 10 ppbv in the metropolitan area where NO\textsubscript{x} is at the tens or hundreds of ppbv levels [Febo et al., 1996; Harris et al., 1982; Winer and Biermann, 1994]. The formation mechanisms and diurnal behavior of HONO are quite different in high-NO\textsubscript{x} urban and low-NO\textsubscript{x} rural environments.

In urban atmospheres, a distinct diurnal variation pattern of HONO concentration has been observed; HONO is built up at night to a maximum and then drops off in the morning as a result of its fast photolytic loss and vertical mixing dilution. Strong correlations between HONO and NO\textsubscript{x} usually exist in high-NO\textsubscript{x} urban environments, suggesting that NO\textsubscript{x} is the predominant precursor for HONO [Acker et al., 2006a; Alicke et al., 2002; Harrison et al., 1996; Reisinger, 2000]. HONO/NO\textsubscript{x} ratio is relatively low in urban atmosphere, mostly in the range of 0.01-0.04 [Kleffmann, 2007; Stutz et al., 2002; 2004]. In recent years, the development of highly sensitive techniques made it possible to make meaningful measurements of daytime HONO concentrations, which have been found to be on the order of a few hundred pptv, much higher than calculated by photo steady state (PSS) [Acker et al., 2006a; Kleffmann et al., 2005].

In contrast to the diurnal pattern observed in urban environments, HONO concentration usually peaks during the daytime in rural environments. During HONO
studies at rural sites [Acker et al., 2004; He et al., 2006; Zhou et al., 2002a], a HONO concentration peak was observed after sunrise. Since fog/dew events occurred frequently during the study period, a dew controlling mechanism was proposed: ground and vegetation surfaces served as HONO sinks due to the scavenging of dew droplets at night; in the morning as dew droplets evaporated, the release of the trapped HONO/nitrite from the surfaces acted as a strong HONO source. In subsequent research [Acker et al., 2006b; Zhou et al., 2007], maximal daytime HONO concentrations and comparably lower nighttime HONO levels were observed at rural mountain sites, which was opposite to the diurnal pattern observed in urban environments. Therefore, a strong daytime source must exist and control the temporal HONO distribution. The ratio of HONO/NO$_x$ is usually around 0.1, but sometimes as high as 1 [Acker et al., 2004; 2006b; Zhou et al., 2002a, 2007]. The correlation between HONO and NO$_x$ is usually poor ($r^2 \leq 0.1$), implicating other NO$_y$ components other than NO$_x$ as the HONO precursor.

1.2 Sources of HONO in the atmosphere

To date the mechanisms leading to HONO formation are still unclear. Neither direct emission nor gas phase reactions are sufficient explanations for the abundance of atmospheric HONO. It is generally accepted that HONO is produced mainly through the heterogeneous processes involving HONO precursors such as NO$_2$ and HNO$_3$ on the surfaces of ground and/or aerosols. However, consensus has not been reached on the exact mechanism.

1.2.1 Direct emissions

Combustion processes are a direct, but small source of HONO [Lammel and Cape, 1996]. For example, high HONO concentrations were observed during biomass burning
in a tropical savannah [Rondon and Sanhueza, 1989] and in an agricultural community [Park et al., 2004]. Vehicle exhaust has been investigated as a urban HONO source [Kirchstetter et al., 1996; Kurtenbach et al., 2001; Li et al., 2008b; Villena et al., 2011]. Significant levels of HONO in vehicle exhausts have been detected, with the calculated emission index of 88 ± 18 mg HONO kg⁻¹ fuel [Kurtenbach et al., 2001]. However, the HONO/NOₓ ratio from vehicle exhaust is no more than 0.008, too small to account for any significant portion of HONO formation needed to sustain its observed concentrations in an urban atmosphere [Lammel and Cape, 1996].

1.2.2 Homogeneous sources

Several homogeneous routes for HONO formation in the atmosphere have been investigated in the last few decades, but none of these processes are likely to be significant net sources of tropospheric HONO. The rate coefficients of gas-phase reactions R1-2, R1-3, and R1-4 are small enough to exclude the reactions from being a significant source of nitrous acid in the atmosphere [Calvert et al., 1994; Kitto and Harrison, 1992; Lammel and Cape, 1996; Tyndall et al., 1995]:

\[
\begin{align*}
\text{NO + NO}_2 + \text{H}_2\text{O} & \rightarrow 2\text{HONO} \quad \text{(R1-2)} \\
2\text{NO}_2 + \text{H}_2\text{O} & \rightarrow \text{HONO} + \text{HNO}_3 \quad \text{(R1-3)} \\
\text{NO}_2 + \text{HO}_2 & \rightarrow \text{HONO} + \text{O}_2 \quad \text{(R1-4)}
\end{align*}
\]

The most considered reaction (R1-5) has a faster rate coefficient \(k_{1.5} = 4.8 \times 10^{12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\). However, since photo-reaction (R1-1) reverses reaction (R1-5) during the daytime, HONO output from reaction (R1-5) is insignificant compared to the observed HONO concentrations [Calvert et al., 1994; Lammel and Cape, 1996]:
In a recent study, formation of HONO in the gas phase has been observed in the photolysis of orthonitrophenols and methyl substituted derivatives \((R1-6)\) [Bejan et al., 2006].

Since HONO yield was found to be linearly dependent on the nitrophenol concentrations and light intensity \((300-500 \text{ nm})\), a photolytic HONO formation rate is estimated to be 100 pptv \(\text{hr}^{-1}\) assuming 1 ppbv of nitrophenol is present. This source might be helpful to explain in part the high concentrations of HONO observed in urban atmospheres. However, it is unlikely to be important in rural environments due to the low concentration of nitrophenols [Kleffmann, 2007].

Other homogeneous HONO sources include the reaction of electronically excited \(\text{NO}_2\) \(\text{(NO}_2^*\text{)}\) with water \((R1-7)\) [Li et al., 2008a], and nucleation of three gases, \(\text{NO}_2\), \(\text{H}_2\text{O}\), and \(\text{NH}_3\) \((R1-8)\) [Zhang and Tao, 2010]. However, the reaction rates and yields of HONO are still under debate [Carr et al., 2009; Li et al., 2009].

\[
\text{NO}_2^* + \text{H}_2\text{O} \rightarrow \text{OH} + \text{HONO} \quad \text{(R1-7)}
\]

\[
\text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) + \text{NH}_3(\text{g}) \rightarrow \text{HONO}(\text{g}) + \text{NH}_4\text{NO}_3(\text{s}) \quad \text{(R1-8)}
\]

1.2.3 Heterogeneous formation

1.2.3.1 HONO night-time sources
In the absence of light, the reaction (R1-9) is the most favored formation mechanism [Elshorbany et al., 2010; Finlayson-Pitts and Pitts, 2000; Harrison et al., 1996; Kleffmann, 2007; Lammel and Cape, 1996]. Unlike the homogenous gas-phase reactions (e.g. (R1-2) and (R1-3)), the observed kinetics of reaction (R1-9) depend on the surface-to-volume ratio of the reaction vessel, clearly indicating a heterogeneous reaction on the surfaces [Finlayson-Pitts and Pitts, 2000].

\[
2\text{NO}_2 + \text{H}_2\text{O} + \text{surface} \rightarrow \text{HONO} + \text{HNO}_3 \quad \text{(R1-9)}
\]

This reaction has been extensively studied in the laboratory on a variety of surfaces such as glass and soot [Finlayson-Pitts and Pitts, 2000; Kleffmann et al., 1998; Lammel and Cape, 1996]. It was found the reaction (R1-9) to be first order in \(\text{NO}_2\) and first order in water vapor [Finlayson-Pitts and Pitts, 2000; Jenkin et al., 1988; Kleffmann et al., 1998; Pitts et al., 1984]. However, there are still many uncertainties in the mechanism.

The reduction of \(\text{NO}_2\) to HONO on soot surfaces has also been observed. Since no \(\text{HNO}_3\) was detected as the product, reaction (R1-10) was postulated:

\[
\text{NO}_2 + \text{red}_{\text{ads}} \rightarrow \text{HONO (g)} + \text{ox}_{\text{ads}} \quad \text{(R1-10)}
\]

where \(\text{red}_{\text{ads}}\) and \(\text{ox}_{\text{ads}}\) denote a reduced and an oxidized site on the soot surfaces, respectively [Ammann et al., 1998]. This reaction may be particularly important in polluted urban areas as well as in the upper troposphere where soots from commercial aircrafts are injected into the atmosphere [Finlayson-Pitts and Pitts, 2000]. The reaction appeared to be very fast within the first few seconds, e.g. 5-7 orders of magnitude faster than other HONO sources. However, it deactivated very quickly on soot surfaces, which limited the amount of HONO that could be generated from this reaction [Arens et al., 2001; Kleffmann et al., 1999]. More recent studies suggest that it is not the soot itself, but
the attached organic species on soot surfaces that reduce NO$_2$ to HONO [Arens et al., 2002; Gutzwiller et al., 2002]. Thus the heterogeneous reduction of NO$_2$ with adsorbed hydrocarbons is of greater importance under atmospheric conditions [Kleffmann, 2007].

### 1.2.3.2 Photolytic sources

While nighttime HONO concentrations can be reasonably explained by direct emissions and the heterogeneous reduction of NO$_2$ as discussed above, the large discrepancies between observed daytime HONO concentration and the calculated photo steady state values point to additional strong photochemical sources [Acker et al., 2006a; 2006b; Beine et al., 2002a; Kleffmann et al., 2003; 2005; Ren et al., 2003; Zhou et al., 2001; 2002a; 2002b; 2007]. The source strength was estimated to be 200-500 pptv hr$^{-1}$ [Acker et al., 2006b; Zhou et al., 2002a; 2003], 500 pptv hr$^{-1}$ [Kleffmann et al., 2005] and up to 2 ppbv hr$^{-1}$ [Acker et al., 2006a; Ren et al., 2003; 2006] for rural, semi-urban and urban environment, respectively. In semi-urban noontime conditions, this photochemical source produces HONO about 60 times faster than all nighttime sources of HONO [Kleffmann et al., 2003]. However, the identification of photochemical sources and their mechanisms are still ongoing, and are a controversial topic in atmospheric chemistry.

In urban environments, photosensitized conversion of NO$_2$ on the surfaces of organic compounds such as aromatic ketones, phenols and humic acid is postulated as a photochemical HONO source. Under irradiation ($\lambda=300$-$420$ nm), the reduction of NO$_2$ was observed 10 times faster than in dark conditions, and the resulting HONO yield was up to nearly 100% [George, et al., 2005; Stemmler, et al., 2006; 2007]. This observation is attributed to the activation of organic films by light to form a reductive photosensitizer, and converts absorbed NO$_2$ into HONO. However, this mechanism is only applicable in
the areas with several ppbv of NO₂, rather than rural and remote regions with low NOₓ concentrations [Kleffmann, 2007].

In rural low-NOₓ environments, the photolysis of deposited HNO₃ and nitrate on the surfaces has been suggested as an important daytime HONO source (R1-11).

\[
\text{HNO}_3/\text{NO}_3^- + h\nu \rightarrow \text{HONO}/\text{NO}_2^- + \text{O}
\]  
(R1-11)

In polar regions, HONO emission was observed over snow surfaces, with concentrations much higher than expected [Beine et al., 2002a; 2003; Dibb et al., 2002; 2004; Honrath et al., 2000; 2002; Zhou et al., 2001]. This was explained by HNO₃/nitrate photolysis in snowpack [Beine et al., 2002a; Zhou et al., 2001]. In a rural site, an artifact HONO signal was observed from a sunlight-exposed glass sample manifold but disappeared after the manifold was shielded from the sunlight or cleaned with water. The artifact was likely photochemically generated from water-soluble NOₓ species such as nitrate or HNO₃ [Zhou et al., 2002b]. In laboratory studies, adsorbed HNO₃ was found to be a key intermediate product during NO₂ heterogeneous hydrolysis, leading to the formation of HONO under irradiation [Finlayson-Pitts et al., 2003; Ramazan et al., 2004; 2006]. Furthermore, significant HONO and NOₓ production was observed in a HNO₃-coated flow reactor, with a photolysis rate constant of HNO₃ 2–6×10⁻⁵ s⁻¹ on Pyrex surfaces under full sun, 1-2 orders of magnitude faster than HNO₃ photolysis in the gas phase or nitrate photolysis in the aqueous phase [Zhou et al., 2003].

However, there are still arguments casting doubt on the mechanism of surface HNO₃ photolysis as a major HONO source. For example, in a chamber study, the photolysis of HNO₃/nitrate was ruled out as a HONO source because significant photolytic HONO formation was observed in the wavelength range of 350-420 nm, corresponding to small
absorption cross sections of gaseous HNO$_3$ [Rohrer et al., 2005]. In addition, the effective quantum yield for HONO formation by nitrate photolysis was expected to be similar to that in aqueous phase and in gas phase, which is too small to account for 1-2 orders of magnitude photoenhanced HONO formation [Kleffmann, 2007].

In a recent laboratory investigation, the absorption cross sections of surface-adsorbed HNO$_3$ were found to be at least 2 orders of magnitude higher than that of HNO$_3$ vapor [Zhu et al., 2008; 2010]. They also found that NO$_2^*$ + OH is the predominant photolysis pathway (if not the only photolysis pathway) for photolysis of HNO$_3$ at 308 nm and NO$_2^*$ quantum yield from HNO$_3$ photolysis was near unity [Zhu et al., 2008; 2010]. Their results clearly indicated this mechanism was enhanced on surfaces. Furthermore, Gao et al. [2006] recently observed the enhanced HONO production and overall photolysis rate of HNO$_3$/nitrate on plant leaves, compared to those on glass surfaces, which were attributed to the catalytic effect of organic matters deposited from ambient air. Handley et al. [2007] observed photochemical HNO$_3$ loss by illuminating films containing nitrate and organic compounds and proposed that the re-NO$_x$-ification process could be an important source of HONO and/or NO$_2$. Since organic compounds are ubiquitously present in ambient environments, the processes of HNO$_3$ / nitrate photolysis on surfaces are very likely to be enhanced in the presence of organic compounds, similar to a mechanism observed for the reaction of NO$_2$ with organic substrates. However, there is no quantitative information available regarding the effects of different types of organics on surface HNO$_3$ photolysis. The photolysis rate constant of atmospheric nitrate aerosols is also undetermined. Further studies are necessary to clarify the mechanism of HONO formation from photolysis of adsorbed HNO$_3$/nitrate on the surfaces.
1.3 Heterogeneous formation of HONO on ground vs. aerosol

Another important issue is in regards to the source regions of HONO formation. Whether heterogeneous formation of HONO occurs mainly on the surfaces of aerosols or on ground surfaces has been a controversial topic.

Lammel and Perner [1988] found that nitrite concentrations in the aerosol liquid phase far exceeded what was expected from Henry’s law equilibrium. They concluded that some reactions of gaseous NO\textsubscript{x} compounds may be enhanced by surfaces of atmospheric aerosols, suggesting that aerosols must be acting as a source of HONO. Acker et al. [2008] identified significant amounts of nitrite in the collected samples of fog, cloud, dew, and rain at both the mountain sites and in the urban areas. They emphasize that fog and cloud droplets (and possibly dew) provide an effective ‘surface reservoir’ for heterogeneous HONO production. Studies have noted the close correlation between HONO peaks and high aerosol surface levels in the foggy episodes [Notholt et al., 1992] and during winter nights [Reisinger, 2000]. This close correlation suggests that significant heterogeneous formation of HONO involves the reaction of NO\textsubscript{2} on the aerosol surfaces. Wang et al. [2003] reported a highly efficient NO\textsubscript{2} to HONO conversion on dust particles; the HONO to NO\textsubscript{2} ratio could reach 19% during nighttime dust storms, while the ratio was rarely over 3% during non-dust-storm nights. Ziemba et al. [2010] observed good correlations between HNO\textsubscript{3} depletion, HONO production and aerosol surface area, suggesting HONO was formed via the heterogeneous conversion of HNO\textsubscript{3} on the surfaces of primary organic aerosols. However, in contrast to the field results, most laboratory work observed either deactivation or very small uptake coefficients in kinetic studies on reactions of NO\textsubscript{2} on particles, implying the minor
importance of aerosol surfaces in the heterogeneous HONO formation [Ammann et al., 1998; Arens et al., 2001; Aumont et al., 1999; Broske et al., 2003; Gerecke et al., 1998; Grassian, 2002; Kalberer et al., 1999; Kleffmann et al., 1998; Kleffmann and Wiesen, 2005; Ndour et al., 2008].

In addition, field measurements provide evidence for heterogeneous HONO generation on ground surfaces, in competition with its deposition process. Harrison and colleagues [Harrison and Kitto, 1994; Harrison et al., 1996] studied HONO flux above grasslands in eastern England using a gradient technique. They observed both upward and downward fluxes at different time depending on the ambient concentrations of NO₂. At NO₂ concentrations above 10 ppbv in semirural areas, the ground surface appeared to be a net source of HONO. At concentrations of NO₂ below 10 ppbv in rural areas, the ground surface acted as a net sink of HONO. Stutz et al. [2002] measured the vertical gradients and fluxes of HONO over a flat grass surface in the polluted atmosphere of Milan. They found no evidence of efficient HONO formation on ground surfaces, likely due to the conflicting and concurrent deposition and formation processes of HONO. He at al. [2006] observed a negative gradient of HONO concentration during the day but a positive gradient at night, as a result of changes in the dominating process on the canopy from photochemical production to dry deposition. This suggests ground surfaces may act as both a source and sink for HONO.

Further supporting the ground surface as a major source of HONO, measurements of nighttime concentrations of HONO were conducted at both urban and non-urban sites [AndresHernandez et al., 1996]. The results showed that although the total aerosol surfaces were comparable at different locations, the HONO/NOₓ ratio was usually
increasing much faster in urban sites than in non-urban sites, suggesting that the heterogeneous HONO formation on permanent surfaces like buildings should be more important than that on atmospheric aerosols. Both Kleffmann et al. [2003] and Veitel et al. [2002] observed the HONO/NO\(_2\) ratio decreased with the increasing altitude of up to 500 m above the ground surface. Kleffmann et al. [2003] also reported that there was no correlation between the HONO/NO\(_2\) ratio and the particle surface area density. Collectively, results from these studies, along with the recent measurements of HONO vertical gradients throughout the various sites using different methods [Sorgel et al., 2011; Villena et al., 2011; Wong et al., 2011; Zhu et al., 2011] all suggest that heterogeneous HONO formation was dominated by processes on the ground surfaces rather than on aerosol surfaces.

In order to estimate the relative importance of ground surfaces and aerosol surfaces in heterogeneous production of HONO, vertical HONO profile measurements are necessary, over the altitudes from surface mixed layer to free troposphere. However, almost all the HONO measurements to date have been ground-based, and thus the reported HONO concentration profiles were all near the bottom of the boundary layer. In addition, a direct HONO flux measurement is essential to accurately quantify the air-surface exchange of HONO and to parameterize boundary layer models to predict photooxidant formation.

1.4 Sinks of HONO in the atmosphere

1.4.1 HONO photolysis as OH source

During the day, photolysis is the dominant HONO sink (R1-1). HONO absorbs sunlight strongly at wavelengths less than 400nm, generating OH and NO with unit
quantum yield [Calvert et al., 1994; DeMore et al., 1997; Finlayson-Pitts and Pitts, 2000]. The estimated $j$-values for HONO dissociation range from 0.089 min$^{-1}$ at $z = 0^\circ$ (Z is solar zenith angle) to 0.004 min$^{-1}$ at $z = 86^\circ$ [Calvert et al., 1994]. Accordingly, HONO’s photodissociation lifetime is from 10 min at noontime to over 1 hour in the early morning. Thus, HONO is considered a major source of OH radical.

In addition to photolysis, HONO also reacts with OH radical (R1-12):

$$\text{OH} + \text{HONO} \rightarrow \text{H}_2\text{O} + \text{NO}_2 \quad (\text{R1-12})$$

However, this reaction is too slow to compete with the loss by photolysis, with a pseudo-first order reaction constant of $\sim 4.5 \times 10^{-5}$ s$^{-1}$ at room temperature, assuming a rate constant of reaction (R1-12) of $4.5 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ [DeMore et al., 1997; Finlayson-Pitts and Pitts, 2000] and a peak OH concentration of $1 \times 10^7$ radicals cm$^{-3}$. Thus, this reaction is only responsible for a small percentage of HONO destruction [Calvert et al., 1994].

Given HONO formation in gas-phase (R1-5), its rapid loss by photolysis (R1-1), and reaction with OH (R1-12), the photo-steady state concentration of HONO, $[\text{HONO}]_{pss}$, is defined as:

$$[\text{HONO}]_{pss} = \frac{k_{OH+NO}[\text{OH}][\text{NO}]}{j_{\text{HONO}} + k_{OH+\text{HONO}}[\text{OH}]} \quad (\text{Eq. 1 - 1})$$

Based on this calculation, $[\text{HONO}]_{pss}$ is typically in the lower pptv range. However, large discrepancies exist between the calculated $[\text{HONO}]_{pss}$ and the field observations during daytime due to the heterogeneous photochemical formation of HONO. This elevated HONO concentration makes it not only the most important source of OH radicals in the
morning, but also throughout the daytime. The contribution of HONO photolysis to OH, \( P_{OH} \):

\[
P_{OH} = f_{HONO} [HONO] - k_{OH+NO} [OH][NO] \quad (Eq. 1 - 2)
\]

can account for up to 81% of the total OH radical initiation sources [Elshorbany et al., 2009; 2010; Ren et al., 2006; Vogel et al., 2003].

