

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2022-390

Anonymous Referee #2

Referee comment on "Fundamental oxidation processes in the remote marine atmosphere investigated using the NO-NO₂-O₃ photostationary state" by Simone T. Andersen et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-390-RC2>, 2022

Andersen et al. use long-term (years) measurements of NO_x, O₃, organic compounds and associated parameters from a remote marine sampling location to evaluate understanding of radical chemistry affecting NO₂/NO ratios and ozone production. This topic is of wide interest as radical chemistry is central to understanding global oxidation processes, and many studies have failed to explain the observed NO_x partitioning in a variety of chemical environments. Strengths of the work are uniqueness of the dataset, and analysis using GEOS-Chem and a detailed chemical box model to evaluate the chemistry.

Overall, I think the paper is well written, provides an excellent review of and links to the prior work on this topic, and has interesting analysis. I think that the paper will deserve publication but that the authors should first consider a few important points concerning the limitations of the measurements and modeling analysis and how that might affect the way that the conclusions are stated.

General comments:

1) The primary conclusion of the paper is that the NO₂/NO ratio observations are consistent with the expected NO → NO₂ oxidants in the cleanest conditions, but more polluted air masses would require significantly more organic peroxy radicals or halogen oxides to explain the observed NO₂/NO ratios. This is first stated in the paragraph beginning on line 354. I am not convinced, however, that there is a clear difference in the behavior between the more pristine and more polluted air masses. In other words, it is not clear to me that one can say the cleaner data definitely are completely explained by the known chemistry whereas the more polluted data have a different behavior. I think a more thorough discussion of the uncertainties of each data point due to precision or artifact uncertainties would help the interpretation of the figures.

For example in Fig 3B while the scatter of data at NO₂ < 20 ppt are hard to distinguish from the 1-1 line, I would not say by eye that the overall trend there is different than at

the higher NO₂ mixing ratios. In Figure 5, while enhancements in acetylene and ethane are associated with higher than expected NO₂, the data with low acetylene and ethane do not cluster around a value of 1 for NO₂_obs / NO₂_pss, but appear to have significantly lower than expected NO₂. I did not see discussion of the lower than expected NO₂ observations. In Figure 6 while the CO < 90 ppb data are centered around a value of 1 for NO₂_obs / NO₂_pss, many of the points are not close to one. Is the width of the histogram explained by the precision of the measurements or is it possible that some of the width here is also evidence for incomplete understanding of the chemistry?

2) As I understand it from this paper and Anderson et al. 2021, a potential positive artifact on the NO₂ measurement from the photolytic converter is assumed to be negligible (Anderson et al., 2021 state that measurements of zero air show 0 – 10 ppt of NO₂, which is assumed to be real NO₂ in the zero air). While I understand the problems/challenges with experimentally determining if there is a real surface artifact, I find it concerning that the potential for a positive artifact in the NO₂ measurement due to illumination of species on the walls of the photolytic converter is assumed to be zero. It is well documented that typically a positive NO signal of at least a few ppt will be generated by illuminating such converters (even quartz ones) even in the presence of synthetic, NO_y-free air (e.g. Gao et al., 1994, Pollack et al., 2010, others). Can the authors please comment in the artifact section in some way on this? What would the impact be if there were a few ppt of fake NO₂ from the converter? Perhaps the lowest measured NO₂ could be used at least as an upper limit of such an artifact. Are there other upper limits that can be stated for such an artifact?

3) I suggest that the authors put a bit more emphasis/discussion on the good agreement shown in Fig. 7 between measured and calculated ozone tendency. It could be argued that this is more important than being able to reproduce the NO/NO₂ ratio, and therefore remaining uncertainties or discrepancies in observed vs calculated NO₂/NO are less important to resolve since the ozone tendency seems nicely explained.

Specific comments by line:

Line 60: Suggest defining RO₂ as 'organic peroxy radicals' rather than just 'peroxy radicals.'

252: Recommend using the symbol *s* rather than defining the ACS acronym.

260: Can you state the width of the LED spectrum?

277: While GEOS-Chem may not show a coherent seasonal pattern for NO_y, clearly there is a lot of real variability that is likely related to airmass origin, and higher NO_y is probably related to pollution sources. PAN for example could matter. Could you comment on the

origin of the variability in GEOS-Chem? Perhaps adding a timeseries of CO to Fig. S7 would be helpful.

292: The GEOS-Chem timeseries of PAN (S7) which seems to be routinely above 20 ppt would suggest that if GEOS-Chem has some skill here the PAN would be above this 6 ppt detection limit frequently, or always. Can you comment on this?

322: Since the calculation of RO₂ is critical to the argument of the paper, it would be helpful to see more information about the relative importance of these measured RO₂ precursors. Is there any correlation between the calculated RO₂ and the pollution indicators? Do the authors think that the missing RO₂ sources could be due to VOCs that are not measured by the GC system at CVAO? If the air is of African origin and possibly influenced by biomass burning, can the authors comment on how sufficient the measured suite of VOCs might be in comparison to recent those reported in more recent papers with comprehensive measurements of biomass burning VOC emissions? Overall, I'm a bit unsure if 'missing' is the right word to use to describe the unaccounted for RO₂, or rather that we should expect there are a number of important organic compounds that were not measured.

460: I would say that the required additional factor for XO is higher than that of RO₂ not because of the difference in rate coefficients, but because the measured/calculated XO is << measured/calculated RO₂.

Figures

Fig1: please provide a colorscale and explanation. Does each point represent the calculated location of an air parcel 10 days prior to arrival at CVAO?

Fig2: Would be nice to mention in the caption the seasons of those campaigns.