



EGUsphere, referee comment RC2  
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## Comment on egusphere-2022-656

Anonymous Referee #2

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Referee comment on "Nitrogen oxides in the free troposphere: implications for tropospheric oxidants and the interpretation of satellite NO<sub>2</sub> measurements" by Viral Shah et al., EGU sphere, <https://doi.org/10.5194/egusphere-2022-656-RC2>, 2022

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This manuscript analyzes NO<sub>x</sub> concentrations and the vertical distribution in the troposphere based on three aircraft campaigns - SEAC<sup>4</sup>RS, DC3 & ATom - and four atmospheric chemistry models - GEOS-Chem, GMI, TM5 & CAMS. The authors present that measurements via LIF and P-CL overestimate NO<sub>2</sub> concentrations in the upper troposphere due to thermal interferences and can be better represented by PSS calculations from measured NO. pNO<sub>3</sub><sup>-</sup> photolysis as a missing NO<sub>x</sub> source in models is evaluated and is found to have a significant contribution, particularly over the oceans which improves the model performance for the ATom mission. Lightning and aircraft emissions are identified as main sources of NO<sub>x</sub> in the free troposphere, with individual contributions varying by latitude and season.

This manuscript is well written and presents an interesting and comprehensive analysis of free tropospheric NO<sub>x</sub> from measurements and models.

My main concerns are that the P-CL NO<sub>2</sub> measurements were not corrected for thermal interferences from e.g. MPN and HNO<sub>4</sub>. This should be done and compared to the LIF measurements and the model results. I suggest some changes to the Figures, i.a. adding letters (a), (b), ... to the subfigures for easier distinction, changing some of the axis scales and adding labels to all axis, but most importantly including error bars. Finally, I recommend the authors to elaborate in more detail how the NO<sub>2</sub> columns were calculated from the measurements and what the uncertainties are. You will find my detailed comments and questions below. Once these points are addressed properly, this paper would be a valuable contribution to the current literature.

Major comments:

Lines 156 ff.: I assume this interference results from thermal decomposition of MPN. Could you go a bit more into detail? How was the correction determined? What's the temperature in the instrument and what is the residence time of the sample gas?

Lines 162 ff.: What's the residence time and the temperature in the photolysis cell (I assume the operation of the LEDs inevitably increases the temperature in the cell)? And how large is the resulting interference? Does thermal decay of  $\text{HNO}_4$  play a role? From Bourgeois et al. (2022), I understand that the wavelength of the LEDs in the photolysis cell is 385nm – do you experience and correct for photolytic interference from HONO?

Table 1: It would be helpful to add the uncertainties of each measurement in the table (e.g. as a fifth column).

Line 196: Do you perform a separate model run for the data along the flight track?

Line 252: How is the factor of 2.39 determined?

Line 278: It looks like the DC3 NO observations show a minimum for the lowest altitude bin. Is this real and if yes, why? Or do you have a small number of observations at this altitude?

Line 284: Do I understand correctly that the P-CL  $\text{NO}_2$  measurements were not corrected for the MPN and  $\text{HNO}_4$  interferences?

Figure 1: I recommend adding letters (a)-(f) to the subfigures for easier distinction. Could you lower the upper x-limit for NO to e.g. 200 or 250 pptv – so the profile is better to see. I find it a bit confusing that black was chosen as the observation in the NO vertical profiles and for the PSS calculation in the  $\text{NO}_2$  vertical profile. The LIF and P-CL observations are also hard to distinguish. I suggest using different colors and potentially decreasing the line width to prevent overlapping. Please add error bars to the modeled data, too.

Lines 307 ff.: So, the PSS is not entirely calculated from observations? - Maybe clarify in the legend of Figure 1.

Lines 312: It might be more accurate to use  $k(\text{NO}+\text{CH}_3\text{O}_2)$  as surrogate for  $k_3=k(\text{NO}+\text{RO}_2)$ .

Line 320: Does jNO2 increase with altitude and plays a role in this, too?

Lines 326 ff.: You can estimate the interference from HNO<sub>4</sub> and MPN with the temperature and the residence time in the instrument assuming first order decay (presented by Reed et al. (2016) and Nussbaumer et al. (2021)). If I see correctly you have measurements of both species available for SEAC<sup>4</sup>RS & DC3 and can calculate the resulting artifact and correct the measurements. For ATom (if needed), you could estimate HNO<sub>4</sub> and MPN via PSS calculations. It could be helpful to compare your measurements with the PSS calculations for SEAC<sup>4</sup>RS & DC3 to see whether using the PSS to calculate HNO<sub>4</sub> and MPN is a valid assumption. You can find the rate constants for the decay here: <https://iupac-aeris.ipsl.fr/#>.

