Response to the comments of Reviewer #1

This paper presents HONO and associated measurements from a ground site in Beijing during the months of June to October, 2021. There is an attempt to assess non-traditional sources of HONO (sources aside from OH + NO) using co-measured NOx and particle loading. There is a serious flaw in the paper that cannot be overcome by revision or further analysis (see below). The full paper as submitted here should be rejected for publication. However, the authors should consider publishing the HONO data and associated summary of measurements from Beijing (there have been many) as an ACP Measurement Report. I have the following General and Specific comments.

Response: We thank Referee #1 for the review and the evaluation of our manuscript. We have fully considered the comments and responded to these comments below in blue text. The revisions in the manuscript are highlighted in yellow color. The response and changes are listed below.

General comments.

1. *The major flaw in this paper is there is only an NO_y measurement at the site, which we know to measure not just NO_x but also PAN, HNO_3, particle, and alkyl nitrates (NOz compounds). The authors try to argue that the impact of NOz compounds is minor. We know that this is not true, especially for the mid-day period when NO_2 is below 10 ppbv, and there is obvious O_3 production (see for example Zhang et al., 2015, Zhang et al., 2023 (which shares some authors with this paper). Under these conditions in particular, equating NO_2 with NO_z will result is errors of factors of 2 -3 at least. All of the interpretation that the authors try to do with this data is fatally flawed.*

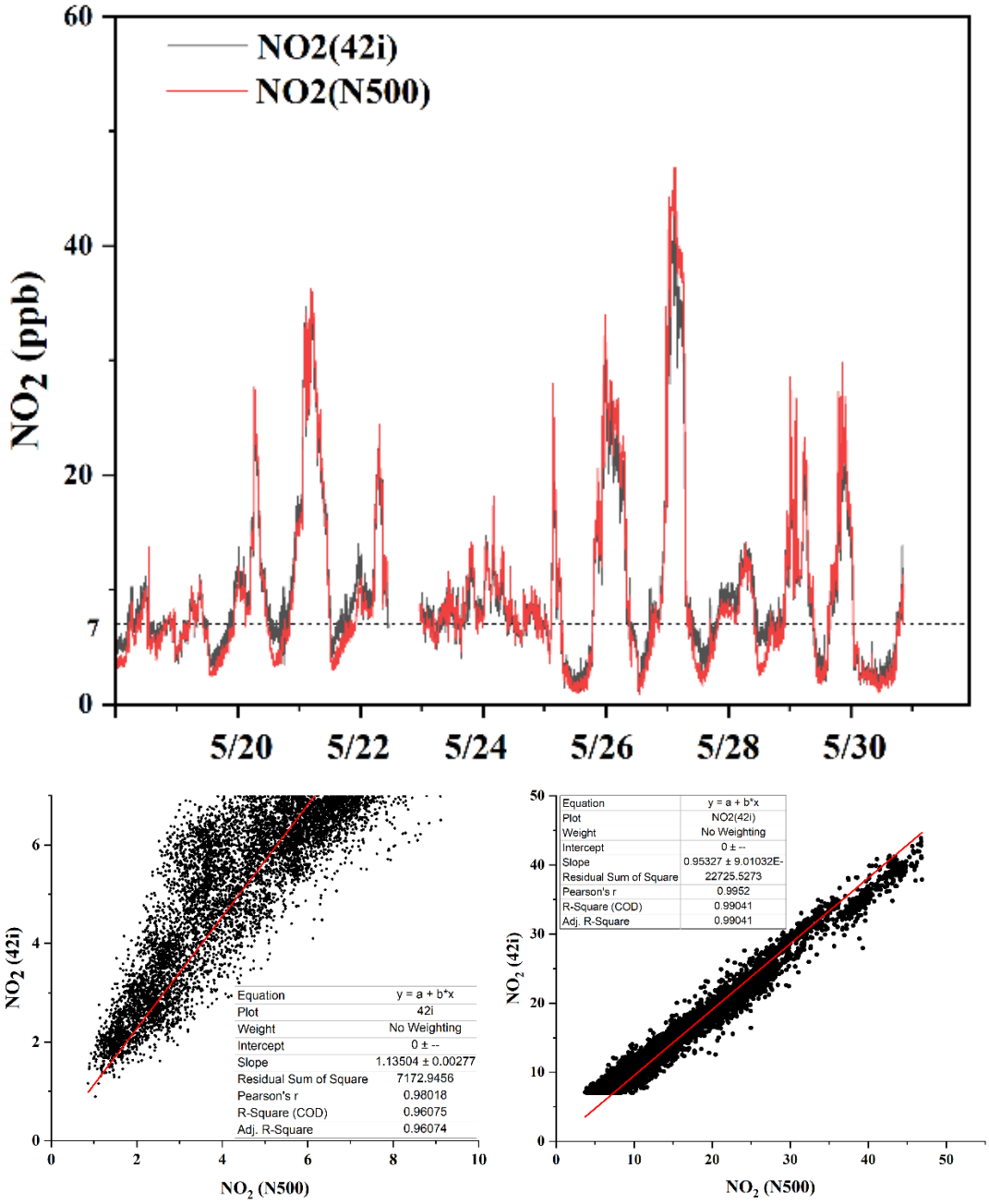
   Actually, due to the employment of a molybdenum NO_2-to-NO converter, the 42i analyzer might overestimate NO_2 concentration for the potential convertion of NOz (NOz = NOy – NOx. e.g., HONO, HNO_3, peroxyacetyl nitrate (PAN), and so on). Based on the articles mentioned (Zhang et al., 2023; Zhang et al., 2015) above, we conducted a period of targeted observations, and two devices were applied: the Teledyne API Model N500 CAPS NOx analyzer and the Thermo Scientific 42i analyzer; the Teledyne API Model N500 CAPS NOx analyzer is a Cavity Attenuated Phase Shift (CAPS), non-chemiluminescent NOx analyzer, which can directly measure NO_2.

