Chemical Characteristics and Ozone Production in the Northern Colorado Front Range

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We use the extensive set of aircraft and ground-based observations from the NSF/NCAR and State of Colorado Front Range Air Pollution and Photochemistry Éxperiment (FRAPPÉ) and the NASA DISCOVER-AQ experiments in summer 2014 together with WRF-Chem simulations to study the ozone production and chemical regimes in the Northern Colorado Front Range (NFR). We apply the Integrated Reaction Rate (IRR) capability that will be released with WRF-Chem version 4 and the chemical tendencies diagnostics and present preliminary results from an in-depth analysis of the ozone formation in various NFR regions for a case study of 12 August 2014. We further apply these diagnostics along WRF online trajectories to assess the chemical evolution of air masses as they are transported from the NFR to the mountains during upslope events. The results show efficient ozone production within the NFR driven by high NOx and high VOCs (specifically higher alkanes and aldehydes) and also continued ozone production during the transport into the mountains.

• Model Simulations and Observations

Case Study: 12 August 2014

Observations: NCAR/NSF C-130 Observations
Surface O_3 from all available monitors

Simulations
- WRF-Chem Version 4.0 beta
- 2-domain setup (12km and 4km)
- IC&BC: ECMWF (meteorology), MOZART-4 (chemistry)
- YSU PBL, Monin-Obukhov Similarity scheme, NOAA Land model
- 51 vertical levels between surface and 50 hPa
- Meteorological initialization every 24 hours at 6 UTC from 10 Aug – 13 August, results are analyzed for 12 August
- Analysis nudging in d01; in d02 until last cycle
- Chemical Mechanism: MOZART-MOSAIC_4_bin
- Emissions (updates based on evaluation with campaign data):
  - Biogenic: MEGAN online (isoprene*0.5, monoterpenes*1.5)
  - Fires: FINN with online plumerise
  - Anthropogenic: NEI 2011v2 (Stu McKeen) with
    - Mobile Emissions -50%
    - Oil and Gas Emissions *2 (not NO_x, C_2H_6 and C_3H_8)

Here we make use of three diagnostics tools available in WRF-Chem: Chemical Diagnostics, Integrated Reaction Rates, Online Trajectories

• Regional Analysis

We conduct analysis for 4 regions (Fig 1) based on emission characteristics: Larger Denver area (**City**) and an area dominated by oil and natural gas production (**OG**) in the NFR; two regions in the Foothills: a region North (**FHnorth**) and a region South (**FHsouth**). The average composition within the boundary layer (PBL) is analyzed. Note that chemistry is not only impacted by the emissions but also by airmass exchange between the regions.

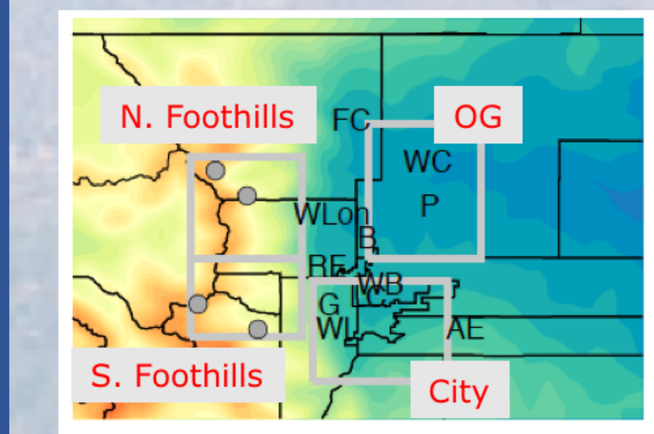

Fig1: Elevation contours and selected regions. Letters indicate NFR surface sites, grey circles the mountain sites.

