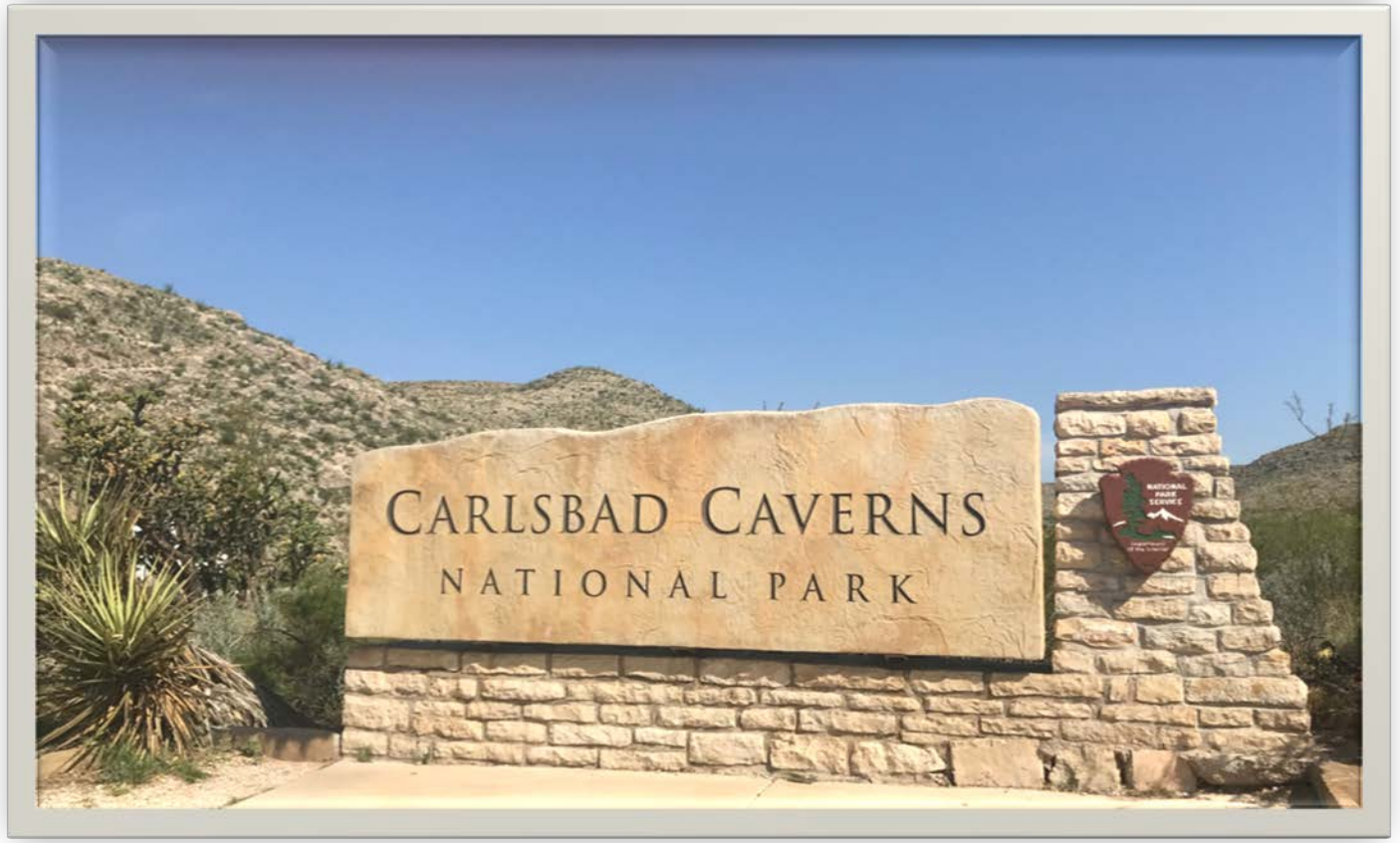
Carlsbad Caverns Intensive Air Quality Study
July – September 2019



Air Resource SPECIALISTS

Carlsbad Caverns Intensive Air Quality Study
July – September 2019

Objectives

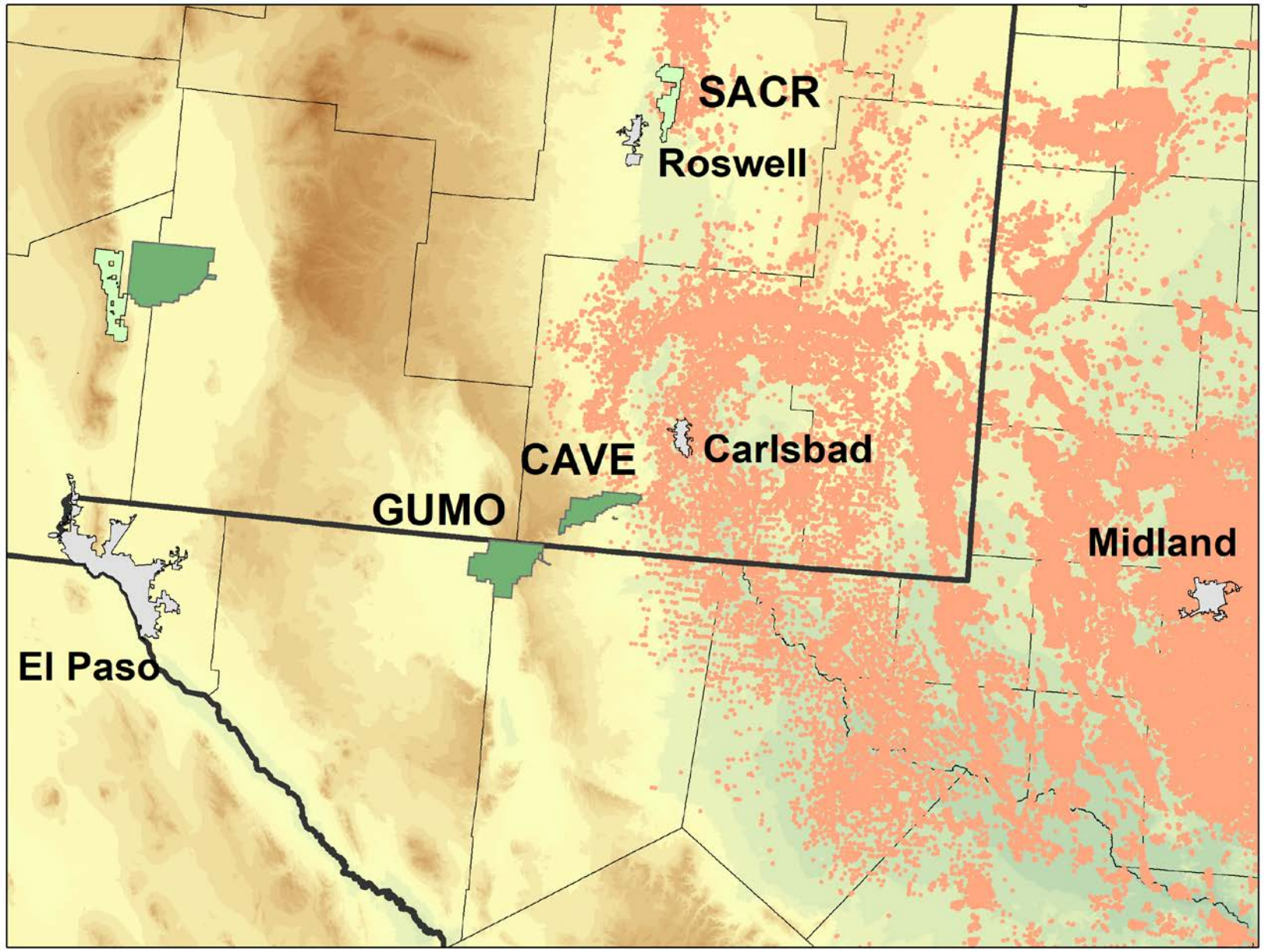
1. What are the primary VOC drivers of regional ozone formation and how might future changes in VOC emissions affect peak ozone at CAVE?

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?

NOTE: ALL DATA AND FINDINGS ARE PRELIMINARY

Wells Near CAVE*



*2017

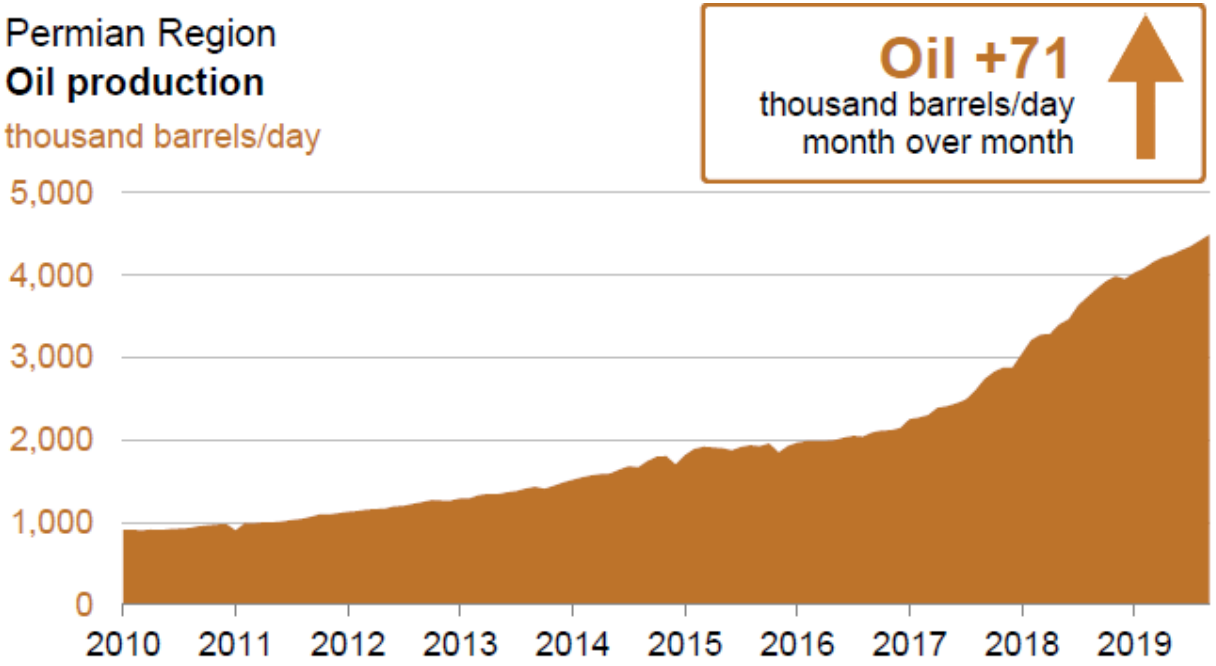
Ozone Exceedances and Design Values 2019