the instruments applied in this targeted observation	
	
N500 NO_X-NO_2-NO analyzer	42i NO-NO_2-NO_X analyzer

The observation period was from May 19th to 31st, 2024. The specific weather conditions these days are shown in the figure below.

Sun.	Mon.	Tues.	Wed.	Thurs.	Fri.	Sat.
19	20	21	22	23	24	25
26	27	28	29	30	31	1
Note: green-excellent, yellow-good, orange-lightly polluted (ozone)						

The comparison plot of NO_2 data during the observation period is shown in the figures below. When the NO_2 concentration is above 7 ppb, there is no significant difference between the two instruments. However, when NO_2 concentration is below 7 ppb, the 42i values are slightly higher than those of the N500, with a corresponding slope of 1.14. Based on this measurement, we have corrected all NO_2 values below 7 ppb during the observation period, as well as the corresponding analysis. We have also provided an explanation in the methods section. (Page 4, line 96-102; SI, Page 7, Figure S1)



References:

Zhang, G., Mu, Y., Zhou, L., Zhang, C., Zhang, Y., Liu, J., Fang, S., and Yao, B.: Summertime distributions of peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) in Beijing: Understanding the sources and major sink of PAN, Atmospheric Environment, 103, 289-296, 10.1016/j.atmosenv.2014.12.035, 2015.

Zhang, H., Tong, S., Zhang, W., Xu, Y., Zhai, M., Guo, Y., Li, X., Wang, L., Tang, G., Liu, Z., Hu, B., Liu, C., Liu, P., Sun, X., Mu, Y., and Ge, M.: A comprehensive observation on the pollution characteristics of peroxyacetyl nitrate (PAN) in Beijing, China, Science of The Total Environment, 905, 166852, 10.1016/j.scitotenv.2023.166852, 2023.

2. *We are given essentially no details about the measurement site and are given only references to describe the HONO measurement. So, we have no idea if the method has interferences, from other N compounds aside from NO_2. We have no idea what materials that might from or store HONO (soil, asphalt) surround the site. At least a brief description of these is necessary.*

   We thank the reviewer for pointing this out. The description of this site has been added in the methods part of the main text.

   (Page 3-4, line 87-92) "Briefly, Chaoyang District was located at the eastern area of Beijing and was one of the six main urban districts (Dongcheng, Xicheng, Haidian, Chaoyang, Shijingshan, and Fengtai) of Beijing. This site was located about 2 km to the north of the North Fifth Road, approximately 0.3 km away from Beiyuan Road, with a high volume of traffic. And this site was located in a mixed-use commercial and residential area, with several shopping malls, residential areas, and office buildings nearby, and there were no obvious sources of industrial pollution. Thus, this site could be considered as an urban site."