Line 329: I don't agree with the generalized assumption that HNO<sub>4</sub> and MPN dissociate with the same efficiency as NO<sub>2</sub>. This largely depends on the temperature and the residence time. NO<sub>2</sub> is subject to photolytic dissociation by the LEDs in the converter (which is mostly temperature independent), while HNO<sub>4</sub> and MPN produce artifacts through thermal dissociation which is strongly temperature-dependent. MPN dissociates at lower temperatures compared to HNO<sub>4</sub>, and therefore produces the NO<sub>2</sub> artifact at a higher efficiency than HNO<sub>4</sub>.

Line 332: How does it change the agreement between PSS NO/NO<sub>2</sub> and P-CL NO/NO<sub>2</sub> when accounting for the thermal interferences?

Line 341: Do you observe fresh lightning peaks in your NO signal which support this statement?

Line 343: It would be helpful to also show the trace gas concentrations as a function of time of the measurement period. Does NO continuously decrease over the period? How long is the measurement period?

Line 345: This likely looks different when correcting the P-CL NO<sub>2</sub> data as described above. Are the changes described for the NO<sub>2</sub> observations with increasing NO<sub>y</sub>/NO molar ratio significant? It looks like the scatter of the 1-minute observations is approximately the same as the increase/decrease of the NO<sub>2</sub> lines.

Line 348: Is [HO<sub>2</sub>]=[RO<sub>2</sub>] a valid assumption? What's the error arising from this assumption?

Equation (4): How did you calculate the ozone loss term via photolysis?

Figure 2: Again, letters (a)-(c) for the subfigures would be helpful to follow in the text. I recommend using the same colors as in Figure 1 for the according measurements /

calculations. Again, LIF NO<sub>2</sub> and P-CL NO<sub>2</sub> are hard to distinguish and it is impossible to see the difference between the 1-minute observations. It could be helpful to use error bars instead. Please add error bars or the 1-minute data points for all species.

Lines 394 ff.: This seems a little bit like a circular argument to me. Wasn't the PSS NO<sub>2</sub> applied for the observations because the model identified a bias in the P-CL & LIF NO<sub>2</sub> measurements (Lines 281 ff.)? And now the model performance is evaluated in comparison to the PSS NO<sub>2</sub>?

Line 403: How do these values compare to PSS calculations of MPN (production via CH<sub>3</sub>O<sub>2</sub>+NO<sub>2</sub> and loss via decay and photolysis)?

Lines 411 ff.: This whole paragraph describes a method which is used in the subsequent section. I recommend shifting this paragraph to section 3.2.

Figure 3 and 4: Consider using letters for the subfigures. Why was the log scale chosen for the x-axis? I would find it more straight forward with a linear scale and it would also be easier to compare to Figure 1. Please add horizontal error bars for all traces.

Lines 447 ff.: How does this compare to the satellite measurements?

Line 471: Could you show a vertical profile of pNO<sub>3</sub><sup>-</sup> somewhere - either in the manuscript or the supplement?

Figure 5: Please add labels to the axis and the color bar.

Line 533: I cannot follow this argument. It looks like measured pNO<sub>3</sub><sup>-</sup> is much larger than the modeled values. Please clarify.

Lines 552 ff.: How are the PSS NO<sub>2</sub> column density and the corresponding AMF determined? Could you provide a more detailed procedure? From Eq. (5) it looks like the viewing geometry of the satellite is required to determine the AMF. How does this apply to PSS or (in situ) measured values?

Lines 562 ff.: Considering a column density of  $\sim 1.3 \times 10^{14}$  molec/cm<sup>2</sup> for GMI, isn't a difference of  $\sim 1 \times 10^{14}$  molec/cm<sup>2</sup> quite large ( $\sim 80\%$ )?

Figure 6: What are the errors on these values?

Line 582: Do these values refer to the annual mean over all layers? Looking at the  $\text{NO}_x$  changes in Figure 7 (up to 400%), the 9% value probably has a large uncertainty. It could be helpful to add the uncertainty e.g. as the  $1\sigma$  standard deviation.

Figure 7: Why do you show two plots with % changes and one with ppb changes?

Lines 615 ff.: Please state the  $1\sigma$  values (or something comparable) for all averages.

Line 672: It looks like for the 30-60°N oceans and the U.S., absolute aircraft emissions are slightly larger in February compared to August, e.g. at 12km altitude for the U.S.  $\sim 70\text{pptv}$   $\text{NO}_x$  in February and  $\sim 30\text{-}40\text{pptv}$   $\text{NO}_x$  in August. Is this significant? Do you have an explanation for that?

Figure 9: Please add error bars, e.g.  $1\sigma$  from averaging at each altitude bin. Please consider using letters (a) and (b) instead of referring to the right and the left panel.

Lines 739 ff.: I am not sure I can completely follow this argument. So, the right panel from Figure 9 show the summed contribution at each altitude plus everything that's above up to 12km? Why do the winter profiles not show 100% at ground level?

Minor comments:

Line 346: shows

Line 613: consider replacing 'worsening' with 'reducing'