

## Reply on Referee Comment RC1 on acp-2021-52

*In the following the comments of the referee are presented (in black) alongside with our replies (in blue) and changes made to the manuscript (in red).*

General statement: The manuscript presents original and valuable experimental results accompanied by global model calculations. Furthermore, it is generally well written and presented. I suggest acceptance of the manuscript for publication, but I have a few minor comments to be considered before the final acceptance.

Dear reviewer, thank you very much for reviewing our manuscript and for the insightful comments. Below we provide detailed responses to your comments.

**Comment 1:** line 35: The wording “NO<sub>x</sub> is a toxic gas” sounds rather odd as NO<sub>x</sub> is not a single gas. To avoid misunderstandings the wording could be revised.

We have revised the sentence. It now says in line 35: Both NO and NO<sub>2</sub> are toxic gases which degrade surface air quality and regulate the abundance of secondary tropospheric oxidants.

**Comment 2:** line 41: The sentence needs revision.

We have revised the sentence. It now says: The U.S. Clean Air Act identified ozone as a criteria air pollutant in the 1970s (Jaffe et al., 2018).

**Comment 3:** line 84: You may also add some earlier references on NO<sub>x</sub>-VOC sensitivity of ozone production by Sillman.

We have added the already cited study of Sillman et al. “Photochemistry of ozone formation in Atlanta, GA – models and measurements” (1995) as a reference and another study by Sillman et al., “O<sub>3</sub>-NO<sub>x</sub>-VOC sensitivity and NO<sub>x</sub>-VOC indicators in Paris: Results from models and Atmospheric Pollution Over the Paris Area (ESQUIF) measurements” to the list of references and as a reference to line 84: (Sillman et al., 1995; Sillman et al., 2003; Duncan et al., 2010, Nussbaumer and Cohen, 2020, Tadic et al., 2020).

**Comment 4:** lines 85-86: Please add a reference for the lifetime of NO<sub>x</sub>.

We have added a reference to lines 85-86 (Beirle et al., 2010).

**Comment 5:** There are a number of NOPR studies based on in situ HO<sub>x</sub> or RO<sub>x</sub> measurements by aircraft or at high altitudes stations which could be considered, e.g. Cantrell et al., 1996, Zanis et al., 2000, Cantrell et al., (2003a), Ren et al., (2008) Olson et al., (2012).

We have added Zanis et al. (2000a; The Role of In Situ Photochemistry in the Control of Ozone during Spring at the Jungfraujoch (3,580 m asl) – Comparison of Model Results with Measurements; <https://doi.org/10.1023/A:1006349926926>) and Cantrell et al. (2003; Peroxy radical behavior during the Transport and Chemical Evolution over the Pacific (TRACE-P) campaign as measured aboard the NASA P-3B aircraft; <https://doi.org/10.1029/2003JD003674>) to the list of references.

We have added the following sentence to the manuscript in line 367 (referencing Zanis et al., 2000a): The negative net ozone tendencies observed between 3 and 5 km altitude for the tropical troposphere stand in opposition to positive net ozone tendencies of about 0.1 ppbv h<sup>-1</sup> (Zanis et al., 2000a) and balance in net ozone tendencies (NOPR ≈ 0) (HOOVER campaign over Europe; Bozem et al., 2017) deduced from previous measurements at similar altitudes at mid-latitudes.

We have added the following sentence to the manuscript in line 449 (referencing Cantrell et al., 2003): Especially the NO compensation mixing ratio (for which ozone production equals ozone loss) reproduces results from previous studies remarkably well. Cantrell et al. (2003) report NO compensation mixing ratios between 10 and 30 pptv over the Pacific, depending on whether modelled or measured HO<sub>2</sub> and RO<sub>2</sub> is used. Another study conducted by Zanis et al. (2000b) in the Swiss Alps also reports balance in net ozone production for similar NO compensation mixing ratios. Note that this second amendment addresses **Comment 17** of our reply. The respective reference (Zanis et al., 2000b) has been added to the list of references.

**Comment 6:** line 211: Should rather be “is practically one or unit” instead of unity.  
We have revised line 211 accordingly.

**Comment 7:** line 211: Should be Tadic et al. (2017).  
We have revised the passage accordingly.

**Comment 8:** line 235: You may also add some earlier references for the calculation of net ozone production (e.g. Lin et al., 1986).

