Response to reviewers for "**Characterization of Ozone Production in San Antonio, Texas Using Measurements of Total Peroxy Radicals".**

We thank both reviewers for their helpful comments. Responses to the individual comments are shown below in red. Line numbers in red refer to the revised submission that does not include tracked changes.

Anonymous Referee #1

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(O3)) and the total peroxy radical production rate, NOx-VOC sensitivity to P(O3), and species contributing to OH reactivity in this region. Mechanisms driving ozone levels in San Antonio, TX were 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(O3) 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 NOx 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.

We were not adequately clear in our description of how we arrived at the isoprene sensitivity for the AQRP campaign. There was no isoprene standard available during the SAFS field deployment for the GC, so the isoprene sensitivity for the GC was not determined in the field. A multi-component standard containing isoprene and six other hydrocarbons measured during AQRP (iso-pentane, *n*-pentane, *n*-hexane, methylcylcopentane, cyclohexane, and benzene) was available during a later campaign, in which the GC had a slightly different setup. The isoprene sensitivity for this configuration was determined, but since the configuration differed from SAFS, this sensitivity could not be directly applied to the data obtained in San Antonio. Instead, the sensitivities of the other six hydrocarbons that were present in standards available at both campaigns were compared. Overall, the mean ratio of sensitivities from SAFS to the second campaign for these six gases was 0.34. So, to determine the isoprene sensitivity for SAFS, the sensitivity for the second campaign was determined by dividing this value by 0.34.

We have updated the wording in the SI to try to make this clearer. We have also included a figure comparing the GC isoprene sensitivity, determined by the method described above, with the PTR sensitivity determined in the field. These are the only two isoprene values available from the campaign so are the only values we could compare. In addition, we now compare the scaled PTR isoprene to observations made by TCEQ at their Floresville monitoring site, which was co-located with the AML.

The isoprene section now reads (Lines 204 – 231 in the SI):

"No isoprene standard was available during SAFS for online calibration of the GC-MS observations, so an isoprene sensitivity was not determined during the campaign. Approximately 6-months after SAFS, a calibration of the same instrument was conducted during a second campaign using a multi-component mixture, including isoprene and 6 other hydrocarbons (iso-pentane, n-pentane, n-hexane, methylcyclopentane, cyclohexane, and benzene) measured during SAFS. To determine a sensitivity for isoprene for SAFS, the sensitivities for the six hydrocarbons during SAFS was compared to that for the second campaign, in which the GC setup differed in both sample trap temperature and detector micro channel plate voltage from the SAFS configuration. The mean ratio of sensitivities from SAFS to the second campaign for the six overlapping hydrocarbons was 0.34 ± 0.10 (1σ), while the slope of a regression line of the SAFS sensitivities to the second campaign sensitivities was 0.38. The isoprene sensitivity for SAFS was then determined by dividing the sensitivity to isoprene at the second campaign by the average of these two values (0.36). The total uncertainty (1σ) in the isoprene observations is estimated as 31%, with the sensitivity uncertainty dominating.

While there was an in-field calibration for the PTR derived isoprene, it was determined that the isoprene concentration in this older calibration tank was most likely lower than the stated value, biasing the PTR results. There were overlapping observations of the PTR and GC derived isoprene values from the start of the campaign to 19 May, after which the GC trap was damaged. So that we have calibrated isoprene observations for the duration of the campaign, we have scaled the PTR derived isoprene to GC values for this overlapping period. The 1-minute averaged PTR data were averaged to the GC sampling time, and a linear least squares regression was used to determine the relationship. This resulted in a fit with an r^2 of 0.91 and a relationship between the two instruments as follows: $[C_5H_8]_{GC} = 0.787[C_5H_8]_{PTR} - 0.15$ (Fig. S7). The normalized mean bias for this relationship was 7%.

To evaluate the scaled PTR isoprene, we compare these values to isoprene measurements made hourly by a GC at the Floresville TCEQ site. The scaled PTR isoprene was averaged to the TCEQ sampling frequency and regressed against the TCEQ isoprene. This yielded a slope of 0.93 with an r^2 of 0.88. There was an offset of 0.10 ppbv between the two data sets with the TCEQ isoprene higher. The excellent agreement between the scaled PTR isoprene and the TCEQ isoprene further validates the isoprene results presented here."

