

# ***Interactive comment on “High resolution vertical distribution and sources of HONO and NO<sub>2</sub> in the nocturnal boundary layer in urban Beijing, China” by Fanhao Meng et al.***

## **Anonymous Referee #3**

Received and published: 1 November 2019

General Comments. Manuscript acp-2019-613 reports results of a nighttime vertical gradient study aimed at determining the sources and sinks of nitrous acid (HONO) in Beijing, China. Measurements were made from an instrumented container capable of ascending and then descending a 325 m tower over an hour, enabling measurements at ground level and up to a height of 240 m. The maximum height achieved means that measurements covered the surface layer, nocturnal boundary layer, and residual layer. Furthermore, the measurement campaign covered three periods of time marked by clean or hazy air masses. The results are then used to draw conclusions about the relative importance of direct (automobile), ground, and aerosol sources of HONO to the airshed.

Printer-friendly version

Discussion paper



The analytical measurements appear to be of high quality. The tower experiments are ideal for elucidating HONO sources and sinks, and it was a good idea to operate simultaneous ground-based and vertically transported IBBCEAS systems. It is not the first time that gradient measurements of HONO and related physical/chemical have been made using a tower/elevator and much of the approach to data analysis and interpretation closely follows previous studies (especially, VandenBoer, et al. J. Geophys. Res. 2013, 118, 10,155–10,171, doi:10.1002/jgrd.50721 and Stutz et al. J. Geophys. Res. 2002, 107, doi:10.1029/2001JD000390). Despite the lack of novelty, the data has the potential to provide insights into myriad processes affecting HONO production and loss in Beijing, an area where frequent high aerosol concentrations mean that multiphase chemistry has a large influence on atmospheric composition. However, I do not feel that sufficient analysis of the data was carried out to support the authors' conclusions. Therefore, I feel that the manuscript is not ready for publication; additional work must be carried out to properly analyze the data and extract the information it holds.

Specific Comments. One of the most important aims of the manuscript is to determine the relative contribution of direct sources vs. ground and aerosol surfaces to overall HONO production at the site. The conclusions are: (1) direct sources are a major source (~51% of total ambient HONO is from combustion); (2) vertical profiles of HONO concentration do not support heterogeneous NO<sub>2</sub>-to-HONO conversion on aerosol surfaces; (3) heterogeneous NO<sub>2</sub>-to-HONO conversion on ground surfaces followed by vertical convection dominate HONO production at night. These conclusions are based on interpretation and discussion of results on p. 11-15, which I found to be unclear and not necessarily supportive of the final conclusions. To be suitable for publication I feel the relative contribution of the various HONO processes need to be quantified in more detail for the full data set and the derivations of those calculations more clearly explained in the text.

There was some ambiguity regarding how the contribution of direct emissions to ambient HONO was determined. It seems to be derived from the HONO/NO<sub>x</sub> ratio mea-

[Printer-friendly version](#)[Discussion paper](#)

sured on days dominated by fresh vehicle emissions, which were identified when  $\text{NO} > 80$  ppb and  $\text{NO}/\text{NO}_x > 80\%$ . The ratio was then used to devise a linear relationship between ambient  $\text{NO}_x$  and direct HONO emissions that is applied over the whole campaign. How this relationship was used to derive the contribution of direct emissions to ambient HONO is not clear. Also, the statement that direct sources constitute 51% of total ambient HONO is generalized for the entire campaign. However, it is clear that the relative contribution of HONO sources will change with time of day, traffic intensity and type of traffic, meteorology. Indeed, it is expected that the HONO mass balance for each nocturnal profile will be different, with each source/sink having a different relative contribution depending on time and meteorology.

When determining the relative contribution of aerosol surfaces to the HONO budget, the authors attempt to quantify HONO production using an assumed uptake coefficient (for  $\text{NO}_2$ -to-HONO conversion) and an aerosol surface area-to-volume ratio from a completely different study, which is supposed to be a typical of winter in Beijing. I don't see how one can justify using a single aerosol surface area-to-volume ratio for the entire campaign, especially since this will vary with time, meteorology, and day (see Table 1). Further, it is not clear why a single value was used since a suite of aerosol measurements were made during the current study; measurements of black carbon, non-refractory PM, and AMS measurements at ground and 260 m height are reported. This data should be used to refine the analysis and make it more specific for each ascent/descent period. I encourage the authors to provide a more in-depth analysis of the contribution of aerosol surface area to HONO processes. I believe there may indeed be evidence for an important role for aerosol here under hazy conditions. For example, clear gradients, denoted by decreasing HONO/ $\text{NO}_2$  ratio with elevation, were only observed on a few occasions, whereas it was more often the case that the HONO/ $\text{NO}_2$  ratio was quite constant over the vertical range. Thus, it is possible that aerosol chemistry may influence this profile, but only a detailed quantitative analysis can tell you this.