3. *The authors basically prescribe nighttime OH, and broadly parameterize daytime OH. We know that there is substantial variability in OH, so these shortcuts will mask much of the chemical dependencies that the authors are trying to uncover in their analyses. In several places the authors try to use slight differences in R^2 to say something about what factors might be more responsible for HONO. In some case these R^2 values are below 0.1, which means neither factor was significant. Such an analysis doesn't tell us anything.*

   Actually, OH concentrations in the atmosphere have high variability. The empirical model applied to calculate the daytime OH concentration was proposed by Rohrer and Berresheim (2006), they found the strong nearly linear correlations between measured OH concentrations and simultaneously observed $J(O^1D)$, despite the fact that OH concentrations were influenced by thousands of reactants. Liu et al. (2019) analyzed this calculation method, the calculated OH concentrations around noon were comparable to the observations in Chinese urban or suburban atmospheres. Based on the research background above, we applied this calculation formula to provide a visual assessment of OH concentrations during the observation period. We have added explanations accordingly in the manuscript. Indeed, a very small R-squared (R^2) value did not explain much, the contents with analysis that $R^2 < 0.1$ were removed.

   (Page 4-5, line 118-123) "……these coefficients adopted here were from the OH studies in the Pearl

River delta (PRD) and Beijing, China (Rohrer et al., 2014; Tan et al., 2017, 2018). According to the summarizing coefficients in different OH observation campaigns in the polluted areas of China (Liu et al., 2019), the comprehensive impact of reactants (e.g., VOCs and NOx) on OH could not compete with that of UV light to OH, the chemical environments of OH could be similar. This could be a reasonable way to derive OH concentration by the equation above."

Reference:

Rohrer, F., and Berresheim, H.: Strong correlation between levels of tropospheric hydroxyl radicals and solar ultraviolet radiation, Nature, 442, 184-187, 10.1038/nature04924, 2006.

Rohrer, F., Lu, K., Hofzumahaus, A., Bohn, B., Brauers, T., Chang, C.-C., Fuchs, H., Häseler, R., Holland, F., Hu, M., Kita, K., Kondo, Y., Li, X., Lou, S., Oebel, A., Shao, M., Zeng, L., Zhu, T., Zhang, Y., and Wahner, A.: Maximum efficiency in the hydroxyl radical-based self-cleansing of the troposphere, Nat. Geosci., 7, 559–563, https://doi.org/10.1038/ngeo2199, 2014.

Tan, Z., Fuchs, H., Lu, K., Hofzumahaus, A., Bohn, B., Broch, S., Dong, H., Gomm, S., Häseler, R., He, L., Holland, F., Li, X., Liu, Y., Lu, S., Rohrer, F., Shao, M., Wang, B., Wang, M., Wu, Y., Zeng, L., Zhang, Y., Wahner, A., and Zhang, Y.: Radical chemistry at a rural site (Wangdu) in the North China Plain: observation and model calculations of OH, HO_2 and RO_2 radicals, Atmos. Chem. Phys., 17, 663–690, https://doi.org/10.5194/acp-17-663-2017, 2017.

Tan, Z., Rohrer, F., Lu, K., Ma, X., Bohn, B., Broch, S., Dong, H., Fuchs, H., Gkatzelis, G. I., Hofzumahaus, A., Holland, F., Li, X., Liu, Y., Liu, Y., Novelli, A., Shao, M., Wang, H., Wu, Y., Zeng, L., Hu, M., Kiendler-Scharr, A., Wahner, A., and Zhang, Y.: Wintertime photochemistry in Beijing: observations of ROx radical concentrations in the North China Plain during the BEST-ONE campaign, Atmos. Chem. Phys., 18, 12391–12411, https://doi.org/10.5194/acp-18-12391-2018, 2018.

Liu, Y., Nie, W., Xu, Z., Wang, T., Wang, R., Li, Y., Wang, L., Chi, X., and Ding, A.: Semi-quantitative understanding of source contribution to nitrous acid (HONO) based on 1 year of continuous observation at the SORPES station in eastern China, Atmos. Chem. Phys., 19, 13289-13308, 10.5194/acp-19-13289-2019, 2019.

Specific comments

4. *The abstract is too long and has too much detail.*

Thank you for this comment. We've streamlined the content in the abstract.

(Page 1, line 11-28)

"**Abstract.** As a key source of hydroxyl (OH) radical, nitrous acid (HONO) has attracted much attention for its important role in the atmospheric oxidant capacity (AOC) increase. In this study, we made a comparative study on the ambient levels, variation patterns, sources and formation pathway

