Decadal Trends and Variability in Intermountain West Surface Ozone near Oil and Gas Extraction Fields

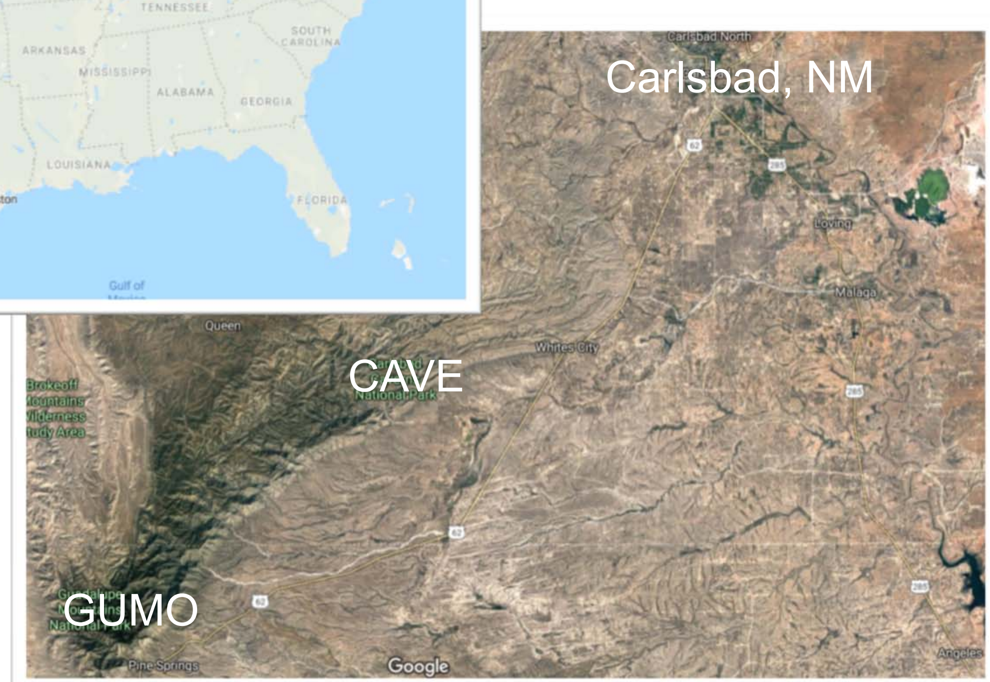
Barkley C. Sive
Air Resources Division
National Park Service

Ying Zhou and Huiting Mao
Department of Chemistry
SUNY ESF

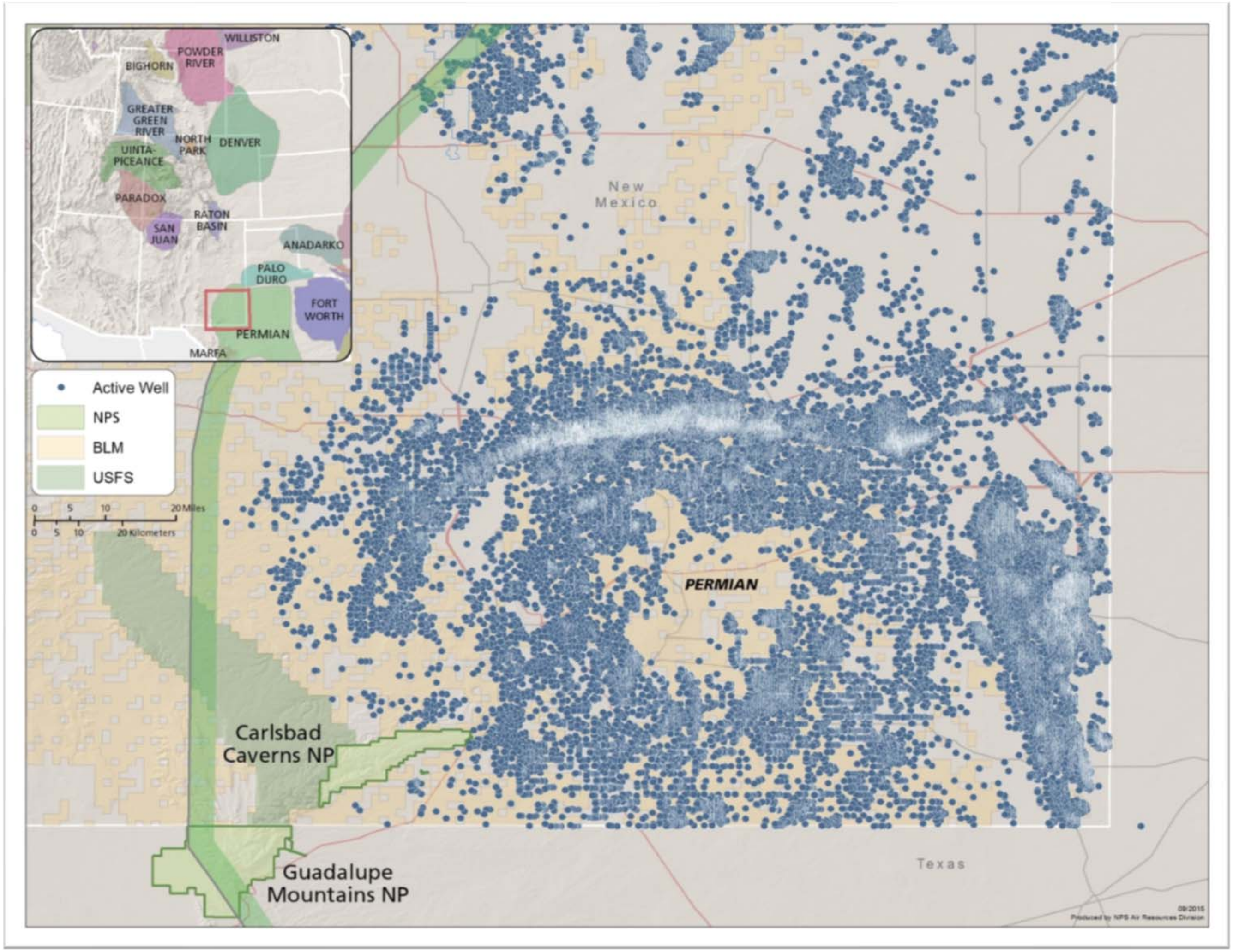
Carlsbad Caverns Intensive Air Quality Study
August-September 2019

1. What are the primary VOC drivers of regional ozone formation and how might future changes in VOC emissions affect peak ozone at CAVE?
2. What is the nitrogen budget in the region and how sensitive is ozone formation to changes in NOx concentrations?
3. What species, e.g. NOx, H_2S, and VOC, contribute to or limit aerosol formation?

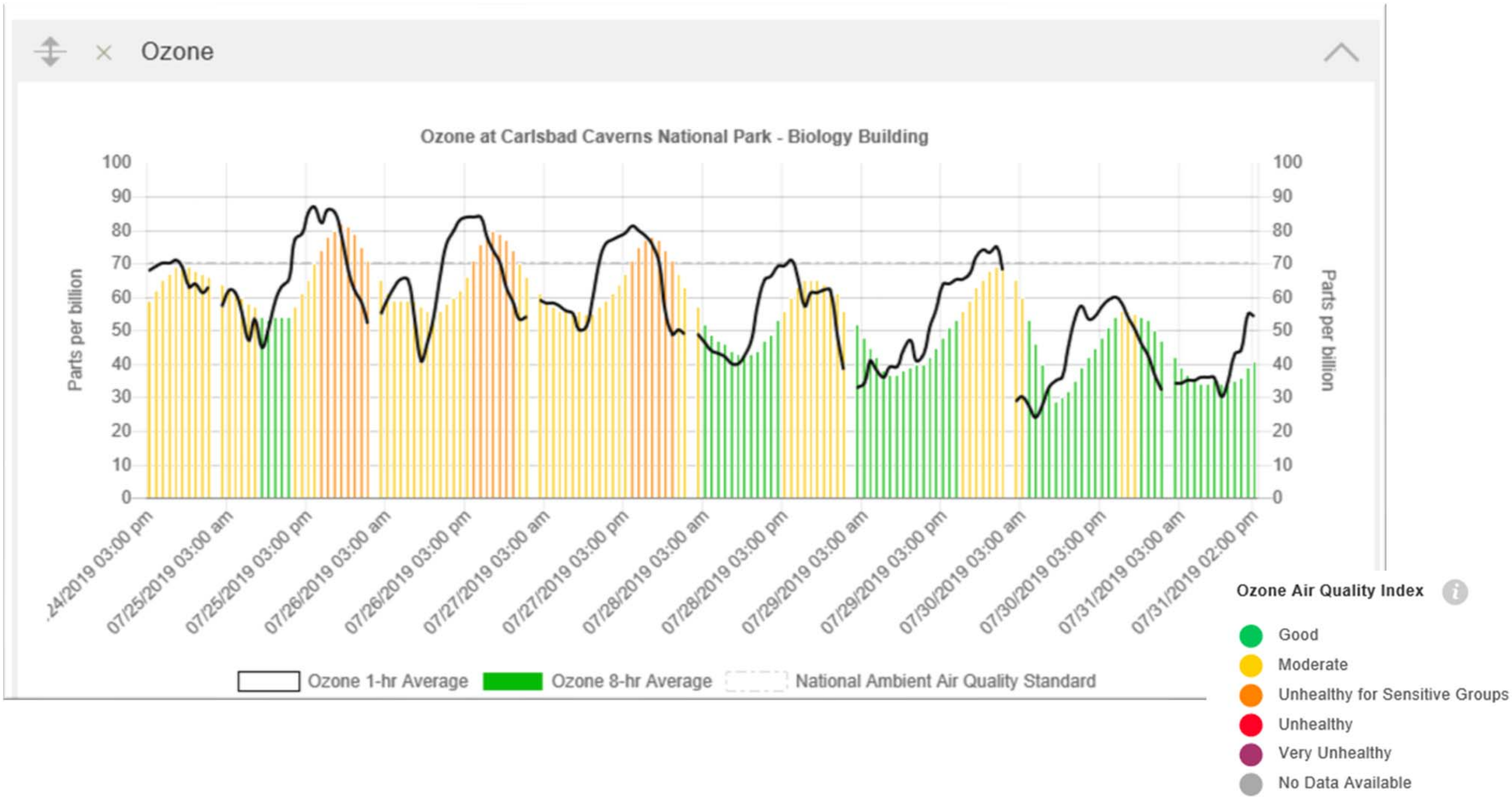
Carlsbad Caverns Intensive Air Quality Study



Wells Near CAVE



Carlsbad Caverns Intensive Air Quality Study August-September 2019



Region 6 8-hr Ozone Exceedance Day Update

preliminary data **(through July 31, 2019)**

Applicable Standard = 70 ppb

	State/Cities	8-hour Ozone Year to Date Exceedance Days	Max. exceedance levels week of 7/26-7/31							Year to Date Air Quality Index Category Totals		
			F	S	S	M	T	W	R	# Unhealthy for Sensitive Groups	# Unhealthy	# Very Unhealthy
	Texas	**# > 70 ppb**										
1.	Houston	21	76							19	2	
2.	Dallas-Fort Worth	17	74	74				71		17		
	Beaumont	3								3		
	Longview	1								1		
	Tyler	1								1		
	El Paso	4	77	75						4		
	Austin											
	San Antonio	4	76							4		
	Corpus Christi											
	Waco											
	Killeen-Temple	2								2		
	Victoria											
	Louisiana											
	Baton Rouge	6								6		
	Pointe Coupee	3								3		
	Shreveport											
	New Orleans											
	Lake Charles											
	Lafayette											
	Lafourche Parish	1								1		
	Oklahoma											
	Tulsa	1								1		
	Oklahoma City	1					72			1		
	Cherokee Tribal											
	Cherokee Fort Smith MSA											
	Quapaw Tribal											
	Arkansas											
	Little Rock											
	Crittenden Co.											
	Shelby Co., TN											
	DeSoto Co., MS											
	New Mexico											
	Albuquerque	2	72				73			2		
	San Juan Co.											
	Southern Dona Ana Co.	6	78	79						6		
3.	Carlsbad	15	78	77						13	2	
	Hobbs	3	73							3		

Notes: 71 - 85 ppb = Unhealthy for Sensitive Groups; 86 - 105 ppb = Unhealthy; >= 106 ppb = Very Unhealthy (based on applicable 70 ppb standard)

