Li et al. present warm season measurements of HONO and related trace gases at a measurement site in Beijing, China. According to these authors, these data and analysis fill a measurement gap for the seasonal understanding of HONO in Beijing. As such, the data and analysis are a reasonable contribution to the literature on this subject and the related topics of the contribution of HONO to free radicals, oxidation capacity, and urban air pollution. It can be published in ACP subject to the comments below.

As with previous literature on this topic, the authors find a large missing or unknown source of HONO. The authors analyze the magnitude of this source, and try to assess the mechanisms that may produce it. This is the weakest part of this paper and one that should undergo major revision. The presented correlations do not appear to support any of the proposed mechanisms. Rather than trying to provide evidence for these sources, the authors would do better to simply evaluate the magnitude of each based on the available data and assess the extent to which each can explain the observations. There do not appear to be meaningful correlations that would support any given explanation for the unknown HONO source, but an analysis of the size of each would still be informative. See specific comments below for recommendations.

There are several other major revisions required – see the specific comments below. Of particular importance are the explicit recognition of vertical gradients in HONO, and the related topic of the contribution of HONO to the OH budget.

This paper has already been reviewed by two other reviewers. One recommended rejection on the basis of NO_2 measured by a molybdenum converter. The authors have addressed this concern, although they could go further with an uncertainty budget for the corrected NOx and all measurements. See specific comments. The second reviewer recommended major revisions based on lack of clarity and consistency in the analyses. I concur with this reviewer, and my recommendations are similar to those of this reviewer. The authors have addressed some of these comments, but have not fully addressed them. See specific comments below.

Response: We are very grateful to Anonymous Referee #3 for reviewing this manuscript so carefully. We have tried our best to improve and made some changes in the manuscript. We have responded to the comments below in blue text. The revisions in the manuscript are highlighted in yellow color. The response and changes are listed below.

Specific comments:

1. *Line 15: Define the emission factor in the abstract – i.e., relative to NOx or some other component of vehicle emissions.*
   Thank you for this suggestion. We have refined this definition (Page 1, line 16).
2. *Line 17: Conversion frequency in the abstract appears to be a first order rate constant. If so, quote as such, and don't give in units of % per hour but rather in s^{-1}. Also check this unit as it seems quite slow as given.*
   Thank you for this suggestion. We have refined the expression by removing the percentage and changing the range values to the average (0.008 h^{-1}). The averaged value is within a reasonable range comparing with Xuan et al. (2023) and Jia et al. (2020), 0.0073 h^{-1} and 0.0078 h^{-1} from August to September, 2018 (Page 1, line 17).
   References:

Xuan, H., Zhao, Y., Ma, Q., Chen, T., Liu, J., Wang, Y., Liu, C., Wang, Y., Liu, Y., Mu, Y., and He, H.: Formation mechanisms and atmospheric implications of summertime nitrous acid (HONO) during clean, ozone pollution and double high-level $PM_{2.5}$ and O_3 pollution periods in Beijing, Sci. Total Environ., 857, 159538, doi: 10.1016/j.scitotenv.2022.159538, 2023.

Jia, C. H., Tong, S. R., Zhang, W. Q., Zhang, X. R., Li, W. R., Wang, Z., Wang, L. L., Liu, Z. R., Hu, B., Zhao, P. S., and Ge, M. F.: Pollution characteristics and potential sources of nitrous acid (HONO) in early autumn 2018 of Beijing, Sci. Total Environ., 735, 11, doi: 10.1016/j.scitotenv.2020.139317, 2020.

3. *Line 50-52: OH + NO is not normally a net source of HONO as it is balanced by photolysis to create a null cycle that does not affect OH or NOx.*

    The content of the introduction mainly summarizes the source-sink characteristics of HONO. OH+NO is an important source of HONO, although it is not a net increase of HOx. We have provided a more detailed explanation in the manuscript. (Page 2, line 43-48)

    "Homogeneous reaction of OH +NO. This is an important source of HONO. Although the reaction of OH+NO, which is the reverse reaction of HONO photolysis, does not contribute to an actual increase in free radicals, the assessment of this reaction pathway is significant for understanding the sources and sinks of HONO. Especially during the winter pollution period in North China Plain, where there is usually a higher concentration of NO, this reaction pathway will contribute to a higher concentration of HONO (Xue et al., 2020).

