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

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Response to interactive comment on manuscript on "Tropospheric HONO Distribution and Chemistry in the Southeast U.S." by D. Parrish

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We completely agree with David Parrish that "Extraordinary claims require extraordinary evidence." However, we disagree that our finding that ". . .the sum of all known NOx-related HONO formation mechanisms was found to account for less 20% of the daytime HONO source in the background terrestrial air masses, ..." is an extraordinary claim. In high NOx environments, such as urban atmosphere and power plant and biomass burning plumes, NOx is known to be the dominant precursor to HONO. How-

ever, in low NOx environments, such as the rural regions in the Southeast US, other precursors become more important. In fact, there have been many reports in literature, based on both field and laboratory results, demonstrating that several processes other than reactions involving ambient NOx can lead to the production of HONO. Nitrate photolysis in snowpack has been found to be a major source for HONO and NOx during the polar spring and summer in the polar regions (Beine et al., 2002, 2008; Honrath et al., 2000, 2002; Zhou et al., 2001). In low-NOx rural and forested regions, photolysis of nitric acid on the forest canopy surface has been found to be the major daytime HONO source (Ye et al., 2016a; Zhou et al., 2002, 2003, 2011). Photolysis of particulate nitrate has been found to be the major HONO source in the low-NOx marine boundary layer (Reed et al, 2017; Ye et al., 2016b). And in agricultural regions, biochemical process in the soils (denitrification or nitrification) has been found to account for the majority of HONO budget (Oswald et al., 2013; Su et al., 2012; Meusel et al., 2018).

We estimated the HONO formation rates from known homogeneous and heterogeneous NOx reactions, with a suit of parameters measured on board the C-130, and found the sum of these mechanisms to contribute less than 20% of the total HONO source strength in the background air masses. Most of the remaining so-called "unknown" 80% can actually be accounted for by the photolysis of particulate nitrate (lines 302 - 331 in the original manuscript). This finding is consistent with several reported laboratory studies that the photolysis of surface nitric acid and particulate nitrate is 2 - 3 orders faster than that of gaseous nitric acid (Baergen and Donaldson, 2013, Ye et al., 2016a, 2017a; Zhou et al., 2003; Zhu et al, 2010, 2015), producing mostly NO2 on clean dry surface (Ye et al., 2016a; Zhou et al., 2003; Zhu et al, 2010) and mainly HONO on natural surfaces and ambient aerosols (Ye et al., 2016a, 2017a).

We would also like to point out that while HONO photolysis can be a significant or even a major HOx source on the ground level in both rural and urban atmosphere (Acker et al., 2006a,b; Elshorbany et al., 2010; Kleffmann et al., 2003, 2005; Villena et al., 2011), it was found unimportant compared to photolyses of O3 and HCHO in the background air masses aloft over the Southeast US. At the observed levels of 5-11 pptv, the answer to the HONO source question is unlikely to significantly affect our understanding of HOx chemistry in the rural troposphere. On the other hand, since HONO was found to be mainly produced from photolysis of particulate nitrate, it is an important intermediate product of a photochemical renoxification process recycling nitric acid and nitrate back to NOx.

We regret that we did not reference the recent paper by Neuman et al. (2016). We prepared and 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 first draft during the subsequent revisions, we failed to update the references. We have referenced and discussed the paper in the revised manuscript (lines 64, 95, 211, 215, 239, 282, 403). It is important to point out that there is no major disagreement in the results between the two aircraft-based studies. Similar to what reported by Neuman et al. (2016), we found that the NOx-related reactions (mainly NO+OH reaction) accounted for nearly all the required HONO source in the large fresh power plant plume (NOx ~ 20 ppbv) encountered during the RF #7 to Ohio River Valley (lines 375-378 in the original manuscript). In the smaller and more diluted power plant plume G in the original Figures 2c and 7b (NOx ~1.8 ppb), NOx-related reactions contribute to a major fraction (52%) of the total required HONO source (the original Figure 7b). In the low-NOx background air masses, the mean HONO concentration was 11.2 ± 4.3 pptv in the PBL and 5.6 ± 3.4 in the free troposphere (Table 2), which is again in agreement the value reported by Neuman et al (2016) “indistinguishable from zero within the 15 parts per trillion by volume measurement uncertainty.” We would further argue that while the CIMS instrument, with detection limits of 40 pptv for 1-s data and 15 pptv for 30-min averaging, is capable of producing high quality data in the plumes, it does not have the sensitivity to measure low levels of HONO in the low-NOx background atmosphere. The conclusion based on its below-detection-limit measurements and on the extrapolations from combustion plumes to low-NOx background atmosphere is not reliable and thus should not be used to rule out the findings based on our measurement

