

# Volatile Organic Compound and Ozone Measurements at Carlsbad Caverns National Park: Impacts of Oil and Natural Gas Operation Emissions on Park Air Quality

## National Park Service, Air Resources Division

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# Carlsbad Caverns Intensive Air Quality Study

## July – September 2019

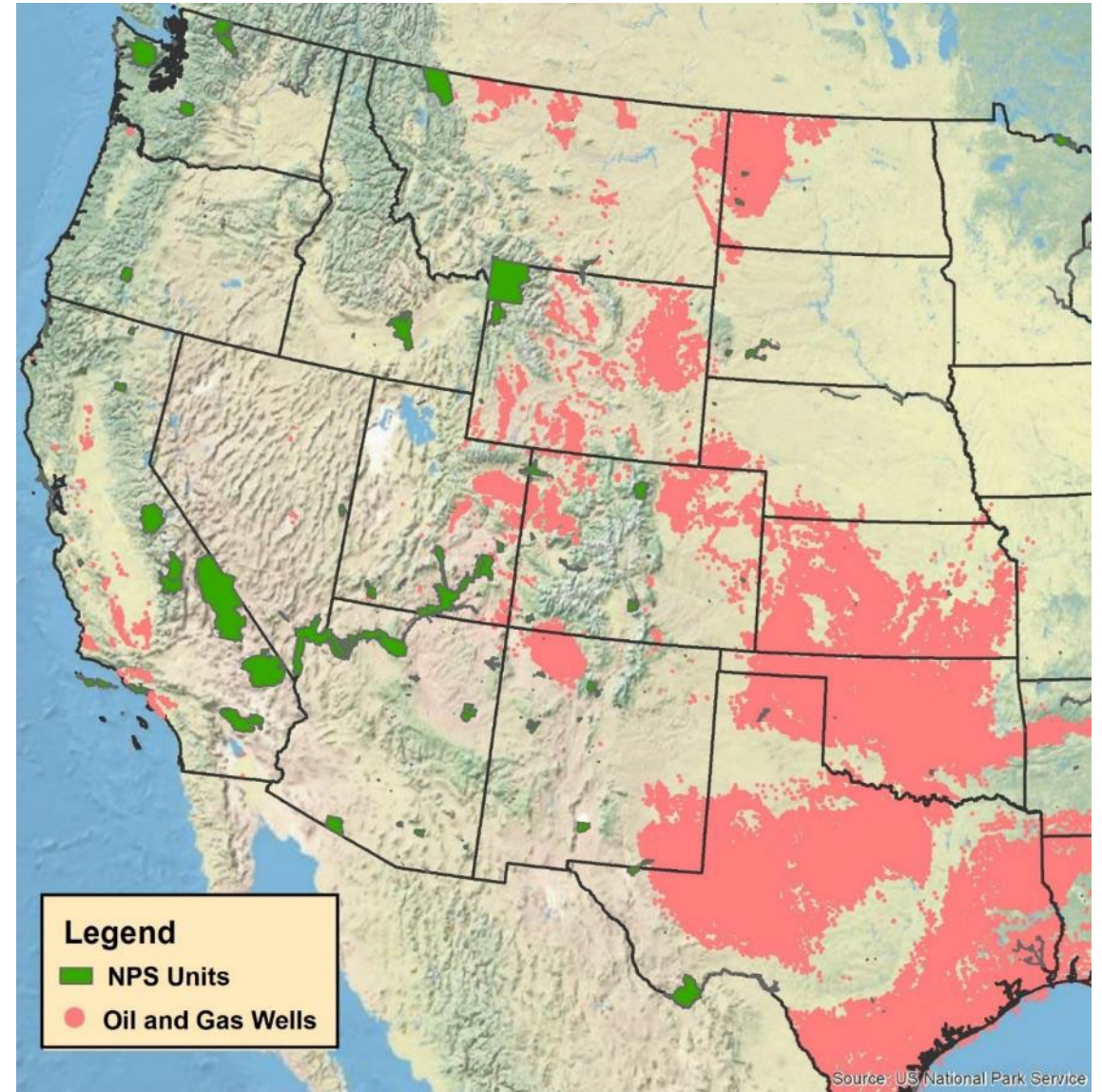
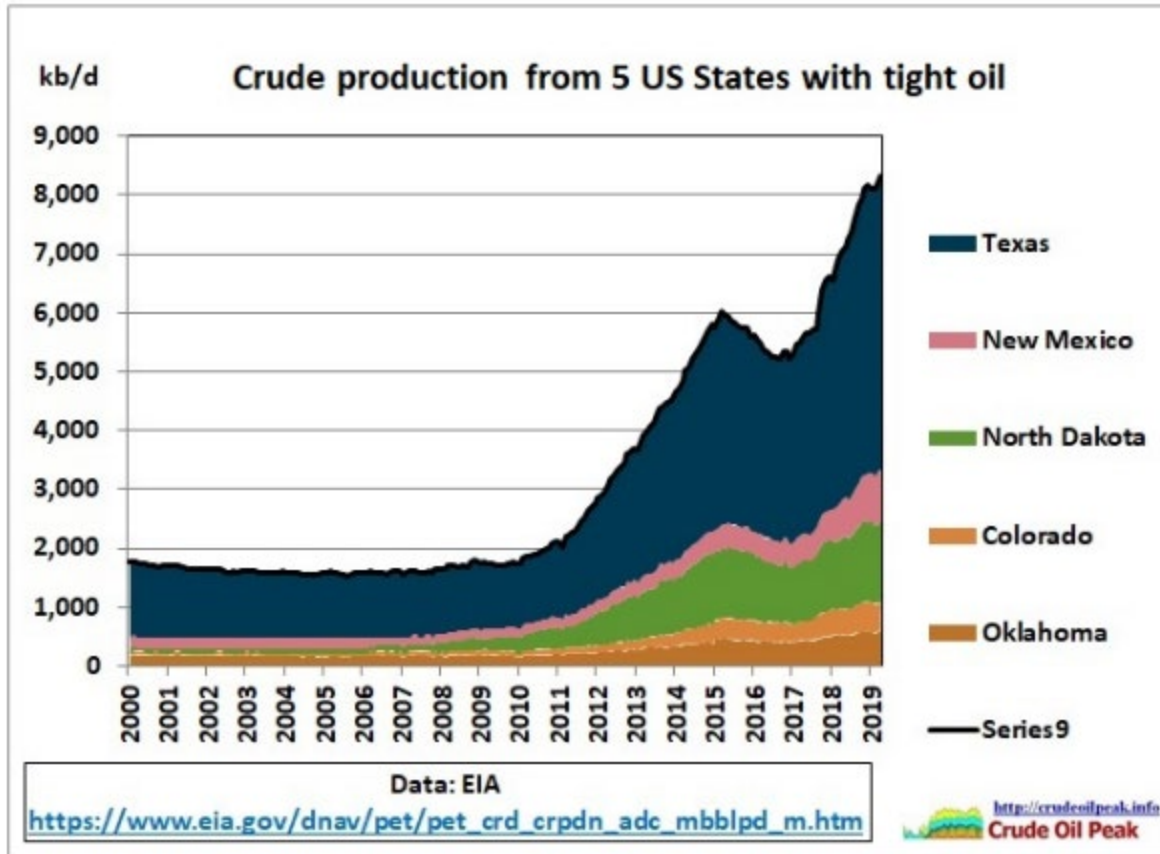
### Objectives

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 NO<sub>x</sub> concentrations?
3. What species, e.g. NO<sub>x</sub>, H<sub>2</sub>S, and VOC, contribute to or limit aerosol formation?

**NOTE: ALL DATA AND FINDINGS ARE PRELIMINARY**

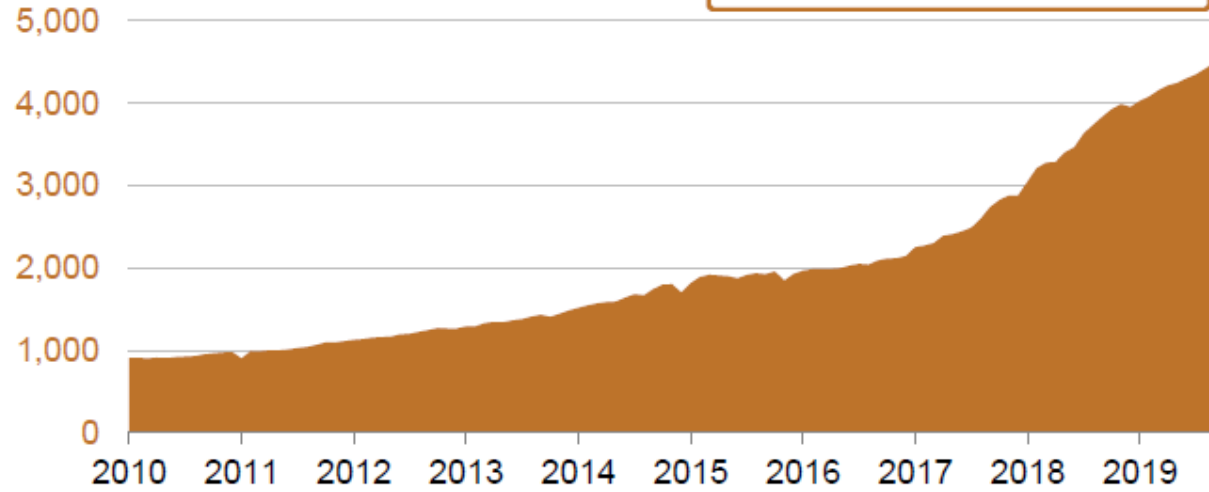


# Extensive Oil & Gas Activities throughout Midwest and West



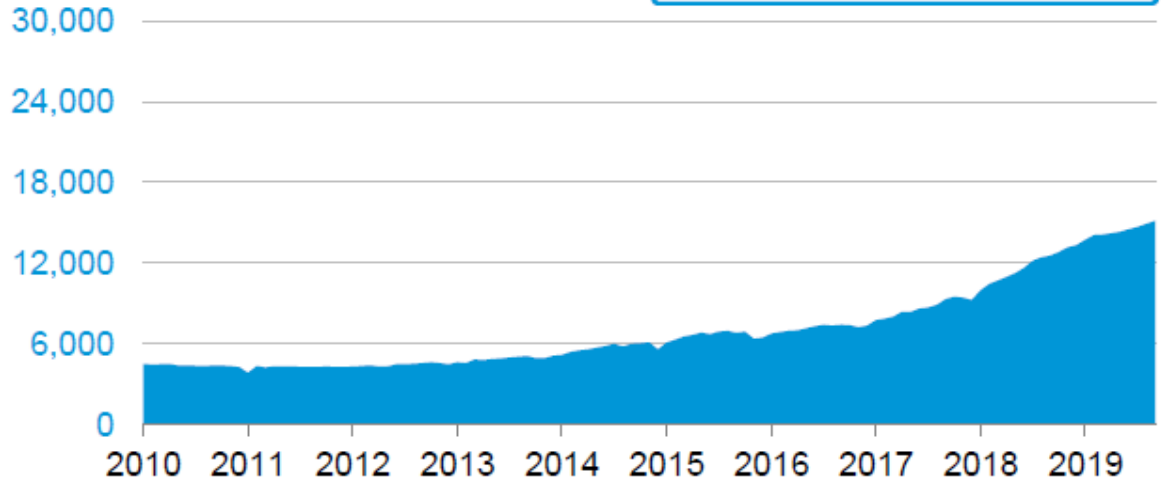


Permian Region  
Oil production  
thousand barrels/day



**Oil +71**  
thousand barrels/day  
month over month

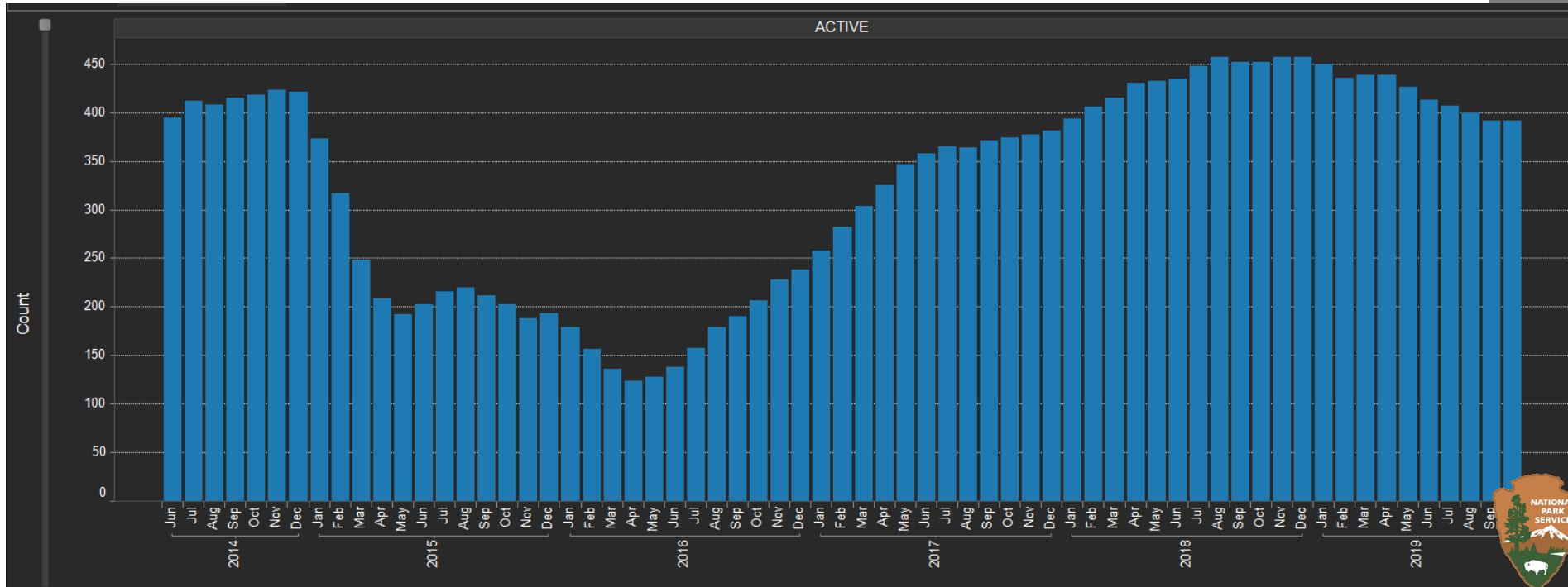
Permian Region  
Natural gas production  
million cubic feet/day



