

Response to referee 2:

The authors would like to thank the anonymous referee 2 for taking the time to review the manuscript. We thank them for their kind and encouraging words, and for the very relevant comments that allowed us to improve the manuscript. Comments by the reviewer are given in black normal font, and our response to the comments is shown in blue. Newly added and modified text in the revised manuscript and supporting information (SI) is given in italics.

The manuscript examined the potential formation pathways for HONO and their impacts on ozone production in a suburban site in the China YRD region during the summertime, using sophisticated field measurements and constrained box model tests. They found that the traditional OH+NO pathway only largely underestimate the observed HONO concentrations. Within several potential pathways, photo-induced NO₂ conversion on the ground is mostly likely the missing HONO source during the day, and NO₂ hydrolysis on the group surface is the major missing source at night. The study also indicated a significant HONO contribution from direct vehicle emissions. They also assessed the contributions of the missing sources to the ozone production, suggesting an important role of HONO in aggravating ozone pollution. The topic is important and relevant. The dataset and analysis are comprehensive and valuable in improving the understanding the secondary pollutions and control policies. This paper is within the scope of ACP and might be of great interest to the broad atmospheric science community. I have a few questions and comments that should be answered before it can be considered for publication.

Thank you for your positive comments.

Specific comments:

Line 36: Should it be “increased by 88%”? $(12.6-6.7)/6.7 = 88\%$

We agree with the reviewer. We have changed the texts accordingly:

Line 36-39:

“The net ozone production rate (6.7 ppb h⁻¹) without observed HONO as a model constraint increased by 88% compared to that (12.6 ppb h⁻¹) with HONO as a model constraint, indicating HONO evidently enhanced HONO production and hence aggravated O₃ pollution in summer seasons.”

Line 64: “which is typically less than 2% NO_x emissions” is confusing. Did you mean the HONO/NO_x ratio is typically less than 2%?

Yes, we mean that HONO/NO_x ratio is typically less than 2%.

Section 3.7 HONO Budget: why did you not include direct emissions, such as vehicle emission, into the HONO production rate? It seems vehicle emission contributed

significantly to this site (~15%).

As suggested, we have taken vehicle HONO emission into consideration. The revised figure was shown below. HONO production by vehicle emission accounted for 22% of the seven HONO sources during nighttime, while it played a minor role during the daytime.

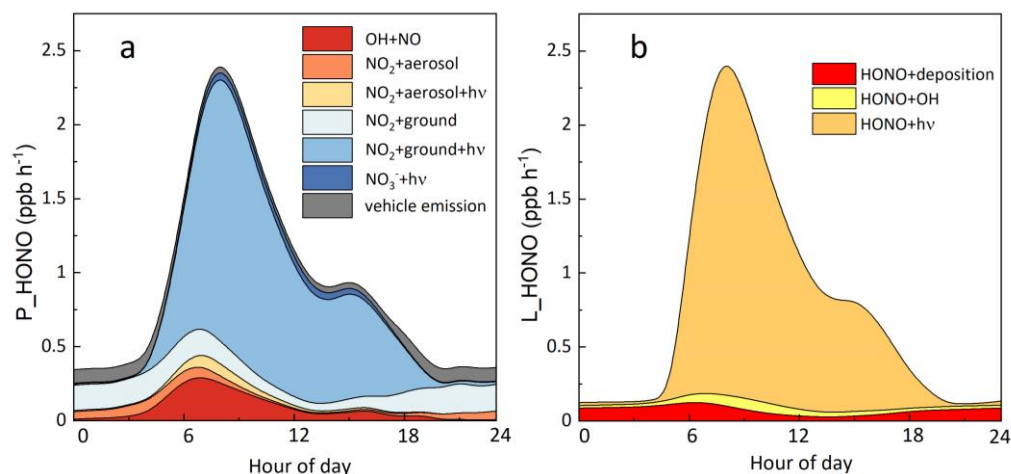


Figure 10: HONO production rates and loss rates by different pathways.

Technical corrections:

Line 28: change it to be “more likely due to”.

We have revised accordingly.

Line 37: Should it be “indicating HONO evidently enhanced O₃ production”?

Thank you for noticing this mistake. We have changed the corresponding texts as follows:

Line 38:

“...with HONO as a model constraint, indicating HONO evidently enhanced O₃ production”.

Line 42: please define “SOA”, also “VOCs”, “PAN” ...in the following text.

Thank you for your suggestion. We have changed “SOA” to “secondary organic aerosol (SOA)”, “VOCs” to “volatile organic compounds (VOCs)”, “PAN” to “peroxyacetyl nitrate (PAN)”.

Line 52-53: may change the sentence to be “several HONO sources, including ..., have been proposed”.

We have changed the texts as suggested:

Line 52-53:

“Till now, several HONO sources, including gas-phase reactions, direct emissions...”

Line 52, 80, 87: replace “varied” with “various”.

“Varied” replaced with “various”, as suggested.

Line 98: please correct the format of the citation.

We have corrected “Fu et al. (Fu et al., 2019)” to “Fu et al. (2019)”.

