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. First, the smog chamber system is inadequately described, and many questions remain in my mind regarding its performance. An adequate description could possibly be added to this manuscript, probably in the supplement, but the authors should consider publishing a stand-alone paper in a journal such as Atmospheric Measurement Techniques (AMT), before attempting to develop this paper describing the results.

We have addressed each of the issues raised by the reviewer in the current paper through a combination of additional measurements and calculations. A chamber model developed by Howard et al (Howard et al., 2008, Howard et al., 2010a, Howard et al. 2010b) was employed as a part of this analysis to quantify the sensitivity of the O_3 response to NO_x perturbations under different experimental configurations. The chemical reaction system used by the chamber model is based on the SAPRC11 chemical mechanism (Carter and Heo, 2013) with wall loss rates based on the measured value of 5% hr^{-1}. The time integration procedures used to solve the set of differential equations that predict concentrations as a function of time are taken from the full UCD/CIT chemical transport model (Venecek et al., 2018; Ying et al., 2007).

Day-specific values of NO, NO_2, and O_3 initial concentrations used in the chamber simulations are based on measurements near the study location. VOC initial concentrations used in the chamber simulations are based on UCD/CIT simulations over the study location. The seasonal profile of the simulated VOC concentrations matches the CO*biogenic trends illustrated in Fig 2 of the manuscript, but the amplitude of the simulated seasonal trend was damped. VOC initial concentrations used in the chamber simulations were therefore scaled to match the amplitude of the CO*biogenic factor. The seasonal pattern of O_3 response to NO_x perturbations predicted by the SAPRC11 chamber model closely matches the measured trends shown in Figure 1. Chamber model calculations will be used as part of each response to the reviewer comments below.

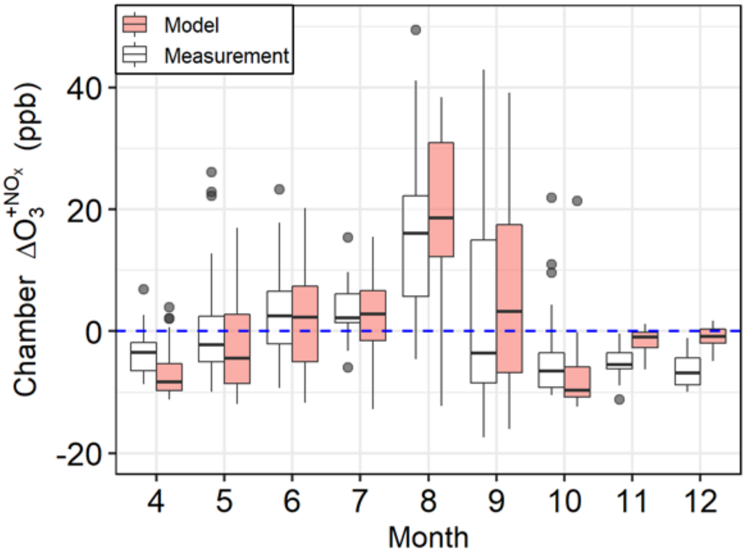

Figure 1. Monthly variation of the $\Delta O_3^{+NO_x}$ predicted by the chamber model (solid box) and directly measured in the chamber (open box) from April to December, 2020 at the Sacramento measurement site.

Issues that should be included in that description are:

- Temperature control of the chambers – It has been widely reported (e.g., Coates et al., 2016) that temperature affects ozone formation. Are the chambers held at ambient temperature in spite of irradiation by the UV lamp panels? (I presume that the chambers are enclosed in a light-tight structure to exclude ambient sunlight – this should be fully described).

The temperature in the reaction chambers was higher than the ambient temperature due to the heating effects of the UV lights. Figure 2 below shows that the difference between the chamber gas temperature and the ambient temperature increased by 5-10°C over the course of each experiment, with the exact temperature profile depending on the measurement month. Despite this temperature increase, all 3 chambers experience the same temperature profile, and so the comparison of O_3 formation between the chambers is not strongly biased by this issue.

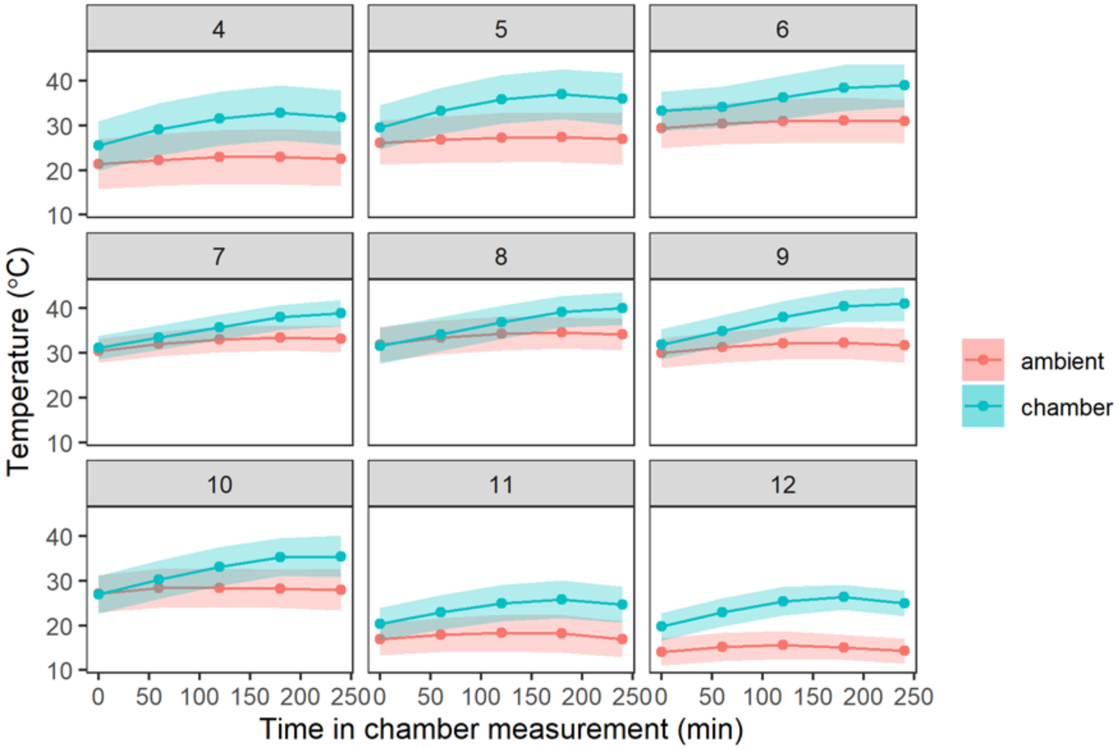

Figure 2. Time series of chamber gas temperature (blue) and ambient temperature (red) for each month from April to December, 2020. The dots show the monthly averaged value, and the shaded area shows the standard deviation of the temperature in each month.

The SAPRC11 chamber model used to quantify the effect of the chamber vs. ambient temperature difference illustrated in Figure 1 above. Figure 3 below shows the calculated $\Delta O_3^{+NO_x}$ during each month of the experiment under the chamber and ambient temperature profiles. 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. This point has been clarified in a new Sensitivity Analysis section added to the revised manuscript.

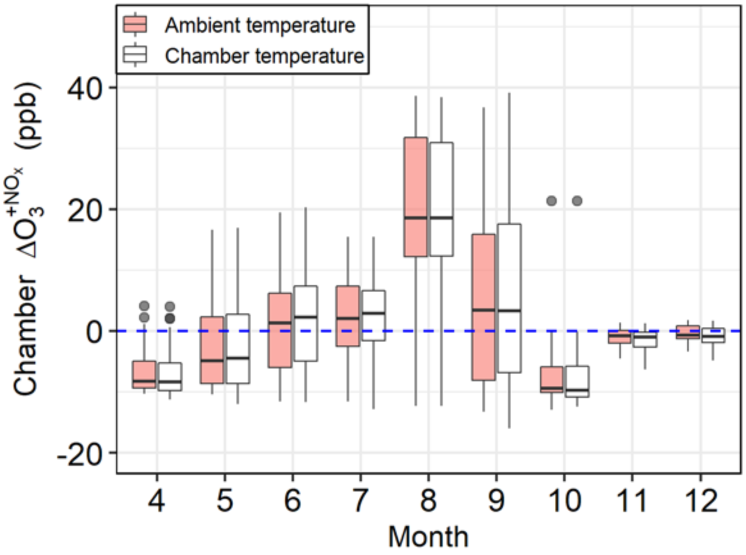

Figure 3. Monthly variation of the predicted $\Delta O_3^{+NO_x}$ under the ambient temperature profile (solid box) and chamber gas temperature profile (open box) from April to December, 2020 at the Sacramento measurement site.