**Gas +229**  
million cubic feet/day  
month over month

Source: EIA

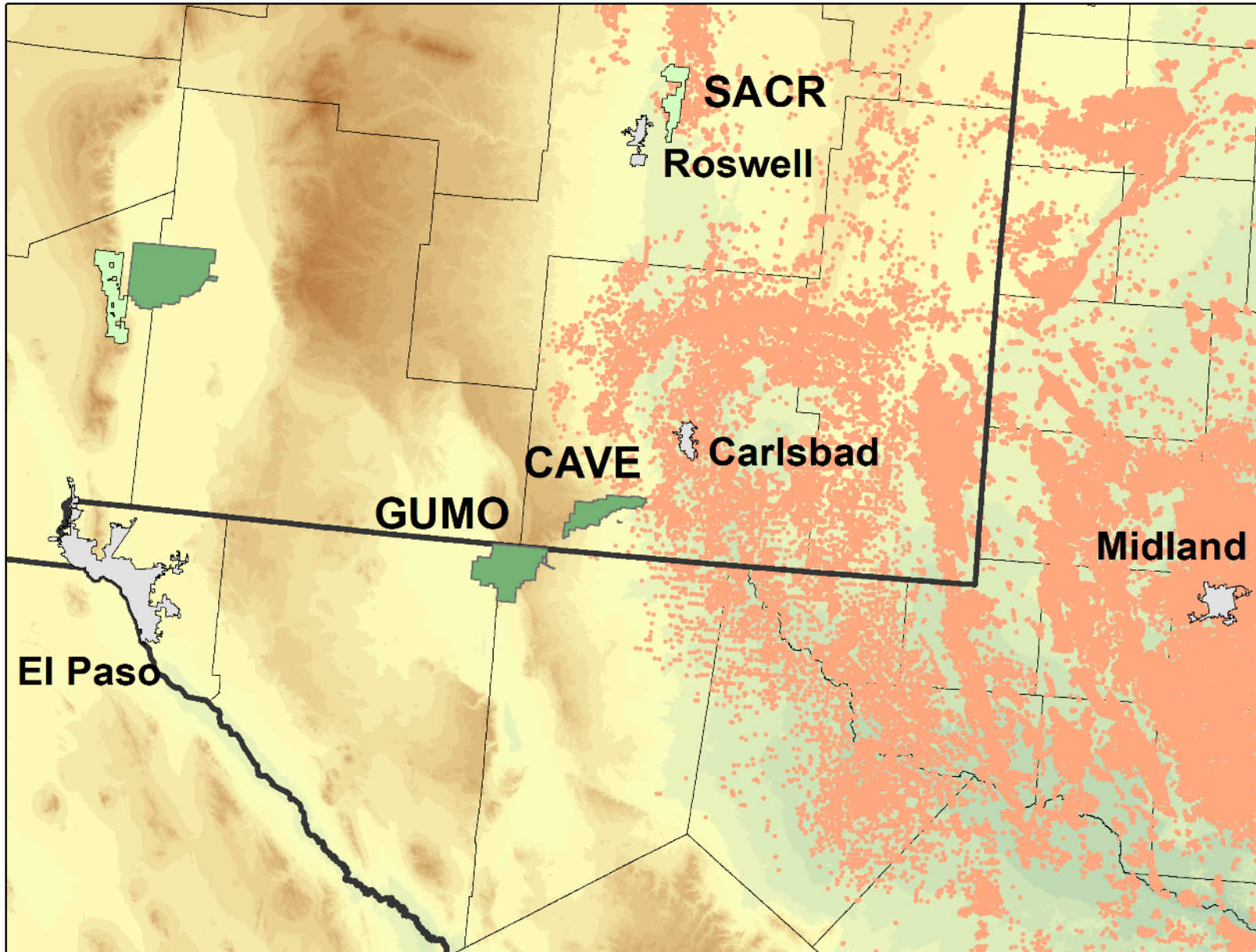
Active Drill Rig Count  
Delaware and Midland Basins



Source: Enverus



# Wells Near CAVE\*



\*2017



## 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
<b>Texas</b>	<b># &gt; 70 ppb</b>
<b>Houston</b>	<b>28</b>
<b>Dallas-Fort Worth</b>	<b>29</b>
Beaumont	4
Longview	1
Tyler	1
El Paso	9
Austin	1
San Antonio	4
Corpus Christi	
Waco	
Killeen-Temple	2
Victoria	
<b>Louisiana</b>	
Baton Rouge	6
Pointe Coupee	3
Shreveport	
New Orleans	
Lake Charles	
Lafayette	
Lafourche Parish	2
<b>Oklahoma</b>	
Tulsa	2
Oklahoma City	2
Cherokee Tribal	
Cherokee Fort Smith MSA	
Quapaw Tribal	
<b>Arkansas</b>	
Little Rock	
Crittenden Co.	1
Shelby Co., TN	2
DeSoto Co., MS	1
<b>New Mexico</b>	
Albuquerque	4
San Juan Co.	
Southern Dona Ana Co.	14
<b>Carlsbad</b>	<b>19</b>
Hobbs	3

# Ozone Exceedances and Design Values 2019

8-hr O3 DV Years	CAVE	Carlsbad, NM	DFW	Houston
2014-2016	67	67	80	79
2015-2017	66	68	79	81
2016-2018	71	74	76	78
<b>2017-2019</b>	<b>74</b>	<b>79</b>	<b>77</b>	<b>81</b>
2018-2020	73	78	76	79
2019-2021*	74	77	76	77

State/Cities	8-hr Ozone Year to Date Exceedance Days
<b>Through Oct 1, 2021</b>	
<b>Texas</b>	<b># &gt; 70 ppb</b>
<b>Houston</b>	<b>20</b>
<b>Dallas-Fort Worth</b>	<b>25</b>
El Paso	16
<b>New Mexico</b>	
Albuquerque	15
San Juan Co.	7
Southern Dona Ana Co.	16
<b>Carlsbad</b>	<b>23</b>
<b>Carlsbad Caverns NP</b>	<b>14</b>
Hobbs	3

\*Preliminary and incomplete

Mark Sather  
U.S. EPA Region 6



2. →  
1. →

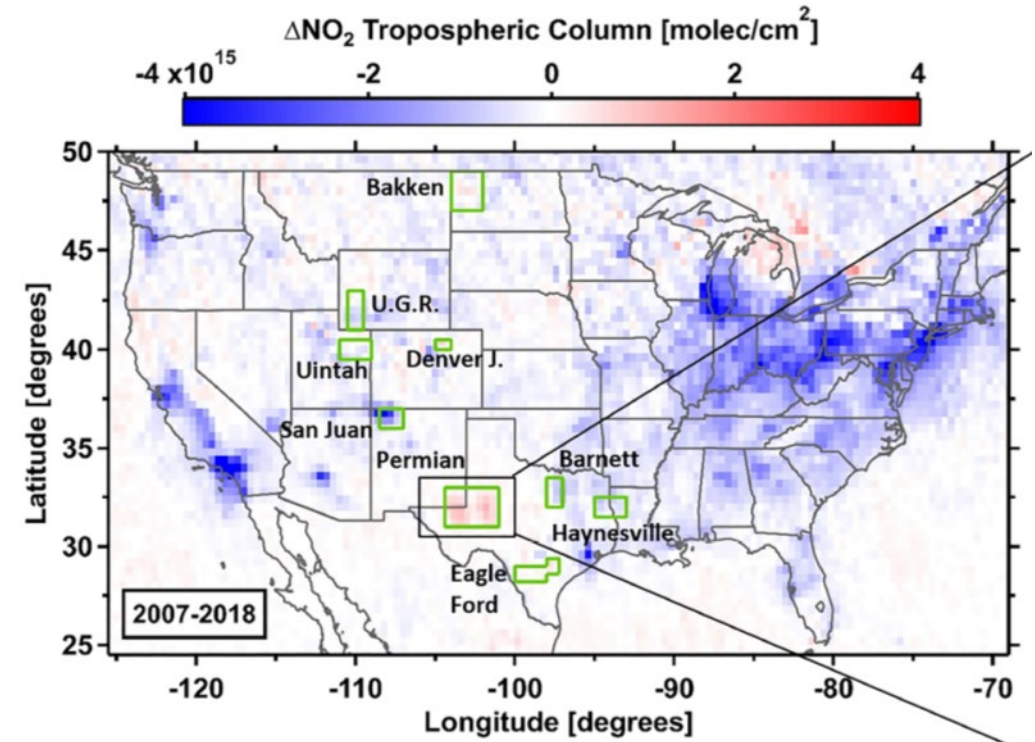
3. →

# Increases in NO<sub>x</sub> and Ozone at Carlsbad Caverns National Park

**Carlsbad Caverns Ozone**  
70 ppb is the national standard

Year	# Exceedance Days	Years	8-hr 4 <sup>th</sup> high O <sub>3</sub>
2016	None	2014-2016	67
2017	None	2015-2017	66
2018	10	2016-2018	<b>71</b>
2019	6	2017-2019	<b>74</b>
2020	9	2018-2020	<b>73</b>
2021	15	2019-2021*	<b>74</b>

\*Preliminary and incomplete



**Trends in NO<sub>x</sub> from satellite data**  
(Dix et al., 2020)





# Years of toxic leaks raise cancer risk in refinery town

Corbin Hiar, E&E News reporter • Published: Thursday, April 2, 2020

April, 2 2020

# Artesia, NM In the news...



Noxious fumes of Tank 57

HollyFi



Claudine Hellmuth/E&E News (graphic); © 2020 Google (map data)

## AIR POLLUTION

### EPA hits N.M. refinery for long-running toxic leak

Mike Soraghan, E&E News reporter

Published: Tuesday, May 12, 2020

May 12, 2020



HollyFrontier Navajo Refining LLC's refinery in Artesia, N.M. HollyFrontier Corp./New Mexico Environment Department

A New Mexico refinery continued operating a leaky tank even after learning that it was causing benzene pollution that ranked as some of the worst in the nation, according to EPA investigators.





# 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<sub>2</sub>, NO<sub>y</sub>
- CH<sub>4</sub>, NH<sub>3</sub>, CO<sub>2</sub>
- PAN, PPN
- Real-time GC: C<sub>2</sub>-C<sub>10</sub> NMHCs, C<sub>1</sub>-C<sub>5</sub> alkyl nitrates, C<sub>1</sub>-C<sub>2</sub> halocarbons, OVOCs, etc.
- PTR-MS: HCHO, MeOH, EtOH, Propyne, HCN, Acetone, Acetic Acid, DMS, Isoprene, Pentanal, MVK/MAC, MEK, Benzene, Toluene, C<sub>8</sub>, C<sub>9</sub> & C<sub>10</sub> aromatics, naphthalene, Terpenes, H<sub>2</sub>S
- PM<sub>2.5</sub> mass and composition (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Acetate, Formate, Glycolate, Oxalate)
- 24-hr NH<sub>3</sub>, HNO<sub>3</sub>, SO<sub>2</sub>, and PM<sub>2.5</sub> composition
- Carbonyl cartridges (10 AM – 5 PM)
- Aethalometer (black carbon)
- NPS/ARS operated real-time O<sub>3</sub>, SO<sub>2</sub>, CO and meteorology





