Hu et al. made PAN observations and investigated its summertime formation with the aid of box modelling and machine learning. The paper provides valuable insights into the summertime formation of PAN and its link to aerosol pollution, which has been an unsolved issue during recent years. The following issues should be addressed before it can be considered for publication.

Response: Thank you for your feedback. We appreciate your acknowledgment of the insights provided in our paper regarding the summertime formation of PAN and its connection to aerosol pollution. We have carefully addressed the issues you raised to ensure the manuscript quality for publication standards. In general replies, we use blue font; red font indicates parts added in the revised manuscript, and blue italic font denotes references.

Major issues:

1. L76-81: The authors should probably further emphasize that Xiamen is a coastal site and give a background understanding on pollution as well as climate characteristics in Xiamen. What differs Xiamen from the sites where PAN was previously already investigated? This might help emphasizing the importance of this study.

Response: Thank you for your feedback. We would like to emphasize that Xiamen presents several unique characteristics that distinguish it from other sites where PAN has been previously studied. Firstly, Xiamen is one of the fastest urbanizing regions in southeast China while also being recognized as one of the cities with the best air quality in China. Its air quality could be seen as a model for the future of other urban regions in China. This makes Xiamen a particularly interesting site for studying PAN, as it offers insight into atmospheric chemistry in a rapidly urbanizing yet relatively clean environment. Geographically, Xiamen is located in a low-latitude coastal area, receiving abundant sunlight and long daylight hours during the summer. This results in strong solar radiation and rapid photochemical conversion rates, which differ significantly from the conditions at many inland or higher-latitude PAN study sites. Furthermore, the city is situated in the East Asian monsoon region, acting as a transport channel for atmospheric pollutants from the Yangtze River Delta and Pearl River Delta regions. This means that Xiamen experiences pollution that is overlapped by both local generation and regional transport. Thirdly, Xiamen's summer climate is influenced by complex meteorological conditions, including typhoons and the West Pacific Subtropical High (WPSH). The WPSH, in particular, creates conditions conducive to the formation and accumulation of photochemical pollutants and particulate matter (Wu et al., 2019). This contrasts with previous PAN studies conducted in regions with less dynamic weather systems. The combination of high temperatures, high humidity, and intense solar radiation, especially in July, likely accelerates both the formation and consumption rates of PAN, making Xiamen an ideal natural laboratory for studying PAN dynamics under high ozone conditions. These factors highlight the importance of this study in understanding the formation mechanisms of PAN in coastal, rapidly urbanizing regions with diverse meteorological influences. We have made the corresponding additions in the revised manuscript as follows (in red font): Xiamen is one of the fastest urbanizing regions in the southeast China and is also one of the coastal cities with the best air quality in China, where the air quality could represent the future of other Chinese urban regions. Between 2018 and 2023, Xiamen ranked among the top 10 cities in China, achieving positions of 7th in 2018, 4th in both 2019 and 2020, 6th in 2021, 9th in 2022, and returning to 7th in 2023 (mee.gov.cn, last assessed October 30, 2014). Xiamen is located in a low-latitude coastal area, with abundant sunlight and long daylight hours during the summer, resulting in strong solar radiation and rapid photochemical conversion rates. The city is typically influenced by the East Asian monsoon and serves as a transport channel for atmospheric pollutants from both the Yangtze River Delta and Pearl River Delta regions. Additionally, during the summer, Xiamen is often affected by complex meteorological conditions such as typhoons and the West Pacific Subtropical High (WPSH). The WPSH creates weather conditions that promote the formation and accumulation of photochemical pollutants and particulate matter (Wu et al., 2019). This setting provides an ideal "laboratory" for investigating the complexities of summertime PAN formation and its relationship with aerosol pollution under high ozone concentrations. In summer, especially in July, high temperatures, high humidity, and intense radiation are likely to accelerate both the formation and consumption rates of PAN.

2. Sect. 2.1 VOCs measurements were not introduced in terms of instrumentation details and observed species. Figures present TVOCs concentrations, how was VOCs constrained within the MCM model if you did not have the individual VOCs species.

