

### General Overview:

The manuscript (egusphere-2024-2631) presents an attractive aspect of the connection of peroxyacetyl nitrate (PAN) to summertime haze and photochemical air pollution. As claimed by the manuscript, summertime PAN formation is quite an important topic. The topic also falls within the scope of the journal Atmospheric Chemistry and Physics (ACP). The authors present data from field observations with high temporal resolution as well as those from a box model and a machine learning model. The authors not only discuss the key factors and mechanisms of PAN formation based on the presented data but also tested the sensitivity of PAN to several other chemical species in the atmosphere. This manuscript is laid out well and shows the knowledge gap it fills. This manuscript is recommended to be published after addressing the concerns and comments below with minor revisions.

Response: Thank you for your thorough review and constructive comments on our manuscript (egusphere-2024-2631). We are delighted to hear that you find our study on the connection of peroxyacetyl nitrate (PAN) to summertime haze and photochemical air pollution to be significant, and that it falls within the scope of the journal Atmospheric Chemistry and Physics (ACP). We also appreciate your recognition of our data analysis and model applications. In response to your feedback, we have carefully considered and made revisions as follow. In general replies, we use blue font; red font indicates parts added in the revised manuscript, and blue italic font denotes references.

### Major Concerns:

Line 227 – 229: It is stated in the manuscript that “The daily variation of PAN exhibits a clear unimodal pattern, with concentrations starting to rise after sunrise and decreasing after 12:00 caused by thermal decomposition of PAN at high temperatures”. However, the diurnal variations of PAN, O<sub>3</sub>, and UV during the clean period as shown in Figure 2 (a) seems to exhibit bimodal patterns, which might not be consistent with and might not support the statement in the manuscript.

Response: Thank you for your valuable comment. We believe that the bimodal patterns of PAN and O<sub>3</sub> during the clean period are primarily influenced by UV radiation. As shown in Figure 2(a), UV also exhibits a bimodal pattern during this period, which likely contributes to the similar behavior of PAN and O<sub>3</sub> concentrations. In contrast, during haze conditions, UV levels remain relatively stable, resulting in the absence of bimodal patterns for PAN and O<sub>3</sub>. We have clarified this point in the revised manuscript to ensure consistency and accuracy in our discussion: **Although PAN and O<sub>3</sub> exhibit a slight bimodal pattern during the clean period, this is primarily due to the bimodal pattern of UV during this time.**

Line 276 – 277: It is stated in the manuscript that “reactions without considered in MCM may enhance PAN generation during hazy periods”. This statement seems to be based on the fact that the slope for the hazy period in Figure 3 (c) is less than 1. However, this statement might be challenged by the facts that the R<sup>2</sup> value is only 0.4708 and that there are multiple simulated PAN concentrations higher than observed PAN concentrations, which make the statement less convincing. It would probably be safer and more convincing to state that some reactions related to PAN generation might be missing in the MCM during the hazy period.

Response: Thank you for your insightful suggestion. You are correct that our initial statement was derived from the slope being less than 1. However, since the intercept is a positive value (0.21) and some simulated PAN concentrations are indeed greater than the observed values, we acknowledge that it would be more accurate to state that **"some reactions related to PAN generation or destruction might be missing in the MCM during the hazy period."** We have revised the manuscript to reflect this clarification.

Line 385 – 387 and 391 – 393: It is stated in Line 385 – 387 that “decreases in NO led to strong negative RIR” and in Line 391 – 393 that “increased NO level would inhibit the production of PAN”. These 2 statements seem to be contradictory to each other. It would be great if these 2 statements could be explained in more detail to make sure that the statements in this manuscript are consistent with each other.

Response: Thank you for pointing out this potential inconsistency. According to the RIR calculation formula (eq. S4 in the supporting information), a negative RIR indicates that after a 20% reduction in NO, the net production rate of PAN is higher than that before the reduction. This means that reducing NO can indeed promote PAN generation, making the two statements not contradictory. To avoid any ambiguity, we have revised Lines 385 – 387 to state: **the RIR of NO was negative, ranging from -0.67 to -0.27 (-0.52 ± 0.13) throughout the observation period.**

Line 457 – 458: The expression of the sentence “This further indicates that, despite the high temperatures, there is still a significant concentration of PAN, suggesting the existence of an unknown compensatory mechanism” seems unclear when it is put right after the sentence “Additionally, the net production rate of PAN becomes negative with PAN constrained”. It might take the reader quite some time and efforts to see if these 2 sentences are logically connected. It might be worth trying to rephrase the sentences to make the expressions more clearly.

Response: Thank you for your constructive feedback. We understand that the connection between these two sentences may not be immediately clear. Because of the high temperatures in summer, if PAN concentrations remain high, this would lead to a large removal rate of PAN by thermal decomposition, ultimately resulting in a negative net production rate of PAN. To enhance readability, we have rephrased this sentence: **However, the observed increasing PAN concentrations indicates that the actual net production rate is positive, suggesting that there are additional sources contributing to PAN generation that are not considered in the MCM mechanism.**

### **Minor Concerns:**

Line 31 – 32: Under the context of the abstract, the meanings of acronyms RIR and EKMA are not clear. The full form “Relative Incremental Reactivity” of RIR is not shown until Section 2.2 (Line 129) while the full form “Empirical Kinetic Modeling Approach” of EKMA is not shown until Section 3.3 (Line 397). It would be great if the full form can appear first in the manuscript before a corresponding acronym is used.