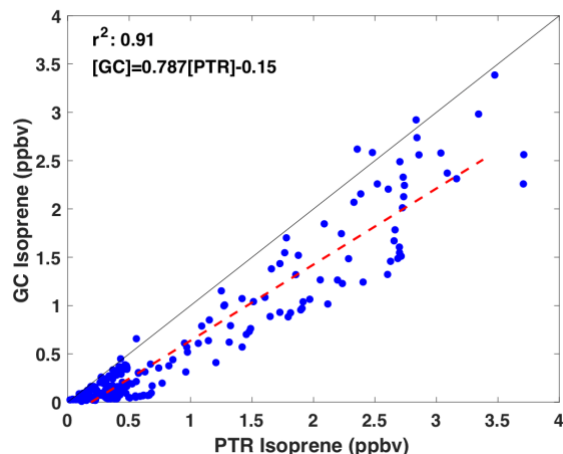



Figure S7: Comparison of isoprene measured by the PTR to observations from the GC. The isoprene sensitivity of the GC was determined several months after the campaign as described in the text.

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.

We have added the following summary of the ECHAMP instrument to lines 182 – 189 in section 2.2.

> "Briefly, ECHAMP measures total XO_2 concentration at a two-minute resolution by reacting peroxy radicals with excess NO and ethane (C_2H_6). Through a series of chain reactions, each XO_2 radical produces approximately 20 NO_2 molecules (depending on the relative humidity (RH)), which are then measured with a commercially available NO_2 monitor. Because this NO_2 monitor also measures ambient O_3 and NO_2 (O_X), a second channel and dedicated NO_2 monitor are used to only measure the sum of [O_3] and [NO_2]. The difference between the two channels, divided by the "amplification factor" of ~20, yields the XO_2 concentration."

Section 2.3 – The calculation of gross P(O3) is presented here, but the authors have measured the majority of the main constituents needed to calculate net P(O3). Thus, P(O3) presented here is presumably overestimated (even if only slightly). I would recommend that, for completeness, the authors calculate net P(O3) as in Sommariva et al., 2011. An estimate of the uncertainty in this calculated P(O3) is also needed.

We have presented values for gross $P(O_3)$ in lieu of net $P(O_3)$ so that the calculated values can be tied directly to observations. Calculating net $P(O_3)$ requires knowledge of both OH and the fraction of total XO_2 comprised of HO_2, neither of which were observed during the campaign.

We have added the following discussion to the text (Lines 265 – 282):

> "The net formation rate of O_3 is equal to $P(O_3)_{Gross} - L(O_3)$. In order to tie $P(O_3)$ completely to observations, we report only gross $P(O_3)$, not net $P(O_3)$. That is, we only calculate the production term (Eq. 2) and not the loss term (Eq. 4) for net ozone production. Calculation of the loss term requires knowledge of the concentration of OH and alkenes as well as the fraction of total XO_2 comprised of HO_2, none of which were measured during SAFS. Alkene concentrations, except for isoprene and monoterpenes, were not measured during

SAFS. Estimating the alkene loss term using concentrations from nearby TCEQ monitoring sites, suggests that O_3 loss due to this pathway is negligible for the data analyzed here, and we omit this from our calculation of ozone loss. To estimate OH and the fraction of XO_2 comprised of HO_2 and to determine whether analyzing only gross $P(O_3)$ affects our conclusions, we used the Framework for 0-Dimensional Atmospheric Modeling (F0AM) box model (Wolfe et al., 2016b) to calculate OH and the fraction of RO_2 comprised of HO_2. A description of the model setup can be found in the SI. For data points that were not modeled due to missing model constraints, these values were estimated from interpolation of modeled values, if observations were made within two hours of a modeled data point, or from site-specific mean daily profiles if no modeled points were available. Using these modeled-derived values for OH and the HO_2 fraction, median $L(O_3)$ for daytime observations at all sites were determined to be 0.90 ppbv/hr, which is 16% of the gross production rate."

We estimate total uncertainty in the gross ozone production rate as 34%, and we described this in the text as follows (Lines 252 – 263);

"At 298 K, k_{NO+HO2} is within 10% of the k values for the reaction of NO with CH_3O_2 and isoprene RO_2 (Orlando and Tyndall, 2012), supporting our choice of k_{eff}. Further, while the reaction of NO with acetyl peroxy radicals is approximately 2.5 times faster than with other peroxy radicals at 298K, box modeling results suggest that these radicals comprise only 5 – 10% of total XO_2, resulting in an average difference in $P(O_3)$ of 15% from the k_{NO+HO2} value used here. This uncertainty is comparable to the total uncertainty of the k_{NO+HO2} rate constant, estimated as 15% (Sanders et al., 2011). As will be shown in Section 3.2, our conclusions are insensitive to the value of k_{eff} chosen. Uncertainty in gross $P(O_3)$ results from uncertainty in the NO and XO_2 measurements, 5% and 25%, respectively, and k_{eff}, whose uncertainty we estimate at 23%, determined by adding the uncertainty in the k_{NO+HO2} rate constant and the uncertainty in the choice of k_{eff} in quadrature. This results in a total $P(O_3)$ uncertainty of 34%."

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.

We agree that the wording describing the estimation of alkene concentrations was confusing. We have expanded this discussion into its own paragraph at the end of the OH reactivity section (Lines 505 – 524) in the revised text:

"Because of the large contribution of alkenes to OH reactivity at other Texas sites (Mao et al., 2010), it is necessary to make an estimate of their importance during SAFS. With the exception of isoprene and monoterpenes, alkenes were not measured onboard the AML and therefore have not been included in the above analysis. To estimate the impact of anthropogenic alkenes on OH reactivity, we include in our calculation of OH reactivity observations of alkenes made at nearby TCEQ monitoring sites, Camp Bullis for UTSA and a site in Floresville co-located with the AML. These sites provide hourly observations of cis-2-butene, trans-2-butene, 1-pentene, cis-2-pentene, trans-2-pentene, ethene, propene, 1,3-butadiene, and 1-butene. Alkene concentrations at the SAFS monitoring sites were assumed to be identical to those at the TCEQ monitoring sites and were interpolated to the

ECHAMP time base. This assumption is likely more accurate for the Floresville site than for UTSA. A regression of hourly averaged *n*-pentane measured onboard the AML to that measured at the Camp Bullis TCEQ site has an r^2 of 0.3, even after maximizing the correlation using a lead-lag analysis. In addition, the maximum *n*-pentane concentrations at the Camp Bullis site are almost a factor of 2 higher than those seen at UTSA. Regressions of cyclohexane and benzene between the two sites show even lower r^2 values. On the other hand, a similar regression of n-pentane at the Floresville site has an r^2 of 0.83. Better agreement at Floresville is to be expected since the AML and TCEQ monitor were co-located.   Total OH reactivity was then recalculated using the estimates of alkene concentrations. Alkenes contribute less than 1% of total reactivity at both UTSA and Floresville for morning and afternoon times."

Are there differences in total XO2 measured and total XO2 modeled that would indicate missing OHR, potentially from alkenes?

This is a good point and is one that we have started to investigate. Preliminary box modeling results using multiple chemical mechanisms overestimate observed XO_2 by 0 to 30%, well within the combined measurement and modeling uncertainty. This would suggest that no additional VOCs, including alkenes, are needed to explain the observed XO_2 and that the OH reactivity reported here is also accurate. We choose not to present those results here, however, because we plan on publishing a separate publication on model results in the coming months. Inclusion of modeling results in this paper, beyond that used for the L_n/Q analysis, would expand the scope of this paper too much, resulting in a paper of unwieldy length.

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(O3) 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 O3 and higher UTSA measured O3, 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 O3 agrees quite well with the UTSA O3. 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 O3 in Fig. S3 or in the discussion, begging the question of whether or not this measurement site provides additional evidence for the observed O3 patterns in this area.

We have added the time series of ozone observations at Pecan Value to Figure S5 (formally Figure S3) and discuss these observations in lines 574 – 577. In particular, we note that on several occasions ozone is lower at the Pecan Valley site than at either Lake Calaveras or at UTSA. This is in line with the idea that there is potentially more ozone titration in the downtown area of San Antonio, and that ozone production rates are not constant across the city.

We agree that an investigation into the evolution of ozone in an air parcel over time warrants further investigation. Future papers using both Eulerian and Lagrangian modeling are going to further investigate this topic, so we do not want to discuss this more fully here. Further, we are reluctant to include further discussion on the topic in this paper because the observations needed to determine $P(O_3)$ at all sites are unavailable. As the comparison between ozone concentrations at Lake Calaveras, Pecan Valley, and UTSA show, it is highly likely that ozone production rates are not constant across the region,

so a simple analysis of multiplying ozone production rates by the amount of time it takes to travel from one site to the other will likely not yield accurate results.

