

Review of Hao et al., 2022: “Measuring and modelling investigation of the Net Photochemical Ozone Production Rate via an improved dual-channel reaction chamber technique”

General Comments:

This manuscript details changes made to a two-chamber system used to directly measure ambient net ozone production rates, sensitivity tests conducted on this system, and a final 0-D box modeling comparison of the chemistry in both chambers and in ambient air for a select measurement day in 2021. The criticality of making such direct P(O₃)_{net} measurements in areas with poor air quality for the purpose of determining efficient O₃ mitigation strategies is not refuted here; this is an important issue globally. However, while it is clear that much work has gone into the manuscript, it requires major revisions both scientifically and grammatically before being referred for publication. Given the nature of the manuscript, I wonder whether submission to Atmospheric Measurement Techniques is more suitable.

Specific Comments:

- In general, the manuscript is structured appropriately, but has a number of grammatical errors within that prevent clear and fluent presentation. The manuscript would benefit from a review by a technical editor. Some suggestions are presented in the technical corrections below.
- Equation (1), the ambient O₃ budget, is also dependent upon entrainment from the stratosphere. Please add this term for completeness.
- The manuscript indicates that the same tests were conducted on the NPOPR system as in other studies (L188-L189). However, several sensitivity tests conducted in previous studies (Sklaveniti et al., 2018; Baier et al., 2017) are missing from this analysis. These include the following: biases on P(O₃)_{net} from temperature differences between the reaction and reference chamber; short-duration baseline drifting in the CAPS monitor (in presence of both dried and humidified air) and HONO production. Given that some of these additional tests have not been conducted, it is difficult to assess whether the NPOPR system described here has significant improvements over other systems described in the literature. Further, a more detailed description of the system, materials used, switching for sample analysis, etc. would be helpful for characterizing potential differences between this chamber system and others described in previous literature.
- A full error quantification and discussion of P(O₃)_{net} is missing from the manuscript's main text. Results are presented for several sensitivity tests in the main text, while results from others presented in the supplemental information. However, not all test results that influence the overall P(O₃)_{net}_error are included in the error budget for P(O₃)_{net}. This includes the loss of O_x in each chamber, the photo-enhanced O_x loss, residence time uncertainty, etc.. A limit of detection is presented in Section 2.4, but is this then later revised in Section 3.2? Each error term in the P(O₃)_{net}_error equation should be clearly defined.
- The potential for O_x loss at high RH and photo-enhanced O_x loss was discussed in supplemental information and a correction factor was devised to exclude this bias, but it is unclear how this correction factor is (or can be) used for ambient measurements; b) which RH range (30-32% is shown, but ambient RH routinely exceeds this value) was tested; c) for which flow rate regime was this correction devised and d) whether this relationship holds for all measurement scenarios. More details are needed here to fully understand the test being conducted and how it can be applied to correct P(O₃)_{net}.
- It is unclear what new information is being presented with the discussion of flow state in L282-L290 and I might suggest that this section could be removed. While the flow may be

considered laminar, it is shown from residence time testing that the fluid within the chambers does not represent a “plug” flow, so reactions on the chamber walls may still produce biases in P(O₃)_{net}.

- Units of ppbv imply a “mixing ratio” in atmospheric chemistry terms, whereas a “concentration” is often referred to in molec cm⁻³ or mol L⁻¹
- Have the authors investigated the potential for a small amount of NO₂ impurity in the NO mixture used for conversion and can you address this potential bias in P(O₃)_{net}?
- L330-339 addresses the fact that O_x(= NO₂+O₃) mixing ratios change over the 2 minute sampling time of each chamber. How do the authors address issues of NO₂ atmospheric variability over the sampling time of the reaction versus the reference chamber, and the subtraction of these alternating two measurements, especially in urban areas? It is difficult to understand the resolution of P(O₃)_{net} in Figure 6 and how the data are averaged (or not?). Can you provide more details on how the data are processed to help the discussion?
- The modeling section could use some work to clarify and condense the information presented. In theory, modeling of the chemistry in both chambers separately seems like a good check on what is actually measured by the NPOPR system, but it is known from previous studies (and this issue is presented here as well) that modeling of HO₂ and RO₂ in ambient air does not match that which is measured (e.g. from Ren et al. 2013). Thus, if HO₂ and RO₂ are not well-captured in the model from parameterized VOCs and reactions therein, it is difficult to use the model to verify the chamber chemistry. Therefore, one suggestion could be to simplify this discussion to compare the ambient photochemistry from the model to the NPOPR system, given modeling limitations.

Technical Corrections:

- L87: You may also choose to reference Baier et al. (2017) here for similar work
- L90: There is no Baier et al. (2021) in references. Do you mean Baier et al. (2015)?
- L98: Could also benefit from citing Baier et al., 2017 for chamber artifact discussion
- L107-108: please re-write for clarity
- L116: change “access” to assess
- L131: change “amounted” to mounted
- L132: Please describe alternating flow more clearly. How do you account for the “transition” period after switching and sampling by the CAPS monitor (i.e. is some portion of the data discarded after transitioning between reaction and reference chambers as in Sklaveniti et al., 2018?)
- L141: How do you assess portability?
- L186: Accuracy implies that P(O₃) is produced as it is in the atmosphere, which cannot be determined here. Better phrasing could be: “to make the NPOPR less prone to biases than other systems” or similar.
- L217: Please calculate the bias in P(O₃)_{net} incurred from O_x loss in the reaction and reference chamber
- Table 1: is some shading missing here?
- Figure 4: Typically, the axes are reversed for a calibration such that y represents known values and x represents those values that are calibrated.
- L360: Please describe what ‘cd’ means for readers
- Figure 5: Please indicate shading in a colorbar, etc.
- Figure 6b): is this an average of the diurnal P(O₃)
- L432: November or December?
- SI L129: perhaps change the word “ingestion” to “loss”?
- SI L135-136 should be Fig. S7a, not S6a
- Figure S7: please add units on figure axes

- Table S7a: Sklaveniti et al., 2018 does not constitute an urban area – please see description within this particular reference and check other sites as well.
- SI Tables S7a/S7b require corrections made to locations. For example, Writtle College is not located in the USA; Houston, USA should be replaced with City, State, Country format like other sites: Houston, Texas, USA, etc.