Tropospheric HONO Distribution and Chemistry in the Southeast U.S.

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Abstract

Here we report the measurement results of nitrous acid (HONO) and a suite of relevant parameters on the NCAR C-130 research aircraft in the Southeast U.S. during NOMADSS 2013 summer field study. Daytime HONO concentrations ranged from low parts per trillion by volume (pptv) in the free troposphere (FT) to mostly within 5 - 15 pptv in the background terrestrial air masses, and to up to 40 pptv in the industrial and urban plumes in the planetary boundary layer (PBL). There was no discernable vertical HONO distribution trend in the PBL above the lowest flight altitude of 300 m, indicating that the ground surface HONO source was not a significant contributor to the HONO budget in the measurement altitude between 300 m and 4.7 km. While there was a strong correlation between the concentrations of HONO and oxides of nitrogen (NO\textsubscript{x} = NO + NO\textsubscript{2}) (R\textsuperscript{2} = 0.52), the sum of all known NO\textsubscript{x}-related HONO formation mechanisms was found to account for less 20% of the daytime HONO source in the background terrestrial air masses, due to the low level of NO\textsubscript{x} and surface area density of aerosol particles. Photolysis of particulate nitrate (pNO\textsubscript{3}) appeared to be the major daytime HONO source in the background terrestrial air masses, based on the measured pNO\textsubscript{3} concentration and the median value of 2.0×10\textsuperscript{-4} s\textsuperscript{-1} for pNO\textsubscript{3} photolysis rate constant determined in the laboratory using ambient aerosol samples collected during the field study.

Within the power plant and industrial plumes encountered, daytime HONO was predominantly produced by secondary formation processes involving both NO\textsubscript{x} and pNO\textsubscript{3} as precursors. While HONO was not a significant OH precursor compared to O\textsubscript{3} under low NO\textsubscript{x} conditions in the air column, it was an important intermediate product of a photochemical renoxification process recycling nitric acid and nitrate back to NO\textsubscript{x}. Finally, the HONO/NO\textsubscript{x} ratio stayed relatively constant for several hours after sunset in the nocturnal residual layer, suggesting no significant night-time volume HONO source existed in the nocturnal residual layer and the nocturnal FT under background conditions.

1 Introduction

Extensive field studies at ground sites have shown that gas-phase nitrous acid (HONO) exists at much higher levels than expected during the day, with a mixing ratio of HONO up to several parts per billion by volume (ppbv) in the urban atmosphere (Acker et al., 2006; Villena et al., 2011) and up to several hundred parts per trillion by volume (pptv) in rural environments (Acker et al., 2006; Kleffmann et al., 2003; Zhang et al., 2009; Zhou et al., 2002, 2011). At the observed concentrations, HONO photolysis (R1) becomes an important or
even a major OH primary source in both urban (Elshorbany et al., 2010; Villena et al., 2011) and rural environments near the ground surface (Acker et al., 2006; He et al., 2006; Kleffmann et al., 2003; Zhou et al., 2003; 2011).

\[
\text{HONO} + h\nu \rightleftharpoons \text{OH} + \text{NO} \quad \text{(R1, R-1)}.
\]

The OH radical is responsible for the removal of primary pollutants, and plays a crucial role in the formation of secondary pollutants, such as O3 and aerosol (Finlayson-Pitts and Pitts, 2000), and thus HONO, as an important OH precursor, plays an important role in atmospheric chemistry.

The removal processes of HONO from the troposphere are relatively well understood, including mainly photolysis, reaction with the OH radical and surface deposition. Photolysis is the dominant sink for HONO during the day (Kleffmann et al., 2003; Oswald et al., 2015; Zhang et al., 2009, 2012), and dry deposition is the major HONO loss pathway at night, especially over wet surfaces (He et al., 2006; VandenBoer et al., 2015). However, HONO sources in the planetary boundary layer (PBL) are numerous. HONO is directly emitted from combustion processes, such as automobile emissions (Li et al., 2008b) and biomass burning (Burling et al., 2010; Trentmann et al., 2003). Due to the relatively short photolytic lifetime of HONO, in the order of 10 min around summer noontime, the impacts of the direct emission on HONO distribution and chemistry is highly localized and limited to the source region during the day. Recent studies have suggested that microbial activities produce nitrite through nitrification or denitrification in the soil, and soil emission may be a significant HONO source for the overlying atmosphere (Maljanen et al., 2013; Oswald et al., 2013; Su et al., 2011). Since the emission of HONO from soils depends on multiple factors, such as the abundance of soil nitrate and ammonia, the soil pH and water content, and microbial types and activities, it is expected that the strength of this HONO emission varies greatly in different environments and thus needs to be further quantified (Oswald et al., 2013).

HONO is a unique species that is produced through heterogeneous reactions of different precursors, such as NO2 and HNO3, on surfaces (R2 - R3):

\[
\text{NO}_2 + \text{H}_2\text{O} \text{ (or organics)} \xrightarrow{\text{surface}} \text{HONO} \quad \text{(R2)}
\]

\[
\text{HNO}_3(s) + h\nu \xrightarrow{\text{orga} \text{nics}, \text{H}_2\text{O}} \text{HONO} + \text{NO}_2 \quad \text{(R3)}
\]

Heterogeneous reactions of NO2 with organics (R2) on the surfaces have been found to be greatly accelerated by sunlight through photosensitization (George et al., 2005; Kleffmann, 2007; Stemmler et al., 2006, 2007) and these reactions are likely the major daytime HONO
Laboratory studies have confirmed that HNO$_3$ undergoes photolysis in sunlight at rates 2 - 3 orders of magnitude greater on the surface than in the gas phase (Baergen and Donaldson, 2013; Du and Zhu, 2011; Ye et al., 2016a, b; Zhou et al., 2003; Zhu et al., 2008), producing NO$_x$ and HONO. In low-NO$_x$ environments, photolysis of nitric acid/nitrate deposited on the surface has been proposed to be the major daytime HONO source near the ground surface (Ye et al., 2016b; Zhou et al., 2003, 2011).