[Printer-friendly version](#)[Discussion paper](#)

Finally, the authors state that ground level HONO production has been corrected for the influence of direct emissions from automobiles. Has this correction been carried out for the production on aerosol surfaces as well? I had a difficult time understanding the rationale of going through all the calculations in section 3.4.3 on the topic of ground level HONO production. It was not clear how equation 4 and 5 were derived. The purpose of these equations is to estimate a HONO conversion frequency, which appears to be the pseudo-first order rate constant associated with the conversion of NO<sub>2</sub>-to-HONO. These values should then be used to compare to the other HONO sources and sinks to evaluate the relative importance of all the various HONO sources/sinks. However, this comparison is not clearly carried out at the end of the paper as I would expect. Instead, starting with line 410 the text veers off subject by deriving a HONO yield from deposited NO<sub>2</sub>. While this may be a useful calculation to carry out, I don't see how it helps the authors reach their research objectives and main conclusions.

In closing, I feel the interpretation of the vertical profiles relies on highly generalized 'back of the envelope' calculations. Such calculations can be very useful in certain cases; however, the quality and quantity of the data provided by this study should allow for a more elaborate analyses. I recommend the authors revisit their data to devise a mass balance for HONO processes where they quantify the sources and sinks for each vertical profile. I expect this approach will provide valuable insights that are not clear from the current presentation of the data.

Specific comments by line number: Lines 45-133: I feel that the introduction lacks an explicit statement of the study's research objective(s). The authors provide a [some-what long] background section reviewing aspects of HONO chemistry that ends with a summary of what they did in their study. The introduction would be far stronger if the authors include a focused discussion of what research objective they hope to achieve. This could be accomplished by stating a hypothesis, following by a plan for how they hoped to test the hypothesis. At the moment, it is only in the second to last sentence of the introduction that one finally learns that a comparison of HONO heterogeneous

[Printer-friendly version](#)[Discussion paper](#)

chemistry on ground vs. aerosol surfaces is the major aim of the work.

64-66: The authors state that hydrolysis of NO<sub>2</sub> on humid surfaces via R2 is considered the most likely explanation for observed HONO concentrations. The authors should be aware that this is not a viable mechanism under atmospherically relevant concentrations of NO<sub>2</sub>. Reaction R2 is too slow and only becomes important when the NO<sub>2</sub> concentration is high enough to promote N<sub>2</sub>O<sub>4</sub> formation. Initial mechanistic studies of this mechanism had to use high NO<sub>2</sub> concentrations due to high instrument detection limits. More recent laboratory studies of this process using state-of-the-science sensitive field-grade instrumentation do not report this chemistry occurring under lower concentrations (50 ppb or less). One can refer to numerous lab studies over the past 10-15 years aimed at studying NO<sub>2</sub> conversion on surfaces containing humic acid reactive sites to learn more about this. It is notable that these studies often include control experiments aimed at quantifying background levels of HONO derived from NO<sub>2</sub> hydrolysis on their experimental system (i.e., in the absence of redox active substrates). These studies consistently show that NO<sub>2</sub>-to-HONO conversion on organic matter and other redox active surfaces produce orders of magnitude more HONO than does R2.

81: The colon after the references should be deleted.

349: The authors attribute a decrease in HONO/NO<sub>2</sub> ratio at RH above 70% to enhanced HONO deposition. While RH does impact HONO uptake (see Donaldson et al. Environ. Sci. Technol. 2014, 48, 375), it would affect NO<sub>2</sub>-to-HONO conversion as well (by enhancing to a point); so there are competing effects here. The abovementioned Donaldson et al. paper suggests that the uptake coefficient for HONO actually decreases with increasing RH.

372: The number listed having units of h<sup>-1</sup> is not a formation rate as stated. Those are units of a first-order rate constant. Rather, units of ppb h<sup>-1</sup> are appropriate for a formation rate. 405: It would be beneficial to provide a visual comparison of all the production rates (calculated in units of mixing ratio per hour). See for example Fig. 11

[Printer-friendly version](#)[Discussion paper](#)

from Vandenboer et al. JGR, 2013, 118, 10,155.

413: I recommend that the authors choose another symbol to represent the compensation point, which they call the HONO yield from deposited NO<sub>2</sub>; the greek letter phi is reserved for the photolysis quantum yield. The symbol “H” used for mixing depth is also confusing. Some readers may mistake this for the Henry’s law constant without reading further into the text. Consider using “d” (for depth) or lower case “h” or “z”, all of which have been used in the past to represent height.

421: Why choose a deposition velocity from the literature, which is derived from completely different studies. Isn’t the point here to model the vertical profile to derive a deposition velocity and the uptake coefficients for NO<sub>2</sub>, HONO, etc. that are specific for the current sampling site?

More general remarks: More work should be devoted to providing error analysis. For example, error bars on data and errors in reported values derived from their analyses. This will be especially important when comparing quantitatively the relative contribution of sources/sinks to ambient HONO. I felt there were too many figures in the text. For example, what is the purpose of showing Figure 5, where the information is more useful plotted in the format shown in Fig. 6, etc. The manuscript could benefit from editing by a native English speaker. Grammatical errors start on the first line of the abstract and persist throughout the manuscript. Lastly, I note that the authors are comparing their IBBCEAS results to data collected on an instrument from Cambridge University. Does this contribution need to be acknowledged in some way (e.g., in the acknowledgement section or author list)?

---

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2019-613>, 2019.

Printer-friendly version

Discussion paper

