Response to Reviewer #1:

Reviewer #1: The authors conducted a study to investigate the variations in tropospheric ozone (O_3) and peroxyacetyl nitrate (PAN) and their precursors at a high-altitude site in the southern Tibetan Plateau. They found that variations in O_3 and PAN were controlled by distinct processes, with O_3 being mostly determined by stratosphere-troposphere exchange (STE), while PAN being mostly influenced by tropospheric chemistry and transport. While local surface O_3 and PAN both revealed net photochemical production during daytime, the variability of PAN was more controlled by photochemical formation processes than O_3. Overall, the manuscript is well organized and fluent in language. The analysis methods and results are scientifically sound. To my knowledge, this is the first study in Tibet presenting simultaneous high time resolution measurements of O_3, PAN as well as its precursors, which are highly valuable data worth publishing. Additionally, this is the first evaluation of PAN formation in Tibet, which also fills in a gap of knowledge. Some minor issues need to be addressed before the manuscript can be accepted for publication.

Response: We thank the reviewer for carefully going through our manuscript and for acknowledging the value of this research. In the following we will provide point-to-point responses to the detailed comments and suggestions.

Reviewer #1: Minor comments:

1. Lines 136-156: A slight concern on the PSCF analysis is that this is typically more suitable for the source analysis of atmospheric components with longer lifetimes, while PAN can have a long-lifetime in the free troposphere, O_3 seems to be more short-lived.

   Response: We thank the reviewer for raising this concern. O_3 indeed has relatively short lifetime in polluted regions, mainly due to its consumption by anthropogenic VOCs and NO_x emissions. However, at remote and pristine high altitude mountain sites such as those in Tibet (including the Lake Nam Co, Mount Waliguan and Xianggelila sites), NO_x levels are extremely low (~50 ppt on average) and concentrations of VOCs are also far lower than in polluted urban regions, which allows O_3 to have a relatively longer lifetime. The global lifetime of O_3 was estimated to be ~22 days (Goldberg et al., 2015), however, Bates and Jacob (2020) introduced an expanded odd oxygen family in the calculation of O_3 lifetimes and reached the conclusion that the global mean O_3 lifetime can reach 73 days. Previous studies at Mt. Waliguan have shown that O_3 can be transported over long distances from Southeast Asia to the northeastern edge of the Tibetan Plateau (Xu et al., 2018). The PSCF analysis was also used together with surface O_3 observations, which identified free tropospheric contributions in the Northwest sector and high anthropogenic contributions

from the Southeastern sector. Thus, using the PSCF analysis on surface O_3 in Nam Co was believed to be adequate.

2. Lines 198-205: The authors only provided Propy-Equivalent VOCs concentrations, however, to put observations into context with those in other studies, it might also be necessary to provide direct VOCs concentrations in ppb or ppbC. How do VOCs levels compare with previous observations in Tibet or similar high-altitude sites around the world? Since the authors discuss O_3 and PAN photochemistry afterwards, this might be important for understanding the difference or similarities in their results with those in literature.

   Response: We thank the reviewer for this suggestion. We added VOCs concentrations (in ppbv) and included a brief comparison between VOCs levels observed in this study and those obtained at other mountain sites, and added a short discussion on sources of VOCs at Nam Co:

   "Alkanes, alkenes and aromatics observed at the Dinghu mountain (1000 m a.s.l.) background site in southern China were 48, 40 and 29 times of those observed at the Nam Co site (Wu et al., 2016). Those in the Rocky Mountain National Park (3498 m a.s.l.) were 1.2, 3.6 and 1.3 times of those observed in this study (Benedict et al., 2019), while those observed during summertime (1994-1996) were 0.9, 14 and 1.6 times of that those in Nam Co (Ma et al., 2002), revealing the extremely low primary VOCs emissions at our site. However, OVOCs concentrations at Nam Co were 1.3 times of those observed in the Rocky Mountains, while only 0.24 times of those previously observed at Mt. Waliguan (Mu et al., 2007), indicating that airmasses in the TP were strongly photochemically aged due to the strong radiation and high oxidative capacity at such high altitudes, with additional influences from natural sources such as plant emissions or animal excrement (mostly from yak and sheep). At Nam Co, concentrations of isoprene and its oxidation products (e.g. MVK and MACR) were very low (0.034 ppb in total), with OVOCs being mostly dominated by formaldehyde, acetaldehyde and acetone (3.2 ppb in total), which have shown elevated concentrations over animal excrement (Mu et al., 2007)."

