Referee 2

This paper uses a 20-year simulation of the EMAC model to demonstrate the reliability of different metrics for defining NOₓ and VOC-sensitive regimes for ozone production in the tropical upper troposphere. They find that these chemical regimes are well defined using the formaldehyde to NO_2 ratio ($HCHO/NO_2$) and the production of HCHO from methyl peroxyradicals ($a(CH_3O_2)$), parametrized as a function of NO mixing ratios. The sensitivity of the chemical regimes to changes in lighting NO_x production is presented as a case study. Overall, the paper is well written and within the scope of ACP. Understanding the drivers of ozone production in the upper troposphere is important for projecting the role of ozone in climate change.

We thank the referee for taking the time to review our manuscript and the positive feedback.

However, discussion should be added explaining how the results of the present study fit in with earlier publications. Additionally, given the role of lightning NO_x and aircraft emissions in the paper, how these emissions are implemented in EMAC should be described in Section 2.3. Please also explain how the 200 hPa pressure level was chosen for this analysis and if it might have an impact on the results, such as the relative importance of lightning NOx and aircraft emissions. In general, the paper spends a lot of time listing details that are summarized in the figures at the expense of communicating the meaning of the results. Examples are given under the specific comments where more concise language would be beneficial.

We have added discussion in view of earlier publications.

Lines 467 ff.: Our results fit well with previous literature on the role of lightning NO_x in O_3 production in the upper troposphere. Grewe (2007) reported that NO_x from lightning is the dominant source of O_3 in the upper tropical troposphere based on simulations with the global climate–chemistry model E39/C. Similar results have been presented by Murray (2016), Schumann and Huntrieser (2007) and Sauvage et al. (2007). While it has been shown previously that ozone production in the UTT is highly dependent on lightning NO_x, this study is the first to extensively study the impact of lightning on the dominant O_3 regime, applying a new indicator $α(CH_3O_2)$, which is valid throughout the entire troposphere.

We have added some information on the implementation of emissions of NO_x from lightning and aircraft in Section 2.3.

Lines 213 ff.: In this work the emissions of NO_x from lightning are following the work of Tost et al. (2007). A constant NO_x emission of ~20,6 kg N/flash is used for cloud-to-ground flashes. The ratio of NO_x production by intra-cloud flashes is lower by a factor of 0.1. The lightning frequency is estimated with the parameterization of Grewe et al. (2001). Here the updraft velocity (used as proxy for convective strength) is associated with cloud electrification and therefore proportional to frequency of the lightning flashes. On the other side, aircraft emissions are prescribed from the CAMS dataset (CAMS-GLOB-AIR v1.1, Garnier et al, 2019).

The 200hPa pressure level was chosen to represent upper tropical tropospheric influence. At this altitude, we capture lightning events, but is not strongly influenced

by transport from the stratosphere. This is also highlighted in Figure 8 of our manuscript. At lower altitudes in the free troposphere, O_3 chemistry is strongly NO_x sensitive due to the absence of NOx sources. In contrast, in the stratosphere O_3 chemistry is strongly VOC sensitive. The UTT at ~200hPa marks the transition area between NO_x and VOC sensitivity, which is strongly impacted by lightning. We have added this information to the text.
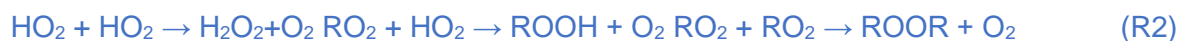
Lines 209 ff.: This pressure level was chosen to represent upper tropospheric influence in the tropics in order to capture lightning events and avoid strong influence of transport from the stratosphere. The choice is also underlined by the results presented in Figure 7 where 200 hPa marks the area of transition from NO_x sensitivity in the free troposphere to VOC sensitivity in the stratosphere, impacted by lightning.

Specific Comments:

- In the introduction, please write out chemical reactions that are described and used again in the paper or are important for understanding the regime metrics.