Mark Sather
U.S. EPA Region 6

Carlsbad Caverns Intensive Air Quality Study
August-September 2019

Artesia, NM
~30 mi N of Carlsbad

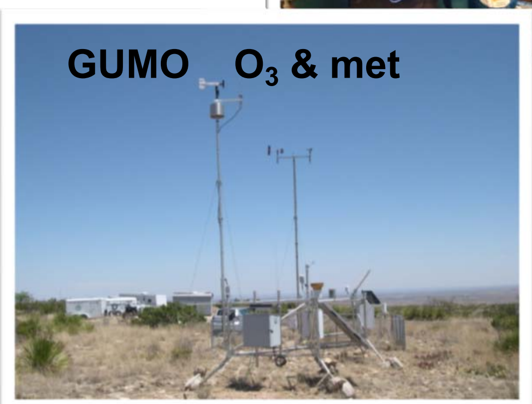
CAVE Study

CH_4, NH_3, CO_2, BC, $PM_{2.5}$

NO, NO_2, NOy

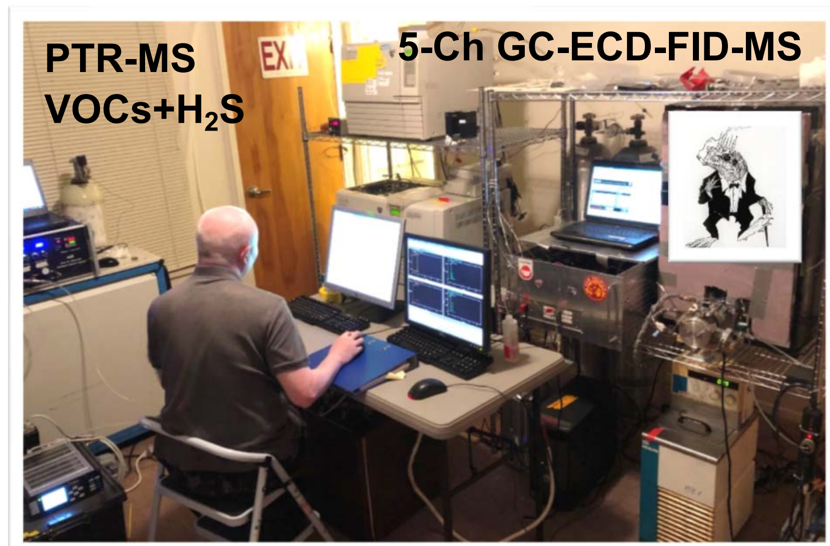
PAN GC

O_3, CO, SO_2 & met



GUMO O_3 & met

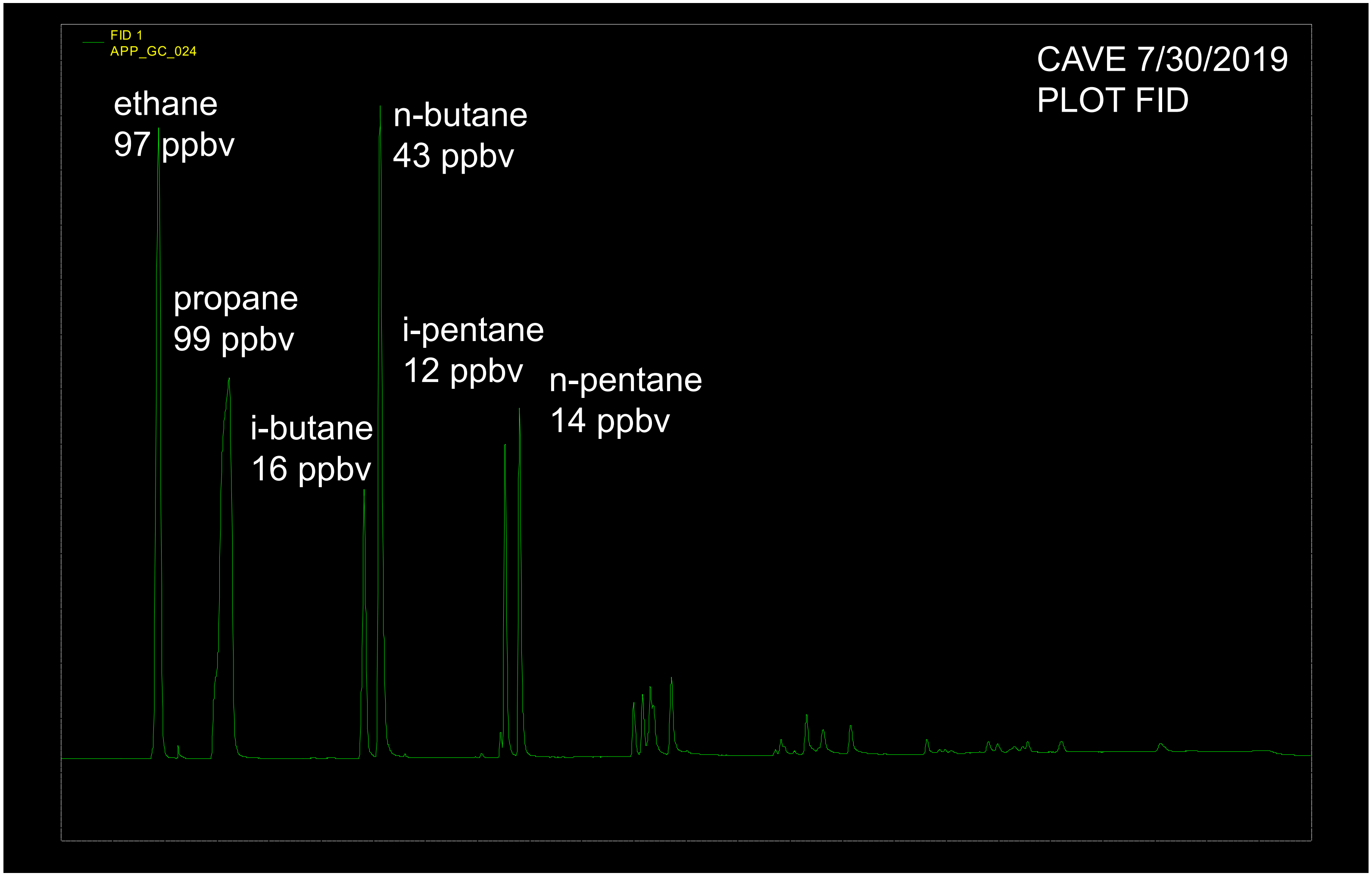
PILS-IC

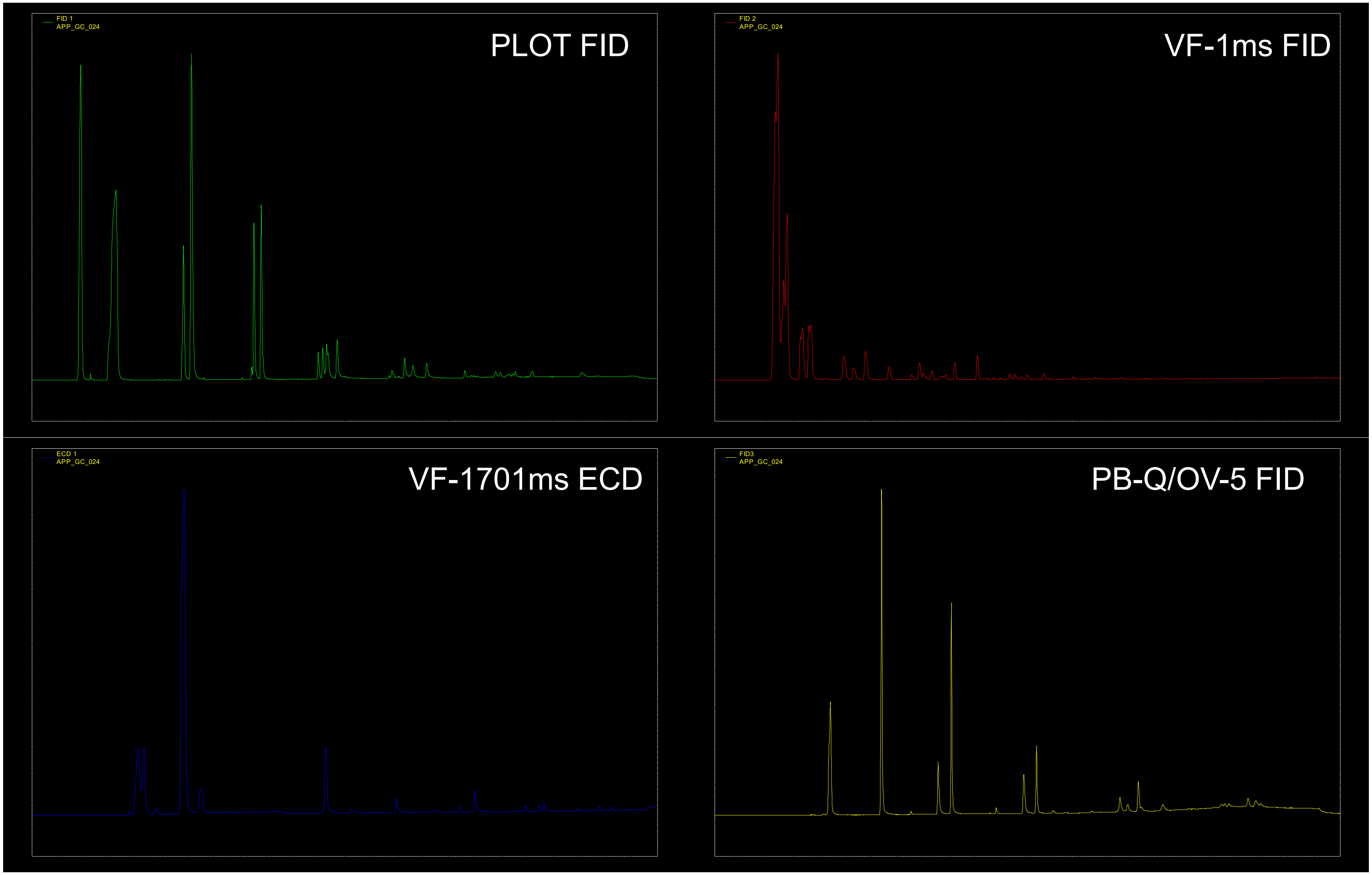


PTR-MS VOCs+H_2S

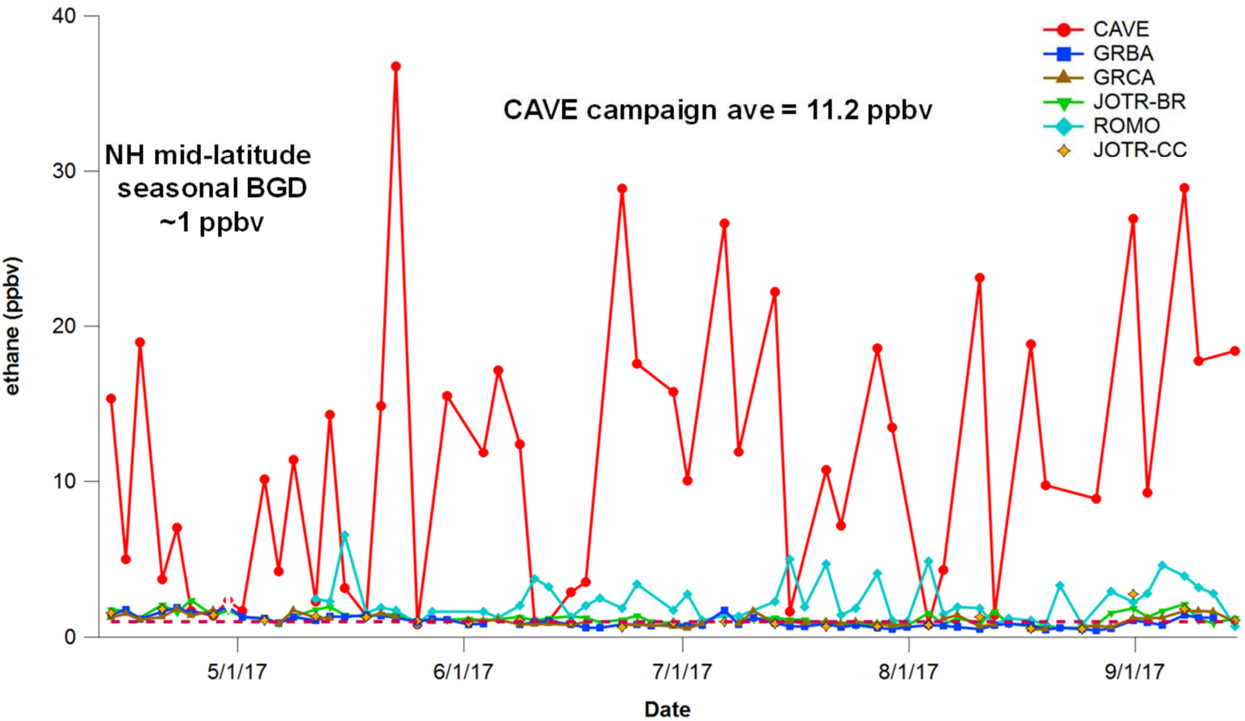
5-Ch GC-ECD-FID-MS

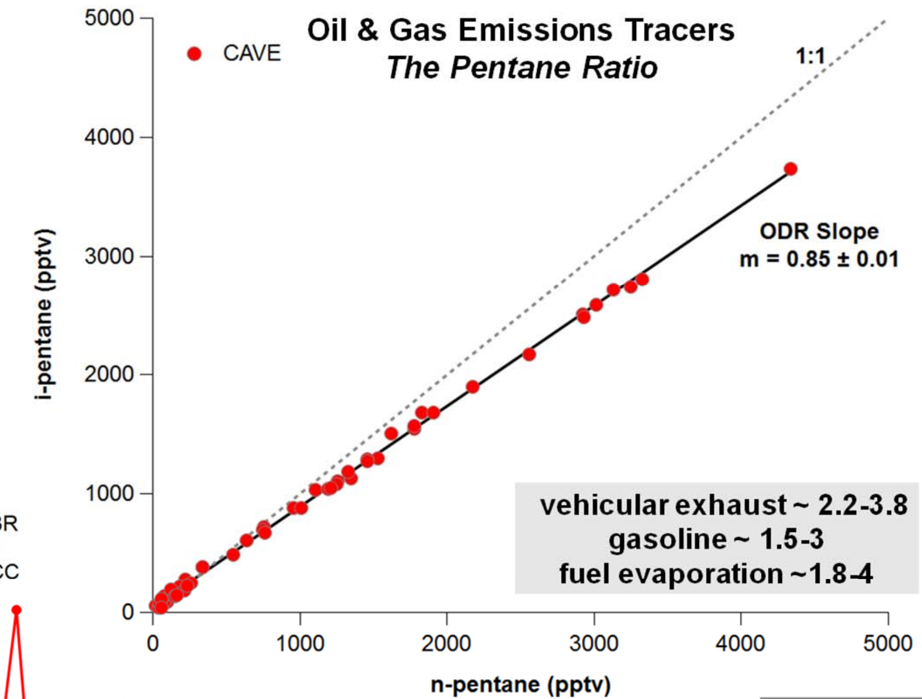
Oil & Gas Signature




FID 1
APP_GC_024
PLOT FID
FID 2
APP_GC_024
VF-1ms FID
ECD 1
APP_GC_024
VF-1701ms ECD
FID3
APP_GC_024
PB-Q/OV-5 FID

Comparison with 2017 Study Results



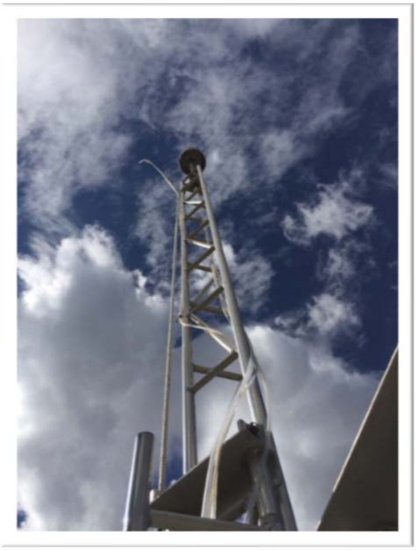


Gaseous Pollutant Monitoring Program

- Operated & maintained network AQ monitors since 1981
- GPMP network grew to 42 stations in the 1990s
- Currently GPMP monitoring in 31 different park units
- Most NPS sites:
    - operated in a regulatory manner
    - part of CASTNET

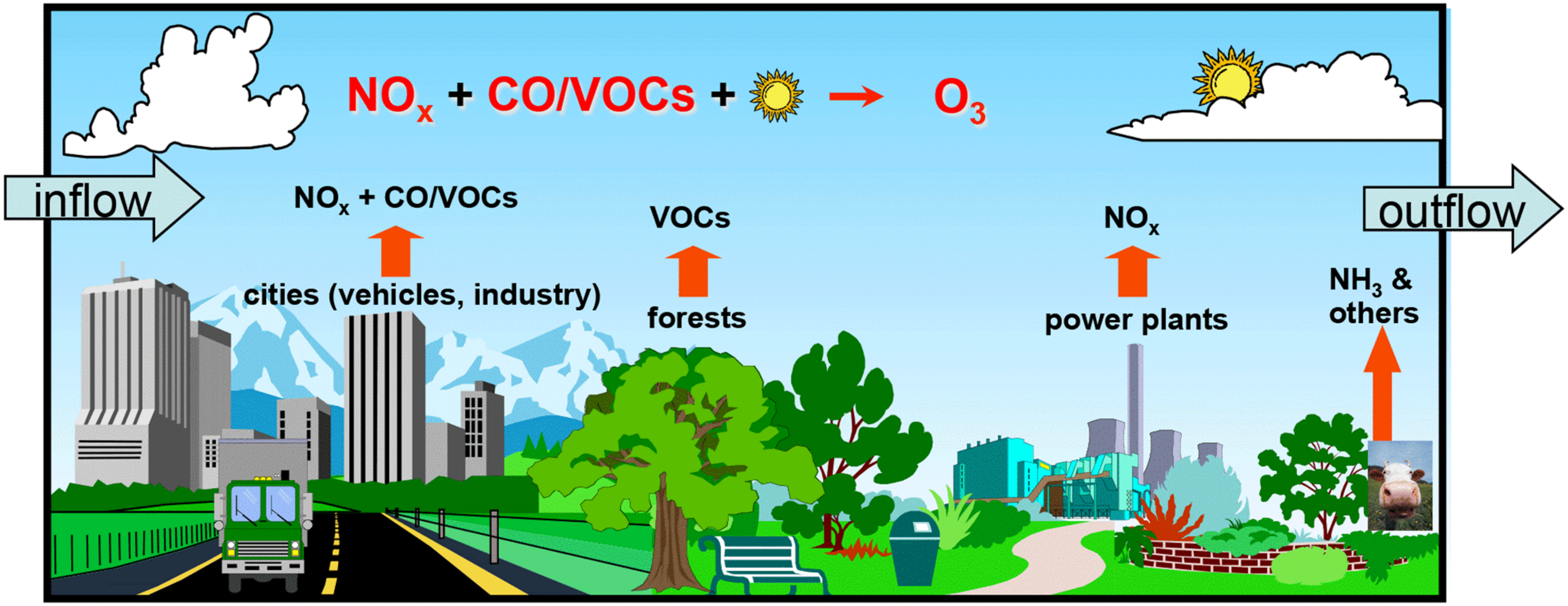
Parameters Measured

Chemical/Physical	Meteorology
Ozone (O_3)	Wind Speed (WS)
Sulfur Dioxide (SO_2)	Wind Direction (WD)
Carbon Monoxide (CO)	Temperature (TMP)
Nitrogen Oxides ($NO+NO_2$, NO_y)	Relative Humidity (RH)
Particulate Matter ($PM_{2.5}$, PM_{10})	Precipitation (RNF)
CASTNET Filter Packs (Acids, base cations, chloride)	Solar Radiation (SOL)