Line 105: from 28 to 76 is more than doubling.

The reviewer is correct. We have changed the corresponding texts as follows:

Line 105-106:

“Recently, this area has witnessed an evident increase in O₃ levels, with O₃ pollution days more than doubling (28 days to 76 days) from 2014 to 2017 (Liu et al., 2020).”

Line 314: Should “Sa” here be the “aerosol surface area density”, rather than “aerosol surface-to-volume ratio”?

Yes, “Sa” represents the “aerosol surface area density”. We have corrected in the revised manuscript accordingly.

Line 345: please correct the format of the citation.

We have changed “Laufs et al. (Laufs and Kleffmann, 2016)” to “Laufs et al. (2016).”

Line 353: change “whether” to be “regardless of whether”.

We have changed accordingly.

Figure 2: Some values on y-axis of CO, PM_{2.5}, and NO₂ overlaps with each other. Please fix that.

As suggested, we have revised the figure as follows:

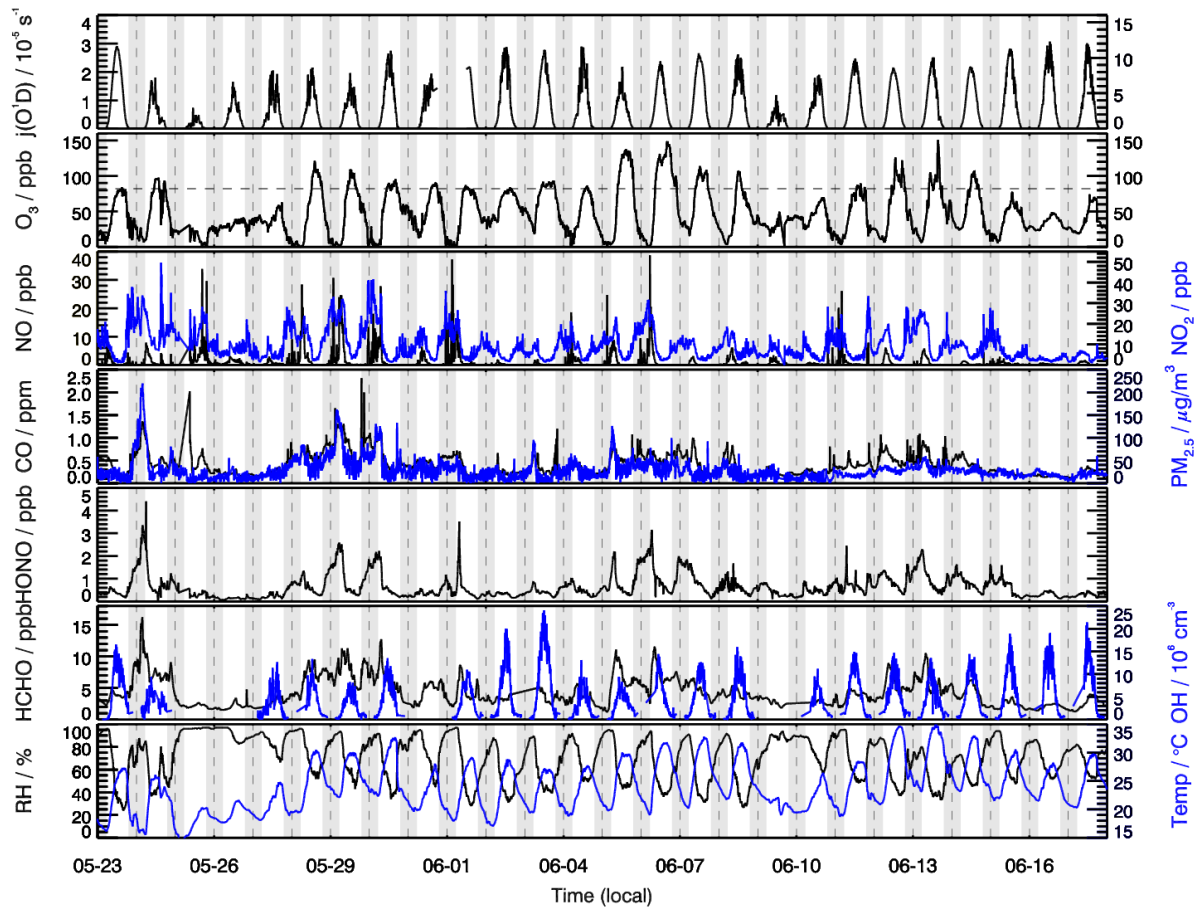


Figure 1: Time series of HONO, O₃, CO, PM_{2.5}, OH, HCHO, NO_x, relative humidity (RH), temperature and j(O¹D) during the EXPLORE-YRD campaign.

Table 1: Why the Reaction of NO₂ hydrolysis only gives 0.5 HONO for 1 NO₂ reacted?

NO₂ hydrolysis reaction proceeds as follows:



Therefore, one NO₂ molecule will lead one 0.5 HNO₃ and 0.5 HONO.