**NO<sub>x</sub>/y**

**PANs**

**O<sub>3</sub>, CO, SO<sub>2</sub>**

**PTR-MS**

**Real-time GC**



**PILS-TOC**

**PILS-IC**

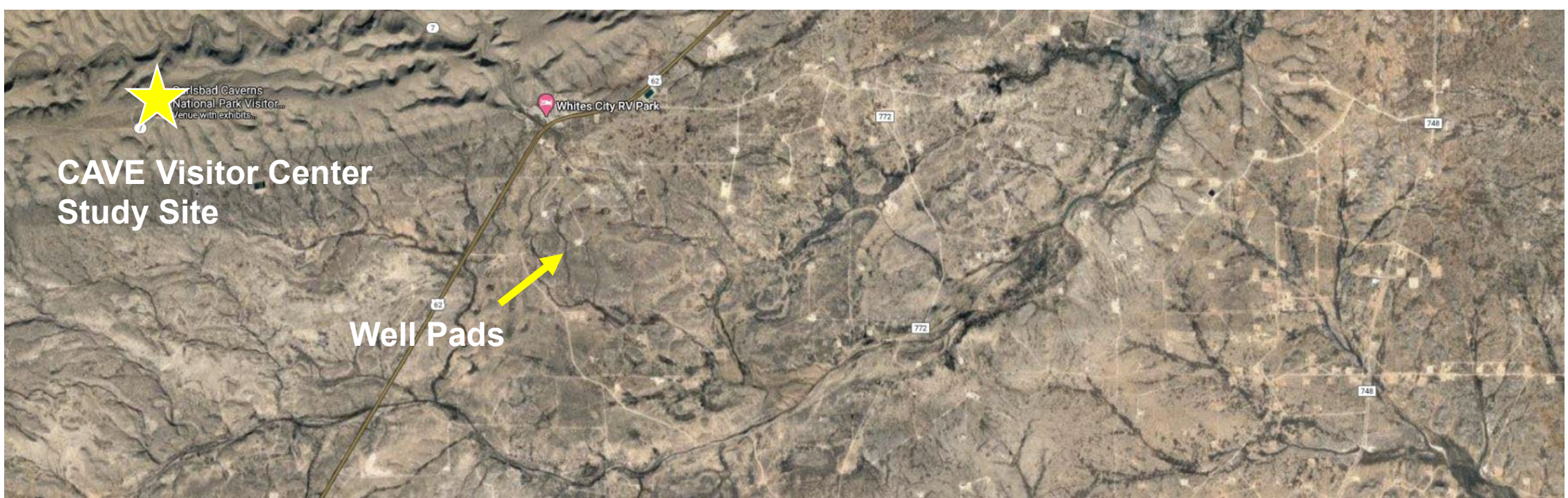
**Picarro, Aethalometer TEOM**

**Inlets, Met**

**Precip, URG, HCHO**





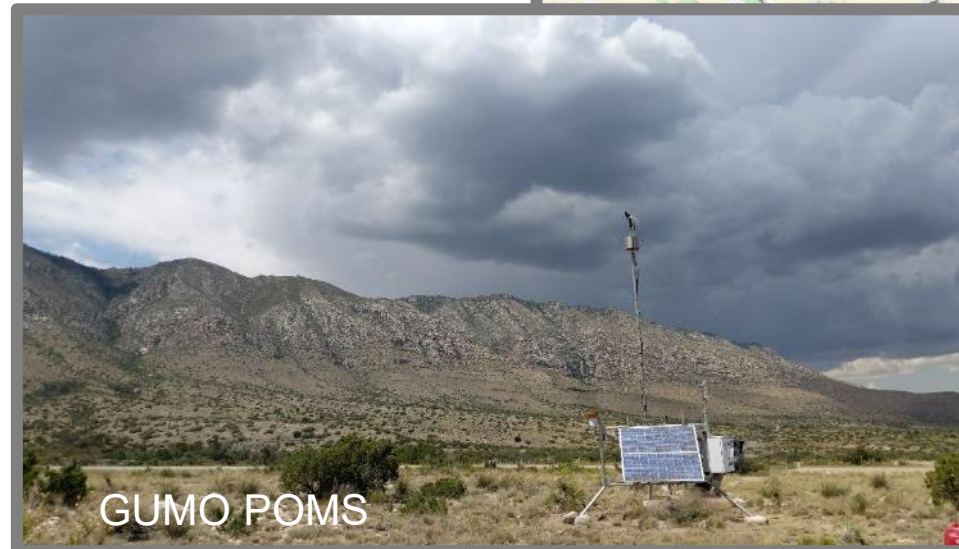
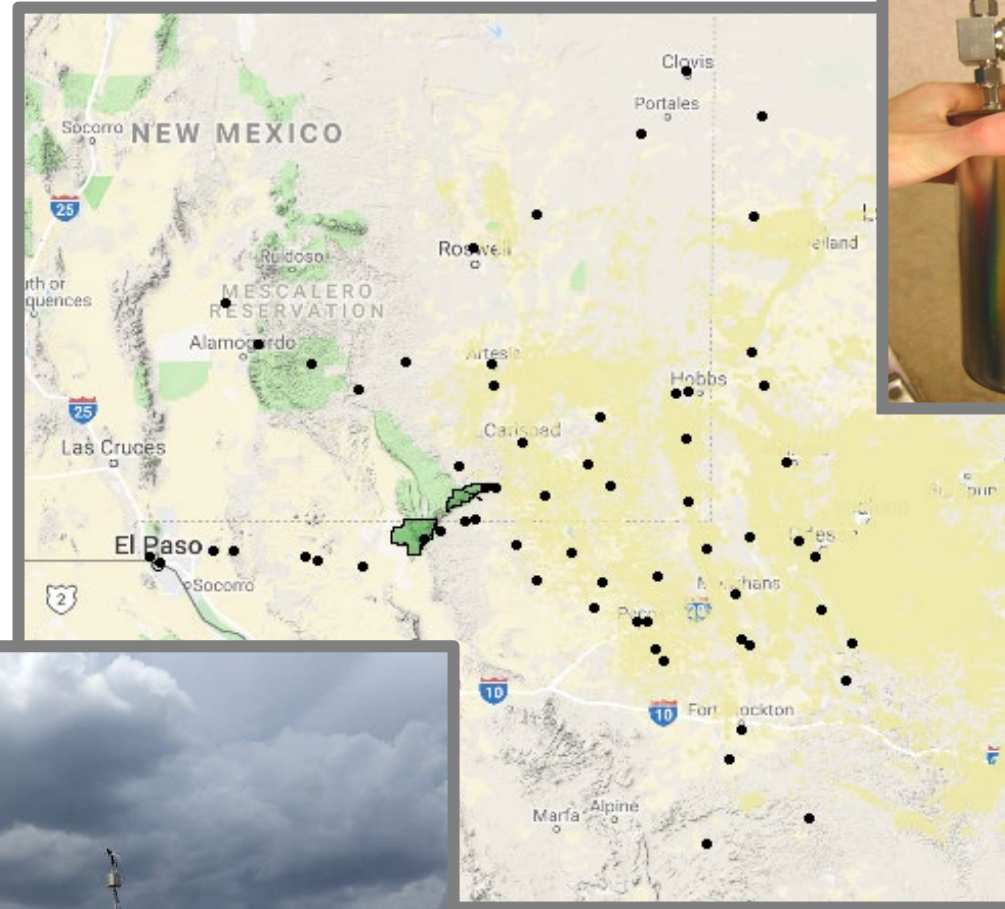




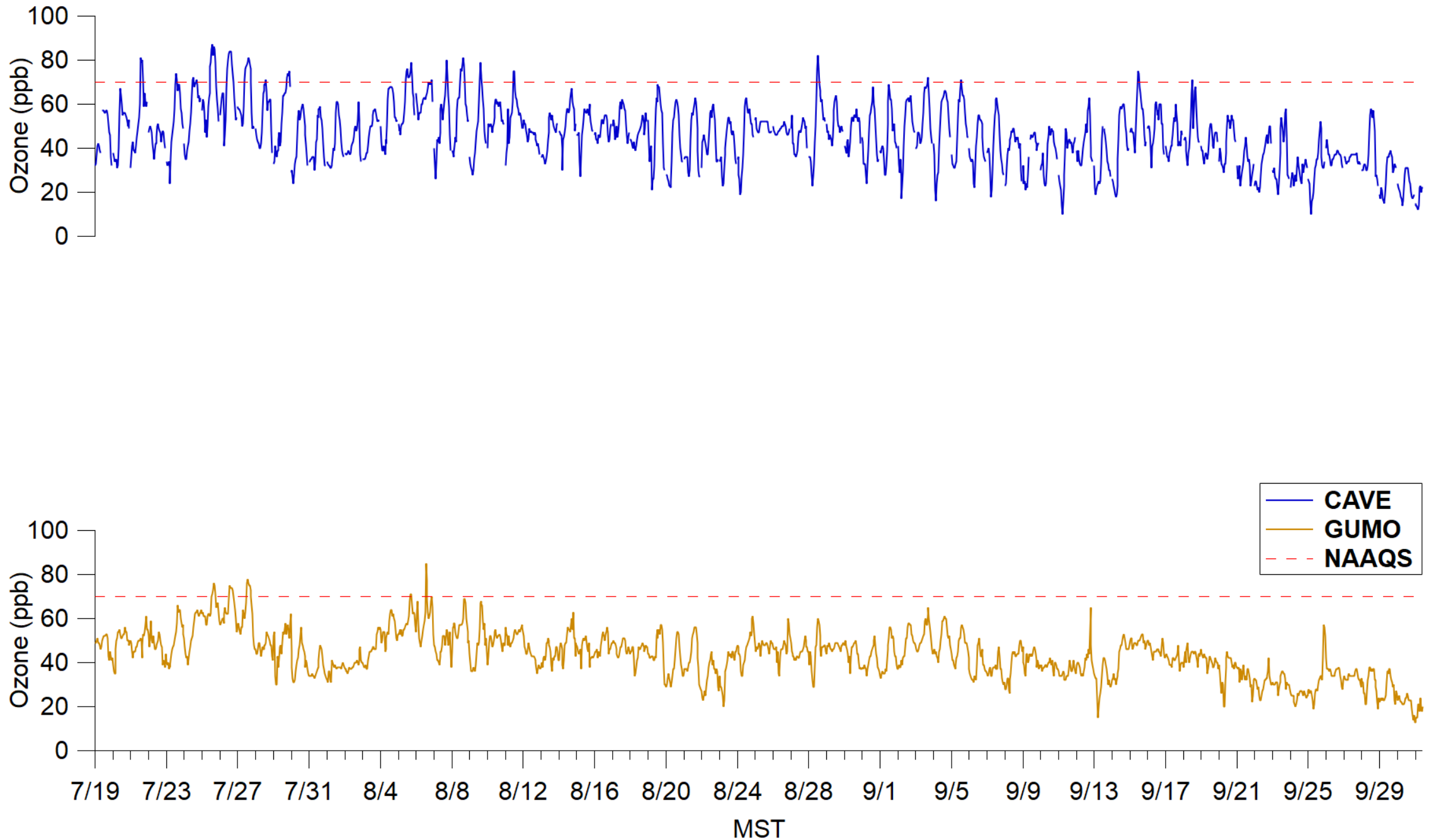
# Carlsbad Caverns Intensive Air Quality Study

## Additional Measurements

- Spatial Samples – 71 canisters
- Grab Samples 7/25 – 7/30 when personnel were at the site until GC system operational (61 canisters)
- Ozone and Meteorology
  - GUMO

