Response to the Interactive comment by Anonymous Referee #1 on "Tropospheric HONO Distribution and Chemistry in the Southeast U.S."

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The manuscript "Tropospheric HONO distribution and chemistry in the Southeast U.S." by Ye et al. presents HONO measurements made during the NOMADSS campaign. The two main claims presented here are: (1) there is more HONO observed than can be explained by known chemistry, and (2) photolysis of particle nitrate accounts for this so-called missing HONO source. The analysis used to make both claims are weak, therefore, unconvincing. Moreover, the analysis on nighttime chemistry and production in power plant exhaust were hastily done and written. This work can be considered for publication only after significant improvements.

Response: We thank the Anonymous Referee #1 for pointing out the shortcomings in our analysis and presentation of the data. We have significantly revised the manuscript accordingly to address the referee's comments and concerns. Here are our responses to the referee's specific comments.

As for (1), the authors claim that because HONO photo-lifetime is 8 minutes, that direct emission of HONO can be disregarded. This is a misinterpretation of the concept of lifetime. Lifetime represents an e-folding time, meaning that ~36% of the original amount still remains after 8 minutes since time zero, or time since emission. If HONO at the emission source is 10 ppb, approximately 50 to 60 minutes is required for HONO to reach 11 ppt, the median HONO level reported. Judging by figure 2, the median HONO value of 11 ppt (what the authors claim is anthropogenic-free HONO) is observed in close proximity to urban plumes (20 to 30 ppt, identified in figure 2). This 50 to 60 minute period is an underestimate since it does not account for re-formation of HONO by OH + NO, both of which are likely to be elevated in urban plumes. Bottom line is that the authors need to demonstrate convincingly that the 11 ppt HONO is not derived from anthropogenic sources (by quantitatively accounting for mixing, emissions, and chemistry), because the case for this so-called 'extra' HONO is the difference between 11 ppt and 2 ppt (amount of HONO expected assuming PSS without this 'extra' source). The analysis as it currently stands in inadequate.

Response: The referee is correct that ~36% of the original HONO remains after one photolysis lifetime. However, we did not "disregard" the contribution from ground HONO source simply because HONO photo-lifetime is 8 minutes. We would first like to point out that there has not been any report in literature for 10 ppbv daytime HONO on the ground level, as the referee assumed. The daytime HONO/NO_x ratio is in the range of 0.05-0.1 in the low-NO_x rural atmosphere (Zhou et al., 2002) and ~ 0.02 in high-NO_x urban environment (Villena et al., 2011). The direct emission HONO/NO_x ratios are even lower, ≤0.01 in automobile exhausts (Kirchstetter et al., 1996; Li et al., 2008) and ~0.002 in power plant plumes (Neuman et al., 2016). The NO_x levels that we observed in the Southeast U.S. was mostly under 0.5 ppbv in the background area and even in the urban plumes; the initial HONO concentration associated with the observed levels of NO_x would be ≤ 50 pptv even if an upper limit HONO/NO_x ratio of 0.1 is assumed. With a transport time of ~1 h from the source, i.e., ~ 5 times of the HONO photolysis lifetime, the contribution from the source would be well below the detection limit of 1 pptv of our HONO instrument. Therefore, we argued that the measured HONO was mostly produced *in* *situ* from precursors such as NO_x and pNO_3 within the air masses during the transport, not from the ground HONO sources.

Our conclusion of no significant contribution from the ground HONO source was also based on the vertical profile of HONO. We examined the vertical profiles of HONO, its precursor, isoprene and potential temperature (Figure 4) in section "3.2 HONO contribution from ground-level sources". Isoprene is a biogenic VOC emitted from ground vegetations (trees) and has a lifetime of ~1 hr. Based on isoprene vertical distribution information, a TBL mixing time can be estimated. The photolysis lifetime of HONO was much shorter than that of isoprene during the daytime NOMADSS flights. If the ground source contributed significant to the TBL HONO budget, a much steeper vertical concentration gradient than that of isoprene should be expected. However, we observed relatively uniform vertical concentration profiles (Figs. 3 and 4), suggesting that contribution from ground HONO source was not important.

