Influence of Oil and Gas Emissions on Summertime Ozone in the Colorado Northern Front Range

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GOAL: DETERMINE THE CONTRIBUTION OF REGIONAL EMISSION SOURCES TO OZONE IN THE COLORADO FRONT RANGE

Why Ozone?
- Toposophic ozone (O₃) is a health hazard and greenhouse gas that alters the radiative balance of Earth’s atmosphere
- Emissions and subsequent oxidation of NOₓ (+ NO + NO₂) in the presence of volatile organic compounds (VOCs) is the only known mechanism for toposophic O₃ production

Why the Front Range?
- The Denver urban area is currently out of compliance with national air quality standards for O₃ for the summer months
- In contrast to the eastern US, many western locations have positive daytime summer O₃ trends (see right)

Possible reasons include increases in:
- Western wild fire activity
- Stratospheric O₃ intrusions
- Pollutant Transport from Asia
- Changes in regional urban and Oil and Natural Gas (O&NG) Emissions

MEASUREMENTS: LOCATION, CAMPAIGNS, AND INSTRUMENTS

The Boulder Atmospheric Observatory (BAO)
- BAO lies between NOₓ and VOC emission sources in the Denver-Colorado Front Range (urban to the south, O&NG to the northeast)
- BAO measurement platform multiple ground sites and 300+ km across with movable carriage for vertically resolved measurements

Field Campaigns
- Summer 2012 – SONNE, Summer Ozone Near Natural Gas Emissions
- Summer 2014 – FRAPPE, Front Range Air Pollution and Photochemistry Experiment

Chemical Tracers of Regional Emission Sources observed at BAO (2014), plotted by wind direction:
- Methane (CH₄)
- Ammonia (NH₃)
- CO and NOₓ (urban activity)

At the BAO Tower: NOₓ and CO peaked slightly to the south (Denver), CH₄ peaked slightly to the north (O&NG activity), but all three are regionally mixed

Chemical tracers do not identify regional emission sources with distinct ozone production efficiencies

SUMMARY & CONCLUSIONS
1. Field measurements from the Boulder Atmospheric Observatory have been used with a photochemical box model to understand air pollution and photochemistry in a region currently out of compliance with national ambient air quality standards for O₃.
2. Observed O₃ Production Efficiencies are scattered around 5 and do not distinguish urban emissions from Oil and Natural Gas using wind direction or chemical tracers as markers of air transport history
3. A photochemical box model indicates that Oil and Natural Gas VOC emissions increase local maximum photochemical O₃ by ~17% and O₃ production efficiency by ~1.3 ppbv/ppbv

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ANALYSIS METHOD #1: OBSERVED O₃ PRODUCTION EFFICIENCY

O₃ Production Efficiency (OPE): Slope of O₃(=O₂ + NOₓ) against NOₓ (= NO + NO₂) as a measure of O₃ molecules produced per NOₓ molecules emitted and oxidized

FRAPPE (2014) Results
- Afternoon O₃ always correlated with photochemically oxidized ammonia (NH₃)
- OPE determined by O₃/NOₓ correlations over short time intervals
- OPE as a metric
- Advantages: independent of air mass age, dependent on air mass composition (i.e., changes with emission source), not sensitive to local circulation
- Limitations: sensitive to nitric acid deposition (i.e., artificially low NOₓ will raise O₃/NOₓ slope), difficult to extract slope in mixed air masses

Methods to Distinguish OPEs from Different Regional Emission Sources...

a) Wind Direction, Speed, and History
- Advantages: simple urban influence air flows from the south and O&NG from the north
- Challenges: Front Range air masses are mixed

b) Chemical Tracers
- Tracers: Methane (CH₄), CO, NOₓ, Ammonia (NH₃) (see Measurements Section)
- Advantages: unique to emission source, relatively low background, dependent on wind history and speed

FRAPPE Case Study – Chemical tracers can be used to identify distinct air masses in this unique instance

Chemical tracers do not identify regional emission sources with distinct ozone production efficiencies

ANALYSIS METHOD #2: OBSERVATIONS + PHOTOCHEMICAL BOX MODEL

Dynamically Simple Model for Atmospheric Chemical Complexity (DSMACC)

- Chemistry described by Marine Chemical Mechanism (MCM 3.1.1)
- ~4000 chemical species, ~15,000 chemical reactions
- Reaction rates calculated by TUV 5.2; then scaled to diurnal average observations

Observational Inputs and Constraints:
- 24-hr simulations, initialized with observations at 1 km local time (MDT) and chemically constrained to SONNE (2012) diurnal average observations of primary VOCs (< 40 compounds), NOₓ, and meteorological parameters (i.e. temperature)
- Observed 2012 Diurnal Profiles of Non-Methane Hydrocarbons (NMHC) Ozone Reactivity, and NOₓ and O₃

Model Results
- On Average, Ozone and Natural Gas (O&NG) VOC Emissions Contribute ~17% to Maximum Simulated Photochemical Ozone (ppbv)
- Maximum Simulated Photochemical Ozone

O&NG VOC Fractions - Gilman, J. et al. ES&T 2013 VOCs emitted from O&NG activity are primarily volatile alkenes. Remaining VOCs predominantly from surrounding urban and agricultural activities
- O&NG VOC fraction removed from the observed Case 1 observation minus daily photochemical ozone by 17.4% and 2.7 ppbv (at observed NOₓ level)
- Remaining O&NG VOC fraction from the observed Case 1 observation minus daily photochemical ozone by 13.2% and 2.2 ppbv (at observed NOₓ level)

Model OPE Results
- Model OPEs are most sensitive to changes in NOₓ mixing ratios and precursor VOCs
- Model Case 1 OPE is within 1 standard deviation of the observed average (5.1 ± 3.6 ppbv/ppbv)
- Model Case 2 OPE is within 1 standard deviation of the observed average (5.1 ± 3.6 ppbv/ppbv)

O&NG VOC Emissions influence simulated OPE by ~1.3 ppbv/ppbv

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