Technical Comments:
All acronyms throughout the manuscript should be defined, including chemical species formulae. In addition, the 'x' in Ox and NOx should appear as a subscript.

All instances of NO_X and O_X are now presented with the "X" as a subscript. We note that we use a capital "X" for this, that when subscripted, can be mistaken for a lower case "x".

Line 27: Define NO and NO2, as well as other chemical species formulae that are used throughout the manuscript.

We have defined these species in the revision.

Lines 43-47: Define chemical species, including O3

These species are now defined. We define O_3 in line 27 since that is the first usage of the species in the main body of the text.

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

We have moved the definition of OH reactivity from section 3.3 to here. See lines 72 – 73.

Line 91: should be ": : :radicals (XO2 = RO2 + HO2) from three sites in the San Antonio area, characterizing the XO2 distribution in the region."

We have made this change. Now lines 94 – 95.

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

We have made this change. See lines 117 – 118.

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

In reference to the uncertainty of the PTR observations, on Lines 154-155, we now say "Typical measurement uncertainties were on the order of 25%." And for the GC observation uncertainties, we now say on Lines 160-163 "While toluene and *m-* and *p-* xylene measurement uncertainty was on the order of 20%, typical measurement uncertainties of other observed species, except isoprene, were on the order of 10%."

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

We have indicated that the uncertainty is 1 sigma. Line 169.

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

We have updated Fig. S1 with the correct flow rates.

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

We have made this change (now Line 209).

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

We have made this change (now Line 357).

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

We have made this change (now Line 371).

Line 345: The claim that P(O3) can be VOC-limited at NO > 200 pptv is hard to discern from Fig. 6 due to the variability in P(O3) at lower P(ROx).

In response to comments by the other reviewer, we now show an additional panel to figure 6 with the data further separated by VOC reactivity. This more clearly shows the peak associated with the transition from NO_x- to VOC-limited chemistry.

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: : :"

We have made this change, although we now define OH reactivity on Lines 72 – 73.

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

We have updated the text to show that a regression of observed n-pentane at UTSA and the Camp Bullis site only has an r^2 of 0.3. This is in contrast to the AML and TCEQ observations, co-located at Floresville which have an r^2 greater than 0.8. (Lines 515 – 521)

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

The paper now reads (Lines 495 – 497):

> "Contributions from alkanes were unimportant at the UTSA site, 1% or less during both morning and afternoon, and contributed only 4-5% at Floresville."

Fig. 2b: White lettering of the measurement locations are difficult to see; I would recommend changes these colors to something more visible.

The labeling for the measuring locations is now yellow with a black outline.

Fig. 3: P(O3) upper quantities are cut off; consider either averaging the P(O3) signal more, or enlarging the y-axis.

We have made this change.

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

We have increased the size of the points to make them more visible and to better distinguish these points from the Ln/Q values.

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

We have added the panel labels to the figure, and changed RO_2 to XO_2 and $P(HO_X)$ to $P(RO_X)$ to match the figure.

Anonymous Reviewer #2

The paper "Characterization of Ozone Production in San Antonio, Texas Using Observations of Total Peroxy Radicals" by Anderson et al. presents observations of total peroxy radicals and supporting measurements at three different sites in San Antonio, TX. The dataset is used to calculate the production rate of ozone and to provide information on the drivers of ozone formation in the area. The manuscript is well written and presented and I recommend after some modifications and clarifications.
Main Comments ————-

The measurements were made at three sites, but most of the discussion seems to be focused on the UTSA site or on aggregated data. The authors do not really use the dataset to explore the geographical differences between the three sites and what could be the underlying causes of these differences. On page 22 for example it is mentioned almost in passing that the VOC profile at the Floresville site is different (less isoprene). Does that change the main conclusions of the paper? Please add more discussion on the other sites.

