

At first we want to thank the reviewer for the very helpful comments to improve the manuscript.

*The Smoydzin et al. manuscript presents analysis and modeling of ozone produced as a result of biomass burning and lightning emissions over the Amazon Basin. The analysis is tied to aircraft observations taken in the UT off the east coast of Brazil. Backward trajectories are computed from points along the flight track, and chemical calculations are performed in a forward Lagrangian model along these trajectories, which pass over fires and areas affected by lightning. The resulting model-calculated ozone is compared with that observed on the flight, and NO<sub>x</sub>-sensitive and VOC-sensitive conditions are estimated. The analysis is probably the best that can be done, but has a number of uncertainties: e.g., biomass burning emissions, lightning NO<sub>x</sub> emissions, magnitude and frequency of convective transport. These uncertainties need to be stressed in the conclusions section of the paper. In general, the text reads well, but more detailed explanations are needed in several locations, as noted in the detailed comments below. In addition, more comparisons with previous results in the literature are needed. My recommendation is that minor revisions are needed.*

**line 10: Why is "eventually" used here? Lightning often occurred in the same regions as the biomass burning or nearby.**

We erased 'eventually'. This word was placed incorrectly in this sentence.

**line 52: Need to add that Fishman et al. (1990) and Watson et al. (1990) used TOMS satellite data to recognize the South Atlantic ozone maximum.**

Thank you for this hint. We extended this sentence mentioning the observation method.

**line 56: There is no Pickering and Simpson reference. It should be Pickering, K.E., A..M. Thompson, J. R. Scala, and J. Simpson. Please correct this in the text and reference list.**

We apologize for this mistake. Unfortunately, there was a typo in our Literature file.

**line 99: No NO<sub>x</sub> observations are mentioned in this sentence. Seems like they are an important piece of the analysis and should be mentioned in the full list of trace gas observations. They are mentioned at the end of the paragraph (line 112) , but should be given more prominence.**

We extended the discussion in section 3.3 in particular regarding VOC and NO<sub>x</sub> chemistry.

**line 140: here it is not clear that the MPTRAC trajectory model does not consider subgrid convective vertical transport, and only uses the grid scale vertical velocities. This needs to be clarified here.**

To discuss this important limitation of Lagrangian trajectory simulations, we added the following in section 2.3.1:

'The ERA5 based MPTRAC simulations do not explicitly represent deep convection since trajectory calculations are only driven by large scale wind fields. However, Lawrence and Salzmann (2008) point out that trajectories should represent the net vertical and long-range transport reasonably. As Lawrence and Salzmann (2008) and Lawrence and Lelieveld (2010) discuss in detail, it can be assumed that the basic regional lofting will be present in lagrangian trajectory simulations using input from global circulation models. It has to be expected that the mean rate of vertical transport is underestimated. A more recent study by Smith et al. (2021) indicates that a significant portion of convective transport processes are represented in trajectory experiments driven by the grid scale wind fields. They further conclude, that convective and boundary layer source regions of upper tropospheric air parcels are consistent with the climatological flow regime in their study region.'

**Line 149: Is the chemistry initiated at the 13-day point of the MPTRAC trajectory?**

Chemistry is indeed initiated at the 13-day point of the MPTRAC trajectories however with excep-

tions: For trajectories having boundary layer contact over the South American continent, chemistry is initiated 24 hours before the last BL contact (in the backward perspective, e.g. if the last BL contact was on day 5 of the MPTRAC backward simulation time, chemistry was initiated on day 6 of the MPTRAC simulation time).

We added this information in section 2.3.2.

**line 158: Need to explain what resolution T42L90MA means.**

This is a spectral resolution with 42 wave numbers in the horizontal and 90 vertical levels reaching into the middle atmosphere; respective gaussian grid representations correspond to  $2.81^\circ$  horizontally and vertical grid spacing between 30 hPa near the surface, 300 hPa in the UTLS and an upper level boundary of 1 Pa.

We added a sentence with this information in the manuscript.

**line 173: Kappa(s) is not defined in Equation 2. I assume this must be the emission factor. Is this correct?**

Indeed! We forgot ( $\kappa$ ) in line 174. → The species emission factors  $\kappa$  are taken.....

**lines 175-176: All biomass burning pollution is being assumed to reside in the BL. How accurate is this assumption? Can you cite references to back up this assumption? Some other models have assumed it is routinely mixed upward to 3 or 4 km by fair weather cumulus clouds.**

Our assumption, that biomass burning emissions are only added as long as trajectories are within the boundary layer is certainly a simplification. The effect of upward mixed emissions you mention, is however included indirectly: In every CAABA-chemistry timestep, air masses at the trajectory position are mixed with ambient air masses from the EMAC model where the process of (large scale) upward lift of emissions is included. EMAC mixing ratios of  $O_3$ ,  $NO_x$ , CO and VOCs show a very strong biomass burning signal over South America throughout the troposphere. Furthermore, the high elevations of the distribution height are often assumed only for mid-latitude biomass burning events, e.g., doi:10.5194/acp-17-2921-2017 Fig. 4. For most events this means, that the plume or injection height is located in the PBL over the South American continent.

