We thank the reviewer for a set of very comprehensive comments. We have used a combination of measurements and model calculations to evaluate how these issues could impact the overall results of the paper. In summary, none of the issues changes the major findings of the manuscript. Our detailed responses for each comment are listed below, along with the changes made to the manuscript to make these findings clear to readers. Our responses to the comments are presented in blue. The comments are shown in black.

1. The authors stated that "A new technique was used to directly measure O3 response to changes in precursor NOx and VOC concentrations.....…"; it will be helpful for the readers to have more detailed description of the measurements and the improvements compared to other recent smog chambers studies.

This comment is similar to the 1st comment from RC2. We have clarified the novel features of the current experiment in the Introduction section of the revised manuscript:

"Mobile smog chambers bridge the gap between laboratory studies and the real atmosphere. Past studies have designed mobile smog chambers to measure the aging of secondary pollutants (i.e., O_3, SOA) from certain emission source (Howard et al., 2008, 2010; Li et al., 2019; Platt et al., 2013; Presto et al., 2011). It is difficult to evaluate sensitivity of secondary pollutants formed from multiple sources using a single smog chamber. Recently, a mobile dual smog chamber system has been used to directly measure the SOA formation in ambient air (Jorga et al., 2020; Kaltsonoudis et al., 2019). Our smog chamber system consists of three chambers designed to simultaneously analyze the non-linear response of NO_x and VOC to O_3 formation. The automated valve and sampling system also allows long-term remote field measurements to evaluate the seasonal trends in O_3 sensitivity."

2. The authors used artificial light to provide constant UV radiation in the chamber experiments, which is different from the real atmospheric conditions. Additionally, the settings of other parameters for the smog chambers, such as temperature, relative humidity, etc., are important in modifying the O_3 formation but they were not provided in the measurement section. More importantly, it is not reasonable to explore the seasonal changes of the O_3 sensitivity using chambers with constant UV radiation. Except for anthropogenic emissions changes, variations of solar radiation play a major role in the seasonal pattern of O_3 formation sensitivity. O_3 formation regime becomes more NO_X-sensitive in warm seasons, which is mainly caused by intensified solar radiation. Increasing solar radiation enhances BVOCs emissions that are light- and temperature-dependent, facilitates photochemical reactions, and promotes development of the planetary boundary layer to decrease near-surface NO_2 concentrations.

This comment is similar to several comments submitted by RC1. We have performed a comprehensive sensitivity analysis to investigate the effects temperature and constant UV radiation on the chamber measurements. We summarize the main points below, and refer the reviewer to the response to RC1 for an expanded discussion that includes plots from the Sensitivity Analysis.

The temperature in the reaction chambers was higher than the ambient temperature due to the heating effects of the UV lights. The difference between the chamber gas temperature and the ambient temperature increased by 5-10^{o}C over the course of each experiment, with the exact temperature profile depending on the measurement month. Despite this temperature increase, all chambers experiences the same temperature profile, and so the comparison of O_3 formation between the chambers is not strongly biased by this issue. SAPRC11 chamber model simulations were used to quantify the effect of the chamber vs. ambient temperature difference. The difference between the chamber and ambient temperature has little effect on the O_3 sensitivity in each month. Temperature effects do not significantly modify the seasonal variation of the measured O_3 sensitivity in the current study. Please see plots in RC1 response.

The UV intensity in the chambers was intentionally maintained at a constant level through all seasons so that the effects of seasonal variation in the ambient concentrations would be more apparent without the added complication of varying UV intensity. A representative average UV intensity was selected for this purpose. As was the case with temperature, all chambers experience the same UV conditions and so this factor is not expected to overly bias the comparison between chambers that acts as the core of the current study. The actual seasonal cycle of UV radiation would generate higher photolysis rates in the summer and lower photolysis rates in the winter that would further amplify the seasonal signal already detected by the measurements with constant UV intensity.