- Light intensity control – It is generally recognized that ozone formation is a function of solar radiation intensity. In the ambient atmosphere, this intensity varies with solar zenith angle on diurnal and seasonal cycles, as well as ambient clouds and meteorological conditions (clouds, aerosol loading, stratospheric ozone column, etc.) Is there a mechanism to allow the chamber light intensity to mimic the ambient light intensity? Most important I suspect is the seasonal cycle of solar radiation intensity. Figure 3 of the paper shows the seasonal cycle of the smog-chamber results; does the experiment mimic the seasonal variation of the solar radiation intensity? If not, how can this “technique … directly measure O3 response to changes in precursor NOx and VOC concentrations in the atmosphere”?

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 summarized in Figure 4 below show that the difference associated with the use of constant UV radiation does not change the seasonal pattern of O_3 sensitivity to NO_x and VOC perturbations. As expected, 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. This information has been added to the new Sensitivity Analysis section in the revised manuscript.

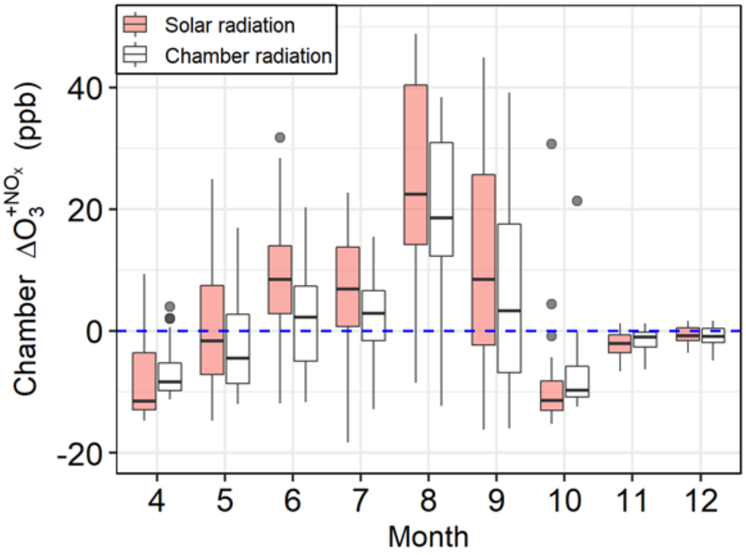

Figure 4. Monthly variation of predicted $\Delta O_3^{+NO_x}$ under constant chamber UV radiation (solid box) and clear-sky solar radiation (open box) from April to December, 2020 in the Sacramento measurement site.

- Blank tests – To develop confidence in the reported results, the authors must show that results of "blank runs" (i.e., filling all three chambers with zero air, adding the standard perturbation amounts of NOx and VOC to the two perturbed chambers, **and irradiating for the standard three hours) result in zero ozone formation** in all three chambers.

As the reviewer surely knows, adding NO_2 to a chamber followed by UV irradiation will definitely form O_3. The check requested by the reviewer therefore cannot result in zero O_3 formation. Furthermore, "blank tests" with zero air and zero O_3 formation are far outside the relevant atmospheric conditions that are the focus of the current study. A much more relevant indicator of the uncertainty in the experimental results is the difference between O_3 formed in different chambers across a range of atmospherically-relevant O_3 concentrations, since these between-chamber comparisons form the basis of the reported data. The results already reported in the manuscript summarize that the uncertainty between O_3 formation in different chambers operated under the same conditions is 1~2% for final O_3 concentrations between 40 – 125 ppb. This information has been highlighted on Figure S2 in the revised manuscript.

Even though the results are far outside the range of atmospherically-relevant concentrations, chambers were filled with zero air and irradiated for 180 min to address the request for a literal blank test. Figure 5 (Figure S2 in the revised SI) shows the results of this “blank” test alongside the original consistency test results measured at atmospherically-relevant O_3 concentrations. The final O_3 concentration in all 3 chambers during “blank” tests were less than 4 ppb and (more importantly) the difference between chambers that forms the basis of the reported O_3 sensitivity was less than 1 ppb (see points near the origin in Figure 5). These results are consistent with the sensitivity reported for atmospherically-relevant O_3 concentrations. This confirms that the O_3 measured in each chamber during normal operation is formed by the reaction of the ambient air plus perturbed gases. Any biases in the ozone formation have similar effects on all chambers and therefore very little effect on the comparison between chambers. This information has been added to the consistency test paragraph in Section 2.1 in the manuscript.

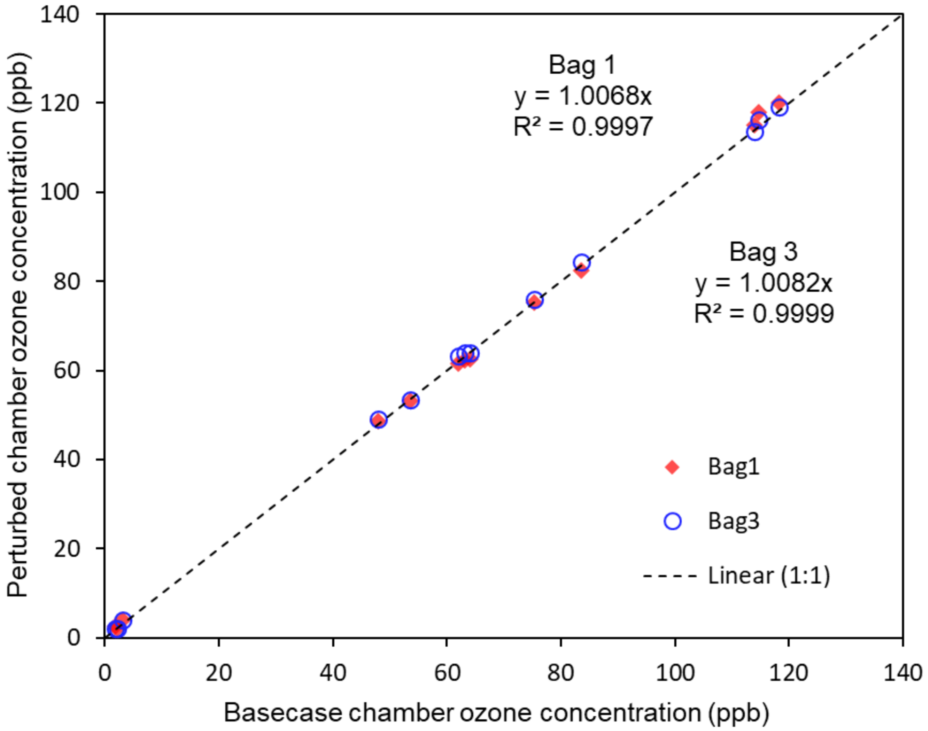

Figure 5. Consistency check of three 1 m^3 FEP bags using equal NO_x-VOC mixture. Points near the origin were measured with zero air. The equation and R^2 shows the linear regression results of O_3 concentration in perturbed chamber to basecase chamber. The 95% confidence intervals (CI) of regression coefficient are (0.996, 1.017) for bag 1, and (1.002, 1.013) for bag 3.

- Ambient condition tests – Again, to develop confidence that the reported results actually "directly measure O_3 response to changes in precursor NO_x and VOC concentrations in the atmosphere" it would seem critical to remove any light-tight shroud around the chambers so that they are exposed to ambient solar radiation, to not operate the UV lamps, and then to compare the ozone evolution in the chamber with the evolution of ambient ozone. Only if the chamber ozone actually tracks the ambient ozone, can it be accepted that a direct measurement of the ozone response is actually obtained.

