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 O₃ production and we regret that this does not seem to be clear enough in the manuscript. Methane forms O₃ within the catalytic HOₓ cycle, initiated by the reaction with OH radicals. Inevitably, CH₄ forms methyl peroxy radicals CH₃O₂ as an intermediate on its way to O₃. And this is precisely the major advantage of the metric α(CH₃O₂) that we are employing to investigate the sensitivity of O₃ 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 CH₃O₂ represent the predominant portion of RO₂ radicals in the upper troposphere which acknowledges and underlines that CH₄ is one, if not the most crucial VOC involved in O₃ production in the UTT. When calculating α(CH₃O₂), CH₃O₂ mixing ratios truncate out of the fraction, and the influence on O₃ sensitivity simplifies to the availability of NO and HO₂ radicals. More important than the abundance of methane for O₃ sensitivity is the abundance of HO₂ radicals, whose availability depends partly on CH₄, but also on OH, CO, other VOCs and O₃.

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 HO₂ is required to adequately represent O₃ precursors and its sensitivity towards them.

Lines 166 ff.: The formation of HCHO from CH₃O₂ through reaction with NO leads to O₃ formation, as NO₂ is formed simultaneously, which can subsequently react to O₃ via photolysis. In contrast, the reaction of CH₃O₂ with HO₂ represents a termination reaction of the HOₓ cycle and therefore decelerates P(O₃). CH₃O₂ here is a proxy for VOCs which form HCHO and O₃ through RO₂. A principal precursor to CH₃O₂ is CH₄, which is oxidized by OH radicals and reacts with O₂ in the first two steps of the catalytic HOₓ cycle. The atmospheric CH₄ concentration is increasing rapidly, with the tropics implicated, suggestive of feedbacks that may accelerate CH₄ growth in future contributing to O₃ formation in the upper troposphere (Griffiths et al., 2021; Nisbet et al., 2023) Other precursors to CH₃O₂ can be acetone, methyl hydroxy peroxide or acetaldehyde through photolysis or reaction with OH radicals (Nussbaumer et al., 2021a). The advantage of considering CH₃O₂ is that it represents an entire group of...
VOCs that can form O₃, including CH₄, instead of handling multiple trace gases and risking incompleteness.

Lines 188 ff.: This method underlines that O₃ sensitivity is dependent on the availability of NO and HO₂ radicals. Individual VOCs do not need to be considered when investigating O₃ sensitivity, as HO₂ 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 CH₄ did not relevantly affect the O₃ 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 CH₄ in the upper tropical troposphere. Figure 6.4 of Szopa et al. (2021) seems to relate to the overall tropospheric O₃ 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 O₃ precursors. We do find an increase in average O₃ 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 HOₓ 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 O₃ sensitivity is induced by changes in HO₂. Therefore, we expect the changes in methane over the past 20 years to have a negligible impact on the dominating O₃ 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 concentration 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 (CH4) is one of the most
important VOC precursors to O3 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 O3 sensitivity is the abundance of HO2 radicals. As significant changes
in HO2 are unlikely in the near future, we believe a sensitivity study regarding CH4 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 NOx are most
important north of 30°N latitude. The share of NOx emissions from aircraft should be
small in comparison to NOx originating from lightning in the upper tropical
troposphere. According to Schumann and Huntrieser (2007), the fraction of aircraft
NOx 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 NOx from aircraft would still be low. Based on our findings,
around 5% of NOx 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 O3 chemistry is NOx sensitive, small changes in NOx can impact O3
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 O3. 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, NOx in the tropical upper troposphere is dominated by lightning emissions, whereas NOx 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 (CO2) and methane (CH4), 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).

References:
