Response to Editor
Manuscript Number: acp-2021-359

Dear Authors,

Thank you for your consideration of the referee comments. The revisions largely address the referee comments. Before accepting this manuscript for publication however, I think that a few additional points require consideration.

We are very thankful to the editor for the time and effort that you have put into reviewing the previous version of the manuscript. The suggestions have enabled us to greatly improve our work. We make sure that each of the comments has been addressed carefully and the paper is revised accordingly. Please see our point-by-point response to the comments given in blue.

Main comment:

1. Further elaboration on the modeling using PAN/CO ratios is required in the manuscript. The equations from Section S1 should be moved to the main text along with a brief explanation.

Following the editor's suggestion, we have moved the equations from the supplement to the main text with corresponding explanation (Lines 258−273).

Additionally, further information is required about how the PAN and CO concentrations are selected for the model. It seems to me that the PAN/CO ratio used in the calculation should be the ratio from the urban environment. Please provide a brief discussion on why you think the PAN/CO ratio selected is appropriate to represent the urban environment.

As shown in **Figure 2b-c**, the increase rates of PAN during pollution days at the SDZ site are much larger than CO. It is known that CO is chemically inert and usually served as an ideal tracer for anthropogenic sources, which can well represent transport processes from pollution sources (Gao et al. 2005; Worden et al., 2013; Chen et al., 2020). Thus, we assume that PAN change rate at the SDZ site due to direct physical transport is identical with that of CO, and PAN/CO ratios change little along the transport from downtown Beijing to the SDZ site, as there are no intense anthropogenic sources along the transport pathway. Here, concentrations of PAN and CO are both from observations at the SDZ site. We have added the sentence in Lines 254−258 as "As shown in **Figure 2b-c**, the increase rates of PAN during pollution days at the SDZ site are much larger than CO. It is known that CO is chemically inert and served as an ideal tracer for anthropogenic sources, which can well represent transport processes from pollution sources (Gao et al., 2005; Worden et al., 2013; Chen et al., 2020). Thus, further evidence of enhanced photochemistry during the pollution episodes comes from the quantitative assessment of direct PAN transport and chemical production using CO as a tracer."

References:

Chen, Y. J., Ma, Q. L., Lin, W. L., Xu, X. B., Yao, J., and Gao, W.: Measurement report: Long-term variations in carbon monoxide at a background station in China's Yangtze River Delta region, Atmospheric Chemistry and Physics, 20, 15969-15982, 10.5194/acp-20-15969-2020, 2020.

Gao, J., Wang, T., Ding, A. J., and Liu, C. B.: Observational study of ozone and carbon monoxide at the summit of mount Tai (1534m a.s.l.) in central-eastern China, Atmospheric Environment, 39, 4779-4791, 10.1016/j.atmosenv.2005.04.030, 2005.

Worden, H. M., Deeter, M. N., Frankenberg, C., George, M., Nichitiu, F., Worden, J., Aben, I., Bowman, K. W., Clerbaux, C., Coheur, P. F., de Laat, A. T. J., Detweiler, R., Drummond, J. R., Edwards, D. P., Gille, J. C., Hurtmans, D., Luo, M., Martinez-Alonso, S., Massie, S., Pfister, G., and Warner, J. X.:

Decadal record of satellite carbon monoxide observations, Atmospheric Chemistry and Physics, 13, 837-850, 10.5194/acp-13-837-2013, 2013.

A brief discussion on biases and limitations of this calculation are also warranted.

It should be noted that PAN/CO ratios are assumed to be constant along the transport pathway in the calculation, leading to underestimation of physical impacts due to PAN thermal decomposition, especially in the afternoon when temperature is high. Thus, change rates due to chemical processes are maximum values that are possible. To remind the reader, we have added the sentence in Lines 273−275 as "It should be noted that the assumption of constant PAN/CO ratio along the transport pathway may lead to underestimation of physical impacts, especially in the afternoon when temperature is high. Therefore, the change rates due to chemical processes calculated by PAN/CO method are maximum values that are possible."