  We have added important chemical reactions. For the HO_x cycle, we kindly ask the reader to refer to the stated literature as it has been published and discussed in detail many times before.

  Lines 45 f.: Deviations from the HO_x cycle, including self-reactions of peroxy radicals, (Reaction (R2)), and the reaction of OH with NO_2 forming HNO_3 (Reaction (R3)), can terminate the formation of ozone.

  $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ $RO_2 + HO_2 \rightarrow ROOH + O_2$ $RO_2 + RO_2 \rightarrow ROOR + O_2$ (R2)

  $NO_2 + OH \rightarrow HNO_3$ (R3)

- Line 44: In terms of surface O_3, knowing if a region is NO_x or VOC sensitive is important for determining regulatory policies for controlling air quality. Please state why knowing the regime is useful for the upper troposphere and connect these concepts to the first two paragraphs of the introduction. This is mentioned later, but motivation should be given upfront.

  We have added some text to underline the importance of investigating dominating O_3 sensitivity at high altitudes.

  Lines 58 ff.: Due to its wide-ranging atmospheric effects, not only on air quality and human health at the surface but also on atmospheric oxidation processes (the self-cleaning mechanism) and on climate change, with the upper troposphere being especially sensitive, it is highly relevant to understand and monitor O_3 levels and the main drivers of its sensitivity also at these altitudes.

- Line 47, "…most of the indicators for either regime are no longer valid.": Please provide a brief explanation why. This sentence might make more sense if it was moved to the description of indicators that are not suitable for the upper troposphere.

Thanks for pointing this out. We have added some text for clarification.

Lines 54 ff.: These metrics are well studied and reported at surface levels. However, most of the indicators for either regime are no longer valid when it comes to the upper troposphere. This is due, for example, to the changing ratios of the investigated trace gases with altitude and the decreasing temperature, which affects chemical rate constants and, therefore, the relevance of specific reactions (e.g., NO_2 + OH).

- Line 67, "Another indicator is the ratio…": I recommend starting a new paragraph to distinguish between metrics that are used in the upper troposphere from ones that are air quality specific. Overall, this is a long paragraph that lists different metrics, and reorganizing the discussion would be helpful to communicate what's relevant for the upper troposphere and why.

The idea of this section is to discuss metrics previously reported in literature, one by one. We have tried to clarify this paragraph by starting a new line for each metric. Generally, none of these metrics is well suited to use for the upper troposphere. They have all been developed for the surface and most of them have not been applied to higher altitudes in the troposphere. The only metric that we found to be applicable for high altitudes is the HCHO to NO_2 ratio, but only in combination with ambient NO mixing ratios as we show later in the manuscript (e.g. Figure 6). So far, absolute values (e.g. lower than 1 for VOC sensitivity or higher than 2 for NO_x sensitivity) have been reported and applied in literature. Due to the strong vertical gradients of the trace gases, these are not applicable in the upper troposphere. We have added text for clarification. Additionally, we have summarized the discussed metrics in Table 1 and we hope this provides some additional clarification for the reader.

Lines 106 ff.: These metrics were developed for the conditions near the surface, and most of them have not been applied to higher altitudes in the troposphere. Of the above metrics, the HCHO to NO_2 ratio is the only one, which we find to be applicable also to high altitudes – but only in combination with ambient NO mixing ratios. We demonstrate this in Section 3.3. So far, absolute thresholds (e.g. lower than 1 for VOC sensitivity or higher than 2 for NO_x sensitivity (Duncan et al., 2010)) have been reported and applied in the literature. Due to the strong vertical trace gas gradients, these absolute thresholds are not applicable in the upper troposphere.