NATIONAL PARK SERVICE

Ground-level ozone formation



- Formed by chemical reactions between oxides of nitrogen (NOx) and volatile organic compounds (VOCs) in the presence of sunlight
- Emissions can travel hundreds of kilometers and can increase ozone in areas far from source regions

https://www.esrl.noaa.gov/csd/news/2016/178_0114.html

U.S. EPA National Ambient Air Quality Standards (NAAQS)

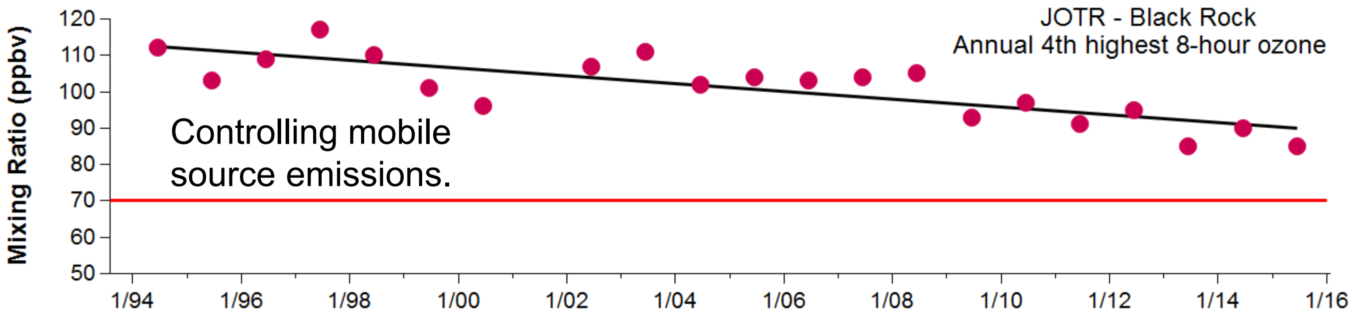
2 kinds of standards:

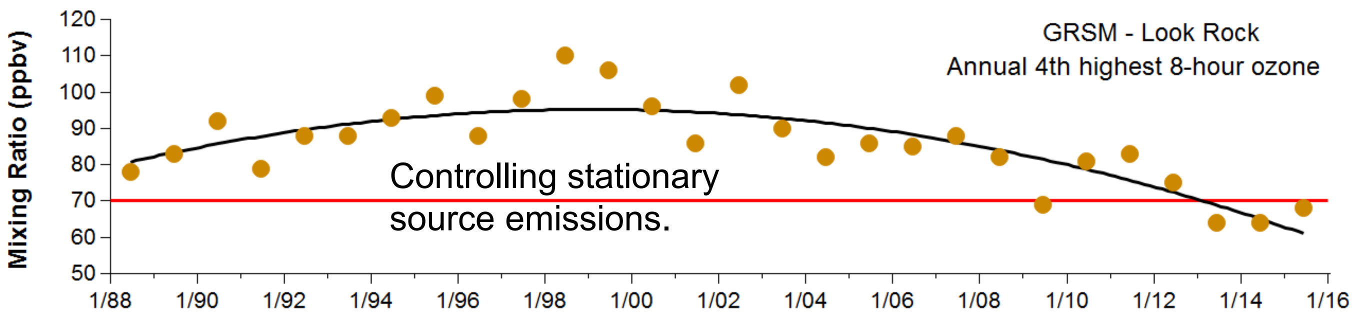
Primary: set to protect public health

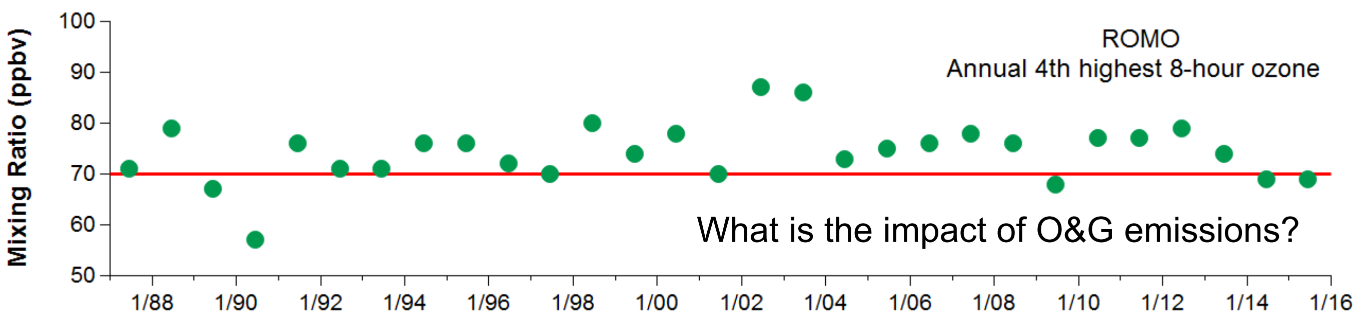
Secondary: set to protect public welfare

Pollutant		Primary/Secondary	Averaging Time	Level	Form
Ozone (O_3)		primary and secondary	8 hours	0.070 ppm	Annual 4th-highest daily maximum 8-hr concentration, averaged over 3 years
Carbon Monoxide (CO)		primary	8 hours	9 ppm	Not to be exceeded more than once per year
			1 hour	35 ppm	
Nitrogen Dioxide (NO_2)		primary	1 hour	100 ppb	98th percentile of 1-hr daily maximum concentrations, averaged over 3 years
		primary and secondary	1 year	53 ppb	Annual mean
Particulate Matter (PM)	$PM_{2.5}$	primary	1 year	12.0 ug/m^3	Annual mean, averaged over 3 years
		secondary	1 year	15.0 ug/m^3	Annual mean, averaged over 3 years
		primary and secondary	24 hours	35 ug/m^3	98th percentile, averaged over 3 years
	PM_{10}	primary and secondary	24 hours	150 ug/m^3	Not to be exceeded more than once per year on average over 3 years
Sulfur Dioxide (SO_2)		primary	1 hour	75 ppb	99th percentile of 1-hr daily maximum concentrations, averaged over 3 years
		secondary	3 hours	0.5 ppm	Not to be exceeded more than once per year

