A31I-0174

Wildfire and soil emissions of NOx observed at a remote mountaintop site in Central California

Elizabeth Asher, Stephen Conley, and Ian Faloona
Department of Land, Air, & Water Resources, University of California

Abstract

Nitric oxide (NO_x) emissions contribute to the production of tropospheric ozone and the nutrient supply fueling primary production. Current global estimates indicate that biomass burning (including wildfires) and soil emissions represent ~5.5 TgN yr^{-1} and ~7.3 TgN yr^{-1} respectively of a ~48.8 TgN yr^{-1} budget (IPCC Report 2013). As domestic air quality standards grow stricter and anthropogenic sources more regulated, however, constraining natural sources of NO_x is critical. NO_x concentrations in wildfire smoke vary based on the age of the smoke plume, the fire intensity and vegetation type. NO_x soil emissions depend on soil moisture, as well as nitrogen storage, temperature, and soil porosity. We present NO_x and ozone (O_3) measurements from a remote mountaintop monitoring site located on Chews Ridge in the coastal mountains of Central California, airborne observations, and soil moisture measurements obtained from a local in situ soil moisture sensor from the summer and fall of 2015 and 2016. Our observations include measurements directly downwind of the Soberanes wildfire, which endured 83 days beginning on July 22, 2016 and burned 132,127 acres.

Hypotheses

1) Biomass burning will lead to net ozone production and elevated O_3 concentrations, even though the Chews Ridge site is typically characterized by net O_3 destruction.
2) Soil emissions of NO_x are related to soil moisture. These emissions constitute a quantifiable natural source of NO_x to this site. However, sustained elevated soil temperatures due to widespread biomass burning could decimate soil microbial populations, yielding lower NO_x soil emissions.

Methods

We collected NO_x and O_3 measurements using the Thermo Scientific Model 42i-TL NOx Analyzer and the 2B Technology Ozone Monitor Model 202 from June, 2015 - December, 2016. Soil moisture data for station Qcs2 is courtesy of the University of Colorado, where GPS receivers in the soil measure ground reflections that are strongly influenced by in soil moisture (Larson et al. 2008). The Oliver Observing station, maintained by the Monterey Institute for Research in Astronomy, provided the meteorological data for Chews Ridge. We also used High Resolution Rapid Refresh (HRRR) meteorology to calculate Hysplit back trajectories between Chews Ridge and the Soberanes fire region.

The instruments were calibrated every ~3 months—the NO_x Analyzer using gas-phase titration of NO with 800 ppb O_3 and the Ozone Monitor with a 2B Technology Ozone Calibrator Model 306. Calibration curves were applied to raw NO_x and O_3 data, and these data were binned hourly for comparison with meteorological data, or binned daily for comparison with soil moisture data.

We calculated the surface emissions from soils using a steady state NO_x measurement, the boundary layer height, z_i, the chemical lifetime of NO_x with respect to OH, τ_NOx, and the entrainment velocity, w_e (equation 1). Based on extensive aircraft surveys in this region, we use an average entrainment velocity of ~1cm s^{-1} (scaled to a 24-hour day from maximum entrainment velocities of ~4 cm s^{-1} at midday (Trousdell et al., 2016; Karl et al., 2013), and a boundary layer height of 800 m. The lifetime of NO_x was estimated using the reaction rate, as 8.2E-12 cm^3 $molec^{-1}$ s^{-1} using a pressure of 865 mb and temperature of 300 K (Sander et al. 2011) and maximum OH concentration (at midday) of ~3-4E6 molec cm^3, yielding a lifetime of ~32 hours.

$$1.\quad Flux_0 = [NO_x]_{SS}\left(\frac{z_i}{\tau_{NOx}} + w_e\right)$$

Although substantial fluctuations in NO_x concentrations (i.e. not a steady state measurement) prevented us from calcuating surface emissions related to the Soberanes wildfire, we did calculate ozone production in July – Nov., 2016. This calculation employed measurements of O_3, NO_x, the photolytic loss of NO_2, J_{NO2}, from the NCAR TUV model, and the reaction rate between NO and O_3 (k_1 = 1.9 E-14; equation 2). NO_2* is used to account for the presence of NO_y confounding the Thermo Scientific NOx measurement and is calculated as 0.75* NOx according to Chu and Meyer (1991).

$$2.\quad O_3\,production = NO\left(JNO_2\frac{NO_{2*}}{NO} - O_3K_1\right)$$

Unfortunately, we are missing meteorological data for the period of September 5 – October 8, 2016 due to a technical malfunction involving data transfer to our server.

