Referee 1

This paper provides a detailed analysis of ozone chemical regimes across the tropics, with a focus on the role of short-lived VOCs. The paper is well written and the analysis is thorough and it provides new insight, but my main concern is that it is missing the big-picture by focusing too much on the details of VOCs. Methane plays a huge role in global (and tropical) ozone production, especially in remote regions dominated by lightning NOx. Methane is increasing rapidly and it is expected to increase over the next few decades, and therefore it will continue to drive ozone production across the tropics, even if NOx emissions were to remain constant. Methane cannot be ignored and this paper needs to consider the role of methane as the background driver of tropical ozone production. I provide more details below, and I touch on a few other items that need to be addressed.

We thank the referee for the time to review our manuscript and for the valuable feedback. We fully agree with the referee that methane plays an important role in O_3 production and we regret that this does not seem to be clear enough in the manuscript. Methane forms O_3 within the catalytic HO_x cycle, initiated by the reaction with OH radicals. Inevitably, CH_4 forms methyl peroxy radicals CH_3O_2 as an intermediate on its way to O_3. And this is precisely the major advantage of the metric $\alpha(CH_3O_2)$ that we are employing to investigate the sensitivity of O_3 towards its precursors. It does not require detailed knowledge about VOCs, but we consider the role of VOCs indirectly through their oxidized intermediates. In fact, we show that CH_3O_2 represent the predominant portion of RO_2 radicals in the upper troposphere which acknowledges and underlines that CH_4 is one, if not the most crucial VOC involved in O_3 production in the UTT. When calculating $\alpha(CH_3O_2)$, CH_3O_2 mixing ratios truncate out of the fraction, and the influence on O_3 sensitivity simplifies to the availability of NO and HO_2 radicals. More important than the abundance of methane for O_3 sensitivity is the abundance of HO_2 radicals, whose availability depends partly on CH_4, but also on OH, CO, other VOCs and O_3.

We have added text in the manuscript in various locations in order to clarify this very important point.

Lines 15 ff.: We show that effectively only the knowledge of the availability of NO and HO_2 is required to adequately represent O_3 precursors and its sensitivity towards them.

Lines 166 ff.: The formation of HCHO from CH_3O_2 through reaction with NO leads to O_3 formation, as NO_2 is formed simultaneously, which can subsequently react to O_3 via photolysis. In contrast, the reaction of CH_3O_2 with HO_2 represents a termination reaction of the HO_x cycle and therefore decelerates $P(O_3)$. CH_3O_2 here is a proxy for VOCs which form HCHO and O_3 through RO_2. A principal precursor to CH_3O_2 is CH_4, which is oxidized by OH radicals and reacts with O_2 in the first two steps of the catalytic HO_x cycle. The atmospheric CH_4 concentration is increasing rapidly, with the tropics implicated, suggestive of feedbacks that may accelerate CH_4 growth in future contributing to O_3 formation in the upper troposphere (Griffiths et al., 2021; Nisbet et al., 2023) Other precursors to CH_3O_2 can be acetone, methyl hydroxy peroxide or acetaldehyde through photolysis or reaction with OH radicals (Nussbaumer et al., 2021a). The advantage of considering CH_3O_2 is that it represents an entire group of

VOCs that can form O_3, including CH4, instead of handling multiple trace gases and risking incompleteness.

Lines 188 ff.: This method underlines that O_3 sensitivity is dependent on the availability of NO and HO_2 radicals. Individual VOCs do not need to be considered when investigating O_3 sensitivity, as HO_2 effectively represents their chemical impact.

Methane is a major ozone precursor especially in the remote atmosphere and it will play a major role in future ozone increases across the tropics (Young et al., 2013), yet methane is not even discussed in this paper. Methane cannot be ignored and needs to be addressed. Please consider the following:

Zhang et al. (2016) ran the CAM-Chem model for 1980-2010 and estimated an increase of the global tropospheric ozone burden of 28.12 Tg (8.9%), due to the increase of anthropogenic emissions and the partial shift of the emissions from mid-latitudes towards the equator. The increase of methane (15% over 30 years) accounted for one quarter of the ozone burden increase. The increase of methane has continued to the present, with rapid increases over the past 5-10 years (https://gml.noaa.gov/ccgg/trends_ch4/). Under a future scenario of high anthropogenic emissions and continuously increasing methane concentrations (Griffiths et al., 2021), the global ozone burden is expected to increase for the remainder of the 21st century (see the ssp370 scenario in Figure 6.4 of Szopa et al., 2021), with increases of approximately 10% from 2014 to 2050.

If we understand correctly, the values presented in Zhang et al. (2016) relate to the entire tropospheric column (not only to the upper troposphere) and we therefore believe these results are not inconsistent with our results. From Figure 3d from Zhang et al. (2016) we understand that CH_4 did not relevantly affect the O_3 change between 1980 and 2010 in the upper troposphere (200hPa ~ 11-13km), where lightning is effective. These findings are in line with our observations of a relatively small increase in CH_4 in the upper tropical troposphere. Figure 6.4 of Szopa et al. (2021) seems to relate to the overall tropospheric O_3 burden as well. Regarding the change of methane over time, our model simulations are not addressing the increase over the last two decades (which may be underestimated). We would like to emphasize that this study does not aim to investigate the change over time in O_3 precursors. We do find an increase in average O_3 from ~65ppbv to ~70ppbv which corresponds to an increase by ~8% and is in line with the value stated by Zhang et al. (2016), however this change is not significant considering the variability of the order of 30 ppbv (~40-50%). This large variability likely arises from the broad geographic area that we are investigating. Additionally, despite the rise in methane level over the past decades, the HO_x budget in the upper tropical troposphere has remained relatively constant, also indicated by the fact that the methane lifetime has not changed relevantly over time (Lelieveld et al. (2016), Naik et al. (2013)). From the perspective of VOC, a change in O_3 sensitivity is induced by changes in HO_2. Therefore, we expect the changes in methane over the past 20 years to have a negligible impact on the dominating O_3 regime.