Ozone Distributions

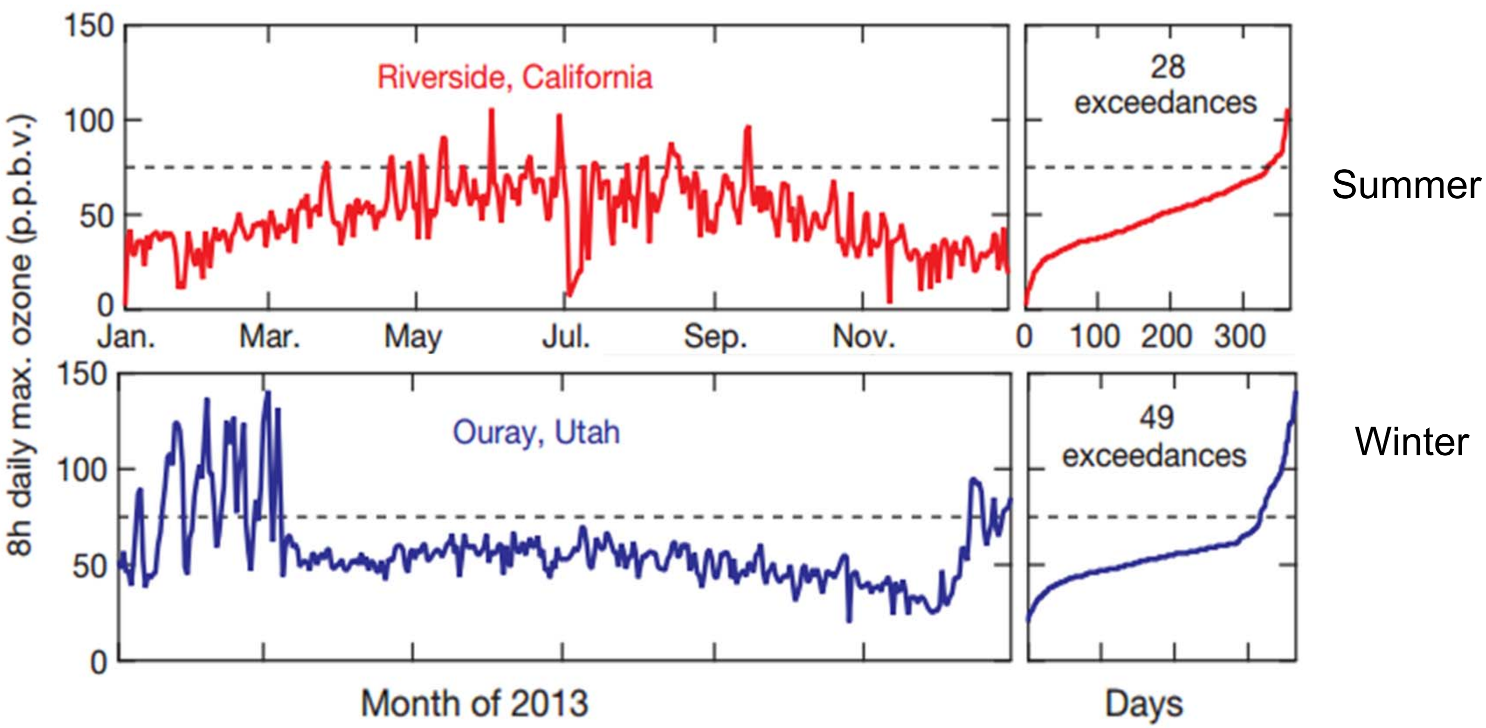






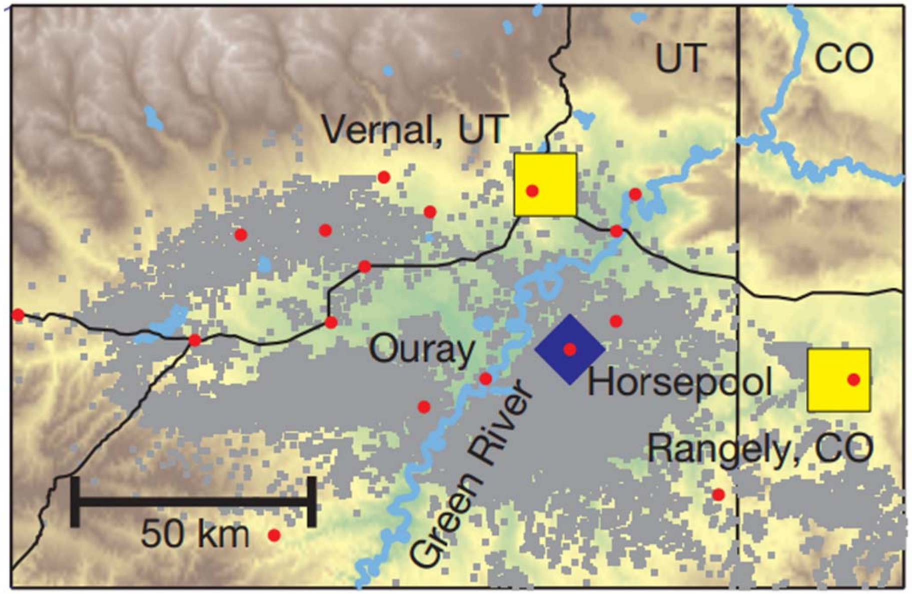
Previous Studies

U.S. National Ambient Air Quality Standard: **70 ppbv**



Edwards et al., 2014

Previous Studies

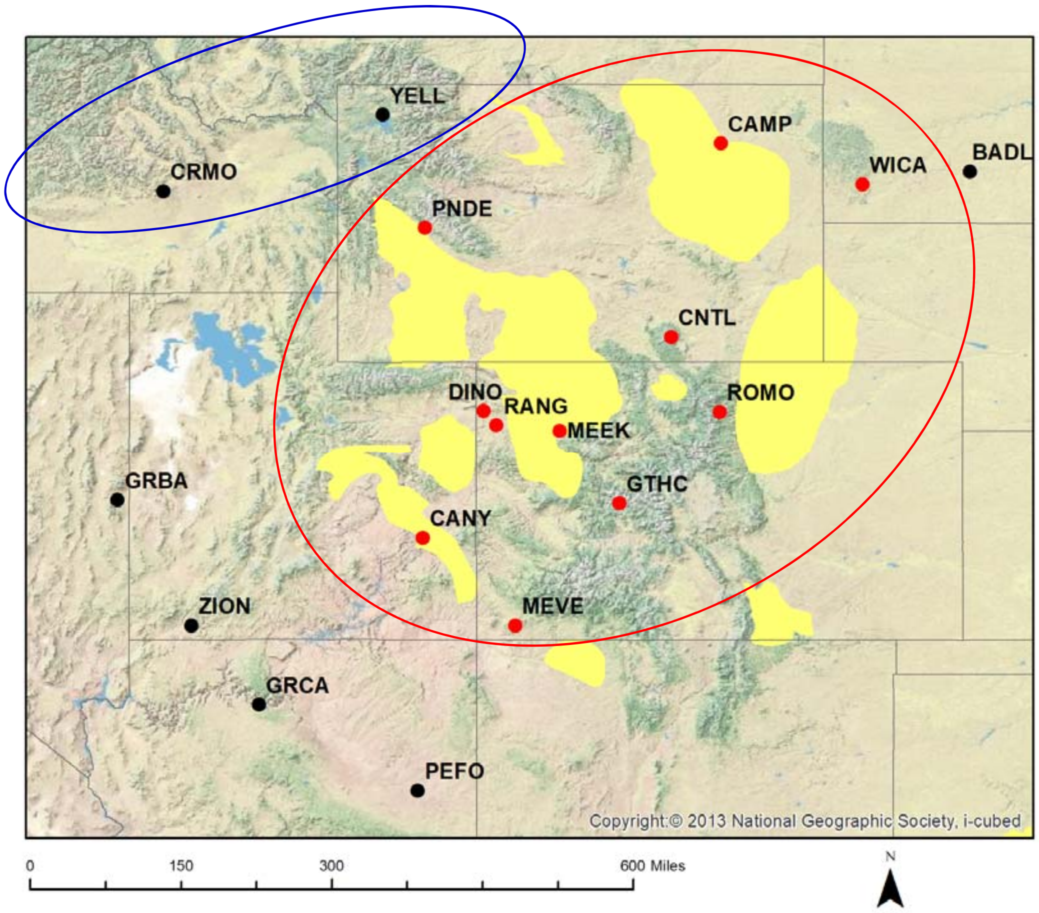


Rapid O_3 production in cold winters:

- High VOC and NO_x emissions in a shallow and stable boundary layer
- Increased photolysis rates due to the snow albedo

How has O&NG extraction affected surface O_3 over the time scale of more than 10 years?

Surface Observations



Data source: National Park Service

2 reference sites:

YELL, CRMO

11 O&NG sites:

- 5 sites within the basins
- 6 sites outside the basins

Trends in the A4DM8HA O_3

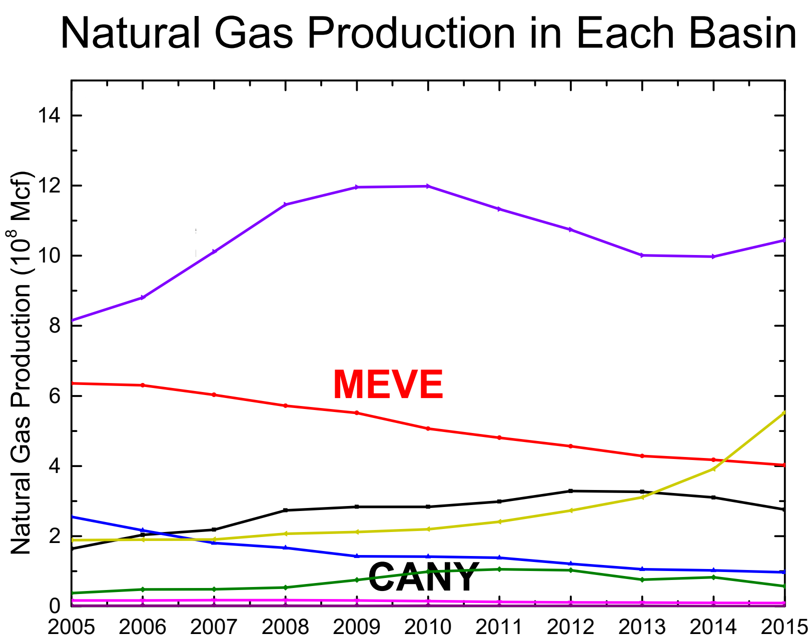
Annual fourth-highest daily maximum 8-hour average (A4DM8HA)