Results

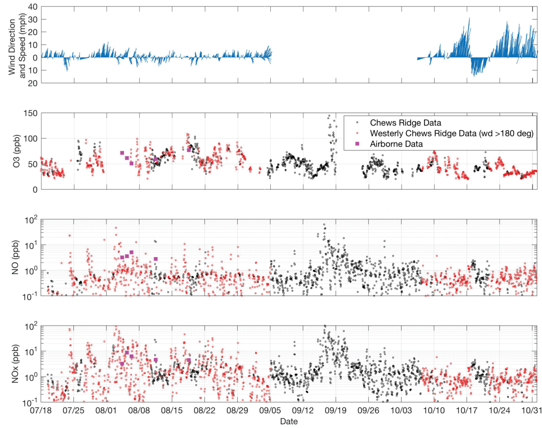


Figure 1. Time series of O_3, NO_x, and NO at Chews Ridge during the Soberanes wildfire of 2016. Concentrations of O_3, NO_x and NO were elevated given westerly winds (i.e. transport from the direction of the fire).

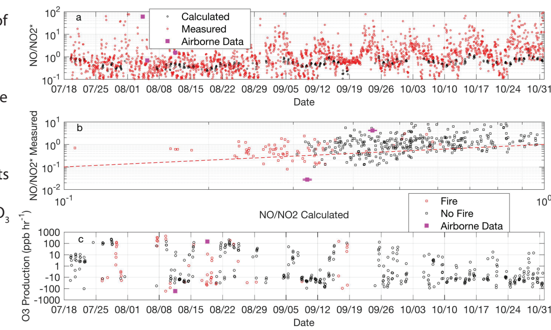


Figure 3. Time series of calculated and measured NO/NO_2* (a), relationship between calculated NO/NO_2* and measured NO/NO_2* - note the 1-1 dashed line (b), and a time series of calculated net ozone production (c). Fire-influenced measurements were determined using an arbitrary chemical criterion (O_3 > 70 ppb; NO_x > 6ppb).

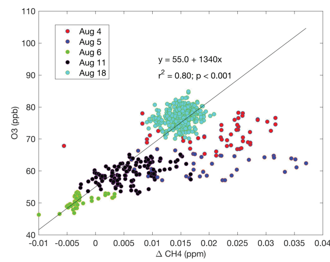


Figure 2. Airborne measurements of CH_4 and O_3 on five flights during the 2016 field campaign (and the Soberanes fire). Strong correlation between O_3 and CH_4 suggests that O_3 was elevated in response to biomass burning.

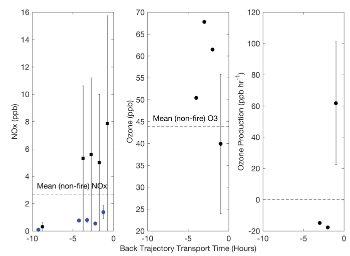


Figure 4. We ran 40 Hysplit back trajectories from July 22 - Sept. 5, each ending at 8pm UTC. We defined a quadrant of potential fire influence based on inspection of satellite images (36.3 – 36.5 N and 121.7 – 121.9 W). Minimum back trajectory times through this quadrant are compared with corresponding NO_x, NO, O_3 and O_3 production. Error bars represent the SD of multiple back trajectories (14 of 40 back trajectories passed through this quadrant within 18 hours).

