Review of "Direct Measurements of Ozone Response to Emissions Perturbations in California" by Shenglun Wu et al.

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**Summary:**

This paper aims to characterize the overall ozone response to NOx and VOC emission reductions in California by synthesizing satellite data with the results of experiments that perturbed the ambient photochemistry through in-the-field smog chamber runs. This is an interesting study that I think possibly can be developed into a useful addition to our understanding of ozone formation in California. However, there are two major shortcomings in the description and interpretation of the smog chamber experiments that prevent a full understanding of the experimental results and significantly impact the conclusions of the paper. These shortcomings are significant enough that I recommend that the paper be rejected until the authors are able to thoroughly address the issues discussed below.

It should be noted that my expertise is in laboratory and field measurements, and that I have little expertise in the interpretation of satellite data. The following comments focus on the smog chamber work; in my view this paper should not be accepted until it is reviewed by someone that does have the necessary experience to thoroughly review the satellite data interpretation.

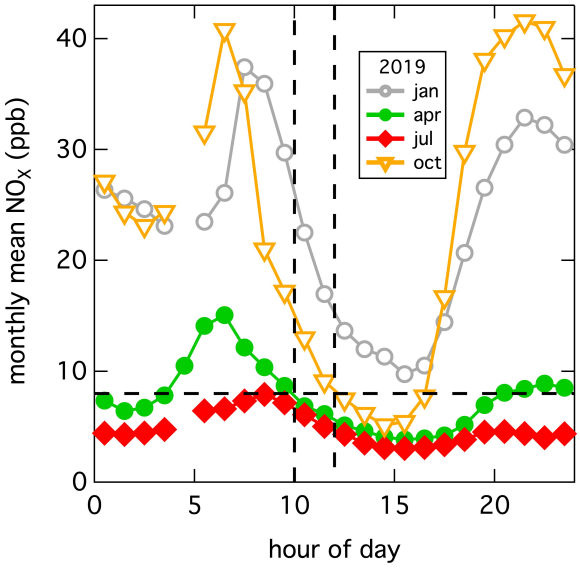
Given my major concerns regarding the smog chamber approach, I am unable to thoroughly review the Results, Discussion and Conclusions of the paper. Such a review must await resubmission of a manuscript that improves the experimental discussion.

**Major Issues:**

1. The first line of the abstract states: "A new technique was used to directly measure $O_3$ response to changes in precursor NOx and VOC concentrations in the atmosphere." However, neither this paper nor any of the references demonstrate the validity of this statement. In this regard, I see three major problems:
   a. 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. 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).
      - 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 $O_3$ response to changes in precursor NOx and VOC concentrations in the atmosphere"?

- 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.
- Ambient condition tests – Again, to develop confidence that the reported results actually "directly measure $O_3$ response to changes in precursor NOx 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.
- 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.




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 NOx and VOC, but likely that does not directly correspond to the sensitivity of the actual ozone concentrations in the ambient Sacramento boundary layer.

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 NOx 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 NOx (i.e., $\Delta O_3^{+NOx}$ 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 NOx 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 NOx perturbations relative to the initial ambient NOx concentrations in the chamber when the experimental run is initiated.

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 $O_3$ concentrations, but slightly increase intermediate $O_3$ concentrations until NOx levels fall far enough to re-enter the NOx-limited regime. The spatial pattern of increasing and decreasing $O_3$ 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.

**Minor Issues:**

1. Lines 54-61: These sentences discuss references that propose causes of the increase of $O_3$ 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 increase. 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).

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).

3. Lines 143-153: This same paragraph discusses the comparison of the $O_3$ increase in the basecase chamber and in the ambient air; that discussion is greatly oversimplified. In the ambient atmosphere, the early morning $O_3$ 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 $O_3$ formation in the chamber, therefore, captures a realistic "worst-case scenario" for surface-level $O_3$ 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).

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.
   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.

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.
   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?
   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.
   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.

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 $\Delta O_3$ 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).

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.

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 NOx, NOy, $O_3$, 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.

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.

**Reference:**

Bianco, L., et al. (2011), Diurnal Evolution and Annual Variability of Boundary-Layer Height and Its Correlation to Other Meteorological Variables in California's Central Valley. Boundary-Layer Meteorology, 140, 491-511, DOI 10.1007/s10546-011-9622-4.

Coates, J., K.A. Mar1, N. Ojha, and Tim M. Butler (2016), The influence of temperature on ozone production under varying NOx conditions – a modelling study, Atmos. Chem. Phys., 16, 11601–11615, doi:10.5194/acp-16-11601-2016.