We have added the suggested reference to the list of references and to line 235/236. However it should be Lin et al., [1988](https://doi.org/10.1029/JD093iD12p15879) (https://doi.org/10.1029/JD093iD12p15879) instead of [1986](#). We have further added Cantrell et al. (2003) as a reference for this sentence.

**Comment 9:** line 242-243: You may add a reference for the selection of the 100 ppbv criterion for stratospheric ozone. For example, see Prather et al., 2011. Other model intercomparison studies generally utilized a chemical tropopause defined at the 150 ppbv.

We have added Prather et al. (2011) to the list of references. Line 242ff now says (the underlined passage is new): Data are filtered for stratospheric influence by removing all data points for which concurrent O<sub>3</sub> is larger than 100 ppbv; a conservative criterion which has been earlier discussed by Prather et al. (2011).

**Comment 10:** lines 251-253: The attribution of high NO<sub>x</sub> above 12 km to lightning NO<sub>x</sub> rather than NO<sub>x</sub> rich stratospheric air is rather speculative, unless if there are some indications from the model results of references for that. Mind also the simultaneous relatively smooth increase of both NO and O<sub>3</sub> (as you also mention in page 10) which may point influence of stratospheric air.

Our argumentation is based the fact that the tropopause is located at about 16-18 km altitude at the ITCZ, which is still about 3-5 km above typical (highest) cruising altitudes of 12 – 14 km during the campaign. Second, although both NO and O<sub>3</sub> show a slight increase above 12 km, the vertical CO profile shows only a slight decrease in average mixing ratios from about 100 ppbv around 12 km altitude to 80 ppbv around 15 km altitude which is statistically insignificant within ±1 standard deviation of the vertical average CO mixing ratio. Assuming that stratospheric influence did play a (more) dominant role in terms of high NO<sub>x</sub>, the decrease in CO should be stronger than observed.

Also we have created two additional figures (added at the end of this reply) showing 2-D latitudinal/altitudinal distributions of measured, tropospheric NO and O<sub>3</sub> during the campaign. Especially the latitudinal/altitudinal NO distribution shows rather local enhancements at the latitudinal range of the ITCZ than intrusion from the stratosphere at the subtropical jet streams. We have further added these two figures discussed here to the supplement (as supplement Figure S5 and Figure S6) and redefined the numbering of the following supplement Figures accordingly. A short passage has been added to the manuscript in line 343: Furthermore, supplement Figures S5 and S6 show 2-D latitudinal-altitudinal distributions of measured, tropospheric NO and O<sub>3</sub>, respectively.

**Comment 11:** line 264: At around 6 km it seems that there is an ozone layer of possible stratospheric origin. You may check this with relevant model diagnostics (e.g. specific humidity, potential vorticity or O<sub>3</sub>S if it is available from the simulation).

There is generally a lower data coverage for altitudes in the free and middle troposphere (between 4 and 10 km). The increase in modelled O<sub>3</sub> at 6 km altitude arises from a few data points with increased mixing ratios at this altitude. A vertical profile of modelled humidity does not reproduce stratospheric influence.

**Comment 12:** lines 280-281: This does not necessarily mean that you totally exclude the influence of mixing with air of stratospheric origin.

No, we do not exclude mixing with air of stratospheric origin. To clarify this, we have added a short notice after the respective sentence in line 281f (underlined passage is new): We again remove stratospheric measurement data by only considering those for which O<sub>3</sub> was below

100 ppbv. Note that this does not necessarily exclude the influence of mixing with air of stratospheric origin.

**Comment 13:** line 308: "...is shown.." should be deleted.

Thanks for noticing. We have removed "is shown" from the sentence.

**Comment 14:** line 368: Although the effect of humidity can be implied from factor  $\alpha$  of Eq. 4 maybe it is also interesting adding in the supplementary material the observed and simulated specific humidity values.

We agree that it makes sense to add a comparison of the vertical profiles of observed and simulated humidity. We have added the following underlined sentence in line 349: We provide a vertical profile of  $\alpha$  calculated based on Eq. 4, for which we obtain good agreement between measurements and simulations, for which we refer to the left graph of Figure S7 in the supplement. Supplement Figure S7 also provides a comparison of vertical profiles of measured and simulated H<sub>2</sub>O mixing ratios. The respective comparison of measured and modelled H<sub>2</sub>O mixing ratios has been added to supplement Figure S7 (which already shows the intercomparison of the vertical profile of  $\alpha$  and  $j(01D)$ ). The revised Figure S7 (updated in the supplement) is included at the end of our reply.