O_3 Concentrations

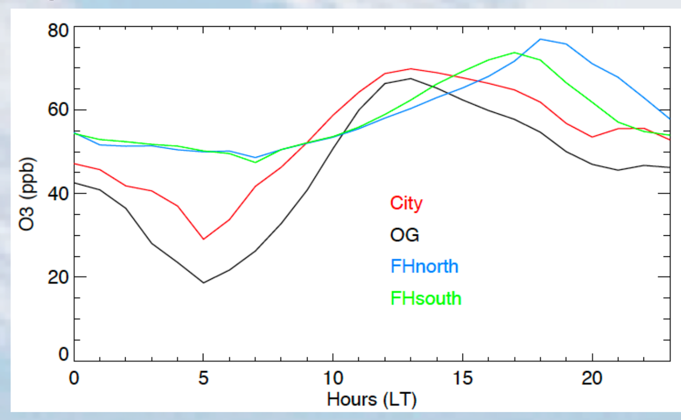

Fig2: Surface O_3 (ppb) for 12 August.

- O_3 in NFR peaks mid-day;
- O_3 is higher for City compared to OG.
- FHnorth and FHsouth peak later after upslope transports NFR airmasses to mountains.
- Peak O_3 is highest for Foothills regions.

O_3 Net Chemical Production Tendencies (Chem_O_3)

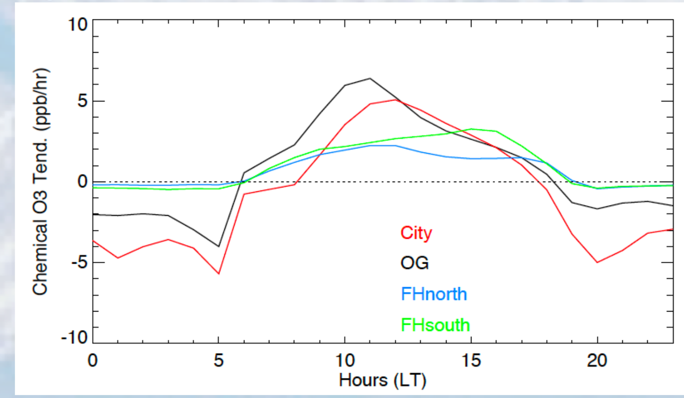

Fig3: Chemical O_3 Tendencies (ppb/hr)

- Chem_O_3 peaks in OG
- Strongest nighttime titration in City (largest NOx)
- Total Chem_O_3 for 8-18LT:
  21 ppb (City
  36 ppb (OG)
  25 ppb (FHsouth)
  17 ppb (FHnorth)

OH Reactivity by VOC

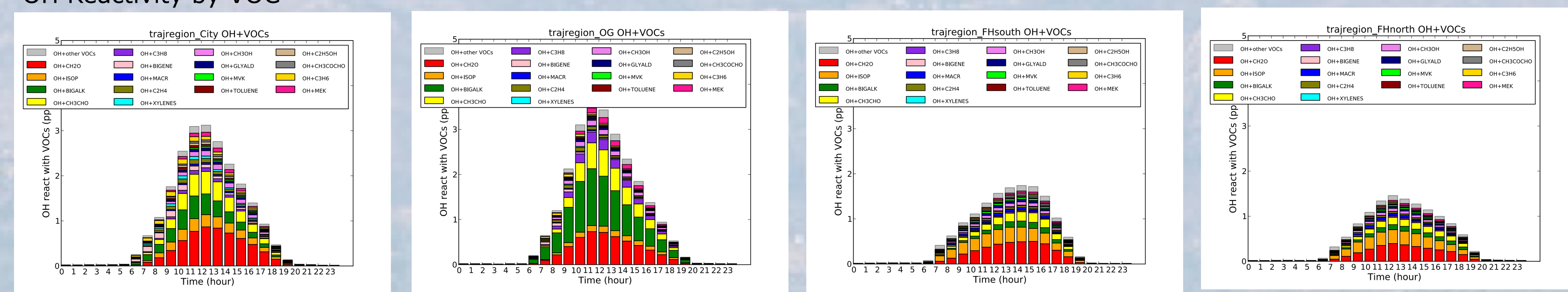

Fig 4: IRR derived total OH reactivity by VOC species.

BIGALK represents lumped higher alkanes.