However, reported contributions of HONO photolysis to HO\(_x\) budgets were calculated using data collected in ground measurement. Thus, the data may not be valid for the air masses beyond the lowest portion of boundary layer. Gradient HONO concentration measurements extended to the whole boundary layer by either an aircraft or a balloon are highly desirable, as the data can be used to identify HONO source regions and quantify the integrated contributions of HONO to the photooxidation capacity in the whole boundary layer [Kleffmann, 2007].

1.4.2 Deposition

Dry or wet deposition is an alternative pathway that removes HONO from the atmosphere. Depending on humidity and nature of the surfaces, the average velocity for dry deposition of HONO ranges from 0.08 to 4.1 cm s\(^{-1}\) [Harrison and Kitto, 1994; Harrison et al., 1996; Stutz et al., 2002]. Because HONO is very soluble in water (H= 60 M atm\(^{-1}\) at room temperature) [Finlayson-Pitts and Pitts, 2000], fog, rain, and dew are all efficient sinks for HONO.

A portion of dry deposition of HONO may be due to the uptake by vegetations. Recently, an exposure experiment was done where HONO was introduced into a chamber with various plant species (sunflower, tobacco, castor, birch), and exposed to light at
wavelengths of 350-750 nm [Schimang et al., 2006]. The results showed that at least 74% of the total HONO loss within the chamber was due to uptake of HONO by several plant species, whereas photolytic losses only contributed 22% and wall losses only accounted for 4%. The uptake was proportional to HONO concentrations and linearly related to stomatal conductance, but limited by diffusion of HONO through the stomata [Schimang et al., 2006]. However, the detailed uptake mechanism can be complicated and has a lot of uncertainties [Sakugawa and Cape, 2007; Sparks, 2009]. Sakugawa et al. [2007] did not find evidence of a fertilizer effect caused by metabolism of uptake HONO in plant leaves. Both Raivonen et al. [2006] and Gao et al. [2006] observed HONO emission from HNO$_3$ photolysis on plant surfaces. These conflicting results may imply that plant surfaces serve as a sink or a source for HONO, depending on ambient HONO concentrations and other conditions.

1.5 Public health impacts

Apart from its potentially important role in tropospheric chemistry, HONO is of toxicological relevance. Upon photolysis, HONO produces NO and OH. Both species are involved in ground-level ozone formation, a well-known secondary air pollutant leading to a variety of health problems including chest pain, coughing, throat irritation, and congestion.

HONO is also an indoor air pollutant—both emitted directly from combustion sources (e.g., gas cooking range) and formed through the heterogeneous reaction of NO$_2$ with water vapor on various surfaces. Indoor levels of HONO measured as a 24-hour average have been reported as high as 8 ppbv, and concentrations measured as a 6-hour average has been reported up to 40 ppbv in normal, in-use buildings and homes [Febo
and Perrino, 1991; Park et al., 2008; Spengler et al., 1993; Weschler et al., 1994]. At high concentration (e.g. ppb level), HONO can cause adverse effects towards mucous membranes and lung function [Beckett et al., 1995; Jarvis et al., 2005; Rasmussen et al., 1995].

HONO can react with organic amines to form nitrosamines, one of the most potent carcinogens [Grosjean, 1991; Pitts et al., 1978]. Third-hand smoke (THS) is defined as residual smoke contamination that remains on surfaces after a cigarette is extinguished [Winickoff et al., 2009]. Only recently has THS been recognized as a contributor to indoor pollution due to the role of indoor surfaces [Petrick et al., 2011]. Sleiman et al. [2010] examined indoor nicotine transformations and found that residual nicotine from tobacco smoke adsorbed to indoor surfaces –including clothing and human skin- reacts with ambient HONO to form carcinogenic tobacco-specific nitrosamines (TSNAs). Given the rapid adsorption and persistence of high levels of nicotine on indoor surfaces, this process represents a long-term health hazard though dermal exposure, dust inhalation, and ingestion [Sleiman et al., 2010].

1.6 Research objectives

Although extensive research has been carried out on HONO chemistry in the troposphere, as discussed above, many unknowns remain, including:

1. How much HONO exists beyond the surface boundary layer? What are HONO sources in the atmosphere beyond the surface boundary layer? Is HONO an important source of HOx above boundary layer?
2. What are the relative contributions of ground and aerosol surfaces in heterogeneous production of HONO? How much HONO is released from ground surface processes?

3. What are the formation mechanisms/precursors of HONO, especially in the rural environment? How do surface organics affect HONO production?

The objective of this dissertation research is to answer some of these questions, i.e., investigate the distribution and sources of HONO in rural troposphere, focusing on HONO as an intermediate product of nitric acid/nitrate re-NO\textsubscript{x}-ification. Specifically, the proposed research is to test and verify the following three hypotheses derived from previous research in our group.

**Hypothesis 1:** Photolysis of HNO\textsubscript{3}/nitrate on ground surfaces, including vegetation, is a dominant daytime HONO source and a major re-NO\textsubscript{x}-ification pathway in the rural atmospheric boundary layer.

**Hypothesis 2:** Photolysis of particulate nitrate in aerosols is a major daytime HONO source and a re-NO\textsubscript{x}-ification pathway in the troposphere above the boundary layer.

**Hypothesis 3:** Organic compounds, such as light-absorbing aromatic compounds, may significantly enhance the HONO production rate by photolysis of HNO\textsubscript{3} on surfaces and nitrate in aerosols.

These three hypotheses were investigated through three projects:

1. Aircraft-based measurements to establish HONO vertical distributions from the surface mixed layer to the free troposphere. The collected information will allow us to calculate the HONO source strength throughout the atmospheric boundary layer
and in the free troposphere, and thus to identify the relative importance of ground surface HONO and \textit{in situ} HONO source (to evaluate hypotheses 1, 2).

2. Ground-based field measurements to quantify the atmosphere-biosphere exchange of HONO. The collected information will allow us to quantitatively assess the HONO contribution from processes on ground/canopy surfaces. The relationship between HONO flux and other physical and chemical parameters, such as temperature, relative humidity, solar UV intensity, NO\textsubscript{x} concentration, and surface HNO\textsubscript{3} loading on leaves, may provide insights into HONO formation mechanisms under different conditions (to evaluate hypothesis 1).

3. Laboratory photochemical experiments to investigate the precursors involved in HONO formation, i.e. the photolysis of HNO\textsubscript{3}/nitrate and organic compounds, and further examine the detailed chemical formation mechanisms (to evaluate hypothesis 1, 2, 3).

Through these research activities, we will gain greater understanding of tropospheric HONO chemistry and HONO’s role in tropospheric reactive nitrogen cycling. If the above hypotheses are confirmed by the research results, there are significant implications in atmospheric chemistry: the troposphere is more photochemically reactive than we previously realized due to the recycling of HNO\textsubscript{3} back to NO\textsubscript{x}, leading to higher production of photooxidants, such as O\textsubscript{3} and OH radicals.
CHAPTER 2. METHODS AND MATERIALS

In this research, HONO, NO\textsubscript{x} and HNO\textsubscript{3} are reactive nitrogen species of greatest interest, analysis of which were made based on the techniques developed by our group [He et al., 2006; Huang et al., 2002]. The technique for NO\textsubscript{2} measurement was developed in the present research.

2.1 Principle of the methods

The principle behind these techniques is the same, namely Griess-Saltzman reaction [Saltzman, 1954] (see Figure 2.1), during which nitrite or nitrogen dioxide is absorbed in pre-mixed reagent of sulfanilamide (SA) and N-(1-naphthyl)-ethylene-diamine (NED) in an acid medium, to form a stable pink azo dye. The intensity of the color is measured spectrophotometrically, and the method is conveniently calibrated with nitrite solution.

![Griess-Saltzman reactions](image)

*Figure 2.1* Griess-Saltzman reactions.
2.2 HONO measurement

The original HONO measurement technique was described in detail by [Huang et al., 2002] and modified by [He et al., 2006]. This technique has been successfully applied by our group in several field campaigns in various atmospheric environments [He, 2006; He et al., 2006; Huang et al., 2002; Zhou et al., 2001; 2002a]. Briefly, ambient HONO was scrubbed by 1 mM phosphate buffer (pH = 7) or de-ionized (DI) water (resistance > 18.2 MΩ cm⁻¹) using a 10-turn glass coil sampler, at scrubbing solution flow rate of 0.25 ml min⁻¹ and the air sampling rate of 2 L min⁻¹. The scrubbed nitrite was derivatized with 2 mM SA and 0.2 mM NED in 25 mM HCl, to form an azo dye within 5 min. The azo dye was detected by light absorbance at 540 nm using a miniature fiber optic spectrometer (USB2000, Ocean Optics) with a 1-m liquid-waveguide capillary flow cell (WPI). The method has detection limit as low as 5 pptv and collection efficiency > 99%. Figure 2.2 showed a schematic diagram of HONO measurement system.

Interference from atmospheric species such as NOₓ, particulate nitrite and other neutral NOᵧ species was below our detection limit in ambient air containing HONO concentrations ≤ 20 pptv, and accounted for ~10% of the overall signal in ambient air containing [HONO] ≥ 20 pptv.

Calibration was performed by introducing aqueous NaNO₂ standard solutions in place of scrubbing solution into the HONO measurement system with the coil sampler bypassed. The signal height was plotted against the nitrite concentration as a calibration curve. The ambient HONO concentration was calculated by:

\[ C_{HONO} = \frac{RT \times C_{NO_2^-} \times F_l}{F_g} \quad (Eq. 2 - 1) \]
where $F_i$ is scrubbing solution flow rate in mL min$^{-1}$; $F_q$ is air sampling flow rate in L min$^{-1}$; $C_{NO_2}$ is nitrite concentrations (nmol L$^{-1}$) in the scrubbed aqueous samples; $C_{HONO}$ is gaseous concentration of HONO in pptv; R is gas constant (0.082 L atm K$^{-1}$ mol$^{-1}$) and T is the absolute temperature at which the mass flow controller is calibrated (293K).

The technique has been modified and improved during each of the following studies.

2.2.1 Aircraft-based measurements

Because atmospheric compositions fluctuate rapidly at any single point as a result of species’ chemical reactivity, lifetime, and atmospheric dispersion, aircraft instruments required fast enough time resolution at an adequate sensitivity to capture both dispersion and chemically-induced changes. To satisfy this requirement, we adjusted operation parameters of original HONO measurement system as following: (1) increased gas sampling flow rate and decreased aqueous scrubbing rate to enrich HONO concentration in sample solution; (2) increased both derivatization reaction rate by increasing acidity in SA/NED reagent and the carrier solution flow rate to minimize sample integration time; (3) replaced the 6-port injection valve with a 8-port injection valve to allow continuous sample collection. All connection tubings were kept as short as possible to reduce the delivery time. Figure 2.2 showed an aircraft HONO measurement system. Typical operation conditions in an aircraft include 1mM phosphate buffer solution (pH=7); reagent of 2 mM SA and 0.2 mM NED in 40 mM HCl; air sampling rate, 3 L min$^{-1}$; scrubbing solution flow rates, 0.2 ml min$^{-1}$; overall carrier solution flow rate, 2.7 ml min$^{-1}$;
derivatization time, 2.5 min. The detection limit (3σ of noise at a low HONO concentration) was 2 pptv. The data collection interval was 1 min.

**Figure 2.2** Upper: schematic diagram of HONO measurement system. Lower: a picture of actual HONO measurement system used in the aircraft.
2.2.2 Ground-based field measurements

HONO measurement system is shown in Figure 2.3. Three HONO measurement systems were used in ground-based field measurements: one for ambient concentration measurement and two for flux measurement. A major improvement over the original method is that a 3-way solenoid valve was used to alternately introduce ambient air or “zero-HONO” air to a coil sampler. The ambient HONO concentrations were derived from the difference between the ambient signals and the “zero-HONO” air. It eliminated the need for carrier solution and significantly reduced the production of waste solution, which is a significant advantage in field measurement. Furthermore, the new design allows for continuous HONO signal collection at a frequency of 0.3 Hz. A 1-ml thermostatic derivatization coil at 55 °C was used to increase derivatization reaction rate as well as to constrain bubble formation in the subsequent procedure. De-ionized (D.I.) water was used as scrubbing solution.

The system was operating on a 30-min cycle controlled by a 3-way solenoid valve: sampling ambient air for 20 minutes and then “zero-HONO” air for 10 minutes to obtain a baseline. A Na$_2$CO$_3$-coated annular denuder was used to generate “zero HONO” air for background correction. While the Na$_2$CO$_3$-coated denuder removed HONO and acidic gases from the ambient air, it allowed most of the potential interfering species such as NO, NO$_2$, PAN, nitrate and aerosol, to pass through (USEPA, 1999). Therefore, interference from these species was mostly eliminated by subtracting the “zero-HONO” signals from the ambient air signals.
Figure 2.3 Schematic diagram of a HONO measurement system used in flux measurement.

Figure 2.4 shows an excerpt of 10-min raw data recorded during flux measurement in the morning of 25 July, 2008. The 90% response time, based on the signal transition from “zero-HONO” air to ambient air, was about 110 s. The ambient concentrations were derived from the difference between the ambient signals and the “zero-HONO” air. The “zero-HONO” baseline drifted only slowly throughout the day, mostly within 2 pptv.
hr⁻¹, in response to factors including concentrations of interfering species (e.g. NOₓ), temperature and reagent age. After removing the transitional data points, 17-18 min of ambient HONO concentration data were collected in each 30-min cycle.

Figure 2.4 An excerpt of 10-min HONO raw data during the transition from the “zero-HONO” baseline to ambient HONO measurement, 25 July, 2008.

The linear dynamic range is 1 - 5000 pptv; above the 5000 pptv level, the response signal becomes non-linear. The response time may be shortened by increasing the rates of scrubbing and reagent flows and by reducing the length of tubing in the liquid flow plumbing. The upper limit of linear dynamic range may be improved by increasing the
rates of scrubbing and reagent flows and by reducing the air sampling flow rate. These measures, however, will increase the lower detection limits.

The lower detection limit of the method, as defined by 3 times of the standard deviation of the signal, is 1 pptv for 2-min averages. The measurement precision, based on side-by-side measurements using multiple HONO systems, is estimated to be better than 2% in the concentration range of 50 pptv to 5 ppbv. An overall uncertainty of ±(1 + 0.05 [HONO]) pptv is estimated, accounting for uncertainties in signal acquisition and processing, air and liquid flow rates, and standard preparation.

### 2.2.3 Laboratory photochemical experiments

In controlled laboratory conditions, design of HONO measurement system is similar to Figure 2.3 except that the solenoid valve and the thermostatic control box were not used. HONO concentration was continuously monitored in the air exiting the photochemical reactor at a frequency of 0.3 Hz. Ultra high-purity nitrogen (Airgas, UHP200) was used as the carrier gas. D.I. water was used as scrubbing solution. Two types of blank controls were used in this study: (1) system dark blank obtained when a sample was not irradiated by covering the photochemical reactor with an Al foil; and (2) reactor exposure blank obtained when an empty reactor was exposed to light. Effective HONO signal was derived by subtracting both blanks from HONO signals during sample irradiation. Therefore, interference from dark reactions and reactor contaminations was mostly eliminated.
The HONO measurement system was operated at a gas flow rate of 400 ml min\(^{-1}\) and a scrubbing solution (D.I. H\(_2\)O) flow rate of 0.24 ml min\(^{-1}\). The scrubbed nitrite was derivatized by 60 mM SA and 0.8 mM NED in 1 M HCl, to form an azo dye within \(~\)2 min. The detection limit is 9 pptv.

### 2.3 Nitrate measurement

Nitrate can be reduced quantitatively to nitrite by copperized cadmium. In this method, cadmium is pretreated with CuSO\(_4\) solution to form a porous metallic copper coating on cadmium surfaces, which catalyze the reduction process of nitrate to nitrite. The conversion of nitrate to nitrite in a mild alkaline solution (pH = 8~8.5) can be described as following:

\[
\text{NO}_3^- + \text{H}_2\text{O} + \text{Cd} \rightarrow \text{NO}_2^- + \text{Cd}^{2+} + 2\text{OH}^- \\
(R \ 2-1)
\]

Further reduction of nitrite to lower oxidation states is slow due to kinetic barriers. The nitrate-to-nitrite conversion efficiency depends on factors such as mixing time, Cd surface to volume ratio, and pH. The produced nitrite thus is determined by the method described above.

In our experiment, Cd granules were pretreated following the procedures of the APHA-AWWA-WPCF standard method [Clesceri et al., 1989]. In brief, 20 g of Cd granules was treated with 100 ml 6 M HCl, followed by rinsing with 200 ml of 2% CuSO\(_4\)5H\(_2\)O solution to from Cd-Cu granules. The treated Cd-Cu granules were packed into a 0.8 cm PFA tubing (1/8” i.d., ¼” o.d.). The Cd reduction column was stored in 1% NH\(_4\)Cl buffer solution (pH=8.5) and was activated prior to use by passing through 50 ml of 1% NH\(_4\)Cl buffer solution containing 5 µM NaNO\(_3\). One percent NH\(_4\)Cl buffer
solution (pH=8) was used as carrier with flow rate of 0.4 ml min\(^{-1}\). Sample dissolved in 1% NH\(_4\)Cl buffer solution was injected at a flow rate of 0.25 ml min\(^{-1}\). After Cd-column, nitrate was reduced quantitatively to nitrite with an on-line copperized cadmium column. Nitrite was derivatized with 2 mM SA, 0.2 mM NED and 40 mM HCl (0.5 ml min\(^{-1}\)) to form azo dye in 1 min, which was detected at 540 nm by a UV-visible miniature spectrometer with a long-path flow cell. NaNO\(_3\) standard solution was used for calibration. A standard curve was obtained by plotting the absorbance of standard against NO\(_3\) concentration. The detection limit of this method is \(~\)10 nM. Nitrate reduction efficiency is \(\geq\) 95% with the sampling flow rate of 0.4 ml min\(^{-1}\). Figure 2.5 showed a schematic diagram of nitrate measurement system.

![Schematic diagram of a nitrate measurement system](image)

**Figure 2.5** Schematic diagram of a nitrate measurement system.
2.4 NO$_2$ measurement

NO$_2$ is a product of nitric acid photolysis, and thus needs to be quantified in the photochemical experiments. The commercial NO$_x$ analyzer (Model 42C Trace Level, Thermo Environmental Instrument) was not suitable to quantify the NO$_2$ concentration and production under our experimental set up (Chapter 5) for two reasons: (1) its detection limit is relatively high (~ 50 pptv), and (2) its air sample flow rate (1.7 L min$^{-1}$) is too high compared to the flow reactor flow rate (0.45 L min$^{-1}$). A measurement method of NO$_2$ was thus developed based on HONO measurement technique (Figure 2.6). Air was drawn into a 40-turn coil sampler and NO$_2$ was scrubbed directly by a SA + NED reagent solution. Azo dye derivative was detected at 540 nm by a UV-visible miniature spectrometer with a long-path flow cell. The NO$_2$ collection efficiency was determined and optimized by varying the length of coil sampler, reagent compositions, gas flow rate and reagent flow rate.

In laboratory photochemical experiment, NO$_2$ measurement system was connected in series with HONO measurement system. HONO was scrubbed by the first coil sampler and NO$_2$ by the second coil sampler (details see Figure 5.1 in Chapter 5). Gas flow rate of 0.4 L min$^{-1}$ and reagent flow rate of 0.5 ml min$^{-1}$ were used as a typical operation condition for NO$_2$ measurement system. Using a 40-turn coil sampler, ~ 60% collection efficiency can be achieved when NO$_2$ reacted with reagent comprised of 60 mM SA and 0.8 mM NED in 2.5 M acetic acid. The detection limit is 15 pptv.
Interference of NO$_2$ on HONO channel at gas flow rate of 0.4 L min$^{-1}$ was investigated. Gas-phase standard of 5-30 ppb was generated by diluting 20 ppm NO$_2$ (Certified, Matheson Tri-Gas Inc., CP) with zero air in a gas mixer (Environics, series 2000), followed by passing through a NaCO$_3$-coated denuder at a flow rate of 6 L min$^{-1}$ to remove the potential contamination of HONO and HNO$_3$ right before reaching the HONO coil sampler. A tee was connected before the inlet of HONO channel, directing a flow of 0.4 L min$^{-1}$ to the inlet and venting the remaining flow of 5.6 L min$^{-1}$. No NO$_2$ signal was observed in HONO channel. Since HONO collection efficiency is nearly 100% in the first channel, the NO$_2$ channel is free of HONO interference.
A standard curve for NO$_2$ measurement was made by introducing the pre-mixed NaNO$_2$ standard solution with SA/NED directly into the downstream of the coil sampler. The signal height was plotted against the nitrite concentration as a calibration curve. The concentration of produced NO$_2$ was calculated as:

$$C_{NO_2} = \frac{RT \times C_{NO_2^-} \times F_l}{0.6 F_g} \quad (Eq. \ 2 - 2)$$

where $F_l$ is scrubbing solution flow rate in ml min$^{-1}$; $F_g$ is air sampling flow rate in L min$^{-1}$; $C_{NO_2^-}$ is nitrite concentrations (nmol L$^{-1}$) in the scrubbed aqueous samples; $C_{NO_2}$ is gaseous concentration of NO$_2$ in pptv; R is gas constant (0.082 L atm K$^{-1}$ mol$^{-1}$) and T is the absolute temperature at which the mass flow controller is calibrated (293K); 0.6 is the NO$_2$ collection efficiency by the 40-turn coil sampler.