We have changed the wording in the final paragraph to indicate that, while the absolute concentration of isoprene was lower at Floresville than at UTSA, it was still the dominant contributor to total OH reactivity. Because of the lower isoprene concentration, however, the total OH reactivity is about a factor of 3 lower at Floresville than at UTSA. The final paragraph (Lines 592 – 607) now reads:

> "While the isoprene concentration at Floresville was significantly lower than at UTSA, it was still the dominant contributor to OH reactivity during the afternoon, although the total OH reactivity was a factor of 3 lower at this site (4 s^{-1}) than at UTSA. Schade and Roest (2016) found a significantly different OH reactivity profile at Floresville than described here, with alkanes accounting for approximately 70% of total OH reactivity, with biogenic VOCs contributing less than 5%. Observed isoprene at Floresville during SAFS was more than an order of magnitude larger than that reported in Schade and Roest (2016), with alkane concentrations consistent between the two studies. When the data used in Schade and Roest (2016) are subset to afternoon times and May through July, the contribution of isoprene to VOC reactivity increases to a median value of 38%, in agreement with the results presented here (Schade, personal communication). The differences between the two studies do suggest that there could be significant seasonal and diurnal variations in OH reactivity. Nevertheless, these results suggest that policies designed to limit O_3 production at the SAFS sites discussed here should initially focus primarily on NO_X reductions as the region is NO_X limited and the primary VOC contributor is biogenic. Further observations and analysis are need to determine whether this holds true in the urban core of downtown San Antonio."

We now also note that the relationship between $P(O_3)$ and NO is consistent among all three sites. They differ in that $P(RO_X)$ and VOC reactivity are significantly lower at Floresville and Corpus than at UTSA, so that ozone production is significantly lower at these sites (Lines 559 – 562).

> "The relationship between $P(O_3)$ and NO was consistent at the three sites, although the lower $P(RO_X)$, NO, and VOC reactivity at Floresville and Corpus Christi led to overall lower ozone production rates as compared to UTSA."

The P(O3) values derived from this dataset are lower than those derived from observations in other areas of Texas, namely Houston. It would be interesting to have a more detailed comparison with the other datasets. Only TRAMP2006 is compared with SAFS (on page 22). Especially the TEXAQS 2006 data (Sommariva et al, 2011) which were obtained with a similar technique could be interesting to compare. Are the differences simply a matter of different VOC emissions? In addition, can you comment on the source of isoprene? If isoprene is dominant at the UTSA site but not at the other sites, do the conclusions of the study regarding NOx-limited conditions in the city still apply?

We have added a paragraph (Lines 530 – 535) comparing our results to those found during DISCOVER-AQ in 2013 in Houston. Near surface $P(O_3)$ had a median value of about 10 ppbv/hr, slightly more than a factor of 2 higher than what was seen at UTSA and a factor of 10 higher than at Floresville and Corpus. While it is difficult from the results published in Mazzuca et al to make a direct comparison to our study, both NO and $P(HO_X)$ were frequently higher in Houston than in San Antonio. Both of these could explain the higher ozone production rates. We do not compare our results directly to Sommariva, et al. because, as they note in their paper, they frequently sampled individual plumes that were not representative of the overall photochemical environment. This is quite evident when comparing the means and medians of ozone production rates at individual sites in Sommariva. We do note that the median rates observed in Sommariva are reasonably in line with Mazzuca. We refrain from making further comparisons because many of the campaigns were conducted more than a decade previous to SAFS, so both emission sources and strength have likely changed at both sites. The new paragraph reads:

> "We have presented observations of O_3, its precursors, and total observations of XO_2 at three sites in the San Antonio region. We also presented determinations of $P(O_3)$ calculated from measurements of total peroxy radicals. Median daytime $P(O_3)$ at UTSA was 4.1 ppbv/hr, compared to just over 1 ppbv/hr at the other two SAFS sites. Ozone production rates at UTSA were still far lower, however, than values observed during campaigns in Houston. Mazzuca et al. (2016) found median near surface gross $P(O_3)$ of about 10 ppbv/hr during the DISCOVER-AQ campaign in the summer of 2013, with values up to 140 ppbv/hr seen over the Houston shipping channel. These values are consistent with previous studies in the region (Sommariva et al., 2011). Higher concentrations of NO and larger production rates of RO_X were seen during DISCOVER-AQ than during SAFS, both of which could lead to higher $P(O_3)$."