2. How consistent is the chemical production rate calculated using the PAN/CO method to that calculated using the PA radical production rates? This would require an estimation of the PA radical loss to obtain the PA radical concentration. It would also require NO2 concentrations, for which the measurement may be influenced by PAN. Nevertheless, I think a rough comparison would be instructive and would support the PAN/CO method.

Following the reviewer's suggestion, we also calculate PAN production rates using estimated PA concentrations. As shown in Section 3.4, PA radical is mainly formed through the reaction between CH_3CHO and OH (R1), and the major sinks of PA are reactions between NO_2 (R2) and NO (R3)

$$CH_3CHO + OH \rightarrow PA + H_2O \quad (R1)$$

$$PA + NO_2 \rightarrow PAN \quad (R2)$$

$$PA + NO \rightarrow CH_3 + NO_2 + CO_2 \quad (R3)$$

Since PA is rather reactive, it may reach steady state and thereby we assume that the rate of PA formation is equal to the rate of loss. Thus, PA radical concentration can be calculated by

$$[PA] = \frac{k_1[CH_3CHO][OH]}{k_2[NO_2]+k_3[NO]}$$

where the reaction coefficients (k) are temperature-dependent (Seinfeld and Pandis, 2006) and PAN production rate can be estimated by $k_2[PA][NO_2]$. **Figure R1** shows the calculated PAN production rates and PA concentrations at the SDZ site on the mornings of the observation period. Using this method, the mean PAN production rate in the morning was 0.25 ppb h^{-1}, and increased to about 0.6 ppb h^{-1} on pollution days. Although these values are slightly lower than those estimated by PAN/CO method (0.27 ppb h^{-1} and 0.73 ppb h^{-1}), the comparable PAN production rates by two different methods also suggest the enhanced photochemistry during pollution days.

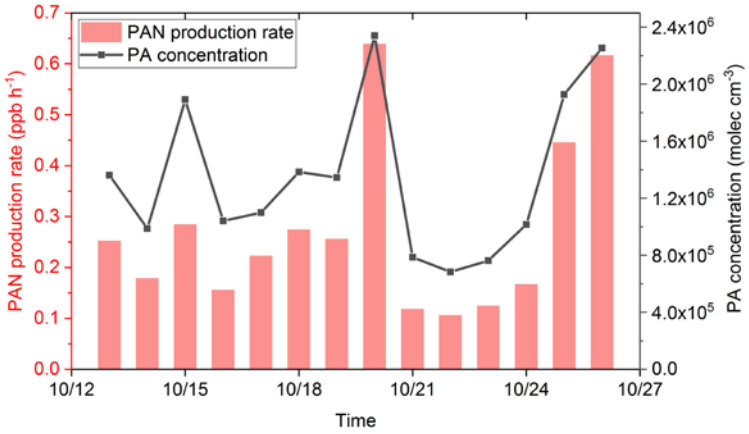

Figure R1. Time series of calculated PAN production rates (ppb h^{-1}) through reaction between PA radical and NO_2 and PA concentrations (molec cm^{-3}) at the SDZ site on the mornings of the observation period.

We have added a rough comparison in Lines 321−326 as "The calculation of PA production rates by CH_3CHO and OH can also help us estimate PA concentration in suppose that PA radical can reach steady state. Thus, we can also obtain PAN production rates by the product of reaction coefficient, PA and NO_2 concentrations (**Method S2**). Using this method, the calculated mean PAN production rate in the morning is 0.25 ppb h^{-1}, and increases to about 0.6 ppb h^{-1} on pollution days (**Figure S2**). Although these values are slightly lower than those estimated by PAN/CO method (0.27 ppb h^{-1} and 0.73 ppb h^{-1}) shown in **Figure 6**, the comparable PAN production rates using two different methods also suggest the enhanced photochemistry during pollution days." Besides, **Figure S2** and **Method S2** are also added in the supplement.

Minor comments

1. Several references to the cold season still remain in the manuscript (e.g. lines 19. 75. 349, and others). Please edit to clarify that it is autumn.

Thanks the reviewer for pointing this out. We have changed "cold season" concerning our observations to "autumn" through the main text.