in warm season (from June to October in 2021) on a basis of a continuous intensive observation in an urban site of Beijing. The HONO concentration showed a larger contribution to OH radical relative to ozone at daytime. The emission factor (EF) from the vehicle emissions, was estimated to be 0.017, higher than most studies conducted in Beijing. The homogeneous production of HONO via reaction of NO + OH, P^{net}_{OH+NO}, were 0.033-0.17 ppb/h. The average nocturnal NO_2 to HONO conversion frequency k_{HONO} were 0.0016-0.011% h^{-1}. In warm seasons, the missing source of HONO, $P_{unknown}$, around noontime were 0.29-2.7 ppb/h. Relatively low humidity and strong solar illumination were conductive to HONO formation in June, which might be due to light-induced heterogeneous reactions of NO_2. In July in Beijing, high humidity condition was beneficial to the heterogeneous reaction of NO_2, and due to the increase of precipitation, more HONO would enter the liquid phase. For days with high humidity and strong sunlight in June and August, photolysis of nitrate was also one important HONO source. For August and September, light-induced reactions of NO_2 on non-aerosol surfaces under relatively low humidity and strong light conditions could be an important HONO source. In addition, the presence of Cl ions and sulfate could enhance the photolysis of nitrate, and this was obvious in July; the presence of organic compounds also could have this effect, which was obvious in June. Not only the HONO concentration but also the HONO source has temporal patterns, even within a season, it varies from month to month. This work highlights the importance of HONO for AOC in warm season, while encouraging long-term HONO observation to assess the contribution of HONO sources over time compared to the capture of pollution processes."

5. *Line 20. What are the units of P_{emis}?*

   The units of P_{emis} were ppb/h, and emission factor (EF) was a dimensionless constant, this has been corrected in the manuscript.

   (Page 1, line 15) "The emission factor (EF) from the vehicle emissions, was estimated to be 0.017, higher than……"

   (Page 11, line 236) "……$\triangle HONO/\triangle NO_x$ value of 0.017 was adopted to estimate the vehicle emissions P_{emis} (ppb/h) contribution to……"

6. *Line 29. The solubility of HONO is very much pH dependent. Below its pKa (3.28) it is not very soluble.*

   Thank you for this comment. We have revised the interpretation in the manuscript.

7. *Line 55. The authors have missed VandenBoer, et al., 2015.*

   Thank you for this comment. This has been added in the manuscript.

   (Page 2, line 46-47) "The release from soil nitrite is one important primary source of HONO (Su et al., 2011; VandenBoer et al., 2015; Wu et al., 2019)"

   (Page 26, Line 667-669) *"*VandenBoer, T. C., Young, C. J., Talukdar, R. K., Markovic, M. Z., Brown, S. S., Roberts, J. M., and Murphy, J. G.: Nocturnal loss and daytime source of nitrous acid through reactive uptake and displacement, Nat. Geosci., 8, 55-60, 10.1038/ngeo2298, 2015.*"*

8. *Line 70. This sentence is meaningless.*

   This sentence has been removed.

9. *Line 89. The authors did not tell us what the impact of their measured HONO on O_3 production was.*

   The correlation between HONO and O_3 was analyzed in Section 3.5. We found that the correlation between ozone and HONO varies in different months, corresponding explanations was added in the manuscript.

   (Page 21, line 443-445) "……the ozone formation and concentration could be affected by various factors, including precursors, meteorological factors, and regional transport, et al., the formation of OH radical by HONO photolysis was a pathway involved in the ROx and NOx cycle of ozone formation, ozone was not directly related to HONO."

10. *Line 113. "was" should be "were"*

    This has been corrected. (Page 4, line 111)

11. *Line 119. OH is going to vary a lot, with dependencies that are very much at the heart of what the authors are trying to get at. This specification is not very useful.*

    Actually, OH concentrations in the atmosphere have high variability. The empirical model proposed by Rohrer and Berresheim (2006) was applied here to calculate the daytime OH concentration. Rohrer and Berresheim (2006) found the strong nearly linear correlations between measured OH concentrations and simultaneously observed $J(O^1D)$, despite the fact that OH concentrations were influenced by thousands of reactants. Liu et al. (2019) analyzed this calculation method, the calculated OH concentrations around noon were comparable to the observations in Chinese urban or suburban atmospheres. Based on the research background above, we applied this calculation formula to provide a visual assessment of OH concentrations during the observation period. And we have added explanations accordingly in the manuscript.

(Page 4-5, line 118-123) "……these coefficients adopted here were from the OH studies in the Pearl River delta (PRD) and Beijing, China (Rohrer et al., 2014; Tan et al., 2017, 2018). According to the summarizing coefficients in different OH observation campaigns in the polluted areas of China (Liu et al., 2019), the comprehensive impact of reactants (e.g., VOCs and NOx) on OH could not compete with that of UV light to OH, the chemical environments of OH could be similar. This could be a reasonable way to derive OH concentration by the equation above."