We have also expanded slightly the comparison to the Schade and Roest study done at Floresville (Lines 597 – 603):

> "Observed isoprene at Floresville during SAFS was more than an order of magnitude larger than that reported in Schade and Roest (2016), with alkane concentrations consistent between the two studies. When the data used in Schade and Roest (2016) are subset to afternoon times and May through July, the contribution of isoprene to VOC reactivity increases to a median value of 38%, in agreement with the results presented here (Schade,

personal communication). The differences between the two studies do suggest that there could be significant seasonal and diurnal variations in OH reactivity. "

We also note that we caution against applying these results to sites beyond the SAFS monitoring sites. The satellite results do suggest that the region as a whole is NO_X-limited in the afternoon, when ozone production rates are the highest.   The paper reads (lines 588 – 591):

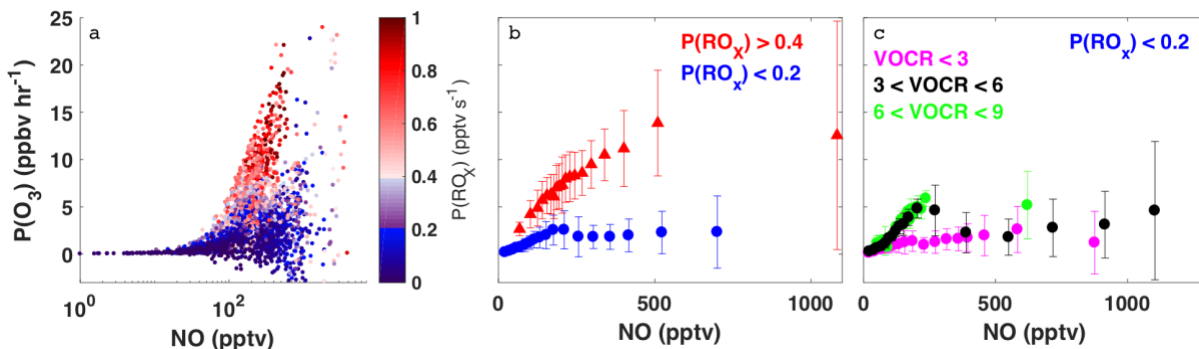
 "While there are trees throughout the San Antonio region, the results at UTSA cannot be extrapolated to areas with far less foliage without further observations. Other VOCs could comprise a larger fraction of total OH reactivity in less vegetated areas."

Figure 7 indicates that most of the time O3 production is NOx-limited, but that there are periods, mostly in the morning, when it is VOC-limited. The text related to figure 6 (on page 16) seems to suggest that VOC limited conditions correspond to periods with low P(ROx). However this is not clear from the discussion. If this is the case, than it should be stated explicitly. On page 21 it is mentioned that the VOC limited periods in the morning correspond to high NOx (presumably rush hour emissions?) but the "flat" part of the blue curve in figure 6 is at intermediate NO levels (200-400 ppt). Are you talking about different sites? Please clarify.

We have expanded the discussion of the diurnal cycle in the ozone production regime to better illustrate this point. We have added an additional panel to figure 6 and to a new supplementary figure (Figure S3) in which, in addition to separating the data by $P(RO_X)$ values we also separate the data by VOC reactivity. Lines 377 – 416 now read:

"Figure 6b demonstrates that the majority of observations made during SAFS were in the NO_X-limited regime. For the high $P(RO_X)$ observations, there is a steady increase in $P(O_3)$ up to the 500 pptv NO bin. Above this point, $P(O_3)$ potentially plateaus, but there were insufficient observations at higher NO to determine the location of the turnover point in ozone production. Because the majority of NO observations at UTSA were less than 500 pptv, we conclude that the site is predominantly NO_X-limited. Further observations at higher NO mixing ratios are required to determine the turnover point for ozone production in this region. The true turnover concentration for NO cannot be easily inferred by inspection of a graph of $P(O_3)$ versus [NO], however, because VOC concentrations are not constant for all points. To see if there is any variation in this relationship with VOCs, we further separate the high $P(RO_X)$ data by their VOC reactivity (Fig. SXa). VOC reactivity (VOCR) was calculated in the same manner as OH reactivity, described in section 3.3, but including only OH reactive VOC's. In addition, VOCs exclusively observed by the GC instrument were not included in the calculation as they were only available until 19 May. For data points with GC observations available, VOC reactivity increased by only 2% in the afternoon and 12% in the morning on average when including the GC observations, suggesting that this omission does not significantly affect the results.   Data were then separated into low (VOCR < 3 s^{-1}), medium (3 s^{-1} < VOCR < 6 s^{-1}), and high (6 s^{-1} < VOCR < 9 s^{-1}) VOC reactivity bins. For the high $P(RO_X)$ case, the relationship is similar for all VOC reactivities, showing a general increase in $P(O_3)$ with NO, further suggesting the majority of observations were NO_X-limited for high $P(RO_X)$. We note that for a constant $P(RO_X)$ value, theoretically $P(O_3)$ is expected to increase with [NO] at approximately the same rate until the turn-over point with little sensitivity to the VOC reactivity. The 5th and 95th percentiles of $P(RO_X)$ for the high $P(RO_X)$ are 0.42 and 0.92 pptv/s, more than a factor of two different.   This