**Comment 15:** line 379: Should rather be: "... is from a factor of 2-3 (below 3 km altitude) to a factor of 10 (above 12 km altitude) stronger ..."

We have applied the suggested change.

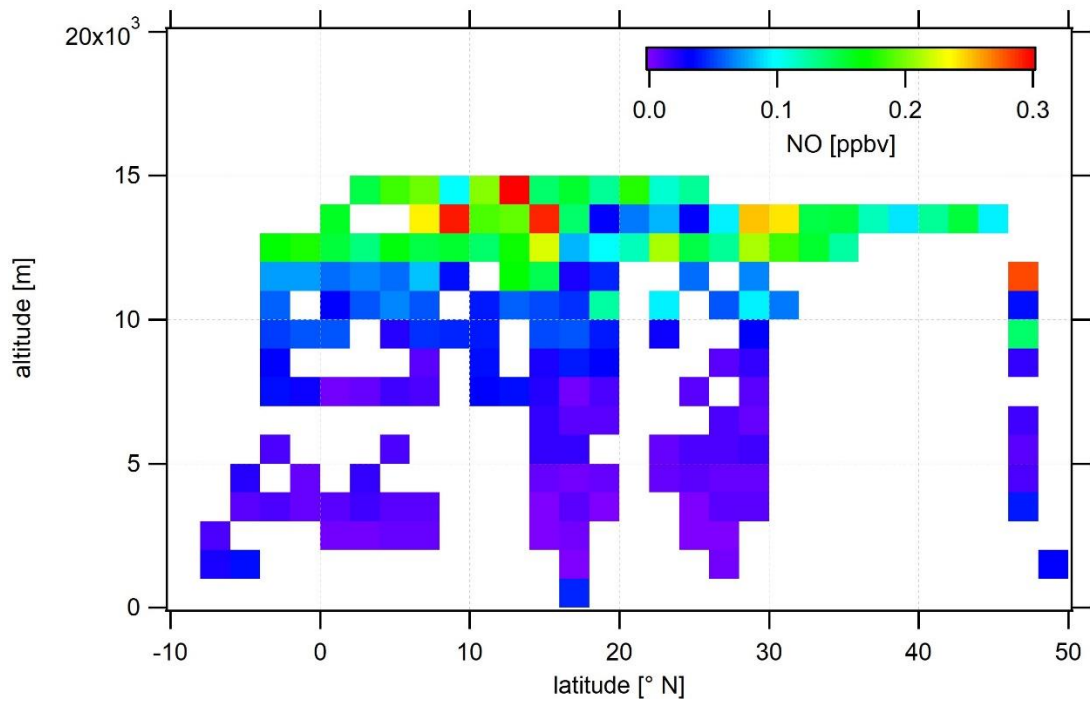
**Comment 16:** Figure 7 is interesting showing the NO dependence of NORP as well as the ozone compensation point (the NO level at which NORP is roughly zero). One possible limitation is the fact that the aggregated bins correspond to different atmospheric layers with different atmospheric characteristics which can possibly induce the spiky signal in the figure.

We agree that the spiky signature in the profile could be due to the variety of different air masses measured during the campaign and corresponding to a certain bin. We have added the following sentence to the passage below the figure (line 453ff): Note that one possible limitation of this figure arises from the fact that the data aggregated in the respective NO mixing ratio bins stem from different atmospheric layers and origins, which causes the spiky signature of the profile for both measurement and model.