3. Lines 212-215: Again, how do NO_2 concentrations compare with previous observations in Tibet (if there are any)? The authors mention that there are natural and anthropogenic emissions in NO_x, can you name the detailed sources influencing NO_x variations at Nam CO? How do these sources impact the diurnal variation of NO_x?

Response: Thank you for the suggestion, we added a brief comparison with previous observations made at Mt. Waliguan in the northeastern Qinghai-Tibetan Plateau. Additionally, we pointed out the possible sources of NOx at Nam Co.

"NO_x levels were only scarcely reported for remote high-altitude locations, mainly due to instrument limitations. NO_2 levels were only slightly higher than the average NO_2 and NO level reported at Mt. Waliguan during summer 1994-1996 (0.048±0.017 ppb) based on filter-pack sampling and spring 2003 (0.043±0.069 ppb) based on chemiluminescence (Ma et al., 2002; Wang et al., 2006). Since Nam Co is located far away from anthropogenic emission sources, NO_x levels here are mainly determined by natural emissions, such as those from soil microbial activities or lightning processes. Additionally, a latest study has proposed that lakes in the TP are strong NO_x emission sources of NO_x (Kong et al., 2022). "

4. Lines 252-260: Here the authors conclude that O_3 and PAN decreases after sunset are caused by dry deposition as well as the cutoff of free-tropospheric input, indicating that local formations O_3 and PAN are weak. However, in the later sections, PAN formation at least was revealed to be strong. Is there a contradiction?

Response: We thank the reviewer for the good question. Lines 252-260 mainly summarizes the conclusions in a previous study on O_3 and PAN at Nam Co. Free tropospheric airmasses were suggested to be richer in PAN, because they were not influenced by dry deposition compared to near surface airmasses. Additionally, it was speculated in their study that PAN precursors observed at Nam Co mainly came from transport and photochemical conversions on their transport pathway, rather than local emissions and photochemical production.

Results in our study, however, have revealed that near surface PAN formation can be strong under observed NO_x and VOCs levels, which even overexplains the observed daytime increases. However, wind speeds were very strong at Nam Co, especially during daytime. Airmasses crossing over Nam Co only had very short residence times. Thus, observed daytime PAN concentrations were not necessarily representative of in situ photochemical formation, but were also greatly influenced by free tropospheric airmasses and PAN formation therein, which partly explained the overestimation of the box-model. From Fig. 12b in the manuscript, it was noted that photochemical PAN formation ends after sunset, thus the overestimated PAN in the box model after sunset mainly resulted from the fact that nighttime PAN loss terms (such as dry deposition) could not consume all the overestimated PAN formed over daytime within the model. Thus, the gradual decrease in observed PAN concentrations after sunset

did not indicate that surface formation of PAN was weak, it only suggests that with no photochemical formation and without additional downmixing from the free troposphere, near surface PAN would be partly lost through dry deposition.

5. Lines 258-264: PAN often revealed high concentrations at moderate PBLH, which the authors explained as *"Whereas PAN in the free troposphere might have had higher variability, which resulted in largely different enhancements of PAN upon down mixing."*. Might it be that local PAN formation was controlling the large variability of PAN?

   Response: The reviewer put forward a very good point. The large variability of PAN might have been the combined effect of high variability in free tropospheric PAN loading and high variability in PAN formation within the observed airmass. The fact that only moderate concentrations of PAN were observed at high PBLH suggests that intensive downmixing of free tropospheric air might have had a dilution effect on local PAN. Thus we modified this part as:

   "Whereas free tropospheric PAN or the surface formation of PAN might have had higher variability, which resulted in largely different responses of PAN with the down mixing of free tropospheric air. Intensive downmixing for free tropospheric air under high PBLH might have even diluted boundary layer PAN concentrations."

Technical comments:

1. Line 18 and later in text: "physiochemical" should be replaced with be "physicochemical".

   Response: Thank you for pointing that out, we changed "physiochemical" to "physicochemical" throughout the entire manuscript.

2. Line 28: "could by" should be "could be explained by"

   Response: Thanks for noticing, we corrected this typing error according to your suggestion.

3. Line 45: Change "nearly proportional to its OVOCs precursors" to "nearly proportionally to its OVOC precursors".

Response: Thank you for the suggestion, we made according changes.

4. Line 440: “reflects” should be “reflect”

   Response: Thanks, this mistake has been corrected.

5. Line 446: The “of” should be “or” in “from the west of from the south”

   Response: Thank you for pointing that out, we corrected it to “or”.

References:

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