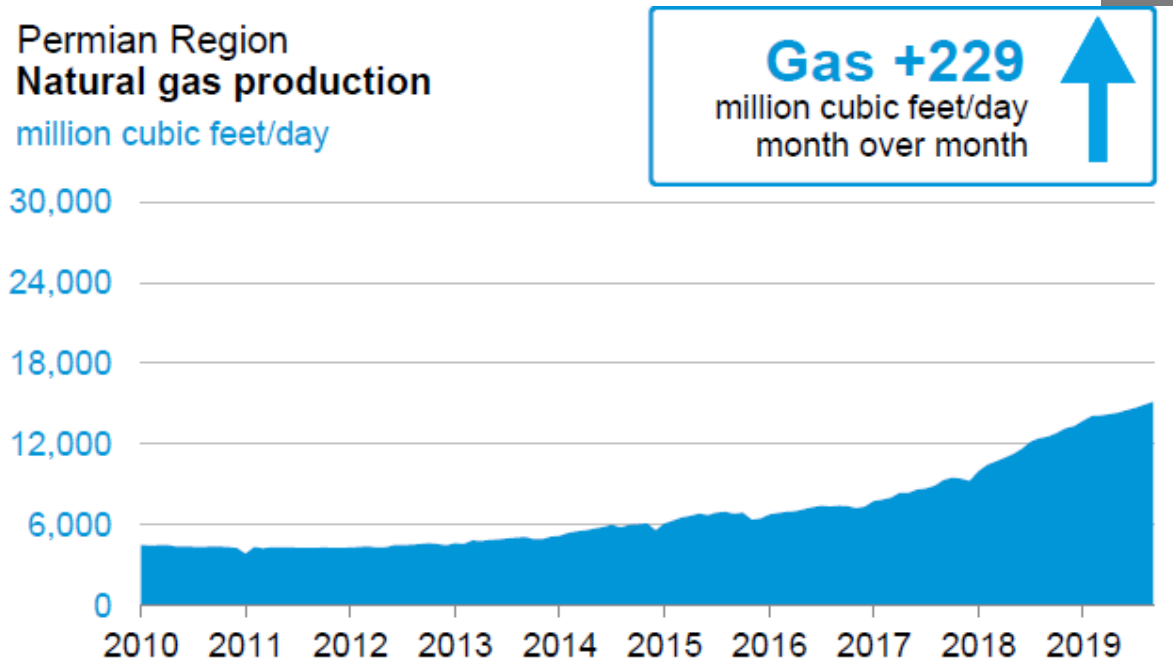
Region 6 8-hr Ozone Exceedance Day Update	
(through October 3, 2019)	
preliminary data	Applicable Standard = 70 ppb
State/Cities	8-hour Ozone Year to Date Exceedance Days
Texas	**# > 70 ppb**
Houston	**28**
Dallas-Fort Worth	**29**
Beaumont	4
Longview	1
Tyler	1
El Paso	9
Austin	1
San Antonio	4
Corpus Christi	
Waco	
Killeen-Temple	2
Victoria	
Louisiana	
Baton Rouge	6
Pointe Coupee	3
Shreveport	
New Orleans	
Lake Charles	
Lafayette	
Lafourche Parish	2
Oklahoma	
Tulsa	2
Oklahoma City	2
Cherokee Tribal	
Cherokee Fort Smith MSA	
Quapaw Tribal	
Arkansas	
Little Rock	
Crittenden Co.	1
Shelby Co., TN	2
DeSoto Co., MS	1
New Mexico	
Albuquerque	4
San Juan Co.	
Southern Dona Ana Co.	14
Carlsbad	**19**
Hobbs	3

2. → Houston
1. → Dallas-Fort Worth
3. → Carlsbad

8-hour O_3 DV	DFW	Houston	El Paso County, TX	Carlsbad, NM
2014-2016	80 ppb	79 ppb	70 ppb	**67 ppb**
2015-2017	79 ppb	81 ppb	71 ppb	**68 ppb**
2016-2018	76 ppb	78 ppb	73 ppb	**74 ppb**
2017-2019*	77 ppb	81 ppb	75 ppb	**79 ppb**
*Preliminary and Incomplete				

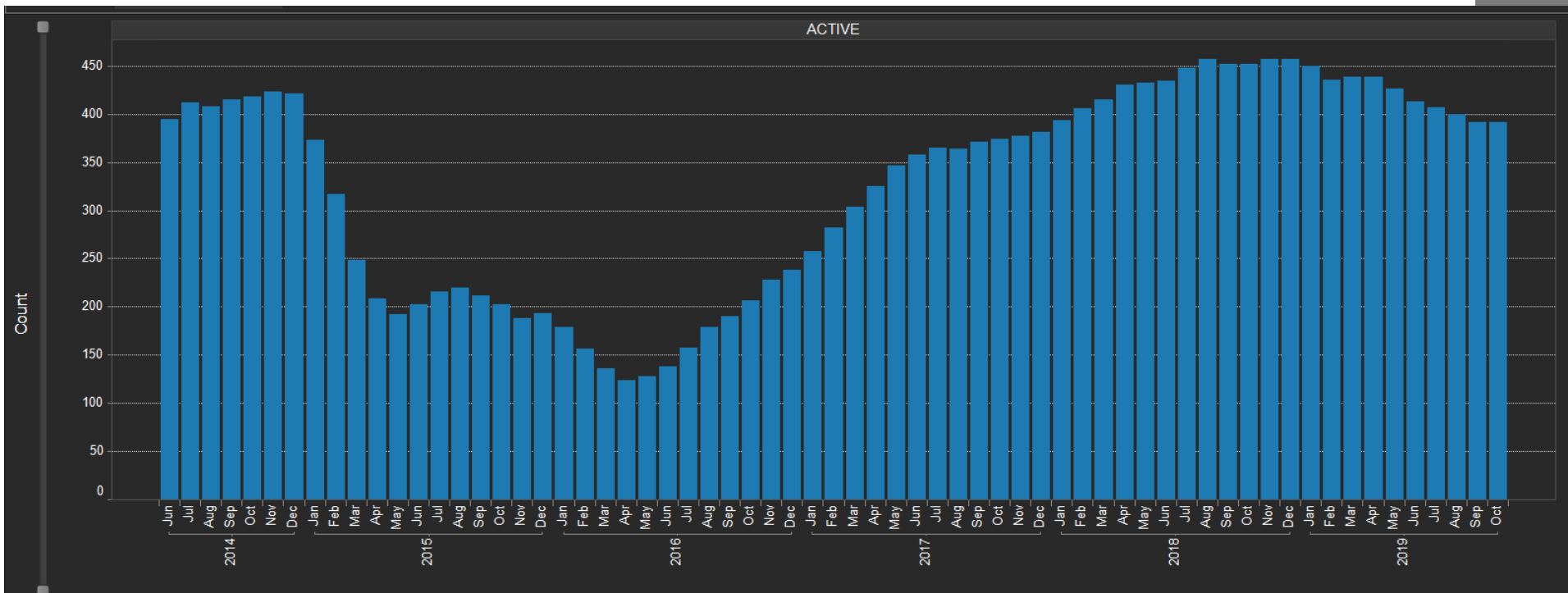
Mark Sather
U.S. EPA Region 6





Source: EIA

Active Drill Rig Count
Delaware and Midland
Basins



Source: Enverus

Carlsbad Caverns Intensive Air Quality Study

Artesia, NM
~30 mi N of Carlsbad

Carlsbad Caverns Intensive Air Quality Study

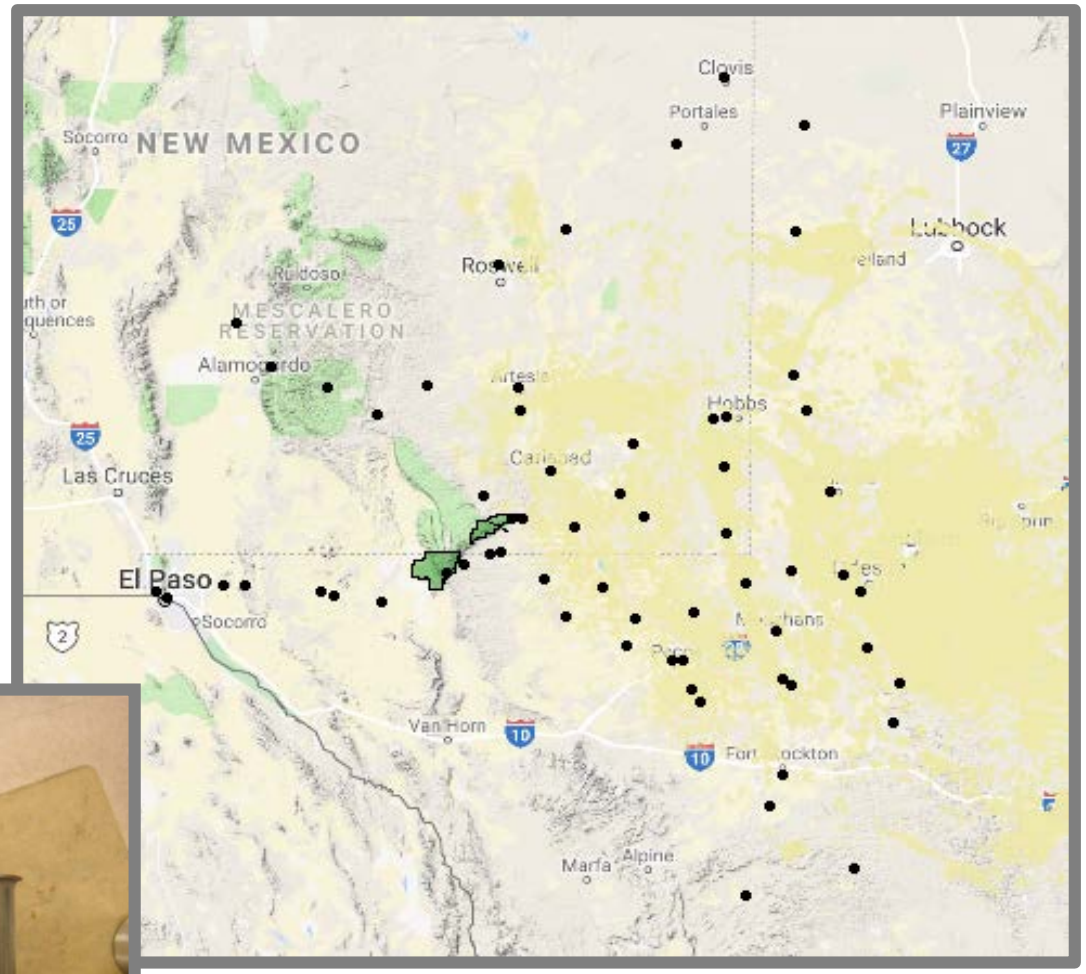
Measurements Setup 7/24 → Shutdown 9/3

- NO, NO_2, NO_y
- CH_4, NH_3, CO_2
- PAN
- Real-time GC: C_2-C_{10} NMHCs, C_1-C_5 alkyl nitrates, C_1-C_2 halocarbons, OVOCs, etc.
- PTR-MS: Formaldehyde, MeOH, EtOH, Propyne, HCN, Acetone, Acetic Acid, DMS, Isoprene, MVK/MAC, MEK, Benzene, Terpenes, Pentanal, Toluene, C8 aromatics, C9 aromatics, naphthalene, C10 aromatics, H_2S
- $PM_{2.5}$ mass and composition (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, Acetate, Formate, Glycolate, Oxalate)
- 24-hr NH_3, HNO_3, SO_2, and $PM_{2.5}$ composition
- Carbonyl cartridges (10 AM – 5 PM)
- Aethalometer (black carbon)
- NPS/ARS operated real-time O_3, SO_2, CO and meteorology