We did not randomly assign an air mass as "background" or "urban" just based on HONO concentrations. In the four daytime research flights (RFs #4, #5, #11 and #17) reported in this manuscript, we conducted our airborne HONO measurements mostly over the rural regions in Southeast U.S., and only sampled urban and power plumes sometimes in RF #11 (Figure 2). A large suite of chemical and metrological parameters were measured onboard the C-130. The identifications of plumes and background air masses were done with the help of plumes tracers like NO_x, and benzene (Figure 7) in original manuscript, further with SO_2, CO, and acetonitrile (Figure S1) in the revised manuscript. And in RF #18, we performed back trajectory calculations to examine the impact of urban plume from Nashville metropolitan area. Indeed, HONO was being produced from its precursors (including the OH-NO reaction the referee mentioned) in the air mass during the transport. The HONO is considered *in situ* produced, not directly emitted. When an air mass was influenced by the urban emission, concentrations of HONO precursors and urban tracers (NO_x, CO, benzene) were higher, and *in situ* HONO production would be higher.

We have significantly revised the discussion in the manuscript in both "3.2 HONO contribution from ground-level sources" and "3.4 HONO chemistry in plumes", to address referee's concerns and to make our argument more clearly.

As for (2), the authors conclude a causal relationship between photolysis of particulate nitrate and HONO based on rather weak correlation (figure 5). That is less than convincing. Moreover, a photolysis rate of 2e-4 sec-1 means a photo-lifetime less than 1.5 hours for particulate nitrates. What are these nitrates? inorganic or organic? Has there been any reports of particle-phase nitrates exhibiting photo-lifetimes on the order of 1.5 hours? Is there a mechanism proposed? What remains in the particle-phase as the nitrate is released as HONO? Is all of the nitrate turn into HONO, or NO or NO2 or HNO3? I am concerned the photolysis conducted in the laboratory is not atmospherically relevant. More information on this lab photolysis experiment may help. How do the nitrate abundances measured with this filter method compare to what other instruments (AMS? PILS?) have measured for particle nitrates? And as for the power plant analysis, the same concerns I have for claim (1) applies here. You cannot assume just because the plume has been transported over 1 hour that none of the HONO observed is anthropogenic in origin. You need to know what the mixing ratio was near the emission point to know whether the HONO measured downwind was or was not directly emitted because the photo-lifetime is an e-folding time, it does not just disappear after 8 minutes. Lastly, citing previous work on the *subject could be useful. Recent work by Neuman et al. 2016 comes to mind (https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1002/2016JD025197).*

Response: We disagree with the referee that our conclusion was based on weak correlation. The conclusion that inorganic particulate nitrate (pNO_3) photolysis is a major HONO source in the air column in Southeast U.S. was first based on directly field observation and HONO budget analysis. With comprehensive parameters related to HONO chemistry were directly measured in our study, we were able to conduct HONO budget analysis. The analysis suggested that known NO_x-related reactions can only sustain a minor fraction of the observed HONO source and there was a major fraction of HONO source strength unaccounted in the air column. If particulate nitrate behaves similarly to surface HNO_3 photochemically, i.e., with a photolysis rate constant 2-3 order of magnitude higher than that in the gas phase (e.g., Baergen and Donaldson, 2013; Reed et al., 2017; Ye et al., 2016b, 2017a; Zhou et al., 2003, 2011; Zhu et al, 2010, 2015), it could be a potentially important HONO precursor. To examine the potential role of pNO_3 as a HONO precursor, we collected aerosol samples on Teflon filters on the C-130 during the NOMADSS field study and determined the photolysis rate constants of particulate nitrate leading to the productions of HONO (a major product) and NO_2 (a minor product). High and highly variable J^N_{pNO3} values were obtained, from 8.3×10^{-5} s^{-1} to 3.1×10^{-4} s^{-1}, with a median of 2.0×10^{-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 = $0\,^{o}$) (Ye et al., 2017b). The laboratory measurement of J_{pNO3} has been described and discussed in detail in our previous paper (Ye et al., 2017b). HONO budget analysis using the median $J^N_{pNO_3}$ value of 2.0×10^{-4} s^{-1} suggests that pNO_3 photolysis can account for most of the remaining HONO source strength (the original Figures 6b and 7b, and now the revised Figures 5b and 6).