    Reference:

    Xue, C., Zhang, C., Ye, C., Liu, P., Catoire, V., Krysztofiak, G., Chen, H., Ren, Y., Zhao, X., Wang, J., Zhang, F., Zhang, C., Zhang, J., An, J., Wang, T., Chen, J., Kleffmann, J., Mellouki, A., and Mu, Y.: HONO Budget and Its Role in Nitrate Formation in the Rural North China Plain, Environmental Science & Technology, 54, 11048-11057, 10.1021/acs.est.0c01832, 2020.

4. *Line 94: NO_2 hydrolysis is not the only potential interference in LOPAP instruments for HONO. For example, HO_2NO_2 is known to interfere with HONO in these systems. Can the authors provide more detail on the phrase "subtracted by a deployed dual channel absorption system" and explain how this corrects for interferences in the LOPAP method?*

    Briefly, the main structure of the instrument sampling unit is a double-channel stripping coil. In the first coil, almost all of the HONO and a small fraction of interfering species (e.g., NO_2, peroxyacetyl nitrate, NO_2^-) are absorbed by deionized water; while in the second channel, only a small fraction of interfering species is absorbed, which could be seen as the comparable conversion ratio in both the first and second channels. Therefore, the HONO concentration output by the instrument is the difference in concentration between the first and second channels. As to the soluble species such as HO_2NO_2, considering its little ambient concentration, especially in warm season, the interfering could be neglected. And we have added this explanation in the manuscript. (Page 3-4, line 89-95)

    Reference:

    Veres, P. R., Roberts, J. M., Wild, R. J., Edwards, P. M., Brown, S. S., Bates, T. S., Quinn, P. K., Johnson, J. E., Zamora, R. J., and de Gouw, J.: Peroxynitric acid (HO_2NO_2) measurements during the UBWOS 2013 and 2014 studies using iodide ion chemical ionization mass spectrometry, Atmospheric Chemistry and Physics, 15, 8101-8114, 10.5194/acp-15-8101-2015, 2015.

5. *Line 102: Does this imply an uncertainty in the analysis that is greater below 7 ppb of NOx? Is an uncertainty budget given? What, in general, is the uncertainty of all the measurements quoted in this paragraph?*

In the comparative observation of two devices, when the NO_2 concentration is less than 7ppb, the fitting results show that the ratio is magnified or reduced by 1.14 times. In terms of uncertainty, the fitting R^2 value is 0.96. Therefore, for the situation where the NO_2 concentration is less than 7ppb, the uncertainty should consider an additional 4% on top of the original 20% measurement uncertainty of the instrument (Yang et al., 2021). Based on the error calculation equation, the overall uncertainty is 20.4%.

Reference:

Yang, X., Lu, K., Ma, X., Liu, Y., Wang, H., Hu, R., Li, X., Lou, S., Chen, S., Dong, H., Wang, F., Wang, Y., Zhang, G., Li, S., Yang, S., Yang, Y., Kuang, C., Tan, Z., Chen, X., Qiu, P., Zeng, L., Xie, P., and Zhang, Y.: Observations and modeling of OH and HO_2 radicals in Chengdu, China in summer 2019, Science of the Total Environment, 772, 144829, 10.1016/j.scitotenv.2020.144829, 2021.