suggests that the differences in the rate of change of P(O₃) with NO for the different VOC reactivities likely results from the wide range of P(RO$_X$) values analyzed.

When looking at all points for the low P(RO$_X$) case (Fig. 6b), there is a small peak in P(O₃) at 200 pptv NO, suggesting that in a low P(RO$_X$) environment, UTSA can be VOC-limited at higher NO mixing ratios. Separating these data points by VOC reactivity, shows more clearly the transition between the NO$_X$- and VOC-limited regimes. For the medium case, P(O₃) first increases with [NO], peaks at 5 ppbv/hr at approximately 200 pptv [NO], and then declines to 2 ppbv/hr at 400 pptv [NO]. This peak and decline suggests that, for P(RO$_X$) < 2 pptv/s, VOC reactivities < 6 s^{-1}, and NO > 200 pptv, the region is VOC-limited. For NO > 400 pptv, there is a slight increase in P(O₃) with [NO], although the spread of data for a given [NO], also increases. For the low VOC reactivity scenario, the range of P(O₃) for a given [NO] is also large compared to the mean P(O₃), making it difficult to determine whether these points obey a similar relationship. As with the high P(RO$_X$) scenario, each bin has a wide range of P(RO$_X$) and VOC reactivities, which could lead to the large spread in data. More observations are needed to further separate the data. Separating the results by location yields the same results, although VOC reactivity at Floresville and Corpus were almost always below 3 s^{-1} due to the lower isoprene concentration at these sites in comparison to UTSA."

Minor Comments ─────────
It would be good to check the sensitivity of equation 2 to the choice of k_eff. Do the results change significantly with another value of k_eff?

We have added a paragraph in section 3.2 in which we discuss a new supplementary figure that shows the relationship between P(O₃) and NO for four different values of k$_{eff}$. While the P(O₃) value obviously changes, the overall relationship does not change, with the majority of points still being NO$_X$-limited. In addition, we note that the uncertainty in the k$_{NO+HO2}$ value is greater than the uncertainty from choosing different, reasonable k$_{eff}$ values. The paragraph (Lines 424 – 430) reads:

"Finally, the results presented here are insensitive to the value of k$_{eff}$ chosen. Figure S4 shows the relationship between P(O₃) and NO for four different values of k$_{eff}$: k$_{NO+HO2}$ (the k$_{eff}$ used in this analysis), k$_{NO+CH3O2}$, k$_{NO+IsopreneRO2}$, and assuming k$_{no+acetyl peroxy}$ for 10% of the value and k$_{NO+HO2}$ for the remainder. While the magnitude of P(O₃) does change with k$_{eff}$, the overall relationship is the same. As mentioned previously, the uncertainty in k$_{NO+HO2}$ is larger than the uncertainty induced by the choice of k$_{eff}$. Additional analysis further suggests that the majority of the observations during SAFS were in the NO$_X$-limited regime."

Shouldn't O1D quenching by O2 be included in equation 3?

Yes, we have corrected this error.

Figure 2. Can you add the outline of San Antonio on the left panel? Is the Floresville site visible on the right panel? And can you use consistent labels? The UTSA site is labelled 1 in one panel and B in the other.

We now show the outline of the city of San Antonio in purple in the left panel. We also use numbers for all locations in both panels, using consistent numbering between the two. We have also expanded the axis limits so that we can show the Floresville SAFS site on panel b.

Figure 5. I assume that is the median of all three sites together?

That is correct. The figure caption now reads:

"…The median value for 15-minute time bins for observations at all sites is shown by the gold trace."