Table 1. Overview of the most common metrics to determine if O_3 chemistry is sensitive towards NO_x or VOC reported in literature. Details can be found in the text.

metric	required parameters	NO$_x$ sensitivity	VOC sensitivity	references	suitability
P(O$_3$)	NO$_x$, O$_3$, HO$_2$, RO$_2$	P(O$_3$) increases with NO$_x$	P(O$_3$) decreases with NO$_x$	Brasseur et al. (1996) Jaeglé et al. (1999) Tonnesen and Dennis (2000a) Tadic et al. (2021)	surface
OPE	NO$_x$ & reaction products (e.g. HNO$_3$, PAN)	high OPEs	low OPEs	Liu et al. (1987) Trainer et al. (1993) Wang et al. (2018a)	surface
weekend O$_3$ effect	NO$_x$, O$_3$	O$_3$ decreases on weekends	O$_3$ increases on weekends	Fujita et al. (2003) Pusede and Cohen (2012) Nussbaumer and Cohen (2020) Sicard et al. (2020) Gough and Anderson (2022)	surface
HCHO to NO$_2$ ratio	HCHO, NO$_2$	high HCHO/NO$_2$ e.g. HCHO/NO$_2$ > 2*	low HCHO/NO$_2$ e.g. HCHO/NO$_2$ < 1*	Sillman (1995) *Duncan et al. (2010) Jin et al. (2020) Xue et al. (2022)	surface
H$_2$O$_2$ to HNO$_3$ ratio	H$_2$O$_2$, HNO$_3$	high H$_2$O$_2$/HNO$_3$ e.g. H$_2$O$_2$/HNO$_3$ > 0.4**	low H$_2$O$_2$/HNO$_3$ e.g. H$_2$O$_2$/HNO$_3$ < 0.4**	**Sillman (1995) Wang et al. (2018b) Vermeuel et al. (2019) Liu et al. (2021) Gough and Anderson (2022)	surface
α(CH$_3$O$_2$)	NO, OH, HO$_2$	α(CH$_3$O$_2$) increases with NO	α(CH$_3$O$_2$) unaffected by NO	Nussbaumer et al. (2021b) Nussbaumer et al. (2022)	entire troposphere

- Line 95, "Khodayari et al…": what region did this modeling study focus on?

Khodayari et al. (2018) have investigated the correlation between lightning NO$_x$ and O$_3$ production on a global scale. We have clarified this in the text.

Line 120 f: (…) where globally a decreasing O$_3$ burden was observed with increasing lightning NO$_x$.

- Paragraph beginning line 88: This is a list of past studies that explored ozone production sensitivity regimes in the upper troposphere. In the results or conclusions, please discuss your findings with respect to these studies.

These studies have explored ozone sensitivity based on metrics, which were developed for the surface. We expect that most of the studies published 20-25 years ago overestimated the rate constant for the reaction of NO$_2$ with OH to form HNO$_3$ (state of knowledge two decades ago), and therefore overestimate the NO$_x$ loss. We have added some discussion to Section 3.3.2 and also highlight this aspect.

Lines 467 ff.: Our results fit well with previous literature on the role of lightning NO$_x$ in O$_3$ production in the upper troposphere. Grewe (2007) reported that NO$_x$ from lightning is the dominant source of O$_3$ in the upper tropical troposphere based on simulations with the global climate–chemistry model E39/C. Similar results have been presented by Murray (2016), Schumann and Huntrieser (2007) and Sauvage et al. (2007). While it has been shown previously that ozone production in the UTT is highly dependent on lightning NO$_x$, this study is the first to extensively study the impact of lightning on the dominant O$_3$ regime, applying a new indicator α(CH$_3$O$_2$), which is valid throughout the entire troposphere.

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  The black curve and grey error shade represent an average of all available data points at 200hPa in the tropics for $\alpha(CH_3O_2)$ binned to NO from the EMAC modeling output. The red line presents a linear fit of the data points for NO < 0.1ppbv and the blue line a linear fit for NO > 0.1ppbv. We have added some details in the figure caption and the text.

  Figure 1. Illustration of how $\alpha(CH_3O_2)$ can serve as a metric to identify the dominant chemical regime. The black line shows the tropical background $\alpha(CH_3O_2)$ binned to NO mixing ratios from the EMAC model output. The grey shading shows the 1σ standard deviation. The red dashed line is a linear fit for NO < 0.1 ppbv and represents NO_x-sensitive O_3 chemistry. The blue dashed line represents VOC-sensitive O_3 chemistry for NO > 0.1 ppbv.

  and

  Line 177 f.: (…) as obtained from the EMAC modeling output.