In terms of ozone production from lightning, methane is a key precursor, first explored above the tropical South Atlantic by Moxim and Levy, 2000. They found that the upper tropospheric ozone maximum above this region was dominated by ozone production from lightning NOx in conjunction with CO/CH4 chemistry. They

suggested an ozone maximum would have existed in this region in preindustrial times. Similarly, Cooper et al. (2006) calculated that 69–84% (11–13 ppbv) of the observed upper-tropospheric ozone enhancement above North America during summer 2004 was due to in situ ozone production from lightning NOx and background mixing ratios of CO and CH4. In situ observations from the NASA DC8 showed very low values of reactive hydrocarbons in the UT, indicating a limited impact from fresh surface emissions. Basically, given plenty of lightning NOx, background methane concenrations and sunny conditions in the tropics, short-lived VOCs aren't required to produce large amounts of ozone.

We agree with the referee and we have added these references to support our findings.

Lines 40 f.: Previous studies have shown that methane (CH_4) is one of the most important VOC precursors to O_3 in the upper troposphere (Moxim and Levy, 2000; Cooper et al., 2006).

The current authors conducted sensitivity tests to understand the impact of lightning NOx, and it would be very informative if they can estimate future changes in ozone with increasing methane. Given that methane has increased almost continuously since the 1980s, and given the high likelihood that it will continue to increase, testing the sensitivity of the model to increased methane should be a priority.

We disagree with the referee regarding the need to perform a sensitivity study for methane. As discussed above, more important than the availability of methane for investigating O_3 sensitivity is the abundance of HO_2 radicals. As significant changes in HO_2 are unlikely in the near future, we believe a sensitivity study regarding CH_4 is outside the scope of this manuscript.

Line 40

"…model run excluding aircraft NOx does not show significant differences compared to the baseline scenario". This result contradicts the recent findings of Wang et al. (2022) who concluded that increasing aircraft emissions are playing a major role in increasing the global tropospheric ozone burden. Please address this discrepancy.

The applicability of the finding of Wang et al. (2022) to the upper tropical troposphere is ambiguous. Actually, this is unlikely because aircraft emissions of NO_x are most important north of 30°N latitude. The share of NO_x emissions from aircraft should be small in comparison to NO_x originating from lightning in the upper tropical troposphere. According to Schumann and Huntrieser (2007), the fraction of aircraft NO_x is close to 7% between 35°S and 35°N (assuming only sources in the UTT are aircraft and lightning) between 1995-2000. Even if these values doubled up to 2019 (Wang et al. 2022 estimated 76% between 1995 and 2017) and lightning remained constant, the fraction of NO_x from aircraft would still be low. Based on our findings, around 5% of NO_x originates from aircraft emissions over Africa, South East Asia and the Atlantic Ocean, and even less in the remaining areas, looking at the period from 2000-2019. When O_3 chemistry is NO_x sensitive, small changes in NO_x can impact O_3 levels, but when it is VOC sensitive due to strong lightning, e.g. over Africa or South America, we do not expect aircraft to have a significant impact on O_3. We added text to highlight this discrepancy with Wang et al. (2022).

Lines 444 f.: This may contradict recent findings by Wang et al. (2022), who presented increases in upper tropospheric ozone in response to increasing aircraft emissions. In our model, NO_x in the tropical upper troposphere is dominated by lightning emissions, whereas NO_x concentrations from aviation in this part of the troposphere are small, with most aircraft emissions occurring north of 30°N latitude.

Line 26

"In the upper troposphere (UT), ozone is the second most important greenhouse gas after water vapor and changes in ozone exert (and will continue to exert) a particularly large impact on the earth's radiative forcing – especially in the tropopause region and the tropical UT (Lacis et al., 1990; Mohnen et al., 1993; Wuebbles, 1995; Lelieveld and van Dorland, 1995; van Dorland et al., 1997; Staehelin et al., 2001; Iglesias-Suarez et al., 2018)."

On the global scale, ozone is the third most important greenhouse gas after CO2 and methane (not including water vapor) and so I'm surprised by this statement that ozone has a greater impact than CO2 and methane on the radiative balance of the UT. I looked at the list of references and none of them seem to make a strong case for this claim. Perhaps this was true decades ago when CO2 and methane concentrations were much lower, but they have increased greatly since the study by Lacis et al. 1990.

The NOAA Annual Greenhouse Gas Index (https://gml.noaa.gov/aggi/aggi.html) has increased by 49% since 1990, driven by increases in methane and CO2 and corresponding to a radiative forcing increase from 2.3 W m-2 to 3.4 W m-2. The index does not include ozone, but the increase in radiative forcing due to ozone from 1990 to 2014 is only about 0.1 W m-2. Figure 1 in the supplement to Skeie et al. (2020) has the most recent update on the height/latitude distribution of ozone's radiative forcing. Do you have any similar plots to compare it to, which would indicate if ozone has a stronger radiative effect in the tropical UT than CO2 or methane?

Thanks for bringing this to our attention. Indeed, our statement was incorrect. We have adjusted the text accordingly and added Skeie et al. (2020) as a reference.

Lines 27 ff.: Ozone is the third most important anthropogenic greenhouse gas after carbon dioxide (CO_2) and methane (CH_4), with a particularly strong impact in the upper troposphere where concentrations of the natural greenhouse gas water vapor are small compared to the surface. Changes in ozone exert (…).

and

Line 2: Ozone is an important contributor to the radiative energy budget of the upper troposphere (UT).

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