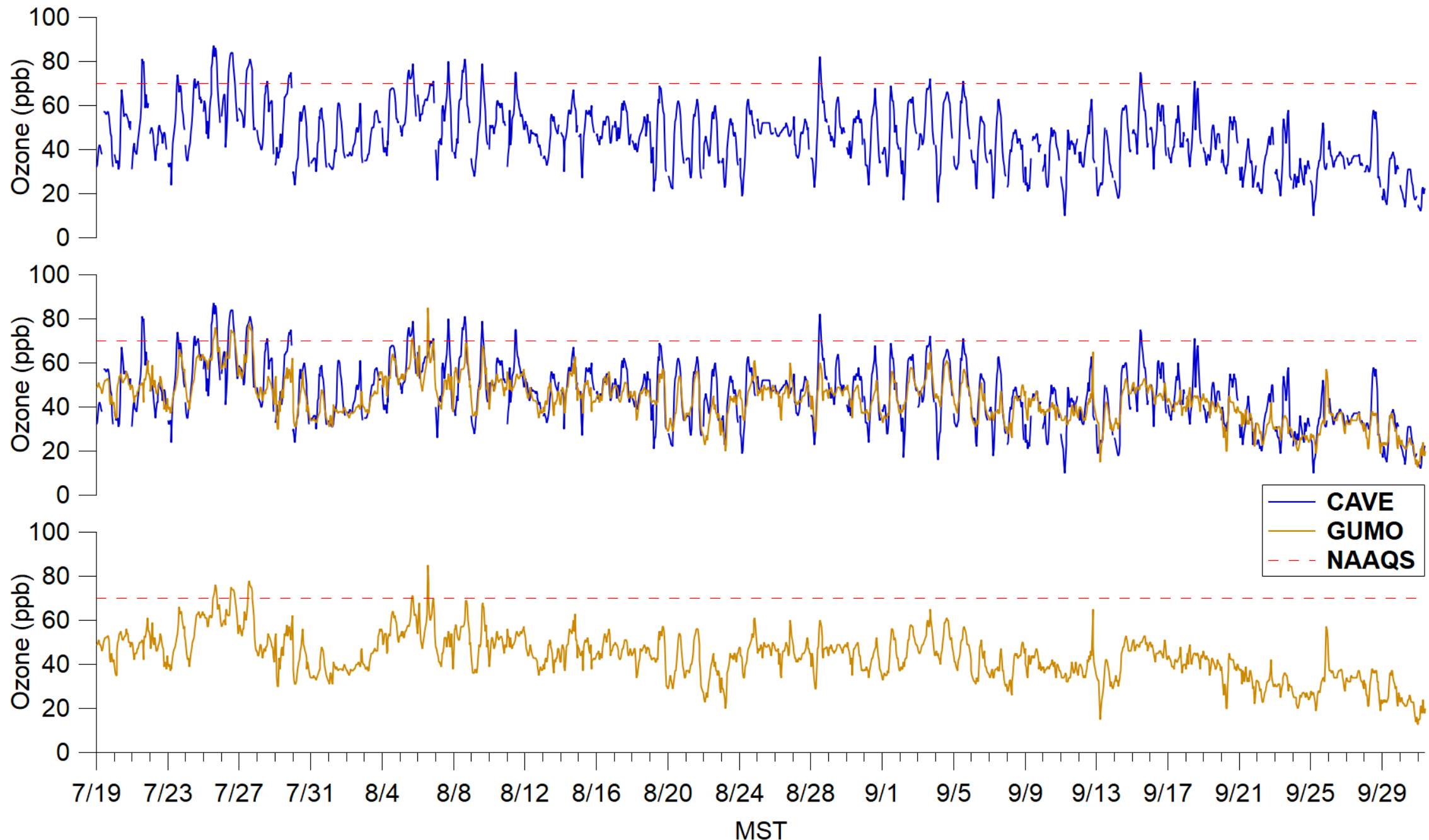


# CAVE and GUMO Ozone Temporal Distributions 2019

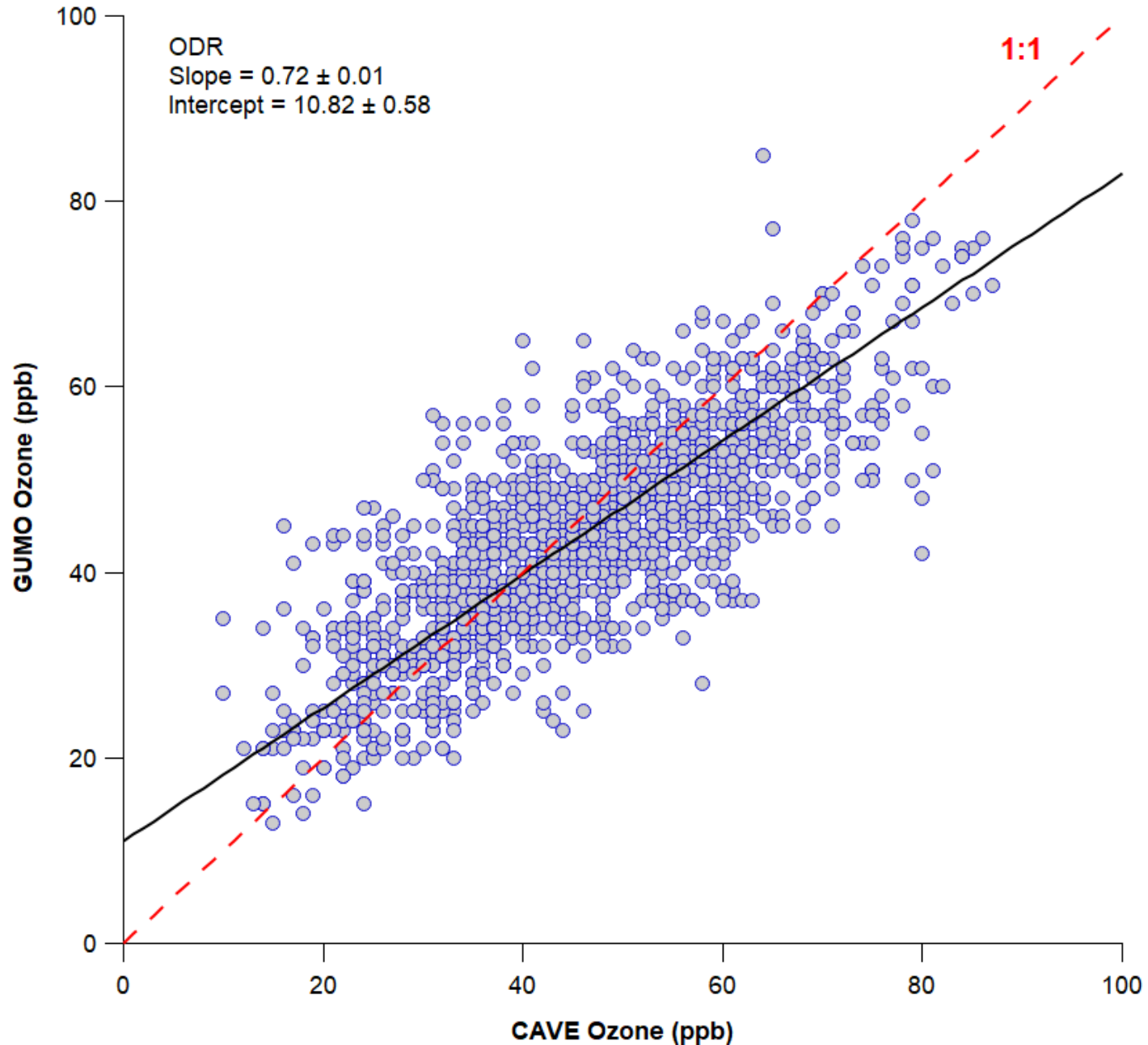




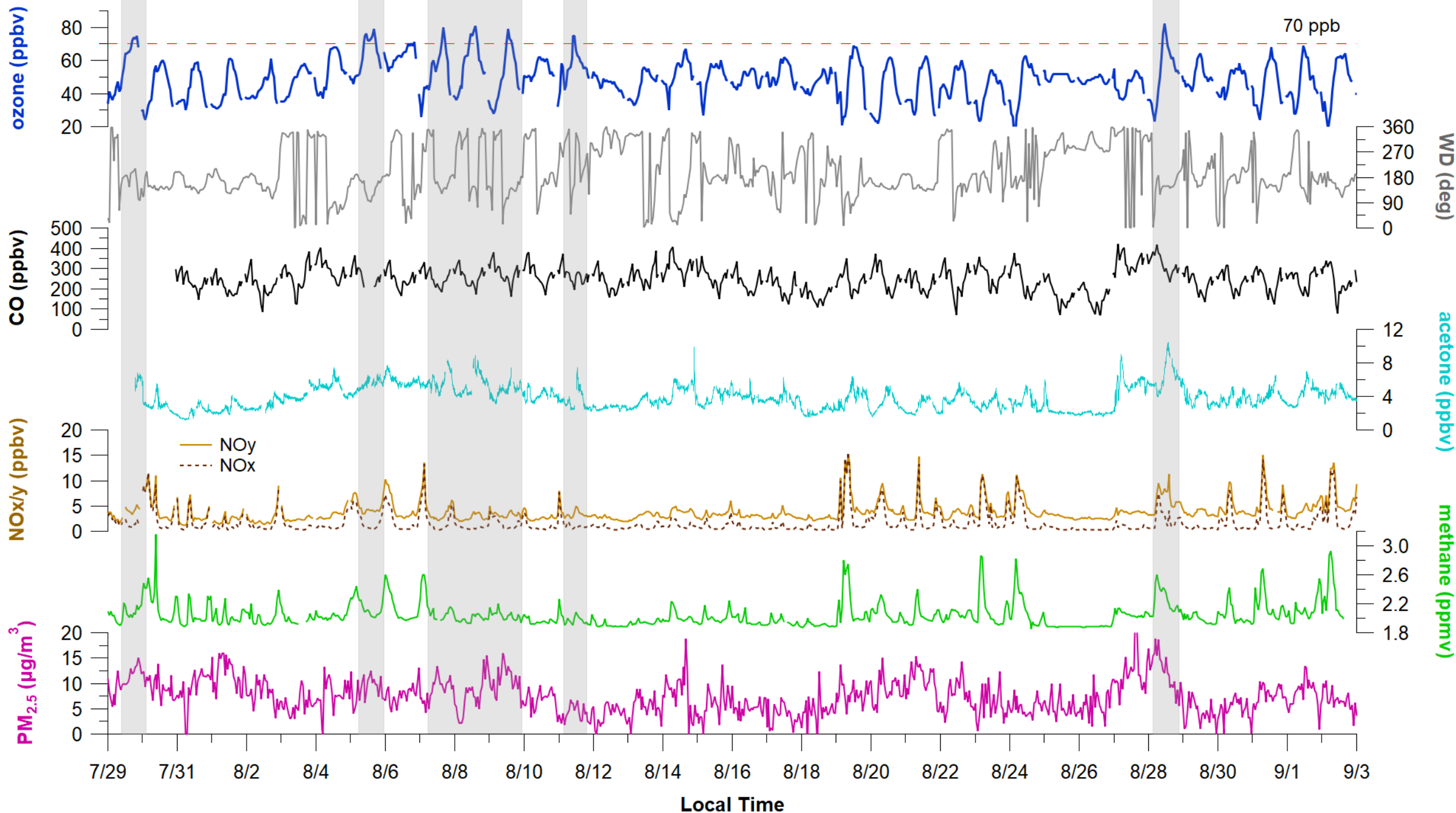
# CAVE and GUMO Ozone Temporal Distributions 2019