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  The black line shows the yearly averages of daily values at local noon of each respective species. The grey shades represent the variability, as 1σ standard deviation of the averaging. We have added this information in the figure caption.

  Figure S1. Development of modeled trace gas mixing ratios in the upper tropical troposphere at 200 hPa from 2000 to 2019. Black lines represent the average of daily mixing ratios at local noon for each year, and the grey shades show the variability, calculated as the 1σ standard deviation of the averaging.

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  We regret that the referee finds this section not clear enough. However, we think it is important to provide a description of the figure, including absolute values, to the reader prior to the interpretation of the results. We have restructured this paragraph and focus on relative comparisons between areas, including maritime and continental areas, as well as northern and southern hemispheric values, and provide absolute average values in brackets instead. We hope this helps to improve the clarity for the reader.

  Lines 238 ff.: During DJF, NO mixing ratios are highest over the tropical continental areas of South America, southern Africa and northern Australia, with average peak values between 0.3 and 0.4 ppbv. In comparison, NO mixing ratios are much lower

over the Pacific and the Indian Oceans (0.09 ± 0.01 ppbv), the Atlantic Ocean (0.12 ± 0.02 ppbv), North Africa (0.10 ± 0.03 ppbv) and South East Asia (0.08 ± 0.01 ppbv). Generally, the mixing ratios over land are much higher than those over the ocean, and the mixing ratios north of the equator (0.09 ± 0.03 ppbv) are lower compared to south of the equator (0.14 ± 0.06 ppbv). During MAM, NO mixing ratios over South America are similar to those during DJF (0.21 ± 0.05 ppbv). NO mixing ratios over Africa are almost twice as high on average compared to DJF and reach peak values of 0.53 ppbv. The relative maxima relocate from South to Central Africa from DJF to MAM and also over the Arabian Peninsula and South Asia, including India. Mixing ratios over Australia are around 0.15 ppbv and approximately half of those during DJF and are similar over South East Asia. During JJA, peak NO mixing ratios are found north of the equator over Central America and North Africa. Average NO mixing ratios are almost 60 % higher in the northern (0.14 ± 0.07 ppbv) compared to the southern tropical hemisphere (0.09 ± 0.02 ppbv). The distribution, therefore, differs drastically from DJF. During SON, NO mixing ratios are similar to MAM and peak over South America and Central Africa.

We performed according adjustments to the remaining sections.

- Line 209, "During DJF…": This should be stated earlier in the discussion, with citation.

We have added this information in the introduction of Section 3.2.1.

Lines 232 ff.: We find large changes throughout the year related to the seasonality of deep convection and the location of the intertropical convergence zone (ITCZ). Deep convection dominates in the southern hemisphere in January, and during July it is most prevalent in the northern hemisphere Yan (2005).

- Line 240: What specifically about your modeled NOPR values is in line with the findings by Apel et al. (2015)?

Apel et al. (2015) observed enhanced O_3 production for high LNO_x, which fits well with our results that NOPR and NO mixing ratios show the same features considering their geographic distribution. We have clarified this in the text.

Lines 283 ff.: These results, showing similar features for NOPRs and NO geographically, are in line with findings by Apel et al. (2015), who reported enhanced ozone production for high lightning NOx over the U.S. during a research flight in June 2012 as part of the DC3 campaign.

- Line 273: What do you mean by "mostly absolute values" here; is this columns of HCHO and NO_2?

With absolute values we mean that in order to determine the dominant sensitivity using the HCHO/NO_2 ratio, in literature absolute thresholds are compared. The ratio is calculated and the resulting number is compared to a threshold, e.g. 1 for a VOC sensitivity or 2 for a NO_x sensitivity (according to Duncan et al., 2010). However, these thresholds (represented by absolute numbers) can vary by location

and have never been explored for the free or upper troposphere. We have clarified this in the text.