The focus of the current study is to maintain UV intensity constant at an atmospherically-relevant level so that changes in O_3 sensitivity can be more directly associated with changes in atmospheric composition. We realize this is not a literal direct measurement of O_3 response, but rather it is a direct measurement of O_3 chemical production that is closer to a direct measurement than any other technique that has been previously demonstrated. If the reviewer (and Editor) feel that the claim of a direct measurement is too strong, then we would agree to soften the language slightly to claim direct measurements of the sensitivity of O_3 chemical production, or "semi-direct" measurements of O_3 sensitivity. The basecase O_3 chemical production rates are consistent with the ambient measurements as discussed below, and so we believe the measurements are atmospherically-relevant.

The first version of the manuscript used measurements from a preliminary experiment in Los Angeles to evaluate whether the chemical production rate of chamber O_3 was consistent with ambient measurements. The lower initial O_3 concentrations shown in that original figure were caused by the time-lag between the start time of ambient air injection and the start time of the chamber measurement. Figure S3 in the revised manuscript (shown as Figure 6 below) has been updated using a more comprehensive analysis over a longer time period for Sacramento to increase confidence in the analysis. Figure 4 shows the weekly-average ozone profile for each month of the year measured in the basecase chamber (dots) and the nearby ambient monitor (solid line). The initial O_3 concentrations in the base case chamber are similar to the ambient O_3 concentration at the start of each measurement period. The chemical production rate of O_3 measured in the basecase chamber is generally consistent with the rate of change in the O_3 concentrations measured at the ambient monitor between 10 am ~ 12 pm. The chemical production rate of O_3 in the chamber is higher than the increase in the ambient O_3 concentration because the ambient concentration is also affected by deposition and transport (Cazorla et al., 2012).

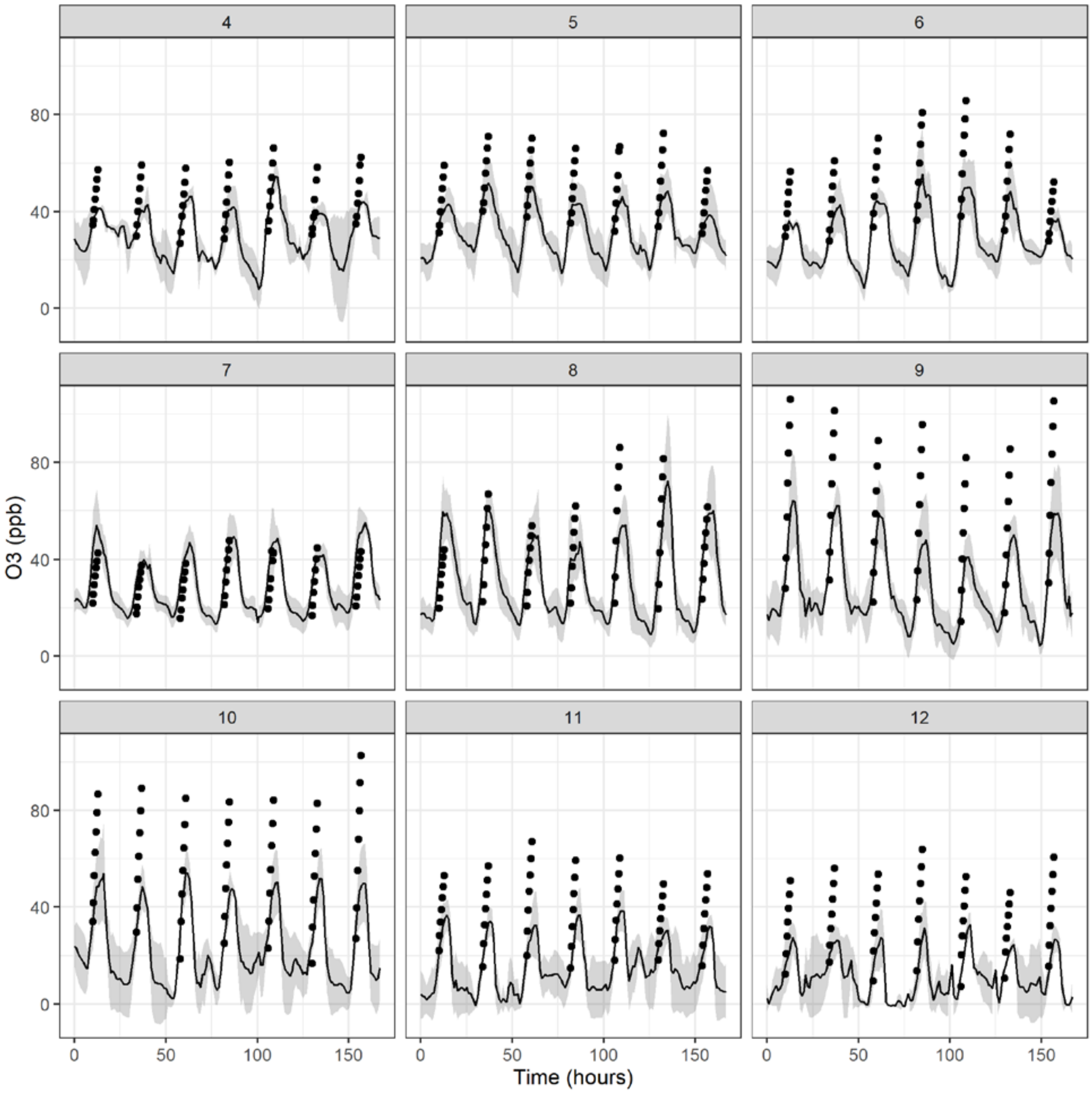

Figure 6. Weekly averaged Ambient (solid line) vs. Chamber (solid circles) O3 concentrations measured in Sacramento for each month from April to December, 2020. The shaded area indicates one standard deviation of the ambient O_3 concentration. Chambers were filled over a ~2hr period followed by a 30 min measurement period before UV lights were turned on. Hour is relative to the start of the experiment. (Appears as Figure S3 in revised manuscript)

The following information will be added to Section 2.1 in the revised manuscript to replace the original paragraph discussing Figure S3.

Weekly-averaged O_3 concentrations in the basecase chamber were compared to weekly-averaged ambient O_3 concentrations measured at the nearby monitoring station from April to December 2020 (Figure S3). The O_3 concentrations in the basecase chamber at the start of each experiment were similar to the ambient O_3 concentrations, indicating that the gas-phase chemical composition related to O_3 formation was not changed while injecting ambient air into the chamber. The O_3 formation in the chamber generally reflects the O_3 chemical production from the in-situ ambient air around 10 am ~ 12 pm in the morning, while the ambient O_3 is influenced by chemical production, mixing, and deposition (Cazorla et al., 2012). As expected, the initial rate of O_3 formation in the chamber is therefore higher than the initial rate of change in the ambient O_3 concentrations. The current experiment is focused on measuring the response of this chemical production rate to changes in precursor NO_x and VOC concentrations because this most closely approximates the local effects of potential emissions control programs.

- Linearity tests – With regard to comment c below, the response of the smog-chamber system to different magnitude perturbation concentrations must be investigated. The figure at right shows example diurnal cycles of the NO_X concentrations in four months, one from each season, measured at the monitoring site adjacent to the smog-chamber location (Fig. S5). In summer and spring (the seasons of most policy relevance) the added NO_2 perturbation (8 ppb) in the smog chamber more than doubles the NO_X concentration. Thus, the physical significance of the derived ozone formation sensitivity is questionable.

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 7 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.

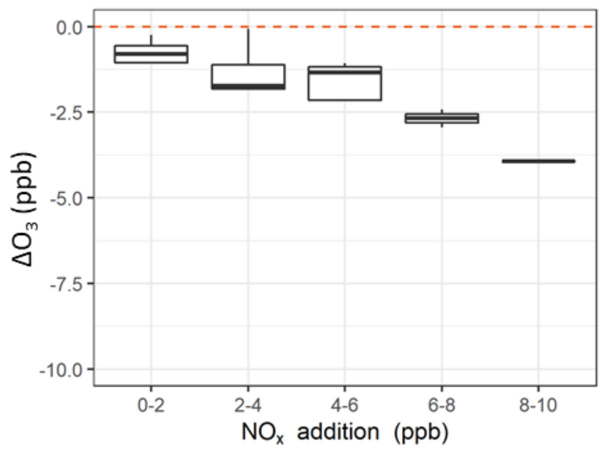

Figure 7. Measured ΔO_3 as a function of different NO_x perturbations. Total number of data points is 24.

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 8 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.

