SURFACE OZONE IN THE NORTHERN FRONT RANGE AND THE INFLUENCE OF OIL AND GAS DEVELOPMENT ON OZONE PRODUCTION DURING FRAPPE/DISCOVER-AQ

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Overview

- Surface ozone ($O_3$) in Front Range
  - Motivations
  - “Background” $O_3$ from surface sites
  - Summer 2014 $O_3$ summary
  - Spatial variability at surface sites

- Case studies
  - Three days
  - Mobile lab drives
  - Surface monitoring stations
  - Discrete air samples in flasks
Motivations

- Surface ozone (O₃) in Front Range
  - Nonattainment area since 2007
  - EPA NAAQS:
    - During summer 2014: 75 ppb for 4th highest 8-hr average daily max averaged over 3 years
    - 2015-present: 70 ppb

- O₃ precursors:
  - VOCs + NOx + sunlight = O₃
  - Statewide NOx reductions but still exceeding O₃ standard
  - VOC sources play a role
  - Oil and gas activities major source of VOCs in the Front Range
“Background” $\text{O}_3$

- Estimated underlying $\text{O}_3$ distribution on days without significant photochemical production to be 45-50 ppb
- Used long-term data from Niwot Ridge on days without significant upslope events

Days w/ peak $\text{O}_3$ <60 ppb (Jun-Aug 2013-2015)
- ~35% of days in Front Range, 56% of days at Niwot Ridge

Days w/ peak $\text{O}_3$ >75 ppb (Jun-Aug 2013-2015)
- ~15% of days in Front Range, 10% of days at Niwot Ridge
Summer 2014 and Spatial Variability

- July 16 – August 16, 2014: FRAPPE and DISCOVER-AQ field campaigns
- Cool and damp during July and August, 2014
- 2014 was low O₃ summer overall
- Some days O₃ high at multiple sites, other days more localized
  - Influence of local and regional precursor sources
  - High O₃ observed throughout Front Range and not confined to Denver area
Case Studies

- Dates: July 23, August 3, August 13, 2014
- Weather summary
  - July 23: max temp 32°C, clear sky after AM
  - August 3: max temp 31°C, clear sky
  - August 13: max temp 33°C, clear sky
- Types of data included
  - Mobile laboratory gas measurements (Aerodyne)
  - Mobile laboratory wind data (Aerodyne)
  - Discrete air samples in flasks (UC Irvine)
  - Surface monitoring sites (CDPHE, NOAA, and NASA)
July 23: O&G emissions, moderate O$_3$ levels

Drive start: 10:00 (LST)
Drive end: 16:10
Surface O$_3$ at monitoring sites:
- BAO: >75 ppb
- Platteville: >75 ppb
- Greeley, Fort Collins, Niwot Ridge all moderate
July 23: O&G emissions, moderate O₃ levels

Wind rose from mobile lab during 14:00-16:10

Gases measured on mobile lab:
- O₃
- Methane (oil and gas, agriculture, landfills, wastewater treatment plants)
- Ethane (oil and gas)
- Carbon Monoxide (urban)
- Ammonia (agriculture)
- Nitrous Oxide (agriculture and wastewater treatment plants)

Low emission levels overall during drive
Increased concentrations at 4:00 PM coincided with regional shift in surface winds
August 3: Mixed emissions, high $\text{O}_3$ day

Drive start: 10:15
Drive end: 18:00 (interrupted at 12:45)
High $\text{O}_3$ at monitoring sites:
- Greeley: >80 ppb
- FTC (both sites): >80 ppb
August 3: Mixed emissions, high O$_3$ day

Wind rose from mobile lab during 11:15-13:00

- Increasing O$_3$ production, ethane, and methane during drive
- Oil and gas influence
- Decreasing CO with increasing O$_3$
- Urban emissions not dominating O$_3$ formation
- Higher ammonia and nitrous oxide
- Agricultural emissions present
- Less potential for O$_3$ production from these sources
August 13: O&G emissions and localized elevated O₃

Drive start: 7:20
Drive end: 14:20
High O₃ at monitoring sites:
- FTC-CSU: peak of ~90 ppb
- Greeley and Platteville: peak of ~70 ppb
August 13: O&G emissions and localized elevated $O_3$

- High $O_3$ in remote area
  - Linked to elevated ethane and methane
  - Likely oil and gas precursor source
- Lower, background levels of agricultural and urban emissions
  - Slightly elevated CO correlated with ethane but not acetylene
- $O_3$ levels at ~30 ppb above background
Conclusions

- "Background" \( \text{O}_3 \) in Front Range \(~40-45\) ppb
- Mobile lab drives measuring \( \text{O}_3 \) at \(30-35\) ppb above "background"
- Influence from four main sectors on local emissions as seen in methane levels:
  - Oil and gas, urban, agriculture, wastewater treatment plants
- Large influence of oil and gas emissions on \( \text{O}_3 \) formation:
  - Some influence of urban emissions on \( \text{O}_3 \)
  - All case studies show potential influence of oil and gas
  - Aug 13 shows most unambiguous evidence of oil and gas as source of \( \text{O}_3 \) precursors with enhancement up to \(30\) ppb of \( \text{O}_3 \)
Additional Slides

Surface Sites NE of Greeley
Isoprene in Flasks
MesoWest Winds August 13
References
Additional NE Sites

Growth Rates
- Pawnee Buttes = 3.30 ppb/hr
- Niwot Ridge = 1.04 ppb/hr
- Briggsdale = 8.30 ppb/hr
- Greeley = 8.80 ppb/hr

All days June, July, August 2013-2015
Additional NE Sites

Days w/ peak $O_3 < 60$ ppb  
Days w/ peak $O_3 > 75$ ppb
Additional NE Sites – 1 Week
Isoprene in Platteville

- Isoprene is the most prevalent naturally occurring biogenic VOC in the northern Front Range and the average mixing ratio measured at the BAO Tower during the summer of 2015 was 0.2 ppb (Abeleira et al., 2017)

- Measurements of isoprene in Platteville
  - July 23 average: 0.04 ppb
  - August 3 average: 0.03 ppb
  - August 13 average: 0.06 ppb

- All case study values less than the 0.2 ppb average measured at BAO Tower during summer 2014. Biogenic VOCs likely did not contribute as much to O₃ production during case studies than during summer 2015.