Response: Thank you for your feedback. The full forms of "relative incremental reactivity (RIR)" and "empirical kinetic modeling approach (EKMA)" have been provided the first time they are mentioned in the manuscript. We appreciate your attention to this matter.

Line 33 and 462: The terminology “deep emission reduction” appears in the manuscript without clear definition. If the definition is similar to that in some previous studies, it would be great to cite the relevant studies with clear definition. Otherwise, it might be helpful to define it in the manuscript.

Response: The term "deep emission reduction" is a technical term that refers to significant efforts in emissions reduction. This term is widely applied in the context of carbon emissions (Deetman et al., 2014), and it can also be used for the reduction of other pollutants.

### References

*Deetman, S., Hof, A. F., & van Vuuren, D. P. (2014). Deep CO<sub>2</sub> emission reductions in a global bottom-up model approach. Climate Policy, 15(2), 253 – 271. <https://doi.org/10.1080/14693062.2014.912980>*

Line 43: It might be better to cite the source of reactions R1 – R3 when they first appear in the description.

Response: Thank you for your suggestion. We have cited the source of reactions R1 – R3 at their first appearance in the manuscript to provide proper attribution and enhance clarity for the readers.

Line 58 – 59: While discussing previous studies on wintertime photochemical air pollution in the manuscript, it would be helpful to cite the source of the statement “it is found that aerosol promotes PAN generation”.

Response: Thank you for your suggestion. We have added the appropriate citation for the statement "it is found that aerosol promotes PAN generation" in the revised manuscript. This would provide proper context and support for the discussion on previous studies regarding photochemical air pollution in wintertime.

Line 59 – 60: While discussing previous studies on wintertime photochemical air pollution in the manuscript, please “Surprisingly high concentrations of OH radical, particularly under hazy conditions, have been observed and are largely attributed to HONO photolysis”.

Response: Added.

Line 139, 283, and 288: The meaning of the acronym OBM is not clear. The full name of the acronym seems to be missing in the manuscript.

Response: Thank you for pointing this out. We have included the full name of the acronym "OBM" in the revised manuscript at the first instance it appears.

Line 144: It might be better if the source of the "SHapley Additive exPlanations (SHAP)" approach can be cited.

Response: Thank you for your suggestion. We have added a citation for the "Shaply Additive explanation (SHAP)" approach in the revised manuscript.

Line 144 – 146: It might be better if some of the studies that have successfully applied the SHAP approach can be cited.

Response: Thank you for your recommendation. We have included citations for several studies that had successfully applied the SHAP approach in the revised manuscript.

Line 188 – 189: The statement "the precursor concentration of PAN is significantly lower than in the northern region" is not quite clear. Is it meant to be It would be helpful if the statement can be clarified.

Response: Thank you for your feedback. We have clarified the statement to specify that "the precursor concentrations of PAN, including NO<sub>2</sub> and VOCs, are significantly lower in the studied area compared to those in the northern region."

Line 190 – 191 figure to support the statement "The correlation between the daily maximum values of PAN and BC is the strongest (R=0.85), followed by O<sub>3</sub> (R=0.75)"?

Response: Thank you for your suggestion. We have included Fig. R1 in the revised manuscript to visually support the statement "The correlation between the maximum daily values of PAN and BC is the strongest (R=0.85), followed by O<sub>3</sub> (R=0.75)".

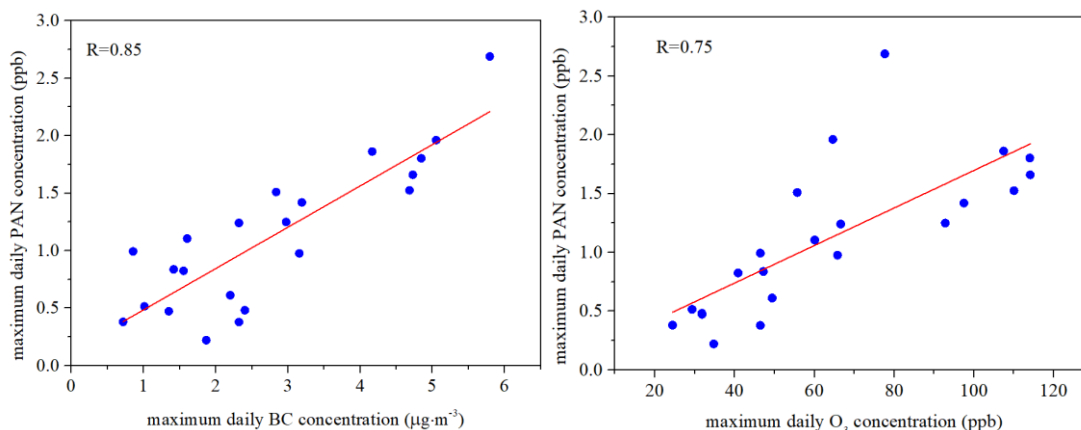


Fig. R1 The correlation between the maximum daily values of PAN and BC (a), as well as the correlation between the maximum daily values of PAN and O<sub>3</sub> (b).

Line 227: It would be helpful if it could be pointed out that the average diurnal patterns of PAN and related variables for clean and hazy conditions are shown in Figure 2 before the contents in Figure 2 are discussed in detail without clearly stating where the contents are shown.