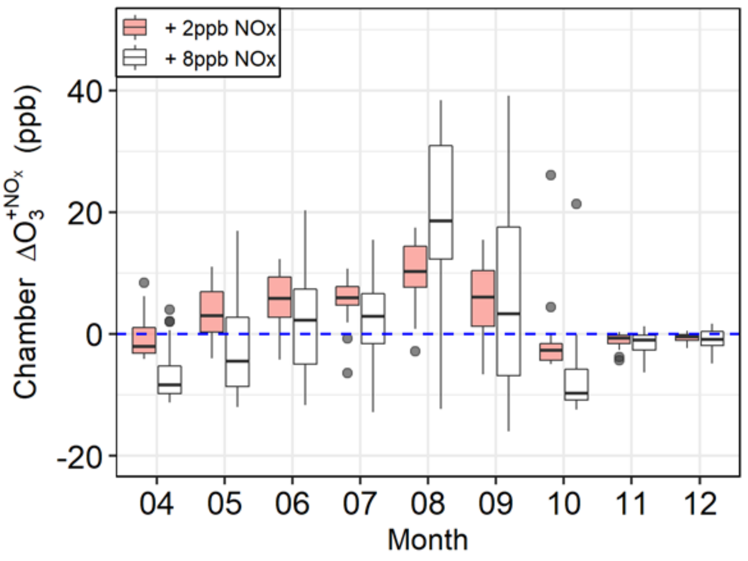

Figure 8. Monthly variation of chamber $\Delta O_3^{+NO_x}$ at Sacramento using NO_2 perturbations of 2 ppb (solid box) and 8 ppb (open box) from April to December, 2020. Simulations are based on the actual chamber UV radiation and chamber temperature profile.

b. Second, I do not believe that the system can actually directly measure ozone sensitivity in the sense that it accurately reflects how actual ambient ozone concentrations would respond to precursor emission changes. In the real atmosphere, during the photochemical active period of a day, ambient air parcels are transported through an air basin. During that transport, dilution and mixing processes occur, fresh emissions are injected into the air parcel and ozone is lost to surface deposition simultaneously with in situ photochemical ozone production. It seems to me that the smog chamber can only reproduce one (albeit very important) aspect of this extremely complex ambient ozone production process. A late morning, integrated air parcel is captured in the chamber, and then the in situ photochemical ozone production is mimicked in isolation from all other processes. This issue should be thoroughly discussed, and the authors should acknowledge that their approach can potentially determine the sensitivity of the in situ photochemical ozone production to precursor NO_x and VOC, but likely that does not directly correspond to the sensitivity of the actual ozone concentrations in the ambient Sacramento boundary layer.

We believe that the measurement does reflect how ambient O_3 concentrations would respond to changes in emissions. The experiment measures the sensitivity of the O_3 chemical production term in response to the concentration of NO_x and VOC. This is the most appropriate measurement of how local emission controls will affect the local O_3 concentrations. The experiment may not directly capture all of the atmospheric processes, but it represents the dominant processes. The agreement between the measured results at ground level and the satellite measurements build confidence that the results are capturing the most important features of the atmospheric system. An enhanced discussion of the issues above has been added to the Sensitivity Analysis section of the revised manuscript.

c. Third, when the sensitivity of ozone is discussed, it is generally understood that the sensitivity is referring to the response of ozone to decreases in precursor NO_x and VOC. However, the smog chamber experiment operates by investigating increases in those precursors. If ozone production chemistry responded linearly to precursor changes, this distinction would be unimportant; however, it is widely acknowledged that ozone chemistry is highly non-linear. Thus, the smog chamber approach must give biased results. For example, if the ambient atmosphere were on the “ridgeline” of the corresponding ozone isopleth diagram, then the smog chamber data would indicate VOC sensitivity, since the ozone production would decrease with added NO_x (i.e., $\Delta O_3^{+NO_x}$ would be negative). But if the experiment could be run with a NOx decrease, rather than an increase, the ozone produced would again decrease, indicating NOx sensitivity. The extent of the bias resulting from the non-linearity of the ozone response depends upon the relative magnitude of the precursor perturbations. A very small, potentially infinitesimal, perturbation would reduce, potentially eliminate, the bias; however to obtain a precisely measurable response, I suspect that the precursor perturbations were rather large relative to the ambient concentrations. Since the NO_x concentrations were actually measured in these experimental runs, a thorough discussion of this potential source of bias should be given in the context of the magnitude of the NO_x perturbations relative to the initial ambient NO_x concentrations in the chamber when the experimental run is initiated.

This question was addressed in the response to the comment about linearity in response to the NO_x perturbation. To summarize, box model calculations confirm that the size of the positive NO_x perturbation does not change the overall observation that O_3 sensitivity transitions from NO_x-rich during winter months to NO_x-limited in summer months. That is why the ground-based measurement trends match the independent TROPOMI satellite measurement trends. If anything, the 8 ppb NO_2 perturbation slightly changes the timing of the transition and damps the magnitude of the O_3 sensitivity during the transition months rather than artificially enhancing the trends. A thorough discussion about this issue is included in the Sensitivity Analysis section of the revised manuscript.

2. This paper emphasizes the policy relevance of the results. The last two sentences of the abstract state: “This challenging situation suggests that emissions control programs that focus on NOx reductions will immediately lower peak O3 concentrations, but slightly increase intermediate O3 concentrations until NOx levels fall far enough to re-enter the NOx-limited regime. The spatial pattern of increasing and decreasing O3 concentrations in response to a NOx emissions control strategy should be carefully mapped in order to fully understand the public health implications.” However, the smog chamber work is analyzed from the perspective of the final ozone concentration in the chamber at the end of the experimental run. The policy relevance would be much more clearly evident in this work if the analysis perspective focused on the ambient MDA8 ozone concentration on the day of each run. In particular, **Figure 6 would be more informative if the x-axis variable were the MDA8 ambient ozone concentration recorded at the monitoring site adjacent to the smog chamber field location** (see Figure S5). A great deal more support must be given before these policy-relevant statements can be accepted. In this regard, the findings must be directly related to

the conditions that produce ambient **MDA8** ozone concentrations that exceed the NAAQS, as discussed in the 2nd paragraph of the Introduction Section of the paper.

Figure 6 in the manuscript (shown as Figure 9 below) was updated to use MDA8 O_3 concentration from the nearby CARB monitoring station as requested. The text in Section 3.1.5 has been revised to describe the updated figure.

"The days with the highest measured O_3 concentrations are of particular interest in the current study since emissions control programs are traditionally tailored to reduce the O_3 design value, which is determined by daily maximum 8-hour average (MDA8) O_3 concentration. Figure 6 illustrates box-and-whisker plots of measured $\Delta O_3^{+NO_x}$, and ΔO_3^{+VOC} at Sacramento binned according to the MDA8 O_3 concentration measured at the monitoring station near the chamber measurement site. The right two bins, corresponding to the O_3-nonattainment days (MDA8 O_3 > 70 ppb), have O_3 sensitivity in the NO_x-limited regime where NO_x addition increases O_3 concentrations and VOC addition has minor effects on O_3 concentrations. These measurements suggest that a NO_x emissions control strategy would be most effective at reducing these peak O_3 concentrations. In contrast, a large portion of the days with MDA8 O_3 concentrations below 55 ppb were in the VOC-limited regime, suggesting that an emissions control strategy focusing on NO_x reduction would increase O_3 concentrations. VOC controls on these intermediate days would be difficult, however, if biogenic VOCs account for the majority of the O_3 formation. This challenging situation suggests that emissions control programs that focus on NO_x reductions will immediately lower peak O_3 concentrations, but slightly increase intermediate O_3 concentrations until NO_x levels fall far enough to re-enter the NO_x-limited regime."