Response: Thank you for pointing this out. The VOC measurements were indeed conducted using a gas chromatography mass spectrometer (GC-FID/MS, TH-300B, Wuhan, China) at an hourly time resolution. This included key VOC species such as alkanes, alkenes, aromatics, and oxygenated VOCs. Detailed information regarding the VOC detection system and calibration procedures is available in our previous study (Liu et al., 2022). Regarding the constraint of VOCs within the MCM model, while the figures in the manuscript present the total VOCs (TVOCs) concentrations, the MCM simulations were constrained by the measured concentrations of individual VOC species from the GC-FID/MS dataset. The individual VOC species were used to initialize and constrain the model inputs. This approach ensures that the MCM model represents the real atmospheric chemistry accurately, based on the observed VOC species. We have included this information in the revised manuscript to clarify the VOC measurements as follow: The VOC measurements were conducted using a gas chromatography mass spectrometer (GC-FID/MS, TH-300B, Wuhan, China) at an hourly time resolution. Detailed information regarding the VOC detection system and calibration procedures is available in our previous study (Liu et al., 2022b).

Reference:

Liu, T., Hong, Y., Li, M., Xu, L., Chen, J., Bian, Y., Yang, C., Dan, Y., Zhang, Y., Xue, L., Zhao, M., Huang, Z., and Wang, H.: Atmospheric oxidation capacity and ozone pollution mechanism in a coastal city of southeastern China: analysis of a typical photochemical episode by an observation-based model, Atmos. Chem. Phys., 22, 2173-2190, 10.5194/acp-22-2173-2022, 2022.

3. L190-192: Does it make sense to correlate daily maximum BC and PAN, when obviously they peaked at very different times of day? BC usually peaks during nighttime under low boundary layer conditions, while PAN peaks during noontime before O_3 due to strong thermal deposition losses. If there were any correlation between BC and PAN, you should at least prove it with a correlation analysis that uses data from the same time of day.

Response: Thank you for this insightful comment. We fully agree that BC and PAN typically peak at different times of the day, with BC usually reaching its maximum during nighttime under low boundary layer conditions, and PAN peaking around noon due to strong photochemical activity. This temporal mismatch indeed leads to poor direct correlation (with a correlation coefficient of only 0.097) when using hourly data. By using the daily maximum, these short-term fluctuations can be smoothed out, showing more clearly the correlations between pollutants and trends in atmospheric chemical processes.

4. L213-214: In addition to O_3 and PAN formation, a great part of TVOCs might have turned into SOA.

Response: We recognize that a significant portion of TVOCs can lead to secondary organic aerosol (SOA) formation. However, our study focuses on O_3 and PAN formation, and since SOA data was lack, we did not include it in our analysis. To avoid ambiguity, we have added the following statement in the revised manuscript: Although it is acknowledged that VOCs can also be converted into SOA, the discussion of SOA is beyond the scope of this study.

5. L231: It would be better if you added the standard deviations to the averaged values.

Response: We appreciate your suggestion and have added the standard deviations to the averaged values in the revised manuscript. The standard deviations for the haze and clean periods are 0.44 and 0.21, respectively.

6. L239-245: If you corrected for thermal losses, would this change the slope of PAN vs. O_3 production?

Response: Considering thermal losses alters the slope of PAN versus O_3 production. Specifically, during haze conditions, the slope increased from 0.009 to 0.1581, and in cleaner periods, it rose from 0.021 to 0.1504 (Fig. R1). This substantial change indicates that the low PAN generation efficiency in our region is largely influenced by thermal decomposition.