The correlation between HONO and its potential precursor pNO_3 (the original Figure 5, and now the revised Figure S1) is quite weak (r^2 ~0.17), as pointed out by the referee. The correlation between the required HONO source and the contribution from particulate nitrate photolysis ($[pNO_3] \times J_{pNO3}$) improved somewhat ($r^2 = 0.34$) (the original Figures 6b, now the revised Figure 5b), but is still not as strong as to be expected from pNO_3 photolysis being the major HONO source. As we explained in the manuscript (lines 338-343), "It may be in part due to the use of a single median J^N_{pNO3} value of ~ 2.0×10^{-4} s^{-1} in the calculations of the ambient J_{pNO_3} and the production rates of HONO in Figure 5b; the actual J^N_{pNO3} values are highly variable, ranging from 8.3×10^{-5} s^{-1} to 3.1×10^{-4} s^{-1} (Ye et al., 2017). HONO source contribution from particulate nitrate photolysis in Figure 5b are thus estimates of the *in situ* HONO production rates from pNO_3 photolysis in different air masses."

The photolysis lifetime of pNO_3 was short using the median value of laboratory determined J_{pNO3}, as the referee pointed out. Many laboratory and field studies have shown the high photolysis rate constant of surface HNO_3 (Baergen and Donaldson, 2013; Ye et al., 2016a; Zhou et al., 2003, 2011; Zhu et al, 2010, 2015) and pNO_3 (Reed et al.; Ye et al., 2017a, 2017b), lending support to our argument that pNO_3 photolysis can be an effective renoxification pathway to recycle nitric acid to photochemically reactive NO_x and HONO. However, we would like to point out that particulate nitrate is in a dynamic equilibrium with gas-phase HNO_3, and that the later accounts for a larger (or even dominant) fraction of total nitrate (pNO_3+HNO_3) and is photochemically inert. The overall photolysis of total nitrate (pNO_3+HNO_3) would be much slower than indicated by J_{pNO3}. In addition, oxidation of NO_x via several pathways will replenish the pNO_3+HNO_3 reservoir. The results reported in this manuscript and in earlier papers (Reed et al., 2017; Ye et al., 2016a) suggest that there is an effective cycling in reactive nitrogen species in the low-NO_x atmosphere, sustaining the observed levels of HONO and pNO_3.

Some mechanisms have been proposed to explain the large enhancement of photolysis rate constant for surface HNO_3 and pNO_3, by 2-3 orders of magnitude compared to that of gas-phase HNO_3. The light absorption by HNO_3 in the UV range has been found to be 1-4 orders of magnitude higher on surfaces of silicon and ice than in the gas phase, with a significant red shift to long wavelength (Du et al., 2011; Zhu et al., 2008, 2015), probably resulting from bond stretching and/or bond deformation (Svoboda et al., 2013). Since the photolysis yield stays relatively high, 0.8-0.9 (Zhu et al, 2010), the resulting effect of the catalytic surface is the enhancement of photolysis rate constant over that in gas phase. In addition, organic and inorganic chromophores on ambient surfaces and in aerosol particles can enhance the photolysis of the associated HNO_3 and nitrate through photosensitization (Ye et al., 2016b, 2017b). We also hypothesized that NO_2 is the dominant primary product of the photolysis of surface HNO_3 and pNO_3, and the produced NO_2 (adsorbed) may react quickly with organics and water molecules on the surface and in aerosol particles to produce HONO as the secondary product. The proposed mechanism explains the laboratory results showing NO_2 as the dominant product from HNO_3 photolysis on clean and dry laboratory surfaces (Zhou et al., 2003; Zhu et al., 2010), while HONO as the major product on natural surfaces and in ambient aerosols (Ye et al., 2016a, 2017b).

We have not got the chance to compare our LPAS pNO_3 method with other instruments. We would like to do that as soon as we have the opportunity.

As to the issue of power plant plumes raised by the referee, the answer is similar to what we just provided for urban plumes. That is, the power plant plumes we encountered were small and relatively diluted with NO_x levels up to 1.8 ppbv (Figures 2 and 7), and the directly emitted HONO would be ≤ 18 pptv ppbv even if a high HONO/NO_x emission ratio of 0.01 is assumed (Neuman et al., 2016). During the 1-h transport time, the remaining HONO concentration from the direct emission would be well below our detection limit of 1 pptv. Therefore, the HONO concentrations in the power plant plumes were mostly produced within the air mass during the transportation, from elevated HONO precursors from anthropogenic sources. In fact, the HONO measured in fresh power plant plumes has been found to be mostly secondarily produced (Neuman et al., 2016).

Lastly, we regret the omission to reference the recent paper by Neuman et al. (2016). We finished our first draft of this manuscript over two years ago, before the publication of the mentioned paper. Although we have made significant changes to the draft during the subsequent revisions, we failed to update the references. The paper by Neuman et al. (2016) has been referenced and discussed in the revised manuscript.

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