

***Interactive comment on* “Tropospheric HONO Distribution and Chemistry in the Southeast U.S.” by Chunxiang Ye et al.**

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

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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.

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

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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 pNO₃ 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 vegetation (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)

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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 SO₂, 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.

We disagree with the referee that our conclusion was based on weak correlation. The conclusion that inorganic particulate nitrate (pNO₃) 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 HNO₃ 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

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pNO₃ 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 NO₂ (a minor product). High and highly variable J_{NpNO₃} values were obtained, from $8.3 \times 10^{-5} \text{ s}^{-1}$ to $3.1 \times 10^{-4} \text{ s}^{-1}$, with a median of $2.0 \times 10^{-4} \text{ s}^{-1}$ and a mean (± 1 standard deviation) of $1.9 (\pm 1.2) \times 10^{-4} \text{ s}^{-1}$, when normalized to tropical noontime conditions at ground level (solar zenith angle = 0°) (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_{(pNO₃)^N} value of $2.0 \times 10^{-4} \text{ s}^{-1}$ suggests that pNO₃ 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 pNO₃ (the original Figure 5, and now the revised Figure S1) is quite weak ($r^2 \sim 0.17$), as pointed out by the referee. The correlation between the required HONO source and the contribution from particulate nitrate photolysis ([pNO₃] × 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 pNO₃ 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_{pNO₃)^N value of $\sim 2.0 \times 10^{-4} \text{ s}^{-1}$ in the calculations of the ambient J_{(pNO₃)^N} and the production rates of HONO in Figure 5b; the actual J_{pNO₃)^N values 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). HONO source contribution from particulate nitrate photolysis in Figure 5b are thus estimates of the in situ HONO production rates from pNO₃ photolysis in different air masses.”}}

The photolysis lifetime of pNO₃ 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 HNO₃ (Baergen and Donaldson, 2013; Ye et al., 2016a; Zhou et al., 2003, 2011; Zhu et al, 2010, 2015) and pNO₃ (Reed et al.; Ye et al., 2017a, 2017b), lending support to our argument that pNO₃ photolysis can be an effective renoxification pathway to recycle nitric acid to photochemically re-

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active NO_x and HONO. However, we would like to point out that particulate nitrate is in a dynamic equilibrium with gas-phase HNO₃, and that the later accounts for a larger (or even dominant) fraction of total nitrate (pNO₃+HNO₃) and is photochemically inert. The overall photolysis of total nitrate (pNO₃+HNO₃) would be much slower than indicated by JpNO₃. In addition, oxidation of NO_x via several pathways will replenish the pNO₃+HNO₃ 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 pNO₃.

Some mechanisms have been proposed to explain the large enhancement of photolysis rate constant for surface HNO₃ and pNO₃, by 2-3 orders of magnitude compared to that of gas-phase HNO₃. The light absorption by HNO₃ 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 HNO₃ and nitrate through photosensitization (Ye et al., 2016b, 2017b). We also hypothesized that NO₂ is the dominant primary product of the photolysis of surface HNO₃ and pNO₃, and the produced NO₂ (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 NO₂ as the dominant product from HNO₃ 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 pNO₃ method with other instru-

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ments. 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.

References

Baergen, A. M., and Donaldson, D. J.: Photochemical renoxification of nitric acid on real urban grime, *Environ. Sci. Technol.*, 47, 815-820, 10.1021/es3037862, 2013.

Du, J., and Zhu, L.: Quantification of the absorption cross sections of surface-adsorbed nitric acid in the 335-365 nm region by Brewster angle cavity ring-down spectroscopy, *Chem. Phys. Lett.*, 511, 213-218, 10.1016/j.cplett.2011.06.062, 2011.

Kirchstetter, T. W, Harley, R.A., and Littejohn, D.: Measurements of nitrous acid in motor vehicle exhaust, *Environ. Sci. Technol.*, 30 (9), 2843–2849, 1996.