SAPRC11 chamber model simulations were used to quantify the effect of seasonal variations in UV intensity. Simulations were carried out using the measured constant UV radiation in the chamber and using the clear sky UV intensity calculated with the routines in the UCD/CIT CTM based on the lat/lon of the measurement site and the day of year. The calculations show that the difference between the constant solar radiation and the seasonally adjusted solar radiation does not change the seasonal pattern of O_3 sensitivity to NO_x and VOC perturbations. The seasonal changes to UV intensity slightly amplifies the magnitude of the seasonal trend in O_3 sensitivity (increase the absolute value of $\Delta O_3^{+NO_x}$), but the overall seasonal pattern is unchanged. Please see plots in RC1 response.

This information has been added to the new Sensitivity Analysis section in the revised manuscript.

3. O_3 formation sensitivity is investigated only by adding 8 ppb NO_X in chamber #1 and 8 ppb surrogate VOCs in chamber #3. Lacking a series of linear experiments with different concentrations of precursor gases, the current conclusions are drawn from the effects of 8 ppb precursor perturbations on O_3 levels of the air masses sampled at one site, which is not sufficient to assess the O_3 formation sensitivity *in situ*, let alone the regional O_3 sensitivity.

This comment is similar to a comment about linearity submitted by RC1. We address this issue using a combination of measurements and chamber model calculations.

O_3 sensitivity measurements were conducted using NO_x perturbations ranging from 1-10 ppb at the UC Davis campus from December 2021 to January 2022 to investigate the non-linear behavior of the chemistry. The results summarized

in Figure 1 below show the O_3 response expressed as ΔO_3 (final O_3 concentration in base case chamber minus final O_3 concentration in NO_x perturbed chamber). The ΔO_3 is negative in all NO_x perturbed tests due to the low VOC emission in winter in Davis, CA (similar to Sacramento). Increasing the magnitude of the NO_x perturbation decreased the ΔO_3 value but did not shift the chemistry into a different regime. It was not possible to make linearity measurements in the NO_x-limited regime during the cold winter season, and so these issues will be further explored using chamber model calculations as described below.

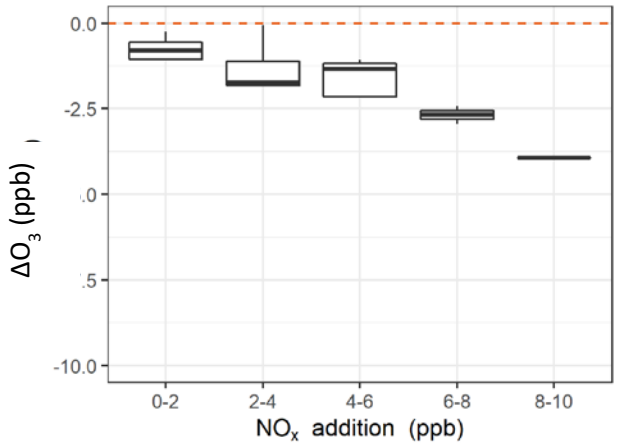

Figure 1. Measured ΔO_3 as a function of different NO_x perturbations. Total number of data points is 24.

The size of the NO_x perturbation used in the chamber experiments is most important when ambient conditions are close to the ridgeline on the O_3 isopleth diagram. An 8 ppb NO_2 perturbation may jump over the ridgeline in this case, suggesting that the chemistry is NO_x-rich rather than NO_x-limited. SAPRC11 chamber model simulations were used to quantify the effect of the 8 ppb NO_2 perturbation vs. a smaller 2 ppb NO_2 perturbation. As shown in Figure 2 below, this issue does not affect the shape of the seasonal trend in O_3 sensitivity measurement, but it does affect the transition months when the atmospheric system changes to NO_x-limited behavior. The conclusions of the paper are not changed by this finding, but the revised figure and associated discussion in the new Sensitivity Analysis section of the revised manuscript help clarify this point for readers.