Lines 317 ff.: In the literature, mostly absolute values for the HCHO/NO$_2$ ratio are used to determine the chemical regime, meaning the ratio is calculated and compared to a certain threshold, for example HCHO/NO2 > 2 for NOx sensitivity and HCHO/NO2 < 1 for VOC sensitivity (Duncan et al., 2010).

- Lines 289 – 318: Please consider more concise wording for the description of Figure 6. What are the main results you want the reader to understand from this Figure?

We have added some text to improve the structure of this section and hope it provides more clarity.

Lines 303 ff.: In this section, we first discuss the background curves (representing an average of all data point), and we subsequently present our findings for the individual areas.

Lines 335 ff.: To investigate individual areas regarding predominant O$_3$ sensitivity, we analyze the location of the area averages along the background. Figure 6(a) shows NO vs α(CH$_3$O$_2$) during DJF. (…)

Lines 370 ff.: In summary, Figure 6 illustrates three important results. First, the transition between NO$_x$ and VOC sensitivity occurs at around 0.1 ppbv NO in the upper tropical troposphere. Second, areas with increased lightning activity tend towards the dominance of VOC sensitivity. And third, the dominating regime changes with the time of the year. We will discuss these findings and their implications in the following.

- Figure 7: Add the season (MAM) to the figure caption.

We have added MAM to the figure caption.

Figure 7. Map of the tropical UT between 30°S and 30°N colored by the slopes of NO vs α(CH$_3$O$_2$) of the data in model grid regions, exemplary for MAM. (…)

- Line 345: Is the 38 ppbv^{-1} value for the slope?

Yes, this value describes the slope. We have added this information.

Line 396: For the free troposphere, we find strong NO$_x$ sensitivity with a maximum slope of 38 ppbv^{-1}.

- Figure 9: If the average backgrounds (or another metric) from the base and other sensitivity studies are shown here, the readers can more easily compare these results to those shown in Figure 6 and S16-S17. Additionally, it might be helpful to move Figure S18 to the main text since the results of the aircraft emission sensitivity study is not currently shown in the main text figures.

Thank you for these suggestions. We have added a comparison of the baseline scenario and the scenario without lightning to Figure S15 of the Supplement. Additionally, we have moved Figure S18 to Figure 10 of the main text in order to show both sensitivity studies (for lightning and aircraft).

Lines 414 f.: Figure S14 of the Supplement shows the subdivision into the four periods (DJF, MAM, JJA and SON), and in Figure S15, we present a comparison between the baseline scenario as a yearly average and the scenario excluding lightning.