12. *Line 141-142. What were the averaging times for these?*

The averaging times referred to here is for the entire observation period, this has been added in the manuscript. (Page 6, Table 1)

13. *Line 158. Don't know what a "brief combing" is.*

Thank you for this comment. This has been corrected in the manuscript.

(Page 7, line 161) "For comprehensive comparative analysis, a review of the HONO observations in Beijing was carried out……"

14. *Line 194-195. This isn't what Figure 4a shows.*

This part of the content has been removed from the manuscript. (Page 8, line 192)

15. *Line 216. Emission factor of what?*

This has been added in the manuscript.

(Page 10, line 213) "……the emission factor of vehicles……"

16. *Line 225. Too many significant figures, only 3 at most are justified.*

Thank you for this comment. All the significant figures in the manuscript have been modified.

17. *Line 241. What are the units?*

This has been added in the manuscript.

(Page 11, line 236) "……$\triangle HONO/\triangle NO_x$ value of 0.017 was adopted to estimate the vehicle emissions P_{emis} (ppb/h) contribution to……"

18. *Line 268. Too many significant figures, only 2 (3 for the last number) at most are justified.*

Thank you for this comment. We have made the corresponding modifications in the manuscript.

19. *Line 280. There is no explanation and justification for this equation.*

This has been added in the manuscript.

(Page 13, line 286-288) "Then the NO_2 to HONO conversion rate (C_{HONO}) was calculated by the combination of C^0_{HONO} (not scaled C_{HONO}) and C^{CO}_{HONO} (CO scaled C_{HONO}), which could reduce the

impact of uncertainties in diffusion process and emissions on the conversion rate."

20. *Line 294. You haven't described the observation location.*

    This has been added in the manuscript.

    (Page 3-4, line 87-92) "Briefly, Chaoyang District was located at the eastern area of Beijing and was one of the six main urban districts (Dongcheng, Xicheng, Haidian, Chaoyang, Shijingshan, and Fengtai) of Beijing. This site was located about 2 km to the north of the North Fifth Road, approximately 0.3 km away from Beiyuan Road, with a high volume of traffic. And this site was located in a mixed-use commercial and residential area, with several shopping malls, residential areas, and office buildings nearby, and there were no obvious sources of industrial pollution. Thus, this site could be considered as an urban site."

21. *Line 3456. The averaging here (monthly) is so broad as to make this statement meaningless.*

    The statement here has been removed. And this table has been removed to SI. (SI, table S3)

22. *Line 373. See previous comment about Henry's coeff.*

    The corresponding explanations in the manuscript have been revised.

23. *Line 425-435. This could all go in the SI, there is nothing new here.*

    This has been removed to the SI. (SI, page 1, line 8-19)

24. *Line 450-459. This could all go in the Conclusions.*

    This part of the content has been moved to the Conclusions. (Page 22, line 465-473)

Referee #2

The study by Li et al. provides an extensive record of HONO measured during a field campaign Beijing, China in 2021. The novelty of this work comes from the fact that it HONO concentration measurements during the summer and autumn months, which have been lacking from previous studies conducted in Beijing, which have mostly occurred during the winter months (Figure 3). Detection of HONO was conducted using a LOPAP system. Analysis of the data was somewhat routine was focused on evaluating potential nighttime and daytime sources of HONO during the campaign, in addition to determining the impact of HONO relative to other OH sources on the oxidative capacity in the region. This approach is typical of many papers that attempt to determine the relative influence of the various HONO sources on observed ambient concentrations. The conclusions or analysis approaches are not novel. After calculating a rate of HONO formation from the unknown daytime source, there is some speculation that it is from photo-enhanced NO_2 conversion or nitrate photochemistry, which may be supported by some of the data, depending on the month. The work is valuable as a record of HONO concentrations from an important urban area during a time of year that is less well studied and alone for that should be probably be published eventually-- after the manuscript is revised for clarity, based on the suggestions below.

