Response to Reviewer #2:

Reviewer #2: This paper reports spring and summer season O_3 and PAN levels and their variations in Tibet and presents an analysis of what has been controlling the changes of those two most important photochemical air pollutants at such a high-altitude site under very clean conditions. Different impacts of transport and photochemistry on O_3 and PAN have been detected, revealing distinct transport pathways and different sensitivity to photochemical formation processes. Overall, the topic of the paper fits well into the scope of Atmospheric Chemistry and Physics, the observation and analysis methods used are scientifically sound and the results revealed sufficient novelty. The manuscript can be accepted for publishing after the following questions have been well addressed.

Response: We thank the reviewer for the detailed review of our manuscript, for all the valuable suggestions, and for approving the value of this research. In the following we provide point-to-point responses to the detailed comments and suggestions.

1. Although the authors reported the contributions of transport or STE and local chemistry to the observed O_3 and PAN concentrations, most of the results are descriptive, particularly before section 3.3. It's better to discuss the results more quantitatively and compare them with relevant studies.

Response: We thank the reviewer for this suggestion and added more quantitative discussions in Sect. 3.1 and 3.2, providing concentration levels of O_3, PAN and their precursors during spring and summer, making comparisons with measurements obtained at other background mountain sites. Detailed changes can be seen in the revised manuscript with tracked changes.

2. The writing style needs to be improved. It is difficult to understand some conclusions because some key information in the figures is omitted.

Response: Thanks for the suggestions, we went through the entire manuscript (including all figure and table captions) and improved its readability.

3. Almost all the modeled PAN concentrations are higher than the observed values, while it is completely opposite for O_3. My question is whether it is suitable to evaluate the importance of local chemistry for O_3 and PAN chemistry using a box model under an extreme environment such as Tibet, where is greatly affected by transport or STE？

Response: Thank you for posing this question. Since the box model was set to represent a surface air parcel, it can only account for near surface chemical processes. The F0AM model is based on the latest version of the most

detailed near-explicit chemical mechanism (Master Chemical Mechanism v3.2), with sufficient observation constraints on O_3 and PAN precursors, as well as sufficient spin-up time to warm up the model, the local photochemistry should be relatively well represented by the model. In the extreme environment of Tibet, STE affects O_3 much more than local photochemistry does, making it difficult to assess the influence of chemical process on O_3 and PAN formation, which is exactly why the measurement-constrained box model was adopted, in the hope to provide more insight into the influence of chemical formation on the variation of O_3. Simulated PAN was consistently higher than observed ones, especially when NO_2 was constrained, suggesting that under observed VOCs and NO_2 levels, local chemical formation would result in even higher PAN concentrations, if it were not for the impact of all kinds of transport processes. Overall, we believe it was suitable to this box model in the evaluation of local photochemistry (that was overshadowed by transport processes within observation data), however, this does not mean that the box-model can be deployed to predict O_3 and PAN at such locations, since transport process had too much impact on their overall concentration variations.

4. Did you warm up the model before simulating? How did you evaluate your model performance?

Response: Thanks for the question. We allowed the model to have a 3-day spin-up time, allowing the formation of various VOCs and intermediate oxidation products. We evaluated the model performance by comparing modelled O_3 net formation with those derived in another study of ours (Y.R. Wang et al., to be submitted to this special issue) based on photo stationary state assumptions using measurement constraints on O_3 precursors as well as radicals (OH, HO_2 and RO_2), which agreed very well with each other. Both studies concluded positive net O_3 formation. Additionally, we made sure that modelled NO concentrations fell into a reasonable range (21±38 ppt).

5. Figure 2b, it is difficult to differentiate the different components of VOCs. Figure 3b, what are the dotted lines

Response: Thanks for pointing that out, this was caused by the insufficient resolution of the figure within the preprint version. We modified the figure as the following:

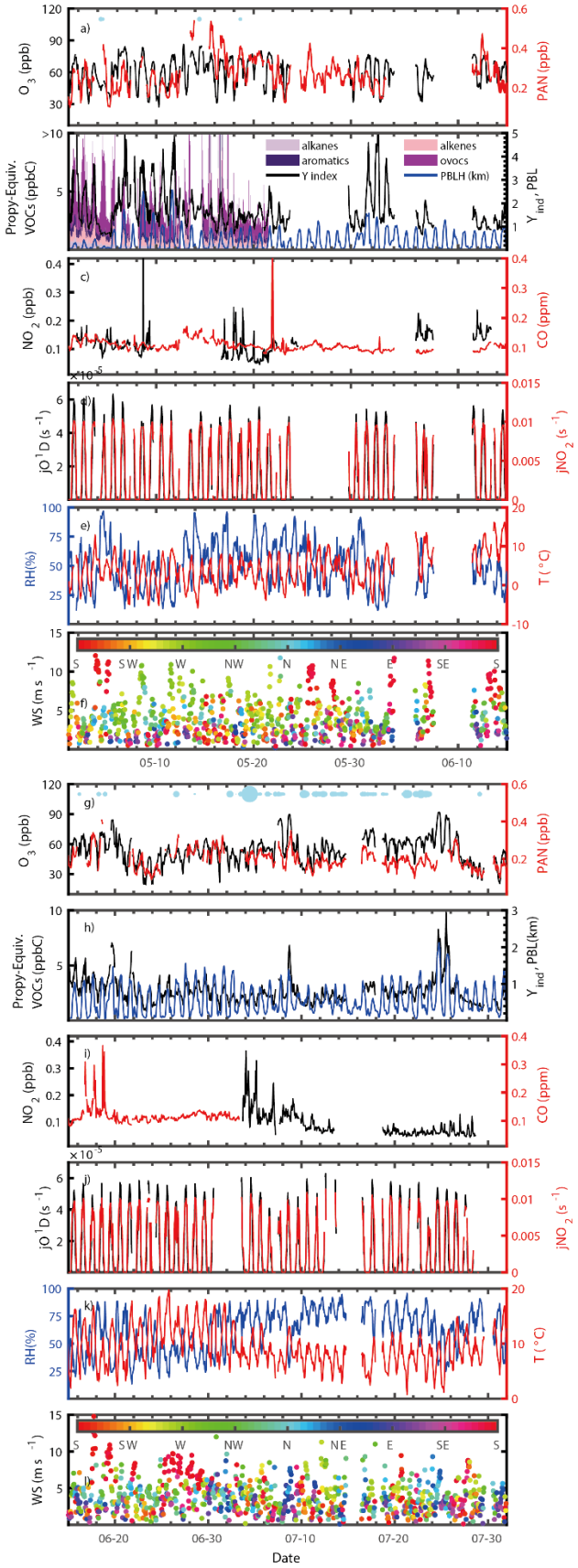

Figure 1. Timeseries of a,g) O_3 (black), PAN (red), b,h) VOCs (bars), Y index (black), PBLH (blue), c,i) NO_2 (black), CO (red), d,j) jO^1D (black), jNO_2 (red), e,k) RH (blue), T (red), f,j) wind

speed and wind direction (colored dots) during the spring (a-f, 1 May to 15 Jun.) and summer (g-j, 15 Jul. to 30 Jul.) period at Nam Co.

6. Please define the w wind, u wind, v wind.

Response: Thank you for the suggestion, we added definitions to the caption of Figure 4, where they first appeared.

7. Line 28: "However, only 0.1% of the springtime day-to-day O_3 variability **could by** STE processes, …". Something is missing in this sentence.

Response: Thank you for noticing, we must have deleted some words by accident. We corrected this sentence to:

"However, only 0.1% of the springtime day-to-day O_3 variability could be explained by STE processes, while 22% was explained during summertime."

8. Line 32: Make sure you really mean "diurnal" here and not "day-to-day".

Response: Thanks for pointing that out. We corrected this sentence to:

"Near surface photochemical formation was unable to account for the high O_3 level observed at NMC, and nor was it the determining factor for the day-to-day variability of O_3. However, it was able to capture events with elevated PAN concentrations and explain its day-to-day variations."

9. Line 115: There should be a comma before "which"

Response: Thanks, a comma was added.

10. Line 288-291: South Asian countries obviously strong pollution sources close to Tibet, revealing PAN transport, especially in summer, however, O_3 transport seemed weaker in comparison (Fig. 8). Is that because of enhanced dry deposition in southerly low altitude airmasses?

Response: There are several reasons behind the fact that southerly airmasses were not obviously linked to high O_3 concentrations. First, tropospheric O_3 concentrations typically increase with altitude, thus airmasses travelling over higher altitudes are more likely linked to higher O_3 concentrations. Secondly, airmasses travelling over heights near earth's surface are influenced by dry deposition as the reviewer suggested. Last, airmasses influenced by fresh stratospheric transport carry much higher O_3 loadings than tropospheric airmasses, which is why high O_3 were mostly linked to westerly and northerly airmasses during spring and summer, respectively.