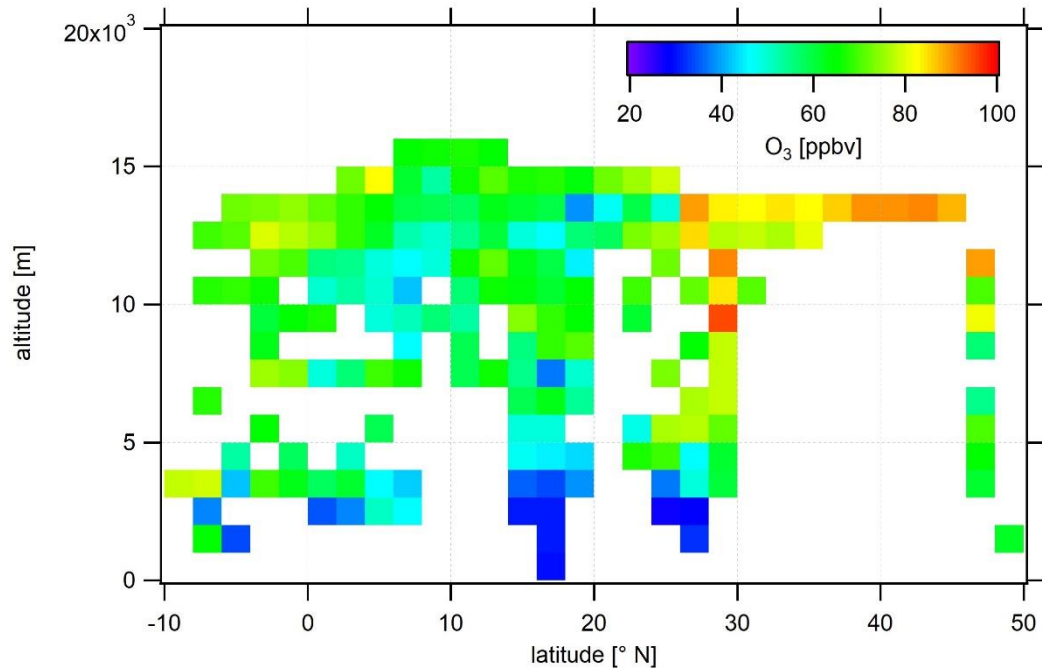
**Comment 17:** line 441: You may also take into consideration the ozone compensation point which was derived in previous studies in the free troposphere and which agrees well with these values (see e.g. Zanis et al., JGR, 2000)

Zanis, P., Monks, P. S., Schuepbach, E., Carpenter, L. J., Green, T. J., Mills, G. P., Bauguitte, S., and Penkett, S. A.: In situ ozone production under free tropospheric conditions during FREETEX '98 in the Swiss Alps, J. Geophys. Res., 105, D19, <https://doi.org/10.1029/2000JD900229>, 2000b has been added to the list of references.

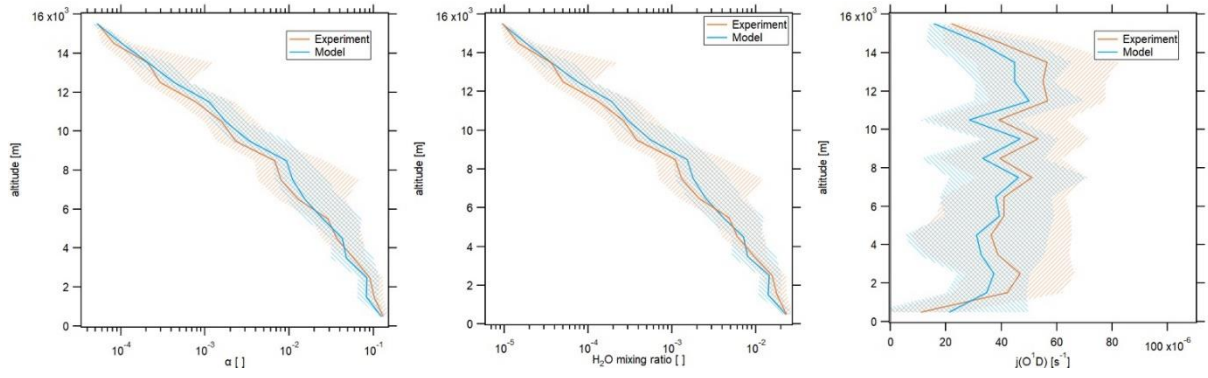
**Comment 17** is being addressed within the answer to **comment 7**.



**Figure S5: Latitudinal/altitudinal distribution of measured, tropospheric NO obtained during the campaign. The data have been aggregated and averaged over a grid width of 2 degree latitude and 1 km altitude.**



**Figure S6: Latitudinal/altitudinal distribution of measured, tropospheric O<sub>3</sub> obtained during the campaign. The data have been aggregated and averaged over a grid width of 2 degree latitude and 1 km altitude.**



**Figure S7: Vertical, tropospheric profile of  $\alpha$  calculated based on measured and simulated data during CAFE-Africa (left graph). Vertical, tropospheric profile of  $H_2O$  mixing ratios calculated based on measured and simulated data during CAFE-Africa (middle graph). Vertical, tropospheric profile of  $j(O^1D)$  (measured and simulated) obtained during CAFE-Africa (right graph). The orange and blue traces represent measured and simulated results, respectively.**