# CAVE and GUMO Ozone 2019

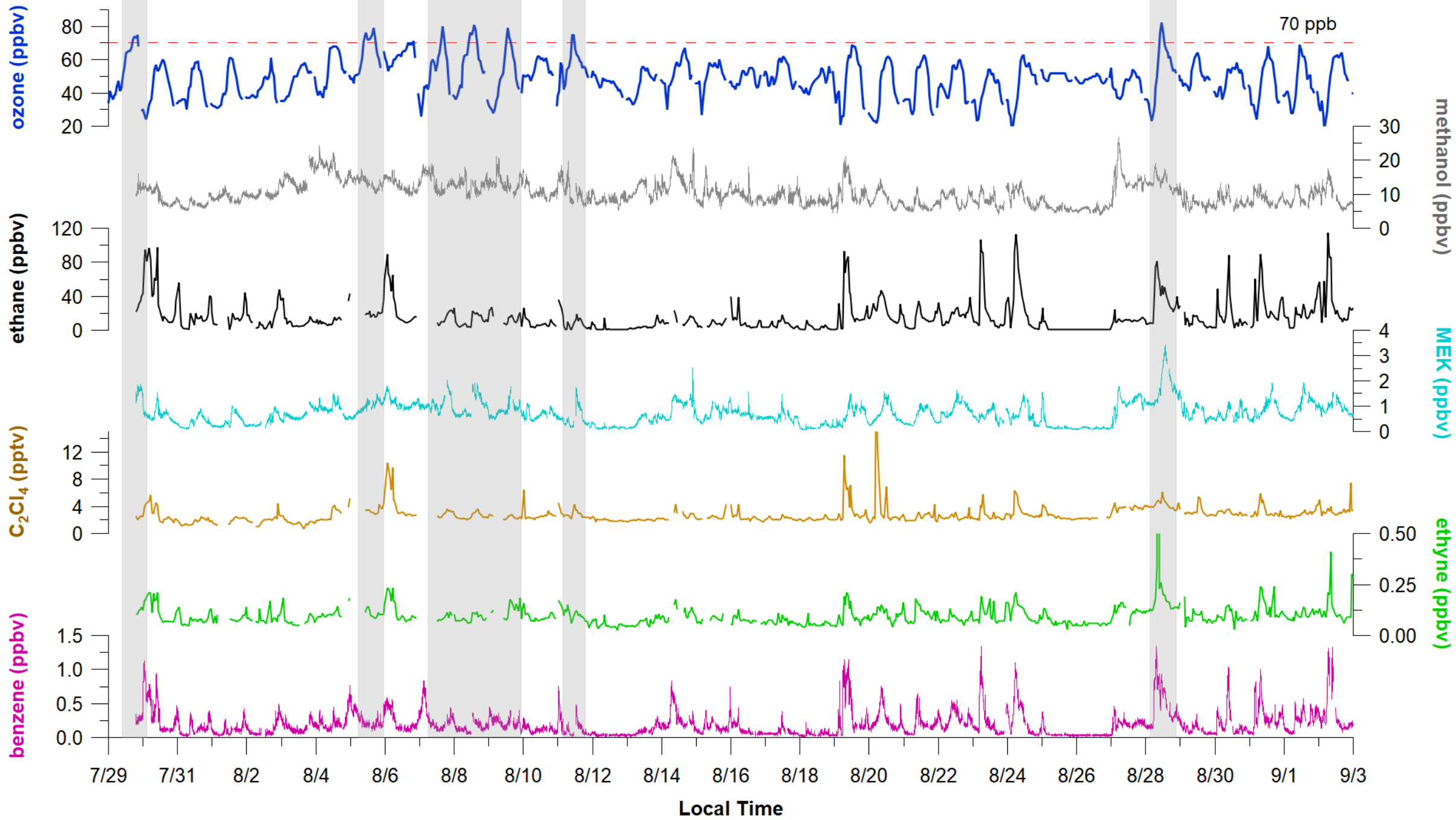


# CAVE Temporal Distributions 2019

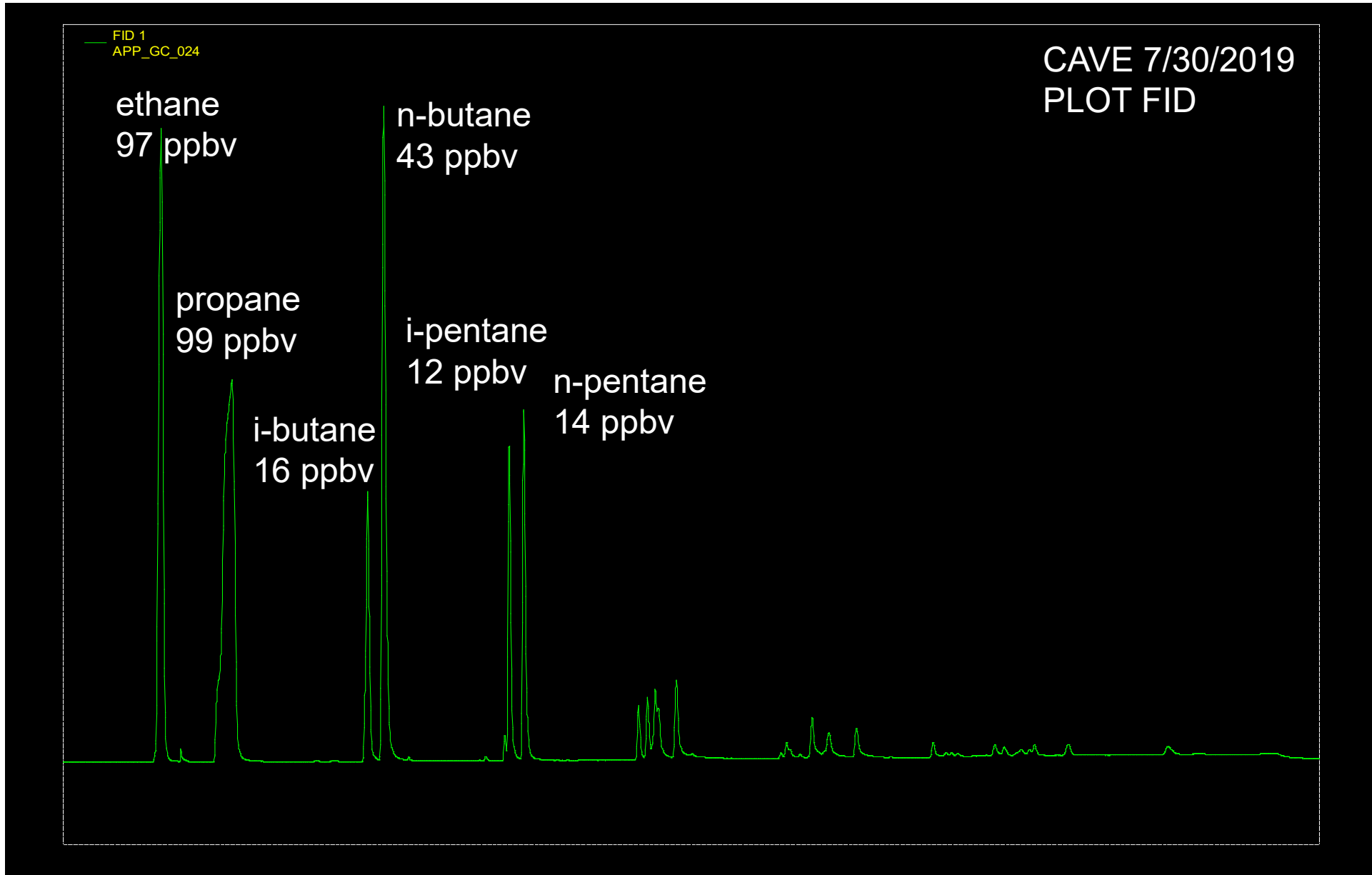




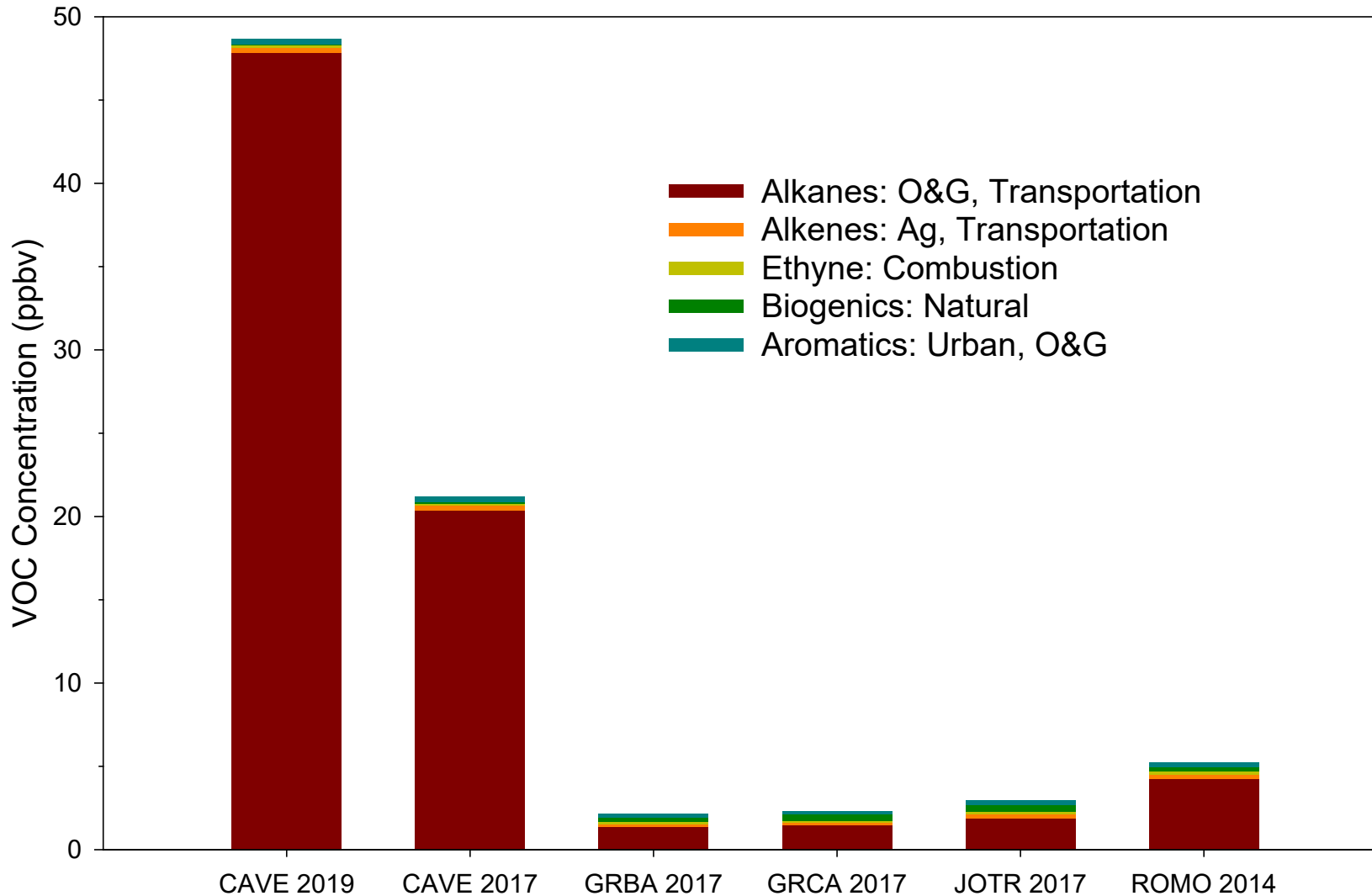
# CAVE Temporal Distributions 2019



# Oil & Gas Signature



# Average VOC Concentration



## Carlsbad Caverns NP

### VOC Mix Dominated by Oil & Gas

#### Carlsbad Caverns NP Sampling Notes

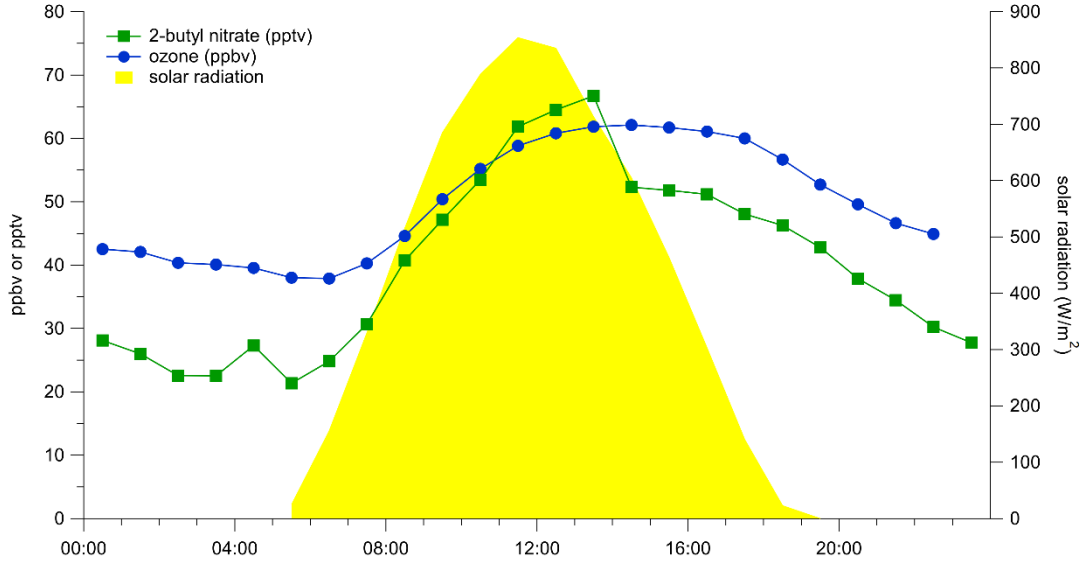
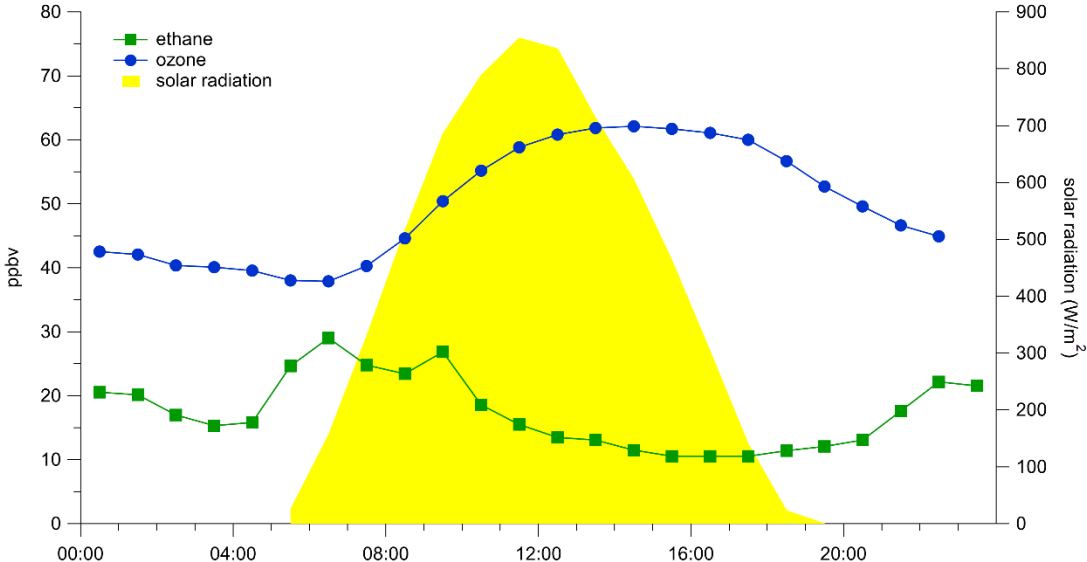
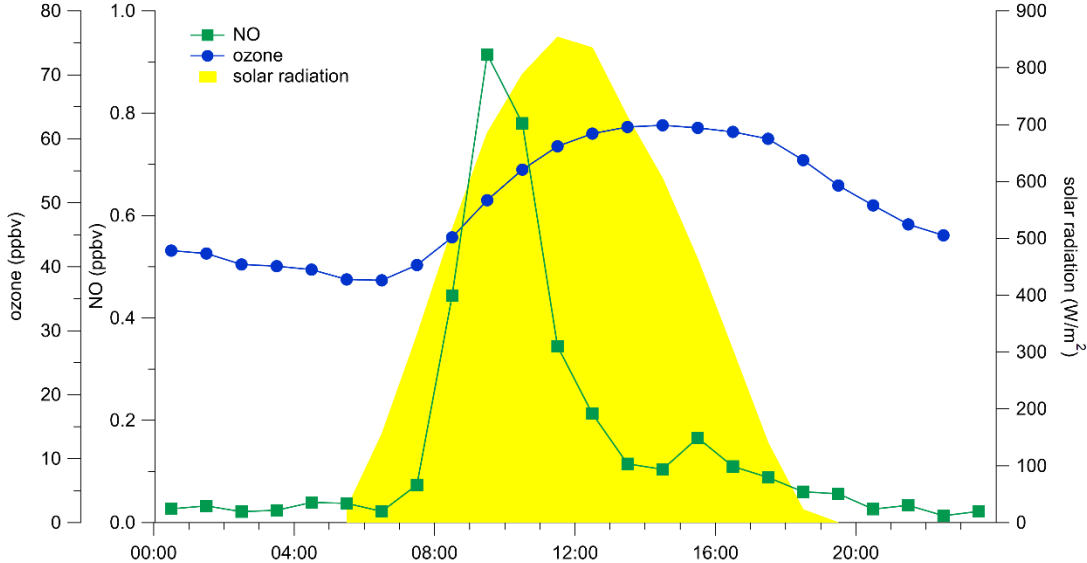
- 2017: Daytime only
- 2019: Hourly diurnal





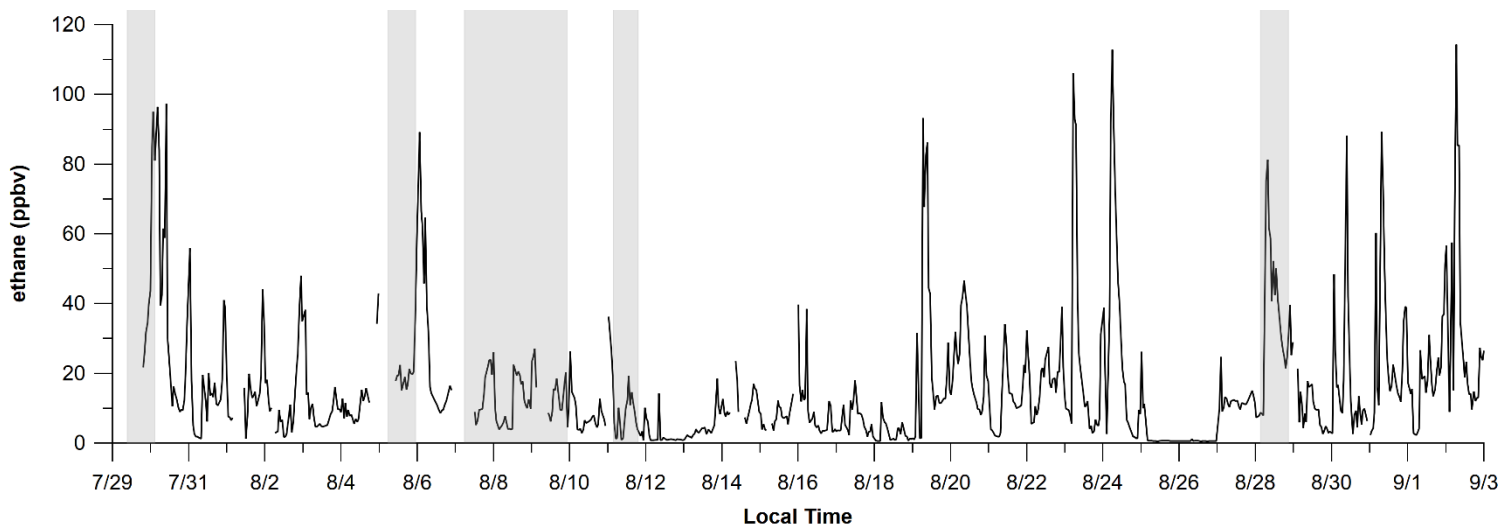
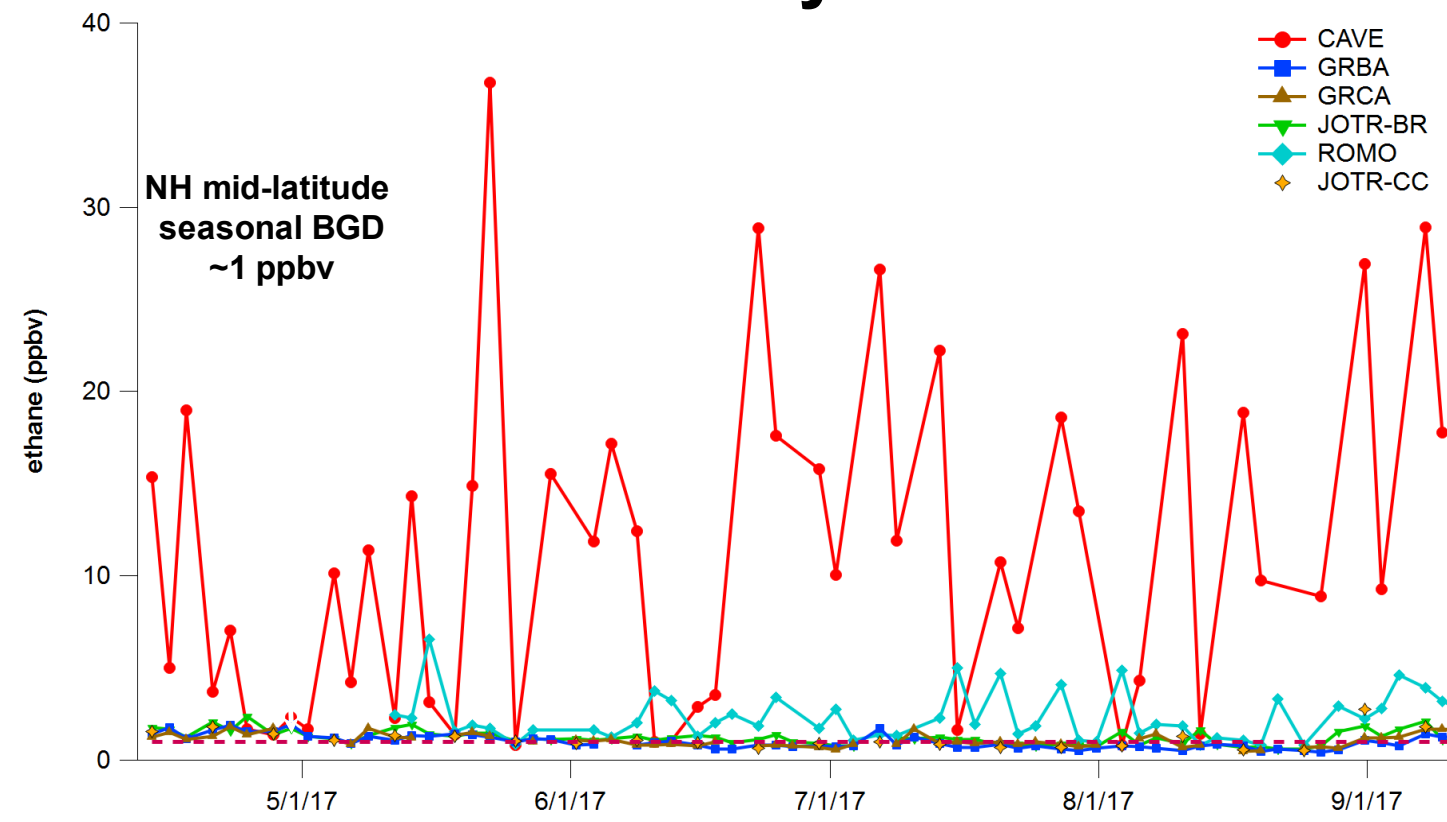
# Diurnal Averages from 2019

- Ozone peaks in the late afternoon
- NO has a morning spike and emissions throughout the day
- VOCs (e.g., ethane) build up overnight and are reacted away during the day + mixing & dilution
- Secondary chemistry products, such as the alkyl nitrates (e.g., 2-butyl nitrate), have a similar diurnal distribution as ozone
- Alkyl nitrates are formed from parent n-alkane in the presence of NOx – high levels indicate abundant sources and local photochemistry