From the fact that northerly low altitude airmasses that originated from the stratosphere revealed significantly elevated O_3, we might deduce that dry deposition might not have had such a strong influence on the depletion of O_3 during its transport.

11. Line 339: make sure of the consistency between “air mass” and “airmass”.

Response: Thanks for the suggestion, we went through the manuscript and changed them all to air mass.

12. Lines 411-412: Since local photochemistry highly overestimates observed concentrations, does that mean that free tropospheric input and PBL growth results in diluted PAN concentrations?

Response: That is a very good point. In fact, prenoon PAN concentrations did not continuously grow with increasing PBLH, only revealing moderate levels at high PBLH. This suggests that intense free tropospheric input might have diluted near surface PAN concentrations. Additionally, the overestimation might also have resulted from the fact that we assumed observed PAN were formed at near surface level in the box model. However, since winds were very strong at Nam Co, observed daytime PAN concentrations might have been more affected by free tropospheric PAN formation, rather than surface formation.

13. Lines 420-421: OVOCs contributed overall largely to the total VOCs concentrations and the authors suggest that PAN revealed certain sensitivity towards OVOCs. Which OVOCs contributed most to the formation of PAN?

Response: We thank the reviewer for the question. According to the modelling results (Fig. S17 below), the production of PA radicals (that formed PAN upon combining with NO_2) was dominated by the oxidation of acetaldehyde, while the oxidation of methylglyoxal, biacetyl and peroxyacetic acid also made small contributions. This conclusion was added to Sect. 3.4:

“Compared to O_3, PAN was sensitive to concentrations of both OVOCs and NO_2, since some of the OVOCs are direct precursors of PA radicals, which combine with NO_2 in PAN formation. ***According to modelling results in Fig. S17, acetaldehyde oxidation contributed majorly to PA radical formation at Nam Co (71.8%), followed by methylglyoxal (9.0%) and biacetyl (5.1%).*** *Still, NO_2 was more decisive of the overall O_3 and PAN production, since without its constraint, O_3 net loss and negligible PAN net formation would be yielded.”*

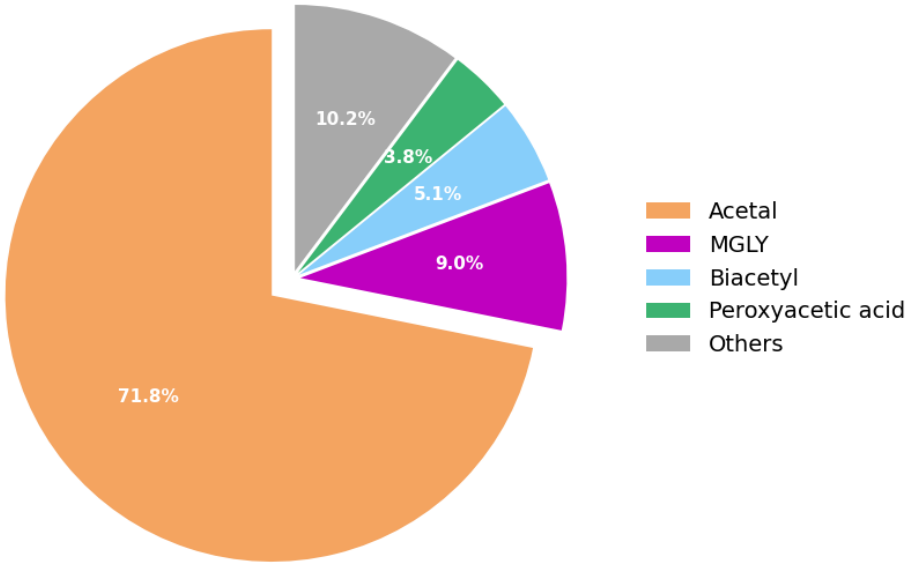

Figure S17. Average relative contribution of first-generation precursors to PA radical formation.

14. Line 445-446: "…, airmasses rich in O_3 were mainly associated with high altitude westerly airmasses that either entered the TP from the west **of** from the south, …" Replace "of" with "or"?

Response: Thanks for noticing, we made an according adjustment.