Response: Thank you for your suggestion. We have added 'Fig. 2' after the sentence 'The average diurnal patterns of PAN and related variables have been averaged separately for clean and hazy conditions'.

Line 274 – 276: Both the R<sup>2</sup> and K values are discussed in the manuscript, but only the R<sup>2</sup> values are defined (Line 152) and shown (Figure 3 (c)). The K values seem to be not defined in the manuscript. It might take the reader some time and efforts to notice that the K values potentially mean the slopes in Figure 3 (c). I would suggest the authors to clearly define

Response: Thank you for your suggestion. The K has been defined in the revised manuscript: Furthermore, the simulated values are closer to the observed values during clean period, reflected in a higher R<sup>2</sup> value (R<sup>2</sup>=0.6782) and a slope value (K) closer to 1 (K=0.9097) (Fig. 3(c)).

Line 279 – 280 (Figure 3): The legend of the figure shows "obs" and "sim" without their definitions. if the legend of the figure

could be defined in and be consistent with the caption of the figure. For example, the caption could be modified as “Comparison of observed (obs) PAN and simulated (sim) PAN”.

Response: Thank you for your suggestion. We agree that clarifying the definitions of "obs" and "sim" in the figure legend would improve consistency and understanding. We have modified the caption to read: Comparison of **observed (obs) PAN and simulated (sim) PAN**, ensuring that the definitions are clearly stated.

Line 282 – 283 and 304 – 305: It might be better if the definition of bias described as “difference between the model simulation values and the observed values” can be expressed mathematically as what values minus what values for the reader to be clear about the mathematic definition.

Response: Thank you for your suggestion. We appreciate the need for clarity, and we have specified that the bias is calculated as **the model simulation minus the observed value**.

Line 283 and 285: Since there are 2 models, a box model and a machine learning model, being used in this study

Response: Thank you for your suggestion. We aim to use a machine learning model to evaluate the reasons behind the biases in the box model simulations. To avoid ambiguity, we have added 'OBM' in the sentence: To identify the key factors influencing the performance of the **OBM** model simulation.

Line 285 – 286: It is stated that “NH<sub>3</sub> is the most significant parameter affecting bias, contributing 19.68 %”. However, it seems that the number 19.68 % is not shown in Figure 4 (a). It would be helpful to clarify whether the contribution of 19.68 % is on average or obtained in some other ways. It would also be great to show such a value in the corresponding figure as described in the manuscript.

Response: Thank you for your suggestion. This proportion is calculated by taking the absolute values of the SHAP values for all features, summing them up, and then dividing the absolute SHAP value of a particular feature by the total sum. In other words, it represents the average proportion of the absolute SHAP value for each feature during the whole observation period.

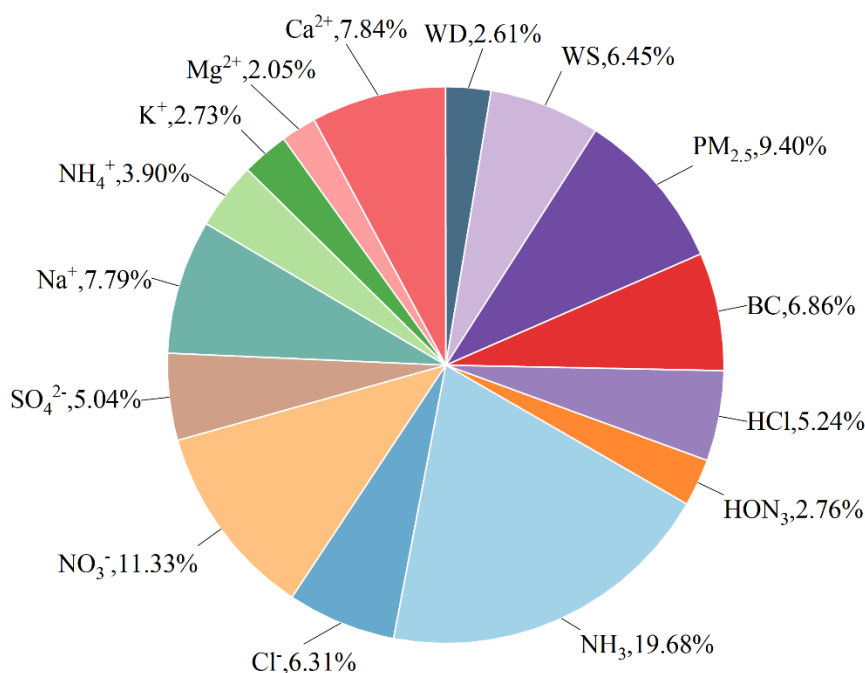


Fig. R2 The average proportion of the absolute SHAP value for each feature during the whole observation period.

Line 294 – 295: It is stated that “NO<sub>3</sub> is the second most significant parameter influencing the bias between the two, contributing 11.33 %”. However, it seems that the number 11.33 % is not shown in Figure 4 (a). Could the authors clarify whether the contribution of 11.33 % is on average or obtained in some other ways? it be possible to show such a value in the corresponding figure as described in the manuscript?

Response: Same as above.

Line 297: It is stated that “PM<sub>2.5</sub> is the third most significant parameter, contributing 9.4 %”. However, it seems that the number 9.4 % is not shown in Figure 4 (a). It would be helpful to clarify whether the contribution of 9.4 % is on average or

obtained in some other ways. It would also be great to show such a value in the corresponding figure as described in the manuscript.

Response: Same as above.