in the low-NOx rural atmosphere. The relative contribution of NOx-related reactions is in the order of power plant plume (NOx ~ 1- 20 ppb) > urban plume (NOx ~ 1 ppb) > background terrestrial air masses (NOx ~100-300 pptv). That is, the relative contribution from NOx-related reactions to the required HONO source is highly dependent on the NOx regimes. While the conclusion we draw in the high NOx regime in large power plant plumes is not different from that by Neuman et al. (2016), our measurements have added new and valuable HONO budget information in low NOx regime to the literature.

We appreciate the question regarding potential problems with experimental design/measurement technique. More detailed descriptions and discussions on HONO measurement technique and set up have been provided in our response to Andy Neuman’s comment (#1 and #2). The wet chemistry-based techniques, including the LPAP used in this study, can provide exceptionally high sensitivity for HONO. However, the measurements by these techniques have been treated with caution and suspicion due to potential interferences from ambient constituents. We have made major and continued efforts in the past two decades to minimize and correct for the potential interferences. For examples, we found that shielding the inlet line from sunlight could prevent photochemical formation of HONO on the inlet wall surface (Zhou et al., 2002b). Results from many field and laboratory tests we conducted so far have indicated that heating the inlet line can effectively minimize the HONO loss to and/or HONO formation from heterogeneous NO2 reactions on inlet wall surface (see Figure 3 in the response to Andy Neuman’s comment). We have used Na2CO3-coated denuder to generate “zero-HONO” air by selectively removing HONO (and acidic species) from ambient air to established measurement baselines. The subtraction of “zero-HONO” air baselines from ambient signals effectively eliminate the potential interference from HONO precursors, such as NOx, PAN and particulate nitrite (Zhang et al., 2012; Figures 1 and 2 in the Response to A.Neuman’s Comment). To check the effectiveness of our background correction procedure and to validate the LPAS technique, we have compared the HONO concentrations measured by the LPAS and by a limb-scanning differential optical absorption spectroscopy (DOAS) instruments on board the C-130 in large power plant plumes during the NOMADSS campaign, and found very good agreement between the two measurements (Ye et al., 2016b). Therefore, we have high confident with our HONO data measured on the C-130 during the NOMADSS field study, and we stand by our findings that the photolysis of particulate nitrate is the major daytime HONO source and NOx-related reactions is an only minor HONO contributor in the low-NOx TBL over Southeast U.S.

References

Acker, K., Moller, D., Wieprecht, W., Meixner, F. X., Bohn, B., Gilge, S., Plass-Dulmer, C., and Berresheim, H.: Strong daytime production of OH from HNO2 at a rural mountain site, Geophys. Res. Lett., 33, L02809,10.1029/2005gl024643, 2006.

Acker, K., et al.: Nitrous acid in the urban area of Rome, Atmos. Environ., 40, 3123-3133, 2006b. Baergen, A. M., and Donaldson, D. J.: Photochemical renoxification of nitrica on real urban grime, Environ. Sci. Technol., 47, 815-820, 10.1021/es3037862, 2013.

Beine, H., Domine, F., Simpson, W. Honrath, R.E., Sparapani, R., Zhou, X., and King, M.: Snow-pile and chamber experiments during the Polar Sunrise Experiment 'Alert 2000': exploration of nitrogen chemistry. Atmos. Environ. 2002, 36, 2707-2719, 2002.

Beine, H., Colussi, A.J., Amoroso, A., Esposito, G., Montagnoli, M., and Hoffmann, M.R.: HONO emissions from snow surfaces, Environ. Res. Lett., 3, 045005, 2008.