Several processes within an air mass may lead to volume, or in situ, production of HONO. The OH+NO reaction (R-1) in the gas phase may be a significant HONO source in high NO$_x$ and photochemically reactive atmospheres (Kleffmann, 2007; Villena et al., 2011), but becomes negligible in low-NO$_x$ environments (Li et al., 2014; Ye et al., 2016b). Two additional gas-phase reactions have been also proposed to produce HONO with in the air column: between excited NO$_2$ (NO$_2^*$) and water vapor (R4) (Li et al., 2008a), and between NO$_2$ and the hydroperoxyl-water complex (HOO$_2$·H$_2$O) (R5a) (Li et al., 2014):

\[
\text{NO}_2^* + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{OH} \quad \text{(R4)}
\]

\[
\text{HOO}_2\cdot\text{H}_2\text{O} + \text{NO}_2 \xrightarrow{\text{a}} \text{HONO} + \text{O}_2 + \text{H}_2\text{O} \quad \text{(R5a)}
\]

\[
\text{HOO}_2\cdot\text{H}_2\text{O} + \text{NO}_2 \xrightarrow{1-\text{a}} \text{products} \quad \text{(R5b)}
\]

However, further laboratory evidence suggests that reaction (R4) is too slow to be important (Carr et al., 2009; Wong et al., 2011). And recent airborne observations have demonstrated that the HONO yield (a) from reaction (R5) is less than 0.03 (Ye et al., 2015).

Almost all HONO measurements to date have been made at ground stations. The observed HONO concentrations reported in the literature represent the HONO levels in the lower PBL under the significant but varying influence of ground surface processes. Thus, it is difficult to distinguish the ground surface HONO sources from the in situ HONO sources.

Measurements of the vertical profile of HONO concentrations and/or HONO fluxes have suggested that ground surfaces can be major HONO sources for the overlying atmosphere in many cases (He et al., 2006; Kleffmann et al., 2003 Stutz et al., 2002; Zhou et al., 2011), but not in some other cases (Villena et al., 2011). A recent HONO flux measurement has suggested that the HONO source from the forest canopy contributed ~ 60% of the measured HONO budget at the measurement height of 11 m above the forest canopy, and the in situ HONO production contributed the remaining ~ 40% (Zhou et al., 2011). Similarly, observational and modeling studies implied a presence of a volume HONO source at 130-m
altitude above Houston, TX (Wong et al., 2012, 2013). The relative importance of in situ HONO production would be expected to increase with altitude due to decreasing influence of the ground surface, at least during the day. Airborne measurements in the air mass above the altitude influenced directly by ground HONO sources should provide more direct and quantitative evidence for in situ HONO production in the troposphere. Indeed, the limited number of airborne measurements available have shown that HONO exists in substantial amounts throughout the troposphere (Li et al., 2014; Ye et al., 2015; Zhang et al., 2009).

Here we report airborne HONO measurement results and findings from five research flights in the Southeast U.S. during the NOMADSS (Nitrogen, Oxidants, Mercury and Aerosol Distributions, Sources and Sinks) 2013 summer field campaign aboard the NSF/NCAR C-130 research aircraft.

2 Experimental

NOMADSS was an airborne field study under the “umbrella” of SAS (Southeast Atmosphere Study). It consisted of nineteen research flights on board the NSF/NCAR C-130 aircraft from June 1, 2013 to July 15, 2013. Parameters observed included HONO, HNO₃, particulate nitrate, NOₓ, O₃, BrO, OH radicals, HO₂ radicals, RO₂ radicals, aerosol surface area densities (size <1 μm), VOCs, photolysis frequencies, and other meteorology parameters. Table 1 summarizes the instrumentation, time resolution, detection limit, accuracy, and references for the measurements.

HONO was measured by two long-path absorption photometric (LPAP) systems based on the Griess-Saltzman reaction (Zhang et al., 2012; Ye et al., 2016b). Briefly, ambient air was first brought into the aircraft through an inlet and then HONO was scrubbed using de-ionized (DI) water in a 10-turn glass coil sampler to ensure high efficiency HONO sampling. The scrubbed nitrite was then derivatized with 5 mM sulfanilamide (SA) and 0.5 mM N-(1-Naphthyl)-ethylene-diamine (NED) in 40 mM HCl, to form an azo dye within 5 min. The azo dye was detected by light absorbance at 540 nm using an optic fiber spectrometer (LEDSpec, WPI) with a 1-m liquid waveguide capillary flow cell (WPI). “Zero-HONO” air was generated by directing the sample stream through a Na₂CO₃-coated denuder to remove HONO and was sampled by the systems periodically to establish measurement baselines. Interference from NOₓ, PAN, and particulate nitrite if any, was corrected by subtracting the baseline from the ambient air signal. Due to the low collecting efficiency of these interfering species in the sampling coil and their low concentrations, the combined interference was estimated to be less...
than 10% of the total signal. Potential interference from peroxynitric acid (HO$_2$NO$_2$) was
suppressed by heating the PFA sampling line to 50 °C with a residence time of 0.8 s. The
HO$_2$NO$_2$ steady state concentration was estimated to be less than 1 pptv at temperatures of 20
- 30 °C in the background PBL (Gierczak et al., 2005), and thus interference from HO$_2$NO$_2$
was negligible. Whereas in power plant plumes and urban plumes in the PBL or biomass
burning plumes in the upper free troposphere (FT), HO$_2$NO$_2$ interference was not negligible.
HONO measurements were corrected by a term of “0.2 × [HO$_2$NO$_2$]$_{SS}$”, assuming an upper
limit HO$_2$NO$_2$-to-HONO conversion efficiency of 0.2 in our system. [HO$_2$NO$_2$]$_{SS}$ refers to the
steady state concentration of HO$_2$NO$_2$, and the upper limit HO$_2$NO$_2$-to-HONO conversion
efficiency of 0.2 was estimated from the ratio of the observed [HONO] to the calculated
[HO$_2$NO$_2$]$_{SS}$ in cold, high altitude air masses under our measurement conditions. In the PBL,
the correction is below 10% of the total signal. The accuracy of HONO measurements was
confirmed by comparison with a limb-scanning Differential Optical Absorption Spectroscopy
(DOAS) (Platt and Stutz, 2008). The agreement between these two instruments was very good
in wide power plant plumes where HONO mixing ratios significantly exceeded the detection
limits of both instruments (Ye et al., 2016b).
Particulate nitrate (pNO$_3$) was quantitatively collected with a frit disc sampler after a
NaCl-coated denuder to remove HNO$_3$ (Huang et al., 2002). The collected nitrate was reduced
to nitrite by a Cd column, and determined using a LPAP systems (Zhang et al., 2012). Zero air
was generated to establish measurement baselines for pNO$_3$ by passing the ambient air
through a Teflon filter and a NaCl-coated denuder to remove aerosol particles and HNO$_3$.
Potential interferences from HONO, NO$_x$ and PAN were corrected by subtracting the
baselines from the ambient air signals.

