

Atmos. Chem. Phys. Discuss., referee comment RC1
<https://doi.org/10.5194/acp-2022-390-RC1>, 2022
© Author(s) 2022. This work is distributed under
the Creative Commons Attribution 4.0 License.

Comment on acp-2022-390

Anonymous Referee #1

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-RC1>, 2022

The authors present analysis using three years of seemingly superb measurements from an excellent measurement site. The conclusions drawn from measurements of NO, NO₂, jNO₂, O₃, CO, and several VOCs is that there are "missing oxidants" that convert NO to NO₂ in the air, and that are not accounted for by past peroxy radical measurements. I recommend it be published after the following major and minor concerns are addressed:

- The detailed model used is only as good and accurate as the inputs (i.e., compound concentrations constrained by measurements), and as impressive as the long-term dataset is, it does not include oxygenated VOCs. As such, it does not seem fair to expect that the models could accurately simulate the actual photochemistry given that it is likely not adequately constrained. Please include a discussion of the impact of unmeasured VOCs, especially oxygenated VOCs. Also please be clear what is meant by the term "missing" – are there reactions missing in the chemical mechanisms?
- The analysis needs a more quantitative handling of the uncertainties. In particular, what is the uncertainty of the calculated quantity [NO₂]_{PSS-ext}? (based on its constituent parts in equation III). For example, in line 343 of the manuscript. See also another comment below regarding the stated measurement uncertainties in Table 2 which require improvement. In numerous places it refers to older peroxy radical measurements and explains that those measurements are highly uncertain, especially at high RH. What are those uncertainties – both as stated in the original papers, and as concluded by the authors today?

Detailed comments

Abstract

Line 29 "...implying 18.5-104 pptV (25th-75th percentile) of missing RO₂ radicals" - the term "missing RO₂ radicals" is unclear. Please clarify as "...of RO₂ radicals missing from photochemical models".

Line 32: "If the missing RO₂ radicals have an ozone production efficiency equivalent to that of..." The term ozone production efficiency is traditionally defined as the number of ozone molecules produced per NO_x molecule. Please use a more accurate and defined term for what you mean in the abstract.

Line 34 (same sentence): "then the calculated net ozone production including these additional oxidants is similar to that observed"

The term "net ozone production" is unclear. Do you mean net ozone production rate (ppb/hr)? or does it mean "net ozone produced", which would be in # of molecules, or possibly mixing ratio (ppb)? Furthermore, it is confusing to refer to the "observed" ozone production rate, since nowhere in the abstract is it explained how that was "observed". Does "observed" actually mean "calculated based on measured quantities"? Please clarify.

Line 37 "and that measured and modelled RO₂ are both significantly underestimated under these conditions." This is the first reference in the abstract to measured RO₂ and as such is quite confusing. Later in the paper it becomes apparent that it is referring to past measurements of RO₂ at this site. Please clarify.

Body of manuscript

54: "Under very polluted conditions, where O₃ is the only oxidant converting NO to NO₂" – I disagree with that statement. There are plenty of very polluted conditions in which there are plenty of peroxy radicals present that also convert NO to NO₂ (e.g., Mexico City, Los Angeles...). This would be better phrased as "Under conditions in which O₃ is the only oxidant converting NO to NO₂, ..." and can clarify that perhaps they are referring to time periods with low sunlight and very high NO (I assume)

72: the equations would be much easier to read if more subscripts were added. i.e., rather than $j_{\text{NO}_2}[\text{NO}_2]$, write as $j_{\text{NO}_2}[\text{NO}_2]$

86: "However, PSS-derived RO_x concentrations are generally higher than both measured and modelled values in rural conditions" – the wording can be tricky and sometimes confusing. The term "modelled" is confusing, since use of the PSS to derive RO_x concentrations is in itself a simple model.

116-117: "However, more recent instruments use "cavity absorption phase shift (CAPS)" - that should be *attenuated* rather than *absorption*, and probably wise to add "spectroscopy" or "spectrometry" afterwards.

124: "... the increase in HO₂ wall loss on wet surfaces" – *humid* surfaces, not *wet* surfaces. "Wet" implies there is a fair amount of liquid water on the surface (rather than a possible thin layer of adsorbed water).

Lines 123 onward describe in detail the sensitivity of chemical amplifiers to humidity and specifics of the RO₂ being sampled. It appears that the main point of this section is to point out that these measurements are not perfect and subject to uncertainties. This is true of course, just as it is for measurements of all compounds. The resulting concentrations and stated uncertainties produced by chemical amplifiers ideally reflect the issues discussed in the text (RH dependence, dependence on organic nitrate and nitrite

formation...). I recommend that this section describing RO₂ measurements by chemical amplifier conclude with a summary of the uncertainties of those measurements as described in the referenced papers. If the authors feel that the measurements are even more uncertain, they should state so explicitly. This might be especially important given that the peroxy measurements were made over 20 years ago.