Carlsbad Caverns Intensive Air Quality Study

Additional Measurements

- Spatial Samples – 71 canisters
- Grab Samples 7/25 – 7/30 when personnel were at the site until GC system operational (61 canisters)
- Several ozone exceedances at the park
- 4 rain events



NOx/y PAN

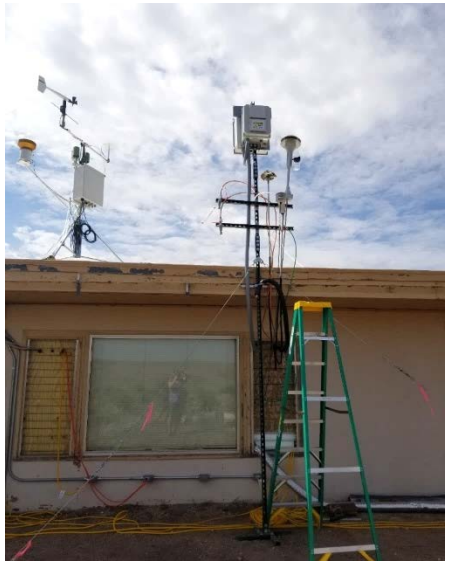
O_3, CO, SO_2

PTR-MS Real-time GC

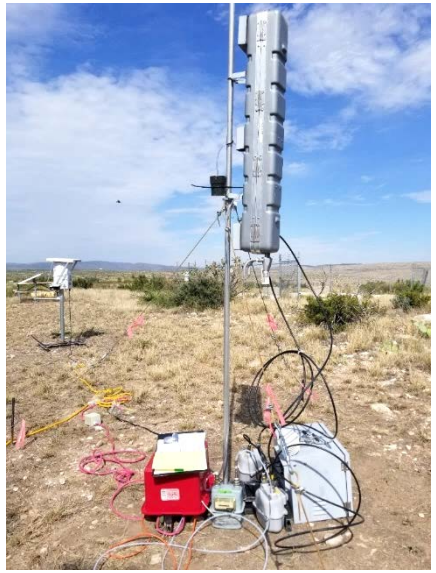
PILS-TOC PILS-IC

Picarro, Aethalometer TEOM

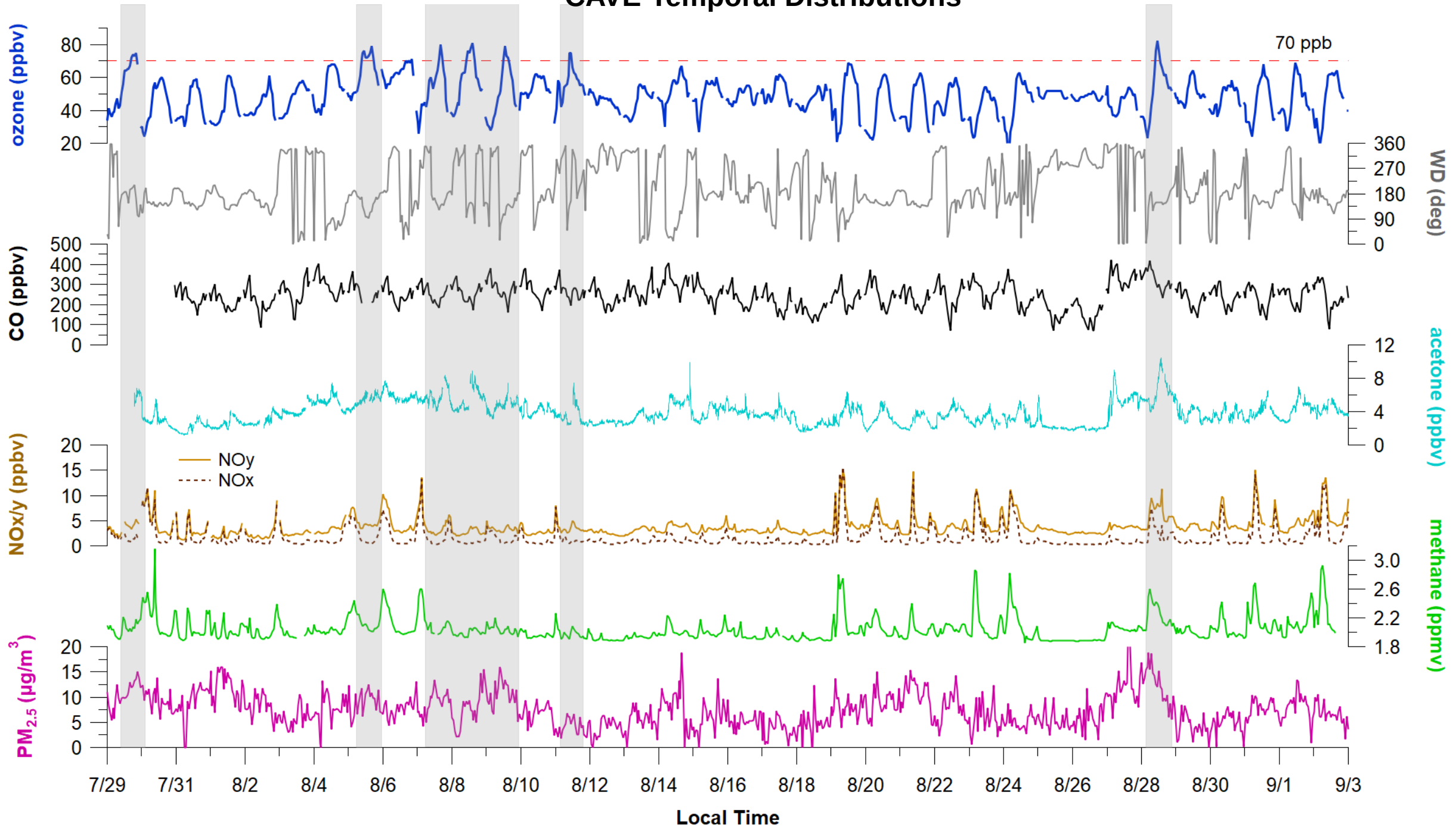
Inlets, Met