The mixing ratios of a large number of non-methane organic compounds (NMOCs)
were measured by Trace Organic Gas Analyzer (TOGA) (Hornbrook et al., 2011a) and
Proton-transfer-reaction mass spectrometry (PTR-MS) (Karl et al., 2003; de Gouw and
Warneke, 2007). The surface area density of fine particles was measured by a Scanning
Mobility Particle Sizer (SMPS). The photolysis frequencies were determined by a Charged-
coupled device Actinic Flux Spectroradiometer instrument (CAFS) (Shetter et al., 2002). The
mixing ratios of HO$_x$ and RO$_2$ radicals were measured by a method based on selected-ion
chemical-ionization mass spectrometry (SICIMS) (Hornbrook et al., 2011b; Mauldin et al.,
2010). The mixing ratios of ozone and NO$_x$ were measured by NCAR’s chemiluminescence
instruments (Ridley et al., 2004). Meteorology parameters were provided by state parameter measurements on board the C-130.

The results from five out of nineteen flights are presented here to discuss vertical HONO distribution and HONO chemistry in the Southeast U.S. The flight tracks are shown in Figure 1.

3 Results and Discussion

3.1 General data description

Figure 2 shows the time series of HONO, NO$_x$, pNO$_3$ concentrations and the measurement altitude for five selected research flights in the Southeast U.S. during the NOMADSS 2013 summer field study. Research flight (RF) #4, RF #5 and RF #17 are race track flights in the background terrestrial areas designed to establish HONO distribution and explore HONO chemistry in background air masses. RF #11 is a race track flight designed to intercept plumes from local power plants and urban areas and explore HONO chemistry therein. All four flights were conducted in the daytime, roughly from 14:00 to 22:00 UTC (10:00 to 18:00 EDT). RF #18 is a race track flight conducted from 20:30 on July 12$^{th}$ to 03:30 on July 13$^{th}$ UTC (16:30 on July 12$^{th}$ to 00:30 on July 13$^{th}$, 2013 EDT), aiming to study the potential night-time HONO accumulation both in the PBL and the FT.

Table 2 summarizes the data statistics for HONO, NO$_x$ and pNO$_3$ measurements in the PBL and the FT, and Figure 3 shows composite vertical distributions of HONO, NO$_x$ and pNO$_3$ concentrations from the five flights in the Southeast U.S. during the NOMADSS 2013 summer field study. HONO, NO$_x$ and pNO$_3$ concentrations show horizontal gradients in every race track flight and vary in different race track flights, reflecting the inhomogeneity of air masses in the region. However, no significant vertical gradient in HONO, NO$_x$ and pNO$_3$ concentrations is apparent, which will be further discussed below. Except in a few power plant plumes and urban plumes mostly encountered in RF #11 (labelled as A-G), most of the data is representative of background terrestrial air masses. The range of the mixing ratio of HONO is 1.1 – 35.9 pptv. The mean ($\pm$1SD) and median values of HONO concentration are 5.4 ($\pm$3.4) pptv and 4.2 pptv in the FT, and 11.2 ($\pm$4.3) pptv and 10.6 pptv in the PBL. HONO levels at ~ 4 pptv are typically found in the background FT, but high HONO concentrations up to 18.2 pptv are also observed in the elevated biomass burning plumes. Many biomass burning plumes were observed during other flights and will be discussed in a future paper. HONO levels at ~ 11 pptv are representative of background conditions in the...
PBL. High HONO levels up to 35.9 pptv are observed in the power plant plumes and urban plumes in RF #11. The HONO distribution and chemistry in these urban and power plant plumes in the Southeast U.S. are specifically discussed below, in comparison with the results for background conditions (RF # 4, #5, and #17). These measured HONO values are consistent with the range of 4 – 74 pptv in the troposphere over Northern Michigan (Zhang et al., 2009), but are significantly lower than other airborne observations (up to 150 pptv) in the morning residual layer over an industrial region of Northern Italy (Li et al., 2014), where the levels of HONO precursors, such as NOx and pNO3, were much higher.

The range of the mixing ratio of NOx is from several pptv to around 1.6 ppbv. The mean (±1SD) and median values of NOx concentration are 96 (±52) pptv and 92 pptv in the FT, and 313 (±174) pptv and 278 pptv in the PBL. The mixing ratios of NOx are mostly between 50 - 150 pptv in the background conditions in the FT and between 200 - 500 pptv in the background conditions in the PBL. Similar to HONO, high values of NOx also occur in the urban and power plant plumes in the PBL (up to 1.6 ppbv) and in the biomass burning plumes in the FT (up to 0.6 ppbv).

Fewer measurement data points are available for pNO3, compared to those for NOx and HONO, due to air bubble formation in the flow cell of the pNO3 system, especially at high altitudes. The range of the mixing ratio of pNO3 is from 2 pptv to 216 pptv, with the mean (±1SD) and median values of 28 (±25) pptv and 21 pptv in the FT, and 78 (±47) pptv and 70 pptv in the PBL. The pNO3 levels were highly variable in both the FT and the PBL. In the FT, the pNO3 levels were often under 10 pptv, but high concentrations up to 115 pptv were also observed in elevated biomass burning plumes. In the PBL, high pNO3 levels were sometimes observed in relative clean conditions; whereas, low pNO3 levels were observed in high HONO and NOx power plant plumes. Both the N(V) level (= [HNO3] + [pNO3]) and the partitioning between HNO3 and pNO3 seem to play roles in determining the pNO3 level.