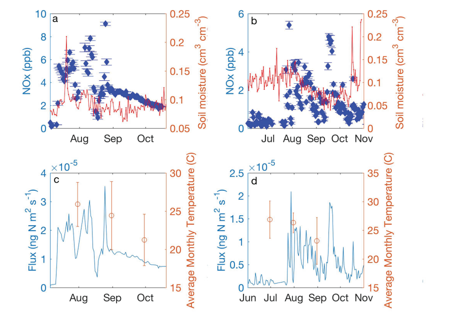
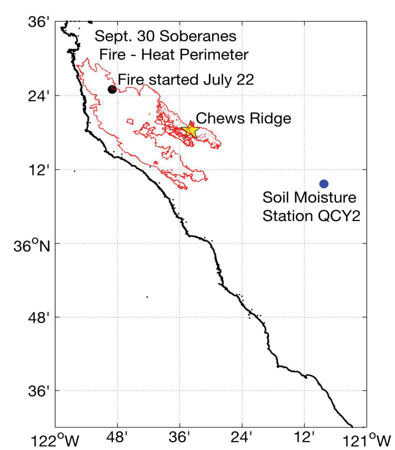


Figure 5. Time series of NO_x at Chews Ridge, local daily measurements of soil moisture and monthly mean temperatures (error bars represent the SD). NO_x was correlated with soil moisture (r^2 = 0.28, p < 0.001).

Map of field site and fire



Conclusions

- We observed elevated O_3 concentrations as a result of the Soberanes wildfire in 2016. (Figures 1 and 2)
- Ozone production at chews ridge is typically negative. During the Soberanes wildfire, however, we calculated apparent high net ozone production at Chews Ridge (>10 ppb hr-1). (Figures 3 and 4)
- Elevated (calculated) ozone production, (measured) ozone concentrations, and NO_x appear related to the transport time from the wildfire. Shorter transport times lead to elevated NO_x and ozone production. Maximum ozone concentrations were observed with transport times > 1 hour. (Figure 4)
- Soil emissions of NO_x at Chews Ridge appear weakly related to local measurements of soil moisture (r^2 = 0.28, p <0.001). This relationship breaks down, however, in 2016 following the Soberanes wildfire. (Figure 5)

Chu, S.H. and E.L. Meyer, 1991. Use of Ambient Ratios to Estimate Impact of NOx Sources on Annual NO2 Concentrations. Proceedings, 84th Annual Meeting & Exhibition of the Air & Waste Management Association, Vancouver, B.C.; 16–21 June 1991. (16pp.) (Docket No. A–92–65, II–A–9).
Karl, T., Misztal, P. K., Jonsson, H. H., Shertz, S., Goldstein, A. H. and Guenther, A. B.: Airborne Flux Measurements of BVOCs above Californian Oak Forests: Experimental Investigation of Surface and Entrainment Fluxes, OH Densities, and Damköhler Numbers, J. Atmos. Sci., 70(10), 3277-287, 2013.
Larson, K.M., E.E. Small, E. Gutmann, A. Bilich, J. Braun, V. Zavorotny, Use of GPS receivers as a soil moisture network for water cycle studies, Geophys. Res. Lett., 35, L24405, doi:10.1029/2008GL036013, 2008.
Sander, S. P., Abbatt, J., Barker, J. R., Burkholder, J. B., Friedl, R. R., Golden, D. M., Huie, R. E., Kolb, C. E., Kurylo, M. J., Moortgat, G. K., Orkin, V. L., and Wine, P. H.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation number 17, NASA Panel for data evaluation, JPL Publication 10-6, Jet Propulsion Laboratory, Pasadena, http: //jpldataeval.jpl.nasa.gov, 2011.
Trousdell, J. F., S. A. Conley, A. Post, and I. C. Faloona (2016), Observing Entrainment Mixing, Photochemical Ozone Production, and Regional Methane Emissions by Aircraft Using a Simple Mixed-Layer Model, Atmospheric Chemistry and Physics Discussions, 1–33, doi:10.5194/acp-2016-635.

Acknowledgements: This project was supported by the San Joaquin Pollution Control District. We would like to extend a personal thank you to PhD student Dani Caputi and undergraduate JeanellSmoot.