Line 307 – 308 and 320 – 321: Since there are data from field observations and model simulations being used in this study, it would be helpful if it could be clearly stated whether the average production and destruction rates of PAN during clean and haze periods are observed or simulated by what model. Although the caption of Figure 5 mentions that they are simulated, it would be great if it could be clearly stated in the paragraph of description as well.

Response: Thank you for your helpful comment. We would like to clarify that the production and destruction rates of PAN mentioned in Lines 307 – 308 are results from the OBM model simulations without the constraint of observed PAN values. In contrast, the rates discussed in Lines 320 – 321 are also from the OBM model simulations but include the constraint of observed PAN values. We have revised the manuscript to clearly state this distinction in the caption of Figure 5: Average diurnal variation of the OBM simulated production, destruction and net rates of PAN during clean (a) and haze (b) without PAN constrained. And average diurnal variation of the OBM simulated production, destruction and net rates of PAN during clean (c) and haze (d) with PAN constrained. Additionally, we have reiterated this information in the relevant paragraph to ensure consistency and clarity: Figure 5 (a) and (b) show the average production and destruction rates of PAN during clean and haze periods, as simulated by OBM without PAN constrained. Figure 5 (c) and (d) show the average production and destruction rates of PAN during clean and haze periods, as simulated by OBM with PAN constrained.

Line 312 – 313: I would appreciate it whether the net production rate of PAN is simulated net production rate or observed net production rate.

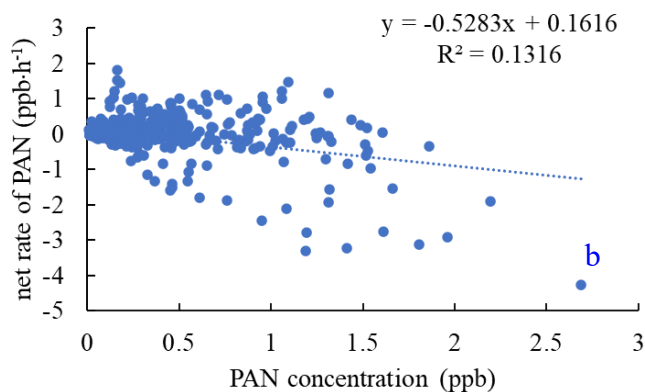
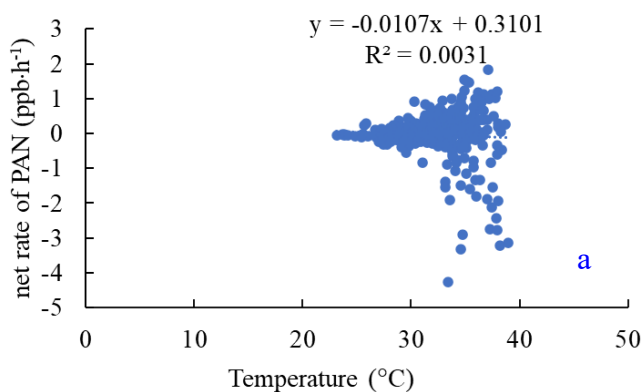
Response: Thank you for your question. The net production rate of PAN mentioned in Lines 312 – 313 is based on the model simulation results. We have ensured this is clearly stated in the revised manuscript: From 6:00 to 12:00 during the haze period, the simulated net production rate of PAN is positive, with an average value of 0.19 ppb·h<sup>-1</sup>. During the clean period, from 6:00 to 12:00, the simulated net production rate of PAN is 0.12 ppb·h<sup>-1</sup>.

Line 313 – 314: Is the diurnal variation of PAN based on observation or simulations? I would suggest the authors to it here.

Response: The result in Lines 313 – 314 is based on observations. We have included this clarification in the revised manuscript: The observed diurnal variation of PAN shows that from 6:00 to 12:00, the average net production rates during the haze and clean periods are 0.20 ppb·h<sup>-1</sup> (Fig. 2(a)) and 0.09 ppb·h<sup>-1</sup> (Fig. 2(b)), respectively.

Line 327 – 329: It is stated that “We conducted a correlation analysis of the net production rate of PAN with temperature, PAN concentration, VOCs, and NO<sub>2</sub>”. However, it seems that only the correlation between the simulated net production rate of PAN and observed PAN concentration is shown in Figure S7. It would be great if the other correlations mentioned in the manuscript can be provided to support the statement.

Response: Thank you for your valuable feedback. We acknowledge that only the correlation between the simulated net production rate of PAN and observed PAN concentration was shown in Figure S7. To address this, we have included additional correlation analyses for the net production rate of PAN with temperature, VOCs, and NO<sub>2</sub> in the revised manuscript as Fig. R3. These results would provide further support for our claims.