# Comparison of 2017 and 2019 Study Results

## 2017



## 2019

Ethane avg = 17.3 ppbv

Hourly sampling exhibited higher diurnal variability

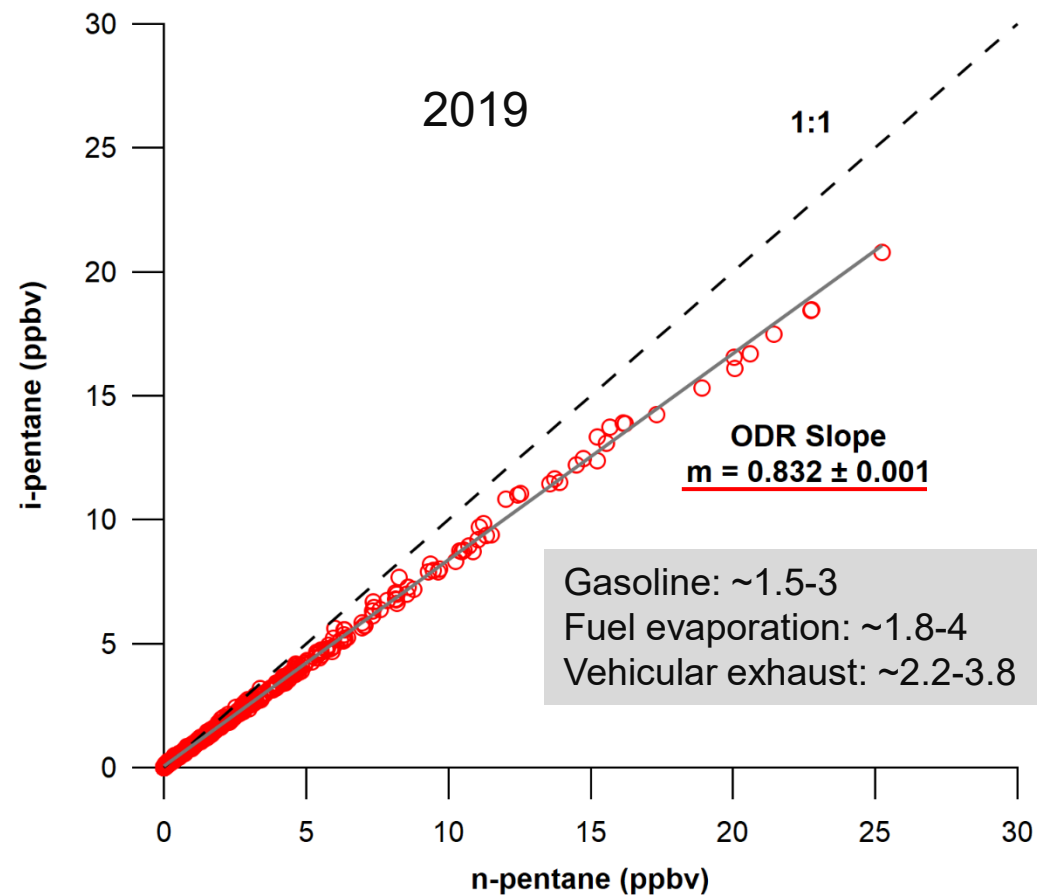
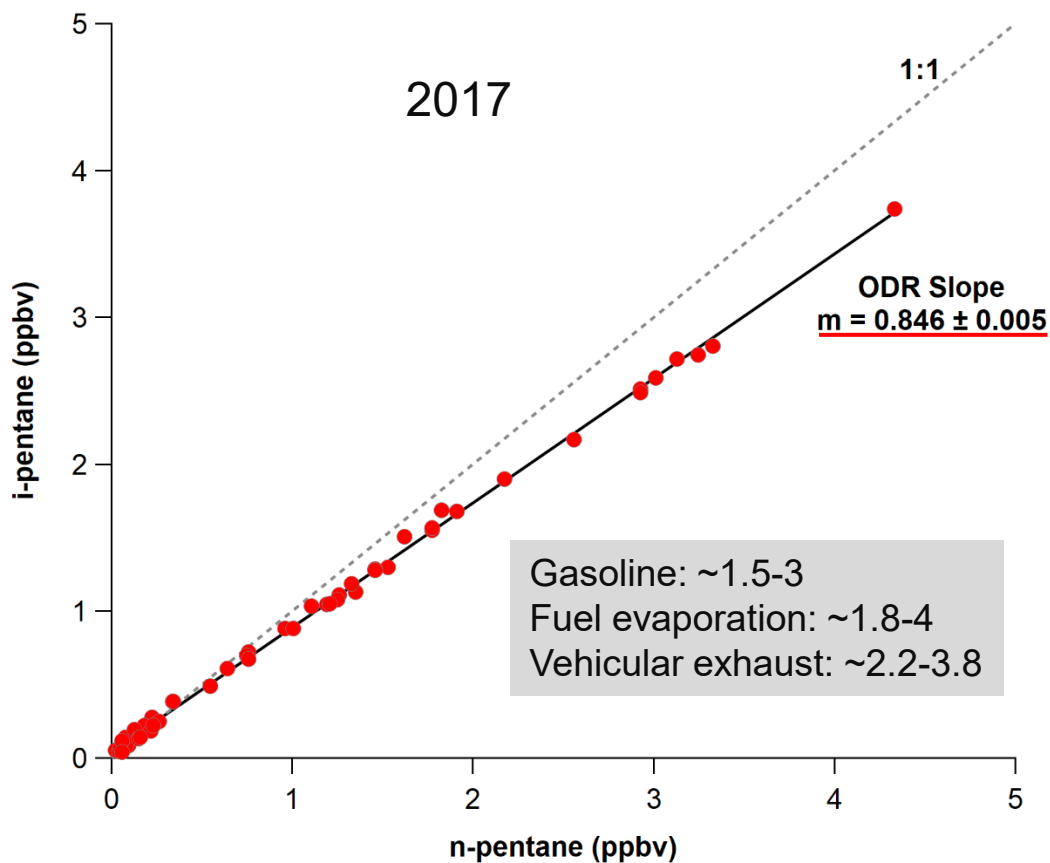
Observed levels  $\geq 100$  ppbv



# Oil & Gas Emissions Tracers

## The Pentane Ratio

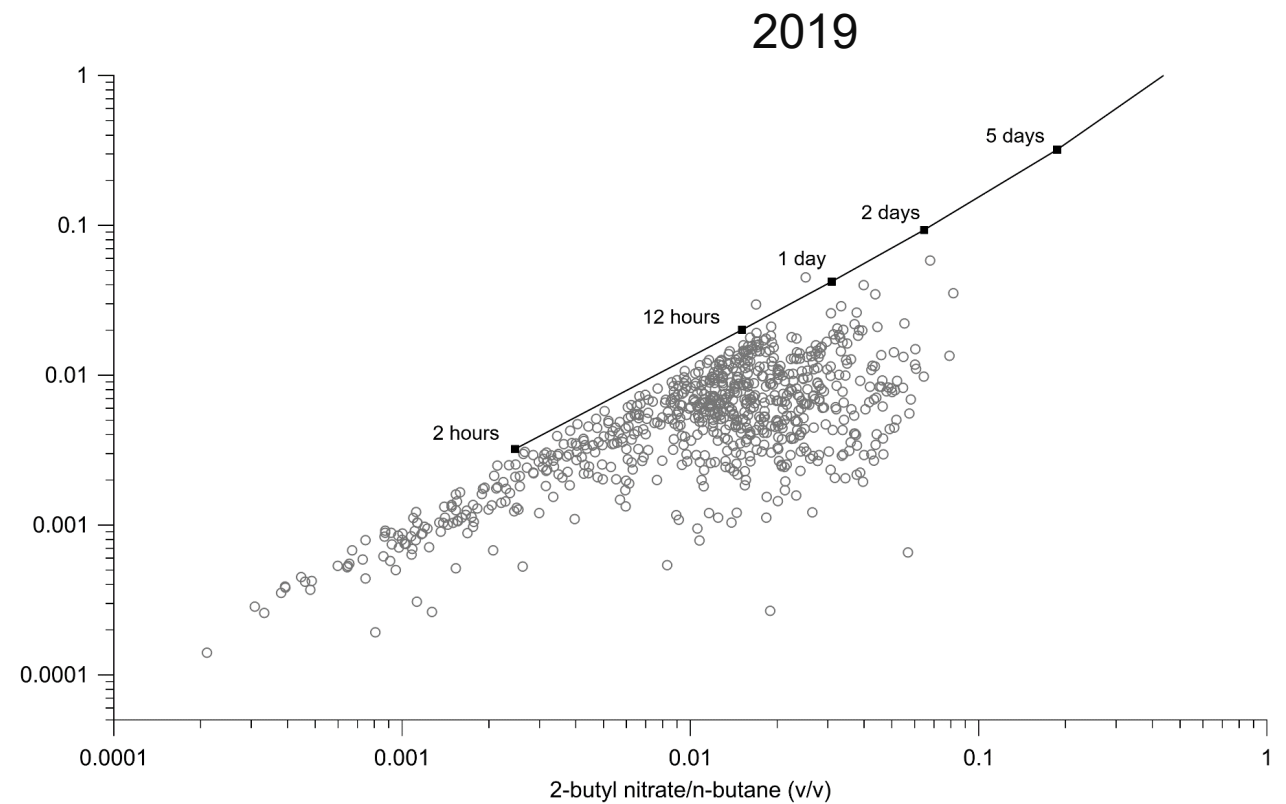
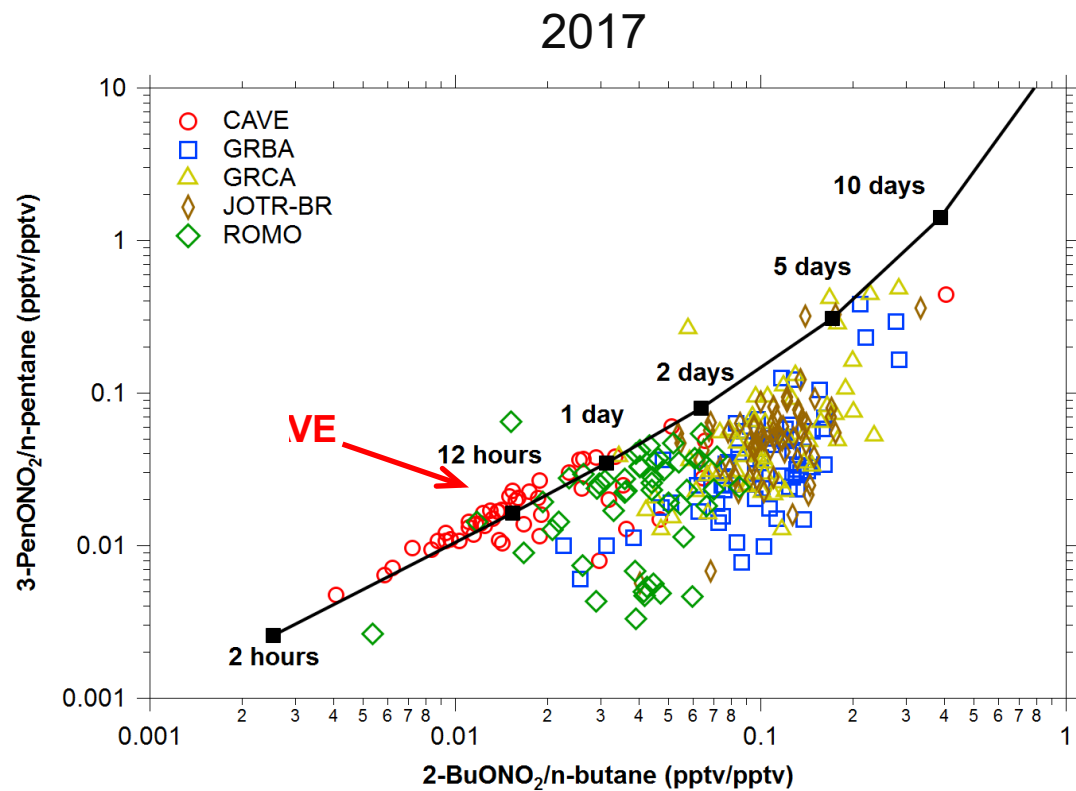
### Carlsbad Caverns National Park 2017 & 2019



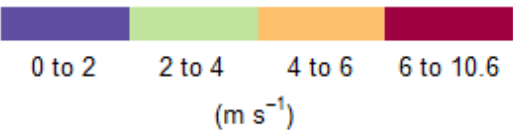
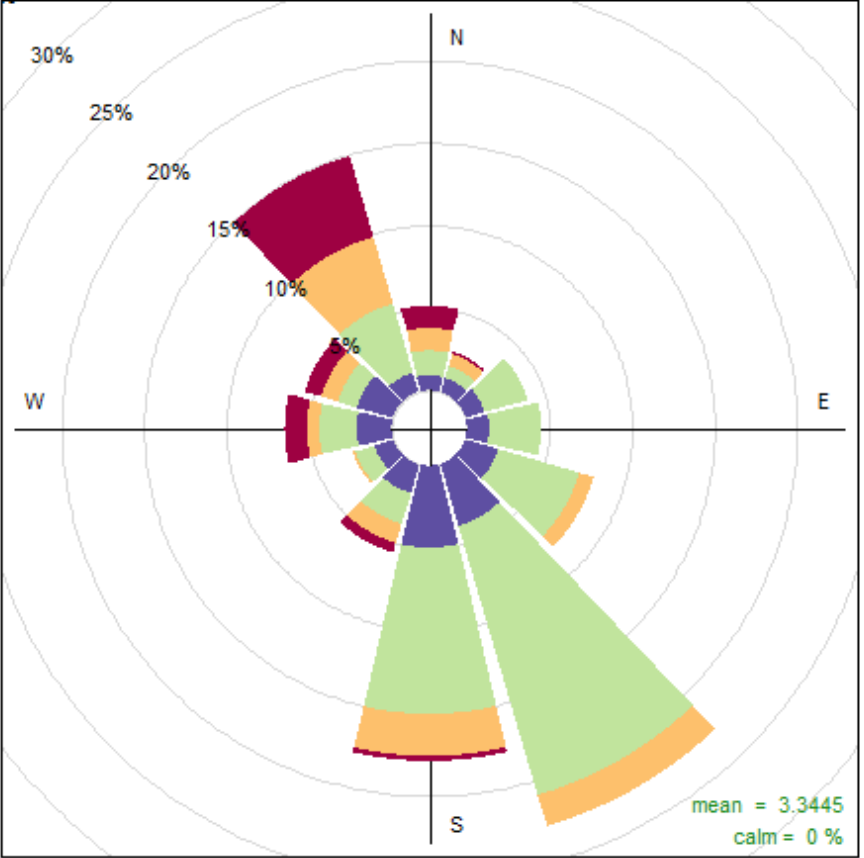


# Photochemical Age using Alkyl Nitrates

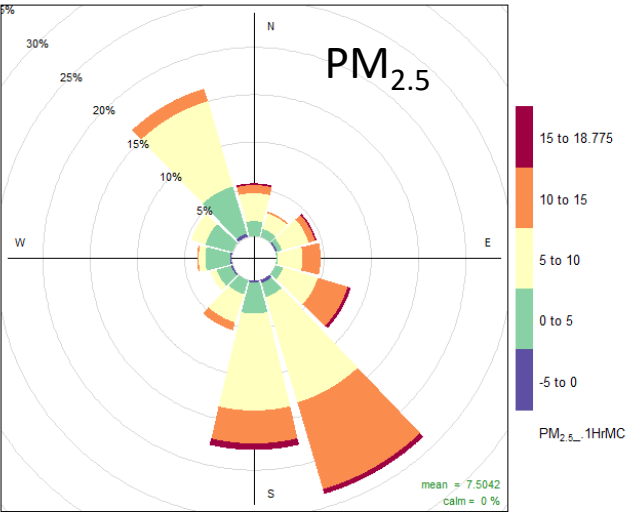
Air mass aging (photochemical age) from ratios of alkyl nitrates to parent n-alkanes illustrate that VOC and  $\text{NO}_x$  emissions are fresh and air masses are impacted by local sources.