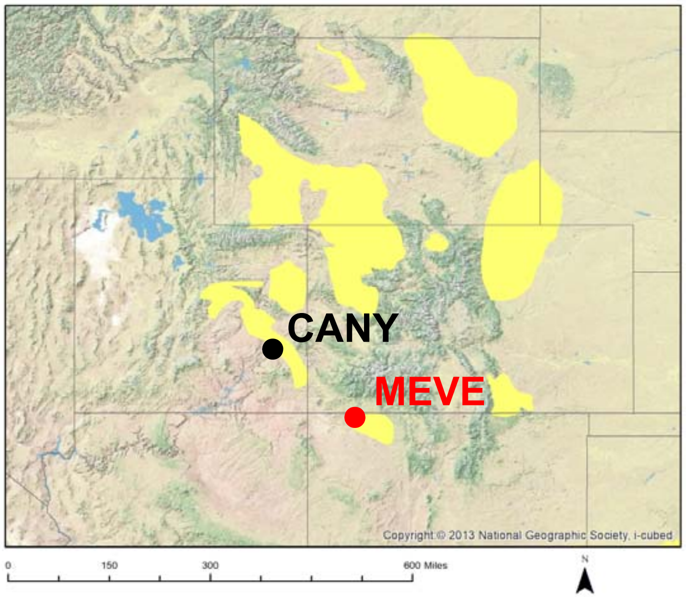
Ozone Design Value

→ National Ambient Air Quality Standards: 70 ppbv

Site	Time Period	Trends (ppbv yr^{-1})
CANY	2005 - 2015	**-0.54 (0.02)** ←
CAMP	2005 - 2015	-0.44 (0.25)
MEVE	2005 - 2015	**-0.76 (<0.01)** ←
ROMO	2005 - 2015	-0.46 (0.23)
WICA	2005 - 2014	**-1.21 (0.05)** ←
CTNL	2005 - 2015	-0.06 (0.78)
GTHC	2005 - 2015	-0.16 (0.64)
PNDE	2005 - 2015	-0.08 (0.75)
CRMO	2007 - 2015	-0.50 (0.23)
YELL	2005 - 2015	-0.17 (0.58)

Decreasing at 2 sites
→Decreasing O&NG Emissions





Mesa Verde National Park (MEVE):
37% decrease in natural gas production

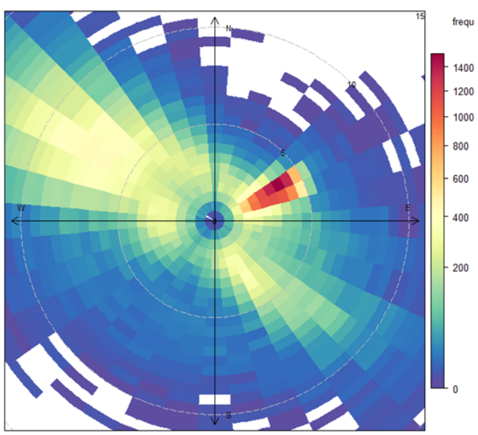
Canyonlands National Park (CANY):
35% of NO_x emission reduction from coal-fired electricity generation

No Trends at 5 Sites
→Increasing O&NG Emissions

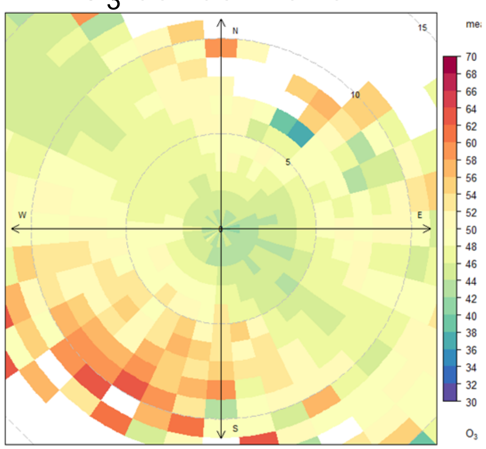
No trends at other sites:

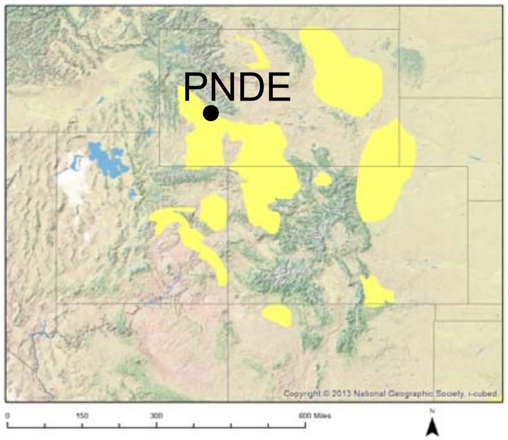
- Increasing O&NG emissions
- Decreasing emissions from other activities

Wind frequency



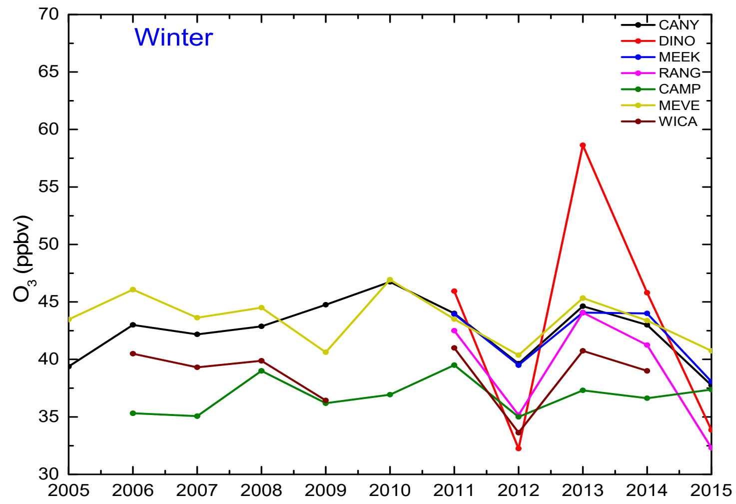
O_3 concentration

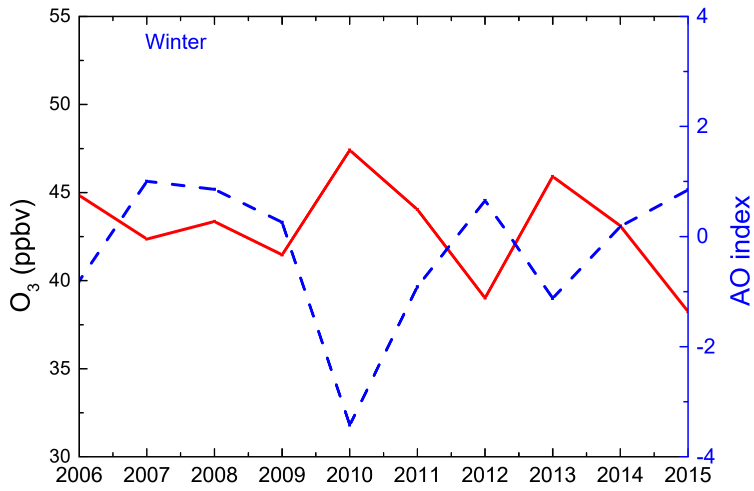




Interannual Variability of O_3 in Winter

Wintertime O_3 was negatively correlated with the AO index.