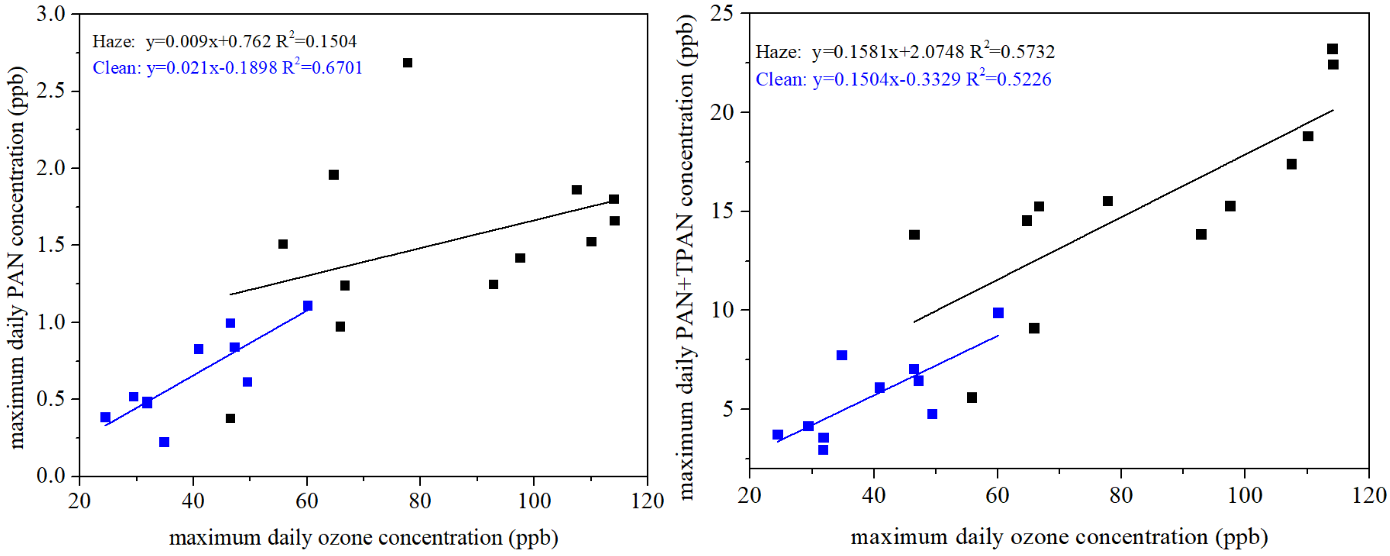

Fig. R1. Correlation between PAN and O_3 maximum daily concentrations during haze and clean (a), and correlation between PAN+TPAN and O_3 maximum daily concentrations during haze and clean (b)

7. L258-259, Fig.2: The wind direction varied differently during clean and haze periods, are daytime northerly winds connected to pollution transport? There was a rise in $PM_{2.5}$ during prenoon hours during haze days, was that connected to stronger secondary formation or transport processes?

Response: The wind direction indeed varied differently during clean and haze periods (Fig. R2). During clean periods, the wind was primarily from the northeast (Fig. R2(a)), while during the haze period, the wind direction was dominated by other directions except for the northeast, particularly the southeast wind (Fig. R2(b)). When the northeast wind blew with high speed, the $PM_{2.5}$ concentration was often low, indicating that the northeast wind primarily acted to clear pollutants, rather than transporting pollution from other regions to the area (Fig. R2(c)). Sulfur oxidation rate and nitrogen oxidation rate (defined as $SOR=SO_4^{2-}/(SO_4^{2-}+SO_2)$ and $NOR=NO_3^-/(NO_3^-+NO_2)$) were commonly used to represent secondary formation of $PM_{2.5}$. During the haze period around noon, the NOR is significantly greater than that during the clean period (Fig. R3(a)), while the SOR is notably higher after 11 o'clock during the haze period compared to the clean period (Fig. R3(b)). However, the wind speed is always greater during the clean period than during the haze period (Fig. R3(c)). The haze is relatively in a stable state, so the reason of the increase in $PM_{2.5}$ during the haze period is more likely to secondary transformation rather than the transport process. If the transport process were dominant, then the $PM_{2.5}$ concentration would be higher during the clean period when the wind speed is greater.

