

Interactive comment on “The promotion effect of nitrous acid on aerosol formation in wintertime Beijing: possible contribution of traffic-related emission” by Yongchun Liu et al.

Anonymous Referee #1

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The work by Liu et al present field measurements of HONO, a key source of radicals in the boundary layer, along with supplementary gas and particle-phase measurements in over a 5-month period in Beijing. The authors used this dataset to probe the sources and their contributions to ambient HONO, with a focus on pollution events. Using a steady state approach, the authors calculated the contributions of different sources to the HONO budget and concluded that traffic emission (via direct emission and conversion of NO by homogenous reactions) was the key source of HONO during winter pollution events. Liu et al present a comprehensive and interesting long-term dataset that enables the authors to perform a budget analysis to investigate the main sources of HONO. The main sources of HONO in Beijing and urban area in general is an open

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research topic, and consequently this work would be of interest to the community, particularly their HONO budget analysis of the haze events.

There are, however, a few issues that in my opinion should be addressed prior to publication. While the manuscript is mostly well written, it is long. For example, Section 3.1 and 3.2 could be much shorter. In my opinion much of the text in these sections is unnecessary and could be reduced, without losing the key points.

The most interesting work is presented in Section 3.3, where a detailed and comprehensive budget analysis is presented. However, throughout section 3.3 some of the calculations and equations need more explanation, as it was not always clear from section 2.2 how they were performed. Some examples are given below in the minor comments. It would also help the reader if the equation used to calculate the rates of emission for each source (i.e. the eqn numbers) were referenced throughout section 3.3.

My major comment is from Section 3.3, the way the OH concentration was estimated is problematic in my opinion. As the authors rightly point out, to measure OH is difficult and requires highly specialized kit and therefore as they did not have access to these instruments, OH concentration needs to be estimated for this study. I am not sure about the way the OH concentration was calculated, as the equations they use (e.g. 13), use the levels of ozone and NO₂. The problem is that during winter, the main source of OH in Beijing is HONO photolysis, as the authors themselves state earlier in the manuscript (Section 3.2, line 288, with references), and is in fact one of their conclusions from Fig 2. Therefore, without considering OH produced from HONO photolysis, how can they be sure that their estimated OH concentration is reasonable, especially in winter? I think that for an atmosphere as chemically complex as Beijing, to estimate the OH concentration requires a box-model approach. It is important as the estimated OH concentration will affect the budget analysis, both sources and loss terms, and therefore the conclusions drawn from it. If this is not possible, then the uncertainties with their approach to estimating OH concentrations should at least be

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discussed/quantified.

Minor comments Line 82: I assume you mean nitrous acid not nitric acid?

Line 112: it would be good to specify that your ACSM was configured for PM2.5, as many of these instruments measure PM1

Line 207: Why does it matter if PM2.5 is above 75 $\mu\text{g m}^{-3}$? I assume you are referring to the regulatory limits, but it is good to be clear on this.

Line 211: I am a bit confused by your explanation for there being more pollution episodes and higher concentrations of BC, CO and PM2.5 in March, as it was the heating season. But isn't February just as cold? So why would there more heating in March?

Line 222: Are the percentages listed for nitrate, chloride and ammonium also monthly means?

Line 226: I am bit surprised that fireworks is regionally transported from Tangshan, are there no fireworks in Beijing?

Line 232-240: As example to one of my main comments above, I found that this paragraph was repeating much of the information presented in the preceding one. Perhaps these two paragraphs could be edited and combined.

Line 272: why have you chosen to subset the data based on 'when the PM2.5 concentration was larger than 50 $\mu\text{g m}^{-3}$ and the RH was less than 90 %'. Furthermore, as you state 'Under these conditions, local chemistry should be more important as 75 % of the wind speed was less than 1.0 m s^{-1} '. Why not then subset the data based solely on wind speed if local sources are of interest?

Line 275: How where these maximal POH-HONO and POH-O3 values calculated? I could not find the equation in the methods or reference.

Line 304: Is it not the production of the OH that changes in winter relative to summer,

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rather than the rate of oxidation of VOC by OH? Please clarify

Line 318-20 and Fig 2: I am not so sure that is 'reasonable to mainly ascribe the increase of OA concentration to local secondary formation initiated by OH radical from HONO photolysis'. This is because if only OH from HONO photolysis was driving secondary formation, then shouldn't the OA/CO peak earlier, as the ambient HONO is essentially run out by 10am?

Line 324: But cant there also be anthropogenic sources of alkenes? For example, isoprene can also be from vehicle emissions (See e.g. Zou et al 2019).

Line 379: at the start of the sentence, you state that hourly NOx EI were available, yet than go to give a yearly emission factor? Why wasn't hourly EI used, and did you consider your measured NOx concentrations, as the diurnal variation in NOx would be important? Please clarify in more detail how the Evehicle was calculated Especially as emission inventories can have significant bias (See for example very recent work for Beijing by Squires et al, 2020).

Line 381: This may be related to the above comment, but how did you report a range for calculated middle value of Evehicle, when the NOx EI rate is constant and the HONO/NOx is constant? Furthermore, what does the middle value refer to? Daily avg? hourly avg? please specify. This applies throughout this section

Line 386: the reported range for the upper limit is the same as reported for the lower limit, I'm guessing a typo?

Line 389: Please give the reference for the emission flux you used, the value and also why grassland was the most appropriate.

Line 397: why does only the middle values for Esoil have uncertainty calculated? Also how did you estimate the uncertainty for Esoil? And why did you use a range of soil water content for lower, middle and upper, why not just use a single value?

Line 416: Please provide more information on the night time temperature dependence

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of OH concentration, and the equations used in this calculation.

Line 419: Please give the reported OH concentrations by Li et al (2018) and Huang et al (2017) and if they were calculated or measured OH levels.

Line 433: How was the HONO from nitrate photolysis calculated? Which equation (give number)? What do these ranges represent?

Line 447: by the end of this paragraph, it was not at all clear to me which uptake co-efficient you actually used. Please clarify.

Line 477-9: the authors state that 'Heterogeneous reactions of NO₂ on aerosol surface and ground surfaces were unimportant compared with other sources because of the very low uptake coefficient'. What do you mean by the very low uptake coefficient, low compared to what? Is the issue more that you used the wrong co-efficient?

Fig 2D: if you take the bottom and top points in Feb/Mar (blue), I am not sure there this a correlation. It would be good to check if you get a similar slope and r² without these 2 points.

References Squires, F. A., Nemitz, E., Langford, B., Wild, O., Drysdale, W. S., Acton, W. J. F., Fu, P., Grimmond, C. S. B., Hamilton, J. F., Hewitt, C. N., Hollaway, M., Kotthaus, S., Lee, J., Metzger, S., Pinguha-Durden, N., Shaw, M., Vaughan, A. R., Wang, X., Wu, R., Zhang, Q., and Zhang, Y.: Measurements of traffic dominated pollutant emissions in a Chinese megacity, *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2019-1105>, in review, 2020. Zou, Yu, Xue Jiao Deng, Tao Deng, Chang Qin Yin, and Fei Li. "One-Year Characterization and Reactivity of Isoprene and Its Impact on Surface Ozone Formation at A Suburban Site in Guangzhou, China." *Atmosphere* 10, no. 4 (2019): 201.

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