Supplement of

Direct measurements of ozone response to emissions perturbations in California

Shenglun Wu et al.

Correspondence to: Michael J. Kleeman (mjkleeman@ucdavis.edu)

The copyright of individual parts of the supplement might differ from the article licence.
1. Configuration of transportable smog chamber system.

The distribution of lights was chosen (shown in Figure S1) 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.
2. Consistency of O₃ formation in smog chambers

A t-test applied to final O₃ concentration in 3 chambers has p-value < 0.03, illustrates the consistency of O₃ formation in 3 chambers.

Figure S2. Consistency check of three 1 m³ FEP bags using equal NOₓ-VOC mixture. Points near the origin were measured with zero air. The equation and R² shows the linear regression results of O₃ 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.
Figure S3. 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 O₃ 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.
4. CO*Biogenic calculation

Temperature and relative humidity-induced enhancement factor for isoprene emissions

\[ T = \frac{\exp[T_1(T_L - T_S)/RT_LT_S]}{1 + \exp[T_2(T_L - T_S)/RT_LT_S]} \]

Where \( T_L \) is the ambient temperature (kelvins), \( T_S \) is the normalizing temperature (301 k), \( R \) is the gas constant (8.314 J K\(^{-1}\)mol\(^{-1}\)), and \( T_1 (= 95100 J mol^{-1}) \), \( T_2 (= 231000 J mol^{-1}) \), \( T_3 (= 311.83 k) \) are empirical coefficient.

\[ H = RH \cdot H_1 + H_2 \]

Where RH is relative humidity (%) and \( H_1 (=0.00236) \) and \( H_2 (=0.8495) \) are empirical coefficients.

\[ CO * Biogenic = [CO] \times T \times H \]

Where [CO] is CO concentration (ppb) measured in the nearby monitoring station.

5. VOC reactivity (VOCR) and CO*Biogenic correlation

Figure S4 shows the correlation between the sum of species measured in the PAMS network multiplied by their O\(_3\) formation potential (= VOCR) vs. candidate surrogate measures of VOC reactivity (= CO and CO*biogenic). The p-value in each panel quantifies the probability that the surrogate has zero correlation with VOCR. The R-value in each panel quantifies the amount variation about the mean value of VOCR that is explained by the surrogate. CO*biogenic explains 36% of the VOCR variability about the mean VOCR value, while CO alone explains 15% of the VOCR variability about the mean VOCR value. CO*biogenic is therefore selected as the preferred (but not perfect) surrogate for VOC concentrations in the current study.

Figure S4. Scatter plot of VOC reactivity vs CO concentration (right) and CO*Biogenic (left) in Sacramento during the years 2010-2019. The shaded area shows the 95% confidence interval of the mean response of the predicted value. The CO, VOC, temperature, and RH data are all from standard monitoring site at Sacramento-Del Paso Manor. Data source: [https://aqs.epa.gov/aqsweb/airdata/download_files.html#Raw](https://aqs.epa.gov/aqsweb/airdata/download_files.html#Raw)
6. Location of chamber measurement site in Sacramento

Figure S5. Map shows the location of the sampling site in Sacramento and surrounding facilities. Powered by ESRI. The North CARB monitoring site (Sacramento - Bercut Drive) collects CO concentration used to calculate CO*Biogenic, the south CARB monitoring site (Sacramento-T Street) collects O₃, NOₓ concentration used as a quality check data source to the chamber measurement.
7. O$_3$ sensitivity measurement calculation

Figure S6. O$_3$ concentration in 3 chambers under the UV exposure during a typical chamber experiment on August 16, 2020 in Sacramento. Lines show the linear regression result of O$_3$ concentration under UV exposure in each chamber.

Figure S6 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 3 hr $O_3^{Bag1}$, 3 hr $O_3^{Bag2}$, and 3 hr $O_3^{Bag3}$). The measured sensitivities $\Delta O_3^{+NOx}$ and $\Delta O_3^{+VOC}$ were calculated using the equation below:

$$\Delta O_3^{+NOx} = 3\text{hr} \ O_3^{Bag2} - 3\text{hr} \ O_3^{Bag1}$$

$$\Delta O_3^{+VOC} = 3\text{hr} \ O_3^{Bag3} - 3\text{hr} \ O_3^{Bag1}$$
8. Comparison between wildfire days and non-wildfire days in TROPOMI data

Figure S7. Monthly box and whisker plot of TROPOMI HCHO and NO2 in wildfire days (solid box) and non-wildfire days (open box) from August to October, 2020. TROPOMI HCHO and NO2 is in the 5km radii buffer of the chamber measurement site in Sacramento.
9. Chamber and satellite $O_3$ sensitivity correlation

Figure S8. Correlation between weekly averaged TROPOMI satellite HCHO/NO$_2$ at other two circular buffers (2.5 km (top) and 7.5 km (bottom)) and the weekly averaged chamber $\Delta O_3^{+NO_x}$ from ground-based measurement. The shaded area shows the 95% confidence interval of the mean response of the predicted value.
Figure S9. Correlation between weekly averaged TROPOMI HCHO/NO₂ at 5 km circular buffers and the weekly averaged \( \Delta O_3^{+NO_x} \) from ground-based measurement during non-wildfire days. The shaded area shows the 95% confidence interval of the mean response of the predicted value. Red regression line generated using ordinary least squares regression. Green regression line generated using reduced major axis regression.
## 10. Monthly variance of TROPOMI HCHO/NO2 in California

