

## ***Interactive comment on “Characterization of Ozone Production in San Antonio, Texas Using Observations of Total Peroxy Radicals” by D. C. Anderson et al.***

### **Anonymous Referee #1**

Received and published: 16 November 2018

Review of ‘Characterization of Ozone Production in San Antonio, Texas Using Observations of Total Peroxy Radicals’ – Anderson et al.

#### General Comments

The manuscript analyzes total peroxy radical observations made by the Ethane Chemical AMPlifier (ECHAMP) in addition to coincident air chemistry measurements aboard the Aerodyne Mobile Laboratory during May 2017 in the vicinity of San Antonio, TX. The authors characterize the gross ozone production rate ( $P(O_3)$ ) and the total peroxy radical production rate,  $NO_x$ -VOC sensitivity to  $P(O_3)$ , and species contributing to OH reactivity in this region. Mechanisms driving ozone levels in San Antonio, TX were

C1

postulated based on upwind measurement sites, as well as other routine measurement sites within the Texas Commission for Environmental Quality monitoring network.

The authors present a cohesive analysis of  $P(O_3)$  in the San Antonio study areas, based on the ECHAMP and accompanying Aerodyne Mobile Laboratory measurements, using model analyses and satellite retrievals to support claims made relating to ozone production sensitivity to  $NO_x$  within this region, with less ozone produced here than in Houston, TX. The authors also find that the main drivers of afternoon OH reactivity are primarily biogenic, in contrast to previous field studies in the area. Publication of this manuscript is recommended after the following points have been addressed.

#### Specific Comments:

Lines 156-163: Some of the major conclusions with respect to OHR are drawn from the PTR isoprene measurements, and while these conclusions relating to the species dominating OHR are unchanged given the calculated isoprene uncertainty, more information is needed to convince readers of the robustness of this measurement and efforts made to appropriately scale the PTR isoprene measurements. In particular, SI Line 207 indicates that the PTR isoprene sensitivity was scaled to the sensitivity in GC isoprene plus six additional hydrocarbons. Which other hydrocarbons were measured and why not directly compare the isoprene sensitivities to each other? Some additional explanation here is needed either in the main text or the SI, perhaps along with a figure of the direct isoprene PTR-GC sensitivity comparisons in addition to the summed PTR-GC sensitivity comparisons.

Section 2.2: While a full description of the ECHAMP measurement can be found in Wood (2017), it would be useful for the reader if the authors very briefly describe the ECHAMP methodology in a few sentences at the beginning of this section.

Section 2.3 – The calculation of gross  $P(O_3)$  is presented here, but the authors have measured the majority of the main constituents needed to calculate net  $P(O_3)$ . Thus,

C2

P(O<sub>3</sub>) presented here is presumably overestimated (even if only slightly). I would recommend that, for completeness, the authors calculate net P(O<sub>3</sub>) as in Sommariva et al., 2011. An estimate of the uncertainty in this calculated P(O<sub>3</sub>) is also needed.

Lines 406-408: More clarification is needed to discuss how the contribution of alkenes to OHR was determined. Presumably, the contribution was determined from adding the alkenes measured at TCEQ sites nearest UTSA and Floresville to the observed mobile laboratory hydrocarbon mixtures at UTSA and Floresville to approximate the difference in OHR, but it is unclear in the text. Another sentence or two here could help to clarify.

Are there differences in total XO<sub>2</sub> measured and total XO<sub>2</sub> modeled that would indicate missing OHR, potentially from alkenes?

Section 4, Lines 448-453: The discussion of ozone production and potential formation mechanisms could be expanded upon more in the discussion. It seems that, instead of hypothesizing the cause of differences between upwind and downwind San Antonio sites, one could examine the change in ozone with time in comparison to calculated P(O<sub>3</sub>) to evaluate whether these areas experience locally-produced versus advected ozone. In the above-mentioned lines, southeasterly winds would seem consistent with the lower Calaveras Lake O<sub>3</sub> and higher UTSA measured O<sub>3</sub>, supporting an urban source or in situ production in the urban outflow. However, there is no mention of the prevailing wind direction before May 17th when the Calaveras Lake O<sub>3</sub> agrees quite well with the UTSA O<sub>3</sub>. Could winds or back trajectories provide any clue to further substantiate causes for the observed ozone levels downwind of the urban core? Finally, there is no mention of the Pecan Valley O<sub>3</sub> in Fig. S3 or in the discussion, begging the question of whether or not this measurement site provides additional evidence for the observed O<sub>3</sub> patterns in this area.

Technical Comments:

All acronyms throughout the manuscript should be defined, including chemical species formulae. In addition, the 'x' in O<sub>x</sub> and NO<sub>x</sub> should appear as a subscript.

C3

Line 27: Define NO and NO<sub>2</sub>, as well as other chemical species formulae that are used throughout the manuscript.

Lines 43-47: Define chemical species, including O<sub>3</sub>

Line 67: A definition of OH reactivity may be needed here as a precursor for subsequent discussion

Line 91: should be "...radicals (XO<sub>2</sub> = RO<sub>2</sub> + HO<sub>2</sub>) from three sites in the San Antonio area, characterizing the XO<sub>2</sub> distribution in the region."

Line 111-112: To clarify your definition of background for this study, it should be defined here as 'upwind of the UTSA site'.

Lines 143-155: A short description of the uncertainties in the GC/PTR observations is needed here.

Line 162: Please denote that the 30% estimated uncertainty is 1 sigma.

Lines 181-182: The flow rates used here are inconsistent with Fig. S1.

Line 195: Should be 'At 15.2 cm downstream ...'

Line 317: 'fresher' should be replaced with 'recently-emitted'

Line 331: 'panel a' should be replaced with 'panel 6a' for clarity

Line 345: The claim that P(O<sub>3</sub>) can be VOC-limited at NO > 200 pptv is hard to discern from Fig. 6 due to the variability in P(O<sub>3</sub>) at lower P(RO<sub>x</sub>).

Line 392-393: To clarify, "The OH reactivity is defined as the sum of the production of the OH reaction rate coefficient for a particular species..."

Line 405: Can the authors quantify 'marginal agreement'?

Line 427: Can authors quantify the alkane contribution at the UTSA site?

Fig. 2b: White lettering of the measurement locations are difficult to see; I would

C4

recommend changes these colors to something more visible.

Fig. 3: P(O<sub>3</sub>) upper quantities are cut off; consider either averaging the P(O<sub>3</sub>) signal more, or enlarging the y-axis.

Fig. 7: Blue dots are difficult to see; the authors may consider fitting a line to these points.

Fig S2: The caption is inconsistent with the legends in the figures

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