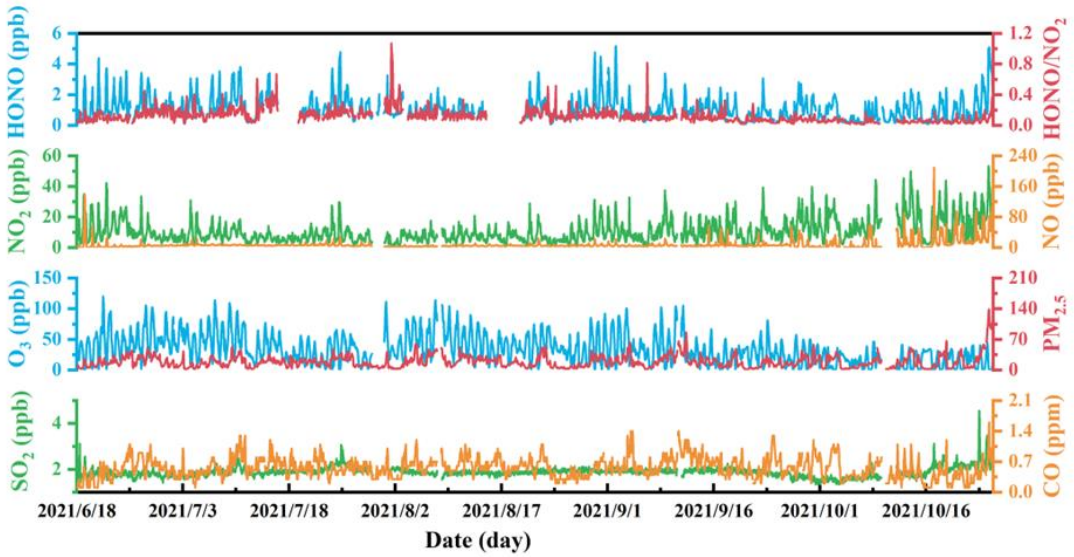
Response: We thank Anonymous Referee #2 for the review and the positive evaluation of our manuscript. We have fully considered the comments and responded to these comments below in blue text. The revisions in the manuscript are highlighted in yellow color. The response and changes are listed below.

1. *Significant figures: There are numerous cases within the text and in tables where too many significant figures are used when reporting numbers (e.g., Table 1 or section 3.1.1, reporting temperature to the hundredth of a degree, or relative humidity to a hundredth of a percent; section 3.1.2, trace gas measurements, etc. many of these measurements are likely not accurate out to that many decimal points and the values should be rounded off appropriately.*

   Thank you for this comment. We have made the corresponding modifications in the manuscript.

2. *Figure 2: This figure was of very poor quality such that it was very difficult to read. The resolution was very low and colors chosen (e.g., yellow or pink) were of low contrast, making it almost impossible to read.*

We have made modifications to Figure 2. (Page 6, line 155)



3. *Section 3.2.1 and Figure 3: I feel it is difficult to make comparisons between HONO concentrations made during different seasons over a 20 year period in Beijing based simply on monthly averages. Error bars or any other indicator of variation in the data is not indicated for these values and it is not clear whether median concentrations may be a better way to report the data. Without consideration of the variation of these concentrations, it is not possible to make conclusions about whether values in summer are higher (in a statistically significant way) than in autumn or winter, etc.*

   To more accurately describe the data reported in the literatures, we have removed figure 3 in the manuscript, the error bars and the other indicators of variation in the data were added in Table S2. The corresponding context in the manuscript has been updated, due to the focus on different aspects in the observations, some on pollution processes and others on longer time scales, we have removed the content related to comparisons from the main text. (SI, Table S2) (main text, page 7, line 161-177)

4. *Line 242: I found the term "corrected HONO concentration ($HONO_{corr}$) confusing. It would help to explain that this is the concentration of HONO in air that is not due to direct vehicular emissions.*

   We have added the explanation in the manuscript.

   (Page 11, line 239-240) "Then the concentration of HONO in air that is not due to direct vehicular emissions (the corrected HONO concentration, $HONO_{corr}$) can be obtained from the following equation……"

5. *Line 251: Symbols for the rate constants should be written with lower case "k" instead of capital letter, which would be understood as an equilibrium constant.*

This has been corrected in the manuscript.

(Page 11, line 249) "……where the rate constants of k_{NO+OH} and $k_{HONO+OH}$ for reactions R1 and R2……"

6. *Line 275: $HONO_{corr}$ is here referred to as the HONO concentration due to heterogeneous NO_2-to-HONO conversion during the nighttime. However, in equation (3) it is all HONO that is not due to direct vehicular emissions. Perhaps a different symbol or term should be used for referring to the nighttime HONO concentrations due solely to NO_2 heterogeneous reaction to avoid confusion.*

This has been modified in the manuscript.