2.5 Chemicals and reagents

Chemicals and reagents used in the experiments are listed in Table 2.1. All chemicals and reagents were used without further purification. All the solutions were prepared with D.I. water purified with a Millipore Milli-Q water system (with resistivity $\geq$18.2 M$\Omega$).
<table>
<thead>
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<th>Chemical</th>
<th>Molecular Formula</th>
<th>Grade (Purity)</th>
<th>Producer</th>
<th>Use</th>
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<td>99.9%</td>
<td>Mallinckrodt</td>
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<td>Fisher</td>
<td>Cd copperization</td>
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<tr>
<td>D-(-)-glucose</td>
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<td>Fluka</td>
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<tr>
<td>3-Nitrophenol</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;NO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>99%</td>
<td>Sigma-Aldrich</td>
<td>Surface coating</td>
</tr>
<tr>
<td>4-Nitrophenol</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;NO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>≥ 99%</td>
<td>Aldrich</td>
<td>Surface coating</td>
</tr>
<tr>
<td>Oxalic acid dihydrate</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;·2H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>≥ 99%</td>
<td>Sigma-Aldrich</td>
<td>Surface coating</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>99+%</td>
<td>Sigma-Aldrich</td>
<td>Surface coating</td>
</tr>
<tr>
<td>Sodium benzoate</td>
<td>C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;Na</td>
<td>99%</td>
<td>Aldrich</td>
<td>Nitrate actinometer</td>
</tr>
<tr>
<td>Sodium carbonate, anhydrous</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>99+%</td>
<td>J.T. Baker</td>
<td>Denuder coating</td>
</tr>
<tr>
<td>Chemical</td>
<td>Molecular Formula</td>
<td>Grade (Purity)</td>
<td>Producer</td>
<td>Use</td>
</tr>
<tr>
<td>--------------------------</td>
<td>-------------------</td>
<td>---------------</td>
<td>---------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>NaOH</td>
<td>99.99%</td>
<td>Aldrich</td>
<td>pH adjust</td>
</tr>
<tr>
<td>Sodium nitrate</td>
<td>NaNO₃</td>
<td>99.9%</td>
<td>J.T. Baker</td>
<td>Cd column activation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Nitrate actinometer</td>
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<td>99.7%</td>
<td>J. T. Baker</td>
<td>Nitrite standard</td>
</tr>
<tr>
<td>Sodium phosphate, bibasic</td>
<td>Na₂HPO₄</td>
<td>99.9%</td>
<td>J. T. Baker</td>
<td>Phosphate buffer</td>
</tr>
<tr>
<td>Sodium salicylate</td>
<td>C₇H₅O₃Na</td>
<td>99+%</td>
<td>Sigma-Aldrich</td>
<td>Actinometry standards</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>C₄H₆O₄</td>
<td>≥ 99%</td>
<td>Sigma-Aldrich</td>
<td>Surface coating</td>
</tr>
<tr>
<td>Sulfanilamide (SA)</td>
<td>C₆H₈N₂O₂S</td>
<td>≥ 99%</td>
<td>Aldrich</td>
<td>Derivatization reagent</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>H₂SO₄</td>
<td>95.7%</td>
<td>Mallinckrodt</td>
<td>pH adjust</td>
</tr>
</tbody>
</table>
CHAPTER 3. AIRCRAFT MEASUREMENT OF HONO VERTICAL PROFILES
IN THE LOWER TROPOSPHERE

Extensive HONO measurements have been conducted in both urban [Acker et al.,
2006a; AndresHernandez et al., 1996; Bari et al., 2003; Huang et al., 2002; Reisinger,
2000; Stutz et al., 2002; 2004] and rural environments [Acker et al., 2004; 2006b; He et
al., 2006; Kleffmann et al., 2003; 2005; Zhou et al., 2002a; 2007]. However, almost all
of the HONO measurements to date have been made on ground-based platforms, and the
reported HONO concentration profiles have all been near the bottom of the boundary
layer (BL). To understand the importance of HONO in tropospheric photochemistry and
to estimate the relative importance of ground surfaces and aerosol surfaces in
heterogeneous production of HONO, vertical HONO profile measurements are necessary,
over the altitudes from the surface mixed layer to the free troposphere (FT).

In this chapter, we report the first aircraft-based measurements of HONO vertical
distribution profiles over a forested region and the Great Lakes. The measurement
altitude ranged from 50-2700 m above the ground level.

3.1 Experimental

Site description. Aircraft measurements were carried out over the northern tip of
the Lower Peninsula of Michigan and the neighboring Great Lakes region (Figure 3.1)
from July 30 to August 6, 2007. During HONO profiling over the land, the aircraft
circled above a mixed deciduous/coniferous forest centered on the PROPHET site of the
University of Michigan Biological Station. HONO concentrations were simultaneously
measured by another student (Honglian Gao) on the top of a 32-m tower located in PROPHET site.

Figure 3.1 Left: locations of sampling sites over the land (★) and major urban and industrial centers in the Great Lakes region. Source: http://www.bestplaces.net/city/michigan/pellston for the map. Upper right: PROPHET site. Lower right: Great lakes.

The surrounding of the PROPHET site has been described in detail by Carroll et al. [2001] and Thorneberry et al. [2001]. The nearest major urban centers are Detroit, Michigan, 350 km to the southeast, and Milwaukee, Wisconsin and Chicago, Illinois, 350 and 450 km, respectively, to the southwest. The shore of Lake Michigan is 25-30 km to the west and northwest, and Lake Huron is 20-45 km to the east and northeast.
HONO profiles over water were measured either over Lake Huron or over Lake Michigan depending on the wind direction during the sampling period to ensure that air mass was transported over water for the last 20 km prior to its arrival. The HONO contribution from the land surface source was thus negligible due to the fast photolysis of HONO during the day.

The major air mass types influencing this area have been identified by Cooper and Moody [2001]. Higher mixing ratios of O₃, CO, NOₓ and NO₂ were generally associated with southerly transport from regions of greater anthropogenic emissions in the contiguous United States. Lower mixing ratios were observed under northerly transport from relatively clean Canadian regions. Figure 3.2 showed locations with NOₓ emissions above 10,000 ton/year, which is of interest because NOₓ is a key precursor of HONO, substantial levels of NOₓ can be transported to the measurement site to cause elevated HONO levels. The arrow indicated the locations of two power plants in the Upper Michigan Peninsula, which affected our observation over the lake.
Figure 3.2 Map of facilities with NO₃ emissions above 10,000 ton/year. The size of the red dot is proportional to the strength of the emission. The arrow indicated the locations of 2 power plants in the Upper Michigan Peninsula. Star indicated the sampling location over the lake on August 6, 2007. Source: US EPA office of Air and Radiation, National Emission Inventory (NEI) database (http://www.epa.gov/air/data/). Data were extracted for year 2002.
**Aircraft and flight summary.** A Beechcraft Duchess twin-engine airplane (Figure 3.3) was used in the study of HONO concentration vertical profiles. A ring laser gyro inertial navigation and global positioning system (INS/GPS) were used to gather inertial information. A temperature sensor was used to record the temperature during the flight. Compared to a large research aircraft (e.g. DC-8), the light aircraft operated in this experiment could travel at an altitude as low as 50 m above the ground surfaces at a relatively low speed (≈ 180 km hr⁻¹). These performances allowed us to examine more details on HONO profiles in the lower BL. On the other hand, limited by the small payload, short endurance and safety concerns associated with a small aircraft, we can only study HONO vertical profiles during daytime in each 2-hr flight session while no other supporting species (such as NO₂) can be measured simultaneously.

*Figure 3.3* A Beechcraft Duchess light aircraft used in the study of HONO vertical profiles.
Each flight took off from Pellston Regional Airport, Michigan (45.6°N, 84.9°W) and lasted 2~3 hr, spending 15-20 min at each altitude to establish HONO concentration profiles. The typical altitudes include 50 - 80 m, 200 – 230 m, 330 – 500 m, 650 – 680 m, 950 – 1300 m and 2500 – 2600 m above ground level (AGL). To assess the changes in HONO vertical distributions throughout the day, missions were conducted at different times of the day.

**Supporting information.** HONO photolysis rate constants were calculated using NCAR TUV model ([http://cprm.acd.ucar.edu/Models/TUV/Interactive_TUV/](http://cprm.acd.ucar.edu/Models/TUV/Interactive_TUV/)). Air mass source regions were identified by back trajectory calculations using the HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model [Draxler, 2003 #618].

### 3.2 Results and discussion

#### 3.2.1 Results summary

The HONO aircraft measurement results have been published in *Geophysical Research Letter* [Zhang et al., 2009]. Eight flights were made over the forested region, three of which were also conducted over the lake. Detailed flight information and measurement results are summarized in Table 3.1. In the BL over the forested region, HONO mixing ratios ranged from 8 to 70 pptv, with a mean of 28 pptv and a median of 29 pptv. The HONO concentrations at the altitudes closest to the ground surfaces were in good agreement with those measured at PROPHET tower during the same periods (Figure 3.4 b-e), and within the HONO concentration range previously reported in the rural atmosphere [Acker et al., 2006; He et al., 2006 ; Zhou et al., 2002, 2007]. Over the Great Lakes, HONO mixing ratios were in the range 21- 32 pptv, with a mean and a median of 26 pptv. HONO mixing ratios in the FT, which started between 1000 m and
1900 m, were low and relatively constant, in the range of 4-17 pptv, with a mean of 9 pptv and a median of 8 pptv.

The variations of the ranges of HONO concentration for different days have a strong dependence on air mass origin, based on backward trajectory calculations. The BL HONO concentrations were high, up to 70 pptv, during polluted southwesterly flow (July 30 - August 1) originating from Chicago and Milwaukee (Figure 3.4 a-c), but were less than 30 pptv during relatively clean northwesterly flow (August 3 - August 6), which originated in Canada (Figure 3.4 d-g). The observations are consistent with the fact that higher concentrations of HONO precursors exist in southerly flow (NOy ~2.9 ppbv and NOx ~1.1 ppbv) than in the northerly flow (NOy ~0.91 ppbv and NOx ~0.46 ppbv)

[Thornberry et al., 2001]
Table 3.1 Summary of the aircraft measurements over the northern tip of the Lower Peninsula of Michigan and the neighboring Great Lakes region during summer of 2007.

<table>
<thead>
<tr>
<th>Flight NO</th>
<th>Date (EDT)</th>
<th>Time (EDT)</th>
<th>Altitude AGL (m)</th>
<th>Air Mass Origin</th>
<th>BL HONO range / mean (pptv)</th>
<th>FT HONO range/ mean (pptv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7/30/07</td>
<td>12:02-14:09</td>
<td>50-2630</td>
<td>SW</td>
<td>25-66 / 41</td>
<td>11-17 / 14</td>
</tr>
<tr>
<td>3</td>
<td>8/01/07</td>
<td>8:18-10:43</td>
<td>70-2680</td>
<td>SW</td>
<td>21-74 / 36</td>
<td>8-12 / 10</td>
</tr>
<tr>
<td>4</td>
<td>8/01/07</td>
<td>13:54-16:25</td>
<td>50-2640</td>
<td>SW</td>
<td>15-42 / 33</td>
<td>10-17 / 15</td>
</tr>
<tr>
<td>4c</td>
<td>8/01/07</td>
<td>16:25-17:07</td>
<td>100</td>
<td>SW</td>
<td>21-32 / 29</td>
<td>N/M</td>
</tr>
<tr>
<td>5</td>
<td>8/03/07</td>
<td>16:13-17:52</td>
<td>50-2610</td>
<td>NW</td>
<td>8-22 / 15</td>
<td>4-8 / 6</td>
</tr>
<tr>
<td>6</td>
<td>8/04/07</td>
<td>8:13-10:17</td>
<td>70-2580</td>
<td>NW</td>
<td>10-52 / 20</td>
<td>7-10 / 9</td>
</tr>
<tr>
<td>7</td>
<td>8/04/07</td>
<td>15:02-17:15</td>
<td>50-2610</td>
<td>NW</td>
<td>22-46 / 33</td>
<td>6-12 / 8</td>
</tr>
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<td>8/04/07</td>
<td>17:15-17:33</td>
<td>100</td>
<td>NW</td>
<td>22-28 / 25</td>
<td>N/M</td>
</tr>
<tr>
<td>8</td>
<td>8/06/07</td>
<td>13:29-15:23</td>
<td>60-2640</td>
<td>NW</td>
<td>12-23 / 20</td>
<td>6-9 / 7</td>
</tr>
<tr>
<td>8c</td>
<td>8/06/07</td>
<td>15:23-16:20</td>
<td>70-1200</td>
<td>NW</td>
<td>12-39 / 28</td>
<td>N/M</td>
</tr>
</tbody>
</table>

a[Zhang et al., 2009]. b The data are not available for the second flight. c Observation over the lakes. N/M – not measured.
Figure 3.4 HONO mixing ratios over the forested region (●), over the Great Lakes (△), and at the PROPHET tower (x), and the potential temperature profiles over the land (−) during summer of 2007. Source: [Zhang et al., 2009].
3.2.2 HONO vertical profiles over the land

All HONO concentration profiles show the highest values near the ground surface, and a general decreasing trend with increasing altitude. In the BL, the HONO vertical profiles were found to be strongly influenced by the air column stabilities, as indicated by the potential temperature profiles (Figure 3.4 a-e). In the morning hours when the air column was relatively stable, significant HONO concentration gradients were observed in the lower BL (Figures 3.4 b, e), suggesting the ground/canopy surface to be a HONO source. These morning HONO profiles are in agreement with previous observations by Kleffmann et al. [2003] showing significant HONO gradients in 190-m nighttime vertical profiles over a forested area in Germany.

Somewhat lower but relatively constant concentrations of HONO above the surface mixed layer probably represent background values from in situ production, i.e. not influenced by the ground surface, due to the stable surface inversion inhibiting vertical mixing. In the morning of August 4 (Figure 3.4e), a significant change in HONO concentration was observed at approximately 70 m above the ground, from 17 pptv measured at ~ 08:30 EDT to 48 pptv at ~10:00 EDT. At 08:30 EDT, the ground surface temperature was 284K, 8K lower than at 70 m (Figure 3.4e). The steep temperature gradient in the stable surface mixing layer prevented vertical mixing of the surface-emitted HONO to the measurement altitude. By 10:00 EDT, surface heating raised the ground surface temperature to about 293K, reducing air column stability and allowing surface HONO to be transported to the measurement altitude.

Several vertical HONO profile/gradient measurements conducted on high towers [He et al., 2006; Kleffmann et al., 2003] or by DOAS with multiple light-path heights
[Stutz et al., 2002; Veitel et al., 2002] have been reported. Although it is difficult to directly compare our results with those from previous studies due to the difference in measurement environments, heights and the times of a day, all studies showed significant vertical HONO gradients within the lower portion of the BL, indicating the ground surface to be a significant HONO source.

We estimated HONO vertical transport by turbulent diffusion using Equation (3.1) [Jacob, 1999].

\[
\sigma = (2K_z \tau_{HONO})^{\frac{1}{2}}
\]

(Eq. 3-1)

In Equation 3.1, \(\sigma\) is the vertical transport distance, \(K_z\) is the turbulent diffusion coefficient, and \(\tau_{HONO}\) is the HONO lifetime. During the morning hours when the BL was stable, as suggested by the temperature profiles (Figure 3.4 b,e), \(K_z\) is in the range of \(10^3 - 10^4\) cm\(^2\) s\(^{-1}\). Assuming a \(\tau_{HONO}\) value of 28 min, most of the surface-derived HONO would be trapped within the lowest 18 - 58m above the canopy surface, resulting in a steep near-surface HONO concentration gradient (Figure 3.4 b, e). Under the near-neutral conditions that we encountered during the afternoons (Figure 3.4 c,d,f,g), the \(K_z\) value is on the order of \(~10^6\) cm\(^2\) s\(^{-1}\). In this case, the vertical transport distance would be \(~350\) m above the canopy surface, assuming a \(\tau_{HONO}\) of 10 min. The increase in the HONO vertical transport distance would result in significant dilution and thus relatively uniform vertical HONO profiles throughout the BL, as observed (Figures 3.4 c, d, f, g) from our measurements. The July 30 data (Figure 3.4a) represents a unique case in which a stable surface layer persisted until solar noon.
3.2.3 HONO vertical profiles over the lake

The HONO concentrations were significantly lower in the lower BL over the Great Lakes than those over the forest, i.e. 29 ± 4 pptv (N = 8) vs 37 ± 3 pptv (N = 14) on August 1, and 25 ± 2 pptv (N = 11) vs 36 ± 3 pptv (N= 11) on August 4 (Figures 3.4c, f), with an exception on August 6 which will be discussed below. Lake surfaces should behave more like a sink of HONO than a source (as in the case of ground surfaces) due to the high solubility of HONO in water (e.g., H~2.6×10^4 M atm^-1 at pH 6). However, a shallow and stable layer of air usually exists over colder water surface and is decoupled from the air aloft, reducing the depositional loss of HONO from the air column to the lake surface. Therefore, the measured HONO concentrations over the lake likely represent the background values supported by in situ HONO production alone.

Higher HONO concentrations over the lake compared to those over the land were observed on August 6 (Figure 3.4 g). Comparison of back trajectories of the air masses at the two sampling locations during the times of measurement indicates that although both air masses arrived from the northwest, the air mass arriving at the Lake Michigan had passed over a significant NO_x source region about 20 hr earlier, where 2 power plants were located in the Michigan Upper Peninsula (Figure 3.2 and 3.5). The land surface HONO source should be negligible since photolysis should have effectively removed all the surface-emitted HONO during the 9-hr travel of the air mass over Lake Michigan. The elevated HONO concentrations over Lake Michigan probably resulted from higher in situ HONO production in this anthropogenically impacted air mass.
Figure 3.5 24-hr backward trajectories (100m AGL) of air masses arriving at the PROPHET site (left, black star) and the sampling location over the Lake Michigan (right, black star) in the afternoon of August 6, 2007. Green stars indicate the locations of 2 power plants in the Upper Michigan Peninsula.

3.2.4 HONO in situ production

One of the major objectives of this research was to characterize *in situ* production of HONO in the air column. The observed median HONO concentrations of ~ 8 pptv in the FT (i.e. typically ≥1500 m AGL) and ~ 25 pptv and ~ 15 pptv in the upper BL (800-1000 m AGL) in the southwesterly and northwesterly flows, respectively, probably represent background HONO concentrations sustained by *in situ* production, because the ground/canopy surface influence is negligible for these altitudes.

Despite the large difference in HONO photolytic lifetime, from 8.3 min at midday to ~30 min in the morning, the observed HONO concentrations did not vary much with time of day (Figure 3.4), suggesting that *in situ* HONO production was photochemical in nature and that ambient HONO was in a near photo-steady state. To maintain the
observed HONO concentrations against photolysis at noontime, an in situ HONO production source of ~57 pptv hr\(^{-1}\) would be required in the FT, and ~180 pptv hr\(^{-1}\) and ~110 pptv hr\(^{-1}\) in the upper BL in the southwesterly and northwesterly flows, respectively, assuming a HONO photolysis rate constant of \(J_{\text{HONO}} \sim 2 \times 10^{-3} \text{ s}^{-1}\).

In the continental FT, the NO\(_x\) level is relatively low, ~40 pptv [Huebert et al., 1990], and the gas-phase NO-OH reaction is only a minor source, i.e., 2 pptv hr\(^{-1}\) or 4\% of the needed in situ production rate, assuming [OH] = 5\times10^6 \text{ molecules cm}^{-3}, [NO] = 2.5\times10^8 \text{ molecules cm}^{-3}, and \(k_{\text{NO} + \text{OH}} = 1.4\times10^{11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) [Atkinson et al., 2004]. In the upper BL, the contribution of the gas-phase NO-OH reaction is estimated to be about 13 pptv hr\(^{-1}\) in southwesterly flow and 5 pptv hr\(^{-1}\) in northwesterly flow, or 5-7\% of the needed in situ production rate, assuming [OH] = 5\times10^6 \text{ molecules cm}^{-3}, and [NO] = 1.3\times10^9 and 5\times10^8 \text{ molecules cm}^{-3} in southwesterly and northwesterly flows, respectively [Thornberry et al., 2001].