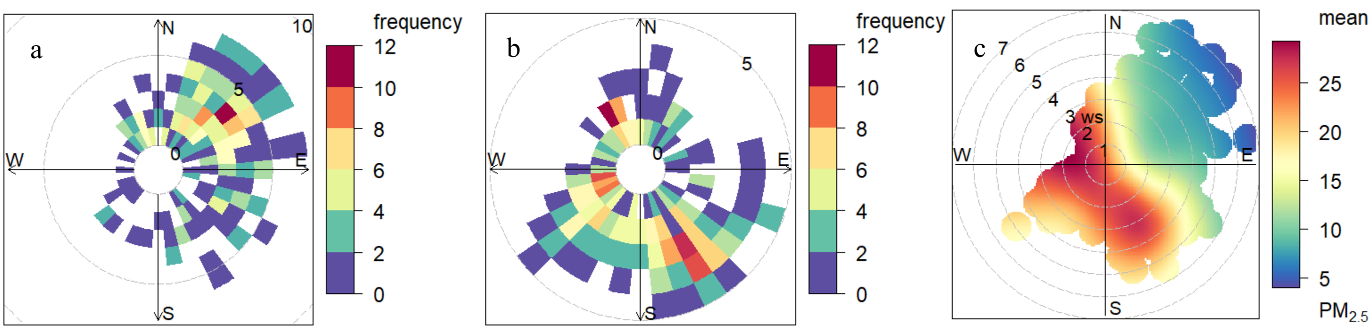

Fig. R2. Polar frequency of wind speed and wind direction for clean (a) and haze period (b), polar plot of $PM_{2.5}$ concentrations for whole observation period (c)

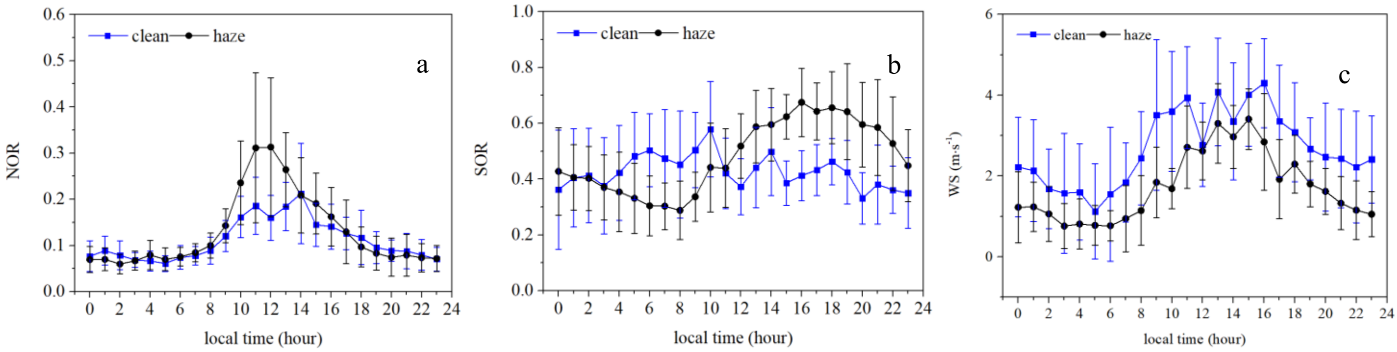

Fig. R3. The diurnal variation of NOR(a), SOR(b), and WS(c)

8. L287-291: NH_3 and HONO often reveal very high correlations in urban regions due to the influence of common vehicle emissions. Was that also the case for Xiamen? Since both were considered in the model, the model must have selected only one variable, would results be different if only HONO and no NH_3 were included? The uptake of aqueous uptake of PAN was introduced to be very weak, what mechanisms do you believe led to strong uptake of PAN on ammonium nitrate aerosols?