(Page 12, line 273) "Nighttime $HONO_{het,night}$ concentration could be estimated……"

(Page 13, line 282-284)

"$$k^0_{HONO} = \frac{[HONO_{corr,night}]_{t2} - [HONO_{corr,night}]_{t1}}{(t_2 - t_1)\overline{[NO_2]}} \quad (5)$$

$$k^X_{HONO} = \frac{(\frac{[HONO_{corr,night}]_{t2}}{[X]_{t2}} - \frac{[HONO_{corr,night}]_{t1}}{X_{t1}})\overline{[X]}}{0.5(t_2 - t_1)(\frac{[NO_2]_{t2}}{[X]_{t2}} + \frac{[NO_2]_{t1}}{[X]_{t1}})\overline{[X]}} = \frac{2(\frac{[HONO_{corr,night}]_{t2}}{[X]_{t2}} - \frac{[HONO_{corr,night}]_{t1}}{X_{t1}})}{(t_2 - t_1)(\frac{[NO_2]_{t2}}{[X]_{t2}} + \frac{[NO_2]_{t1}}{[X]_{t1}})} \quad (6)$$

$$k_{HONO,het-night} = \frac{1}{2}(k^0_{HONO} + k^{CO}_{HONO}) \quad (7)$$"

7. *Equations 5-7: The rational/derivation of these equations is not clear and symbolism is very unclear and there are several typos in the equations. Besides the [$HONO_{corr}$] term described above, it was confusing to use the symbol "C" for a conversion frequency since C is used often to represent concentration, and the units of the "conversion frequency" suggest they are first-order rate constants. Also, it is not clear why the conversion frequencies are scaled to CO concentrations. A clarification would be useful here.*

Thank you for this suggestion, the content mentioned in the comment has been modified in the manuscript. The explanation of rational/derivation of these equations has been added, and the symbol for a conversion frequency has been corrected to "k", the reasons for the application of CO concentration is also added in the manuscript.

(Page 12-13, line 273-288)

"Nighttime $HONO_{het-night}$ concentration could be estimated from the heterogeneous reaction (R3, the mechanism of heterogeneous formation of HONO, and this was first order in NO_2 and H_2O (Alicke

et al., 2002)), and the conversion frequency of HONO ($k_{HONO,het\text{-}night}$) could be expressed as Equation 7. We determined the HONO formation by assuming a linear increase of its mixing ratio during a time interval (t_2-t_1). Since the mechanism summarized in R3 was first order in NO_2, the HONO formation was proportional to the NO_2 concentration. The conversion frequency was also assumed to be independent of gas phase water (Kleffmann et al., 1998), the average nighttime conversion frequency was determined by Equation 5,6, and 7. In order to eliminate the influence of direct emission and diffusion, CO was chosen as the reference species used for normalization:

$$2NO_2 + H_2O \xrightarrow{\text{ground,aerosol surface}} HONO + HNO_3 \quad \text{(R3)}$$

$$k^0_{HONO} = \frac{[HONO_{corr,night}]_{t2} - [HONO_{corr,night}]_{t1}}{(t_2 - t_1)\overline{[NO_2]}} \quad (5)$$

$$k^X_{HONO} = \frac{\left(\frac{[HONO_{corr,night}]_{t2}}{[X]_{t2}} - \frac{[HONO_{corr,night}]_{t1}}{X_{t1}}\right)\overline{[X]}}{0.5(t_2 - t_1)\left(\frac{[NO_2]_{t2}}{[X]_{t2}} + \frac{[NO_2]_{t1}}{[X]_{t1}}\right)\overline{[X]}} = \frac{2\left(\frac{[HONO_{corr,night}]_{t2}}{[X]_{t2}} - \frac{[HONO_{corr,night}]_{t1}}{X_{t1}}\right)}{(t_2 - t_1)\left(\frac{[NO_2]_{t2}}{[X]_{t2}} + \frac{[NO_2]_{t1}}{[X]_{t1}}\right)} \quad (6)$$

$$k_{HONO,het-night} = \frac{1}{2}\left(k^0_{HONO} + k^{CO}_{HONO}\right) \quad (7)$$

where $\overline{[NO_2]}$ was the mean value of NO_2 concentration between time t_2 and t_1, k^0_{HONO} was the conversion frequency which was not scaled, and k^X_{HONO} was the conversion frequency scaled with reference gases X (CO). Then the NO_2 to HONO conversion rate (k_{HONO}) was calculated by the combination of k^0_{HONO} (not scaled k_{HONO}) and k^{CO}_{HONO} (CO scaled k_{HONO}), which could reduce the impact of uncertainties in diffusion process and emissions on the conversion rate."

Reference (Page 24, line 590-591)

Kleffmann, J., Becker, K. H., and Wiesen, P.: Heterogeneous NO_2 conversion processes on acid surfaces: Possible atmospheric implications, Atmos. Environ., 32, 2721-2729, 10.1016/s1352-2310(98)00065-x, 1998.

8. *Table 3: This table compares HONO conversion frequencies and production rates and forms the basis of a comparison. I recommend including errors and when comparing values from this study to others, one should conduct and report results of the appropriate statistical tests of significance.*

   Thank you for this suggestion. The errors have been added in the manuscript.