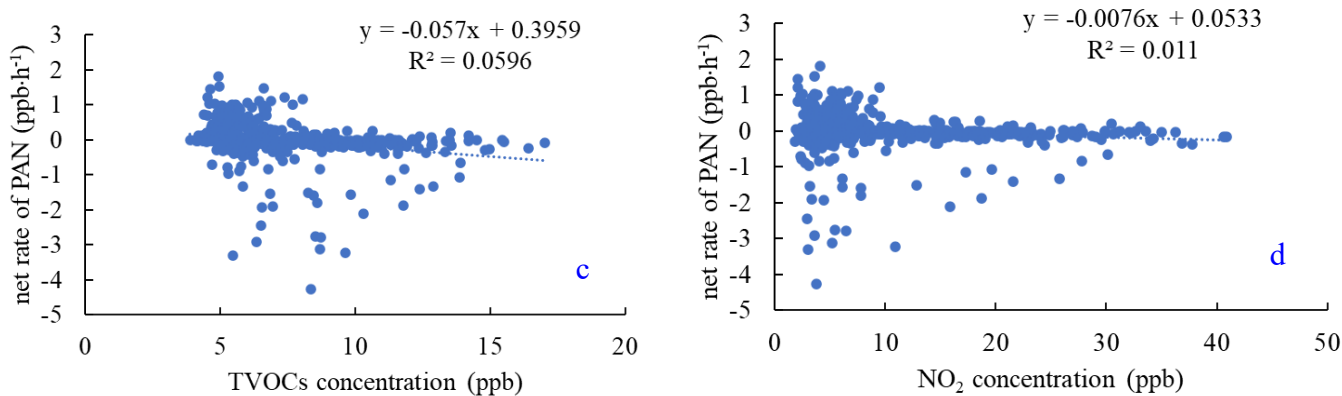


Fig. R3 Correlation analysis of the net production rate of PAN with temperature (a), PAN (b), TVOCs (c), and NO<sub>2</sub> (d) concentration, respectively

Line 330 – 332: It is stated that the sensitivity experiments are shown in Figure 5, but it seems that the sensitivity experiments are actually shown in Figure 6.

Response: Thank you for pointing this out. We have clarified that the sensitivity experiments are indeed shown in Figure 6, not Figure 5, and we have corrected this in the revised manuscript.

Line 331, 333, 335, 337, and 347 (Figure 6): Could the authors state in the text and caption of the figure whether the net production rate of PAN is simulated net production rate of PAN or not?

Response: Thank you for your suggestion. We have clarified in the text and the figure caption that the net production rate of PAN refers to the simulated net production rate.

Line 349 – 350: It is stated that “budget analysis of PA’s production and consumption pathways is frequently used”. However, only 1 study is cited to support this statement, which might not be convincing. It might be better if more studies are cited to support the statement that the method is frequently used. Otherwise, it might be safer and more convincing to state that the method has been used with only 1 citation.

Response: Thank you for your valuable feedback. I acknowledge that citing only one study may not convincingly support the statement regarding the frequency of budget analysis for PA's production and consumption pathways. I have revised the manuscript to include additional studies that demonstrate the widespread use of this method: Given the swift equilibrium between R2 and R4 at high temperatures, budget analysis of PA's production and consumption pathways are frequently used to detail the mechanisms behind PAN formation (Sun et al., 2020; Liu et al., 2022a; Liu et al., 2024).

Line 351: It would be helpful if it is clearly stated whether the diurnal patterns are simulated diurnal patterns or not.

Response: Thank you for your insightful comment. We have clarified in the revised manuscript that the diurnal patterns presented are simulated patterns: Figure 7 illustrates the diurnal patterns of the primary production and loss pathways for the PA radical simulated by OBM across different periods.

Line 356 – 357: It is stated that “the conversion of PAN into PA radical through thermal decomposition had high correlations with temperature during both haze and clean days”. It would be appreciated if a figure of correlations can be provided to support the statement.

Response: Thank you for your suggestion. We have included Fig. R4 showing the correlation between PAN thermal decomposition and temperature. From the figure, it can be observed that during clean days, the temperature is linearly correlated with PAN thermal decomposition, with an  $R^2$  value of 0.82; however, when using an exponential correlation, the  $R^2$  increases to 0.95. Similarly, during haze days, the linear correlation has an  $R^2$  of 0.77, but the exponential correlation significantly improves it to 0.91. Therefore, in the revised manuscript, we have changed the statement to: the conversion of PAN into PA radical through thermal decomposition had high exponential correlations with temperature during both haze ( $R^2=0.91$ ) and clean days ( $R^2=0.95$ ) (Fig. S13).



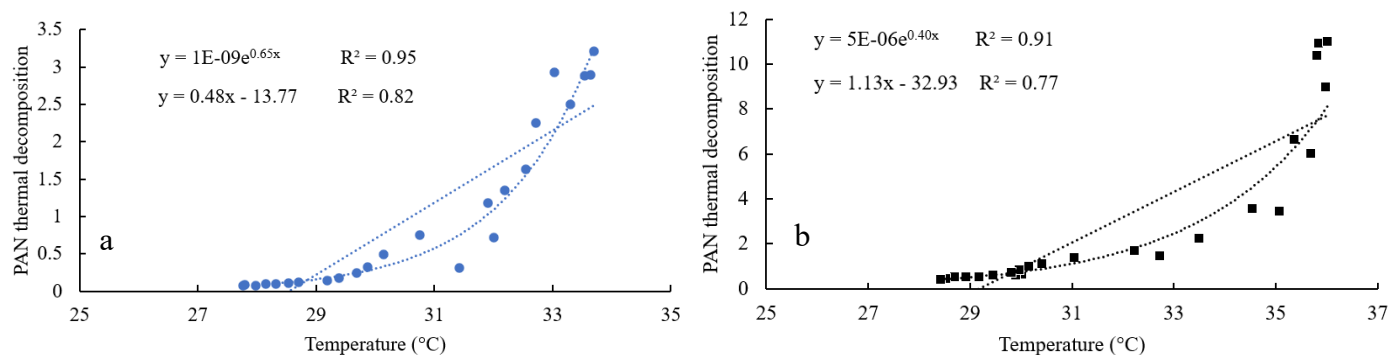


Fig. R4 Correlation between temperature and PAN thermal decomposition during clean (a) and haze (b) period.

