Impacts of Oil & Natural Gas Operations and Urban Emissions on Air Quality in Rocky Mountain National Park during FRAPPÉ

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15 July - 18 August 2014 Colorado Front Range

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FRAPPÉ: National Science Foundation (NSF) State of Colorado DISCOVER-AQ: NASA Others: NOAA, GO₃ Project, NPS, EPA https://www2.acd.ucar.edu/frappe

FRAPPÉ AND DISCOVER-AQ

- Two major field campaigns FRAPPÉ and DISCOVER-AQ - merged to study air quality in the Colorado Front Range in summer 2014 and fill measurement gaps.
- Measurements collected from surface stations, upward looking lidars and profilers, mobile vans, balloons and sondes, and four aircraft.
- Together with satellite data and model analysis provides the most comprehensive characterization of air quality ever conducted in the region.
 - Improve development & evaluation of emission control strategies
 - Allow better modeling of present and future air quality for decision making
 - Identify optimal locations for surface monitoring sites making the network more efficient and more representative
 - Refine and verify satellite data for air quality planning in the Front Range.



Question: Is there a measureable impact from O&G operations at ROMO?

- Historical ozone record at ROMO
- Ozone at 2 sites in ROMO during FRAPPÉ
- VOC distributions and source characterization
- 2 case studies upslope and stratospheric intrusion
- Box modeling results & calculations to determine O₃ production from O&G



Rocky Mountain National Park, CO Site: Longs Peak

Historical Perspective of ROMO for Summer 2014



NATIONAL PARK SERVICE Rocky Mountain National Park, CO Site: Longs Peak

Historical Perspective of ROMO for Summer 2014



ROMO is a Class I area and suffers from multiple air quality problems including elevated ozone and harmful levels of nitrogen deposition.



Rocky Mountain National Park Measurements

Objective: Supplement continuous monitoring occurring at ROMO during FRAPPE intensive period.

Key areas of NPS interest: Oil & gas impacts, N deposition, O_3

Ongoing measurement programs:

IMPROVE, AMoN, NADP, CASTNet (O₃, met, filter packs)

Additional Measurements during FRAPPÉ

VOC GC PTR-MS PAN GC CO, NH_3, NO_x, NO_y MARGA **Spatial sampling:** VOCs with canisters URG annular denuder system Portable O₃ - Trail Ridge Road

Alkanes ethane propane i-butane n-butane i-pentane n-pentane cyclopentane n-hexane n-heptane n-octane n-nonane

Alkenes ethene propene t-2-butene 1-butene i-butene c-2-butene

OVOCs

methanol

acetaldehyde

MEK

MVK+MACR

acetic acid

Alkynes ethyne

Biogenics isoprene **α-pinene**

β-pinene

Aromatics

benzene

toluene

ethylbenzene

m+p-xylene

o-xylene

Halocarbons C2HCI3 **C2CI4** CH3I CH2Br2 CHBrCl2 CHBr3

Alkyl Nitrates

MeONO2

EtONO2

i-PrONO2

n-PrONO2

2-BuONO2

3-PenONO2

2-PenONO2



Ozone: Longs Peak and Trail Ridge Road



Ozone: Longs Peak and Trail Ridge Road









Urban Study Comparison of Light NMHCs



1) Swarthout et al., 2015; 2) Baker et al., 2008; 3) Katzenstein et al., 2003; 4) Swarthout et al., 2013.

Oil and Gas Wells







10 15 20



Oil & Gas Emissions Tracers The Butane and Pentane Ratios



Oil & Gas Emissions Tracers The Butane and Pentane Ratios



Transect Samples



Transect Samples









Date



Date



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Photochemical Age using Alkyl Nitrates



Photochemical Age using Alkyl Nitrates



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Stratospheric Intrusion Event on August 23, 2014



Stratospheric Intrusion Event on August 23, 2014



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Local Time





Photochemical Age using Alkyl Nitrates



Photochemical Age using Alkyl Nitrates



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Upslope and Stratospheric Intrusion Events Box Modeling with BOXMOX



Net ozone production rates ~25 ppb/h during upslope

Ozone Production from O&G during an Upslope Event



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Ozone Production from O&G during an Upslope Event

Compound	XS O ₃ Production (ppbv)	
EtONO ₂	18.4	
i-PrONO ₂	17.9	
n-PrONO ₂	19.8	(vdq
2-BuONO ₂	18.1	Ozone (p
3-PenONO ₂	18.1	
2-PenONO ₂	16.5	
Average	18.2 ± 1.1	



Ozone Production from O&G during an Upslope Event

O₃/RONO₂ Method

$X5 O_3$ Produced: 18.2	vaqo		
Peak 1 hr $O_3 = 74$	<u>XS O₃ (ppbv)</u>	<u>% of XS O₃</u>	<u>% O₃ from O&G</u>
BGD1 $O_3 = 50$	24	76%	25%
BGD2 $O_3 = 44$	30	61%	

RONO₂ Diurnal Cycle Method

 XS O_3 Produced: 14.9 ppbv

 Peak 1 hr $O_3 = 74$ XS O_3 (ppbv)
 % of XS O_3 % O_3 from O&G

 BGD1 $O_3 = 50$ 24
 62%
 20%

 BGD2 $O_3 = 44$ 30
 49%

Net ozone production rates ~25 ppb/h during upslope ~15-18 ppbv excess ozone at ROMO from O&G



Summary

- ROMO is a Class I area and afforded the highest level of air quality protection under the law. Parks should be the cleanest areas in the U.S. (CAA and NPS Organic Act).
- Trail Ridge Road and Longs Peak sites tracked well; highest O₃ levels at high elevation.
- Mixed signature of urban and oil and gas emissions observed at Longs Peak site.
- NMHC distributions similar to summertime measurements in SW PA; mixed urban and oil and gas operations.
- Elevated ozone and VOCs during upslope events, transport from the E and SE.
- Highest levels of alkanes associated with oil and gas operations based on i-pentane/npentane ratio (i-butane/n-butane).
- Net ozone production rates of ~25 ppb/h during the Aug 18-19 upslope event.
- Upwards of ~18 ppbv excess ozone at ROMO during this event.

Is there a measureable impact from O&G production operations? Because O&G emissions are often coupled with urban emissions, this results in a significant ozone production potential for ROMO during upslope events (~20-35%).



Future O&G Developments to the West of ROMO?

- Studies have demonstrated that oil and gas emissions are a significant contributor to pollutant loading (& ozone formation) during upslope events.
- Currently, air masses coming from the west/northwest are relatively "clean" in comparison. If the western side of the park is also allowed to degrade, this will only exacerbate an ongoing problem.





Map Produced by NPS ARD, 2017 Shale Basins Data Layer Produced by EIA, 2011. Well data for CO, WY & UT from COGCC (2017), WYOGCC (2015) & UT DNR (2015), respectively.



Perspective on Potential Impacts



Data from BAO Tower in Weld Co. Winter 2011 Extremely high levels VOCs Ozone precursors Local and downwind impacts

Data from THRO in ND Fall 2013 - Winter 2014 Extremely high levels VOCs Secondary chemistry marker (2-BuONO₂) Haze events from O&G emissions (PM_{2.5}) "Photochemical Clock" for verification Local and fresh emissions from O&G

Potential to behave like Uintah and Upper Green River Basins – Wintertime ozone









Hour

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Hour



Diurnal Profiles from ROMO



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Transect Samples on August 18, 2014



