We completely agree with David Parrish that “Extraordinary claims require extraordi-
nary 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 extraordin-
ary 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 pho-
tolysis 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 ni-
trate 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 heteroge-
nenous 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 “un-
known” 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
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.

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 differen-
tial 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 NOx-related reactions is an only minor HONO contributor in the low-NOx TBL over Southeast U.S.

References


Villena, G., et al.: Vertical gradients of HONO, NOx and O3 in Santiago de Chile,


Please also note the supplement to this comment: https://www.atmos-chem-phys-discuss.net/acp-2018-105/acp-2018-105-AC2-supplement.pdf