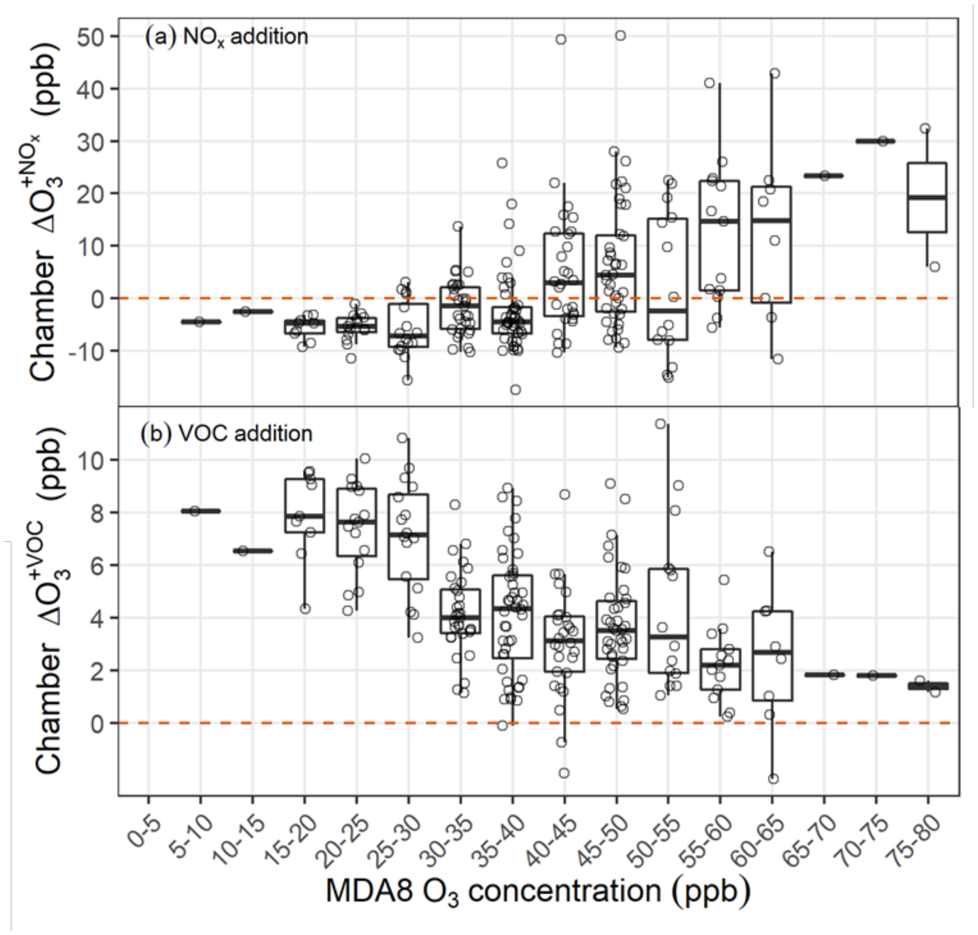

Figure 9: Boxplot of O_3 sensitivity to NO_x and VOC as a function of MDA8 O_3 concentration. (Appears as Figure 6 in revised manuscript)

Minor Issues:

1. Lines 54-61: These sentences discuss references that propose causes of the increase of O3 design values in some air basins between the years 2015 – 2018. However, many of the cited references were published before that increase occurred, so they obviously do not directly address that increases. This discussion must be improved with the inclusion of appropriate references. To my knowledge tenable proposed causes include the influences of wildfire emissions and particularly pronounced heat waves; however the causes the authors discuss in these lines really are not tenable. For example, "growing importance of precursor VOC emissions not previously accounted for in the planning process" could possibly account for a slowing of the ozone decrease, but (unless those emissions increased markedly over that short 2015 – 2018 period) could not account for an increase. Similarly, climate has not changed markedly over that short 2015 – 2018 period, so this cause also is not tenable. If the authors wish to discuss this rather minor feature of Figure 1 (i.e., there are other wiggles in the trend of similar magnitude), then they should do so in a rigorous manner. Perhaps a cause could be sought that accounts for the increase in some (e.g. SoCAB and San Diego as discussed in the manuscript), but not in other Southern California air basins (e.g., South Central Coast Air Basin, which is adjacent to SoCAB).

The text in the Introduction section has been modified to include additional explanations and references as shown below.

"O_3 levels are often described by the maximum 8-hr average concentration that occurs within each day. The annual fourth-highest daily maximum 8-hr average concentration averaged over three years has special regulatory significance. This "design value" determines whether the region containing the monitor complies with the O_3 NAAQS. O_3 design values in California decreased steadily between the years 1980 and 2019 (Figure 1) due to the success of emissions control programs that reduced concentrations of precursors broadly divided into two groups: oxides of nitrogen (NO_x) and volatile organic compounds (VOCs) (Parrish et al., 2016; Simon et al., 2015). Continued progress after the year 2010 has been slower, and O_3 design values even increased in some air basins between the years 2015 – 2018 (Figure 1). Multiple factors have been proposed to explain the lack of further reductions in O_3 concentrations in recent years. These potential factors include: (i) growing importance of precursor VOC emissions not previously accounted for in the planning process as major sources such as transportation have been controlled (McDonald et al., 2018; Shah et al., 2020), (ii) an imbalance in the historical degree of NO_x and VOC reductions (Cox et al., 2013; Parrish et al., 2016; Pollack et al., 2013; Steiner et al., 2006), or (iii) more frequent heat waves (Jacob and Winner, 2009; Jing et al., 2017; Pusede et al., 2015; Rasmussen et al., 2013; Weaver et al., 2009) and wildfires (Jaffe et al., 2013; Lindaas et al., 2017; Lu et al., 2016; Singh et al., 2012) as a consequence of climate change. All these theories are supported to varying degrees by indirect measurements or model predictions, but there is an absence of strong direct evidence that identifies dominant factors contributing to the increased O_3 concentrations. The uncertainty that lingers over the recent O_3 trends suggests that fresh approaches are needed to directly verify the optimum emissions control path."

2. Lines 143-153: This paragraph is not persuasive. The statement “The initial O_3 concentration in the basecase chamber was similar to the ambient O_3 concentration, indicating that the gas phase chemical composition related to O_3 formation is not modified during chamber injection” requires more discussion. Figure S3 clearly indicates that the initial O_3 concentration in the basecase chamber was always significantly (10-30 ppb) below the ambient concentrations at the initial time. This issue and its impacts on the entire analysis must be thoroughly discussed. I suggest that this discussion include an expanded time scale for some specific examples so comparison between the basecase chamber and ambient air is much more clearly illustrated. Further, the tests included in Fig. S3 were conducted in Los Angeles (an urban area with very different ozone levels and presumably photochemical environment) than Sacramento, where the primary field work was conducted (e.g., see Figure 1 of the paper).

This issue has been answered as a part of response for Ambient condition test in Major issue section. The text related to this issue is copied below:

The first version of the manuscript used measurements from a preliminary experiment in Los Angeles to evaluate whether the chemical production rate of chamber O_3 was consistent with ambient measurements. The lower initial O_3 concentrations shown in that original figure were caused by the time-lag between the start time of ambient air injection and the start time of the chamber measurement. Figure S3 in the revised manuscript (shown as Figure 6 below) has been updated using a more comprehensive analysis over a longer time period for Sacramento to increase confidence in the analysis. Figure 4 shows the weekly-average ozone profile for each month of the year measured in the basecase chamber (dots) and the nearby ambient monitor (solid line). The initial O_3 concentrations in the base case chamber are similar to the ambient O_3 concentration at the start of each measurement period. The chemical production rate of O_3 measured in the basecase chamber is generally consistent with the rate of change in the O_3 concentrations measured at the ambient monitor between 10 am ~ 12 pm. The chemical production rate of O_3 in the chamber is higher than the increase in the ambient O_3 concentration because the ambient concentration is also affected by deposition and transport (Cazorla et al., 2012).

3. Lines 143-153: This same paragraph discusses the comparison of the O3 increase in the basecase chamber and in the ambient air; that discussion is greatly oversimplified. In the ambient atmosphere, the early morning O3 increase is largely driven by mixing down of ozone rich air from aloft as the boundary layer rapidly grows during that period. In the SoCAB, the land-sea breeze circulation affects the diurnal ozone cycle during the day. The statement “The O3 formation in the chamber, therefore, captures a realistic “worst-case scenario” for surface-level O3 formation under conditions where atmospheric mixing cannot dilute the NOx and VOC concentrations that build up in the nocturnal ground-level stagnation layer.” is simply not justified – the conditions inside the chambers are very different from ambient conditions. These differences must be thoroughly discussed – not simply “hand waved” away. It should be realized that the predominant growth of the convective boundary layer generally approaches its maximum extent by noon, which is the time that the experimental run begins (e.g.. see Figures 4-7 of Bianco et al., 2011).