The remaining > 90\% of the needed HONO in situ production could derive from sources involving a range of HONO precursors, such as photolysis of nitrophenols in the gas phase and on surfaces [Bejan et al., 2006; Rohrer et al., 2005], photo-enhanced heterogeneous reactions involving NO\(_2\) on organic surfaces [George et al., 2005; Stemmler et al., 2006], and photolysis of HNO\(_3\)/nitrate on and in aerosol particles [He et al., 2006; Zhou et al., 2003]. Because the air over the measurement area around the PROHET site is relatively clean with respect to anthropogenic VOCs, the first mechanism is unlikely to be important. More details on source strengths of photolysis of HNO\(_3\)/nitrate on and in aerosol particles will be discussed in chapter 5.
3.2.5 HONO contribution from the ground/canopy surfaces

We estimated the contribution of surface processes on the ground/canopy to BL HONO ($P_{\text{surface}}$) as expressed as a flux by Equation (3.2), by subtracting the *in situ* HONO production from the overall HONO source strength needed to sustain the observed HONO concentration in the air column throughout the BL, assuming a photo-steady state.

$$P_{\text{surface}} = J_{\text{HONO}} \times \left[ \sum (C_{\text{HONO}}^i \times \Delta Z_i) - C_{\text{HONO}}^o \times Z \right] / RT \quad (\text{Eq. 3-2}).$$

In Equation 3-2, $J_{\text{HONO}}$ is HONO photolysis rate constant, $Z$ is BL height, $C_{\text{HONO}}^i$ is the average HONO concentration in the height interval $\Delta Z_i$, and $C_{\text{HONO}}^o$ is the background HONO concentration, i.e., the HONO concentration observed in the upper BL or over the lake where ground surface contribution can be neglected (Figure 3.4). The calculated $P_{\text{surface}}$ was in the range from $3.6 \times 10^{-7}$ moles m$^{-2}$ hr$^{-1}$ in the northwesterly flow during the morning of August 4 to $2.8 \times 10^{-6}$ moles m$^{-2}$ hr$^{-1}$ in the southwesterly flow during the early afternoon of August 1, with a mean of $9 \times 10^{-7}$ moles m$^{-2}$ hr$^{-1}$ and a median of $8 \times 10^{-7}$ moles m$^{-2}$ hr$^{-1}$. The HONO emitted from the ground/canopy surfaces accounted for 16 – 27% of the overall HONO in the BL, most of which was distributed in the lower portion of the BL.

The calculated HONO contribution from the ground/canopy surface is in good agreement with the HONO flux measured at the PROPHET site in summer of 2008, which showed a noontime mean of $7 \times 10^{-7}$ moles m$^{-2}$ hr$^{-1}$ (see details in Chapter 4). The mean $P_{\text{surface}}$ value of $9 \times 10^{-7}$ moles m$^{-2}$ hr$^{-1}$ represented a significant fraction of the summer noontime NO$_x$ downward flux mean of $1.5 \times 10^{-6}$ moles m$^{-2}$ hr$^{-1}$ at the PROPHET site [Hill et al., 2005]. Thus, a significant fraction of the deposited N is recycled back
into the atmosphere as, effectively, NO\textsubscript{x} [Zhou et al., 2003]. That is consistent with the results of Hill et al. [2005], who found that much of the nitrate that dry deposits to the forest canopy at this site appeared to be recycled to the atmosphere.

### 3.2.6 HONO contribution as OH source

Photolysis of HONO is a significant source of the OH radical in the lower BL, i.e. up to 390 pptv hr\textsuperscript{-1} at midday, similar to that reported for rural ground measurement sites [Acker et al., 2006b; Kleffmann et al., 2003; Kleffmann and Wiesen, 2005; Ren et al., 2006; Zhou et al., 2002; 2007], and on the order of 20% of the total photolytic HO\textsubscript{x} production observed on the canopy level at the PROPHET site [Tan et al., 2001]. However, HONO photolysis is only a minor OH source, ~55 pptv hr\textsuperscript{-1}, in the FT and can be neglected when compared to the source from ozone photolysis.

### 3.3 Summary

We present the first HONO vertical profiles in the atmospheric BL and the lower FT over a forested region in northern Michigan and the neighboring Great Lakes, measured from a small aircraft in summer of 2007. The HONO mixing ratios ranged from 4 to 17 pptv in the FT and from 8 to 74 pptv in the BL.

The HONO distribution pattern was strongly influenced by the air column stability, i.e., strong negative HONO gradients existed in stable BL in the morning hours, whereas the HONO distribution was relatively uniform in the unstable and well-mixed BL in the afternoons.

The ground surface was a major source of HONO in the lower BL. The presence of substantial daytime HONO in the FT (~8 pptv) and in the upper BL (25 pptv) suggests that a significant in situ source of HONO exists in the air column.
CHAPTER 4. HONO FLUX MEASUREMENT

ABOVE A NORTHERN MICHIGAN FOREST CANOPY

Results from aircraft measurement of HONO vertical profiles indicated that the ground/canopy surface was a major source of HONO in the lower boundary layer. To assess quantitatively the source strength of HONO on ground surfaces, measurement of exchange flux of HONO between the ground and the atmosphere is essential. However, there are only a few HONO flux measurements reported in literature [Beine et al., 2005; 2006; Harrison and Kitto, 1994; Honrath et al., 2002; Stutz et al., 2002; Zhou et al., 2001], all of which were made based on an indirect gradient method over grassland or snowpack. In the absence of direct flux measurements, an accurate estimate of the gradient of mean concentration can be difficult due to the large scatter of the measurements and the influence of chemical transformation during the turbulent transport process [Galmarini et al., 1997].

In this research, a relaxed eddy accumulation (REA) system coupled with modified coil sampling/(SA +NED) HONO measurement system [Huang et al., 2002] was developed for direct measurement of HONO flux. Measurements of vertical HONO flux along with HONO ambient concentrations were made simultaneously over a forest canopy at the PROPHET site from July 17 to August 7, 2008.

In this chapter, details regarding the principles, designs and operations of REA HONO flux system were described. The system was deployed and characterized in a
field campaign. The results quantitatively reveal the role of ground surfaces on HONO heterogeneous formation. The correlations of HONO behaviors and its precursors (e.g. NO\textsubscript{x} and HNO\textsubscript{3}) were examined in more details through a case study.

4.1 Experimental

Site description. Measurements were conducted at the PROPHET site at the University of Michigan Biological Station (45°30’ N, 84°42’ W, elevation 238 m). A map and the detailed description of the site were included in Chapter 3. During this field campaign, HONO fluxes and concentrations were measured continuously and concurrently on the top of a 31-m scaffolding tower, ~11 m above the canopy.

REA flux system. HONO flux system was developed based on relaxed eddy accumulation (REA) technique which involves conditional sampling of air into updraft and downdraft components at a constant flow rate [Bowling et al., 1998]. The duration of sampling for each component is only related to the frequency at which the wind eddy changes in vertical direction. Air samples collected in each component were accumulated over a collection period before determination of concentrations. The Flux \((F)\) is calculated using the following relationship [Businger and Oncley, 1990]:

\[
F = \beta \sigma_w (\bar{C}_{up} - \bar{C}_{dn})
\]

\((Eq. 4-1)\)

Where \(\beta\) is an empirically determined coefficient with a value of ~ 0.6 over a smooth surface [Businger and Oncley, 1990; Westberg et al., 2001], \(\sigma_w\) is the standard deviation of vertical wind sector over the collection period, and \(\bar{C}_{up}\) and \(\bar{C}_{dn}\) are the average concentrations of HONO in the updraft and downdraft components, respectively.
A schematic of a REA HONO flux system and its field installation are shown in figure 4.1, consisting of a three-dimensional sonic anemometer and two HONO measurement systems. A CSAT3 3-D sonic anemometer (Campbell Scientific) was mounted at ~11 m above the canopy level on an arm extending ~ 1.5 m away from the west side of the tower facing the prevailing wind, and was used to acquire wind speed at 10 HZ. During flux measurement, the value of $\sigma_w$ was determined by the vertical wind from the previous 30-min period. A dynamic threshold (deadband) $w_T = \sigma_w/2$ was used to increase the concentration difference between the reservoirs [Bowling et al., 1998; Pattey et al., 1993]. The vertical component of the instantaneous wind velocity, $w$, was compared to a threshold $w_T$. Based on this comparison, a laptop computer was used to control the switching of two 3-way valves for conditional sampling (Table 4.1): for $w > w_T$, ambient air was collected into an updraft component and zero air flowed through a downdraft component; for $w < -w_T$, ambient air was sampled into a downdraft component and zero air flowed through an updraft component; for $-w_T < w < w_T$, zero air flowed into both components.

A deadband can be used to improve the sensitivity of the measurement and prolong the life of the REA valves. However, a deadband will result in some uncertainty in the concentration difference measurement by decreasing the effective sampling time [Oncley et al., 1993]. A reduction of the coefficient $\beta$ was also reported to be associated with the use of a deadband [Pattey et al., 1993]. In our experiment, data collected during very calm periods (i.e., when $|w| \leq w_T$ for more than 95% of the sampling period) were excluded in flux calculations.
Figure 4.1 Upper: a schematics of a REA HONO flux measurement setup, consisting of a 3-D sonic anemometer and 2 HONO measurement systems. Lower: The actual instrumentation during the field study.
Two HONO measurement systems described in chapter 2 were used to measure HONO concentrations in the up and down air drafts. The systems were operated over the same 30-min cycle as the ambient measurement system. During the 20-min measurement mode, both up and down systems were doing condition sampling (Table 4.1). Sample flow rate in each of the three channels (up + down + ambient) was maintained at a constant rate of 2 L min\(^{-1}\). Ambient air was pulled into scrubbing samplers through a 2.2-m PFA tube (3.2-mm ID) inlet extended near the anemometer probe (Figure 4.2), at a total flow rate of 6 L min\(^{-1}\). A 200 ms delay before valves responded to the vertical wind signal was set to compensate for time lags from the inlet to REA valves.

**Table 4.1** Sampling status in the 3 HONO measurement systems in a 30-min cycle

<table>
<thead>
<tr>
<th>System</th>
<th>‘Measurement’ (20 min)</th>
<th>‘Zero’ (10 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Updraft</td>
<td>ambient air when ( w &gt; w_T ), otherwise zero air</td>
<td>zero air</td>
</tr>
<tr>
<td>Downdraft</td>
<td>ambient air when ( w &lt; -w_T ), otherwise zero air</td>
<td>zero air</td>
</tr>
<tr>
<td>Ambient</td>
<td>ambient air</td>
<td>zero air</td>
</tr>
</tbody>
</table>

**Figure 4.2** The ambient air inlet extended near the anemometer probe.
The computer used for HONO concentration and flux measurements has a data acquisition program based on LabVIEW to collect and process wind data from 3D anemometer and to control valves. During operation, HONO signals in up, down and ambient channels were shown in three Ocean Optics windows respectively; wind information and REA valves status were monitored in a LabVIEW interface (see figure 4.3).

![A LabVIEW interface used in HONO concentration and flux measurements.](image)

**Figure 4.3** A LabVIEW interface used in HONO concentration and flux measurements.

**Calibration.** Calibration for the ambient concentration channel was described in Chapter 2. For HONO flux measurement, the signal area was integrated above the baseline and was plotted against the amount of nitrite, calculated from the NaNO₂ standard concentration, delivery flow rate and time. Three full-range, multipoint calibrations were conducted at the beginning, middle, and end of the campaign. A single
point calibration was made for every batch of reagent solutions, which usually lasted for 2 days. Correlation coefficients $r^2$ were $\geq 0.999$ for both sets of calibration curves.

**Ultraviolet radiation and photolysis rate constant calculation.** The total solar ultraviolet intensity between 295 nm and 385 nm was measured using an Eppley TUVR radiometer ($UV_{measured}$) with a detection limit of 0.3 W m$^{-2}$ and overall uncertainty of 10% [Carroll et al., 2001]. The radiative transfer model (http://cprm.acd.ucar.edu/Models/TUV/Interactive_TUV/) was used to calculate HONO photolysis rate constant ($J_{HONO}^{model}$) and total ultraviolet intensity between 295nm and 385nm ($UV^{model}$) for clear sky conditions, taking into account the climatological O$_3$ column and aerosol optical depth, time of day and month, and location of the sampling site. Correction was made for variable cloud cover using the following equation:

$$J_{HONO} = J_{HONO}^{model} \times \frac{(UV_{measured} / UV^{model}) \times (UV^{measured*} / UV^{model*})}{(UV_{measured} \times UV_{measured*} / UV^{model} \times UV^{model*})} \quad (Eq. \: 4 - 2)$$

where the $UV^{measured*}$ and $UV^{model*}$ are the modeled and measured UV intensities at solar noon under clear sky.

**Other measurements.** NO$_x$: NO and NO$_2$ were measured by a research group at Purdue University using a custom-built analyzer and the chemiluminescence technique described by [Ridley and Grahek, 1990]. For 5-minute averaged data, the detection limit was 7 pptv for both NO and NO$_2$. Meteorological parameters including temperature, dew point, precipitation, relative humidity and weather conditions were acquired through the website (http://www.wunderground.com). Back trajectories at both 50 m and 500 m above the ground level were calculated using HYSPLIT (HYbrid Single-Particle
Lagrangian Integrated Trajectory) Model [Draxler and Rolph, 2003] to identify the air source region.

4.2 HONO flux system performance

As most surfaces are not perfectly flat, the vertical wind fluctuations are often affected by the mean horizontal wind [Chahuneau et al., 1989]. During the 2 weeks prior to the measurement of HONO flux at this site, 3-D wind data were collected by the anemometer for coordinate transformation, by which wind data collected during flux measurement were aligned with the mean wind streamlines. Thus, when $w = 0$, the average flux of dry air perpendicular to the surfaces of interest is zero. An example of raw data of vertical wind velocity and HONO signals are shown in the upper panel in Figure 4.4. It is apparent that vertical wind fluctuated around zero (red trace), with length of individual updraft or downdraft capable of triggering the valves (i.e. $|w| > w_T$) in the range of 0.1 – 20 s, resulting in ambient air sampling in the updraft channel ($w > w_T$) or in the downdraft channel ($w < -w_T$). The add-up of two HONO traces for the updraft (red trace) and the downdraft (green trace) (Figure 4.4, upper panel) was lower than that for ambient concentration channel (blue trace) since the flux valves opened to the ambient air only a fraction of the time during the 20-min sampling period when $|w| > w_T$. 
Figure 4.4 Examples of raw and processed data collected during a 2-hr period on July 25, 2008.
To quantify HONO collected in each channel during each sampling period, the area of the signal above the “zero-HONO” air baseline was integrated and converted into moles based on the calibration curve. The integrated HONO concentration was derived from the moles of HONO divided by the ambient air volume sampled when the valve was triggered. The middle panel in Figure 4.4 shows the integrated concentrations in the updraft and downdraft channels along with standard deviation of vertical wind ($\sigma_w$) during the sampling cycle. The 20-min averaged HONO flux was then derived from the $\sigma_w$, $\bar{C}_{up}$ and $\bar{C}_{dn}$ information in the middle panel using equation 4.1 (lower panel, Figure 4.4).

To ensure the data quality, data collected in the very calm periods were not used for flux calculation, i.e., when $|w| \leq w_T$ for more than 95% of the sampling period. The flux values were usually low during the very calm period, due to the small $\sigma_w$. The overall precision is estimated to be within $\pm (8 \times 10^{-8} + 0.15 \times F_{HONO})$ mol m$^{-2}$ hr$^{-1}$, estimated from uncertainties associated with HONO measurements in both up and down channels, the volume of ambient air collected during the periods when valve was triggered ($w > w_T$ for the updraft channel and $w < -w_T$ for the downdraft channel), and the $\sigma_w$ derived from vertical measurement.

4.3 Results and discussion

4.3.1 Results summary

A highlight of the HONO flux measurement results has been published elsewhere [Zhou et al., 2011]. A complete data set with discussions of cases is presented here. Figure 4.5 shows HONO fluxes and ambient HONO concentrations during the
measurement campaign. Overall, upward HONO fluxes were observed most of the time over the measuring period, with occasional downward fluxes during the rain, fog and dew events. An upward maximum of $4.7 \times 10^{-6}$ moles m$^{-2}$ hr$^{-1}$ was observed during the day after a high NO$_x$ and NO$_y$ event and a downward maximum of about $-2 \times 10^{-6}$ moles m$^{-2}$ hr$^{-1}$ was observed during a rain event. The average of flux is $0.37 \times 10^{-6}$ moles m$^{-2}$ hr$^{-1}$.

Ambient HONO concentrations ranged from 10 pptv during rain events to 189 pptv during a pollution event at night, with a mean of 49 pptv.

![Figure 4.5](image_url)

**Figure 4.5** Time-series of HONO flux (in red), ambient HONO concentration (in blue).
Figure 4.6 shows diurnal variations in hourly-averaged medians of HONO flux, HONO mixing ratio and Eppley UV intensity over the measurement period. On average, the HONO flux exhibits a strong diurnal variation pattern, with a minimum (~0.1×10^{-6} mol m\(^{-2}\) hr\(^{-1}\)) during the night and a maximum (~0.7×10^{-6} mol m\(^{-2}\) hr\(^{-1}\)) during noontime and early afternoon. It should be pointed out that the actual daytime HONO flux from the forest canopy may be slightly greater than that measured 11 m above the canopy, due to the photolytic loss of HONO during diffusive turbulent transport, by an upper limit of ~10% around noontime. The HONO mixing ratios also exhibited a significant diurnal variation pattern, with a daytime maximum of 70 pptv around noontime and a minimum of around 20 pptv around the time of sunset (Figure 4.6) [Zhou et al., 2011]. Similar diurnal variation patterns in HONO mixing ratios have been reported in other rural sites [Acker et al., 2006a; Zhou et al., 2002a; 2007]. On average, the photolysis of HONO contributed about 340 pptv hr\(^{-1}\) of OH production, similar to those reported for this and other rural sites, between 250-560 pptv hr\(^{-1}\) [Acker et al., 2006a; Zhang et al., 2009; Zhou et al., 2007].
Diurnal variations in hourly averaged median values of UV, HONO mixing ratio, and HONO flux measured from July 15 to August 10, 2008. The vertical bars are the 25 and 75 percentile ranges. Source: [Zhou et al., 2011].
4.3.2 Forest canopy as a HONO source or a sink

The canopy was a net source for HONO at UMBS most of the time indicated by the observed upward HONO flux (Figure 4.5). Substantial levels of HONO existed during the day, despite the effective photolytic loss, reaching an average maximum of about 70 pptv around solar noon. To sustain the observed concentration, a strong HONO source, about 350 pptv hr\(^{-1}\) on average around noontime, was needed.

Zhou et al. [2011] estimated the effect of canopy surface on the observed HONO mixing ratios, based on a 1-D transport of HONO, assuming that the horizontal distribution of HONO is uniform. The change in average HONO mixing ratios (\(\bar{C}_{HONO}\), in pptv) with time above unit area of canopy surface can be expressed by:

\[
\frac{d\bar{C}_{HONO}}{dt} = \frac{F_{HONO} RT}{HP} \times 10^9 + P_{HONO} - L_{HONO} \quad (Eq. 4 - 3)
\]

where \(F_{HONO}\) (mol m\(^{-2}\) hr\(^{-1}\)) is HONO flux over the canopy; \(P_{HONO}\) (pptv hr\(^{-1}\)) is in situ HONO production from gas-phase and particle-phase reactions; \(L_{HONO}\) (pptv hr\(^{-1}\)) is in situ HONO loss; \(H\) (m) is the HONO mixing height within one lifetime of HONO; \(R\) (L atm K\(^{-1}\) mol\(^{-1}\)) is the gas constant; \(T\) (K) is the absolute temperature, \(P\) is the atmospheric pressure (in atm). During daytime when photolysis is the dominant HONO loss pathway, Eqs. 4-3 and 4-4 apply,

\[
L_{HONO} = J_{HONO} \bar{C}_{HONO} \quad (Eq. 4 - 4)
\]
\[ H = \sqrt{2K_z/J_{\text{HONO}}} \quad (Eq. 4-5) \]

where \( J_{\text{HONO}} \) is HONO photolysis rate constant, \( K_z \) is the eddy diffusivity coefficient.

Assuming a midday \( F_{\text{HONO}} \) of \(~7\times10^{-7}\) moles m\(^{-2}\) hr\(^{-1}\), \( J_{\text{HONO}} \) of \(~5\) hr\(^{-1}\), \( \bar{C}_{\text{HONO}} \) of 70 pptv, and \( K_z \) of \(~3.6\times10^{4}\) m\(^{2}\) hr\(^{-1}\) (or \(~1\times10^{5}\) cm\(^{2}\) s\(^{-1}\)) [Jacob, 1999], the contribution of the HONO flux from the canopy was \(~140\) pptv hr\(^{-1}\) if averaged over an air column of 120m, and \(~200\) pptv hr\(^{-1}\) at the observation height of 32 m above ground. Calculations indicated that this source of HONO accounted for a major fraction, \(~57\%)\, of the observed HONO; the remaining 43\% was from volume HONO production mechanisms such as gaseous NO-OH reactions and heterogeneous reactions involved NO\(_x\) and HNO\(_3\) on aerosol surfaces [Zhou et al., 2011].

However, the canopy can also be a net HONO sink, as indicated by occasional downward fluxes during rain events (e.g. July 17, 20, 29), and fog and dew events (e.g. July 19, 27) (Figure 4.5). The wet canopy seemed to enhance the dry deposition of HONO and/or prevent HONO from being released once produced by heterogeneous reactions, in agreement with previous observations [He et al., 2006; Zhou et al., 2002a].

4.3.3 HONO precursors

It is generally believed that atmospheric HONO is produced mostly by heterogeneous reactions involving HONO precursors such as NO\(_x\) [George et al., 2005; Lammel and Cape, 1996; Stemmler et al., 2006; 2007] and HNO\(_3\) [Zhou et al., 2002a; 2002b; 2003; 2007; 2011]. In forested areas, forest canopy surfaces account for the majority of the surface area in the atmospheric boundary layer, and thus serve as sites for the heterogeneous reaction leading to HONO formation under favorable conditions.
In low-NO \textsubscript{x} environments, photolysis of HNO\textsubscript{3} deposited on ground/canopy surface has been proposed to be the major daytime HONO source [Zhou et al., 2002a; 2003; 2007]. To test this hypothesis, 16 sets of leaf samples (6 leaves per set) were collected from the top of the forest canopy for surface nitrate measurement [Zhou et al., 2011]. The daytime HONO flux was found to be strongly correlated ($r^2 = 0.69$) with the surface nitrate photolysis potential, defined as the product of surface nitrate loading and the surface nitrate photolysis rate constant calculated from Eppley UV intensity. Therefore, it was concluded that photolysis of HNO\textsubscript{3} deposited on the canopy surface was the major mechanism responsible for the observed HONO flux from the canopy into the atmosphere [Zhou et al., 2011]. The strong upward HONO flux during the day indicates that photolysis is an important sink for the deposited HNO\textsubscript{3}, thus an important atmospheric re-NO\textsubscript{x}-ification pathway.