6. *Line 117: What is the uncertainty associated with estimating OH via equation 1? See comments above re: uncertainty budget.*

   Equation 1 in the manuscript is cited from Liu et al. (2019). The values of coefficients a, b, and c in this equation were adopted from the OH studies in the Pearl River delta (PRD) and Beijing, China (Rohrer et al., 2014; Tan et al., 2017, 2018). The influence of the uncertainty of the coefficients was estimated, results showed that the errors of OH increased with the increase of $J(O^1D)$, but the ratios of error to mean value of OH radicals were in an acceptable range of 0.37-0.55. In other words, the OH radical concentration calculated through this formula was within a reasonable range and would not subvert the relative conclusions in this study. We have added the explanation in the manuscript. (Page 4-5, line 120-122, line 125-126)

   References:

   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, doi: 10.5194/acp-19-13289-2019, 2019.

   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.

7. *Line 123: Is there a reference to the nighttime OH at 2e-5? This is quite a high number. Does this matter for the subsequent analysis? What is the source of nighttime OH at this level? A sustained OH of this magnitude would require a large, non-photolytic source. If not important to the*

subsequent analysis, suggest neglecting nighttime OH.

The nighttime OH radicals mostly come from the ozonolysis of alkenes (Ren et al., 2013; Tan et al., 2019). However, due to limitations in measuring methods, there is a lack of relevant data. The value of 2e-5 is calculated based on the formula. According to the comments, we have removed the subsequent analysis related to nighttime OH radicals.

Reference:

Ren, X., van Duin, D., Cazorla, M., Chen, S., Mao, J., Zhang, L., Brune, W. H., Flynn, J. H., Grossberg, N., Lefer, B. L., Rappenglück, B., Wong, K. W., Tsai, C., Stutz, J., Dibb, J. E., Thomas Jobson, B., Luke, W. T., and Kelley, P.: Atmospheric oxidation chemistry and ozone production: Results from SHARP 2009 in Houston, Texas, Journal of Geophysical Research: Atmospheres, 118, 5770-5780, 10.1002/jgrd.50342, 2013.

Tan, Z., Lu, K., Jiang, M., Su, R., Wang, H., Lou, S., Fu, Q., Zhai, C., Tan, Q., Yue, D., Chen, D., Wang, Z., Xie, S., Zeng, L., and Zhang, Y.: Daytime atmospheric oxidation capacity in four Chinese megacities during the photochemically polluted season: a case study based on box model simulation, Atmospheric Chemistry and Physics, 19, 3493-3513, 10.5194/acp-19-3493-2019, 2019.

8. *Line 171-174: The premise is hard to follow here – why should HONO sources remain constant? HONO should follow NOx (stated earlier), so variation in NOx should lead to variation in HONO.*

Thank you for this comment. We have removed this part of the content.

9. *Line 211: Provide more justification for the use of 2 μg m^{-3} to exclude biomass burning. For example, what is the ratio of HONO/K$^+$ that would allow assessment of biomass burning as a source of HONO?*

According to studies on the influence of biomass burning on HONO chemistry (Nie et al., 2015), when K$^+$ concentration is higher than 2 μg m^{-3} and the ratio of K$^+$ to PM$_{2.5}$ is larger than 0.02, the plumes are defined as biomass burning samples. While the samples with K$^+$ concentrations lower than 2 μg m^{-3} and a ratio of K$^+$ to PM$_{2.5}$ smaller than 0.02 are categorized as non-biomass burning samples. We have added this explanation in the manuscript. (Page 10, line 211-214)

Reference:

Nie, W., Ding, A. J., Xie, Y. N., Xu, Z., Mao, H., Kerminen, V. M., Zheng, L. F., Qi, X. M., Huang, X., Yang, X. Q., Sun, J. N., Herrmann, E., Petäjä, T., Kulmala, M., and Fu, C. B.: Influence of biomass burning plumes on HONO chemistry in eastern China, Atmos. Chem. Phys., 15, 1147–1159, doi: 10.5194/acp-15-1147-2015, 2015.

10. *Line 251: The OH concentration at night is taken from literature and not observed. Is this level consistent with the observed NO and NO$_2$? Such high levels of NOx would have the effect of greatly reducing nighttime OH, so the literature values would also have to have similar NOx levels. The high inferred levels of OH are not plausible without also demonstrating that there is a large OH source. Absent such an analysis, the nighttime HONO source from OH + NO should be omitted. It is almost certainly the case that the quoted values are an upper limit, perhaps a large upper limit, to the actual contribution of this reaction at night.*

Following the suggestions, we have removed all contents related to the OH radicals at nighttime.