Table S1. Monthly averaged TROPOMI satellite HCHO/NO2 for all air basins in California

| Air Basin        | N  | Feb | Mar | Apr | May | June | July | Aug  | Sept | Oct  |
|------------------|----|-----|-----|-----|-----|------|------|------|------|------|
| Northeast Plateau| 1701 | 4.7 | 3.5 | 3.4 | 5.7 | 12.4 | 10.9 | 11.0 | 6.8  |
|                  |     | (1.9) | (1.3) | (1.2) | (1.2) | (2.4) | (2.2) | (1.7) | (0.9) |
| North Coast      | 1349 | 5.0 | 4.1 | 4.1 | 5.2 | 12.6 | 11.5 |      |      |      |
|                  |     | (1.6) | (1.1) | (1.5) | (1.1) | (2.8) | (2.2) | 9.4  | 6.5  |
| Sacramento       | 1643 | 3.9 | 3.2 | 3.4 | 4.7 | 11.3 | 10.7 | 5.9  |      |      |
| Mountain Counties| 1329 | 3.6 | 3.5 | 3.3 | 4.5 | 11.9 |      | 10.8 | 7.0  |      |
|                  |     | (1.4) | (1.4) | (1.3) | (0.9) | (2.3) | 9.8  | (1.8) | (2.4) | (1.7) |
| Lake County      | 144  | 4.5 | 4.0 | 4.5 | 5.0 | 10.2 | 12.1 | 10.3 | 5.9  |      |
|                  |     | (1.1) | (1.2) | (1.1) | (1.0) | (1.4) | (2.0) | (2.2) | (0.7) |      |
| Lake Tahoe       | 40   | 2.4 | 2.8 | 2.6 | 3.5 | 11.2 | 11.7 | 6.2  |      |      |
| Great Basin      | 3.4  | 2.7 | 3.3 | 5.0 | 10.2 | 10.6 |      |      |      |      |
| Valleys          | 1492 | (1.2) | (1.2) | (1.4) | (1.0) | (1.7) | (2.6) | 8.3  | 1.9  | 9.9  |
|                  |     | (1.2) | (1.2) | (1.4) | (1.0) | (1.7) | (2.6) | 8.3  | 1.9  | 9.9  |
| San Francisco    | 1.8  | 2.4 | 2.6 | 3.6 |      |      |      |      | 3.8  |      |
| Bay              | 583  | (0.9) | (0.8) | (0.9) | (0.8) | 6.2  | 6.5  | 6.0  | 7.4  | 1.6  |
| San Joaquin      | 2.6  | 2.6 | 3.3 | 4.3 |      |      |      |      |      | 6.4  |
| Valley           | 2473 | (1.4) | (1.3) | (1.4) | (1.2) | 8.2  | 8.7  | 7.5  | 7.7  | 1.6  |
|                  |     | (1.4) | (1.3) | (1.4) | (1.2) | 8.2  | 8.7  | 7.5  | 7.7  | 1.6  |
| North Central    | 2.8  | 2.9 | 3.7 | 4.9 |      |      |      |      | 5.6  |      |
| Coast            | 542  | (0.7) | (1.0) | (1.0) | (0.8) | 7.4  | 8.4  | 7.4  | 8.2  | 1.2  |
|                  |     | (0.7) | (1.0) | (1.0) | (0.8) | 7.4  | 8.4  | 7.4  | 8.2  | 1.2  |
| Mojave Desert    | 2766 | 2.6 | 2.6 | 3.7 | 4.5 |      |      |      | 5.3  |      |
| South Central    | 791  | 2.7 | 2.6 | 3.9 | 5.2 |      |      |      | 6.7  |      |
| Coast            | 1.1  | 1.5 | 2.5 | 3.4 |      |      |      |      |      | 3.0  |
| South Coast      | 689  | 0.6 | 0.7 | 0.9 | 0.7 | 8.8  | 9.4  | 8.5  | 9.6  | 1.3  |
|                  |     | (0.6) | (0.7) | (0.9) | (0.7) | 8.8  | 9.4  | 8.5  | 9.6  | 1.3  |
| Salton Sea       | 663  | 2.5 | 3.1 | 3.9 | 4.8 |      |      |      | 4.8  |      |
| San Diego County | 429  | 0.6 | 0.6 | 0.6 | 0.6 | 7.2  | 7.7  | 7.1  | 6.5  | 1.1  |
|                  |     | (0.6) | (0.6) | (0.6) | (0.6) | 7.2  | 7.7  | 7.1  | 6.5  | 1.1  |

Note: Mean (SD) of TROPOMI (HCHO/NO2) shown.
Figure S10. Spatial distribution of O₃ sensitivity regime based on TROPOMI satellite (HCHO/NO₂) ratios in Los Angeles for April – October 2020. Light area is in NOₓ-limited regime (HCHO/NO₂ > 4.6), dark area is in NOₓ-saturated regime (HCHO/NO₂ <= 4.6).
11. Sensitivity analysis

Figure S11. 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.
Figure S12. Effect of temperature, radiation, and perturbation amount on the monthly variation of the predicted chamber ∆O₃^{VOC} from April to December, 2020 at the Sacramento measurement site. Open box constantly shows the calculation under chamber measurement condition (chamber temperature, radiation, and 8ppb VOC perturbation). Solid box reflects the calculation under the change of different condition: (a) under the ambient temperature profile; (b) clear-sky solar radiation; (c) perturbation amount effect: 2 ppb VOC perturbations; (d) the combination of ambient temperature, solar radiation, and 2ppb VOC perturbation.
Figure S13. Measured ΔO₃ as a function of different NOₓ perturbations. Total number of data points is 24.

Reference

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.

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., Mitloehner, F., Stackhouse, K., Green, P. G., Flocchini, R. G. and Kleeman, M. J.: Direct measurements of the ozone formation potential from livestock and poultry waste emissions, Environ. Sci. Technol., 44(7), 2292–2298, doi:10.1021/es901916b, 2010a.

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, 2010b.

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.

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.