The concentrations of NO\textsubscript{x} and HONO and HONO flux were measured simultaneously over two weeks (Figures 4.7 and 4.8), allowing us to examine the role of NO\textsubscript{x} as a HONO precursor at this site. During the day, NO\textsubscript{x} and HONO flux is found not to be correlated at any significant level ($r^2 = 0.01$), suggesting NO\textsubscript{x} was not a significant daytime HONO precursor responsible for the upward flux from the forest canopy. The correlation between NO\textsubscript{x} and daytime HONO concentration is slightly improved but still weak ($r^2 = 0.10$), reflecting some degree of contribution from the volume HONO production under high-NO\textsubscript{x} conditions during southerly flow.
Figure 4.7 Correlations between the HONO flux (left axis, open circles) and ambient NO\textsubscript{x} concentrations, and between ambient HONO (right axis, open triangles) and NO\textsubscript{x} concentrations during the night (22:00 - 06:00 EDT, panel a) and during the day (08:00 – 18:00 EDT, panel b). The data are hourly averages, excluding the rain, fog and dew events. The lines are the least-square fits for the data.
During the nights free of rain or dew, the contribution of the dark heterogeneous NO\textsubscript{x} reaction to the observed HONO flux increased, as indicated by the improved correlation between HONO flux and NO\textsubscript{x} ($r^2 = 0.37$, Figure 4.7). The even stronger correlation between concentrations of HONO and NO\textsubscript{x} ($r^2 = 0.56$, Figure 4.7) accounts for both the HONO produced at the forest canopy and the HONO transported in the air mass, and suggests that NO\textsubscript{x} was the major HONO precursor when photolysis of HNO\textsubscript{3} on surface was absent.

### 4.3.4 A case study

The behavior of HONO during the initial two days of this campaign is examined in more detail to illustrate the processes discussed above as a case study (Figure 4.8). During the morning of July 17 before sunrise, the concentrations of HONO and NO\textsubscript{x} varied in sync when air masses switched from clean northwesterly flow to more polluted southwesterly flow [Cooper et al., 2001]. Both ambient HONO and NO\textsubscript{x} concentrations were rising rapidly, from 40 pptv to 160 pptv and from 700 pptv to 2600 pptv, respectively. The strong correlation between the concentrations of HONO and NO\textsubscript{x} ($r^2 = 0.89$, $N = 7$, hourly averages) and the negative HONO flux during the early morning period suggests that most of the observed ambient HONO during the period was produced within the air mass on the way to the measurement site, probably by heterogeneous NO\textsubscript{x} reactions on aerosol surfaces.

After sunrise, the HONO flux was mostly positive, reaching $\sim 1.7 \times 10^{-7}$ moles m\textsuperscript{-2} hr\textsuperscript{-1} around 11:00 EDT, with an exception of slight negative flux ($\sim -0.1 \times 10^{-7}$ moles m\textsuperscript{-2} hr\textsuperscript{-1}) at 11:30 EDT when NO\textsubscript{x} reaching a peak of 4500 pptv. Several similar brief negative
HONO fluxes occurred throughout the campaign, mostly coinciding with rapid increase in NO\textsubscript{x} and with relatively high ambient HONO concentrations. This phenomenon may be caused by the concentration diffusion from elevated levels of HONO in the air above down to the relatively clean air within the forest canopy during the early phase of pollution episodes.

**Figure 4.8** Two days of time-series of HONO flux (open circles, lower panel, left axis), ambient HONO concentration (open triangles, lower panel, right axis), $\sigma_w$ (crosses) and NO\textsubscript{x} (open squares, upper panel, left axis), and $J_{\text{HONO}}$ (line, upper panel, right axis). The two thick horizontal lines at $J_{\text{HONO}} = 0$ in the upper panel indicate two periods of light rain.
In the afternoon, HONO flux remained significantly positive, between 0.1 and 1.1 \( \times 10^{-6} \) moles m\(^{-2}\) hr\(^{-1}\) despite the significant decrease in NO\(_x\) to around 1000 pptv level. Furthermore, both HONO flux and ambient HONO concentrations seemed to modulate with the fluctuation of HONO photolysis rate constant, suggesting significant contribution of photochemical production of HONO at the forest canopy to the overlying atmosphere.

Light rain and drizzle started around 8 pm (EDT) and continued intermittently throughout the night, as indicated by the thick line on the X axis of the upper panel in Figure 4.8. When surfaces were wet, the forest canopy became a sink rather than a source for HONO [He et al., 2006; Zhou et al., 2011]. As a result, the net HONO flux was negative, and ambient HONO concentration remained low, mostly within 20-30 pptv. However, there was significant fluctuation in HONO flux before and around midnight, probably due to high wind variability during this period. The following period (4:00-7:00 EDT) was very calm with the vertical wind speed \( w \) lower than the threshold \( w_t \) value of 0.1 m s\(^{-1}\), resulting in a data gap in HONO flux.

It was intermittent clouds in the morning of July 18; both HONO flux and ambient HONO concentration remained low. The sky became clear shortly after noontime; both HONO flux and ambient HONO concentration start to increase, reaching a HONO flux maximum of 4.6 \( \times 10^{-6} \) moles m\(^{-2}\) hr\(^{-1}\) and a maximum daytime HONO concentration of 165 pptv in the early to mid afternoon. It is especially worthy to point out that the air arriving at the site during this period of time changed from southwesterly (polluted) to northwesterly (clean), and that NO\(_x\) levels dropped from \(~1500\) pptv to \(~400\) pptv. This anti-correlation between NO\(_x\) and HONO flux suggests that ambient NO\(_x\) was not a
significant precursor for the HONO produced at the canopy surface. During the southwesterly flow period during the previous day and night, HNO₃ as well as organics might have deposited from the “dirtier” southwesterly air mass and accumulated on the leaf surfaces at the top of forest canopy. When exposed to solar UV radiation, the photolysis of the deposited HNO₃ [Zhou et al., 2003; 2011], enhanced by the presence of organics (see chapter 5), was probably the dominant HONO production mechanism responsible for the higher upward flux and the high ambient HONO concentration.

The HONO flux as well as the ambient HONO concentration decreased in the late afternoon and evening as the solar radiation and the photolytic HONO source decreased. There were, however, some spikes in HONO flux and HONO concentration before midnight, probably associated with a change in air masses. Indeed, the back trajectory calculation indicates that air flow changed from northwesterly to southwesterly and then back to northwesterly during the ~4 hours before midnight.

4.4 Summary

A HONO flux measurement method has been developed based on the relaxed eddy accumulation approach. One 3-D sonic anemometer and 2 HONO measurement systems were deployed in the setup. The overall precision is estimated to be within ± (8×10⁻⁸ + 0.15 F_HONO) mol m⁻² hr⁻¹, with 20-min averaged data point per 30 min.

The methods for ambient HONO concentrations and HONO flux measurements have been successfully deployed at the PROPHET site during the summer of 2008. The mean HONO concentration was 49 pptv and mean HONO flux was 0.37×10⁻⁶ moles m⁻² hr⁻¹. Both ambient HONO concentration and HONO flux showed significant diurnal
variations, with noontime maximum means of ~70 pptv and ~0.7×10^{-6} moles m^{-2} hr^{-1} respectively, and a HONO minimum mean of ~20 pptv around sunset, and a minimum HONO flux mean of ~0.1×10^{-6} moles m^{-2} in the early morning before sunrise.

During the day, there was no significant correlation between NOx and HONO flux, suggesting that NOx was not an important precursor responsible for HONO production in the low-NOx atmospheric boundary layer over a forest. During the night, improved correlation between NOx and HONO flux/concentration suggests that NOx was the major HONO precursor. Photolysis of HNO3 deposited on canopy surface was likely to be the major mechanism responsible for the observed daytime HONO flux and may serve as an important remobilization pathway for the deposited HNO3 to photolabile species in the atmosphere.
CHAPTER 5. PHOTOLYSIS OF NITRIC ACID AND AEROSOL NITRATE AS A HONO SOURCE

In the aircraft HONO profile measurements (Chapter 3), significant levels of HONO were observed in the upper boundary layer and lower free troposphere as well as in the air column over the Great Lakes. Since HONO transported from ground surfaces is negligible in these areas, significant \textit{in situ} HONO sources must exist to sustain the observed HONO concentrations against its photolytic loss. Photolysis of aerosol nitrate was suggested to be an important or even a major daytime HONO source \cite{Zhang et al., 2009}. During HONO flux measurement over a forest canopy (Chapter 4), we observed mostly upward HONO flux, and found a strong correlation between daytime HONO flux and the product of the surface nitrate photolysis rate constant $J_{\text{HNO}_3}$ and nitrate loading on the leaf surfaces \cite{Zhou et al., 2011}. This result supported our hypothesis that the photolysis of HNO$_3$ on canopy surface is the dominant daytime HONO source in the low-NO$_x$ rural boundary layer \cite{Zhang et al., 2011; Zhou et al., 2011}. Previous photochemical studies in our group have confirmed that the photolysis of adsorbed HNO$_3$ on Pyrex glass and other environmentally relevant surfaces was enhanced by 1-2 orders of magnitude faster than in aqueous/gas phase, and that NO$_2$ and HONO are the primary products released in the photolytic process \cite{Zhou et al., 2003}. Furthermore, the fast conversion of NO$_2$ to HONO on organic surfaces under irradiation has been reported in the literature recently \cite{George et al., 2005; Stemmler et al., 2006; 2007}. Since organic compounds are ubiquitously present in ambient environments such as aerosol particles and on leaf surfaces, this research was aimed to examine the processes of HNO$_3$ photolysis on surfaces in presence of organic compounds and nitrate aerosol photolysis.
Results from this research would contribute towards further support of the Re-NO$_3$-ification mechanism and pinpointing HONO sources in the atmosphere.

In this chapter, we first examined HNO$_3$ photolysis on substrates coated with HNO$_3$ and different model organic compounds with an emphasis on organic effects on the photolysis rate and photolytic product yields. Then, we investigated the photolysis of aerosol nitrate and discussed the influence of spatial and temporal variation. Finally, we interpreted our field observations in the aircraft measurement and HONO flux measurement through the laboratory results.

5.1 Experimental

Experimental Setup. A schematic diagram of photochemical experimental setup is shown in figure 5.1. A cylindrical Teflon vessel (ID: 4” Depth: 1”) was used as the photochemical flow reactor with a quartz window on top for irradiation. During light exposure, a model surface (e.g. glass, leaf) previously coated with HNO$_3$ and organics was exposed to UV light ($\lambda > 290$ nm). Ultra high-purity nitrogen (Airgas, UHP200) was used as the carrier gas. The carrier gas bubbled through a thermostatic water bubbler at $9.25 \pm 0.5 \ ^\circ \text{C}$ at a flow rate of 450 ml min$^{-1}$, and then passed through a long thermal-equilibration coil (PFA, 1/4” OD, 1/8” ID, 4.5 m in length) before reaching the photochemical reactor. When the moisture-saturated cool air from the water bath was warmed up to room temperature of between 21-22 $^\circ \text{C}$ in the equilibrium coil the relative humidity (RH) was about 50%. The residence time of carrier gas was about 30 seconds in the photochemical flow reactor. Gaseous products released from the surfaces were carried out by the carrier gas, and was collected by two coil samplers connected in series, at a flow rate of 400 ml min$^{-1}$, the first scrubbing HONO and the second scrubbing NO$_2$. 

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(Chapter 2). With 100% of HONO being collected in the first channel, the NO$_2$ channel is free of interference. The minor outflow of ~50 ml min$^{-1}$ from the reactor is monitored by bubbling into water to indicate a positive pressure maintained in the reactor. In the flow measurement system, the collection efficiency of HONO and NO$_2$ are 100% and 60% respectively and the detection limits are 6 pptv and 15 pptv respectively.

**Figure 5.1** A schematic diagram of photochemical experimental setup to study HNO$_3$ photolysis on surfaces.
The UV irradiation was conducted in a confined space: a photochemical safety reaction cabinet (0.5m × 0.5m × 0.9m, ACE Glass, model 7836). A 450-watt medium pressure mercury arc lamp (ACE Glass, model 7825) was used as a light source placed about 20cm above the reactor. A typical spectrum of this lamp is shown in Figure 5.2. As light of \( \lambda < 290\text{nm} \) is absorbed efficiently by \( \text{O}_3 \) in atmospheric conditions, we adapted the lamp to the wavelength of interest by filtering it with both a Pyrex sleeve to remove low wavelength UV light (<290nm) and a quartz well filled with circulated water to remove heat-generating infrared light. The main emission peaks used in our experiment were at 295, 314, 335, 360, 400, 435, 545, and 575 nm. Temperature in the photochemical reactor increased slightly during irradiation, by 1-2 °C. Corresponding RH in the reactor was 50% in the dark and 45% when irradiated. All tubing used in the cabinet was wrapped by aluminum foil to shield from the UV light.

![Figure 5.2](http://www.gewuv.com)  

**Figure 5.2** A typical medium pressure mercury arc lamp spectral distribution. Source: http://www.gewuv.com.
**Background level and corrections.** Background levels of HONO and NO\(_2\) from two sources need to be removed from the sample: signals from dark condition, and signals from the empty reactor during irradiation. The former is related to unknown dark reactions which are beyond the scope of this research. The latter is likely due to reactions of contaminants such as organics and deposited HNO\(_3\) on the reactor wall. Half of the latter background value was deducted from sample signals because only the reactor top surface was involved in sample exposure, while the reactor bottom was covered by the model surface during sample exposure.

Since both photolytic products HONO and NO\(_2\) are photolabile, their photolysis loss in the reactor during irradiation was also considered. With a residence time of about 30 seconds, less than 5% of HONO was photolyzed to OH and NO, and thus the photolysis loss of HONO was neglected. However, about 25% loss of NO\(_2\) was observed when a gaseous NO\(_2\) standard (Matheson Tri-Gas Inc., CP) was introduced into the irradiated reactor. A 25% correction was made in calculation of NO\(_2\) yield.

In sum, the production rate (nmol s\(^{-1}\)) of HONO, \(P_{\text{HONO}}\), and production rate of NO\(_2\), \(P_{\text{NO}_2}\), were calculated by:

\[
P_{\text{HONO}} = \frac{C_{\text{st}} - C_{:\text{sd}} - (C_{:\text{tr}} - C_{:\text{rd}})/2}{60 \times 1000} \times F_t \times \frac{450}{400} \tag{Eq. 5 - 1}
\]

\[
P_{\text{NO}_2} = \frac{C_{\text{st}} - C_{:\text{sd}} - (C_{:\text{tr}} - C_{:\text{rd}})/2}{60 \times 1000} \times F_t \times \frac{450}{400} \times \frac{1}{0.6 \times 0.75} \tag{Eq. 5 - 2}
\]
where $C_{si}$, $C_{sd}$, $C_{ri}$ and $C_{rd}$ represent HONO (or NO$_2$) concentration (nM) formed in sample irradiation, sample dark, empty reactor irradiation and empty reactor dark respectively; $F_1$ is the scrubbing solution flow rate of 0.24 ml min$^{-1}$ and 0.4 ml min$^{-1}$ for HONO and NO$_2$ respectively; the coefficient $\frac{450}{400}$ is for correction of minor outflow loss from the reactor; coefficient 0.6 is the collection efficiency in the NO$_2$ channel and 0.75 is for photolysis loss of produced NO$_2$ before evacuation from the reactor.

The production rate constant (s$^{-1}$) of HONO, $j_{\text{HNO}_3 \rightarrow \text{HONO}}$, production rate constant of NO$_2$, $j_{\text{HNO}_3 \rightarrow \text{NO}_2}$, and the overall photolysis rate constant of absorbed HNO$_3$/nitrate, $J_{\text{HNO}_3}$, were determined by:

$$j_{\text{HNO}_3 \rightarrow \text{HONO}} = \frac{p_{\text{HONO}}}{A_{\text{HNO}_3}} \quad (Eq. 5 - 3)$$

$$j_{\text{HNO}_3 \rightarrow \text{NO}_2} = \frac{p_{\text{NO}_2}}{A_{\text{HNO}_3}} \quad (Eq. 5 - 4)$$

$$J_{\text{HNO}_3} = j_{\text{HNO}_3 \rightarrow \text{HONO}} + j_{\text{HNO}_3 \rightarrow \text{NO}_2} \quad (Eq. 5 - 5)$$

where $A_{\text{HNO}_3}$ is the amount of HNO$_3$/nitrate exposed to light (see nitrate measurement in this section).

**Surface preparation.** In most of photochemical experiments, a piece of sandblasted borosilicate glass surface (Pyrex) was used as the model surface. The effective surface area under irradiation was 62 cm$^2$. Before applying surface coatings, the glass surface was cleaned thoroughly with Micro-90 cleaning solution (Cole-Parmer) then rinsed by ethanol and DI water repeatedly. The cleaned glass surface was dried in a vacuum desiccator before use. Organics and HNO$_3$ were co-adsorbed on the surfaces by adding 0.1 ml of mixture of HNO$_3$ and organic solutions and spreading it out uniformly.
on model surface with a hydrophobic Teflon blade. The concentrations of HNO$_3$ and organics in the mixture are known. Organic solutions were made from their corresponding sodium salt for better water solubility and were acidified to pH ~ 4 with 1 M H$_2$SO$_4$ before mixed with a HNO$_3$ solution. The HNO$_3$-organics-coated surface was allowed to dry overnight in the vacuum desiccators. In order to keep the organics on the surfaces during overnight stay in the desiccators, only the organics with very low volatility were selected.

**Aerosol sampling.** Ambient aerosol samples were collected using Teflon filters (Sartorius, pore size 0.45µm) in the locations of downtown Albany, Delmar and Whiteface Mountain, representing aerosols in urban, suburban/rural and remote environments, respectively. In downtown Albany, aerosol samples were also collected in different seasons: summer, fall and winter. Additionally, two stacked filters were used for collecting some aerosol samples; the second filters were then used as a blank to correct for exposure artifacts from adsorbed HNO$_3$. In this set photochemical experiments, aerosol samples on filters were placed in the photochemical flow reactor and irradiated directly. The results were used to extrapolate aerosol nitrate photolysis in the atmosphere.

**Nitrate measurement.** After irradiation, a total volume of 5-10 ml 1% NH$_4$Cl buffer solution (pH = 8.5) was added into the Pyrex glass plate several times or into a tube holding aerosol sample filter to extract HNO$_3$/nitrate and organics on the surface or in the aerosol sample. Nitrate was reduced quantitatively to nitrite immediately with an on-line copperized cadmium column (0.3 cm ID, 0.8 cm in length) and was detected at 540 nm by a UV-visible spectrometer with a 1-m long-path flow cell. The details for
nitrate measurement method have been given in chapter 2. The detection limit of this method is \( \sim 10 \text{ nM} \). Photolysis loss of surface-adsorbed \( \text{HNO}_3 \) during 15min of UV irradiation was calculated to be below 5\% [Zhou et al., 2003] and was neglected in the calculations of total nitrate amount. Assuming that the adsorbed \( \text{HNO}_3 \) is evenly distributed on the illuminated surface, \( \text{HNO}_3 \) surface density was calculated by dividing total \( \text{HNO}_3 \) amount by the surface area. A value of \( 1 \times 10^{-5} \text{ moles m}^{-2} \) [Masel, 1996] represents a monolayer \( \text{HNO}_3 \) density on surface.

**Measurement of light absorbance by organic compounds.** Aerosol sample filters were rinsed with 25 ml of 1\% \( \text{NH}_4\text{Cl} \) buffer solution, followed by filtering through a 0.20 \( \mu \text{m} \) pore surfactant-free-cellulose-acetate membrane (Corning) prior to light absorbance measurement. Sample absorbance spectra in the wavelength of 200-600nm were scanned using a UV-Visible spectrometer (JENWAY, model 6405) with 1-cm path length and 1\% \( \text{NH}_4\text{Cl} \) buffer solution as reference. Absorbance at 300 nm was frequently used to indicate organic content in natural waters and soil and was found to be closely correlated to sample’s photochemical reactivity [Grzybowski, 2000; Harvey et al., 2009; Kieber et al., 1990], hence the absorbance at 300nm was used as a proxy for organic content in aerosol samples in our experiment. The absorbance at wavelengths of 280 nm, 300 nm, 320 nm, 340 nm, 360 nm and 380 nm were also compared, with no significant impact on conclusions found.