- OH reactivity largest in OG and in Foothills ~1/3rd of NFR regions.
- HCHO, BIGALK and isoprene play most important role in all regions. Others contribute ~10-30%.
- While BIGALK and isoprene are mostly from emissions, HCHO has both, emissions and chemical production
- Most dominant VOC in OG is BIGALK followed by HCHO and CH3CHO (acetaldehyde). C_3H_8 also plays larger role.
- Most dominant VOC in city is HCHO followed by acetaldehyde and BIGALK.
- Isoprene higher for City than OG (green parks and gardens).
- Importance of isoprene increases in Foothills (due to biogenic emissions)

• Model Evaluation

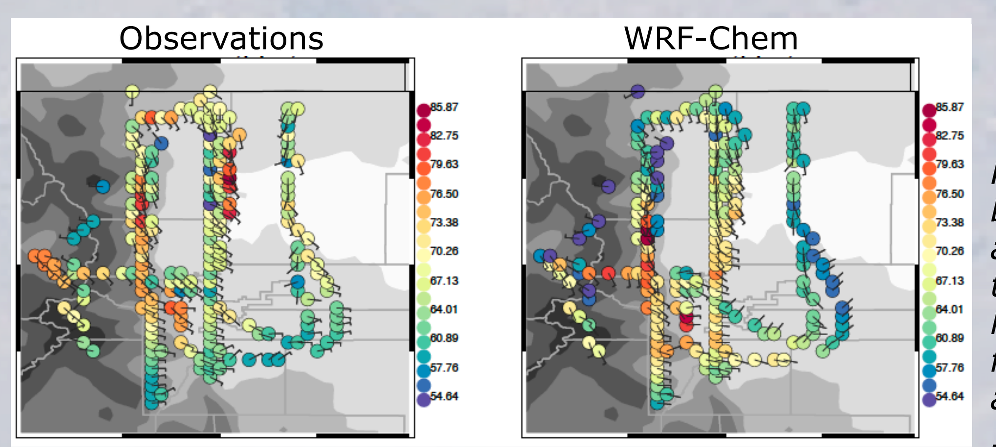

Fig 10: O_3 (ppb) below 1500m agl along C130 flight track for both flight legs combined (Leg1 from ~12-15:30LT and Leg2 from 16:30-20:30 LT).

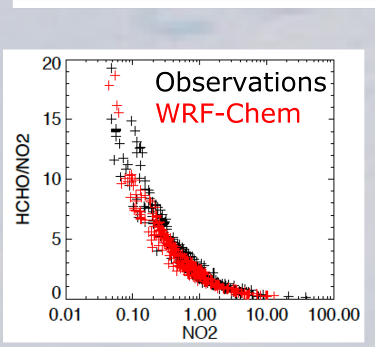

Fig 10: $HCHO/NO_2$ ratio as function of NO_2 (ppb) for C-130 data below 1500m agl.

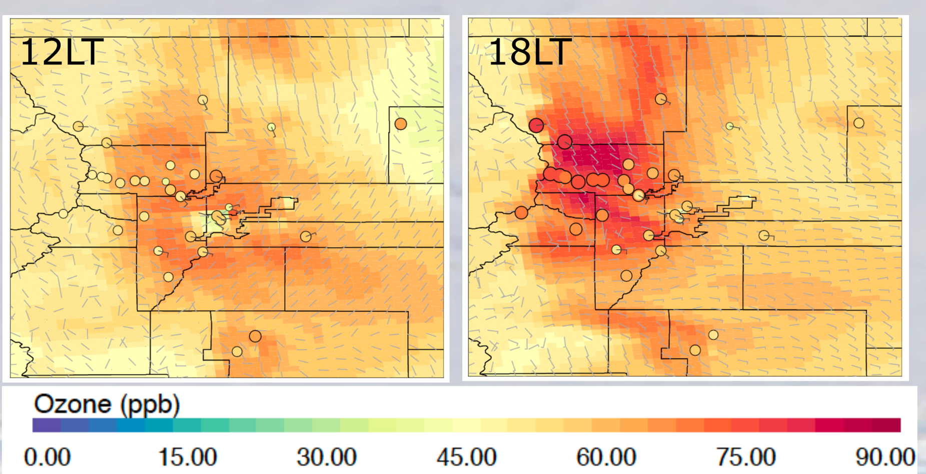

Fig 11: O_3 surface concentrations (ppb) and winds from WRF-Chem and surface monitors.