**LNO<sub>x</sub>:**

**lines 178 - 184: The methodology for computing the LNO<sub>x</sub> emissions is not at all clear. Does a single GLM flash in a grid cell trigger LNO<sub>x</sub> emissions? Is a count of the GLM flashes in a grid cell set in the LNO<sub>x</sub> emission calculation? If so, this needs to be mentioned. The statement "We chose a LNO<sub>x</sub> emission factor leading to the addition of approximately 0.02 ppb NO per CAABA timestep." confuses the explanation, where a few lines earlier the 250 moles NO per flash is mentioned. Is the 0.02 ppb also per flash? Is this the total amount that is added per flash and then distributed in the vertical according to Pickering et al. (1998)? This paragraph needs to be totally rewritten.**

**Figure 4 (top): here we see counts of lightning flashes encountered by the trajectories for the first time. So, perhaps these counts are included in the emission calculations. Lines 178-184 need to better explain this.**

(1)

We rephrased and shortened the section, explaining strictly how LNO<sub>x</sub> emissions are treated in our model setup (l.178-183):

If a specific trajectory crosses a lightning event detected by the GLM sensor on board GOES-16 (see Fig. 1), a constant emission of 0.02 ppb NO is added to the NO concentration at this particular CAABA simulation time of the trajectory.

(2)

We renewed the schematic overview plot in Fig. 1, showing only 1 example trajectory which hope-

fully facilitates understanding the model setup.

**Equation 3:** Need to better explain what this equation represents. Maybe quote Nussbaumer et al. (2023): "Alpha(CH3O2) represents the share of methyl peroxy radicals forming HCHO with NO and OH versus the reaction with HO2 yielding CH3OOH". However, of what value is this equation if the OH + CH3O2 reaction is not included in the chemical mechanism?

(1) A comment in advance: We use exactly the same chemistry setup in our CAABA simulations as Nussbaumer et al. (2023), (personal communication with Andrea Pozzer).

(2) We follow your suggestion and add a more detailed explanation of the  $\alpha(\text{CH}_3\text{O}_2)$  equation referencing Nussbaumer et al. (2023)

(3) The reaction rate of the reaction ( $\text{CH}_3\text{O}_2+\text{OH}$ ) is on average 2 orders of magnitude smaller than both other reactions considered in the  $\alpha$  calculation. While the reactions of  $\text{CH}_3\text{O}_2$  with NO and  $\text{HO}_2$  have rates in the order of 3 ppt/s and 0.3 ppt/s, the reaction rate ( $\text{CH}_3\text{O}_2+\text{OH}$ ) is in the range of 0.003 ppt/s.

**line 206:** Figure 3 is being called in the text before Figure 2.

Figure 2 is mentioned in line 153 for the first time, Figure 3 in line 206.

**line 219:** The longitude range of SASH is given, but not the latitude range.

We added this information:

The South Atlantic subtropical high (SASH) was positioned relatively stable over the south-west Atlantic between  $40^\circ$ - $20^\circ$ W in longitudinal direction and **between  $40^\circ$ - $20^\circ$ S in latitudinal direction....**

**In the discussion of the results of calculated ozone production with regard to the aircraft observations, the authors should include a comparison with the magnitude of ozone production downwind of deep convection shown in Pickering et al. (1996).**

Thank you for this important reminder.

Pickering et al. (1996) calculated a net  $\text{O}_3$  production of 5-6 DU ( $\approx 167$ - $201$  [ $\text{molec cm}^{-3}$ ]\* $10^{-9}$ ) over 8 days after the convective event integrated over the outflow layer between 8 and 16km altitude.

Our simulated 7-day integrated net  $\text{O}_3$  production is comparable to the values given by Pickering et al. (1996), though our simulations show a larger mean value of 304 [ $\text{molec cm}^{-3}$ ]\* $10^{-9}$  (see Tab. 1, we included this table in the manuscript)

	median	mean	std
<i>BB</i>	1558.91	2095.29	1875.41
<i>FLASH_BL</i>	580.23	566.97	179.20
<i>FLASH_noBL</i>	55.20	56.58	9.23
<i>REST</i>	38.79	40.70	5.73
<i>ALL</i>	258.85	304.55	212.79

Table 1: Median, mean and standard deviation of the net  $\text{O}_3$  production for trajectories of each simulation scenario [ $\text{molec cm}^{-3}$ ]\* $10^{-9}$  and the entire trajectory ensemble (ALL). Values are calculated for 7 days backward since trajectories have been started at the flight track.