Response: We conducted a correlation analysis between NH_3 and HONO, and found that when using all data, the R^2 between the two is only 0.13. However, when focusing only on the morning rush hours (6, 7, and 8 AM), the R^2 increases to 0.60 (Fig. R4). This phenomenon suggests that in Xiamen, HONO and NH_3 are likely both emitted from motor vehicles. The concentration of NH_3 in urban environments has significantly increased due to the over-reduction of NO_x in catalytic converters used in automobile exhaust systems (Behera et al., 2013). The OBM model only considered HONO as a constraint, as NH_3 is not included in the default MCM mechanism. To investigate whether NH_3 affects PAN formation, we used machine learning to incorporate variables such as NH_3, $PM_{2.5}$, ws (wind speed), and wd (wind direction), which were not input into the OBM model. The difference between the OBM model simulation values and the observed values was used as the target for exploration. The previous study (Pratap et al., 2021) demonstrated that when the pH of the solution is 4.3, ammonium sulfate solution can promote approximately 30% more gaseous organic compounds to dissolve in the solution compared to pure water. Additionally, with constant pH, the higher the concentration of ammonium sulfate solution, the stronger the promotion effect has. It's a pity that this literature does not discuss the specific mechanism; future research could focus on this mechanism.

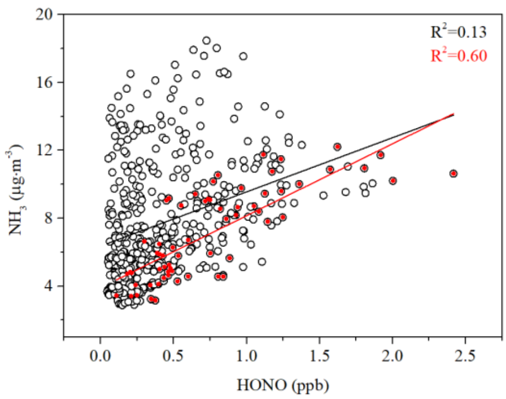

Fig. R4 The scatter plot of HONO and NH_3, where black hollow circles represent all hourly data, and red solid circles represent morning peak hours (6, 7, and 8 AM).

9. L294-297: How does NO_3^- promote PAN formation? Might it be common enhanced formation of NO_3- and PAN during atmospheric processes that led to these results?

Response: A PAN-forming rection involving NO_3 is the following:

$$CH_3COO + NO_3 \rightarrow PAN$$

The above NO_3 reaction predicts a direct proportion between the concentration of NO_3 and the rate of PAN formation, which is a relationship demonstrated experimentally as plotted in Fig. R5(a). However, I previously misunderstood; the NO_3 here refers to a radical, not nitrate.

Yes, it is indeed possible that a common source or physical processes contribute to the enhanced formation of both NO_3^- and

PAN during atmospheric processes. Nitrate is predominantly formed from the gaseous precursor NO*x* through secondary reactions in the atmosphere, which is similar to the main formation pathway of PAN, as PAN is produced during the oxidation of volatile organic compounds in the presence of NOx. We conducted a correlation analysis between PAN and NO_3^- and found a significant positive correlation at the 0.01 level, with a correlation coefficient of 0.374. Additionally, both PAN and NO_3^- exhibit daily variations, peaking around noon (Fig. R5(b)), suggesting they may share a common source. We have made corresponding modifications in the revised manuscript: considering the significant positive correlation between PAN and NO_3 at the 0.01 level, with a correlation coefficient of 0.374, and the fact that both reach their peaks around noon (Fig. S11), it is likely that they have a common source. Thank you for your question and for suggesting this possibility, which makes our assumptions and conclusions more convincing.