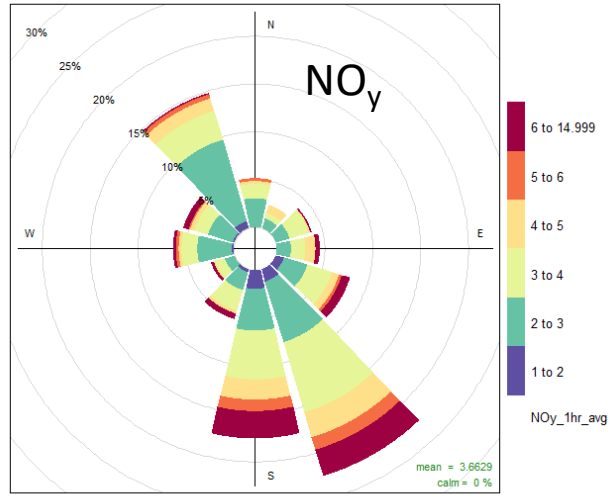
# Distribution of Winds and Wind Speed



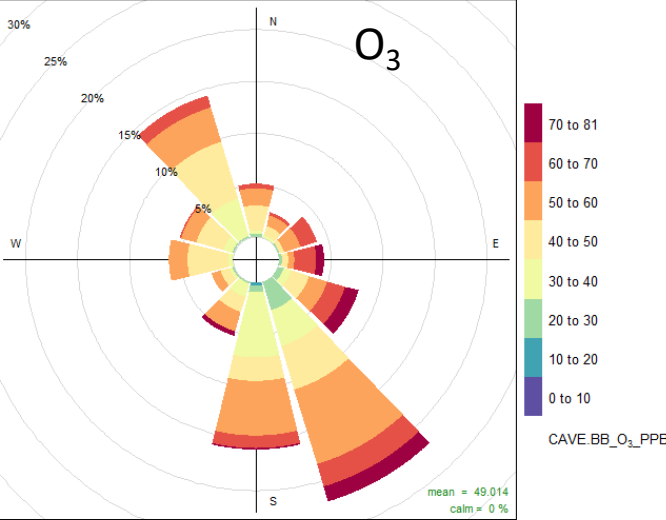
Frequency of counts by wind direction (%)



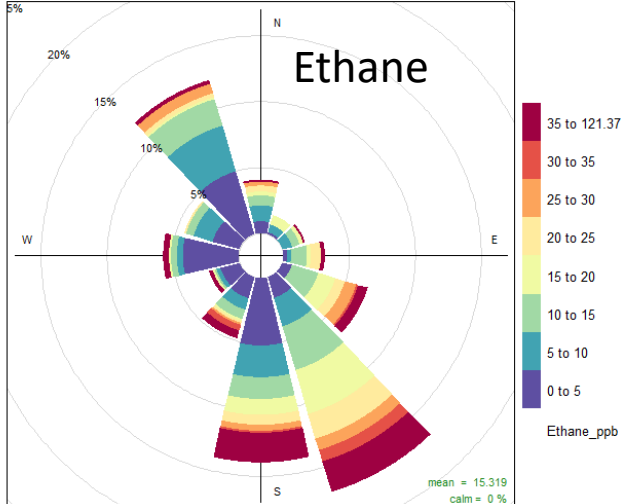
Frequency of counts by wind direction (%)



Frequency of counts by wind direction (%)



Frequency of counts by wind direction (%)

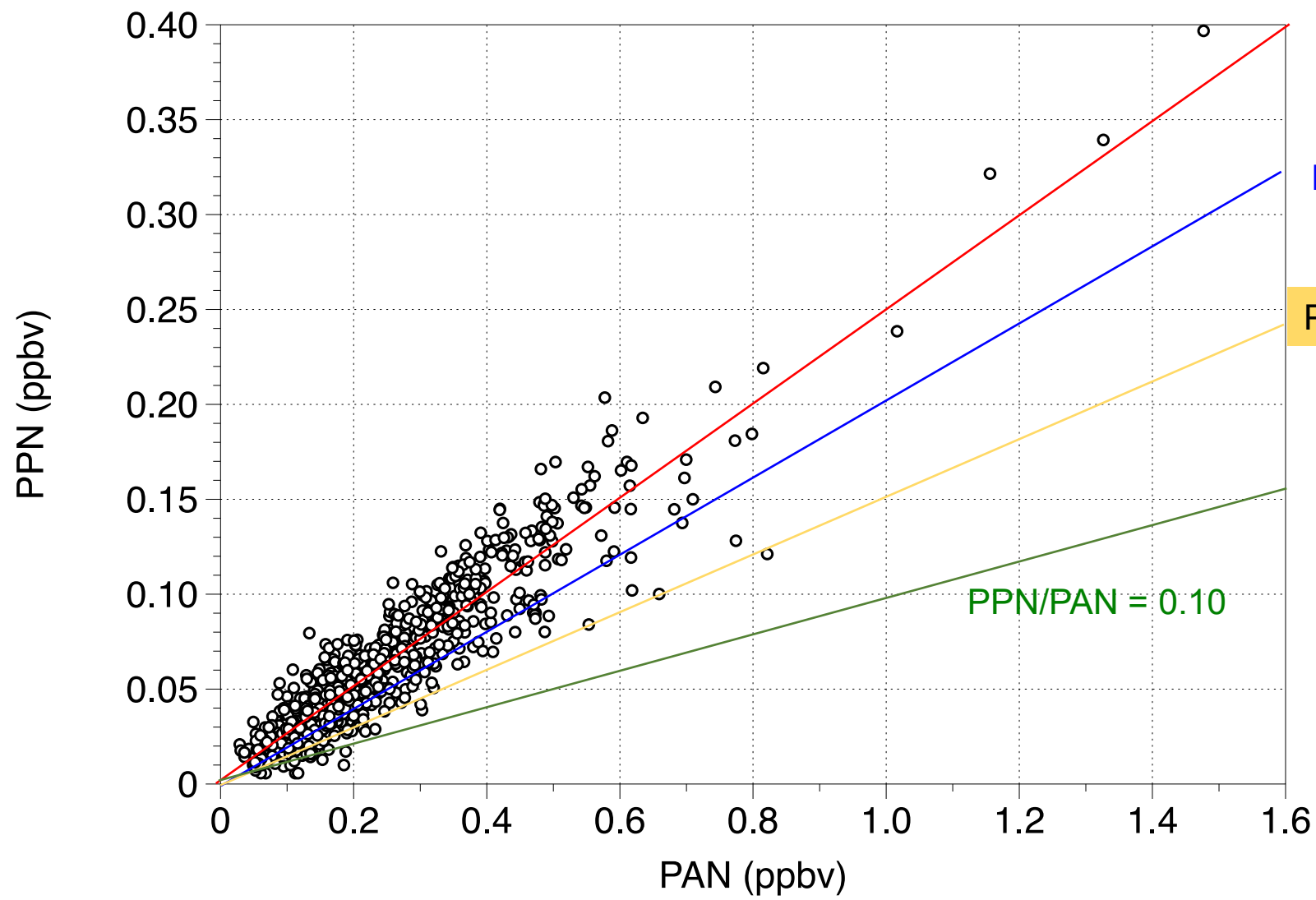


Frequency of counts by wind direction (%)



# PAN "family" can also help identify contribution of VOC sources to O<sub>3</sub> formation

PPN/PAN ratios clearly indicate anthropogenic VOC-NO<sub>x</sub> photochemistry



PPN/PAN = 0.25  
Highest ratio in TEXAS AQ 2000  
*Roberts et al. [2000]*

PPN/PAN = 0.20

PPN/PAN = 0.15

PPN/PAN = 0.10

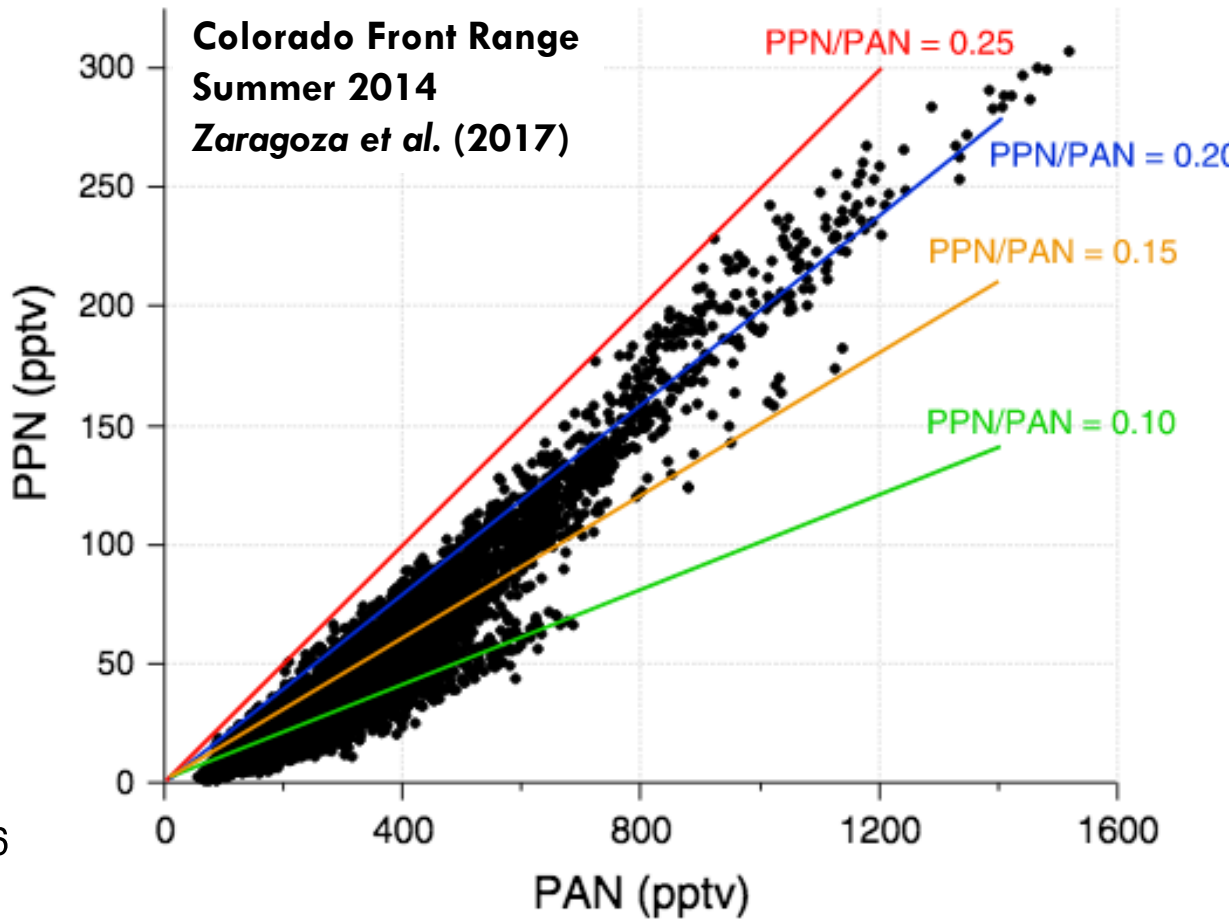
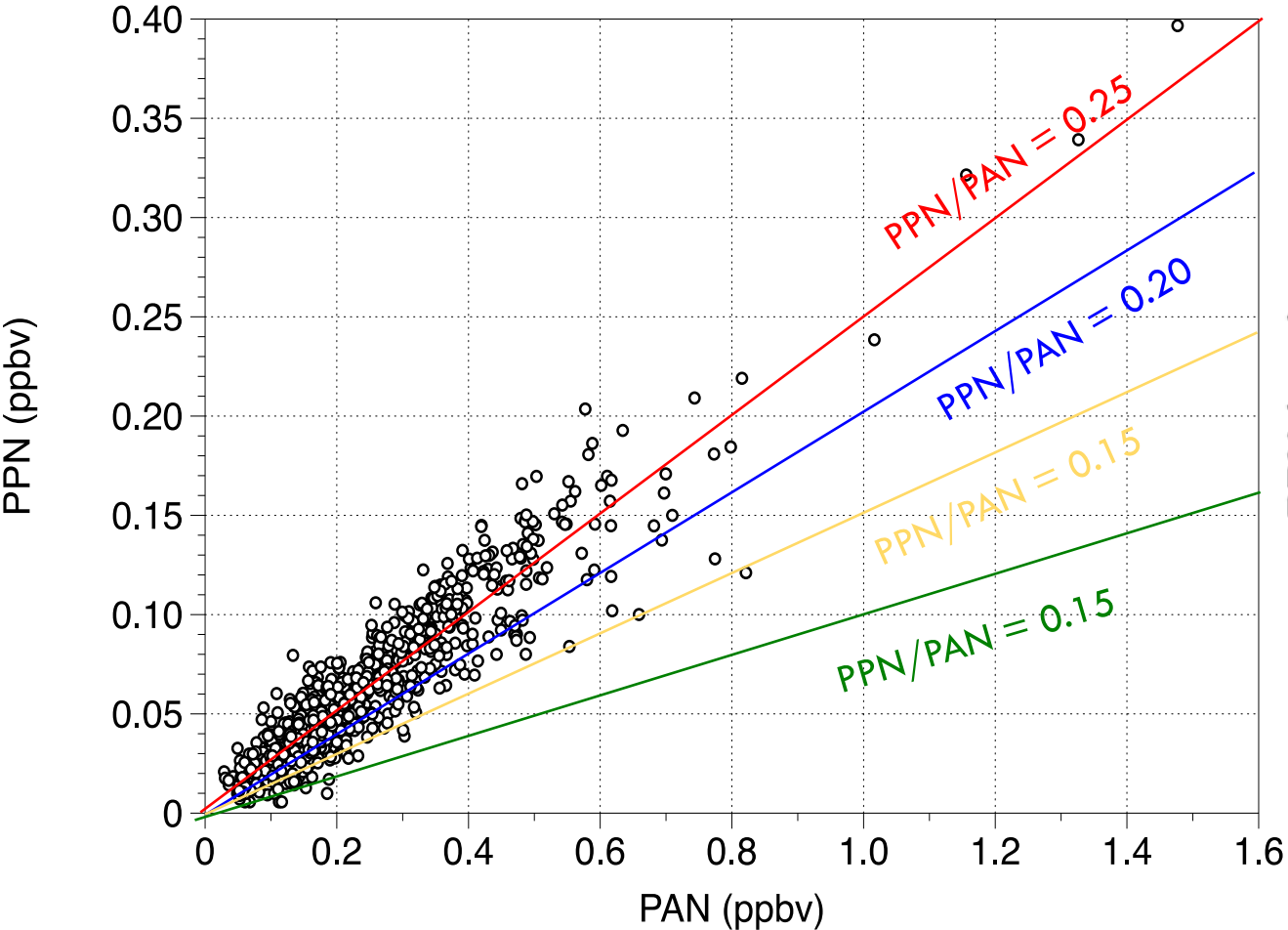
Areas dominated by anthropogenic VOCs  
*Roberts et al. [2003]*  
*Roberts et al. [1998a/b]*  
*Roberts et al. [2003]*  
ALSO average afternoon maximum in Boulder in 1987

