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.

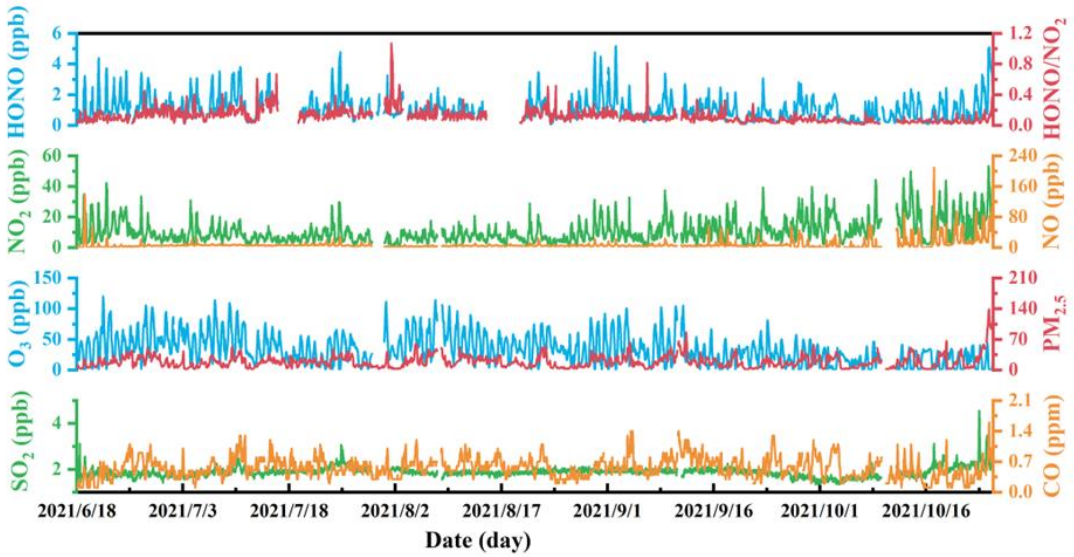
Response: We thank Anonymous Referee #2 for the review and the positive evaluation of our manuscript. We have fully considered the comments and responded to these comments below in blue text. The revisions in the manuscript are highlighted in yellow color. The response and changes are listed below.

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.