- Transport errors in the morning in the Eastern NFR bring too much oil/gas emissions into the city resulting in incorrect representation of emission transport and in spatial distribution of O_3 concentrations. (⇒ ozone is too high in City and too low in OG)
- Overall, however, WRF-Chem represents the chemical characteristics (e.g. $HCHO/NO_2$ ratios)
- Model slightly overpredicts surface O_3 and better represents the afternoon compared to the morning in line with aircraft data.
- WRF-Chem represents well the strong upslope flows on this day.

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• Origin of HCHO in OG & City region

We conducted a sensitivity run without direct emissions of HCHO to estimate the contribution of direct emissions vs chemical production.

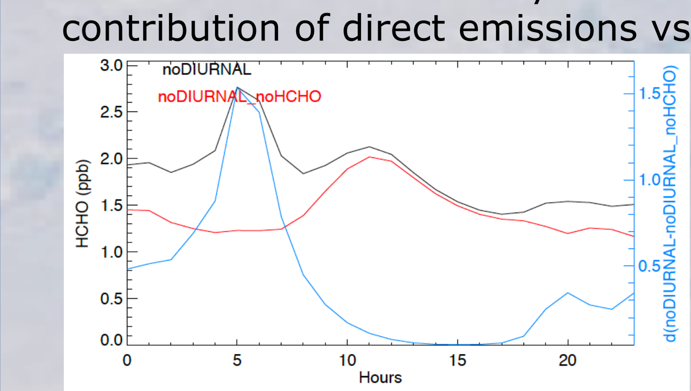

Fig 5: Absolute HCHO for the two runs and difference. Results for OG area.

HCHO reduction up to ~50% in OG and ~25% in City (not shown) early morning, small for other times. With direct emissions, HCHO diurnal concentrations peak early morning when O_3 production is low. Midday peak in HCHO, when O_3 production is high, is mostly due to chemical production -> Small changes in O_3 (< 0.5 ppb).

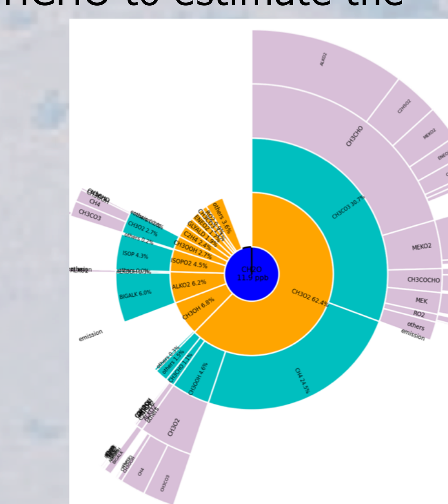

Fig 6: Origin of chemically produced HCHO for OG area.

A large part of HCHO chemical production is traced back to BIGALK, CH_4 and CH3CHO.

• Trajectory Analysis

Concentrations, tendencies, and IRR analysis along WRF trajectories. Trajectory 196 (T196) is shown as example.

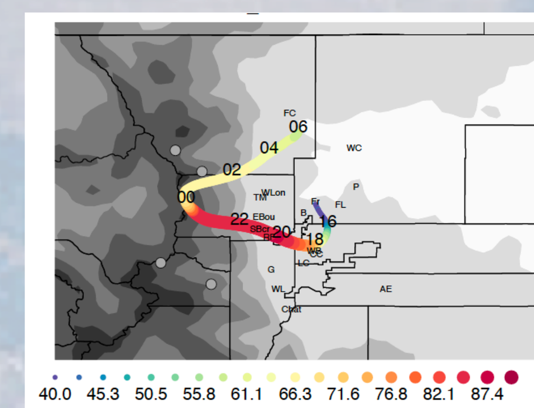

Fig 7: O_3 (ppb) along T_196 with time (UTC). T196 was released near surface in OG at 14 UTC (8 LT). SE flow changes to upslope ~18 UTC (12 LT). T196 travels towards Foothills, not going over Denver; in PBL until 00 UTC (18 LT).