9. *Lines 334-343: This paragraph compares the production rate of HONO due to "unknown sources" derived from this work to values previously reported in the literature. It is one continuous string of values with references and as such is extremely difficult to read. I recommend including all this information in a table or figure to facilitate comparison.*

Thank you so much for this suggestion. This paragraph has been modified and all the information has been included in a table.

(Page 15, line 344)

"Table 4. The $P_{unknown}$ values in this work and reported literatures."

Date		value (ppb/h)	location	literatures
Summer	18 August to 16 September, 2018	0.49	Beijing	Xuan et al., 2023
	June to July, 2019	0.59	Beijing	Li et al., 2021
	24 July to 6 August, 2015	0.75	Xi'an	Huang et al., 2017
	1 June to 31 August, 2018	0.98	Nanjing	Liu et al., 2019
	8-20 March, 2005	1.7	Santiago	Elshorbany et al., 2009
	25 May to 15 July, 2018	2.1	Beijing	Liu et al., 2021a
	June to August, 2021	2.3	Beijing	This work
	1 June to 31 August, 2016	3.0	Jinan	Li et al., 2018
	20 June to 25 July, 2016	3.8	Beijing	Wang et al., 2017a
	August, 2018	4.5	Xiamen	Hu et al., 2022
Autumn	27 September to 9 November, 2018	0.65	Guangzhou	Yu et al., 2022b
	September to October, 2021	1.0	Beijing	This work
	October, 2018	2.1	Xiamen	Hu et al., 2022
	23 August to 17 September, 2018	2.3	Beijing	Jia et al., 2020
	22 September to 21 October, 2015	3.1	Beijing	Wang et al., 2017a

10. *A number of correlations are explored between P-unknown and various other data metrics (e.g., trace gas concentrations, light intensity, $PM_{2.5}$ concentrations, and products thereof). A number of correlations are reported using R values as an indicator of the quality of the fit. However, it is unclear whether these correlations are statistically significant. Please provide information on statistical significance. Also, with respect to the correlations, I am uncomfortable with choosing only the months that support a given hypothesis. For example, it was noted that there is a strong correlation ($R = 0.62$) between P-unknown and (JNO_2 x NO_2 x $PM_{2.5}$) in June, although this is the only month where this correlation seems to be significant. Yet, this is taken to be evidence for a light-induced heterogeneous reaction for NO_2-to-HONO conversion. Why would this relationship only exist in June and not during other months. Same for the correlations with various salt concentrations in October (lines 400-405).*

Thank you for this suggestion. The statistical significance of the correlations (P value) was added in Table S4 and in the main manuscript. Indeed, making an assumption based on the data from just a

few months would be somewhat hasty. Therefore, we have added qualifiers such as "in this observation" to the corresponding inferences.

11. *Section 3.5: This section explores the relationships between HONO concentrations, $PM_{2.5}$ and ozone concentrations in the dataset. A positive correlation between particle pollution and HONO concentration in summer was taken to be evidence that particles are the source of HONO. However, correlation does not imply causation and it is possible that both $PM_{2.5}$ and HONO are stem from the same sources (i.e., their concentrations would both increase during pollution events) and it is also possible that high HONO concentrations can lead to higher oxidative capacity and therefore higher rates of aerosol formation.*

    Thank you for this comment. According to the suggestions above, the explanations about the relationships between HONO and $PM_{2.5}$ concentrations have been updated.

    (Page 21, line 434-438). "One possible explanation of this phenomenon was that the increase in particle pollution in summer and autumn might lead to the formation of HONO and an increase in its concentration. Another possible explanation was that high HONO concentrations could lead to higher oxidative capacity and therefore higher rates of aerosol formation. There was also a possible explanation as both $PM_{2.5}$ and HONO were stem from the same sources (i.e., their concentrations would both increase during pollution events)."

12. *Supporting Information figures and tables: Place each figure or table on its own page and ensure that the figure captions are on the same page as the graphs or tables.*

    This has been corrected in Supporting Information. All figures and tables are placed within a single page width, and the captions are on the same page as the graphs or tables.

13. *Figure S1: What does the symbol WD and WS stand for. Please define.*

    "WD" is wind direction and "WS" is wind speed, these have been added in Figure S2. (SI, page 8)

14. *Lastly, although I felt the language used in the manuscript was relatively clear to understand, it would benefit from proofreading/editing by a native English speaker.*

    Thank you for this suggestion. We will take your suggestions and enhance our English writing skills in our subsequent work.