2. There are several locations where I think the manuscript overstates aspects of the work. For instance, line 25 "proving is too strong a word and in line 30 "fully explain" is not appropriate given the type of model used. Similar comments apply to line 92 ("suggest" may be more appropriate than "explain"), line 101 ("perfect" should be deleted), line 245 ("exclude" should probably be replaced with something along the lines of "deemed to be unlikely").

To avoid overstating aspects of the work, we have changed the wording as follows:

Line 25: "also demonstrating the strong local photochemistry."

Line 30: "Our observational results suggest the cause of rapid increase of PAN during haze events in autumn at a rural site of the NCP"

Line 92: "Our results suggest the cause of rapid PAN increase over the rural NCP"

Line 101: We have deleted "perfect".

Line 245: "PAN increases in the morning resulted from planetary boundary layer evolution are deemed to be unlikely"

3. Line 139: I believe that model of NOx analyzer may detect some PAN as NO2. Given the focus of the manuscript, it may be useful to remind the reader of this.

Thanks the editor for pointing this out. To remind the reader, we have added the following sentence in Line 141: "It is noteworthy that parts of PAN could be considered as NO_2 because of the disadvantage of model 42i analyzer."

4. Line 160: Although the concentrations are in table S2, it would be helpful for the reader if you provide representative ranges for the different locations you are discussing.

Following the reviewer's suggestion, we have provided the representative ranges for different locations in the main text. Please see in Lines 160−164.

5. Line 184: The reduction in photolysis rates is not evident from the data provided in the figures or the tables. Please include this data either in the main text or in the SI.

We have added the following sentence in Lines 218−219: "As shown in **Figure 4j**, daytime $J_{O(^1D)}$ on 10/20 and 10/25 were 3.1×10^{-6} s^{-1} and 4.3×10^{-6} s^{-1}, which were 47% and 26% lower than that on clean days (5.8×10^{-6} s^{-1})." Besides, we have also deleted the text about photolysis in Line 182 and revised the corresponding sentence as "This result suggests the potential enhanced local photochemistry at the SDZ site on pollution days during autumn."

6. Figure 3a (northwesterly winds line 201) seems inconsistent with Fig. 1b (northeasterly/southwesterly lines 101-102). Is this due to the averaging used or the height? Please clarify.

The ERA5 data shows that the wind at 925 hPa at the SDZ site is northwesterly (**Figure 3a**), while the observed wind at 10 m from meteorology observatory is northeasterly (averaged wind direction: 33°). This discrepancy is mainly due to different height. As shown in **Figure R2**, the wind at 10 m near the SDZ site derived from the EAR5 data is northeasterly, consistent with **Figure 1c**. To clarify it, we have revised the sentence in Line 200 as "During the observation period, the SDZ site was affected by a high-pressure system in the west associated with northwesterly wind in the upper boundary layer."

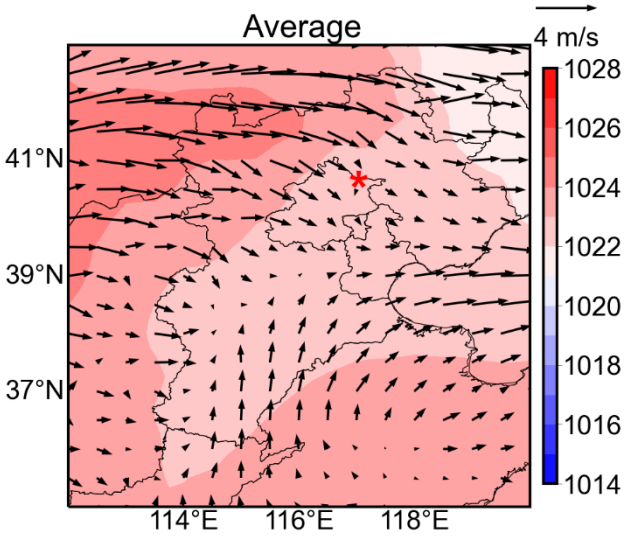

Figure R2. Winds at 10 m and sea level pressure (hPa) derived from ERA5 data averaged during 10/13−10/27. The red asterisk shows the location of the SDZ site.