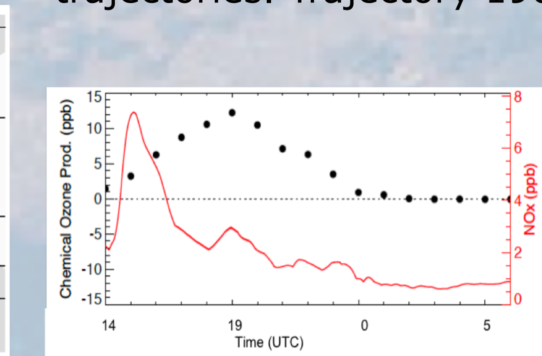

Fig 8: Chem_O3 (ppb/hr) and NOx (ppb) along T196.

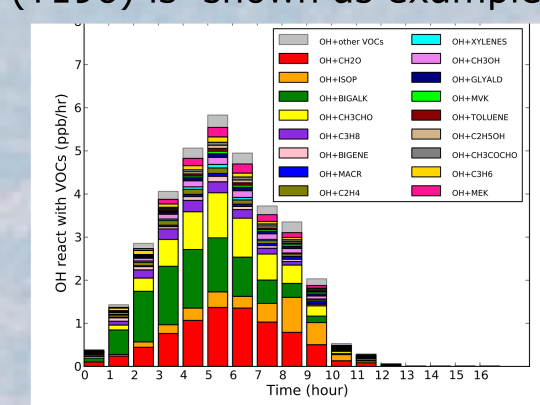

Fig 9: T196 IRR derived total OH reactivity by VOC species.

- Peak Chem_O_3 ~10 ppb/hr; OH reactivity ~6 ppb/hr
- Continued O_3 production during transport into mountains
- HCHO, BIGALK and acetaldehyde are major contributors
- Isoprene contribution increases in afternoon when T196 is in Foothills (biogenic sources)

Summary

The combined analysis of three different WRF-Chem diagnostics is used to study the relevance of VOCs on O_3 production in the NFR. The most relevant VOCs for O_3 production are estimated as HCHO, BIGALK (lumped higher alkanes, mostly from oil and gas emissions) and CH3CHO. A sensitivity study without HCHO direct emissions suggests HCHO is more strongly impacted by photochemical production than direct emissions. Similar results are found for CH3CHO. BIGALK plays a major role in the chemical production of both species. The findings are in line with results from the FRAPPÉ State of Colorado final report where oil and gas emissions were identified as one of the major drivers of O_3 pollution and with studies that concluded a large contribution from higher alkanes (Hornbrook at el., AGU 2016; McDuffie et al., 2016). O_3 production continues during the transport of NFR airmasses into the mountains with the relative importance of isoprene increasing as fresh emissions from biogenic sources become the only fresh emission source.

McDuffie, E.E., et al., J. Geophys. Res. Atmos., 121, doi:10.1002/2016JD025265, 2016.
Hornbrook at al. AGU Fall Meeting 2015, https://agu.confex.com/agu/fm15/meetingapp.cgi/Paper/74084

Acknowledgement

The data for this paper are publicly available at the FRAPPÉ/DISCOVER-AQ data archive (http://www-air.larc.nasa.gov/missions/discover-aq/discover-aq.html). The authors thank the State of Colorado/Colorado Department of Public Health and Environment and the National Science Foundation (NSF) for funding of FRAPPÉ and NASA for funding of DISCOVER-AQ. The authors acknowledge the use of WRF-Chem version 4.0 beta and Stu McKeen at NOAA for providing the NEI 2011 emissions inventory. The National Center for Atmospheric Research is sponsored by the National Science Foundation.