Line 364 – 366: It would be clearer to the reader if it could be stated what “these four pathways” mentioned in the statement are. The pathways are shown in Figure 7, but it would be clearer if they could be described in the paragraph as well.

Response: Thank you for your valuable feedback. We appreciate your suggestion to clarify what “these four pathways” are. We have included a brief description of each pathway in the paragraph to enhance clarity for the reader: Production rates of PA from other pathways related to precursors, including OVOCs, radical cycling, MGLY, and CH<sub>3</sub>CHO, showed single-peak patterns around noon, which suggested that the PA radical generated from these pathways was primarily increased by intense solar radiation at noontime (Sun et al., 2020).

Line 377: It is stated that “The primary contributor to the PAN destruction rate was the reaction between PA and NO<sub>2</sub>”, but it seems that this sentence is meant to describe the PA destruction rate instead of the PAN destruction rate.

Response: Thank you for pointing this out. We have revised the sentence to clarify that it refers to the PA destruction rate rather than the PAN destruction rate.

Line 381 (Figure 7): Are the PA radical production and destruction rates simulated or not?

Response: Thank you for your question. Yes, both the PA radical production and destruction rates were simulated in our study. We have clarified this point in the revised manuscript to avoid any confusion: Figure 7. PA radical production and destruction pathways simulated by OBM on (a) clean days and (b) haze days.

Line 416 and 421: It is stated that “ΔHO<sub>2</sub> and ΔOH are positive for most periods” and that “ΔRO<sub>2</sub>, ΔNO<sub>2</sub>, and ΔNO are negative for most periods”. It might be better if there are specific numbers to quantitatively support the statements since there are also multiple periods with negative values of ΔHO<sub>2</sub> and ΔOH and multiple periods with positive values of ΔRO<sub>2</sub>, ΔNO<sub>2</sub>, and ΔNO shown in Figure 9.

Response: Thank you for your suggestion. We have included specific numerical values to quantitatively support the statements regarding ΔHO<sub>2</sub>, ΔOH, ΔRO<sub>2</sub>, ΔNO<sub>2</sub>, and ΔNO. This would provide clearer support for the trends described and address the variability shown in Figure 9: As shown in Fig. 9, ΔHO<sub>2</sub> and ΔOH are positive for most periods, accounting for 72.16% and 70.83%, respectively, indicating that the PAN mechanism promotes the generation of HO<sub>2</sub> and OH. Over the entire period, ΔHO<sub>2</sub> is 8.43×10<sup>-5</sup> ppb (Table S1), with no significant difference between clean and hazy periods, being 8.18×10<sup>-5</sup> ppb and 8.64×10<sup>-5</sup> ppb respectively. OH behaves similarly, with ΔOH being 4.55×10<sup>-7</sup> ppb over the entire period, and also showing no significant difference between clean and hazy periods, being 4.93×10<sup>-7</sup> ppb and 4.23×10<sup>-7</sup> ppb respectively (Table S1). The increase in simulated OH and HO<sub>2</sub> concentrations suggests that PAN photochemistry is in favor of radical formation and AOC at this site (Liu et al., 2024). Unlike HO<sub>2</sub> and OH, ΔRO<sub>2</sub> and ΔNO<sub>2</sub> are negative for most periods, accounting for 53.22% and 67.23%, respectively, because PAN formation uses up PA and NO<sub>2</sub>, the reduction in PA leads to a decrease in the amount of RO<sub>2</sub>. Over the entire period, ΔRO<sub>2</sub> is -6.45×10<sup>-4</sup> ppb, with no significant difference between clean and hazy periods, being -6.11×10<sup>-4</sup> ppb and -6.5×10<sup>-4</sup> ppb respectively (Table S1). The average value of ΔNO<sub>2</sub> during the entire observation period is -0.17 ppb respectively, with significant differences between hazy and clean periods (Table S1). Specifically, ΔNO<sub>2</sub> is -0.22 during hazy periods and only -0.11 during clean periods, indicating that the PAN mechanism consumes more NO<sub>2</sub> during hazy periods. Although ΔNO is positive for most periods, accounting for 78.79%, the overall mean is -0.01, with significant differences between hazy and clean periods (Table S1). ΔNO is -0.05 during hazy periods, showing an inhibitory effect, while

it is 0.03 during clean periods, showing a promoting effect.

Line 417, 419, 423, and 424: The statistic term “significant difference” appears multiple times in the manuscript. It would be more convincing if the significance levels to determine whether there would be statistically significant differences or not are clearly stated in this study.

Response: Thank you for your comment. I have included the results of the independent samples T-test in the revised manuscript, as shown in Table R1. From the table, it is evident that  $\Delta\text{NO}_2$  and  $\Delta\text{NO}$  exhibit significant differences between the clean and hazy periods at the 0.01 significance level, while  $\text{HO}_2$ ,  $\text{OH}$ , and  $\text{RO}_2$  do not show significant differences.