3.2 HONO contribution from ground-level sources

There are several ground-level HONO sources that may contribute to the HONO budget in the overlying atmosphere. They include anthropogenic sources, such as power plant and automobile emissions (Li et al., 2008b), and natural processes, such as soil emission (Maljanen et al., 2013; Oswald et al., 2013; Su et al., 2011), heterogeneous reactions of NO2 (Acker et al., 2006; George et al., 2005; Ndour et al., 2008, 2009; Ramazan et al., 2006) and...
surface HNO$_3$ photolysis (Ye et al., 2016b; Zhou et al., 2003, 2011). Since HONO photolytic lifetime is relatively short, e.g. 8 - 16 min in RF #4, RF #5, RF #11 and RF #17, a steep negative vertical gradient of HONO concentration would be expected if a significant contribution originated from the ground. The lack of a significant vertical gradient in the measured HONO concentrations (Fig. 3) thus suggests that the ground contribution is either limited to the shallow layer of the boundary layer near the ground, below the C-130 lowest flight altitude of 300 m, or small relative to the *in situ* production of HONO in the air column (Ye et al., 2017).

To further examine the potential HONO contribution from the ground sources, vertical profiles of HONO, NO$_x$, and pNO$_3$, are compared with those of potential temperature (K) and isoprene measured, for example, in the first race-track of RF#4 from 11:00 – 12:15 LT (Fig. 4). Indeed, the measurements conducted in the PBL from 300 m to 1200 m were above the unstable surface layer, as indicated by the constant potential temperature (Fig. 4e). The vertical distribution of isoprene originating from the ground can be expressed with the following equation (Eq. 1):

$$\ln\left(\frac{C}{C_0}\right) = -\frac{k\tau}{H} h = -\frac{h}{h^*}$$

(Eq. 1)

where, $C$ and $C_0$ are its concentrations near the ground and at the altitude $h$, $k$ is the pseudo-first order degradation rate constant, $H$ is the boundary layer height, $\tau$ is the average mixing time in the PBL, and $h^* (= H/(k\tau))$ is its characteristic transport height within one degradation lifetime of isoprene. According to the best fit of (Eq.1) to the observed isoprene data (Fig. 4d), its characteristic transport height $h^*$ is estimated 692 m for isoprene. Assuming isoprene is mainly oxidized by the OH radical whose average concentration is estimated at $3 \times 10^6$ mole cm$^{-3}$ in the PBL (Kaser et al., 2015), the pseudo-first order degradation rate constant of $~3.0 \times 10^4$ s$^{-1}$ (or the degradation rate of $~0.93$ h$^{-1}$) is determined for isoprene. Based on a boundary layer height of $~1.2$ km (Fig. 4e), an average PBL mixing time $\tau$ is estimated to be $~1.6$ h between 11:00 – 12:15 LT of RF #4. With a photolytic lifetime of $~11$ min for HONO, the estimated characteristic transport height of HONO is 138 m between 11:00 – 12:15 LT in RF #4, well below 300 m, the lowest flight altitude of the C-130 aircraft during this field study. Therefore, the instrument on-board the C-130 would not detect the HONO contribution from the ground sources during this race-track profiling around noontime. However, it is interesting to note that there was a slight increase in HONO concentration at the two lowest altitudes (Fig. 4a), which may be attributed to the increasing concentrations of its precursors, NO$_x$ and pNO$_3$ (Fig. 4b, c), both which are much longer lived than HONO.
Apart from the rapid photolytic loss of HONO, the rate of vertical mixing plays an important role in limiting the transport height of HONO in the PBL. The vertical mixing of the PBL is enhanced from the morning to the afternoon, as the ground surface is heated by solar radiation gradually during the day. The average mixing time in the PBL is reduced from ~ 3 h in the morning, to ~ 1.5 h around noontime, and to ~ 30 min in the afternoon, determined from isoprene gradients from RF #4, #5 and #17. The characteristic transport height of HONO would be ~ 500 m in the afternoon, i.e., some of the ground emitted HONO could survive and be transported to lower measurement altitudes, and thus may be detected by our profile measurements. However, the contribution from ground HONO sources to the observed HONO concentrations in the PBL above 300 m appear to be limited, as indicated by the lack of consistent vertical HONO gradient above the altitude of 300 m (Fig. 3a) in all the race track flights.

### 3.3 Daytime HONO chemistry in low NOx areas

After removing the data measured in the urban and power plant plumes, the daytime HONO concentrations are mostly within the range of 5 - 15 pptv throughout the PBL in the background terrestrial areas in the five race-track research flights. Photolysis of HONO is its dominant sink, with a photolysis lifetime of 8 - 16 min during these four daytime flights (RF #4, RF #5, RF #11, and RF #17). Therefore, there must be a significant volume HONO source, up to 200 pptv h\(^{-1}\), within the air mass to sustain the observed HONO concentrations. Both NO\(_x\) and pNO\(_3\) are potential HONO precursors in the air column. Figure 5 shows the correlation analysis of HONO with NO\(_x\) and pNO\(_3\) in the background terrestrial air masses during the five flights. While HONO correlates relatively well with NO\(_x\) (\(r^2 = 0.52\)), with a fitted HONO/NO\(_x\) ratio around 0.04, it only weakly correlates with pNO\(_3\) (\(R^2 = 0.14\)) (Fig. 5).

It may appear at first that NO\(_x\) is a more important HONO precursor than pNO\(_3\). However, the detailed analysis below suggests that NO\(_x\) is only a minor precursor to the observed HONO, and photolysis of pNO\(_3\) is the major in situ HONO source.