Figure S15. Comparison of the plots shown in Figure 6 ($\alpha(CH_3O_2)$, O_3 and the HCHO/NO_2 ratio binned to NO mixing ratios) for the modeling scenario with (bottom row) and without lightning (top row). The baseline scenario is here shown as a yearly average. Black lines show averages of all data points, and grey shades present the 1σ standard deviation. Colored data points show the averages for the indicated areas with the 1σ error.
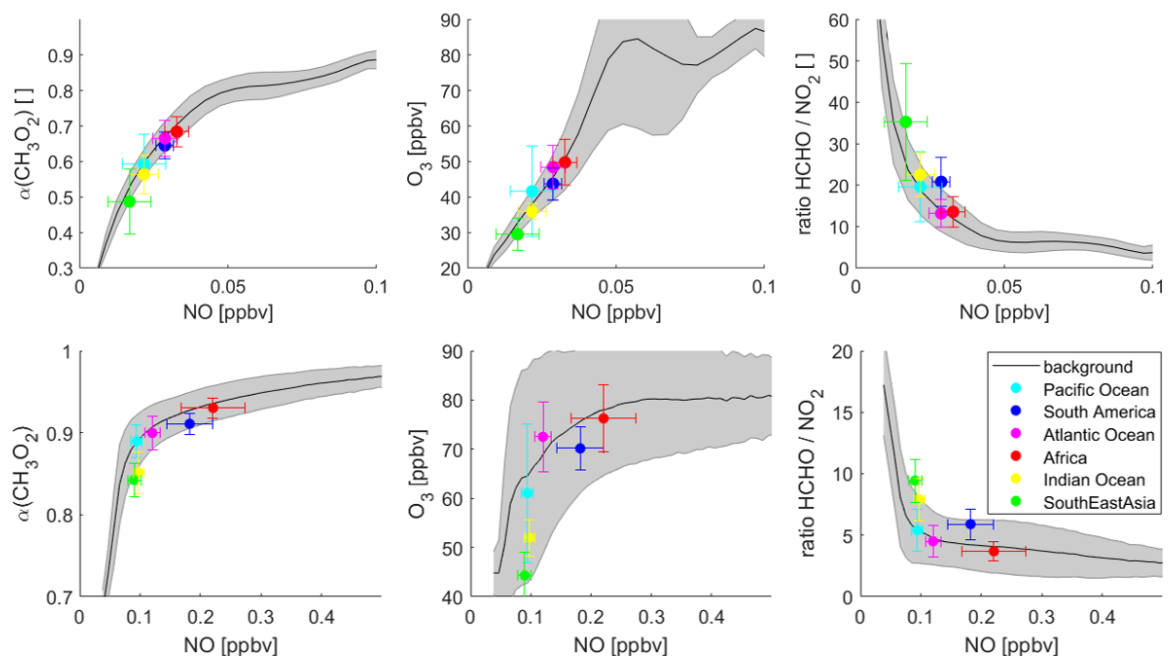
- Line 378: What do you mean by "the absolute values" here? Is this referring to the ratio for individual regions?

We are trying to say that the course of the black line is similar for both scenarios (baseline and excluding lightning), but the values for the HCHO/NO_2 ratio are notably higher for the scenario where lightning was excluded. We have rephrased this for clarification.

Line 429 f.: The course of the average values (black line) is again similar to the one for the baseline scenario, but the values for the HCHO/NO_2 ratio are higher.

- Lines 406 – 412: How do these results fit in with past studies?

We have added some text to account for past studies.

- Line 417: Was an additional run without aircraft emissions conducted?

Yes, a model run without aircraft emissions was performed. We have added this in the conclusion section.

Lines 477 ff.: One model run considers a baseline scenario and four additional ones were run with halved, doubled and excluded lightning NO_x emissions, as well as excluded NO_x aircraft emissions.

- Lines 437- 441: Citations should be provided for these statements.

We have added several references indicating that NO_2 measurements in the upper troposphere suffer from drawbacks e.g. thermal reservoir species (methyl peroxy nitrate) which release NO_2 in instrumental parts with elevated temperatures.

Lines 502 f.: NO_2 measurements tend to suffer from the unselective detection or artifacts from reservoir species, which makes accurate quantification challenging (Reed et al., 2016; Jordan et al., 2020; Andersen et al., 2021; Nussbaumer et al., 2021b)

- Conclusion section: The discussion of the role of lightning in the conclusions is terse and doesn't explain how the study reached these results or how it fits in with the current literature.

We mostly discuss the role of lightning in Section 3.3.2 as part of the sensitivity study. We have added some extra discussion, particularly in regard to the literature (see above).

Lines 467 ff.: Our results fit well with previous literature on the role of lightning NO_x in O_3 production in the upper troposphere. Grewe (2007) reported that NO_x from lightning is the dominant source of O_3 in the upper tropical troposphere based on simulations with the global climate–chemistry model E39/C. Similar results have been presented by Murray (2016), Schumann and Huntrieser (2007) and Sauvage et al. (2007). While it has been shown previously that ozone production in the UTT is highly dependent on lightning NO_x, this study is the first to extensively study the impact of lightning on the dominant O_3 regime, applying a new indicator $\alpha(CH_3O_2)$, which is valid throughout the entire troposphere.