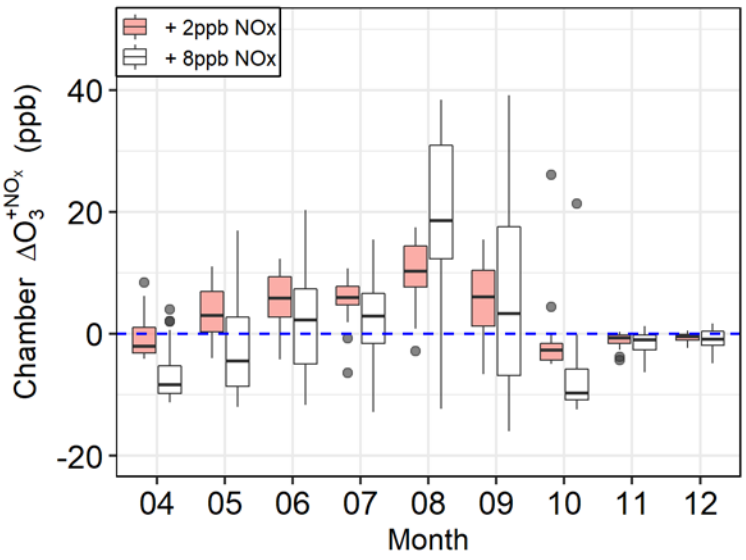

Figure 2. Monthly variation of chamber $\Delta O_3^{+NO_x}$ at Sacramento using NO_2 perturbations of 2 ppb (solid box) and 8 ppb (open box) from April to December, 2020. Simulations are based on the actual chamber UV radiation and chamber temperature profile.

4. O_3 production sensitivity is determined by the ratio of NO_x to VOCs. Adding constant 8 ppb NO_x or surrogate VOCs to experimental air masses sampled in different seasons with various precursor concentrations could lead to varying perturbations for the ratio, possibly contributing to the measured seasonal variations in O_3 production sensitivity.

The experimental design intentionally holds multiple factors constant so that the effects of changes in atmospheric composition on O_3 formation sensitivity are more apparent. The size of the perturbations for the NO_x and VOC surrogates were one of these constant factors. The ambient air does go through a seasonal cycle of NO_x/VOC levels as summarized on the isopleth diagram in Figure 5 of the original paper. The constant perturbation displayed by the arrows in this figure that point towards the ridgeline of the isopleth.

The chosen size of the constant perturbation (+8 ppb) may mask the exact location of the ridgeline in the O_3 isopleth diagram. We evaluate this issue using SAPRC11 chamber model simulations. The response above indicates that this issue does not change the overall shape of the seasonal shift in O_3 sensitivity from NO_x-rich in the winter to NO_x-limited in the summer. To investigate whether the constant amount of perturbation would change our conclusion in this paper, we use the same chamber model and calculate the O_3 sensitivity under two conditions: (i) Add constant 2 ppb of NO_x; (ii) increase ambient NO_x by 20%. The second case would investigate the O_3 sensitivity when NOx perturbations are very small in the summer season. Figure 3 shows the result of this analysis. Increasing NOx by 20% produces the same seasonal trend in O_3 sensitivity as adding a constant 2 ppb or 8 ppb of NOx, but the smaller size of

the perturbation reduces the O_3 response. This issue does not change the shape of the seasonal trend in O_3 sensitivity measurement, but it does affect the transition months when the atmospheric system changes to NO_x-limited behavior.

As a final note, we once again point out that the ground-based chamber measurements are in very good agreement with the TROPOMI satellite $HCHO/NO_2$ measurements. The similar trend of $HCHO/NO_2$ and ΔO_3^{+NOx} indicates that the seasonal variation of O_3 sensitivity measured from chamber experiment exists in the real atmosphere.

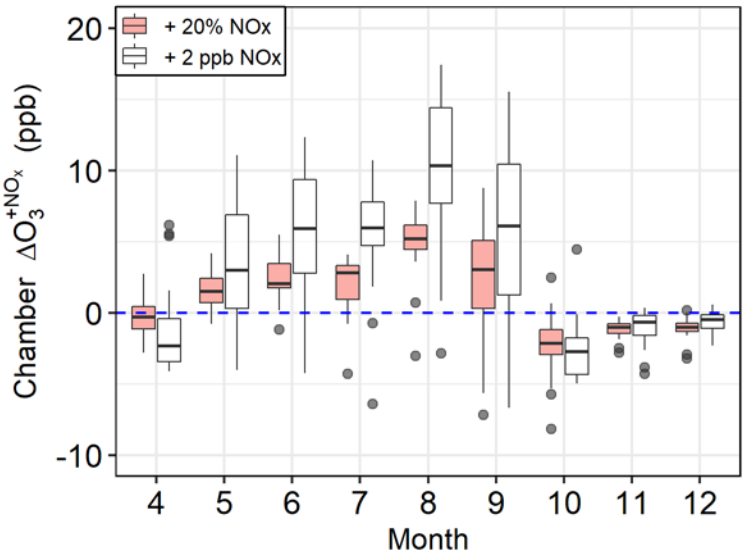

Figure 3. Monthly variation of predicted $\Delta O_3^{+NO_x}$ with NO_x perturbation at 20% (solid box) and constant 2ppb (open box) from April to December, 2020 at the Sacramento measurement site.