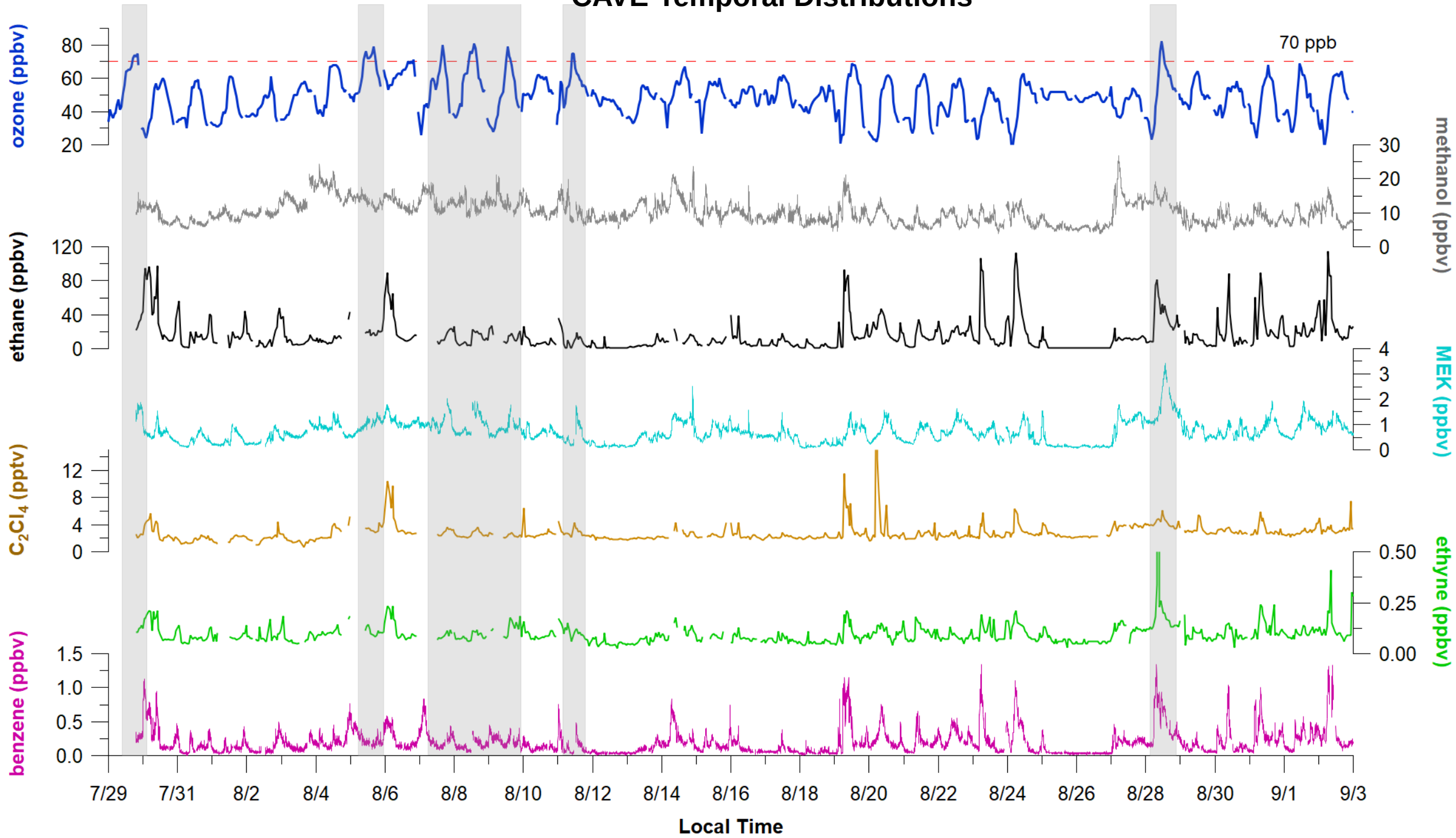
Precip, URG, HCHO



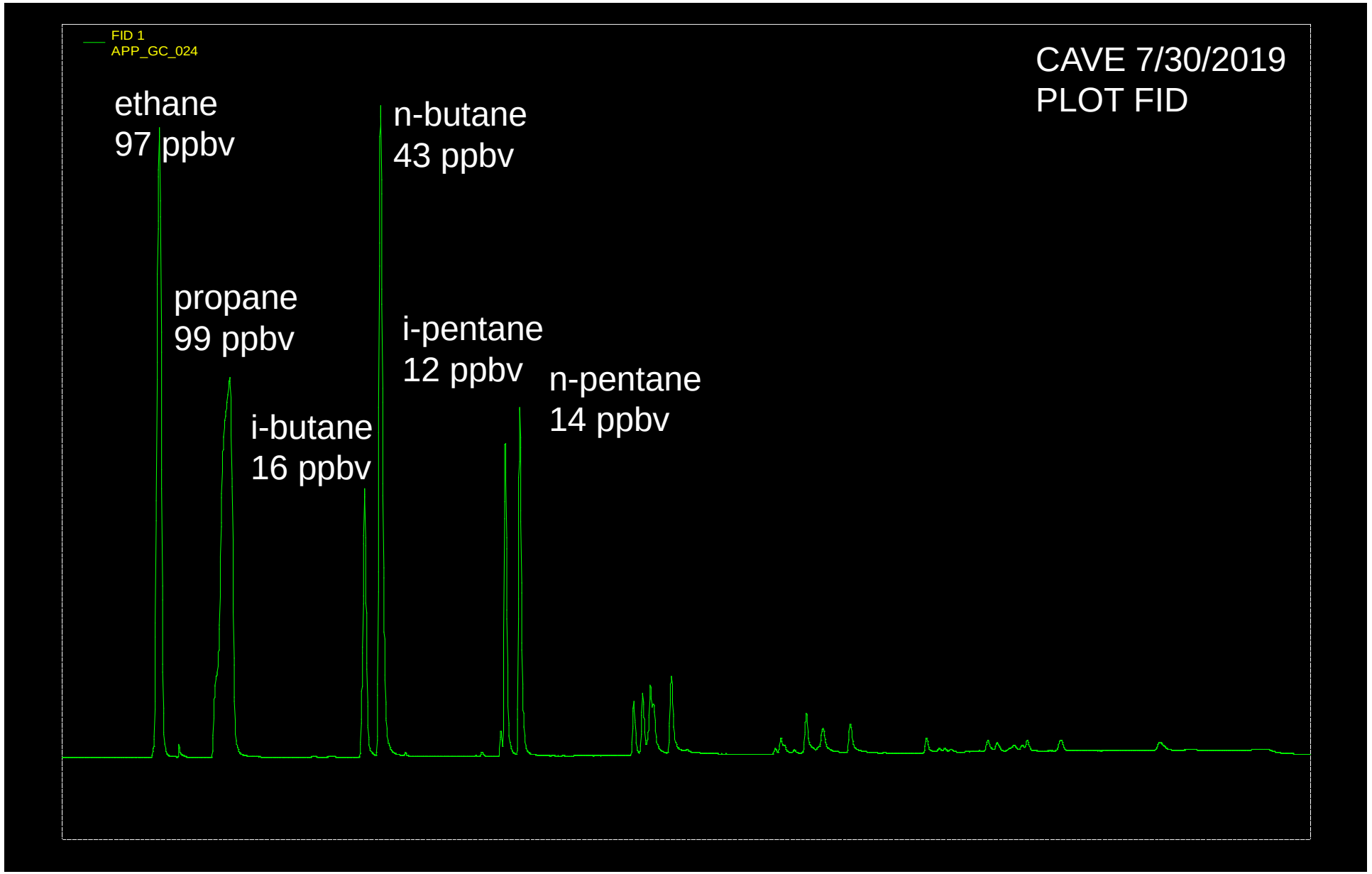
CAVE Temporal Distributions



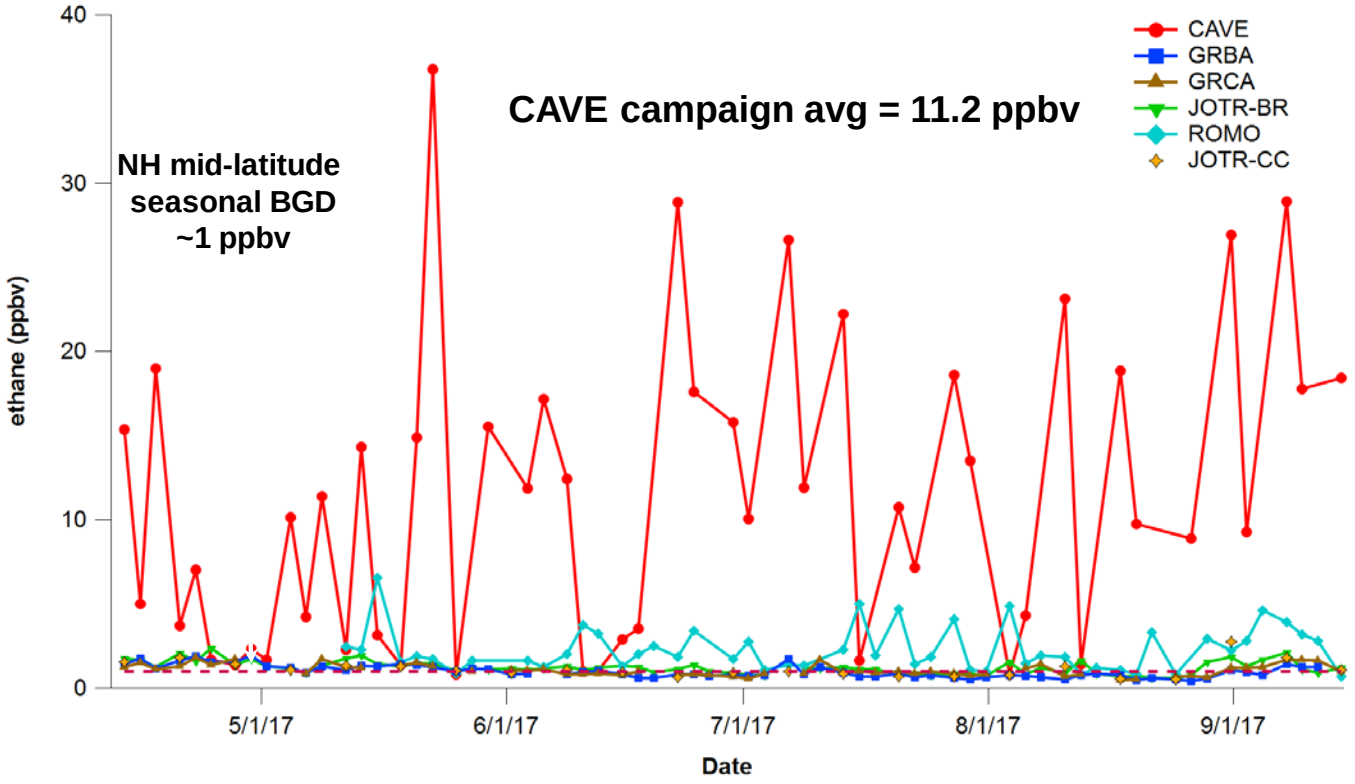
CAVE Temporal Distributions



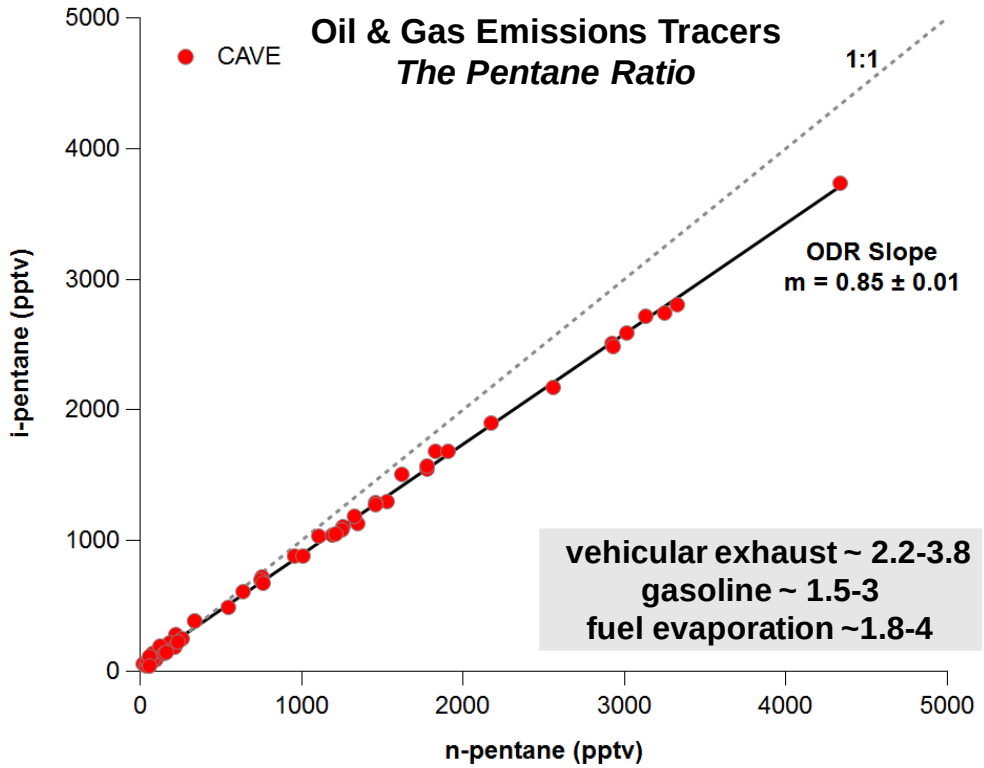
Oil & Gas Signature

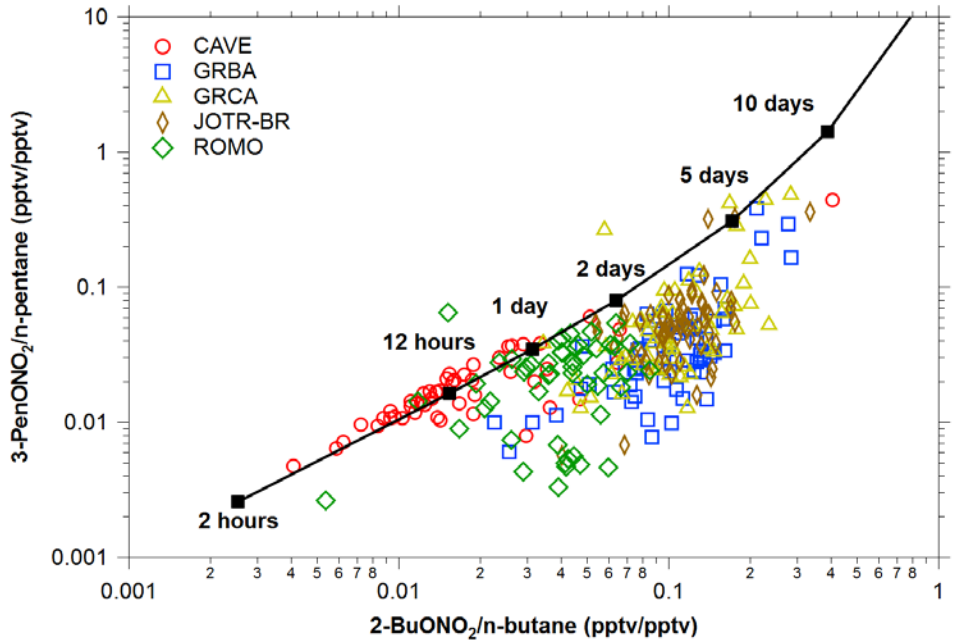


Comparison with 2017 Study Results



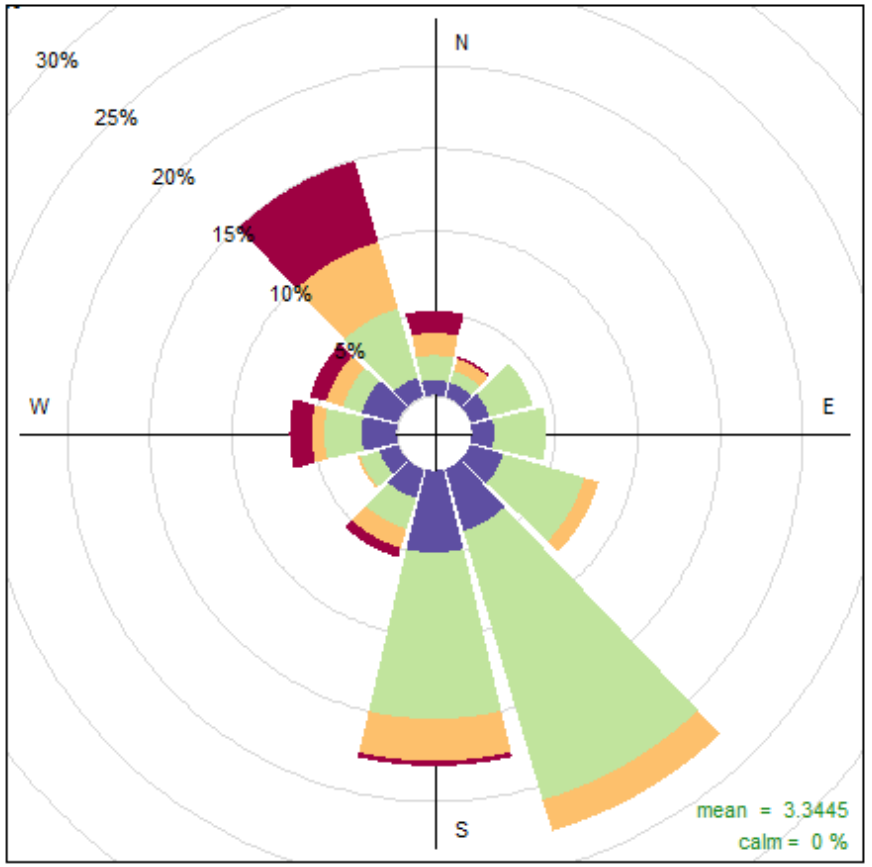
Ethane avg 2019 = 16.0 ppbv
Hourly sampling exhibited higher diurnal variability
Regularly observed levels >100 ppbv