The description of Figure S3 has been revised in the main manuscript. It's also shown in the Major issue about Ambient condition test section. The revised paragraph is copied below:

Weekly-averaged O_3 concentrations in the base case chamber were compared to weekly-averaged ambient O_3 concentrations measured at the nearby monitoring station from April to December 2020 (Figure S3). The O_3 concentrations in the base case chamber at the start of each experiment were similar to the ambient O_3 concentrations, indicating that the gas-phase chemical composition related to O_3 formation was not changed while injecting ambient air into the chamber. The O_3 formation in the chamber generally reflects the O_3 chemical production from the in-situ ambient air around 10 am ~ 12 pm in the morning, while the ambient O_3 is influenced by chemical production, mixing, and deposition (Cazorla et al., 2012). As expected, the initial rate of O_3 formation in the chamber is therefore higher than the initial rate of change in the ambient O_3 concentrations. The current experiment is focused on measuring the response of this 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.

4. Many of the figures show linear regression fits. However, It appears that there may be shortcomings and errors in some of them. These issues should be checked and corrected if necessary; specifically:

a. Figure S2. Confidence limits (preferably 2 sigma or 95%) for the slopes should be included to indicate that the slopes are indeed consistent with unity.

The Figure S2 has been updated as mentioned in Major issue. The confidence interval has been added in the caption of Figure S2.

b. Figure S4. Given the large scatter in the data points and the small correlation coefficients, the exceedingly small p values, and the relatively small shaded areas appear to me to not be realistic (and the meaning of the shaded areas should be defined.) Please check all such fits in all figures to be sure the fitting is properly calculated.

The calculation has been checked. The shaded area indicates the 95% confidence interval of the mean response of the predicted value. The confidence interval of the mean response is tighter than the scatter in the individual data points. The meaning of the shaded area has been described in the caption of all such plots in both the manuscript and SI)

5. The discussion of the VOC and CO relationships (lines 155-173) requires improvement.

a. The statement “Biogenic sources do not emit CO and so any correlation between biogenic VOCs and CO purely reflects the utility of CO as an indicator of atmospheric mixing that equally affects all sources” is incorrect and misleading. An important source of CO is partial oxidation of biogenic VOCs, so their correlation is more complex than indicated here. Further, atmospheric mixing does not equally affect all sources, since the result of mixing is dependent on the background concentrations in the diluting air.

The statement has been revised as “Biogenic sources do not emit CO but biogenic VOCs can react in the atmosphere to produce CO (Hudman et al., 2008). CO also acts as an indicator of atmospheric mixing that equally affects all primary sources.”

b. The quantity CO*Biogenic is not clearly defined. Where were the sites of those VOC measurements? More details of the “temperature and relative humidity-induced enhancement factor for isoprene emissions” must be given. The cited reference is now 30 years old; in the intervening 3 decades a great deal has been learned about biogenic VOC emissions. Is this “enhancement factor” consistent with current understanding?

The Model of Emissions of Gases and Aerosols from Nature (MEGAN) model is widely used to estimate the BVOC emissions. The temperature response used in our manuscript is based on the published MEGAN temperature response (Guenther et al., 2012). We believe this factor is still appropriate for use in the current study.

c. Given the quoted R value in Fig. S4, it should be mentioned that use of CO*Biogenic as an approximate surrogate for VOCR only captures ~36% of the variance of VOCR at the site where the CO and VOCR measurements were made.

This information has been added into the revised manuscript in last paragraph in Section 2.1.

d. It should be explicitly stated whether the CO and VOC measurements were made at the same monitoring site, and the location of this site relative to the location of the chamber measurements should be discussed.

CO and VOC are from the same monitoring site in Sacramento. A detailed description of the data sources has been added in the revised SI. The location of CO and VOC data source is the closest monitoring site to the chamber measurement site that have both CO and VOC data available.

6. Section 2.3. The brief experimental description is not adequate. Questions that occur to me include: How can air be sampled from the chambers without disturbing the environment? Do the sides of the chamber gradually collapse? If the sides collapse, what fraction of the air is exhausted through the sampling process over the 210-minute experimental run? Why is a linear extrapolation required? Section 2.1 reports that ozone loss rates were 5%/hour in the chambers; was correction made for this loss rate? Figure S2 indicates that the perturbed chambers gave 1 to 2%

greater ozone production than the base chamber; was correction made for this difference? How many experimental runs were made over the 11 month period of Figure 2, and included in the box and whisker plots? In addition to an expanded experimental discussion that answers these questions, I suggest including sample chamber measurement data from a typical experimental run as a section in the Supplement. That section should clearly describe all steps included in the process of deriving the DO3 values of Figure 3 from the 3-hr time series of concentration measurements. It would also be useful to indicate the number of experimental runs included in each box and whisker plot in Figure 3 (and in subsequent figures).

All monitors exhaust through tubing that is released several meters away from the trailer at the ground level. The nearby CARB monitoring station is several hundred meters away from the trailer and so it is not influenced by trailer operations. One experiment was conducted each day, releasing a total of 3 m^3 to the ambient air over a 3–4 hour period. This low level will not influence nearby measurements. These points are clarified in the Methods section of the revised manuscript.

The chamber sides collapse as air is withdrawn from the chamber. The total sample flow rate for all monitors is approximately 3 L/min. Seven measurements with a duration of 10 min are made from each chamber resulting in a total sample volume of 210 L air, or approximately 21% of the chamber volume (leaving 79% of the total air in the chamber). The shape of the chambers is not greatly distorted at any point during the experiment. These points are clarified in the Methods section of the revised manuscript.

The sequential sampling strategy means that measurements from different chambers are always made at different times. There will always be a difference of at least 10 min between O_3 measurements in each chamber. We fit a linear regression to O_3 concentrations as a function of time to enable a comparison of O_3 concentrations at the same time at the end of each experiment. These points are clarified in the Methods section of the revised manuscript.

The ozone loss rate of 5% per hour was used to correct the O_3 concentration in each chamber before we apply the linear regression. This point is clarified in the Methods section of the revised manuscript.

Figure S2 shows the reproducibility of O_3 formation in the three chambers. From the coefficient of the linear regression, the O_3 concentration in the perturbed chamber may have ~ 1% difference with the concentration in the basecase chamber. This is the uncertainty of the chamber comparison, not the bias, and so it was not necessary to correct the comparison between chamber measurements. The ~1% uncertainty of O_3 formation from three chambers is acceptable for the O_3 sensitivity analysis. This point is clarified in the Methods section of the revised manuscript.

There are 222 experiment runs from Apr 14 to Dec 20, 2020 (out of a total of 251 days). We will add this information in the main text. The example of a typical day of results is shown below will be added to the revised SI:

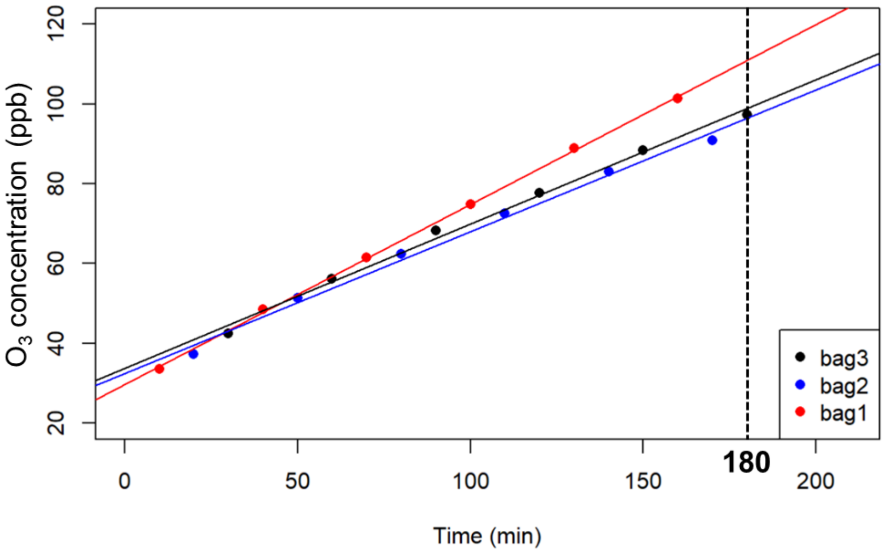

Figure S?. O_3 concentration in 3 chambers under the UV exposure during a typical chamber experiment on August 16, 2020 in Sacramento. Lines shows the linear regression result of O_3 concentration under UV exposure in each chamber.