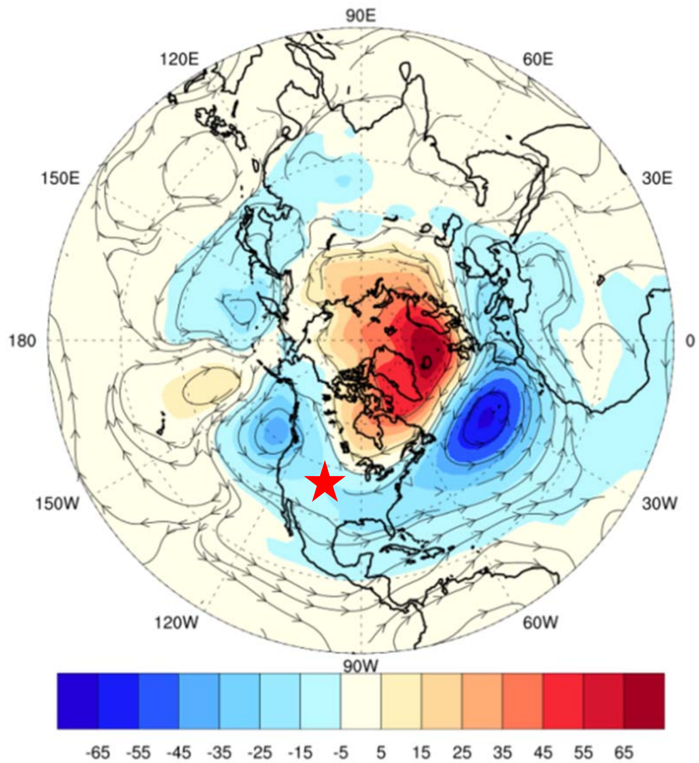
<u>In negative AO:</u>

High O_3 at sites **within the basins**.

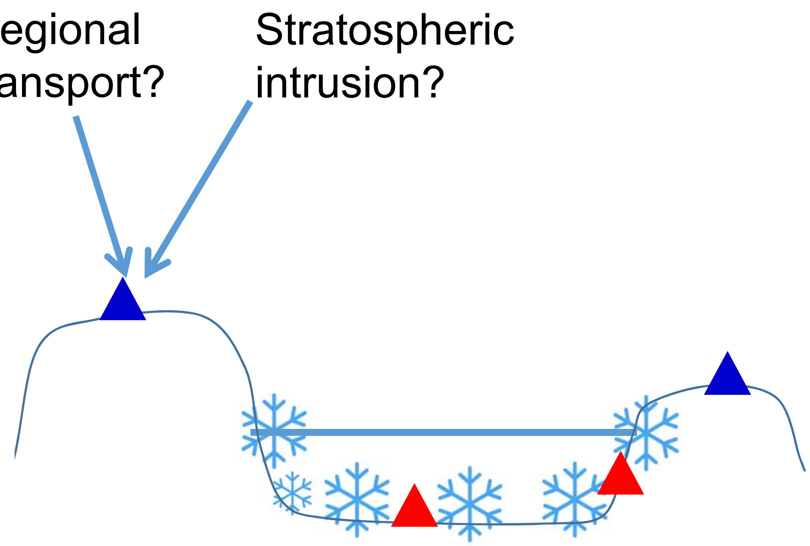
High O_3 at sites **outside the basins**.

Impact of Arctic Oscillation

Negative AO → High O_3



Difference in 850 hPa geopotential height between high O_3 years and low O_3 years



Regional Transport

Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) Model

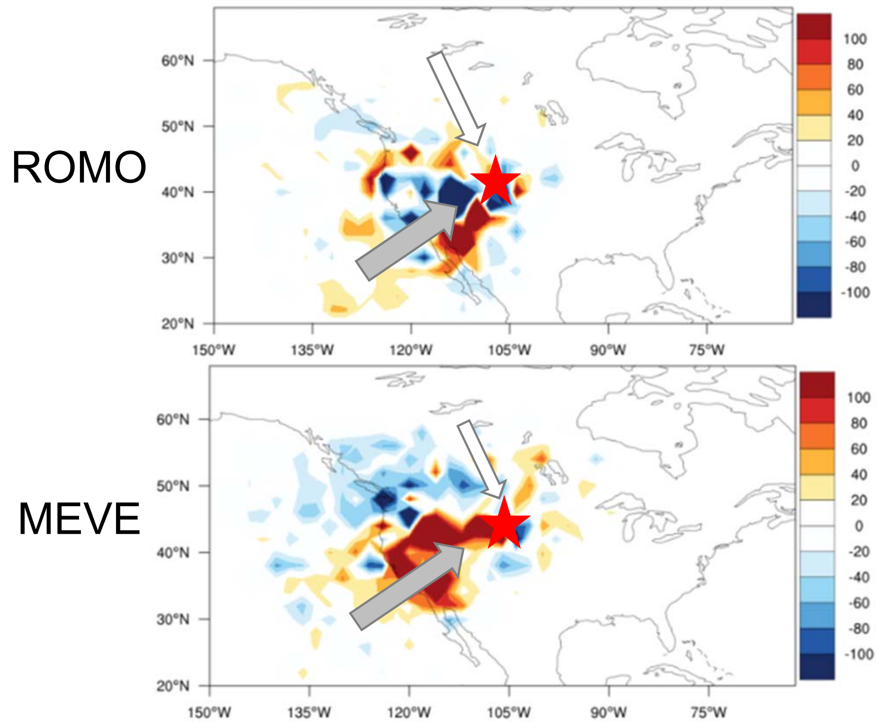
- Determine the origin of air masses and establish source-receptor relationships.

Difference in trajectories between negative and positive AO years

In negative AO years:

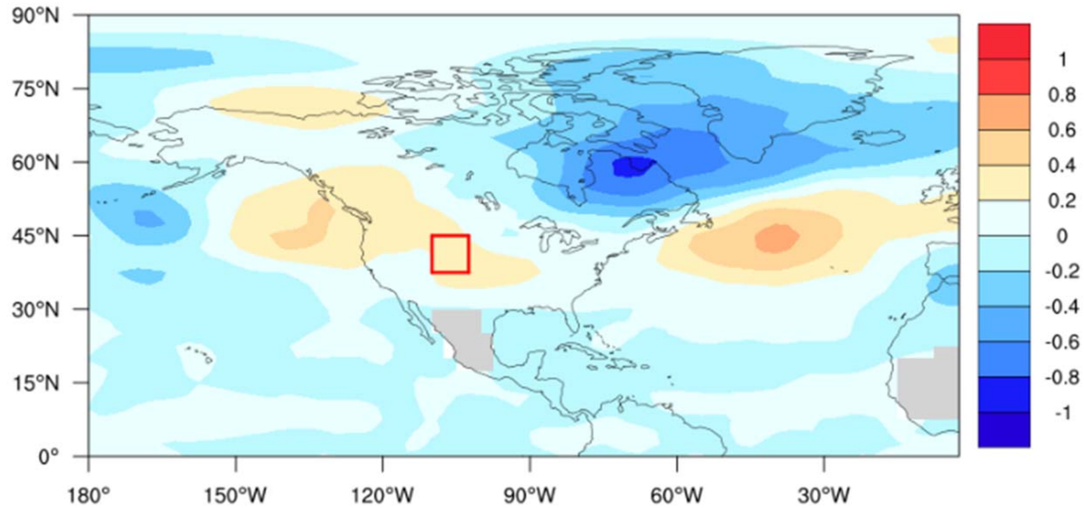
- >80% more trajectories from surface of the west coast.

- ~20% more trajectories from higher altitudes in the north.



Stratospheric Intrusion

Potential Vorticity



Difference in potential vorticity at 315K between negative and positive O_3 years

In Negative AO (high O_3) years:

- Positive anomalies of ~0.5 pv over the Intermountain West.

Summary

- Decadal trends in the A4DM8HA O_3 were investigated over 2005 –2015 for 13 rural/remote sites in the U.S. Intermountain West.
- No trends were observed in A4DM8HA O_3 at two reference sites, located upwind of & minimally influenced by emissions from O&NG basins.
- Trends, or a lack thereof, varied widely at other 11 sites in/near O&NG basins resulting from different controlling factors rather than a simplistic, uniform one.
- Demonstrates the importance and utility of long-term ground based ozone and gaseous pollutant monitoring networks.