7. Line 213/Figure 4: The temperature on 10/20 appears to be lower than the temperature on the preceding days. Furthermore, from Fig. 4f there appears to be extremely little variability in the mean or median temperature between the clean days and either 10/20 or 10/25. It suggests that the result of a positive temperature anomaly is not statistically significant. Further discussion/clarification is warranted.
Statistical results show that the daytime temperatures on 10/20 and 10/25 were 14.1 °C and 15 °C, which were 0.6 °C and 1.5 °C higher than clean days (13.5 °C), as illustrated in **Figure 4f**. In fact, the temperature on 10/20 was higher than most clean days except for 10/17−10/19.

8. Lines 375-378: The comparison of photolysis rates is not particularly meaningful without further information about the different measurements. What times of year are the measurements? Are these all compared at the same time of day? Does the HCHO concentration or the photolysis rate drive the differences?
Thanks. We have removed the comparisons of HCHO photolysis rate.

Technical
1. Line 46: These compounds are oxidation products of various NMHCs. Please correct the wording.
Corrected. Thanks.

2. Line 49: OH is the primary oxidant during the day, not necessarily the primary radical. Please revise.
The sentence in Line 49 has been revised as “During the daytime, hydroxyl (OH) radical is usually considered as the primary oxidant in the troposphere.”

3. Line 123: Please make sure all relevant gases are listed. The use of “etc” suggests that perhaps they are not. For instance, is MGLY measured? The calculations in section 3.4 suggest that it was.
Following the editor’s suggestion, we have deleted “etc” in Line 123. In fact, we did not obtain the MGLY concentration using the PTR-ToF-MS instrument during the observation period, owing to lack of its standard gas. We estimate the PA production rate from MGLY oxidation using a previously reported MGLY concentration in autumn 2018 at the SDZ site, which has been stated in Section 3.4.

4. Line 124: Please provide the length of the inlet.
Added. The length of the inlet is 3 m.

5. Line 127/Table S1: The time resolution of the PTR measurements is inconsistent. Please fix.
The PTR measurement has a time resolution of 5 minutes. To keep consistent, we have added the sentence “The measurement has a time resolution of 5 minutes.” in Lines 126−127.

6. Line 199: Please define SLP at its first use.
Added.

7. Line 237: I believe this should be 12:00 pm (noon), not 12:00 am (midnight).
Corrected. Similar changes have been made through the main text.

8. Line 286: Photolysis rates should be given as J and then subscript species name.

Corrected. Similar changes have been made throughout the main text and the supplement.

9. Line 310: The sentence implies that Figure 4e shows wind direction, but instead it shows wind velocity. Please make the text and figures consistent.

In **Figure 4**, positive V values denote southerly winds, while negatives represent northerly winds. We have added the information in Line 212, and changed "meridional wind speed" to "meridional wind" in the figure caption.

10. Line 330: I think "calculated" rather than "observed" is a better choice since HOx production is calculated and not measured.

We have changed "observed" to "calculated" here. Thanks a lot.

11. Line 333: I think you mean to say that the production rate of OH from HO2+NO is higher than the HOx sink from HO2+HO2. The current wording though implies that HO2+HO2 also produces HOx. Please clarify. Similarly in Table S3, the "production rate" column labeling is misleading/confusing. Production rate of what? I think HO2+HO2 is a loss rate.

Thanks the editor for pointing this out. We have changed the sentence in Lines 353−356 as "Recycling of HO_2+NO contributes to OH formation while HO_2+HO_2 is the important sink of HO_x in the troposphere. Calculated results show that the OH at the SDZ site can be immediately produced through reaction of NO+HO_2 as the production rate of NO+HO_2 is remarkably higher than HO_2 loss rate through HO_2+HO_2 (**Table S3**)." Besides, we have changed "production rates" to "reaction rates" in **Table S3**.

12. Please label reactions in the supplement differently from the main text so that the reader isn't confused as to which R1 you refer.

We have labeled reactions in the supplement as (1), (2), etc. to distinguish from (R1), (R2) in the main text.