**Figure 5:** What do the gray shaded areas represent?

This is only a misleading effect of the colour code chosen and the large range of  $\text{O}_3$  loss/production rates: (Trajectory) Points in the plots having a net  $\text{O}_3$  loss/production rate close to zero have a grayish colour (see colourbar at 0). As there are many points with rather small  $\text{O}_3$  loss/production rates, some areas in the plot appear gray shaded. We only show data points with  $L(\text{O}_3) < -0.01$   $\text{ppt s}^{-1}$  and  $P(\text{O}_3) > 0.01$   $\text{ppt s}^{-1}$  in the revised version.

**Line 275: "Enhancing LNOx emissions....." Is this an additional experiment with larger LNOx emissions that is not represented in Figure 5? The magnitude of enhancement needs to be mentioned, and the results illustrated somewhere (may in Supplement).**

As simulations with our base model setup show a very good agreement between observed and simulated NO mixing ratios in particular for flight ST06, where BB emissions have almost no impact on (upper tropospheric) NO mixing ratios there was actually no need to enhance LNOx emissions (NO plots shown in the supplement). Nevertheless, we performed a set of sensitivity simulations enhancing LNOx emissions by a factor 2.

We rephrased the sentence:

In a sensitivity simulation (not shown here), we enhanced LNOx emissions by a factor 2. This leads however to a tremendous overestimation of NO mixing ratios compared to the flight observations. Even with these unrealistically high NO mixing ratios,  $P(O_3)$  does not increase significantly as air masses in the regions of lightning are mainly in a VOC sensitive regime, (Fig. 5f)) in particular for all *FLASH\_noBL* trajectories (Fig. 5 f),h)).

**Line276: ".....mainly in VOC-sensitive regions". Based on the labeling in Figure 5b, it looks likely there is mostly NOx-sensitive conditions. Need to specify what values of  $\alpha(CH_3O_2)$  define NOx- vs. VOC- sensitive conditions.**

The  $\alpha(CH_3O_2)$  theory introduced by Nussbaumer et al. (2021) has from our point of view many advantages but one mayor disadvantage: There is no absolute, always valid threshold value dividing a dataset into NOx-/VOC sensitive regimes. Nussbaumer et al. (2023) define the NO<sub>x</sub> sensitive O<sub>3</sub> regime by a linear fit for all data points having NO mixing ratios < 0.1 ppbv. However, they only consider data points at the 200hPa model level between 30° S and 30° N. For our dataset however, a threshold value of 0.1 ppbv would not make sense as we have trajectory points with exceptionally high NO mixing ratios (due to fresh and very high biomass burning emissions), a regime which can usually not be found in a global chemistry climate model. Therefore,  $\alpha(CH_3O_2)$  remains a relative measure of VOC/NO<sub>x</sub> sensitive regimes with a large transition region.

We had originally decided to use the same x-axis range for all plots in figure 5 which is rather large due to the very high biomass burning NO emissions. This x-axis range gives however, a misleading picture for plots e)-h). We reduced the x-axis range for these plots. As a consequence, also in these plots a (horizontal) VOC limited regime at high  $\alpha(CH_3O_2)$  values is visible. In the revised version of the manuscript, we describe more detailed the differences between plots in Figure 5, in particular 5e) and 5f).

#### **Model setup uncertainties**

**lines 235 - 237: Here finally it is mentioned that only grid scale vertical motion is used in MPTRAC. The authors are correct that this will underestimate the number of BB trajectories that are lifted by convection. It will also take longer time for them to be uplifted than in reality.**

We added your last sentence in line 237.

**The potential mismatch between lightning flash location and the uplift by convection is a significant uncertainty in the modeling approach, and needs to be stressed more significantly in the text.**

**Line 282-284: Here the potential mismatch of GLM flashes and the times and locations of ERA5 deep convection is mentioned. This could have a major impact on the P(O3) for the FLASH trajectories. Need to emphasize this uncertainty more strongly.**

As an initial evaluation of our model setup we compared daily means of ERA5 and GOES cloud top height as an indication for convective/lightning events. GOES cloud (and lightning) data have a very high temporal and spatial resolution with details which cannot be captured by a reanalysis dataset. However, we considered the agreement in the spatial patterns of the cloud top height (especially high clouds in the South American outflow region and the major burning region, 0-

15°S, 60-80°W) as good enough to use the observed lightning events in our trajectory analysis. If we had instead implemented a lightning parameterisation scheme based on ERA5 dynamical and microphysical parameter, there would be as well an uncertainty in the lightning representation and subsequently in the calculated amount of lightning NO emissions. We considered the uncertainty to be smallest by using the most detailed lightning satellite product available and consider it as less likely that we underestimate the number of lightning events along the trajectories.