11. *Line 308-310: Vertical gradients in HONO are well known (e.g., multiple references from Stutz et al., see below, Vanden Boer et al. 2013). Why would vertical transport be negligible?*

We have carefully read the literatures. And according to literatures mentioned above (Wong et al., 2011; Wong et al., 2012; Wong et al., 2013; Pinto et al., 2014; Stutz et al., 2002; Wang et al., 2006; VandenBoer et al., 2013; Young et al., 2012), photolytic HONO formation at the ground is the major formation pathway in the lowest 20 m, while a combination of gas-phase, photolytic formation on

aerosol, and vertical transport is responsible for daytime HONO between 200-300 meters above the ground. In our work, the measurement was conducted on the rooftop of one building, about eight meters above the ground. Therefore, the contribution of vertical transport to the near-surface HONO source is not significant. We have revised the statement in the manuscript and added the related literatures to the manuscript. (Page 12-13, line 283-288)

References

Wong, K.W., H.J. Oh, B.L. Lefer, B. Rappenglück, and J. Stutz, Vertical profiles of nitrous acid in the nocturnal urban atmosphere of Houston, TX. Atmos. Chem. Phys., 2011. 11(8): p. 3595-3609.

Wong, K.W., C. Tsai, B. Lefer, C. Haman, N. Grossberg, W.H. Brune, X. Ren, W. Luke, and J. Stutz, Daytime HONO Vertical Gradients during SHARP 2009 in Houston, TX. Atmos. Chem. Phys., 2012. 12: p. 635-652.

Wong, K.W., C. Tsai, B. Lefer, N. Grossberg, and J. Stutz, Modeling of daytime HONO vertical gradients during SHARP 2009. Atmos. Chem. Phys., 2013. 13(7): p. 3587-3601.

Pinto, J.P., J. Dibb, B.H. Lee, B. Rappenglück, E.C. Wood, M. Levy, R.Y. Zhang, B. Lefer, X.R. Ren, J. Stutz, C. Tsai, L. Ackermann, J. Golovko, S.C. Herndon, M. Oakes, Q.Y. Meng, J.W. Munger, M. Zahniser, and J. Zheng, Intercomparison of Field Measurements of Nitrous Acid (HONO) during the SHARP Campaign. Journal of Geophysical Research: Atmospheres, 2014: p. 2013JD020287.

Stutz, J., B. Alicke, and A. Neftel, Nitrous acid formation in the urban atmosphere: Gradient measurements of NO_2 and HONO over grass in Milan, Italy. Journal of Geophysical Research-Atmospheres, 2002. 107(D22).

Wang, S., R. Ackermann, and J. Stutz, Vertical profiles of NOx chemistry in the polluted nocturnal boundary layer in Phoenix, AZ: I. Field observations by long-path DOAS. Atmos. Chem. Phys., 2006. 6: p. 2671-2693.

VandenBoer, T.C., S.S. Brown, J.G. Murphy, W.C. Keene, C.J. Young, A.A.P. Pszenny, S. Kim, C. Warneke, J. de Gouw, J.R. Maben, N.L. Wagner, T.P. Riedel, J.A. Thornton, D.E. Wolfe, W.P. Dubé, F. Öztürk, C.A. Brock, N. Grossberg, B. Lefer, B.M. Lerner, A.M. Middlebrook, and J.M. Roberts, Understanding the role of the ground surface in HONO vertical structure: High resolution vertial profiles during NACHTT-11. J. Geophys. Res., 2013. 118(17): p. 10155-10171.

Young, C.J., R.A. Washenfelder, L.H. Mielke, H.D. Osthoff, P. Veres, A.K. Cochran, T.C. VandenBoer, H. Stark, J. Flynn, N. Grossberg, C.L. Haman, B. Lefer, J.B. Gilman, W.C. Kuster, C. Tsai, O. Pikelnaya, J. Stutz, J.M. Roberts, and S.S. Brown, Vertically resolved measurements of nighttime radical reservoirs in Los Angeles and their contribution to the urban radical budget. Environ. Sci. Technol., 2012. 46: p. 10965-10973.

