

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

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General comments

"Extraordinary claims require extraordinary evidence" is a phrase made popular by Carl Sagan [Rational Wiki]. This is particularly relevant to the Ye et al. [2018] paper. The authors make the extraordinary claim that “. . .the sum of all known NO_x-related HONO formation mechanisms was found to account for less 20% of the daytime HONO source in the background terrestrial air masses, . . .”. If this claim were true, it would possibly force a reassessment of our understanding of HO_x and NO_x budgets of the troposphere, depending on the details of the other 80% of the (unknown) sources. However, the evidence presented Ye et al., [2018] does not justify that claim. In fact, Neuman et al. [2016] conclude: “Outside of recently emitted plumes from known combustion sources, HONO mixing ratios measured several hundred meters above ground level were indistinguishable from zero within the 15 parts per trillion by volume measurement uncertainty. The results reported here do not support the existence of a ubiquitous unknown HONO source that produces significant HONO concentrations in the lower troposphere.” The conclusion of these two studies disagree strongly, yet the reported measurements were made from different aircraft with different instrumentation, but in the same region of the country over the same time period, summer 2013. Unfortunately, Ye et al., [2018] do not discuss or even cite Neuman et al. [2016]. The differences in the results reported in these two papers point to clear experimental problems in the measurements. Until these problems are resolved, the extraordinary claim of Ye et al. [2018] should not be published.

References

Neuman, J. A., et al. (2016), HONO emission and production determined from airborne measurements over the Southeast U.S., J. Geophys. Res. Atmos., 121, 9237–9250, doi:10.1002/2016JD025197.

Rational Wiki, https://rationalwiki.org/wiki/Extraordinary_claims_require_extraordinary_evidenceh

Ye, C., et al. (2018), Tropospheric HONO distribution and chemistry in the Southeast U.S., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-105>.

Response: We completely agree with David Parrish that “Extraordinary claims require extraordinary evidence.” However, we disagree that our finding that “. . .the sum of all known NO_x-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 NO_x environments, such as urban atmosphere and power plant and biomass burning plumes, NO_x is known to be the dominant precursor to HONO. However, in low NO_x 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 NO_x can lead to the production of HONO. Nitrate photolysis in snowpack has been found to be a major source

for HONO and NO_x 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-NO_x 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-NO_x 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 NO_x 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 HO_x 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 HO_x 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 NO_x.

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 NO_x-related reactions (mainly NO+OH reaction) accounted for nearly all the required HONO source in the large fresh power plant plume (NO_x ~ 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 (NO_x ~1.8 ppb), NO_x-related reactions contribute to a major fraction (52%) of the total required HONO source (the original Figure 7b). In the low-NO_x 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-NO_x background atmosphere. The conclusion based on its below-detection-limit measurements and on the extrapolations from combustion plumes to low-NO_x background atmosphere is not reliable and thus should not be used to rule out the findings based on our measurement in the low-NO_x rural atmosphere. The relative contribution of NO_x-related reactions is in the order of power plant plume (NO_x ~ 1- 20 ppb) > urban plume (NO_x ~ 1 ppb) > background terrestrial air masses (NO_x ~100-300 pptv). That is, the relative contribution from NO_x-related reactions to the required HONO source is highly dependent on the NO_x regimes. While the conclusion we draw in the high NO_x 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 NO_x 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 NO_x, 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 confidence 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 NO_x-related reactions is an only minor HONO contributor in the low-NO_x TBL over Southeast U.S.

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