We performed a series of sensitivity simulations adding lightning NO emissions also one timestep before and after a trajectory crosses a flash detected by GOES. This leads to higher NO mixing ratios along these trajectories but does not change our conclusion, i.e., that lightning emissions alone can by far not be responsible for the observed amounts of O<sub>3</sub> during flight ST19.

**lines 358-359: Comparison with Pickering et al. (1996) needs some revision: "...who link enhanced UT O<sub>3</sub> levels observed in aircraft data and O<sub>3</sub> soundings from Natal (northeast Brazil coast site) with biomass burning over central Brazil and deep convective transport of these emissions accompanied by a contribution from lightning."**  
We rephrased this section following your advice.

We generally extended and rephrased the 'Discussion and Conclusions' section:

**With regard to LNO<sub>x</sub>, some comparison should be included with the NO<sub>x</sub> observations along the coast of Brazil that were primarily lightning related that were presented by Dickerson et al. (1984, Atmospheric Environment).**

We added: [Dickerson, 1984] present NO observations taken along the Brazilian coast in December 1983 on board of a commercial aircraft along a similar flight track as for flights ST06 and ST19. They observed smaller mixing ratios of NO in the northern hemisphere ( $\approx$  0-30 ppt) compared to the southern hemisphere ( $\approx$  50-150 ppt, in the latitude range between -25° and 0°S) and attribute this difference to enhanced lightning activity over the South American continent and assume that biomass burning does not play a role for upper tropospheric NO level in December. If this is true, the difference in their observations and our observed NO mixing ratios, being at the same locations more than a factor two higher than reported by Dickerson et al. (1984) provides a further indication that our observations are strongly impacted by biomass burning.

**Conclusions: Need to add some statement concerning NO<sub>x</sub>- vs. VOC-sensitive conditions found in the modeling. Can these results be compared with other UT O<sub>3</sub> sensitivity studies?**

We extended the discussion section:

Most studies analysing O<sub>3</sub> production regimes focus on the boundary layer or lower troposphere often with the purpose to quantify the impact of different emission sources on O<sub>3</sub> production which enables the development for mitigation strategies to diminish air pollution. Few studies investigate NO<sub>x</sub> and VOC related O<sub>3</sub> production regimes in the upper troposphere. Based on their modeling study using the EMAC model, [Nussbaumer et al., 2023] conclude, that in the ITCZ over continental areas, in particular Africa and South America, ozone chemistry is mostly VOC sensitive or in the transition regime which is in agreement with our findings for the UT over South America. Following the discussion in [Nussbaumer et al., 2023], older studies assuming a NO<sub>x</sub> sensitive O<sub>3</sub> regime over the US and the North Atlantic based on aircraft observations (Jaeglé et al., 1998; Wennberg et al., 1998; Jaeglé et al., 1999) presumably overestimated the reaction between NO<sub>2</sub> and OH as it is known today that the reaction rate of NO<sub>2</sub> and OH is much lower than previously assumed. An early study by [Pickering et al., 1990] reported a VOC-sensitive regime over the USA at 11 km altitude based on measurements in June 1985 and model simulations. A more recent study by [Tripathi et al., 2025] also comes to the conclusion, that O<sub>3</sub> formation in a NO<sub>x</sub> rich upper troposphere (due to lightning) is limited by the abundance of VOCs. However, [Tripathi et al., 2025] also use the EMAC model in a similar configuration as used in our study thus it is likely that both

studies reveal the same conclusions.

## References

- [Dickerson, 1984] Dickerson, R. (1984). Measurements of reactive nitrogen compounds in the free troposphere. *Atmospheric Environment (1967)*, 18(12):2585–2593. CACGP Symposium on Tropospheric Chemistry Part II.
- [Nussbaumer et al., 2023] Nussbaumer, C. M., Fischer, H., Lelieveld, J., and Pozzer, A. (2023). What controls ozone sensitivity in the upper tropical troposphere? *Atmospheric Chemistry and Physics*, 23(19):12651–12669.
- [Pickering et al., 1990] Pickering, K. E., Thompson, A. M., Dickerson, R. R., Luke, W. T., McNamara, D. P., Greenberg, J. P., and Zimmerman, P. R. (1990). Model calculations of tropospheric ozone production potential following observed convective events. *Journal of Geophysical Research: Atmospheres*, 95(D9):14049–14062.
- [Tripathi et al., 2025] Tripathi, N., Krumm, B., Edtbauer, A., Ringsdorf, A., Wang, N., Kohl, M., Vella, R., Machado, L., Pozzer, A., Lelieveld, J., and Williams, J. (2025). Impacts of convection, chemistry, and forest clearing on biogenic volatile organic compounds over the amazon. *Nature Communications*, 16.