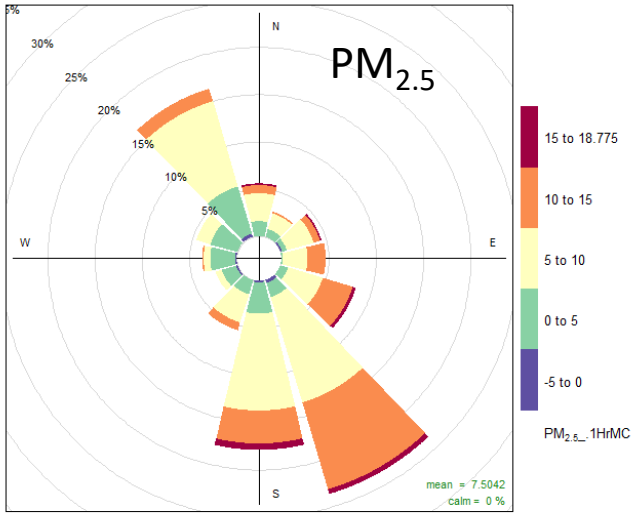


Photochemical Age using Alkyl Nitrates

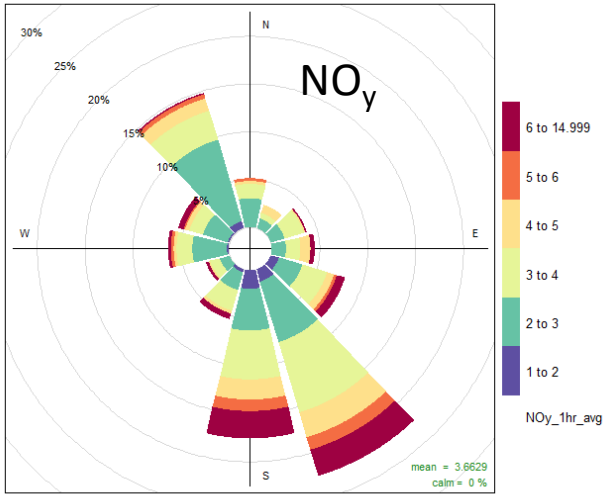
Distribution of Winds and Wind Speed



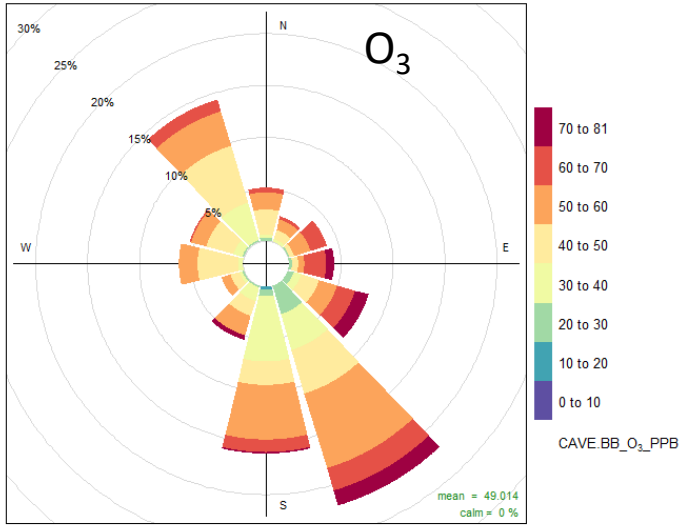
Frequency of counts by wind direction (%)



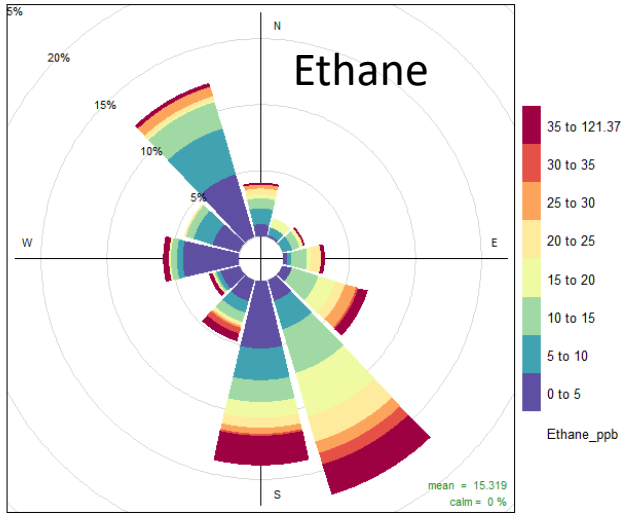
Frequency of counts by wind direction (%)



Frequency of counts by wind direction (%)

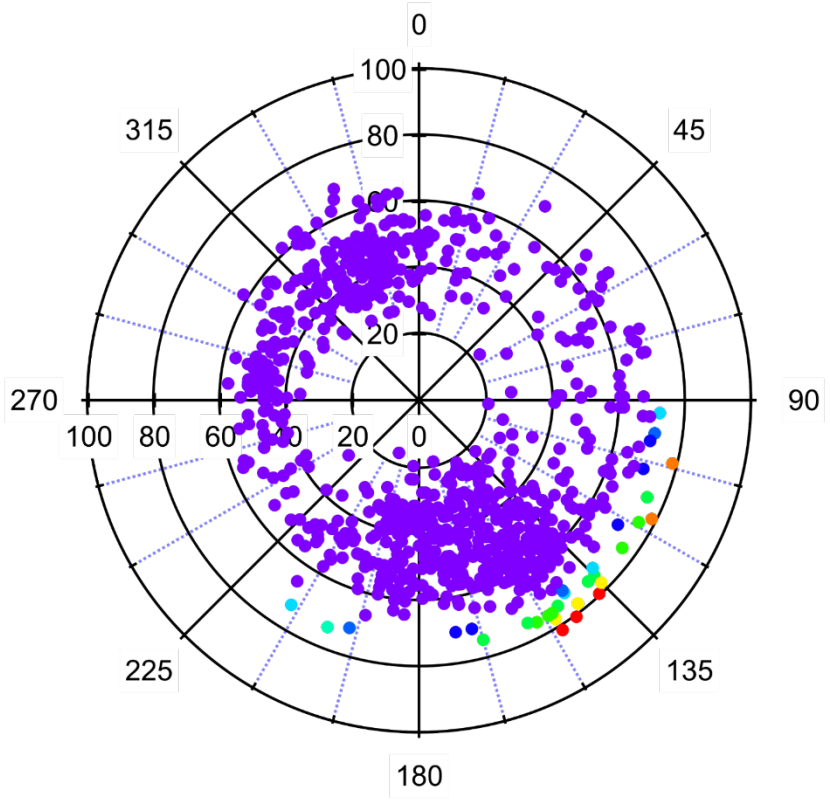


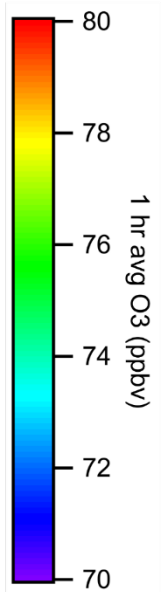
Frequency of counts by wind direction (%)