12. *Line 366-367: If the phenomenon is not evident in four of the five months, then it is clear that there is not evidence for it. The conclusions should clearly state this finding rather than implying that it operates in June only.*

Thank you for this comment. We have modified the corresponding descriptions. (Page 16, line 342-346)

"In our work, good correlation between $P_{unknown}$ and product of JNO_2 and RH was found in June. However, this phenomenon was not evident in other four months. The phenomenon was not evident in four of the five months, this showed that in this observation there was not strong evidence for this conclusion. As shown in Table S4, June had the lowest RH and the highest JNO_2 value, the other four months had relative higher RH (due to the precipitation) and lower JNO_2 value. This phenomenon may be closely related to meteorological conditions and requires further research for

validation"

13. *Line 371-374: The analysis is very confusing. There is a correlation of the unknown source with the product of jNO$_2$, NO$_2$ and PM$_{2.5}$ that is evident only in June? If so, there is no evidence for such a source, and the conclusion should state this. Additionally, none of the R values (which all produce r^2 well under 0.5) are convincing. The assumed variations account for far less than half of the observed variability (r^2 values all well smaller than 0.5).*

Thank you for this comment. We have removed this section of the analysis.

14. *Line 375-381: Similar comment to above. The correlations presented offer no evidence for the source being tested. One could instead simply calculate the magnitude of the source based on previous literature and compare this to the observed P$_{unknown}$. The observations themselves appear to provide no evidence.*

Thank you for this comment. We have removed this section of the analysis.

15. *Line 389: Same comment. Based on the correlation coefficients presented, the conclusion should be that there is no evidence for this source, but that it could contribute based on prior literature.*

Thank you for this comment. We have made modifications to the corresponding explanations. (Page 17, line 364-365)

"However, the phenomenon above were not evident in four of the five months, this showed that in this observation there was not strong evidence for these conclusions, but that they could contribute based on prior literatures"

16. *Line 407-409: The conclusion is flawed, since the source should not vary from month to month without an obvious mechanism. A more likely explanation is simple variation in the data, which can simply be presented as an average and standard deviation rather than as a time varying source. This comment was prominent in previous reviews and should be addressed.*

Thank you for this suggestion. We have removed this section of the analysis.

17. *Section 3.4.3: There is an important caveat missing in this section in that it pertains to the OH source at the altitude of the measurement. Since vertical gradients in HONO are well known (see above) but not measured here, the analysis must be specified as a local analysis at a fixed height rather than characteristic of the entire mixed layer. The actual contribution to OH is smaller, and likely much smaller, than shown here when integrated across the mixed layer.*

Thank you for this comment. We have added the corresponding limiting conditions in the manuscript. (Page 17, line 367-368)

"the OH production rate from HONO (P$_{OH-HONO}$) at the CRAES observation site was calculated in this work"

18. *Also in this section, there is no comparison to the photolysis of formaldehyde, a large and known HOx source in urban areas. Presumably this is due to the lack of formaldehyde measurements. If so, this should be clearly stated, and it should also be stated that the analysis is not a full HOx budget.*

Thank you for this suggestion. Indeed, we did not measure formaldehyde in this work, and we have added the explanations in the manuscript. (Page 17, line 368-369)

"As the formaldehyde was not measured in this work, which was a large and known HO$_x$ source in urban areas, thus the analysis here was not a full HO$_x$ budget."

19. *Lines 418-420: What is P$_{OH-O3}$? Is this O$_3$ photolysis to O$_{1D}$ followed by reaction with water vapor?*

P$_{OH-O3}$ is the production rate of OH radical via O$_3$ photolysis to O1D followed by reaction with water vapor. And we have added the explanation in the manuscript. (Page 17, line 371-372)