The photo-stationary state HONO concentration ([HONO\(_{ps}\)]) was calculated using Equation 2 that takes into account all the known HONO source contributions from NO\(_x\)-related reactions, including gaseous reactions of OH and NO (R-1), excited NO\(_2\) (NO\(_2^*\)) and water vapor (R4) (Carr et al., 2009; Li et al., 2008a), NO\(_2\) and the hydroperoxyl-water complex (HO\(_2\)-H\(_2\)O) with an upper limit HONO yield of 3% (R5a)(Li et al., 2014; Ye et al., 2015), and heterogeneous reaction of NO\(_2\) on aerosol surfaces (R2) using an upper limit
uptake coefficient of $10^{-4}$ reported in the literature (George et al., 2005; Monge et al., 2010; Ndour et al., 2008, 2009; Stemmler et al., 2006, 2007):

$$[HONO]_{pss} = \frac{k_{-1}[NO][OH]+k_4[NO_2][H_2O]+ak_3[NO_2^+][H_2O]+k_2S_{aerosol}[NO_3]}{J_{HONO}+k_{OH-HONO}[OH]}$$  \hspace{1cm} (Eq. 2)

where $S_{aerosol}$ is the aerosol surface area density. Under typical daytime conditions in the PBL with the median measured values of reactants, the upper limit $[HONO]_{pss}$ value is less than 2 pptv, much lower than the median measured HONO concentration of ~ 11 pptv. Figure 6a shows the relationship ($r^2 = 0.44$) between the photolytic HONO loss rate with the sum of HONO production rates from all the NOx-related reactions calculated with upper-limit reaction rate constants. A slope of about 0.19 indicates that the contribution from these NOx-related reactions to the volume HONO source is minor in the background troposphere, despite the good correlation between HONO and NOx. The high HONO/NOx ratios up to 0.24 in the low-NOx air masses are indicative of more important contributions from other HONO precursors, such as pNO3.

Photolysis of HNO3 on surfaces has been found to proceed at a much higher rate than in the gas phase (Baergen and Donaldson, 2013; Du and Zhu, 2011; Ramazan et al., 2004; Ye et al., 2016b; Zhou et al., 2003; Zhu et al., 2008), with HONO as the major product on environmental surfaces (Ye et al., 2016a, 2017). Furthermore, photolysis of particulate nitrate has been found to be the major daytime HONO source in the marine boundary layer (Ye et al., 2016b). To examine the role of particulate nitrate as a potential HONO source in the troposphere, aerosol samples over the terrestrial areas were collected on Teflon filters on board the C-130 aircraft during the NOMADSS 2013 summer field study and were used in the light-exposure experiments to determine the photolysis rate constants for particulate nitrate in the laboratory. The determined pNO3 photolysis rate constant ($J_{pNO3}^N$) varies over a wide range, from $8.3 \times 10^{-5}$ s$^{-1}$ to $3.1 \times 10^{-4}$ s$^{-1}$, with a median of $2.0 \times 10^{-4}$ s$^{-1}$ and a mean (± 1 standard deviation) of $1.9 \pm 1.2 \times 10^{-4}$ s$^{-1}$, when normalized to tropical noontime conditions at ground level (solar zenith angle = 0°), and the average HONO to NO2 relative yield is 2.0 (Ye et al., 2017). Figure 6b shows the relationship between the photolytic HONO loss rate ($J_{HONO} \times [HONO]$) and the volume HONO production rates from pNO3 photolysis ($2/3 \times J_{pNO3}^N \times [pNO3]$). The median $J_{pNO3}^N$ of $\sim 2.0 \times 10^{-4}$ s$^{-1}$ was used to calculate the ambient $J_{pNO3}$ by scaling to $J_{HONO}$:

$$J_{pNO3} = J_{pNO3}^N \times \frac{J_{HONO}}{7.6 \times 10^{-4} \tau^{-1}}$$  \hspace{1cm} (Eq. 3),
where \( J_{HNO_3} \) is the photolysis rate constant of gas-phase HNO\(_3\) calculated from light intensity measurement on the C-130 aircraft, and \( 7.0 \times 10^{-7} \text{ s}^{-1} \) is the photolysis rate constant of gas-phase HNO\(_3\) under the tropical noontime condition at ground level (solar zenith angle = 0°). A slope of 0.67 can be derived from Figure 6b, suggesting that pNO\(_3\) photolysis is the major volume HONO source. However, the \( r^2 \) of 0.31 is not as strong as expected from pNO\(_3\) photolysis being the major volume HONO source. The lower than expected correlation coefficient may be due to the fact that only a single median \( J_{pNO_3}^N \) value of \( \sim 2.0 \times 10^{-4} \text{ s}^{-1} \) is used in the calculations of the ambient \( J_{pNO_3} \) and the production rates of HONO in Figure 6b, while the actual pNO\(_3\) photolysis rate constants determined from seven NOMADSS aerosol samples are highly variable, ranging from \( 8.3 \times 10^{-5} \text{ s}^{-1} \) to \( 3.1 \times 10^{-4} \text{ s}^{-1} \) (Ye et al., 2017). The production rates of HONO in Figure 6b are thus only rough estimates of the in situ HONO production rates from pNO\(_3\) photolysis in different air masses.

HONO photolysis has been found to be an important or even a major OH primary source in the atmosphere near the ground surface (Elshorbany et al., 2010; He et al., 2006; Kleffmann et al., 2003; Villena et al., 2011; Zhou et al., 2011). However, HONO is not a significant daytime OH precursor in the background troposphere away from the ground surface. Based on the measurement results in this study, the contribution of HONO photolysis to the OH source budget (mean ± SD) is 52 ± 22 pptv h\(^{-1}\) in the PBL and 28 ± 20 pptv h\(^{-1}\) in the FT, respectively, less than 10% of the OH production contributed by O\(_3\) photolysis. However, since HONO is mainly produced from photolysis of particulate nitrate, it becomes an important intermediate product of a photochemical renoxification process recycling nitric acid and nitrate back to NO\(_x\). The regenerating rate of NO\(_x\) of about 52 pptv h\(^{-1}\) via HONO photolysis is equivalent to an air column NO\(_x\) source of \( \sim 2 \times 10^6 \text{ mol m}^{-2} \text{ h}^{-1} \) in the 1- km PBL, a considerable supplementary NO\(_x\) source in the low-NO\(_x\) background area.