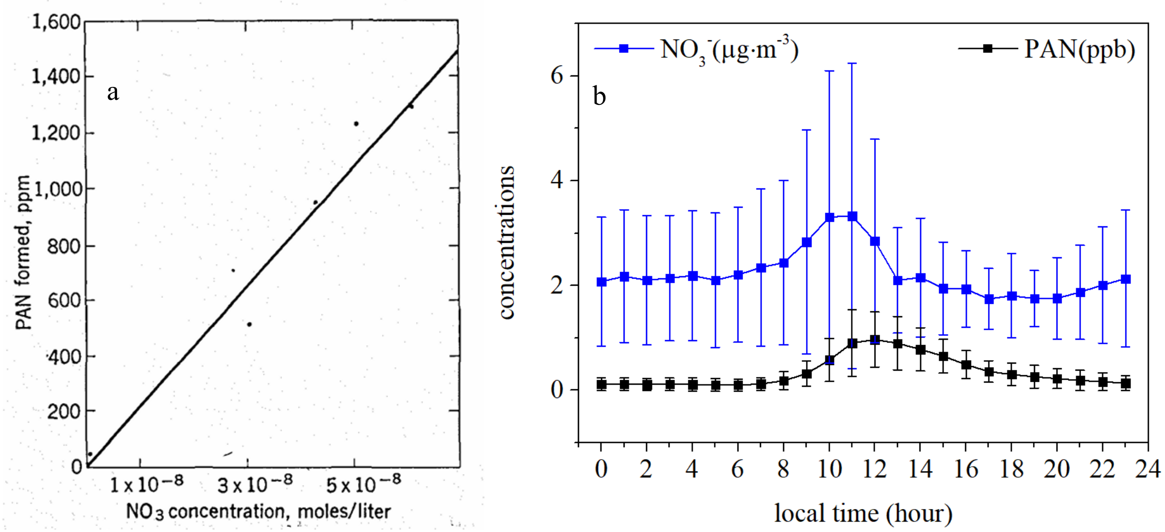

Fig. R5 First order dependence of PAN formation on NO_3 concentration (a) (this figure is from the literature Hanst 1971), diurnal variation of PAN and NO_3^- (b).

10. L321-327: If I am understanding things correctly, constraining PAN within the model would lead to the following results: if constraints are larger than model estimates, the model would add to thermal degradation losses leading to lower net production and vice versa. Since the model performed fairly well in simulating PAN production and could relatively accurately reflect its atmospheric level, why were there negative net production during haze conditions, when PAN was constrained? Since temperature and precursor constraints were the same, do you suggest that constrained concentrations were higher than those simulated by the model? However, simulated PAN was often higher than observed ones when there were no constraints. Isn't that in contradiction? Adjusting PAN constraints to 0.2 times that of actual values is far below those modelled without PAN constraints, why?

Response: Your understanding is correct. Constraining PAN with observational values would lead to similar results: if the observational values are higher than the model estimates, the model would account for the increased losses by thermal degradation, resulting in lower net production; conversely, if the observational values are lower than the estimates, the model would reduce losses by thermal degradation, leading to higher net production. This aligns with the PAN formation and loss processes. The model generally performed well in simulating PAN production and reflecting its atmospheric levels, achieving an IOA of 0.75. However, the simulation performance was lower during haze periods compared to clean periods. During clean periods, the linear fit between the observed and simulated values had an R^2 of 0.68, with a K value of 0.91, while during haze periods, the R^2 dropped to 0.47, and the K value decreased to 0.75. From Fig. R6(a), we can see that the net PAN production rates with PAN constrained turn negative when PAN concentrations are high, and most of these occurrences are during haze periods. To provide a clearer view of how the net PAN production rate is influenced by the constrained PAN concentrations, we created the scatter plot in Fig. R6(b). From Fig. R6(b), we can see that the larger the observed PAN values exceed the simulated values, the more the net production rate with PAN constraints falls below the rate without PAN constraints. The case without PAN constraints can essentially be viewed as constrained by the simulated values. When the observed PAN values are lower than the simulated values, the net production rate constrained by the observed PAN is higher than that constrained by the simulated values. Additionally, the net PAN production rate constrained by 0.2 times the observed values is significantly higher than the net production rate without PAN constraints (Fig. R7). This is also because the lower the PAN concentration, the smaller the thermal degradation, which leads to a higher net PAN production rate.