Table R1. The independent samples T-test between haze and clean period

	Haze (mean $\pm$ stdev)	Clean (mean $\pm$ stdev)
$\Delta\text{HO}_2$	$8.64\times 10^{-5} \pm 8.49\times 10^{-4}$	$8.18\times 10^{-5} \pm 5.76\times 10^{-4}$
$\Delta\text{OH}$	$4.23\times 10^{-7} \pm 1.37\times 10^{-5}$	$4.94\times 10^{-7} \pm 1.49\times 10^{-5}$
$\Delta\text{RO}_2$	$-6.55\times 10^{-4} \pm 2.28\times 10^{-3}$	$-6.11\times 10^{-4} \pm 1.43\times 10^{-3}$
$\Delta\text{NO}_2$	$-0.22 \pm 0.48^{**}$	$-0.11 \pm 0.27$
$\Delta\text{NO}$	$-0.05 \pm 0.17^{**}$	$0.03 \pm 0.09$

Note: \*\* The significance level is 0.01 between haze and clean period.

Line 420: The meaning of the acronym AOC is not clear. The full name of the acronym seems to be missing in the manuscript.

Response: Thank you for your comment. The full name of the acronym AOC, "atmospheric oxidative capacity," have been added to the manuscript to ensure clarity.

Line 429 – 430: the definition of “The difference of  $\text{HO}_2$ ,  $\text{OH}$ ,  $\text{RO}_2$ ,  $\text{NO}_2$ , and  $\text{NO}$  between base scenario with PAN mechanism and scenario without PAN mechanism” could be expressed mathematically as what values minus what values for the reader to be clear about the mathematic definition.

Response: Thank you for your comment. We have clarified the mathematical definition by explicitly stating that it represents the values from the base scenario with the PAN mechanism minus the values from the scenario without the PAN mechanism: **Figure 9.** The time series of  $\Delta\text{HO}_2$ ,  $\Delta\text{OH}$ ,  $\Delta\text{RO}_2$ ,  $\Delta\text{NO}_2$ , and  $\Delta\text{NO}$ . The  $\Delta\text{HO}_2$ ,  $\Delta\text{OH}$ ,  $\Delta\text{RO}_2$ ,  $\Delta\text{NO}_2$ , and  $\Delta\text{NO}$  is calculated as the base scenario with the PAN mechanism minus the scenario without the PAN mechanism.

Line 432 – 434: The term “inhibition rate” appears in the manuscript without clear definition. It would be helpful to define it in the manuscript.

Response: Thank you for your comment. We have added a clear definition of "inhibition rate" in the manuscript to ensure clarity: As shown in Fig.10 (a), the PAN mechanism inhibited 85.80% of net ozone production during the entire observation period, with inhibition rates (the percentage of negative  $\Delta\text{Net}(\text{O}_3)$ ) of 83.75% and 87.50% during clean and haze periods, respectively. This result is consistent with previous spring observations at the same site, where the inhibition rate was 83% (Liu et al., 2022).  $\Delta\text{Net}(\text{O}_3)$  is calculated as the base scenario with the PAN mechanism minus the scenario without the PAN mechanism.

Line 440: It would be clearer if it could be stated that the precursors mentioned here are precursors of what specific chemical species.

Response: Thank you for your suggestion. We have clarified that the precursors mentioned in line 440 specifically refer to  $\text{NO}_x$  and  $\text{VOCs}$ : Under the condition of low precursors (including  $\text{NO}_x$  and  $\text{VOCs}$ ), competition among these precursors may limit their secondary transformation, thus resulting in inhibition (Liu et al., 2024).

Line 440: It would be clearer if it could be stated what “their” means in the sentence with the term “their secondary formation”.

Response: Thank you for your feedback. “Their” refers to these precursors. To avoid ambiguity, I have revised this sentence to: Under the condition of low precursors (including  $\text{NO}_x$  and  $\text{VOCs}$ ), competition among these precursors may limit their secondary transformation, thus resulting in inhibition (Liu et al., 2024).

Line 451: It would be clearer if the units for the number 0.009 could be stated.



Response: Thank you for your comment. The unit for the number 0.009 is also ppb/ppb, and we have added this unit to the revised manuscript for clarity.

Line 456: It would be helpful if it is clearly stated whether the net production rate of PAN is simulated net production rate of PAN or not.

Response: Thank you for your suggestion. We have clarified that the net production rate of PAN mentioned is the simulated net production rate of PAN. This has been explicitly stated in the revised manuscript.

Figure S6 term “their product” in the caption should be clearly described along with the mathematic expression  $O_3 \times JO_1D$  to be consistent with the axis labels of the figure.

Response: Revised.

Figure S7: It seems that the axis labels of abscissa and ordinate are missing.

Response: Added and shown as Fig. R3.

Figure S8: It might be clearer for the reader to see the variations of time series if the axis limits could be adjusted closer to the minimum and maximum of each time series.

Response: Thank you for your feedback. The current axis limits were set to emphasize that these reactions are almost negligible compared to the  $RO_2 + NO_2$  reaction. As shown in Fig. R5, even when we minimize the range of the vertical axis as much as possible and apply the same range to other sources, we still find that the variations from other sources are nearly negligible (Fig. R6).