Elshorbany, Y. F., Kleffmann, J., Kurtenbach, R., Lissi, E., Rubio, M., Villena, G., Gramsch, E., Rickard, A. R., Pilling, M. J., and Wiesen, P.: Seasonal dependence of the oxidation capacity of the city of Santiago de Chile, Atmos. Environ., 44, 5383-5394, 10.1016/j.atmosenv.2009.08.036, 2010.

Honrath, R. E., Peterson, M. C., Dziobak, M. P., Dibb, J. E., Arsenault, M. A., and Green S. A.: Release of NOx from sunlight-irradiated midlatitude snow, Geophys. Res. Lett.,

27, 2237-2240, 2000.

Honrath R. E., Lu, Y., Peterson, M.C., Dibb, J.E., Arsenault, M.A., Cullen, N.J., and Steffen, K.: Vertical fluxes of NOx, HONO, and HNO3 above the snowpack at Summit, Greenland Atmos. Environ., 36 2629-40, 2002.

Kleffmann, J., Kurtenbach, R., Lorzer, J., Wiesen, P., Kalthoff, N., Vogel, B., and Vogel, V.: Measured and simulated vertical profiles of nitrous acid - Part I: Field measurements, Atmos. Environ., 37, 2949-2955, 2003.

Kleffmann, J., et al.: Daytime formation of nitrous acid: A major source of OH radicals in a forest, Geophys. Res. Lett., 32, doi:10.1029/2005GL022524, 2005.

Meusel, H. et al.: Emission of nitrous acid from soil and biological soil crusts represents an important source of HONO in the remote atmosphere in Cyprus, Atmos. Chem. Phys., 18, 799–813, 2018.

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. Oswald, R., et al.: HONO emissions from soil bacteria as a major source of atmospheric reactive nitrogen, Science, 341, 1233-1235, DOI: 10.1126/science.1242266, 2013.

Reed, C. et al.: Evidence for renoxification in the tropical marine boundary layer, Atmos. Chem. Phys., 17, 4081–4092, 2017.

Ren, X., et al.: OH and HO2 chemistry in the urban atmosphere of New York City. Atmos. Environ. 37, 3639-3651, 2003.

Su, H., Cheng, Y. F., Oswald, R., Behrendt, T., Trebs, I., Meixner, F. X., Andreae, M. O., Cheng, P., Zhang, Y., and Poschl, U.: Soil Nitrite as a Source of Atmospheric HONO and OH Radicals, Science, 333, 1616-1618, 10.1126/science.1207687, 2011.

Villena, G., et al.: Vertical gradients of HONO, NOx and O3 in Santiago de Chile, Atmos. Environ., 45, 3867-3873, 2011.

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, 2016a.

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

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

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

Zhou, X., H. J. Beine, H.J., Honrath, R.E., Fuentes, J.D., Simpson, W., Shepson, P.B., and J. W. Bottenheim, J.W.: Snowpack photochemical production as a source for HONO in the Arctic boundary layer in spring time, Geophys. Res. Lett, 28:4087-4090, 2001.

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, 2002a.

Zhou, X., He, Y.,Huang, G.,Thornberry, T.D.,. Carroll, M.A., and Bertman, S.B.: Photochemical production of HONO on glass sample manifold wall surface, Geophys. Res. Lett, 29, doi:10.1029/2002GL015080, 2002b.

Zhou, X., Gao, H., He, Y., Huang, G., Bertman, S. B., Civerolo, K., and Schwab, J.: Nitric acid photolysis on surfaces in low-NOx environments: Significant atmospheric implications, Geophys. Res. Lett., 30, 2217, 10.1029/2003gl018620, 2003.

Zhou, X., G. Huang, G., Civerolo, K., Roychowdhury, U., and Demerjian, K.L.: Summertime observations of HONO, HCHO, and O3 at the summit of Whiteface Mountain, New York, J. Geophys. Res., 112, doi:10.1029/2006JD007256, 2007.

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., 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 2015, 119, 4907-4914, 2015.

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