### 3.4 HONO chemistry in plumes

One of the objectives of RF #11 was to study the chemistry of HONO in urban and coal fired power plant plumes. The arrows and corresponding labels in Figures 2 and 7 indicate the urban plumes (A – C) and power plant plumes (D - G). Benzene was used as the tracer of urban plumes (Liu et al., 2012; Shaw et al., 2015). Benzene peaks were observed in all urban plumes (A – C), but not in the power plant plumes (D – G). The power plant plumes were generated from high-intensity point sources, and thus had features of narrow but high peaks of both HONO and NO\(_x\) concentrations in the time-series plots (Figs. 2 and 7). In contrast, the
urban plumes were generated from area sources and thus were shown as broad peaks of HONO and NO\textsubscript{x} in the time-series plot with low levels of NO\textsubscript{x} (mostly below 500 pptv) (Fig. 2). There were a few sharp but small NO\textsubscript{x} peaks within the broad urban plumes, reflecting the contributions of some point sources in the urban areas. The observed HONO/NO\textsubscript{x} ratio was around 0.02 in the power plant plumes, lower than that of ~ 0.05 in urban plumes and in background terrestrial air masses. Based on the distances between measurement locations from the power plants or the centre of urban area and the observed wind speed, the transport times of these power plant plumes were estimated to be ≥1 h, over 5 times longer than HONO photolysis lifetime of 8 - 16 min. Therefore, most of the observed HONO in the power plant plumes was produced \textit{in situ} within the air masses. Since the typical emission ratio of HONO/NO\textsubscript{x} is less than 0.01 in the fresh power plant plumes and automobile engines (Kurtenbach et al., 2001; Li et al., 2008b), the elevated HONO/NO\textsubscript{x} ratios observed in the plumes suggest the presence of other HONO precursors, such as pNO\textsubscript{3}.

Figure 7b shows the time-series plot of HONO budget within the air masses sampled by the C-130 aircraft during flight RF# 11, comparing its photolysis loss rate with its production rates from pNO\textsubscript{3} photolysis and from all the NO\textsubscript{x}-related reactions combined. Photolysis of particulate nitrate appears to be the major volume HONO source in all urban plumes and in most of the power plant plumes except for plume G observed here (Fig. 7b). NO\textsubscript{x} was generally more important as a HONO precursor in the power plant plumes than in the urban plumes and in low-NO\textsubscript{x} background terrestrial air masses, due to higher levels of NO\textsubscript{x} (up to 1.6 ppb in Fig. 7a), OH radical and aerosol surface density. For example, all the NO\textsubscript{x}-related reactions combined contributed up to 52% of the total volume HONO source required to sustain the observed HONO concentration in plume G (Fig. 7b). In fresh power plant plumes encountered during the RF #7 to Ohio River Valley (X. Zhou, unpublished data), over 20 ppb NO\textsubscript{x} was detected, and the NO\textsubscript{x}-related reactions were found to account for almost all the required HONO source to sustain the observed HONO. The power plant plumes undergo rapid physical and photochemical evolution during the day, such as dilution and NO\textsubscript{x}-into-HNO\textsubscript{3} conversion. Thus, the relative contributions from NO\textsubscript{x}-related reactions and particulate nitrate photolysis as HONO sources change rapidly as the plumes age.

### 3.5 Night-time HONO chemistry

HONO accumulation near the ground surface during the nighttime has been widely observed (Kleffmann et al., 2003; Oswald et al., 2015; 2008; Stutz et al., 2002, 2010; VandenBoer et
al., 2013, 2014, 2015), contributed by various anthropogenic and natural HONO sources on the ground. The main objective of RF #18 was to study the night-time HONO evolution in both the nocturnal residual layer and the nocturnal FT. After sunset, the surface cooling promotes the formations of an inversion layer near the ground surface and a nocturnal residual layer above; the contribution from ground HONO sources then becomes negligible to the air masses beyond the surface inversion layer. Meanwhile, no effective HONO sinks, such as photolysis, oxidation by OH and dry deposition, exist in the nocturnal residual layer. Thus the HONO accumulation, if any, is a net contribution from dark heterogeneous NO\textsubscript{2} reaction on aerosol surfaces (R2).

The C-130 flew in an elongated race track pattern along a north-south direction, about 140 km from Nashville, TN (Fig. 1), alternating between the PBL (1200 m) and the FT (2500 m), from late afternoon to midnight local time (Fig. 2). In the FT, HONO and NO\textsubscript{x} concentrations were relatively stable throughout the afternoon and the night, staying around 4 ppt and 90 pptv respectively. The lack of night-time HONO accumulation is expected from the low levels of HONO precursors, mostly NO\textsubscript{2}, and surface area of aerosol particles in the FT (Fig. 2).

The conditions in the PBL were far more variable and complicated. There were strong horizontal gradients of NO\textsubscript{x}, pNO\textsubscript{3} and HONO in the PBL, with higher concentrations at the southern end and lower concentrations at the northern end of the flight track. Back-trajectory analysis using NOAA’s HYPLIT model (Stein et al., 2015) indicates that the encountered air masses in the PBL at the southern end passed over Nashville, about 140 km northeast of the sample area, with a transport time of about 6 h (Fig. 8a), while the air masses at the northern end stayed to north of Nashville (Fig. 8b). Therefore, the anthropogenic emissions from the metropolitan area of Nashville contributed to the higher concentrations of pollutants observed at the southern end of the flight track. There were also trends of increasing concentrations of NO\textsubscript{x}, pNO\textsubscript{3} and HONO with time after the sunset (Fig. 2). This was probably a result of less dispersion and dilution of anthropogenic pollutants, including NO\textsubscript{x}, as the PBL became more stable after sunset. Furthermore, as time progressed from late afternoon into evening and night, the air masses were less photochemically aged during the transport from the source areas, due to the decreasing solar light intensity and shorter solar light exposure time.