Li, Y. Q., Schwab, J. J., and Demerjian, K. L.: Fast time response measurements

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of gaseous nitrous acid using a tunable diode laser absorption spectrometer: HONO emission source from vehicle exhausts, *Geophys. Res. Lett.*, 35, 2008.

Neuman, J. A., et al.: HONO emission and production determined from airborne measurements over the Southeast U.S., *J. Geophys. Res. Atmos.*, 121, 9237–9250, doi:10.1002/2016JD025197, 2016
Reed, C. et al.: Evidence for renoxification in the tropical marine boundary layer, *Atmos. Chem. Phys.*, 17, 4081–4092, 2017.

Svoboda, O.; Kubelova, L.; Slavicek, P.: Enabling forbidden processes: Quantum and solvation enhancement of nitrate anion UV absorption, *J. Phys. Chem. A*, 117, 12868–12877, 2013.

Villena, G., Kleffmann, J., Kurtenbach, R., Wiesen, P., Lissi, E., Rubio, M. A., Croxatto, G., and Rappengluck, B.: Vertical gradients of HONO, NO_x and O₃ in Santiago de Chile, *Atmos. Environ.*, 45, 3867–3873, 2011.

Ye, C., et al.: Rapid cycling of reactive nitrogen in the marine boundary layer, *Nature*, 532, 489–491, 2016a.

Ye, C., Gao, H., Zhang, N., and Zhou, X.: Photolysis of nitric Acid and nitrate on natural and artificial surfaces, *Environ. Sci. Technol.*, 50, 3530–3536, 2016b.

Ye, C., Heard, D.E., and Whalley, L.K.: Evaluation of novel routes for NO_x formation in remote regions, *Environ. Sci. Technol.*, DOI: 10.1021/acs.est.6b06441, 2017a.

Ye, C., Zhang, N., Gao, H., and Zhou, X.: Photolysis of particulate nitrate as a source of HONO and NO_x, *Environ. Sci. Technol.*, DOI: 10.1021/acs.est.7b00387, 2017b.

Zhou, X., Civerolo, K., Dai, H., Huang, G., Schwab, J., and Demerjian, K.: Summertime nitrous acid chemistry in the atmospheric boundary layer at a rural site in New York State, *J. Geophys. Res.*, 107, doi:10.1029/2001JD001539, 2002.

Zhou, X., Gao, H., He, Y., Huang, G., Bertman, S. B., Civerolo, K., and Schwab, J.: Nitric acid photolysis on surfaces in low-NO_x environments: Significant atmospheric

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implications, *Geophys. Res. Lett.*, 30, 2217, 10.1029/2003gl018620, 2003.

Zhou, X., Zhang, N., TerAvest, M., Tang, D., Hou, J., Bertman, S., Alaghmand, M., Shepson, P. B., Carroll, M. A., Griffith, S., Dusanter, S., and Stevens, P. S.: Nitric acid photolysis on forest canopy surface as a source for tropospheric nitrous acid, *Nature Geosci.*, 4, 440-443, 10.1038/NGEO1164, 2011.

Zhu, C. Z., Xiang, B., Zhu, L., and Cole, R.: Determination of absorption cross sections of surface-adsorbed HNO₃ in the 290-330 nm region by Brewster angle cavity ring-down spectroscopy, *Chem. Phys. Lett.*, 458, 373-377, 2008.

Zhu, C., Xiang, B., Chu, L.T., and Zhu, L.: 308 nm Photolysis of nitric acid in the gas phase, on aluminum surfaces, and on ice films, *J. Phys. Chem. A*, 114, 2561-2568, 2010.

Zhu, L., Sangwan, M., Huang, L., Du, J., and Chu, L.T.: Photolysis of nitric acid at 308 nm in the absence and in the presence of water vapor, *J. Phys. Chem. A*, 119, 4907-4914, 2015.

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<https://www.atmos-chem-phys-discuss.net/acp-2018-105/acp-2018-105-AC3-supplement.pdf>

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