The last sentence of the paragraph could easily be left off, since similar statements apply to all analytical measurement techniques: "It is therefore important to determine the optimal concentrations of reagent gas for each individual instrument as it could vary with what material has been used in the reactor". Similarly, it is important for each chemiluminescence instrument to use the proper ozone concentrations and flow rates, and for HOx LIF instruments to operate with the correct laser settings, NO flow rates....etc.

141: "The production of O₃ (P(O₃)) can be calculated using equation (VI)" insert the word *rate* after *production*

157: "In regions where the net O₃ production is negligible or negative" again this is ambiguous wording, especially in light of the above note regarding the same term "net O₃ production" (line 34). Please define what is meant by "net O₃ production" – the rate? The change in O₃ concentration over time?

Line 159 and 177: O₃ should be [O₃], or written as "O₃ concentration"

Line 180: define what is meant by "photochemical regime".

181 onward, and Table 1: Although later in the text the authors do a good job evaluating the possible interferences in the Chemi-photolytic converter technique, it is noteworthy that all almost all of the NO₂ measurements from Table 1 were made with chemiluminescence and a photolytic converter. The only study that used cavity ring-down spectroscopy (Tadic et al. 2020) appeared to find agreement between ROx(PSS) and ROx(model).

181 – 189: “The large uncertainties associated with ROx measurements, especially at high humidities...” again, the authors really need to include the stated uncertainties from the chemical amplifier measurement papers themselves, and if they believe that the true uncertainties are higher, then they should state so. By how much higher would the uncertainties need to be to have agreement with ROx(model) or ROx(PSS)? Furthermore, is “high humidity” defined as greater than 80%, say, or greater than 50%? What is the range of humidity values observed during daytime at this site?

Table 2: The “accuracy” column is very confusing. For NO, NO₂, O₃, CO, and CH₄ an absolute mixing ratio is listed (e.g., 4.4 ppt), but for all the VOCs, a percentage is listed. The NO and NO₂ values undoubtedly need an accuracy listed in percentage, presumably determined largely by the calibration methods. Perhaps the 1.4 ppt and 4.4 ppt for the NO and NO₂ are actually the 1 sigma precision values? For what time averaging interval? The value for O₃ seems erroneously low – 0.07 ppb! Please fix. The uncertainty of these measurements is crucial given their use in equations II and III.

Section 3.1.1: given the detailed treatment of the NO₂ measurement artefact, it would be useful to include either a spectrum of the blue LEDs or to simply state its spectral width (FWHM).

Line 261-262: “If NO₂ is the product then it will be photolysed to NO with the same efficiency as NO₂ in the ambient air” This does not seem correct, as for an interfering compound it’s a two-step process and thus the NO₂ formed will have less exposure time to the UV radiation (e.g., X --> NO₂ --> NO, rather than NO₂ --> NO). An interfering compound that is converted to NO₂ in the photolysis cell should have a lower efficiency at making NO than NO₂ does.

264: “Organic nitrates, HNO₃, and NO₃ do not photolyse at 385 nm and have therefore not been included in the evaluation of photolytic artefacts” Is this true for all organic nitrates?! There are many kinds – alkyl nitrates, hydroxy-alkyl nitrates, peroxy acyl nitrates...

Line 273: "making it highly likely that a significant fraction of HONO is lost on the manifold before the air is introduced to the NO_x instrument due to the high surface reactivity of HONO (Pinto et al., 2014)" What is the manifold made of? Glass? Teflon? If it's Teflon, then the quoted section seems like an overstatement. Have loss rates of HONO on surfaces been presented in other studies? Pinto et al 2014 appears to have little to say about surface losses and does not conclude that surface losses played a big role in that comparison study.

331: Both of the references which provided the RO₂+HO₂ measurements by chemical amplifiers (Hernández et al., 2001 and Burkert et al., 2001) were from 21 years ago. Do changes in background NO_x and O₃ affect the context of their inclusion in figure 2?

343: "Daily midday values of [NO₂]PSS ext were calculated using equation III" What is the combined uncertainty of [NO₂]PSS ext? Note that this is an important area where the uncertainties of the past chemical amplifier measurements can be addressed quantitatively, as it is part of equation III. This is a crucial area of revision.

Line 361: "the abundance of NO on ..." although the term "abundance" is commonly used synonymously with "concentration", I advise against it in this case as NO molecules were anything but abundant!