**Actinometry.** Effective UV intensity was monitored using a nitrate actinometer [Jankowski et al., 1999; 2000]. The principle behind this method is that photolysis of nitrate produces photochemically reactive \( \text{OH} \) radicals which react with benzoic acid to form hydroxybenzoic acids (HBA), including salicylic acid (SA). Photon exposures
(time-integrated irradiances) were quantified from the photochemical production of SA. In our experiment, 5 ml of solution containing 1 mM sodium benzoate and 1 mM sodium nitrate was added in a quartz cuvette and irradiated in the photochemical reactor for 15 min. The produced SA in the actinometer was quantified by fluorescence spectrometer (Hitachi L-7480) at an excitation wavelength of 305 nm and an emission wavelength of 410 nm. Actinometry was performed each time after a batch of samples was irradiated or when changing a new lamp. The aqueous nitrate photolysis rate, \( J_{\text{NO3}^-} \) (s\(^{-1}\)), was calculated by:

\[
J_{\text{NO3}^-} = \frac{[SA]}{0.001 \times 0.2 \times t} \quad (Eq. 5 - 6)
\]

where [SA] in units of M, is the concentration of SA produced in the actinometer during irradiation; 0.001 is the concentration of nitrate (M\(^{-1}\)) added in the actinometer, 0.2 is the production yield of SA from the reaction of OH radical and benzoate, and t (sec) is the irradiated duration. All data was normalized to the tropical noontime condition with an aqueous nitrate photolysis rate of \(3.0 \times 10^{-7}\) s\(^{-1}\).

### 5.2 Results and discussion: HNO\(_3\) photolysis on model organic surfaces

#### 5.2.1 Results overview

All photochemical experiments were conducted at 45-50% RH in UHP N\(_2\) at ambient temperature and pressure. Figure 5.3 upper panel showed the typical signals from a photochemical experiment using the Pyrex glass surface coated with 20\(\mu\)mol m\(^{-2}\) of HNO\(_3\) and 16 \(\mu\)mol m\(^{-2}\) of salicylic acid; the irradiated organic blank was coated with 16 \(\mu\)mol m\(^{-2}\) of salicylic acid only. In dark condition, little to no HONO and NO\(_2\) were present in the carrier gas; the signals were used as baseline to be subtracted from the
irradiated signals in the results. Upon irradiation, both HONO and NO₂ concentrations increased immediately, then dropped quickly in the first few minutes and then decreased gradually with the consumption of surface reactants during irradiation. When the lamp was turned off, the signals of HONO and NO₂ quickly reduced to baseline again. It is evident that the increase in HONO and NO₂ flow is in response to processes on the glass surface during irradiation. HONO was the major product during irradiation observed in almost all of our photochemical experiments.

The significant high production rate at the beginning of irradiation was also observed in the photolysis of HNO₃ on a pure borosilicate glass surface [Zhou et al., 2003] and was attributed to the catalysis by some more reactive sites on the surface. Similarly, the study on HONO formation on soot surfaces also reported the significant reduction in HONO production rate after the first few seconds due to the consumption of the reactive surface sites [Kalberer et al., 1999]. In a study where organics were coated on the surfaces in same fashion as the present experiment, a laser scan microscope was used to inspect the coating film, showing the uneven distributions of organic structures on the surfaces due to solvent evaporation [Arens et al., 2002]. These studies may suggest that certain organic-abundant sites on the surfaces are responsible for the initial higher production rate in this experiment. Figure 5.3 lower panel showed five consecutive irradiation sessions of the same surface under the same experimental conditions as in upper one. Ignoring the dark period, both panels have almost the same profile pattern, indicating that the reactive surface sites cannot be regenerated.
Figure 5.3 Concentrations of HONO (solid line) and NO$_2$ (dotted line) in the effluent gas from a flow reactor. Upper panel: sample during one-hour irradiation; organic blank (grey line) during 15 min irradiation; Lower panel: sample during 5 cycles of 10-min irradiation. Photolysis of NO$_2$ during irradiation was corrected.
To investigate the effect of organics on HONO and NO$_2$ production by photolysis of HNO$_3$ on surfaces, a wide variety of model organic compounds were used. All model organic compounds used do not contain nitrogen to make sure that HNO$_3$ is the only source of nitrogen. Overall, 14 types of organic compounds were investigated and their chemical structures are shown in figure 5.4. Humic acid and aromatic compounds such as salicylic acid are of special interest because they are either abundant on the earth’s surface or highly light-absorbing in UVB (290-320nm) region. Several isomers of phenolic compounds were examined for comparison of the effective structures. Glucose and some carboxylic acids were selected for comparison with aromatic compounds; they are common species in plants or aerosols.

![Chemical structures of model organic compounds used in photochemical experiment.](image)

Figure 5.4 Chemical structures of model organic compounds used in photochemical experiment.
Organic blank experiments were performed in which the surface was coated only with equal amount of organic compound (salicylic acid in the case of figure 5.3), and was irradiated under the same experimental conditions. Without the addition of HNO$_3$, photolysis of organics resulted in much lower signal compared to HNO$_3$ photolysis, ~ 17% for HONO and 27% for NO$_2$. Since the signal profiles were similar to that in HNO$_3$ photolysis, it was assumed that the HONO and NO$_2$ signals observed from organic blank experiment may have been caused by the nitrate impurity in the 99+% of sodium salicylate we used, or by contamination during handling (e.g. deposition of HNO$_3$ vapor from sample plate during overnight dry in the same desiccator). Our explanation was confirmed by the detection of low concentration of nitrate in organic coating after the organic blank experiment. Since we determine surfaces nitrate content after irradiation, ‘organic blank’ was directly used as a sample containing lower amount of nitrate in all experiments. It is also important to point out that in this photochemical experiment, we found that the HNO$_3$ photolysis rate constant changes as a function of HNO$_3$ mass, with the fastest HNO$_3$ photolysis rate constant in the lowest amount of HNO$_3$. More details on HNO$_3$ photolysis rate and rate constant will be discussed in later sections. As is the case for salicylic acid coating in figure 5.3, the HNO$_3$ photolysis rate constant can be an order of magnitude faster in lower amounts of nitrate, which may account for the relatively high ratios of HONO and NO$_2$ yields in the ‘organic blank’ experiment.

The amount of HNO$_3$ and organic compounds in the coating films were examined as factors in HNO$_3$ photolysis. Typically, ~1.1 µmol m$^{-2}$ or ~25 µmol m$^{-2}$ HNO$_3$ was coated on the model surfaces to represent the monolayer (≤10 µmol m$^{-2}$) and multilayer conditions respectively; ~16 µmol m$^{-2}$ organics was co-adsorbed with HNO$_3$ onto the
substrate to form 1~2 layers of coverage assuming they have the same monolayer density as HNO₃ molecule. Table 5.1 summarized the effect of different organic compounds on the HNO₃ photolysis rate constant under the typical concentration conditions. All photolysis rate constants listed in table 5.1 were calculated from the initial highest production rate and were normalized to tropical noon time conditions.

The observed $J_{\text{HNO}_3}$ values are at least 2 orders of magnitude greater than the nitrate photolysis rate constant of $\sim 3 \times 10^{-7} \text{ s}^{-1}$ in aqueous solutions [Jankowski et al., 2000; Mack and Bolton, 1999] and the HNO₃ photolysis rate constant $\sim 7 \times 10^{-7} \text{ s}^{-1}$ in gas phase. In absence of organic compounds in coating films, the pure HNO₃ photolysis on the surface has a rate constant of $\sim 2 \times 10^{-5} \text{ s}^{-1}$. The same value at 50% RH was also reported by Zhou et al., [2003]. In the presence of organic compounds in coating films, the photolysis of HNO₃ is strongly dependent on the types of organics. Both functional groups and substitution patterns affect the photolysis process. Among aromatic compounds, salicylic acid and hydroquinone enhanced the HNO₃ photolysis rate constant by approximately one order of magnitude, while their isomers and humic acid have less significant effect on the HNO₃ photolysis rate constant. For benzoic acid and 3-hydroxybenzaldehyde, no enhancement was observed, which is likely due to the evaporative loss of organic coating during the overnight dry procedure. Unlike aromatic compounds, glucose and carboxylic acids do not absorb light in the wavelength range of our light source. It is therefore surprising that the presence of citric acid or oxalic acid on the surface also increased the HNO₃ photolysis rate by about one order of magnitude.

The possible mechanisms will be discussed in more details in later sections.
Table 5.1 Organics (~16 µmol m$^{-2}$) effects on the photolysis rate constant of HNO$_3$ on the surfaces

<table>
<thead>
<tr>
<th>Surface Condition</th>
<th>N</th>
<th>Monolayer HNO$_3$: ~ 1.1 µmol m$^{-2}$</th>
<th>Multilayer HNO$_3$: ~ 25 µmol m$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$J_{\text{HNO}_3}$ $\times 10^5$ s$^{-1}$</td>
<td>$J_{\text{HNO}_3^*}$ $\times 10^5$ s$^{-1}$</td>
</tr>
<tr>
<td>HNO$_3$ only</td>
<td>5</td>
<td>1.6 ± 0.4</td>
<td>0.5 ± 0.2</td>
</tr>
<tr>
<td>Humic Acid *</td>
<td>2</td>
<td>3.4</td>
<td>0.8</td>
</tr>
<tr>
<td>Salicylic Acid</td>
<td>2</td>
<td>19</td>
<td>9.7</td>
</tr>
<tr>
<td>3-Hydroxybenzoic Acid</td>
<td>1</td>
<td>4.1</td>
<td>3.1</td>
</tr>
<tr>
<td>4-Hydroxybenzoic Acid</td>
<td>1</td>
<td>3.6</td>
<td>3.4</td>
</tr>
<tr>
<td>Benzoic Acid</td>
<td>1</td>
<td>2.0</td>
<td>1.4</td>
</tr>
<tr>
<td>3-Hydroxybenzaldehyde</td>
<td>1</td>
<td>1.3</td>
<td>0.8</td>
</tr>
<tr>
<td>Catechol</td>
<td>1</td>
<td>8.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>1</td>
<td>5.8</td>
<td>0.3</td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>1</td>
<td>25</td>
<td>1.9</td>
</tr>
<tr>
<td>Salicylic Acid + Hydroquinone</td>
<td>1</td>
<td>15</td>
<td>5.0</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>2</td>
<td>9.1</td>
<td>2.4</td>
</tr>
<tr>
<td>Oxalic Acid</td>
<td>1</td>
<td>10</td>
<td>2.8</td>
</tr>
<tr>
<td>Succinic Acid</td>
<td>1</td>
<td>1.8</td>
<td>1.7</td>
</tr>
<tr>
<td>Ascorbic Acid</td>
<td>1</td>
<td>4.1</td>
<td>0.7</td>
</tr>
<tr>
<td>Glucose</td>
<td>1</td>
<td>2.4</td>
<td>1.9</td>
</tr>
</tbody>
</table>

*Humic Acid = 1.6 mg m$^{-2}$
5.2.2 Enhancement of surface HNO₃ photolysis by organics

The effects of salicylic acid, catechol and humic acid on HNO₃ photolysis on the surfaces will be examined in more details in the following sections. These three compounds are of particular interest because they represent the high, moderate and low reactivity of organic compounds in HNO₃ photolysis process in our photochemical experiment.

Figure 5.5 shows the effects of different types of organic compounds on the surface-HNO₃ photolysis rate. HNO₃ photolysis rate was determined by the total production rate of HONO and NO₂. In the presence of salicylic acid and catechol in the coating film, the HNO₃ photolysis rate was significantly enhanced by at least a factor of 4 for catechol and more than one order of magnitude for salicylic acid.

The photolysis of surface HNO₃ is more effective in monolayer thickness (10⁻⁵ mol m⁻² or < 62 nmol in our experiment) than in multilayer thickness. This is manifested in the decreasing photolysis rate constant from monolayer to multilayer HNO₃ surface concentration, as seen in figure 5.6. The photolysis rate constant initially decreases rapidly with HNO₃ surface concentration within the monolayer range, and then much more slowly or levels off within multilayer range. The different behavior of the HNO₃ photolysis rate constant shown between the monolayer and multilayer is not surprising because surface interaction is expected to be more effective in catalyzing HNO₃ photolysis when there are less HNO₃ molecules present on the surfaces. The mechanism for surface enhancement may be related to the red shift of HNO₃ light absorption cross-section or an increase in quantum yield [Zhou et al., 2003; Zhu et al., 2008]. The stack-up of HNO₃ molecules in the multilayer condition makes the bulk behave more like in
gas phase or in liquid phase, where nitrate photolysis rates are $7 \times 10^{-7} \text{ s}^{-1}$ [Finlayson-Pitts and Pitts, 2000] and $3 \times 10^{-7} \text{ s}^{-1}$ [Jankowski et al., 1999; Mack and Bolton, 1999] respectively.

**Figure 5.5** HNO$_3$ photolysis rate as a function of HNO$_3$ amount in the absence and presence of organic compounds on the surface. Dashed lines represent the best (power) fit for each data series. Slopes from each point on the curves to ‘0, 0’ point can be regarded as the corresponding photolysis rate constants. Glass surface area is ~ 62 cm$^2$. Monolayer HNO$_3$ amount is ~ 62 nmol.
Figure 5.6 A log-log plot of photolysis rate constant as a function of surface HNO$_3$ density in absence and in presence of organic compounds on the surface. Legend is the same as in Figure 5.5. The dashed lines are the best fit for each data series. The inset showed data on linear scales.

Extrapolating the trend line in figure 5.6 to the lower end of surface HNO$_3$ density (e.g. 0.01 $\mu$mol m$^{-2}$), the corresponding photolysis rate constant is $\sim 5\times10^{-4}$ s$^{-1}$ for surface HNO$_3$ only, and $5.5\times10^{-3}$ s$^{-1}$ for surface HNO$_3$ with salicylic acid present. These numbers are a factor of 20 larger than the reported values in table 5.1 for a monolayer HNO$_3$ concentration of 1.1 $\mu$mol m$^{-2}$, which we normally used as the proxy for monolayer condition. The very high photolysis rate constant in very low HNO$_3$ concentration may
account for the intercepts of photolysis rate in figure 5.5, caused by HNO₃ contamination on the reactor wall.

In contrast to the effectiveness of humic acid shown in the conversion of gaseous NO₂ to HONO [Stemmler et al., 2006], the addition of humic acid in the coating film showed only a slight increase in photolysis rate compared to the pure HNO₃ condition, indicating a low reactivity of humic acid in HNO₃ photolysis compared to comparable amount of salicylic acid and catechol. A typical humic acid film in our experiment has a surface loading of 0.16 µg cm⁻², about a factor of 50 less than the concentration of 8 µg cm⁻² used in literature [Stemmler et al., 2006]. The much smaller amount of humic acid we added to form the organic film may account for the low reactivity of humic acid showed in our experiment. Our explanation is supported by a study on irradiated ice containing humic acid [Bartels-Rausch et al., 2010], in which the linear trend between HONO production rate and humic acid concentration has been observed. Humic acid in higher concentration can thus be expected to enhance HNO₃ photolysis on the surface.

In order to examine the effect of organic loadings on surface HNO₃ photolysis, we coated model surfaces with different concentrations of organic solutions while remained HNO₃ concentration constant. However, due to the evaporative loss of HNO₃ during overnight drying procedure, exposed HNO₃ amount varied in photochemical experiments. Figures 5.7 shows the results from a group of experiments using salicylic acid, in which all data points can be fitted by a same power curve. The inset clearly showed that even though the salicylic acid loading on the surfaces varied by 2 orders of magnitude, the HNO₃ photolysis rate constant remained unchanged. Therefore, HNO₃ photolysis is independent of the salicylic acid loading.
Figure 5.7 A log-log plot of HNO$_3$ photolysis rate constant as a function of exposed HNO$_3$ amount in presence of different salicylic acid loading. The red arrow indicated data points showed in the insets. The inset is log-log scale of HNO$_3$ photolysis rate constant as a function of salicyl acid loading while the surface HNO$_3$ density is the same. In contrast, data points in Figure 5.8 with different catechol loading cannot be fitted by the same curve and the inset in Figure 5.8 clearly shows positive correlation between HNO$_3$ photolysis rate constants with the catechol loading on surfaces. The difference indicated that organic compounds may alter the process of HNO$_3$ photolysis in various mechanisms. As a highly light-absorbing compound, salicylic acid may act more like a
photosensitizer than a reactant in HNO₃ photolysis process, transferring the energy to HNO₃ molecule during the irradiation, then being deactivated to its initial energy state.

The dependence of HNO₃ photolysis rate on catechol concentration suggested that catechol is consumed in the process (e.g., reacting with the OH radical produced in the HNO₃ photolysis process or transferring a proton to produced NO₂ leading to formation of HONO). These reactions are in favor of HNO₃ photolysis.

Figure 5.8 A log-log plot of HNO₃ photolysis rate constant as a function of exposed HNO₃ amount in presence of different catechol loading. The inset showed log-log scale of HNO₃ photolysis rate constant as a function of catechol loading while the surface HNO₃ density is similar.
5.2.3 Organics effects on the relative yields of photolytic products

A previous study has confirmed that significant levels of HONO and NO\textsubscript{x} (mainly in the form of NO\textsubscript{2}) are produced from HNO\textsubscript{3} photolysis on surfaces and the production of HONO is greatly enhanced by the presence of water, with the HONO/NO\textsubscript{x} ratio 0.03 at ~0% RH and ~1 at 50% RH [Zhou et al., 2003]. The study also suggested that NO\textsubscript{2} is the major primary photolytic product, while HONO may be the secondary product formed by the further reaction of NO\textsubscript{2} with H\textsubscript{2}O on the surface [Zhou et al., 2003].

In contrast, in our experiment conducted on the Pyrex glass surface at ~50% RH, HONO was the major product in the HNO\textsubscript{3} photolysis process, as observed throughout the study no matter whether organic compounds were doped in the coating films. The inconsistency for pure HNO\textsubscript{3} coating may be a result from the different HNO\textsubscript{3} sources used in each study. In a previous study, a gas-phase HNO\textsubscript{3} permeation source was used to coat flow reactor surface, while a diluted HNO\textsubscript{3} solution was used in this study, followed by a dry period prior to irradiation. In the latter case, HNO\textsubscript{3}-H\textsubscript{2}O complexes can be readily developed on the surface, and once formed, remain adsorbed even after pumping or purging with dry gas for many hours [Ramazan et al., 2004]. In an additional experiment, we studied the effect of surface residual water on the HNO\textsubscript{3} photolysis process. Three groups of Pyrex glass surfaces were coated with same amount of HNO\textsubscript{3} and were allowed to dry in a desiccator for 3, 50, and 120 hours respectively prior to irradiation. The results in Figure 5.9 show that both production rates of HONO and NO\textsubscript{2} increased and the ratio of HONO/NO\textsubscript{2} decreased as water molecule on the surfaces decreased. Given 120 hours for dryness, the ratio of HONO/NO\textsubscript{2} is ~1. The result is also consistent with the observation in Zhou et al. [2003] that the overall production rate of
(NO$_x$ + HONO) increased when RH changed from 50% to ~ 0%. Thus we concluded that surface water molecules both reduce the occurrence of HNO$_3$ photolysis (e.g. by competing for surface active sites or quenching the excited HNO$_3$ molecules) and facilitate the transformation of photolytic-produced NO$_2$ to HONO.

Figure 5.9 HNO$_3$ photolysis rate constant (+, left Y-axis) and HONO/NO$_2$ yield ratio from HNO$_3$ photolysis on Pyrex surface as a function of drying time. Experiment was conducted at 50% RH.

In presence of organic compounds in the coating film, HONO yield was increased as shown in Figure 5.10. With the addition of salicylic acid and catechol, HONO yield increased by about an order of magnitude during irradiation. However, NO$_2$ yield changed differently: increased with salicylic acid; remained constant for catechol;
decreased with humic acid. This variation may be associated with the different mechanisms by which organic compounds affected the photolysis process. In several recent laboratory studies it has been revealed that HONO is a product of a photoenhanced reaction of NO\(_2\) with the organic compounds on the surface \([\text{Bartels-Rausch et al.}, 2010; \text{George et al.}, 2005; \text{Stemmler et al.}, 2006]\). Upon irradiation, surface HNO\(_3\) is photolyzed to produce NO\(_2\) as a major primary product as suggested \([\text{Zhou et al.}, 2003]\), followed by the reaction of adsorbed NO\(_2\) with organics to produce HONO. This pathway will result in the decrease of NO\(_2\) and the increase of HONO. Similarly, organic compounds can also effectively react with OH radical – another immediate photolytic product – to drive the forward reaction of HNO\(_3\) photolysis leading to increased yields for both NO\(_2\) and HONO. Furthermore, aromatic organic compounds may act as a photosensitizer for HNO\(_3\) photolysis, which will also increase the production yields of NO\(_2\) and HONO.
Figure 5.10 Comparison of HNO₃ photolytic product yields in the presence and absence of organic compounds on the surfaces.
5.2.4 Effects of surface activity on photolysis of HNO₃

In addition to Pyrex glass, HNO₃ photolysis on several other surfaces such as metals and leaves was also investigated. It appears that the nature of the substrate has a strong influence on the reactivity and the type of photolytic product of HNO₃ photolysis.