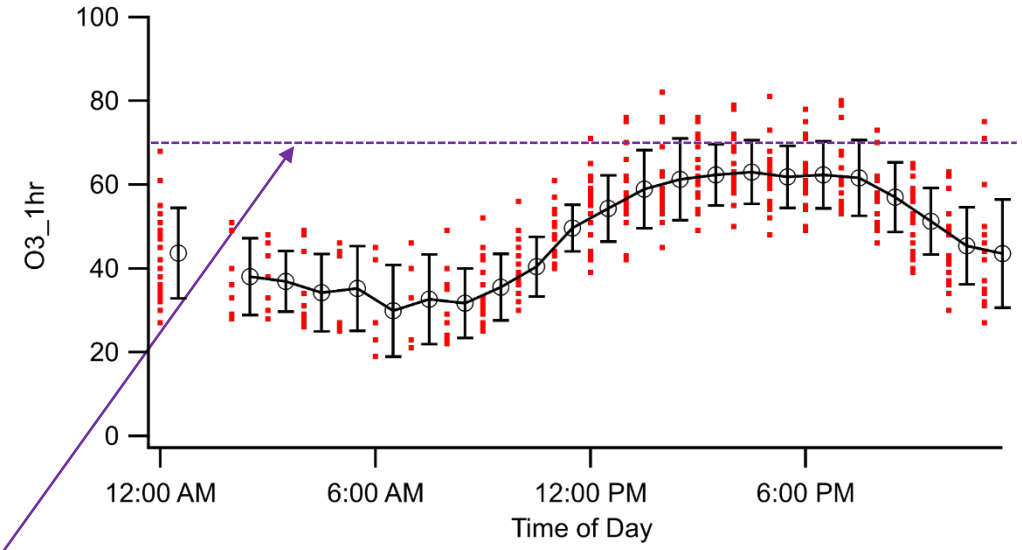
Frequency of counts by wind direction (%)

Ozone enhancements above the national standard are most frequently observed when the wind is from the southeast.





Photochemical production of ozone is typically largest in the afternoon.



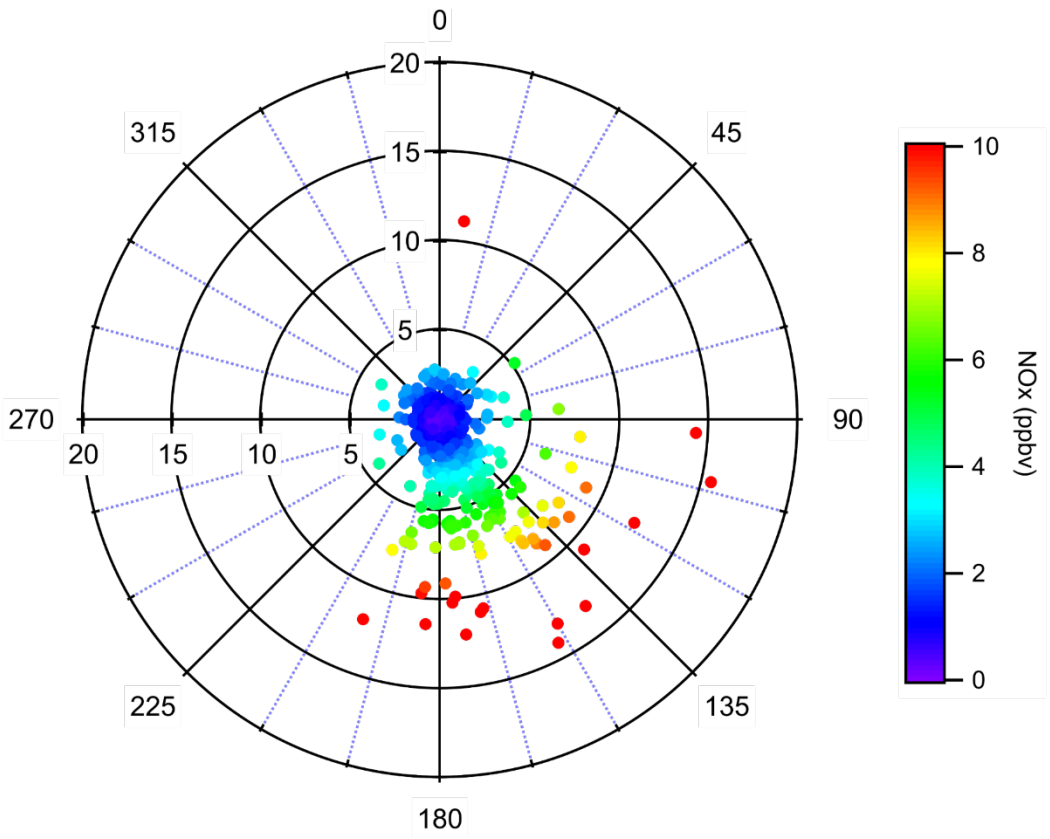
National Standard = 70 ppbv

Preliminary O_3 and winds from ARS Live Weather & Air Quality Data.
Data points represent 1-hour average O_3 collected between 27 July and 3 Sept 2019.

Diurnal profile limited to when the wind direction was from the southeast (between 90 and 180˚)

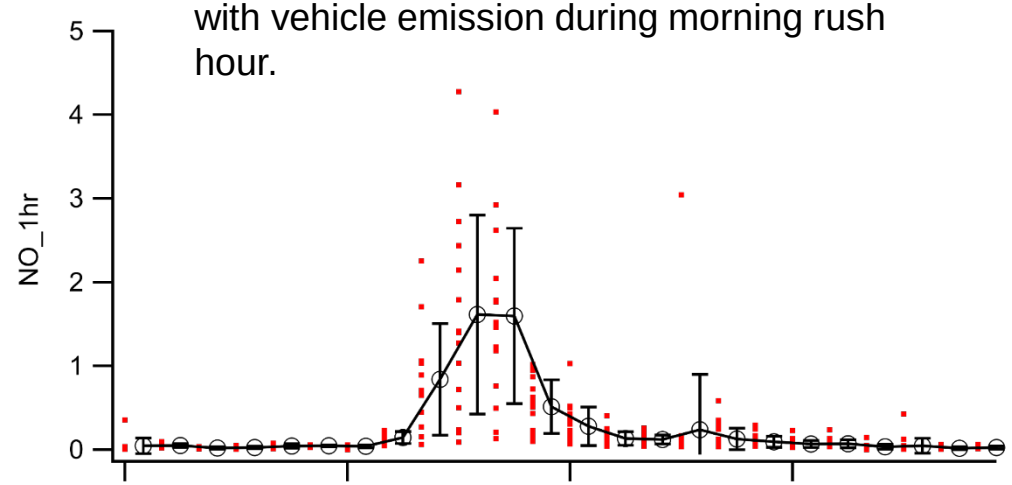
Enhancements in NOx emissions are most frequently from the southeast.

$NOx = NO + NO_2$

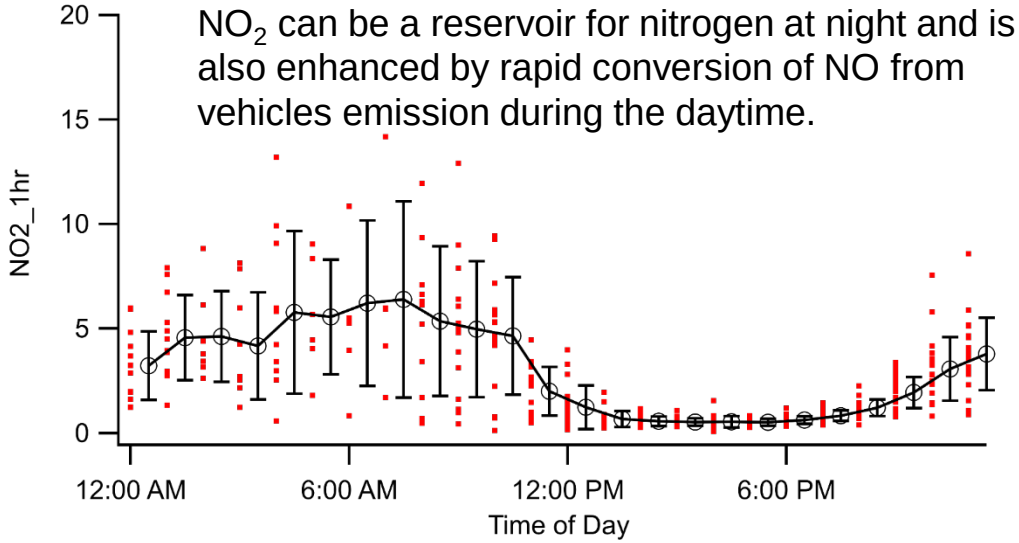


Data points are 1-hour average NO_x collected between 27 July and 3 Sept 2019.

NO enhancements are typically associated with vehicle emission during morning rush hour.