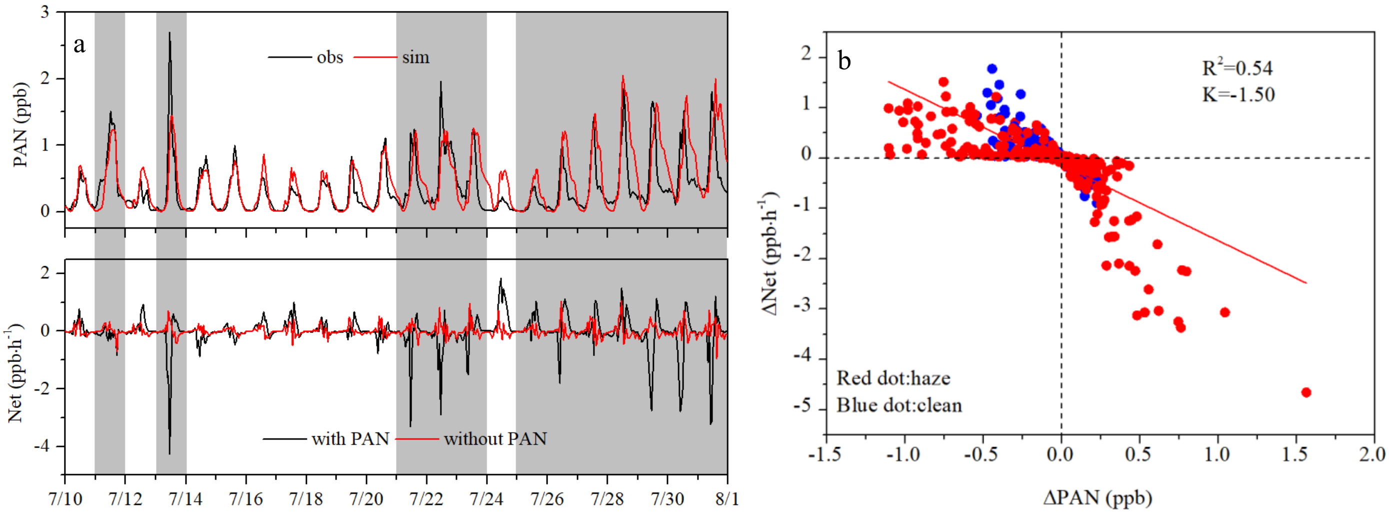

Fig. R6 Time series of observed PAN, simulated PAN, net PAN production rate with PAN constraints, and net PAN production rate without PAN constraints (a), with the shaded areas indicating haze periods; scatter plot of the difference between observed PAN and simulated PAN (ΔPAN) versus the difference between net PAN production rates with and without PAN constraints (ΔNet) (b).

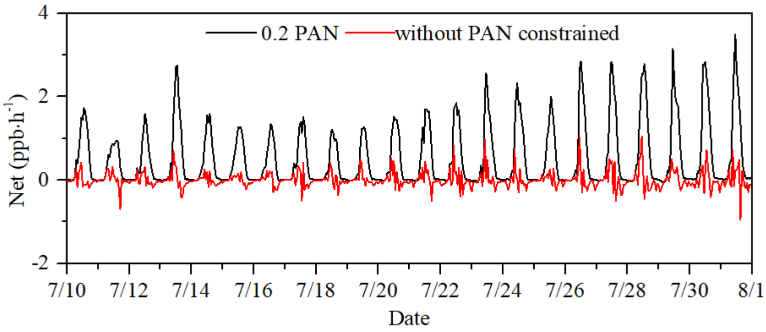

Fig. R7 Net PAN production rates simulated by OBM with 0.2 times the observed PAN values as constraints and without PAN constraints.

11. L379: I recommend a brief summary on which factors played the dominant role in boosting PA production rates on haze days.

Response: Thank you for your valuable feedback. The thermal decomposition of PAN played the dominant role in boosting PA production rates on haze days, followed by from CH_3CHO, MGLY, radical cycling and other OVOCs. And we have added the following sentence in the revised manuscript: In summary, the thermal decomposition of PAN played the dominant role in boosting PA production rates during both clean and haze periods, followed by contributions from CH_3CHO, MGLY, radical cycling, and other OVOCs.

Minor issues:

1. L22-24: Grammatically incorrect, please rephrase.

Response: Thank you for pointing this out. I have rephrased the section to correct the grammatical errors. The revised text now reads: Notably, PAN has been observed at unexpectedly high concentrations (maximum: 3.04 ppb) during the summertime. The daily maximum values of PAN showed a stronger correlation with black carbon (BC) (R=0.85) than with ozone (O_3) (R=0.75), suggesting a close connection between summertime haze and photochemical pollution.