For example, in the pure HNO₃ condition (figure 5.11), HNO₃ photolysis on Al surfaces is about an order of magnitude faster than on Pyrex glass surfaces. Our observation is supported by the higher absorption cross sections of HNO₃ on Al surfaces than on fused-silica surfaces by a factor of 3.5 at 295 K [Zhu et al., 2010]. The cross section of HNO₃ on the Al surface is suggested to be enhanced by the dipole formed between the Al surface and HNO₃ molecules [Zhu et al., 2010]. It’s likely that a similar dipole also exists between adsorbed HNO₃ and glass surfaces, but the repulsive force between the O atom in SiO₂ structures and adsorbed HNO₃ makes the enhancement smaller than on Al surfaces. Another plausible explanation for the effect of Al surfaces on pure HNO₃ photolysis is related to the well-know photoelectric effect in which electrons are ejected from metals as a consequence of their absorption of light. Since metal Al has threshold energy equal to 0.66 × 10⁻¹₈ J/photon, light with wavelengths shorter than 300 nm can satisfy the energy quota to eject photons from an Al surface to cause substrate excitation [Zhou et al., 1991]. In this process, the resulted excited electrons attached to HNO₃ molecules to form an excited state, resulting in bond breakage. However, the light source is filtered with a Pyrex sleeve with a UV cut-off wavelength at 290nm and a transmittance of <30% at 300 nm, ruling out this mechanism as an important process.
Figure 5.11 Comparison of pure HNO\textsubscript{3} photolysis on an Al surface and on a Pyrex glass surface at 50\% RH.

Consistent with the observation on Pyrex surfaces, photolytic product yields on Al surfaces were altered by water vapor and the presence of organic compounds in the coating film. The percentages of NO\textsubscript{2} in total photolytic products (HONO + NO\textsubscript{2}) are \~100\%, \~90\% and \~35\% in corresponding to the conditions of pure HNO\textsubscript{3} coating at \~0\% RH and 50\% RH, and in the presence of organic compounds at 50\% RH. The results on Al surfaces again confirmed that NO\textsubscript{2} is the immediate major product from photolysis of HNO\textsubscript{3} on the surface and the organic compounds on the surfaces are in favor of HONO formation.
We also observed the lower reactivity of soda-lime glass (e.g. windowpane, bottles) surface toward HNO₃ photolysis compared to the Pyrex glass. This may be due to the higher alkali and alkaline earth oxidant (e.g. Na₂O, CaO and MgO) content in soda lime glass than in Pyrex glass. The alkaline surface sites of soda-lime glass are expected to trap NO₃⁻ thus restrain the formation and release of gaseous products from the surface. Similarly, HONO and NOₓ emission by snowpack was observed at Alert and Summit but not in the European high Arctic (Ny-Alesund), which was attributed to alkaline snow surface modified by the deposition of sea salt in a marine environment [Beine et al., 2003].

5.2.5 Proposed reaction mechanism

Although our experimental conditions do not allow us to investigate the in-depth mechanisms of HNO₃ photolysis on the surfaces, a literature review on similar processes will help us to formulate a reaction mechanism for the surface HNO₃ photolysis leading to HONO formation.

Using 308nm excimer laser photolysis coupled with cavity ring-down spectroscopy, the Zhu group recently investigated HNO₃ photolysis in the gas phase and on the fused silica, aluminum and ice surfaces [Zhu et al., 2010; Zhu et al., 2008]. They found that NO₂* + OH is the predominant photolysis pathway (if not the only photolysis pathway) for photolysis of HNO₃ in the gas-phase and on surface at 308nm. On Al surfaces, NO₂* quantum yield from HNO₃ photolysis is near unity. The 308 nm absorption cross sections of HNO₃ on each surface were determined to be at least 2 orders of magnitude higher than that in gas phase, which was attributed to either the red-shift of HNO₃
absorption spectrum or the deformation of original HNO₃ planar structure under the influence of surfaces. These findings lend support to our proposal that NO₂ is the major immediate product from HNO₃ photolysis at relatively low energy (≥ 300nm). Their results also confirmed our observation that the photolysis rate of surface-adsorbed HNO₃ is 1-2 orders of magnitude faster than that of HNO₃ vapor.

A paper recently published in Science [Li et al., 2008] suggested that the reaction between electronically excited nitrogen dioxide, NO₂*, and water vapor is an important atmospheric source of the hydroxyl radical and leads to HONO formation:

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

We proposed similar reaction occurs on the surface as soon as NO₂* is produced from surface HNO₃ photolysis, if water molecules exist on surface. Furthermore, we proposed that in the presence of organic compounds on the surfaces, organic molecules can substitute H₂O to react with NO₂* leading to the conversion of NO₂ to HONO.

Indeed, in two recent studies, fast photosensitized formation of HONO in the reaction of NO₂ on organic surfaces (e.g., aromatic hydrocarbons and humic acids) was observed [George et al., 2005; Stemmler et al., 2006]. The rate of photosensitized reaction was accelerated by 1-2 orders of magnitude in comparison to the dark reaction. The authors proposed that a photo-produced reductive species was formed on the organic surfaces during the irradiation, which converts NO₂ into HONO. Similar patterns of HONO formation were observed in photolysis of HNO₃ on the organic substrates in our experiment, e.g. decreasing HONO yields with time, and saturated HONO production rate with the initial NO₂/HNO₃ concentrations. It is, therefore, more likely that the same intermediate product was produced from NO₂ and HNO₃ precursors when exposed to
irradiation in these experiments, followed by similar reaction mechanism leading to the formation of HONO. Here we proposed that NO$_2^*$ is the intermediate product. In addition to aromatic compounds, we found that some compounds without light-absorbing properties such as citric acid and oxalic acid also resulted in high HONO production yield during HNO$_3$ photolysis. This indicated that photons are not necessarily absorbed solely by organic compounds as the earlier authors proposed [George et al., 2005; Stemmler et al., 2006], but can also be absorbed by HNO$_3$/NO$_2$ leading to the production of NO$_2^*$.

As organic impurities are omnipresent in the ambient environment and the photolysis of nitrophenols were identified as a new HONO source [Bejan et al., 2006], the mechanism of direct HNO$_3$ photolysis was challenged by possibility of the photolysis of adsorbed organic nitrates, nitro compounds etc., formed in the heterogeneous reactions of HNO$_3$ and organics [Kleffmann, 2007]. In order to evaluate the importance of nitrophenol photolysis as a HONO source, we conducted two experiments. In the first experiment, we studied the photolysis of model nitrophenol compounds (e.g. 2-, 3-, 4-nitrophenol and 2, 4-dinitrophenol) by exposing glass surfaces coated with nitrophenols to UV light. Among all four types of model nitrophenols we investigated, 2-nitrophenol was found to be highly volatile, nearly ~100% evaporated during our overnight drying procedure. Thus the small contribution of 2-nitrophenol to HONO formation was assumed to be largely caused by nitrate impurity. Photolysis of 3-nitrophenol and 2, 4-dinitrophenol caused product signals at wavelengths of 470 nm and 500 nm respectively, deviating from 540 nm which we normally used for quantifying HONO production. As in all HNO$_3$ photolysis experiments, we did not observe product signals at these wavelengths; the interference from these two compounds can be ruled out. Efficient
HONO formation observed during photolysis of 4-nitrophenol on glass surfaces was linearly correlated with the concentration of 4-nitrophenol, with the rate constant of $2.3 \times 10^5$ s$^{-1}$. This result is comparable to the photolysis of 2-nitrophenols in the gas phase [Bejan et al., 2006].

In the second experiment, we examined the possible composition changes from freshly prepared organic coating solutions to surface extract solution after overnight drying and conditioning for the three isomeric hydroxyphenols, that is, catechol, resorcinol and hydroquinone. The three compounds were selected from all model organic compounds we investigated because if they react with HNO$_3$ the structures of their products are most likely close to nitrophenols. By comparison of the light absorption spectrum, we found no change in absorbance before and after coating for resorcinol and hydroquinone at the wavelength of >300nm, indicating no nitrophenols were formed on the surface. However, a new product was formed with the maximum light absorption at ~415 nm from catechol-HNO$_3$ coated surface during the overnight drying/conditioning. Assuming the new product is 4-nitrophenol, which has the maximum light absorption at ~400 nm, its photolysis contributed to up to ~14% of produced HONO when a glass surface coated with HNO$_3$ and catechol was irradiated. Therefore, nitrophenols are not likely to be significant intermediate products of HNO$_3$-organic reactions on the surface and not a significant precursor of HONO in our surface HNO$_3$ photolysis experiments.

Based on these past findings and our experimental evidence, the following mechanism is proposed for the formation of HONO from HNO$_3$ photolysis on surfaces. When exposed to UV light, HNO$_3$ molecules on the surface absorb the energy, with an
efficiency ~3 orders of magnitude greater than in gas phase [Zhu et al., 2010], then jump from ground state to excited state (R5-2).

\[
HNO_3^{\text{(ads)}} + h\nu \leftrightarrow HNO_3^*^{\text{(ads)}} \quad \text{(R5-2)}
\]

The bond breakage of excited HNO\textsubscript{3} molecules produces OH and excited NO\textsubscript{2} (NO\textsubscript{2}*) (R5-3); certain fraction of these 2 products may recombine to form HNO\textsubscript{3} (R5-3’).

\[
HNO_3^*^{\text{(ads)}} \leftrightarrow OH^{\text{(ads)}} + NO_2^*^{\text{(ads)}} \quad \text{(R5-3, R5-3’)}
\]

When H\textsubscript{2}O and/or organic molecules are present on surface, NO\textsubscript{2}* may react rapidly with H\textsubscript{2}O and organics to produce HONO (R5-4 and 5-5), or is quenched by the third body (O\textsubscript{2}, N\textsubscript{2}, H\textsubscript{2}O and surface in our experiment) to return to ground state as NO\textsubscript{2} (R5-6).

\[
NO_2^*^{\text{(ads)}} + H_2O \rightarrow OH^{\text{(ads)}} + HONO^{\text{(ads)}} \quad \text{(R5-4)}
\]

\[
\text{Org}^{\text{(ads)}} + NO_2^*^{\text{(ads)}} \rightarrow \text{Products}^{\text{(ads)}} + HONO^{\text{(ads)}} \quad \text{(R5-5)}
\]

\[
NO_2^*^{\text{(ads)}} + M \rightarrow NO_2^{\text{(ads)}} + M \quad \text{(R5-6)}
\]

Surface-absorbed HONO and NO\textsubscript{2} are released from surface to gas phase under acidic condition (R5-7 and R5-8).

\[
\text{HONO}^{\text{(ads)}} \rightarrow \text{HONO}^{\text{(g)}} \quad \text{(R5-7)}
\]

\[
\text{NO}_2^{\text{(ads)}} \rightarrow \text{NO}_2^{\text{(g)}} \quad \text{(R5-8)}
\]

In the presence of organic chromophore on the surfaces, photons may be captured (R5-9) and then the energy is transferred to HNO\textsubscript{3} molecules (R5-10).

\[
\text{Org}^{\text{(ads)}} + h\nu \leftrightarrow \text{Org}^*^{\text{(ads)}} \quad \text{(R5-9)}
\]

\[
\text{Org}^*^{\text{(ads)}} + HNO_3^{\text{(ads)}} \leftrightarrow HNO_3^*^{\text{(ads)}} + \text{Org} \quad \text{(R5-10)}
\]
Through this photosensitization process, more HNO₃ molecules become excited and readily for photolysis, but organics may not be consumed and behaved more like photocatalysts. Organics may also react with photo-produced hydroxyl radical on surface (R5-11), preventing the recombination of NO₂* and OH the (R5-3’)

\[
\text{Org}_{\text{(ads)}} + \text{OH}_{\text{(ads)}} \rightarrow \text{Product} \quad \text{(R5-11)}
\]

Therefore, the presence of organics on the surface may enhance the HONO production from HNO₃ photolysis on surface by reaction with NO₂* (R5-5), and enhance the overall photolysis rate through photosensitization (R5-9 and R5-10) or by removing reactive product, OH radical (R5-11) and thus preventing the recombination of the products (R5-3’).

It should be pointed out here that some of our observations are not fully in agreement with the above mechanism. For example, we found that the organic enhancement on HNO₃ photolysis does not correspond to the reaction rates of organic compounds and hydroxyl radical (R5-11). Further studies are necessary to clarify the mechanism of the photolysis of HNO₃ on the surfaces. Overall, surface organics significantly accelerated HNO₃ photolysis process, with HONO as the major product.

5.3 Results and discussion: nitrate aerosol photolysis

The atmosphere, whether in urban or remote areas, contains significant concentrations of aerosol particles sometimes as high as \(10^7\)-\(10^8\) cm\(^{-3}\) [Seinfeld and Pandis, 2006]. The unique surfaces on aerosols provide important sites for heterogeneous reactions to take place. Given the abundance of nitrate and organic materials in the chemical compositions of aerosols, if mechanisms similar to the ones we proposed above proceed on aerosol surfaces, significant HONO (and NO₂) emission from
photolysis of aerosol nitrate can be expected. Further studies on photolysis of particulate nitrate were conducted using aerosols collected in urban (downtown Albany), suburban/rural (Delmar, NY, depending on wind directions) and remote areas (Whiteface Mountain, NY). To avoid sampling artifacts from adsorption of gaseous HNO$_3$, in some experiments an additional filter was placed behind the aerosol-sampling filter during collection and was used as exposure blank control to correct for the artifact signal from adsorbed HNO$_3$, assuming that both filters are in adsorption equilibrium with ambient gaseous HNO$_3$, but only the first filter collects aerosol particles. In our results we found that the median percentages of sampling artifacts in corresponding sample signals were 0.4% (0.2-33%, n = 12) for Albany samples, 2% (1-23%, n = 8) for Delmar samples and 3% (1.6-16%, n = 3) for WFM samples. These artifacts were corrected for all our results discussed below.

Upon irradiation, aerosol nitrate was photolyzed efficiently, producing a considerate amount of HONO and NO$_2$. An example is shown in figure 5.12. A similar behavior of HONO and NO$_2$ formations was observed, i.e., HONO and NO$_2$ yields decreased during photolysis of aerosol nitrate and HNO$_3$ on glass surfaces, indicating that the same mechanisms are responsible for this photochemical process on/in aerosol particles as on laboratory surfaces.
Figure 5.12 An example of formations of HONO (solid line) and NO\textsubscript{2} (dotted line) during the photolysis of aerosol nitrate. The aerosol sample was collected on a Teflon filter at the rate of 1 L min\textsuperscript{-1} for 16.5 hours in downtown Albany in November, 2010. Experimental conditions are the same as the experiment conducted on the glass surface.

As shown in Figure 5.13, nitrate photolysis rate on aerosol surfaces showed similar non-linear dependence on nitrate loading as we observed on the glass surface. These production rate values should be a lower estimates in the corresponding ambient air masses for the two following reasons: (1) Aerosol nitrate contents collected on the filter may be lower than the actual ambient concentrations due to evaporative loss of semi-volatile NH\textsubscript{4}NO\textsubscript{3} during aerosol collection; (2) the photolysis rate constant of aerosol nitrate may be underestimated due to the aggregation and self-shading of particles when large volume air samples are collected.
It is interesting to note that Albany aerosol samples collected in summer and winter both deviated from the average trendline but in the opposite directions. The former has much higher photolysis rate than expected from the trendline while the latter photolyzed less efficiently than expected. Such variance is not random, but can be explained by the difference in chemical compositions of aerosol samples.

Figure 5.13 Photolysis rate of aerosol nitrate as a function of nitrate loading. Photolysis rate refers to the total production rate of (HONO + NO₂). Experimental conditions are the same as the experiment conducted on the glass surface. The dashed line is the trendline for all data points. AlbSum: aerosol samples collected in Albany in summer (June, 2009); AlbWin: aerosol samples collected in Albany in winter (January and February, 2009); AlbNov: aerosol samples collected in Albany in November (2010); Del: aerosol samples collected in Delmar (October, 2010); WFM: aerosol samples collected in Whiteface mountain (August-September, 2008).
During the winter, almost all HNO₃ that is available is transferred to the particulate phase after reaction with NH₃ to form NH₄NO₃. In the summer, however, the two facts that NH₄NO₃ highly evaporated due to the higher temperature and the higher summertime concentrations of sulfate in the northeastern United States easily acidify the aerosol make the nitrate present mainly in the form of HNO₃ [Seinfeld and Pandis, 2006]. As we explained in section 5.2.4, HNO₃ is more readily to be photolyzed than its salt form, resulting in a much higher photolysis rate for summer nitrate aerosol. Indeed, the faster surface photolysis of HNO₃ than NH₄NO₃ has been confirmed by another experiment conducted in our group (Gao, unpublished data).

The seasonal variation of organics fraction in aerosols may be another factor contributing to this rate difference. Organics fraction in aerosols has been reported to be higher in summer than in winter in New York City [Zhang et al., 2007], which may also be true for Albany. Furthermore, we collected a larger volume (15-58 m³) of summer aerosol samples than winter samples (11-15 m³), also leading to higher levels of organics in the summer aerosol samples. As shown in figure 5.14, the higher levels of organic compounds in summer aerosols may contribute to the faster photolysis rate.

In figure 5.14, water-soluble organic compounds are indicated by the UV absorbance at 300nm, which showed a good linear relationship with the photolysis rate of nitrate. The varieties of organic contents in the aerosol samples were determined by sampling volume, sampling location and seasons. The increase in UV absorption can be attributed to two factors: higher concentrations of organic compounds and the stronger UV absorption at 300nm by certain organic compounds. This result confirmed our
conclusion that nitrate photolysis is enhanced by the presence of organic compounds and also supported the proposed photosensitization mechanism.

Figure 5.14 Linear regression of photolysis rate of aerosol nitrate versus UV absorbance at 300nm. Symbols have the same meaning as in Figure 5.13.

Figure 5.15 showed the photolysis rate constant of aerosol nitrate as the function of nitrate concentration in the air. Unlike on glass surface where the photolysis rate constant decreased rapidly with HNO₃ surface density within monolayer range, the rate constant for most nitrate aerosols is relatively flat except for winter aerosol samples collected in Albany, probably cause by the slower photolysis of NH₄NO₃ that accounted for majority of particulate in winter. Photolysis rate constants for aerosol nitrate are in the order of 10⁻⁴, relatively higher than for HNO₃ on glass surface. In fact, the photolysis
rate constant of aerosol nitrate may be underestimated due to the aggregation and self-shading of particles when large volumes of air samples are collected. The fast rate constant can be attributed to the relatively high ratio of organics to nitrate on aerosol unit surface. In addition, mineral oxides such as TiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$ in aerosols may be also responsible for the higher rate constant since recent modeling and field observations suggested that they act as reactive surfaces in heterogeneous reactions or photocatalysts contributing to HONO formation [Dentener et al., 1996; Gustafsson et al., 2006; Ndour et al., 2008; Wang et al., 2003].

Figure 5.15 Photolysis rate constant of aerosol nitrate as a function of nitrate concentration (both in logarithmic scale). Symbols have the same meaning as in Figure 5.13.
Table 5.2 summarized the results of photolysis of aerosol nitrate. The photolysis rate constant of aerosol nitrate showed considerable variance even for aerosols collected in same season at the same location. For example, $j_{\text{HNO}_3 \rightarrow \text{HONO}}$ varied by about a factor of 7 for aerosol samples collected at the Delmar site, ranging from $5.6 \times 10^{-5}$ s$^{-1}$ to $4.1 \times 10^{-4}$ s$^{-1}$. However, such variability reflects the real difference in aerosol samples, since results are in agreement within $\pm 20\%$ for parallel samples collected simultaneously. A number of factors such as meteorology, temperature, the transport of pollution, the emission of aerosols and their precursors can cause the significant variation in the concentrations and chemical compositions of atmospheric aerosols even over shorter timescales (e.g. hours) [Seinfeld and Pandis, 2006].

Although variability exists, the results in table 5.2 still showed a general trend in the photolysis of aerosol nitrate. First, photolysis rate constant of aerosol nitrate is higher for the samples collected in summer than in winter, as a result of lower $\text{NH}_4\text{NO}_3$ content in the summer due to its thermal dissociation. Second, photolysis rate constant of aerosol nitrate increases from urban to rural/remote area. Lastly, HONO is the predominant product during photolysis of aerosol nitrate, with a mean HONO/NO$_2$ ratio of 8.5. The last two conclusions are most likely related to the ratio of organic/nitrate and the types of organic compounds. The aerosol organic matter was reported to be dominated by oxygenated organic species, which on average accounted for 64% and 95% of the total organic aerosol in urban and rural/remote sites respectively [Zhang et al., 2007]. The abundance of organics in the aerosols may greatly enhance the overall photolysis rate through photosensitization (R5-9 and R5-10) and consumptions of primary products (R5-5 and R5-11), and increase the relative yield of HONO by reaction (R5-5). However,
firm conclusions on photolysis of nitrate aerosol cannot be made until more samples are collected and examined.