Figure S? shows an example of the time series of chamber O_3 concentration under the UV exposure. The time in x-axis reflects the UV exposure duration time in the chamber. Each dot is 10-min averaged O_3 concentration corrected by O_3 wall loss rate. Dots with different colors correspond to different chambers. Linear regression was applied to O_3 concentration in each chamber shown as solid lines. The projected O_3 concentration at the end of the 180-min UV exposure time was calculated based on the regression results (hereafter referred to as $3hr\ O_3^{Bag\ 1}$, $3hr\ O_3^{Bag\ 2}$, and $3hr\ O_3^{Bag\ 3}$). The measured sensitivities $\Delta O_3^{+NO_x}$, and ΔO_3^{+VOC} were calculated using the equation below:

$$\Delta O_3^{+NO_x} = 3hr\ O_3^{Bag\ 2} - 3hr\ O_3^{Bag\ 1}$$

$$\Delta O_3^{+VOC} = 3hr\ O_3^{Bag\ 3} - 3hr\ O_3^{Bag\ 1}$$

7. In this regard, Figure S1 seems to indicate that four lamps were mounted on the floor of the middle chamber, and eight were mounted on the floor of each end chamber. Does this difference in the figure reflect the reality of the chambers? If so, please explain why this arrangement was used, and give more discussion regarding why this arrangement does not bias the results.

Figure S1 exactly represents the light configuration used in the experiment. The three smog chambers are contained in a single rectangular enclosure with reflective wall panels. The length of the enclosure is approximately 0.5 m longer than the combined length of the chambers. This geometry uses space efficiently but the distance between the reflective end walls and the outside chambers is different than the distance between the reflective end walls and the center chamber. The distribution of lights was chosen to achieve equal UV intensity for each chamber in this geometric configuration. Multiple light configurations were tested with UV measurements at each chamber. The configuration summarized in Figure S1 achieved the most uniform distribution of UV among the chambers. The consistency of O_3 formation in all chambers initialized with the same composition confirms that the light distribution produces the same photolysis rates in each chamber. Moreover, the chamber named bag1,2,3 in the consistency test only represent the position of chamber in the system. The actual chambers were rotated during the consistency checks to verify that the equivalent O_3 formation across chambers was not caused by compensating errors. These points have been clarified in the text associated with Figure S1 in the revised manuscript.

8. The discussion of Figure 2 is not adequate. Why are there no TROPOMI measurements in November and December? Reading the figure caption seems to indicate that CO measurements were made in the ground-based chambers; however, Section 2.1 seems to indicate that only NO_x, NO_y, O_3, temperature and relative humidity were measured in the chambers. Please explain clearly how the CO*biogenic values were determined. Evidently the isoprene concentrations in Figure 2 were measured at an EPA PAMS site; Figure S5 indicates two monitoring sites. It should be indicated which (if either) of those sites reported the isoprene measurements discussed here. The meaning of the lines in the box and whisker plots should be explicitly indicated, here and in later figures.

TROPOMI data for November and December were not available during the first round of data analysis for this paper. We have updated the Figure 2 and Figure 3 (shown below) in the revised manuscript with TROPOMI data through December 2020. TROPOMI data in November and December matches well with the chamber measurement. The CO data was collected from a nearby CARB monitoring site that have CO concentration available in Sacramento. The Figure S5 indicates the monitoring site for ambient CO, NO_x, and O_3 concentration. The caption has been revised to correspond the site to each pollutant species. The EPA PAMS site information has been added in the revised SI in Section 5.

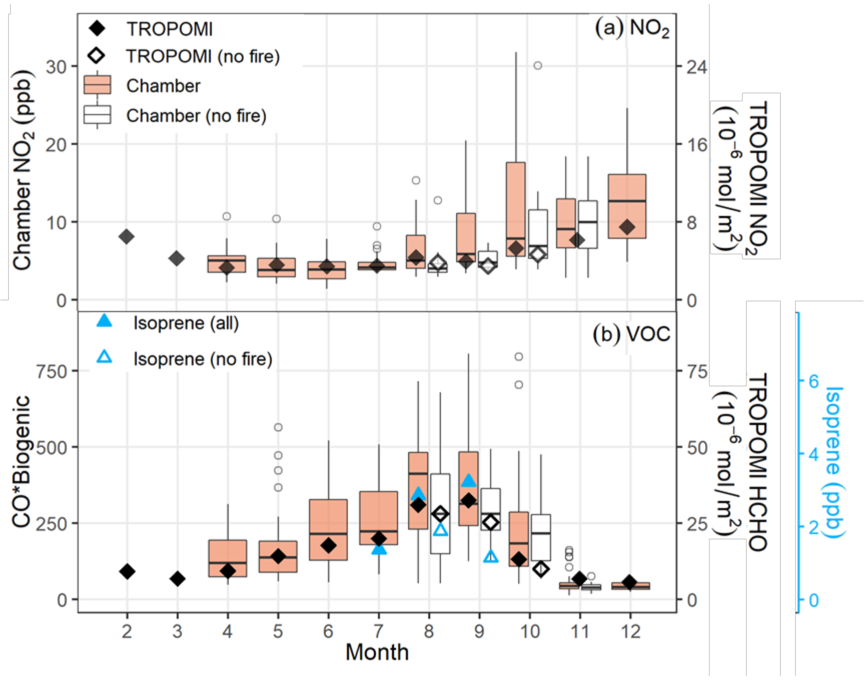

Figure 1. Monthly concentrations of NO$_2$ (panels a) and CO*Biogenic/HCHO/Isoprene (panels b) from February to December 2020. Ground-based chamber measurements use the left axis with results shown as box and whisker plots. TROPOMI measurements use the right axis and are shown as diamonds. Isoprene from ground monitoring station shown as blue triangles. The open box and points show the results after removing wildfire days.

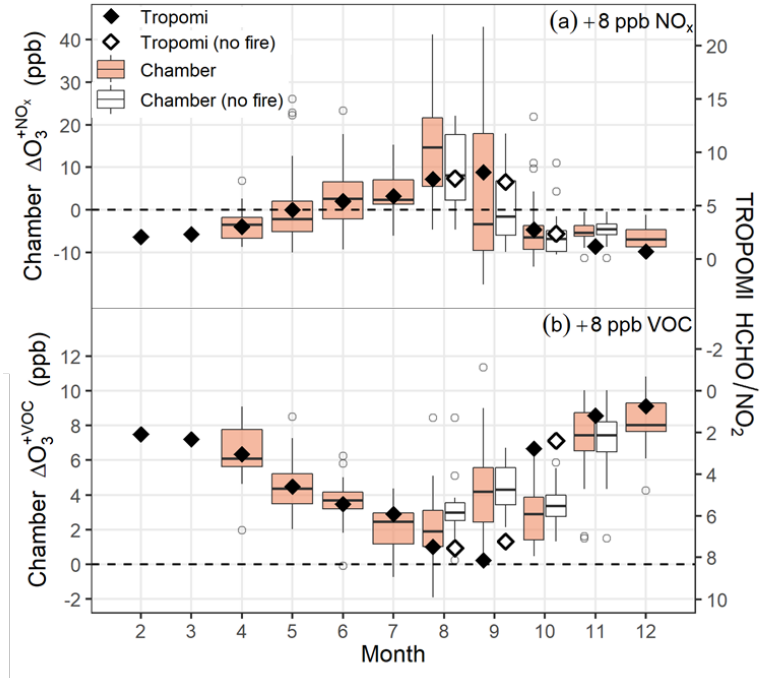

Figure 2. Monthly variance of TROPOMI HCHO/NO$_2$ (diamond) and ΔO$_3$ (box) due to NO$_x$ addition ($\Delta O_3^{+NO_x}$) and VOC addition (ΔO_3^{+VOC}) from April to December including wildfire days (top) and without wildfire days (bottom).

9. The final paragraph of Section 3.1.1 discusses VCPs, but requires improvement. VCP emissions are not related to either CO emissions or isoprene emissions (except if isoprene is one of the VCPs). Thus, there is no reason to expect seasonal pattern similarity between VCPs and CO*biogenic values, or between VCPs and isoprene. Nevertheless, there is nothing here to indicate that VCPs are not important (or even dominant) in driving ozone production in Sacramento (although I agree that this is very unlikely). This paragraph should be modified or eliminated.