2. L27-28: The number of valid digits should be unified across the manuscript.

Response: Thank you for your valuable feedback. We have retained two decimal places for the data in lines 27 and 28, and changed the four decimal places in other sections of the manuscript to two decimal places.

3. L76: "Ximen"→"Xiamen"

Response: Revised.

4. L85-86: Grammatically incorrect, please rephrase.

Response: Thank you for pointing this out. I have rephrased the section to correct the grammatical errors. The revised text now reads: Using machine learning with XGBoost, we identified the key factors that affect the OBM model's simulation results and clarified the mechanisms linking haze pollution to photochemical air pollution, as indicated by PAN and O_3.

5. L161-162: Grammatically incorrect, please rephrase.

Response: Thank you for pointing this out. I have rephrased the section to correct the grammatical errors. The revised text now reads: Combined with the synoptic situation shown in Fig. S4, the 8th typhoon of 2018, Typhoon Maria, made landfall on the morning of the 11th at Huangqi Peninsula in Lianjiang County, Fujian.

6. L177: by "daily maximum average" do you mean "maximum daily average"?

Response: Yes, it refers to the maximum daily average. We have made the corresponding correction in the revised manuscript.

7. L218: Mt. Waliguan is a global background station.

Response: Thank you for raising this point. Mt. Waliguan is indeed a Global Atmosphere Watch (GAW) background station. I have made the corresponding revision in the manuscript accordingly.

8. Fig 8c: It is quite difficult to differentiate between clean and haze dots without enlarging the figure, please select colors with larger contrasts.

Response: Thank you for the suggestion. I have updated the figure with colors that have larger contrasts and increased the size of the dots to better differentiate between clean and haze points (Fig. R8).

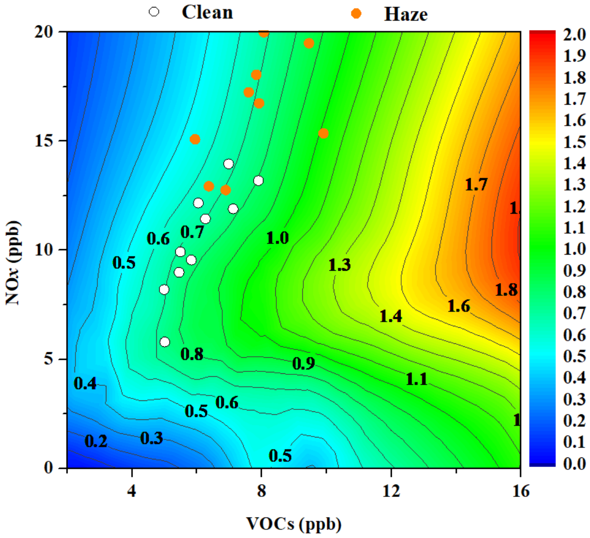

Fig. R8 The isopleth diagrams of PAN formation

9. Figure labels are often too small and hard to read.

Response: Thank you for your observation. We have increased the size of the figure labels to improve readability in the revised manuscript.

Reference

Behera, S. N., Sharma, M., Aneja, V. P., and Balasubramanian, R.: Ammonia in the atmosphere: a review on emission sources, atmospheric chemistry and deposition on terrestrial bodies, Environ. Science and Pollution Research, 20, 8092-8131, 10.1007/s11356-013-2051-9, 2013.

Liu, T., Chen, G., Chen, J., Xu, L., Li, M., Hong, Y., Chen, Y., Ji, X., Yang, C., Chen, Y., Huang, W., Huang, Q., and Wang, H.: Seasonal characteristics of atmospheric peroxyacetyl nitrate (PAN) in a coastal city of Southeast China: Explanatory factors and photochemical effects, Atmos. Chem. Phys., 22, 4339-4353, 10.5194/acp-22-4339-2022, 2022.

Pratap, V., Carlton, A. G., Christiansen, A. E., and Hennigan, C. J.: Partitioning of Ambient Organic Gases to Inorganic Salt Solutions: Influence of Salt Identity, Ionic Strength, and pH, Geophysical Research Letters, 48, 10.1029/2021gl095247, 2021.