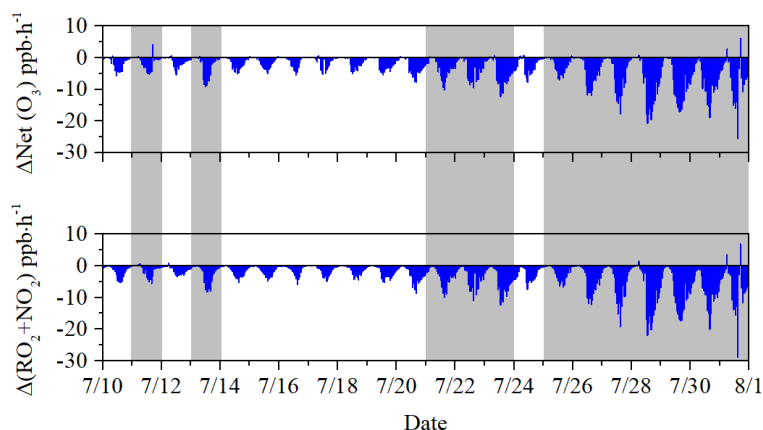


Fig. R5 Time series plot of  $\Delta Net(O_3)$  and the reaction of  $\Delta(RO_2+NO_2)$ . These values are calculated as the base scenario with the PAN mechanism minus the scenario without the PAN mechanism.

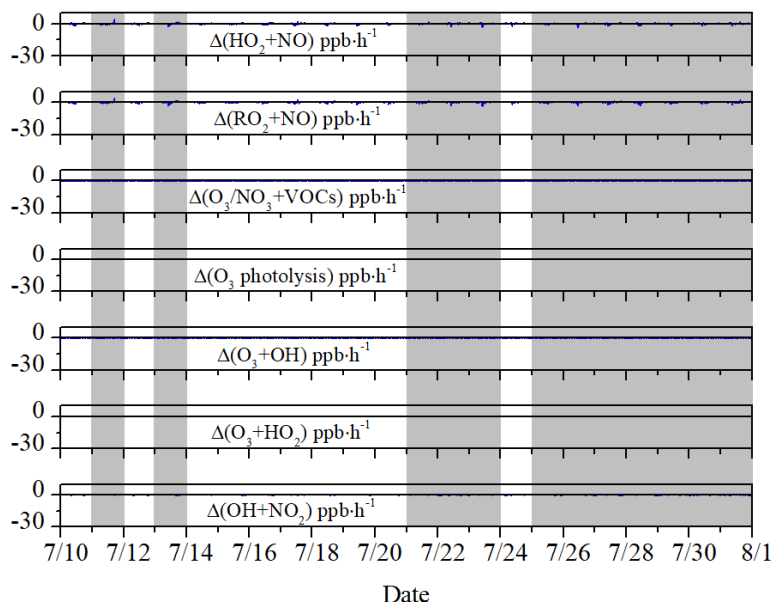


Fig. R6 Time series plot of the reaction of  $\Delta(\text{HO}_2+\text{NO})$ ,  $\Delta(\text{RO}_2+\text{NO})$ ,  $\Delta(\text{O}_3/\text{NO}_3+\text{VOCs})$ ,  $\Delta(\text{O}_3 \text{ photolysis})$ ,  $\Delta(\text{O}_3+\text{OH})$ ,  $\Delta(\text{O}_3+\text{HO}_2)$ , and  $\Delta(\text{OH}+\text{NO}_2)$ . These values are calculated as the base scenario with the PAN mechanism minus the scenario without the PAN mechanism.

**Technical Comments:**

Line 76: “Ximen” seems to be a typographical error of “Xiamen”.

Response: Revised.

Line 199 – 201: The sentence “PM<sub>2.5</sub> concentrations during the haze period were significantly higher than during the clean period, being 2.49 times that of the clean period” might be corrected as “PM<sub>2.5</sub> concentrations during the haze period were significantly higher than those during the clean period, being 2.49 times those of the clean period”.

Response: Revised.

Line 204 – 205: The sentence “During the haze period, ozone concentrations were also significantly higher than during the clean period, being 2.04 times that of the clean period” might be corrected as “During the haze period, ozone concentrations were also significantly higher than those during the clean period, being 2.04 times those of the clean period”.

Response: Revised.

Line 435: The “Fig. S11” seems to be meant as “Fig. S8” since there are only 8 figures in the supporting information.

Response: Revised.

Figure S5: The axis label of the abscissa “maximum daily ozone concentration (PAN)” seems to be a typographical error of “maximum daily ozone concentration (O<sub>3</sub>)”.

Response: Revised as Fig. R7

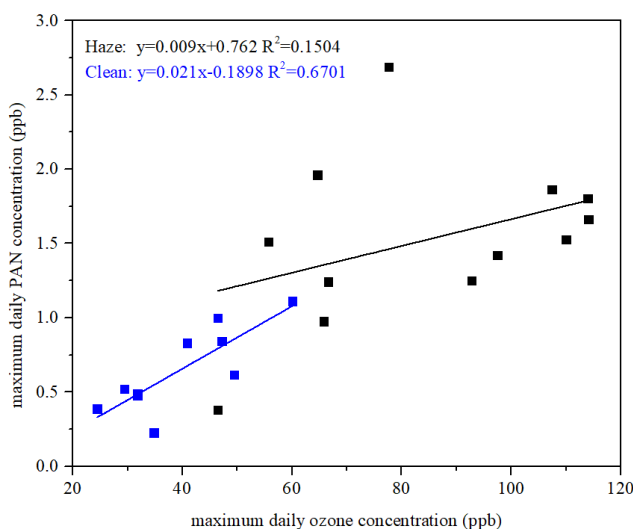


Fig. R7 Correlation between PAN and O<sub>3</sub> maximum daily concentrations during haze and clean.