### Table 5.2 Summary of photolysis of aerosol nitrate

<table>
<thead>
<tr>
<th>Location</th>
<th>N</th>
<th>Date Mon-Yr</th>
<th>(j_{\text{HONO}} \times 10^5 \text{ s}^{-1})</th>
<th>(j_{\text{NO}_2} \times 10^5 \text{ s}^{-1})</th>
<th>Yield Ratio HONO / NO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albany</td>
<td>12</td>
<td>Jan-09</td>
<td>1.9</td>
<td>0.4</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Jan-09</td>
<td>1.9</td>
<td>0.3</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Feb-09</td>
<td>0.8</td>
<td>0.2</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Feb-09</td>
<td>0.5</td>
<td>0.1</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Jun-09</td>
<td>3.5</td>
<td>0.7</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Jun-09</td>
<td>4.5</td>
<td>0.7</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Jun-09</td>
<td>6.6</td>
<td>1.2</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nov-10</td>
<td>12</td>
<td>1.1</td>
<td>10.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nov-10</td>
<td>9.1</td>
<td>1.6</td>
<td>5.7</td>
</tr>
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<td>9.2</td>
<td>1.7</td>
<td>5.4</td>
</tr>
<tr>
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<td></td>
<td>Nov-10</td>
<td>7.1</td>
<td>1.1</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nov-10</td>
<td>5.8</td>
<td>1.0</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mean ± std</td>
<td>5.2 ± 1.4</td>
<td>0.8 ± 0.5</td>
<td>-</td>
</tr>
<tr>
<td>Delmar</td>
<td>8</td>
<td>Oct-10</td>
<td>41</td>
<td>8.3</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Oct-10</td>
<td>13</td>
<td>4.4</td>
<td>3.0</td>
</tr>
<tr>
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<td></td>
<td>Oct-10</td>
<td>17</td>
<td>1.3</td>
<td>13.1</td>
</tr>
<tr>
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<td></td>
<td>Oct-10</td>
<td>14</td>
<td>1.2</td>
<td>11.7</td>
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<td></td>
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<td>Oct-10</td>
<td>6.8</td>
<td>0.6</td>
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<td>0.5</td>
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<td>0.8</td>
<td>8.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mean ± std</td>
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<td>2.2 ± 2.7</td>
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<td></td>
<td></td>
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<td>0.7</td>
<td>10.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mean ± std</td>
<td>20 ± 20</td>
<td>2.3 ± 3.2</td>
<td>-</td>
</tr>
</tbody>
</table>
5.4 Comparison and interpretation of field results

5.4.1 Aircraft measurement

In aircraft measurement, we constantly observed median HONO concentrations of ~8 pptv in the free troposphere (> 1500 m above the ground level) and ~20 pptv in the upper boundary layer (800-1000 m above the ground level), both of which were considered as background HONO concentrations sustained by in situ HONO production since the ground/canopy surface influence is negligible for these altitudes [Zhang et al., 2009]. To maintain the observed HONO concentrations against photolysis at noontime, an in situ HONO production source of ~57 pptv hr\(^{-1}\) and ~150 pptv hr\(^{-1}\) would be required in the free troposphere and upper boundary layer respectively, assuming a HONO photolysis rate constant of \(J_{\text{HONO}} \approx 2 \times 10^{-3} \text{ s}^{-1}\).

In the literature, the concentrations of aerosol nitrate in free troposphere varied widely from 7-2000 pptv [Bahreini et al., 2003; Galasyn et al., 1987; Huebert and Lazrus, 1980; Norton et al., 1992; Schneider et al., 2006], mainly due to the uncertainties in different techniques and variations of underlying emission sources. We used 65 pptv as the concentration of aerosol nitrate in the free troposphere, taken from the measurement made by Huebert and Lazrus [1980] over western North America and the Pacific Ocean because it is geographically similar and proximate to our sampling site in aircraft measurement. In surface layer, aerosol nitrate was reported to be within < 23 to 338 pptv in this site [Thornberry et al., 2001]. As aerosol nitrate vertical profiles in the above literatures did not show a significant change in nitrate concentration in boundary layer, we assumed 150 pptv in the upper boundary layer. An average of photolysis rate constants of aerosol nitrate (except winter aerosol samples) derived in our experiment is
~ $1.2 \times 10^{-4}$ s$^{-1}$. In free troposphere, a factor of ~1.3 should be applied due to the more efficient solar radiation (http://cprm.acd.ucar.edu/Models/TUV/Interactive_TUV/). By our calculations, ~ 35 ppt hr$^{-1}$ and 64 ppt hr$^{-1}$ of HONO was produced by the photolysis of aerosol nitrate in the free troposphere and upper boundary layer, accounting for 60% and 43% of total HONO source, respectively. This result indicated that the photolysis of HNO$_3$/nitrate on and in aerosol particles is the major in situ HONO source.

The remainder of HONO in situ production could derive from a variety of sources, such as the gas-phase NO-OH reaction which was estimated to be a minor source, contributing only 4-7% of the in situ HONO production [Zhang et al., 2009], photo-enhanced heterogeneous reactions involving NO$_2$ on organic surfaces[George et al., 2005; Stemmler et al., 2006; 2007], and photolysis of nitrophenol in the gas phase and on surfaces [Bejan et al., 2006; Rohrer et al., 2005]. Since the air at UMBS is generally relatively clean with respect to anthropogenic VOCs, the last mechanism is unlikely to be important.

5.4.2 HONO flux measurement above forest canopy

Above the forest canopy, positive upward HONO fluxes were observed most of the time during the measurement period in summer 2008, with an average of $3.7\times10^{-7}$ mol m$^{-2}$ hr$^{-1}$ and a noontime maximum mean of $7\times10^{-7}$ mol m$^{-2}$ hr$^{-1}$ [Zhang et al., 2011; Zhou et al., 2011]. With the photolysis rate constant of HNO$_3$ on the surfaces, $j_{\text{HNO}_3-\text{HONO}}$, derived in this experiment, we are able to evaluate whether the observed HONO flux was resulted from the photolysis of deposited HNO$_3$ on the canopy surface. The 16 sets of leaf sample yield a median value (±1σ) of nitrate loading on canopy leaf surface of $(8.3 \pm 3.1) \times 10^{-6}$ mol m$^{-2}$. In Figure 5.6, at such nitrate densities, photolysis rate constants varied from
0.79×10^{-5} to 7.7×10^{-5} s^{-1} in correspondence to different surface coating (by pure HNO_3 or by salicylic acid + HNO_3, with HONO to be the dominant product, ~72%). The calculated HONO flux ranges from 1.7×10^{-7} to 16×10^{-7} mol m^{-2} hr^{-1}; the observed noontime HONO flux well fell within this range. The large variability in HONO flux, as discussed in Chapter 4, can be attributed to the influence from a range of factors such as ambient moisture, the types of organic compounds and solar radiation. The agreement of calculations based on our laboratory results with our field observations supports our hypothesis that the photolysis of deposited HNO_3 on canopy surface is the dominant daytime HONO source for the lower atmospheric boundary layer.

5.5 Summary

Upon irradiation, HNO_3 on the surfaces can be photolyzed, producing HONO and NO_2. HNO_3 photolysis rate constant (J) decreases with HNO_3 density on the surfaces. Within monolayer range (≤ 10 umol/m^2), J varies largely over 1 order of magnitude; in multilayer range (> 10 umol/m^2), J slowly decreased.

Organics present on the surfaces significantly enhanced the HNO_3 photolysis rate by up to one order of magnitude. The presence of organics is in favor of HONO production. HONO is the major product and NO_2 is the minor product in this re-NO_x-ification process under the condition of 50% RH.

Photolysis of aerosol nitrate has similar mechanisms as HNO_3 photolysis on model organic surfaces. The greater J value observed in aerosol nitrate photolysis was attributed to higher ratio of organic/HNO_3 on aerosol surfaces than on the glass surfaces. The J values may vary considerably in space and time.
Experimental data well explained the *in situ* HONO production in aircraft measurement and the observational HONO flux above forest canopy surface. Results of these experiments, in addition to the past literature, indicate that the photolysis of HNO$_3$/nitrate on and in aerosol particles is the major *in situ* HONO source during the day, and the photolysis of HNO$_3$/nitrate on forest canopy is the dominant HONO source for the lower atmospheric boundary layer in the rural environments.
CHAPTER 6. SUMMARY AND FUTURE RESEARCH

In this research, the chemistry of HONO in the rural troposphere has been investigated through aircraft-based measurement, tower-based flux measurement and laboratory photochemical experiments. The major findings and contributions from this research are summarized in this chapter. Among the major contributions to the understanding of tropospheric chemistry from this dissertation research, we are the first to:

✓ Establish and report HONO profiles on an aircraft platform ranging from surface boundary layer to the free troposphere;
✓ Directly measure and report HONO flux above a forest canopy;
✓ Examine photochemical HONO formation from the photolysis of HNO$_3$/nitrate on organic surfaces and on/in atmospheric aerosols.

The quantitative results from this research confirmed the hypothesis proposed by our group in previous studies, i.e., photolysis of HNO$_3$/nitrate on surfaces is a major daytime HONO source and an important re-NO$_x$-ification pathway in the troposphere [Zhou et al., 2001; 2002a; 2002b; 2003; 2007].

HONO vertical distribution was examined from 50 m – 2600 m above the rural forest region in summer 2007. The HONO mixing ratios ranged from 4 to 17 pptv in the free troposphere and from 8 to 74 pptv in the boundary layer. HONO vertical distributions strongly depended on air column stability: sharp negative HONO gradients existed in stable boundary layer in the morning hours, whereas the HONO distribution
was relatively uniform in the unstable and well-mixed boundary layer in the afternoons. Both the abundance of HONO near ground surfaces and the influence of the boundary layer stability on its vertical distribution indicated that ground surfaces, including vegetation, are a major HONO source for the atmospheric lower boundary layer. Photolysis of HNO$_3$/nitrate on and in aerosol particles is likely to be the major \textit{in situ} HONO source, sustaining the large fraction of the observed HONO levels over bodies of water and in the free troposphere.

Ambient HONO and vertical HONO flux were measured simultaneously at the rural PROPHET site in summer 2008. The mean HONO concentration was 49 pptv and mean HONO flux was $0.37 \times 10^{-6}$ moles m$^{-2}$ hr$^{-1}$. Both ambient HONO concentration and HONO flux showed significant diurnal variations, with noontime maximum means of ~70 pptv and $0.7 \times 10^{-6}$ moles m$^{-2}$ hr$^{-1}$ respectively, and a HONO minimum mean of ~20 pptv around sunset, and a minimum HONO flux mean of $0.1 \times 10^{-6}$ moles m$^{-2}$ in the early morning before sunrise. The significant upward HONO flux occurred during the day contributes a major fraction (~60%) of the observed daytime HONO concentrations (~70 pptv) at 10 m above the forest canopy. Photolysis of HNO$_3$ deposited on canopy surface was likely to be the major mechanism responsible for the observed daytime HONO flux and may serve as an important remobilization pathway for the deposited HNO$_3$ to photolabile species in the atmosphere.

Results from laboratory photochemical experiments showed that the kinetics of the re-NO$_x$-ification process is complicated, depending on the surface availability for the heterogeneous reaction and the nature of the surfaces. In the absence of organic compounds on the surfaces, photolysis of surface-adsorbed HNO$_3$ has a rate constant of
~2 ×10^{-5} \text{ s}^{-1}, releasing \text{NO}_2 and HONO as the products with near equal relative yields, at 50\% RH on grounded Pyrex glass. This reaction is 1-2 orders of magnitude faster than in aqueous/gas phase. In the presence of organics on the surfaces, the photolytic process was greatly accelerated by up to ~10 times, with HONO as the major product and \text{NO}_2 as the minor product under ambient atmospheric conditions. An average of photolysis rate constants of aerosol nitrate (except winter aerosol samples) derived in our experiment is \sim 1.2 \times 10^{-4} \text{ s}^{-1}. The greater J value observed in aerosol nitrate photolysis was attributed to higher ratio of organic/HNO_3 on aerosol surfaces than on the glass surfaces. A mechanism is proposed for the formation of HONO from surface HNO_3/nitrate photolysis, involving \text{NO}_2^* as the primary product, followed by abstraction of H atoms from organic compounds and/or water molecules on surface.

With photolysis rate constants derived from this research, photolysis of aerosol nitrate accounts for 60\% and 43\% of observed HONO concentrations in the free troposphere and upper boundary layer respectively, assuming concentrations of aerosol nitrate are 65 pptv and 150 pptv in the free troposphere and the upper boundary layer respectively. Photolysis of nitrate loading on canopy surface at noontime provides HONO flux from 1.7 \times 10^{-7} \text{ to } 16 \times 10^{-7} \text{ mol m}^{-2} \text{ hr}^{-1}; the observed noontime HONO flux with an average of +3.7 \times 10^{-7} \text{ mol m}^{-2} \text{ hr}^{-1} and a noontime maximum mean of +7 \times 10^{-7} \text{ mol m}^{-2} \text{ hr}^{-1} well fell within this range. Experimental data well explained the \textit{in situ} HONO production in aircraft measurement and the observational HONO flux above forest canopy surface. Results of these experiments, in addition to the past literature, indicate that the photolysis of HNO_3/nitrate on and in aerosol particles is the major \textit{in situ} HONO source during the day, and the photolysis of HNO_3/nitrate on forest canopy is the
dominant HONO source for the lower atmospheric boundary layer in the rural environments.

Dry deposition of HNO$_3$ has long been recognized as the dominant sink of HNO$_3$ and NO$_x$ in the troposphere. However, the present research suggested that HNO$_3$ is not a perfect sink of NO$_x$ in the troposphere. At an observed lower limit of HNO$_3$ photolysis rate constant, $J_{HNO3}$, $2 \times 10^{-5}$ s$^{-1}$, the photolysis lifetime of surface HNO$_3$ is about 14 hours when exposed to full sun. In presence of organic compounds on the surfaces in real conditions, the lifetime of surface HNO$_3$ can be as short as one hour. During the summer, daily accumulative solar radiation is approximately 8-9 hours of the radiation present at noon [Finlayson-Pitts and Pitts, 2000]. This means that a major portion of the sunlight-exposed HNO$_3$/particulate nitrate on ground surfaces and in aerosols would be recycled back to the overlying atmosphere as NO$_x$ and HONO on a daily basis. If the surface photochemistry of HNO$_3$ on Pyrex and of nitrate in aerosols observed in our lab occurs in a similar fashion on other surfaces such as leaves, rocks and soil, it can serve as a significant or even major re-NO$_x$-ification pathway.

In the low-NO$_x$ environment where direct anthropogenic NO$_x$ emission is low, the remobilization of deposited HNO$_3$ and aerosol nitrate back to the atmosphere can be an important to supply the overlying atmosphere with a new source of photochemically reactive nitrogen species, e.g. HONO and NO$_x$. With this new sources of HONO and NO$_x$, the atmospheric boundary should be more photochemically reactive than we previously realized, leading to higher production of photooxidants such as OH radicals and O$_3$. The effect of re-NO$_x$-ification of HNO$_3$/nitrate on ground surfaces and in aerosols on the tropospheric chemistry is illustrated in Figure 6.1. Our results from field
and laboratory studies strongly recommend that atmospheric boundary layer models should take this surface process into consideration, especially for understanding the photochemistry in rural areas.

Figure 6.1 Effects of the photolytic remobilization of HNO$_3$/nitrate ("re-NOx-ification") on ground surfaces and in aerosols on tropospheric chemistry. The red arrows are the process investigated and quantified in this research.

The contribution of this dissertation research to the field of atmospheric chemistry also includes the development and improvement of several measurement techniques. The HONO flux measurement technique has been developed based on the relaxed eddy
accumulation approach, deploying a 3-D sonic anemometer and two HONO measurement systems. The overall uncertainty is estimated to be within $\pm (8 \times 10^{-8} + 0.15 F_{HONO})$ mol m$^{-2}$ hr$^{-1}$, with a 20-min averaged data point per 30 min. A major improvement was made upon existing HONO measurement techniques. A 3-way solenoid valve was used to alternately introduce ambient air or “zero-HONO” air to a coil sampler. The ambient HONO concentrations were derived from the difference between the ambient signals and the “zero-HONO” air. The lower detection limit of the method is 1 pptv for 2-min averages, with an overall uncertainty of $\pm (1 + 0.05 [HONO])$ pptv. A technique for NO$_2$ measurement was developed based on SA/NED scrubbing using a coil sampler, followed by detection of the color formed. Under experimental conditions in this research, a collection efficiency of 60% and a detection limit of 15 pptv can be achieved.

There are also some limitations in this research. During aircraft measurement, NO$_x$ was not measured simultaneously due to the limited space in the small aircraft; aerosol nitrate was not determined due to the insufficient sample amount collected. During flux measurement, dry deposition of HNO$_3$ on top of the tower was not examined and directly correlated to observed HONO flux. During laboratory photochemical experiment, the behavior of sample aerosols may vary from the individual aerosols suspended in the air due to the aggregation and self-shading of particles when large volume air samples are collected; organic species in aerosol samples were present in trace amount, thus cannot be identified by our low resolution IR spectrum; the proposed mechanism for the surface HNO$_3$ photolysis leading to HONO formation were based on our experimental evidence and literature review on similar processes.
In the future research, field measurement of HONO should be made along with other parameters, such as NO\textsubscript{x}, HNO\textsubscript{3}, particulate nitrates, HO\textsubscript{x}, aerosol size distribution and composition, organics, and light intensity, in different seasons e.g. summer and winter, on various locations e.g. forest, grassland, snowpack and lake, and at different altitude. The temporal and spatial distributions of HONO and the relevant parameters in these different environments will provide further understanding on the chemistry of HONO in troposphere, such as its sources and sinks, and the detail formation mechanisms. Our measurement techniques for HONO, HNO\textsubscript{3} and NO\textsubscript{2} are all based on azo dye derivatization using Griess-Saltzman reagent. Our ready-to-use HONO flux system has the potential to be modified into a portable and low-cost flux measurements system for gaseous HNO\textsubscript{3} and NO\textsubscript{2}, which will allow one more flexibility in exploring diverse areas in atmospheric research.

Further laboratory studies are necessary to examine the unanswered questions regarding the mechanism of HONO formation from photolysis of HNO\textsubscript{3} on the surfaces in presence of organic compounds. The unanswered questions and uncertainties include: what functional groups and substitution patterns are most effective in enhancing the HNO\textsubscript{3} photolysis process? What the exact reaction steps are in this process? Is the same controlling mechanism responsible for the photolysis of HNO\textsubscript{3} on surfaces and particulate nitrate on/in aerosols? More organic species and measurement techniques are needed in the future studies. Furthermore, in the present research, high-level of HONO emission from HNO\textsubscript{3} photolysis on an aluminum surface was observed in dark conditions as well as during irradiation. Photocatalytical formation of HONO in the reaction of NO\textsubscript{2} on TiO\textsubscript{2} surfaces has also been reported in the literature. Mineral oxides such as TiO\textsubscript{2},
$\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$ may act as reactive surfaces in natural conditions (e.g., in aerosols) to catalyze HNO$_3$ photolysis, which should be investigated in future studies. Lastly, the small sample size of aerosols (N = 23) in this research prevented us from making firm conclusions about photolysis of nitrate aerosols. Collecting more aerosol samples and repeating the photochemical experiment are necessary to elucidate the importance of aerosols related to reactive nitrogen species chemistry.
REFERENCES


Carr, S., D. E. Heard, and M. A. Blitz (2009), Comment on "Atmospheric Hydroxyl Radical Production from Electronically Excited NO2 and H2O", *Science*, 324, -. 


Draxler, R. R., and G. D. Rolph (2003), HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website
(http://www.arl.noaa.gov/ready/hysplit4.html), NOAA Air Resources Laboratory, Silver Spring, MD.


Li, S. P., J. Matthews, and A. Sinha (2009), Response to Comment on "Atmospheric Hydroxyl Radical Production from Electronically Excited NO2 and H2O", *Science*, 324.


Stutz, J., B. Alicke, R. Ackermann, A. Geyer, S. Wang, A. B. White, E. J. Williams, C.
W. Spicer, and J. D. Fast (2004), Relative humidity dependence of HONO

Stutz, J., B. Alicke, and A. Neftel (2002), Nitrous acid formation in the urban atmosphere:
gradiant measurements of NO2 and HONO over grass in Milan, Italy, *J. Geophys.

Tan, D., I. Faloona, J. B. Simpas, W. Brune, P. B. Shepson, T. L. Couch, A. L. Sumner,
M. A. Carroll, T. Thornberry, E. Apel, D. Riemer, and W. Stockwell (2001), HOx
budgets in a deciduous forest: Results from the PROPHET summer 1998

Thornberry, T., M. A. Carroll, G. J. Keeler, S. Sillman, S. B. Bertman, M. R. Pippin, K.
Ostling, J. W. Grossenbacher, P. B. Shepson, O. R. Cooper, J. L. Moody, and W.
R. Stockwell (2001), Observations of reactive oxidized nitrogen and speciation of
NOy during the PROPHET summer 1998 intensive, *J. Geophys. Res.*, 106,
doi:10.1029/2000JD900760, 902001

Tyndall, G. S., J. J. Orlando, and J. G. Calvert (1995), Upper Limit for the Rate

Veitel, H., B. Kromer, M. Mossner, and U. Platt (2002), New techniques for
measurements of atmospheric vertical trace gas profiles using DOAS,


site in New York State, *J. Geophys. Res.*, 107, 4590,

Zhou, X., H. Gao, Y. He, G. Huang, S. B. Bertman, K. Civerolo, and J. Schwab (2003),
Nitric acid photolysis on surfaces in low-NOx environments: significant

Photochemical production of nitrous acid on glass sample manifold surface,

Summertime observations of HONO, HCHO, and O3 at the summit of Whiteface

Zhou, X., N. Zhang, T. Michaela, D. Tang, J. Hou, S. B. Bertman, M. Alaghmand, P. B.
Shepson, M. A. Carroll, S. Griffith, S. Dusanter, and P. S. Stevens (2011), Nitric
Acid Photolysis on Forest Canopy Surface as a Tropospheric Nitrous Acid Source,
*Nature Geoscience*.

Zhou, X. L., H. J. Beine, R. E. Honrath, J. D. Fuentes, W. Simpson, P. B. Shepson, and J.
W. Bottenheim (2001), Snowpack photochemical production of HONO: a major
source of OH in the Arctic boundary layer in springtime, *Geophys. Res. Lett.*, 28,
4087-4090.

interfaces, 13, 73-220.