Because of the large spatial and temporal variations in the concentrations of HONO and its precursors in the PBL (Fig. 2), it is difficult to directly evaluate the nighttime HONO accumulation from HONO measurements alone. The concentration ratio of HONO and its
dominant nighttime precursor, NO₂, can be used as an indicator of nighttime HONO accumulation. As the air masses at measurement altitude of 1200 m decoupled from the ground-level processes after sunset, the HONO production from heterogeneous NO₂ reaction (R2) on aerosol surface becomes the only HONO source, and can be expressed by the following equations (Eq. 4 and Eq. 5):

\[
P(\text{HONO}) = \frac{1}{4} \times \left[ \frac{s}{v} \right] \times \sqrt{\frac{R T}{\pi M}} \times \gamma \times [\text{NO}_2] \quad \text{(Eq. 4)}
\]

\[
\frac{P(\text{HONO})}{[\text{NO}_2]} = \frac{1}{4} \times \left[ \frac{s}{v} \right] \times \sqrt{\frac{R T}{\pi M}} \times \gamma \quad \text{(Eq. 5)}
\]

where \(\left[ \frac{s}{v} \right]\) is the specific aerosol surface area density, \(R\) is the gas constant, \(K\) the absolute temperature, \(M\) the molecular weight of NO₂, and \(\gamma\) is the dark uptake coefficient of NO₂ leading to HONO production. The NO₂-normalized HONO accumulation over time, \(\Delta \frac{[\text{HONO}]}{[\text{NO}_2]}\), can then be calculated by equation (Eq. 6):

\[
\Delta \frac{[\text{HONO}]}{[\text{NO}_2]} \sim \frac{1}{4} \times \left[ \frac{s}{v} \right] \times \sqrt{\frac{R T}{\pi M}} \times \gamma \times \Delta t \quad \text{(Eq. 6)}
\]

Assuming a dark uptake coefficient \(\gamma\) of \(1 \times 10^{-5}\) of NO₂ on aerosol (George et al., 2005; Monge et al., 2010; Ndour et al., 2008; Stemmler et al., 2006, 2007) with a \(\left[ \frac{s}{v} \right]\) value of \(\sim 10^{-4}\) m⁻¹, a relative HONO accumulation rate, \(\Delta \frac{[\text{HONO}]}{[\text{NO}_2]}\)/\(\Delta t\) of \(\sim 0.0003\) h⁻¹ is estimated using the equation (Eq. 6), equivalent to a HONO accumulation of 0.13 pptv hr⁻¹ at a constant NO₂ concentration of 400 pptv. Such a low HONO accumulation rate is below our measurement detection limit. Indeed, the calculated HONO to the NOₓ ratio using the measurement data stayed almost unchanged with time (Fig. 9), well within the observational variability after the sunset, suggesting no significant volume production of HONO in the nocturnal boundary layer.

4 Conclusions

Substantial levels of HONO existed during the day in both the PBL (median ~ 11 pptv) and the FT (median ~ 4 pptv) over the Southeast U.S. during the NOMADSS 2013 summer field study. It appears that ground HONO sources did not significantly contribute to the HONO budget in the PBL above the minimum measurement heights of 300 m. Photolysis of particulate nitrate was the major volume HONO source in the background low-NOₓ air masses, while NOₓ was only a minor HONO precursor. Up to several tens pptv of HONO
were observed in coal fired power plant plumes and urban plumes during the day; the major
HONO precursor could be either NO\textsubscript{x} or pNO\textsubscript{3} depending on the chemical characteristics and
photochemical age of the plumes. No significant night-time HONO accumulation was
observed in the nocturnal residual layer and the free troposphere, suggesting no significant
night-time volume HONO source due to low levels of NO\textsubscript{x} and specific aerosol surface area.
HONO was not a significant daytime OH precursor in the rural troposphere away from the
ground surface; however, HONO mainly produced from photolysis of particulate nitrate could
provide a renoxification pathway. The NO\textsubscript{x} regeneration rate of about 52 pptv h\textsuperscript{-1}
in rural PBL is a considerable supplementary NO\textsubscript{x} source in a low-NO\textsubscript{x} background region.

Acknowledgements

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References


Carr, S., Heard, D. E., and Blitz, M. A.: Comment on "Atmospheric hydroxyl radical production from electronically excited NO$_2$ and H$_2$O", Science, 324, 2009.


Table 1. Measurements from the NOMADSS 2013 summer study used in this analysis.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Instrument</th>
<th>Time</th>
<th>Resolution</th>
<th>Detection Limit</th>
<th>Accuracy</th>
<th>References</th>
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<tr>
<td>HONO</td>
<td>LPAP</td>
<td>200 s</td>
<td>1 pptv</td>
<td></td>
<td>20%</td>
<td>(1, 2)</td>
</tr>
<tr>
<td>pNO</td>
<td>LPAP</td>
<td>360 s</td>
<td>2 pptv</td>
<td></td>
<td>30%</td>
<td>(1, 2, 3)</td>
</tr>
<tr>
<td>HNO_3</td>
<td>LPAP</td>
<td>20 min</td>
<td>2 pptv</td>
<td></td>
<td>30%</td>
<td>(1, 2, 3)</td>
</tr>
<tr>
<td>NO</td>
<td>CI</td>
<td>1 s</td>
<td>2 pptv</td>
<td></td>
<td>10%</td>
<td>(4)</td>
</tr>
<tr>
<td>NO_2</td>
<td>CI</td>
<td>1 s</td>
<td>40 pptv</td>
<td></td>
<td>15%</td>
<td>(4)</td>
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<tr>
<td>O_3</td>
<td>CI</td>
<td>1 s</td>
<td>100 pptv</td>
<td></td>
<td>5%</td>
<td>(4)</td>
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<tr>
<td>OH</td>
<td>SICIMS</td>
<td>30 s</td>
<td>*5×10^4</td>
<td></td>
<td>30%</td>
<td>(5, 6)</td>
</tr>
<tr>
<td>HONO</td>
<td>DOAS</td>
<td>60 s</td>
<td>- 30 pptv</td>
<td></td>
<td>20%</td>
<td>(7)</td>
</tr>
<tr>
<td>Photolysis Frequencies</td>
<td>CAFS</td>
<td>6 s</td>
<td></td>
<td></td>
<td>10-15%</td>
<td>(8)</td>
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<tr>
<td>Surface area density</td>
<td>SMPS/UHSAS</td>
<td>65 s/1 s</td>
<td></td>
<td></td>
<td>20%</td>
<td>(9)</td>
</tr>
<tr>
<td>VOCs</td>
<td>PTRMS</td>
<td>15 s</td>
<td></td>
<td></td>
<td>20%</td>
<td>(10, 11)</td>
</tr>
<tr>
<td>VOCs/organic nitrates</td>
<td>TOGA</td>
<td>20 s</td>
<td></td>
<td></td>
<td>20%</td>
<td>(12)</td>
</tr>
</tbody>
</table>

