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.*

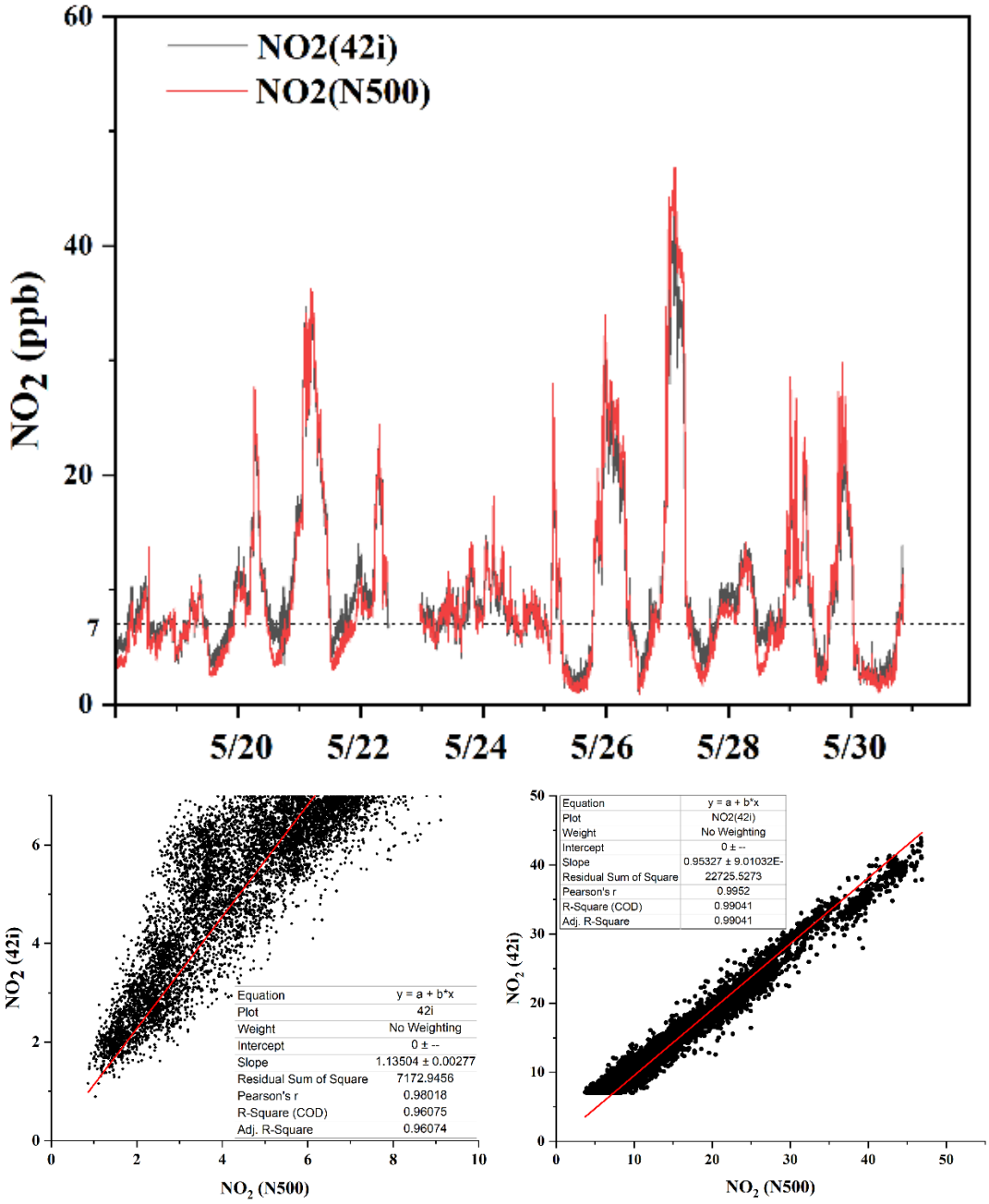
   Actually, due to the employment of a molybdenum NO_2-to-NO converter, the 42i analyzer might overestimate NO_2 concentration for the potential convertion of NOz (NOz = NOy – NOx. e.g., HONO, HNO_3, peroxyacetyl nitrate (PAN), and so on). Based on the articles mentioned (Zhang et al., 2023; Zhang et al., 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)