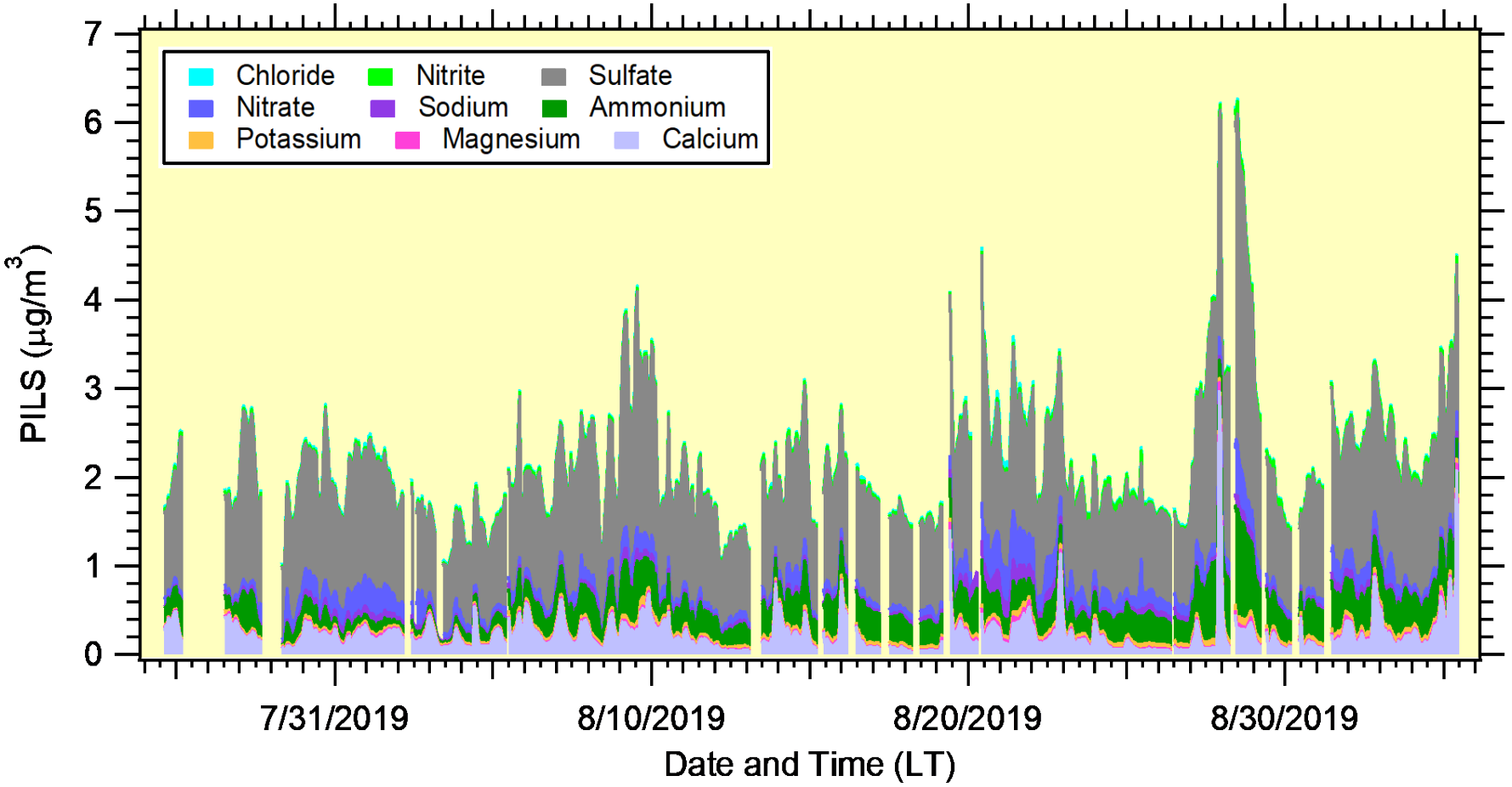


NO_2 can be a reservoir for nitrogen at night and is also enhanced by rapid conversion of NO from vehicles emission during the daytime.



Diurnal profiles limited to when the wind direction was from the southeast (between 90 and 180˚)

Time Series of Inorganic Ions

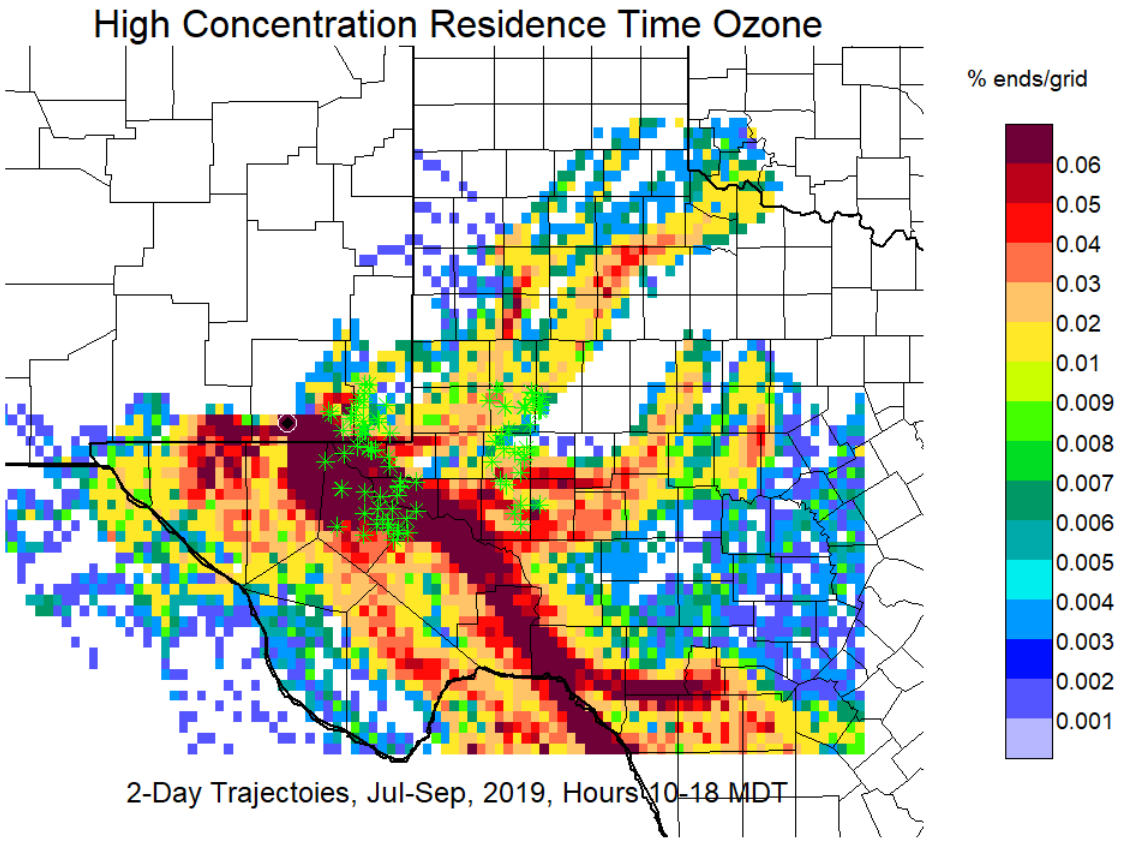


-Sulfate dominates mass

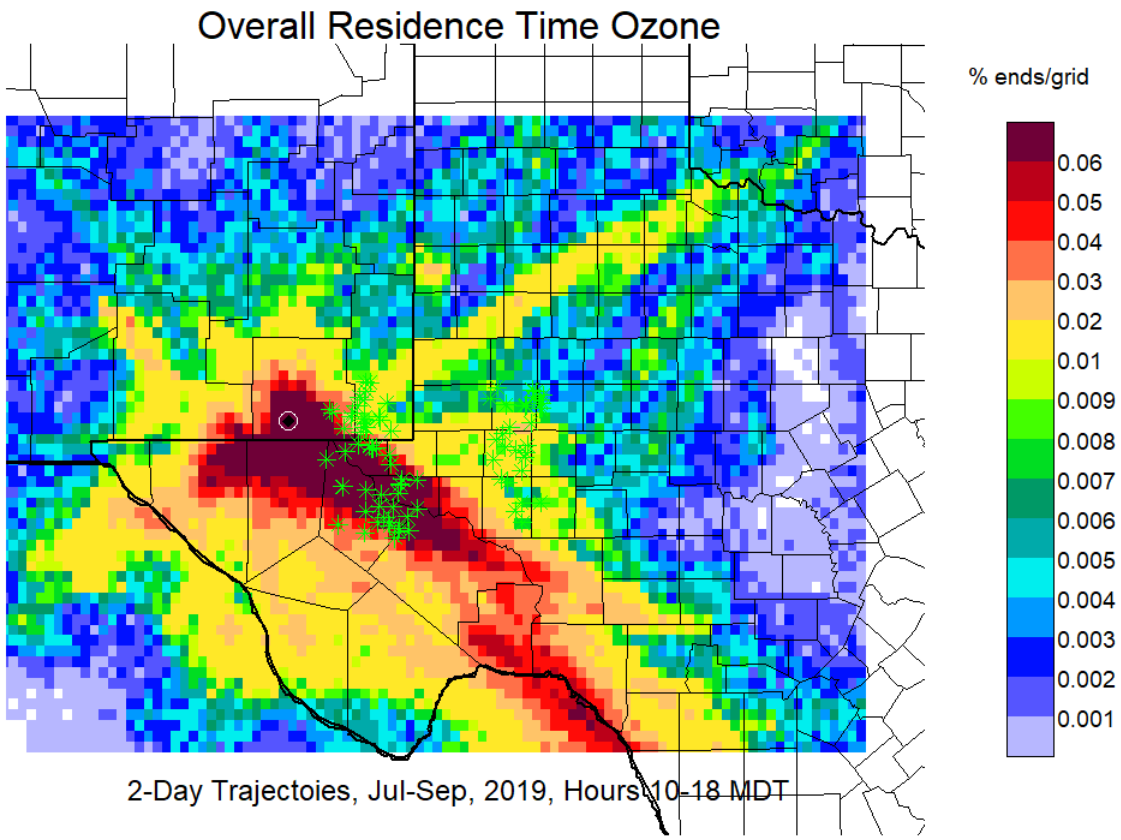
-Although ammonium present, not always main cation

High Residence Time Analysis

High Concentration Residence Time (HRT)