The statements suggest that possible increased VCP emission from sanitizing products due to COVID-19 likely did not change the seasonal trend of VOC. This paragraph did not say that VCP is not an important precursor of O_3 formation, but it discusses the potential influence of COVID-19 on VOC emission in Sacramento. This paragraph correctly notes that the seasonal trend of BVOC is more consistent with the measured trends in Sacramento. We believe the paragraph was clear as originally written.

References

Carter, W. P. L. and Heo, G.: Development of revised SAPRC aromatics mechanisms, Atmos. Environ., 77, 404–414, doi:10.1016/J.ATMOSENV.2013.05.021, 2013.

Cazorla, M., Brune, W. H., Ren, X. and Lefer, B.: Direct measurement of ozone production rates in Houston in 2009 and comparison with two estimation methods, Atmos. Chem. Phys., 12(2), 1203–1212, doi:10.5194/acp-12-1203-2012, 2012.

Cox, P., Delao, A. and Komorniczak, A.: The California Almanac of Emissions and Air Quality - 2013 Edition. [online] Available from: https://www.arb.ca.gov/aqd/almanac/almanac13/almanac13.htm, 2013.

Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K. and Wang, X.: The model of emissions of gases and aerosols from nature version 2.1 (MEGAN2.1): An extended and updated framework for modeling biogenic emissions, Geosci. Model Dev., 5(6), 1471–1492, doi:10.5194/GMD-5-1471-2012, 2012.

Hudman, R. C., Murray, L. T., Jacob, D. J., Millet, D. B., Turquety, S., Wu, S., Blake, D. R., Goldstein, A. H., Holloway, J. S. and Sachse, G. W.: Biogenic versus anthropogenic sources of CO in the United States, Geophys. Res. Lett., 35(4), doi:10.1029/2007GL032393, 2008.

Jacob, D. J. and Winner, D. A.: Effect of climate change on air quality, Atmos. Environ., 43(1), 51–63, doi:10.1016/j.atmosenv.2008.09.051, 2009.

Jaffe, D. A., Wigder, N., Downey, N., Pfister, G., Boynard, A. and Reid, S. B.: Impact of wildfires on ozone exceptional events in the western U.S., Environ. Sci. Technol., 47(19), 11065–11072, doi:10.1021/es402164f, 2013.

Jing, P., Lu, Z. and Steiner, A. L.: The ozone-climate penalty in the Midwestern U.S., Atmos. Environ., 170, 130–142, doi:10.1016/j.atmosenv.2017.09.038, 2017.

Lindaas, J., Farmer, D. K., Pollack, I. B., Abeleira, A., Flocke, F., Roscioli, R., Herndon, S. and Fischer, E. V.: Changes in ozone and precursors during two aged wildfire smoke events in the Colorado Front Range in summer 2015, Atmos. Chem. Phys., 17(17), 10691–10707, doi:10.5194/acp-17-10691-2017, 2017.

Lu, X., Zhang, L., Yue, X., Zhang, J., Jaffe, D. A., Stohl, A., Zhao, Y. and Shao, J.: Wildfire influences on the variability and trend of summer surface ozone in the mountainous western United States, Atmos. Chem. Phys., 16(22), 14687–14702, doi:10.5194/acp-16-14687-2016, 2016.

McDonald, B. C., De Gouw, J. A., Gilman, J. B., Jathar, S. H., Akherati, A., Cappa, C. D., Jimenez, J. L., Lee-Taylor, J., Hayes, P. L., McKeen, S. A., Cui, Y. Y., Kim, S. W., Gentner, D. R., Isaacman-VanWertz, G., Goldstein, A. H., Harley, R. A., Frost, G. J., Roberts, J. M., Ryerson, T. B. and Trainer, M.: Volatile chemical products emerging as largest petrochemical source of urban organic emissions, Science (80-.)., 359(6377), 760–764, doi:10.1126/science.aaq0524, 2018.

Parrish, D. D., Xu, J., Croes, B. and Shao, M.: Air quality improvement in Los Angeles—perspectives for developing cities, Front. Environ. Sci. Eng., 10(5), doi:10.1007/s11783-016-0859-5, 2016.

Pollack, I. B., Ryerson, T. B., Trainer, M., Neuman, J. A., Roberts, J. M. and Parrish, D. D.: Trends in ozone, its precursors, and related secondary oxidation products in Los Angeles, California: A synthesis of measurements from 1960 to 2010, J. Geophys. Res. Atmos., 118(11), 5893–5911, doi:10.1002/jgrd.50472, 2013.

Pusede, S. E., Steiner, A. L. and Cohen, R. C.: Temperature and Recent Trends in the Chemistry of Continental Surface Ozone, Chem. Rev., 115(10), 3898–3918, doi:10.1021/cr5006815, 2015.

Rasmussen, D. J., Hu, J., Mahmud, A. and Kleeman, M. J.: The ozone-climate penalty: Past, present, and future, Environ. Sci. Technol., 47(24), 14258–14266, doi:10.1021/es403446m, 2013.

Shah, R. U., Coggon, M. M., Gkatzelis, G. I., McDonald, B. C., Tasoglou, A., Huber, H., Gilman, J., Warneke, C., Robinson, A. L. and Presto, A. A.: Urban Oxidation Flow Reactor Measurements Reveal Significant Secondary Organic Aerosol Contributions from Volatile Emissions of Emerging Importance, Environ. Sci. Technol., 54(2), 714–725, doi:10.1021/acs.est.9b06531, 2020.

Simon, H., Reff, A., Wells, B., Xing, J. and Frank, N.: Ozone trends across the United States over a period of decreasing NOx and VOC emissions, Environ. Sci. Technol., 49(1), 186–195, doi:10.1021/es504514z, 2015.

Singh, H. B., Cai, C., Kaduwela, A., Weinheimer, A. and Wisthaler, A.: Interactions of fire emissions and urban pollution over California: Ozone formation and air quality simulations, Atmos. Environ., 56, 45–51, doi:10.1016/j.atmosenv.2012.03.046, 2012.

Steiner, A. L., Tonse, S., Cohen, R. C., Goldstein, A. H. and Harley, R. A.: Influence of future climate and emissions on regional air quality in California, J. Geophys. Res., 111(D18), D18303, doi:10.1029/2005JD006935, 2006.

Venecek, M. A., Cai, C., Kaduwela, A., Avise, J., Carter, W. P. L. and Kleeman, M. J.: Analysis of SAPRC16 chemical mechanism for ambient simulations, Atmos. Environ., 192, 136–150, doi:10.1016/J.ATMOSENV.2018.08.039, 2018.

Weaver, C. P., Liang, X. Z., Zhu, J., Adams, P. J., Amar, P., Avise, J., Caughey, M., Chen, J., Cohen, R. C., Cooter, E., Dawson, J. P., Gilliam, R., Gilliland, A., Goldstein, A. H., Grambsch, A., Grano, D., Guenther, A., Gustafson,

W. I., Harley, R. A., He, S., Hemming, B., Hogrefe, C., Huang, H. C., Hunt, S. W., Jacob, D. J., Kinney, P. L., Kunkel, K., Lamarque, J. F., Lamb, B., Larkin, N. K., Leung, L. R., Liao, K. J., Lin, J. T., Lynn, B. H., Manomaiphiboon, K., Mass, C., Mckenzie, D., Mickley, L. J., O'Neill, S. M., Nolte, C., Pandis, S. N., Racherla, P. N., Rosenzweig, C., Russell, A. G., Salathé, E., Steiner, A. L., Tagaris, E., Tao, Z., Tonse, S., Wiedinmyer, C., Williams, A., Winner, D. A., Woo, J. H., Wu, S. and Wuebbles, D. J.: A preliminary synthesis of modeled climate change impacts on U.S. regional ozone concentrations, Bull. Am. Meteorol. Soc., 90(12), 1843–1863, doi:10.1175/2009BAMS2568.1, 2009.

Ying, Q., Fraser, M. P., Griffin, R. J., Chen, J. and Kleeman, M. J.: Verification of a source-oriented externally mixed air quality model during a severe photochemical smog episode, Atmos. Environ., 41(7), 1521–1538, doi:10.1016/J.ATMOSENV.2006.10.004, 2007.