*in molecules cm\(^{-3}\)

LPAP: long-path absorption photometric (LPAP) systems
CI: 4-channel chemiluminescence instrument
SICIMS: selected-ion chemical-ionization mass spectrometer
DOAS: Differential Optical Absorption Spectroscopy
CAFS: Charged-coupled device Actinic Flux Spectroradiometer
SMPS: Scanning Mobility Particle Sizer
UHSAS: Ultra-High Sensitivity Aerosol Spectrometer
PTRMS: Proton Transfer Reaction Mass Spectrometry
TOGA: Trace Organic Gas Analyzer

References: (1) Zhang et al., 2012; (2) Ye et al., 2016b; (3) Huang et al., 2002; (4) Ridley et al., 2004; (5) Hornbrook et al., 2011b; (6) Mauldin et al., 2010; (7) Platt and Stutz, 2008; (8) Shetter et al., 2002; (9) Flagan, 2011; (10) Karl et al., 2003; (11) de Gouw and Warneke, 2007; (12) Hornbrook et al., 2011a.
Table 2. Data statistics for HONO, NO\textsubscript{x} and pNO\textsubscript{3} measurements both in the PBL and the FT from the five Southeast U.S. research flights during the NOMADSS 2013 summer field study.

<table>
<thead>
<tr>
<th></th>
<th>HONO, pptv</th>
<th>NO\textsubscript{x}, pptv</th>
<th>pNO\textsubscript{3}, pptv</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PBL</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range</td>
<td>3.1 - 35.9</td>
<td>81 - 1635</td>
<td>7 - 216</td>
</tr>
<tr>
<td>Mean ± SD</td>
<td>11.2 ± 4.3</td>
<td>313 ± 174</td>
<td>79 ± 47</td>
</tr>
<tr>
<td>Median</td>
<td>10.6</td>
<td>278</td>
<td>70</td>
</tr>
<tr>
<td><strong>FT</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range</td>
<td>1.1 - 18.2</td>
<td>&lt;10 - 582</td>
<td>2 - 115</td>
</tr>
<tr>
<td>Mean±SD</td>
<td>5.4 ± 3.4</td>
<td>96 ± 52</td>
<td>28 ± 25</td>
</tr>
<tr>
<td>Median</td>
<td>4.2</td>
<td>92</td>
<td>21</td>
</tr>
</tbody>
</table>
Figure 2. Time series of altitude, HONO, NOx and pNO3 in five flights (RF #4, RF #5, RF #11, RF #17 and RF #18) in the Southeast US during the NOMADSS 2013 summer study. In RF #11, A-C indicate urban plumes, and D-G indicate coal-fired power plant plumes. The time is in UTC.
Figure 3. Vertical distributions of concentrations of HONO (a), NO\(_x\) (b), and pNO\(_3\) (c) in the five selected flights in the Southeast US during the NOMADSS 2013 summer study.
Figure 4. Vertical distributions of concentrations of HONO (a), NO\textsubscript{x} (b), pNO\textsubscript{3} (c), isoprene (d) and potential temperature (e) in the PBL during the first race-track of RF\#4 from 11:00 – 12:15 LT (16:00 – 17:15 UTC), June 12, 2013. The small open circles represent the 1-min data points, the large solid circles the mean values for each race-track measurement altitude. The line in (d) is the best fit of (Eq. 1) to the isoprene data: \( h = 5.97 - 0.692 \ln C \), \( r^2 = 0.93 \).
Figure 5. Correlation analysis of HONO with NO\textsubscript{x} (a, \(r^2=0.52\)) and pNO\textsubscript{3} (b, \(r^2 = 0.14\)) in the southeast US during the NOMADSS 2013 summer study. Data points in the urban and power plant plumes have been excluded.
Figure 6. Correlation analysis of main HONO sink ("HONO×J_{HONO}") with contribution from particulate nitrate photolysis, pNO$_3$×J$_{pNO3}$ (a) and with contribution from NO$_x$ related reactions (b) in the southeast US during the NOMADSS 2013 summer study. The line represents the least-squares fitting ($R^2=0.44$, intercept = -0.57 and slope = 0.19 for Figure 6a; $R^2=0.31$, intercept = 0.05 and slope = 0.67 for Figure 6b).
Figure 7. HONO budget analysis in RF #11 in the Southeast US during the NOMADSS 2013 summer study. “HONO sink” is the HONO loss rate contributed by photolysis and the reaction of HONO with OH radicals, “NOx related reactions” is the sum of HONO productions by all known NOx reactions, and “pNO3 photolysis” is the HONO source contributed by photolysis of pNO3.
Figure 8. Back trajectory analysis of air masses encountered in the PBL in RF #18 in the Southeast US during the NOMADSS 2013 summer study. The air masses arriving at the southern point of the flight tracks were found to pass over the metropolitan area of Nashville (the black circle, panel a), while those at the northern point to stay to the north of the area. The back trajectory analysis was made using NOAA’s online HYSPLIT model (http://www.arl.noaa.gov/HYSPLIT_info.php).
Figure 9. The evolution of HONO/NO\textsubscript{x} ratio in the nocturnal boundary layer during the RF#18. The red circles and blue squares are the median HONO/NO\textsubscript{x} values under the conditions of NO\textsubscript{x} \leq 400 pptv and NO\textsubscript{x} > 400 pptv, respectively. The horizontal bars indicate the averaging time periods and the vertical bars the one standard deviation of HONO/NO\textsubscript{x} ratios. The black dashed line is the least squared fit to the data, and the green dashed line indicates a slope of $3 \times 10^{-4}$ hr\textsuperscript{-1}. The sunset time at the sampling location was 0:40 UTC.