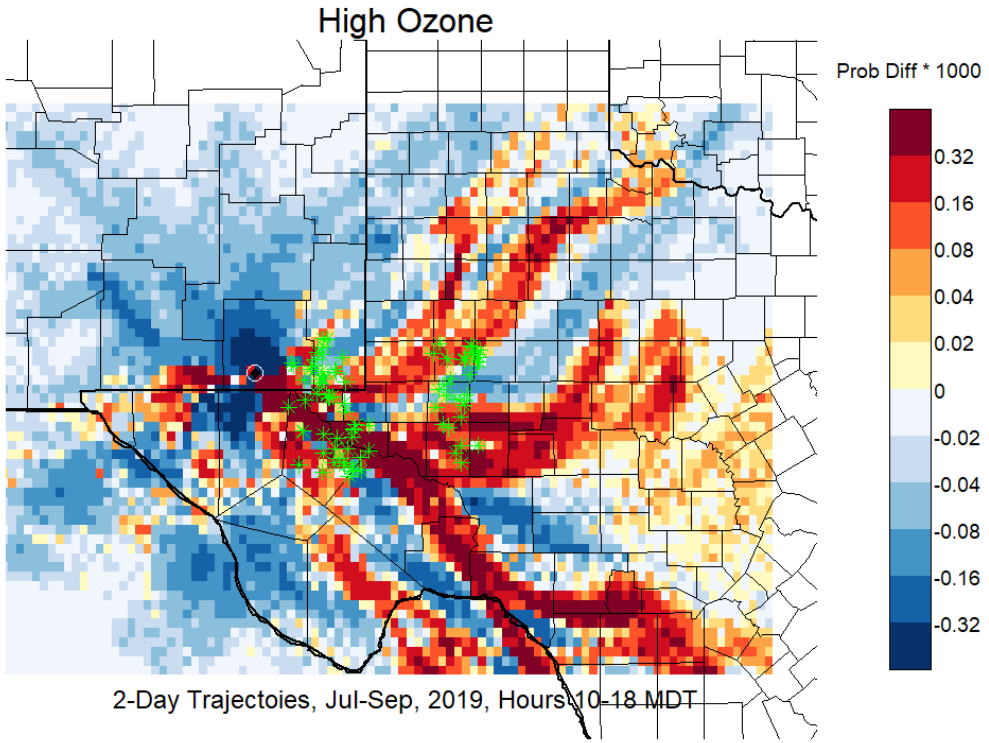


Overall Residence Time (ORT)

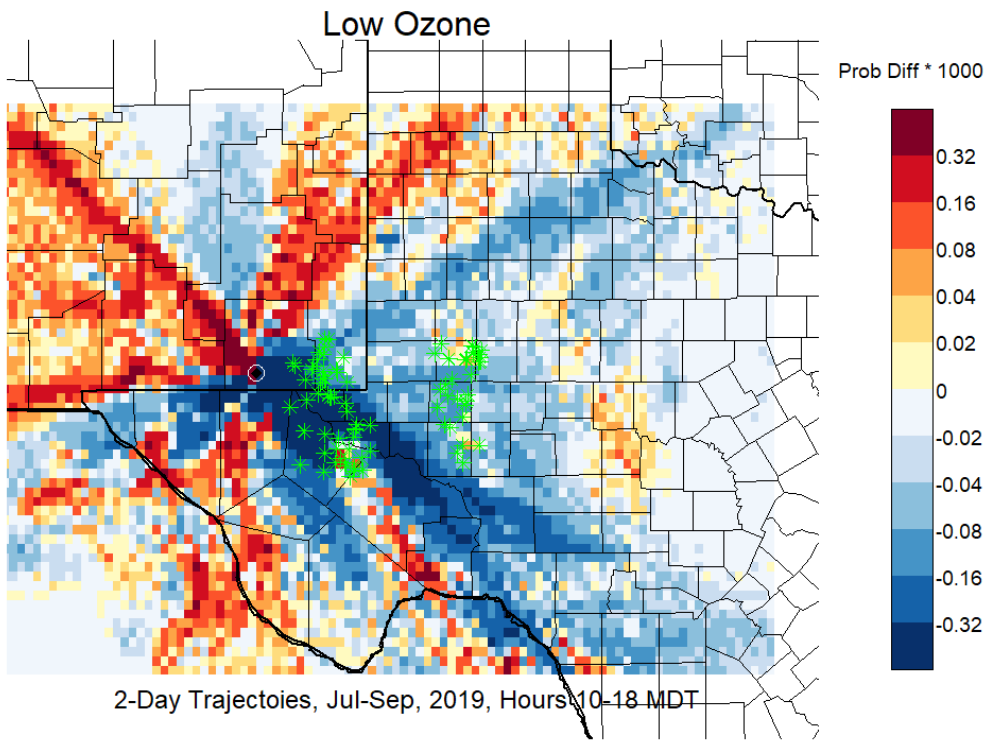


High Residence Time Analysis

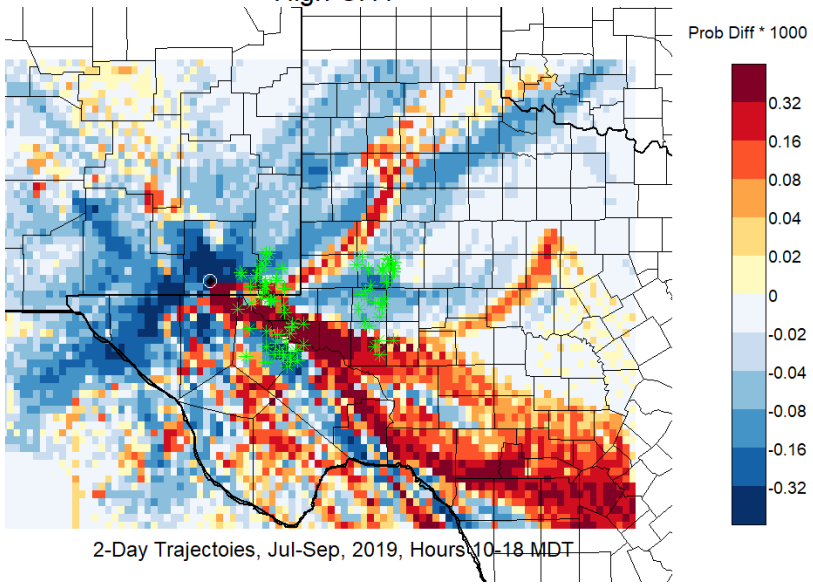
Highest 10% ozone = 74 ppb



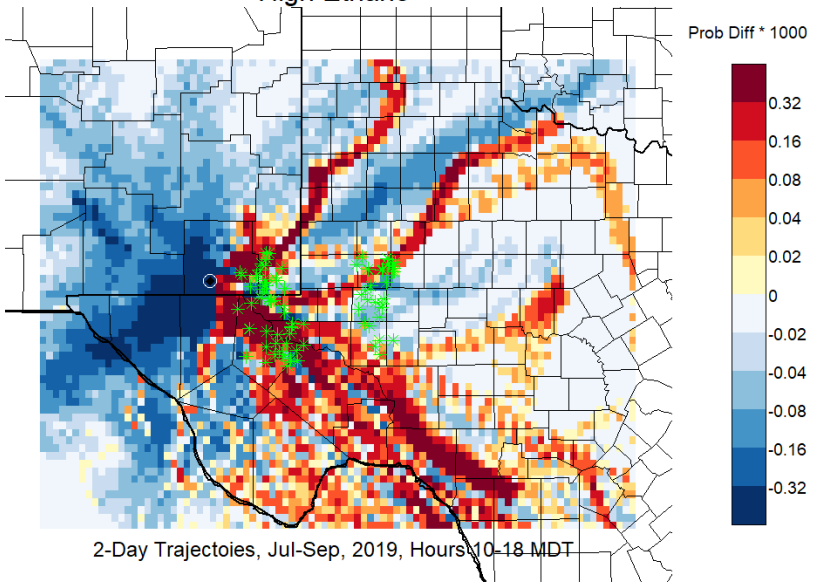
Lowest 10% ozone = 48 ppb



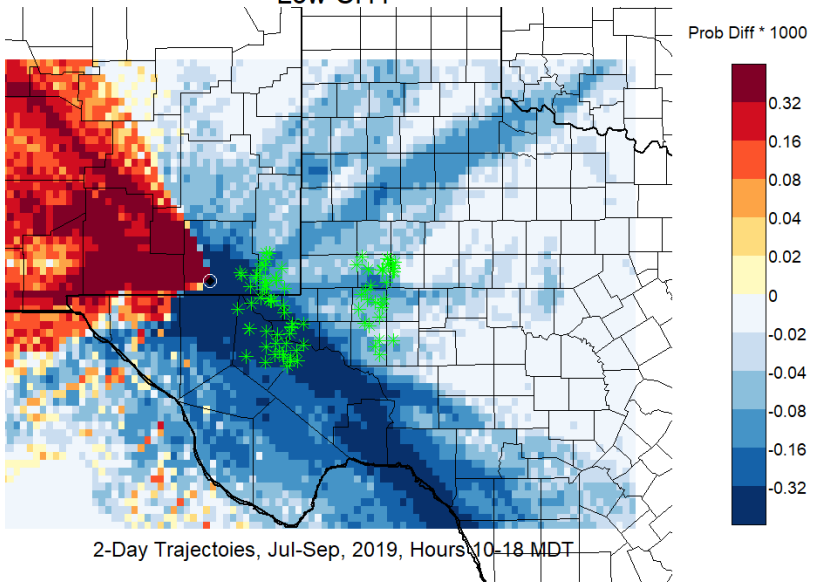
High CH4



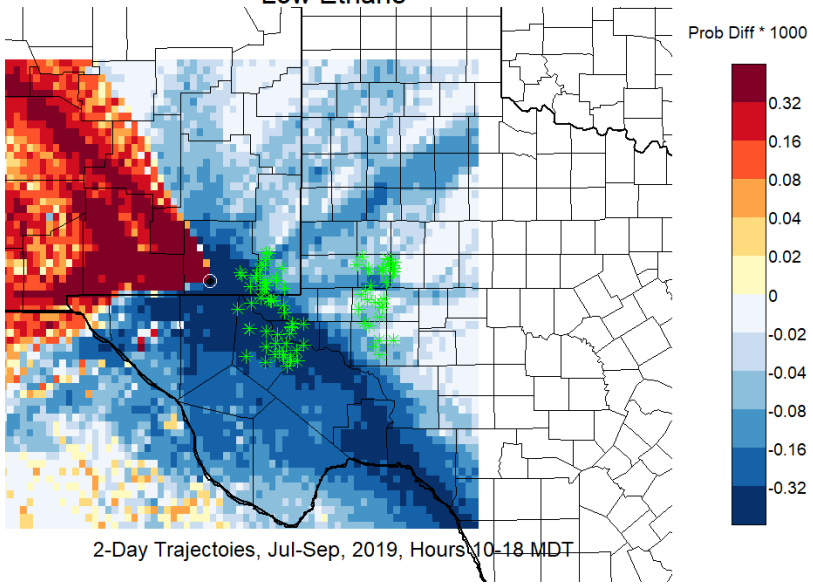
High Ethane



Low CH4



Low Ethane



Summary

- High levels of light alkanes, consistent with O&G emissions
- Multiple 8-hour ozone exceedances during study
- Highest levels of ozone and other pollutants (e.g. oxidized VOCs, reactive N, etc.) were transported from SE
- $PM_{2.5}$ ~10 µg/m^3, ranging from 2 to 15 µg/m^3
- Appears ~50% of the $PM_{2.5}$ mass is water-soluble (includes WSOC)

Future work: A lot to do, but a very rich and comprehensive data set that will allow for a detailed understanding of AQ impacts at CAVE.