5. While smog chamber experiments have been used to simulate the photochemical reactions occurring in the atmosphere, the experiments can not accurately represent the complex real atmospheric conditions. This should be taken into consideration in discussing ozone sensitivity to the precursor gases and in drawing conclusions about emissions control policies

We acknowledge that the current experimental design does not capture all of the complexity in the real atmosphere. Mixing processes in the real atmosphere continue to change the composition at ground level as the planetary boundary layer grows throughout the afternoon. Fresh emissions will continue to impact the chemistry of O_3 formation. Only 3D chemical transport models can attempt to represent all of these competing effects, but measurements are needed to help evaluate those model calculations. The current experiment is focused on measuring the response of the chemical production term to changes in precursor NO_x and VOC concentrations because this most closely approximates the local effects of potential emissions control programs. No technique will be perfect, but we believe

that the current measurements add information to the weight of science approach used to design effective emissions control programs.

These limitations to the current study have been clarified on Sensitivity Analysis section of the revised manuscript.

Reference

Howard, C. J., Yang, W., Green, P. G., Mitloehner, F., Malkina, I. L., Flocchini, R. G. and Kleeman, M. J.: Direct measurements of the ozone formation potential from dairy cattle emissions using a transportable smog chamber, Atmos. Environ., 42(21), 5267–5277, doi:10.1016/j.atmosenv.2008.02.064, 2008.

Howard, C. J., Kumar, A., Malkina, I., Mitloehner, F., Green, P. G., Flocchini, R. G. and Kleeman, M. J.: Reactive organic gas emissions from livestock feed contribute significantly to ozone production in central California, Environ. Sci. Technol., 44(7), 2309–2314, doi:10.1021/es902864u, 2010.

Jorga, S. D., Kaltsonoudis, C., Liangou, A. and Pandis, S. N.: Measurement of Formation Rates of Secondary Aerosol in the Ambient Urban Atmosphere Using a Dual Smog Chamber System, Environ. Sci. Technol., 54(3), 1336–1343, doi:10.1021/acs.est.9b03479, 2020.

Kaltsonoudis, C., Jorga, S. D., Louvaris, E., Florou, K. and Pandis, S. N.: A portable dual-smog-chamber system for atmospheric aerosol field studies, Atmos. Meas. Tech., 12(5), 2733–2743, doi:10.5194/amt-12-2733-2019, 2019.

Li, Y., Alaimo, C. P., Kim, M., Kado, N. Y., Peppers, J., Xue, J., Wan, C., Green, P. G., Zhang, R., Jenkins, B. M., Vogel, C. F. A., Wuertz, S., Young, T. M. and Kleeman, M. J.: Composition and Toxicity of Biogas Produced from Different Feedstocks in California, Environ. Sci. Technol., doi:10.1021/acs.est.9b03003, 2019.

Platt, S. M., Haddad, I. El, Zardini, A. A., Clairotte, M., Astorga, C., Wolf, R., Slowik, J. G. and Universit, A.: Secondary organic aerosol formation from gasoline vehicle emissions in a new mobile environmental reaction chamber, , 9141–9158, doi:10.5194/acp-13-9141-2013, 2013.

Presto, A. A., Nguyen, N. T., Ranjan, M., Reeder, A. J., Lipsky, E. M., Hennigan, C. J., Miracolo, M. A., Riemer, D. D. and Robinson, A. L.: Fine particle and organic vapor emissions from staged tests of an in-use aircraft engine, Atmos. Environ., 45(21), 3603–3612, doi:10.1016/J.ATMOSENV.2011.03.061, 2011.