More AVOCs

More BVOCSs



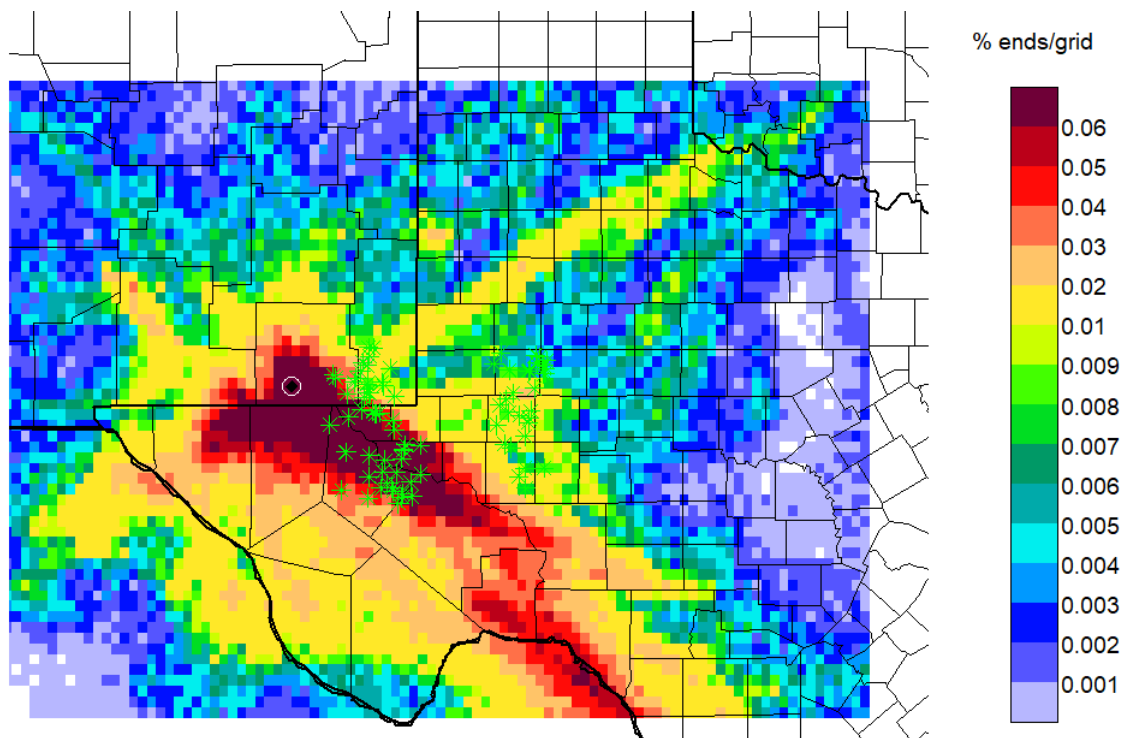
PPN/PAN ratios during elevated periods are within range observed in Front Range.



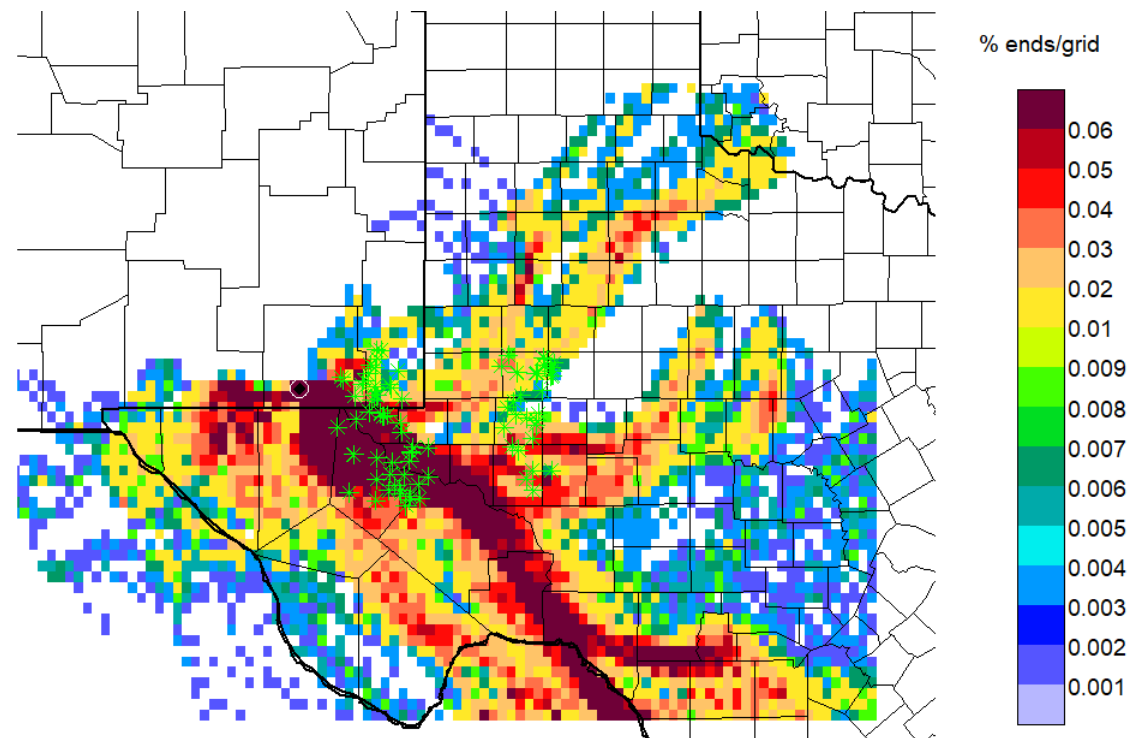


# High Residence Time Analysis

## Overall Residence Time (ORT) Ozone



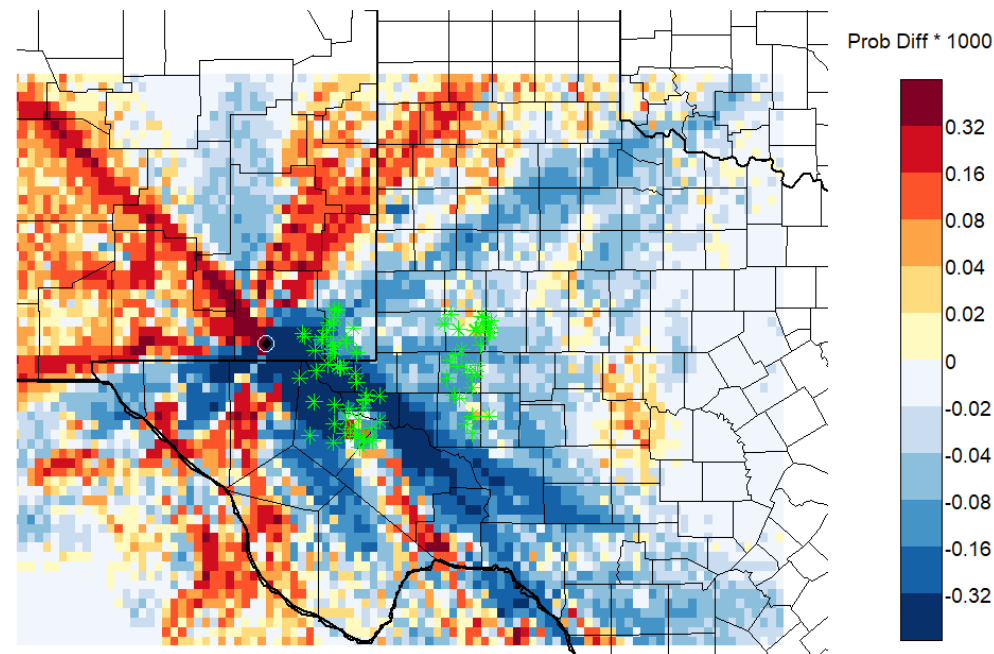
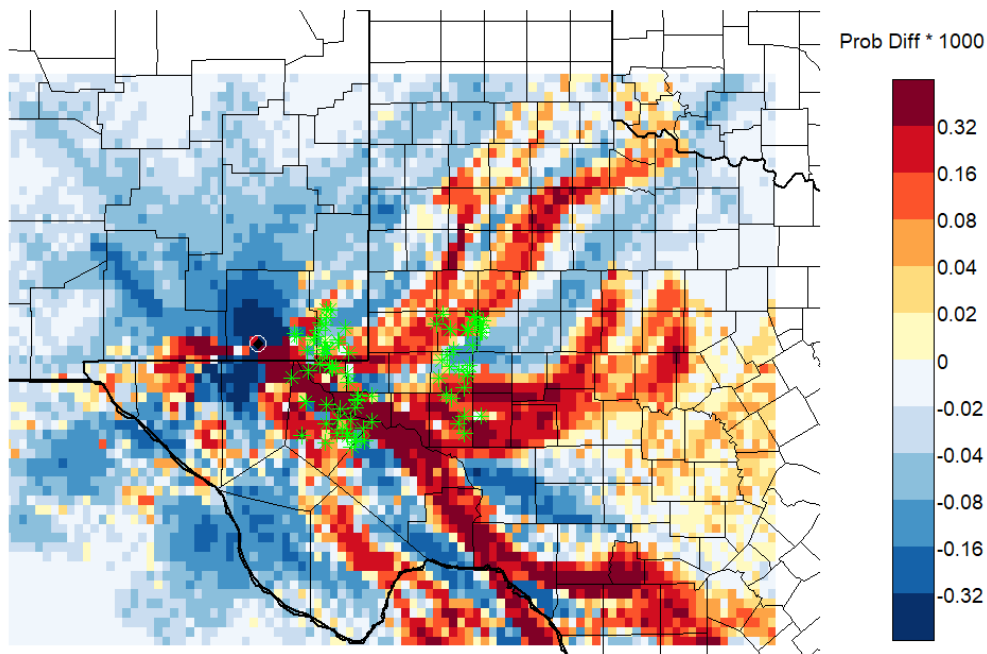
## High Concentration Residence Time (HRT) Ozone



# High Residence Time Analysis

Highest 10% ozone = 74 ppb

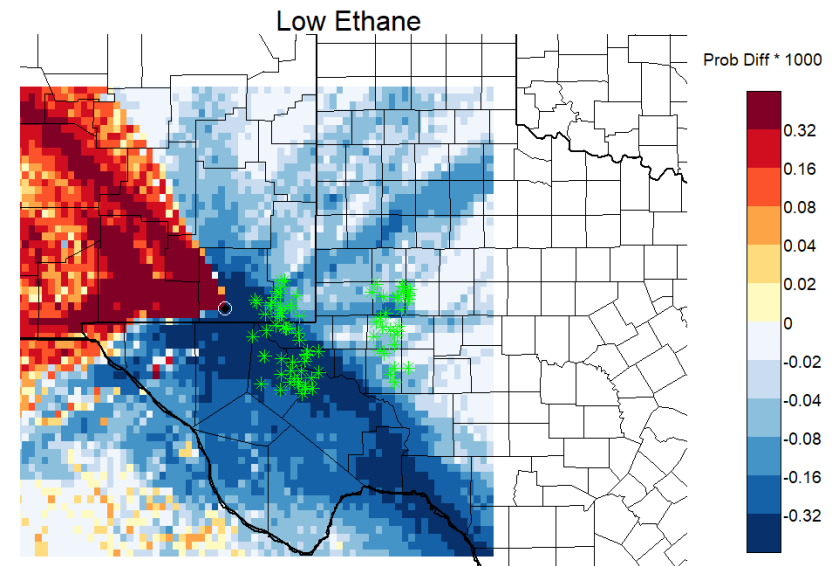
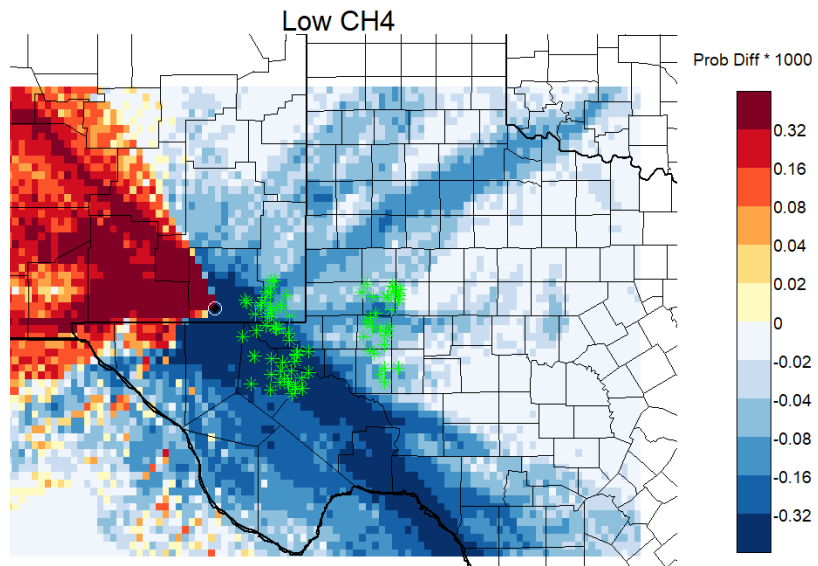
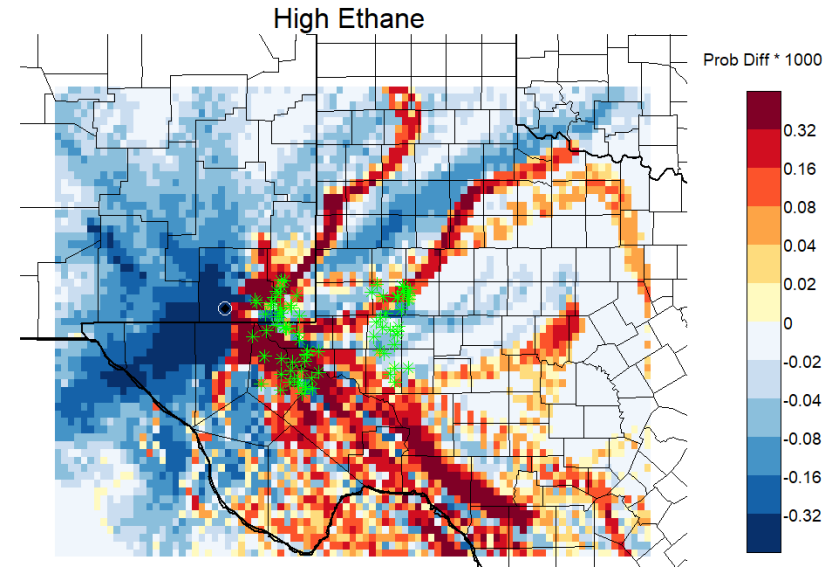
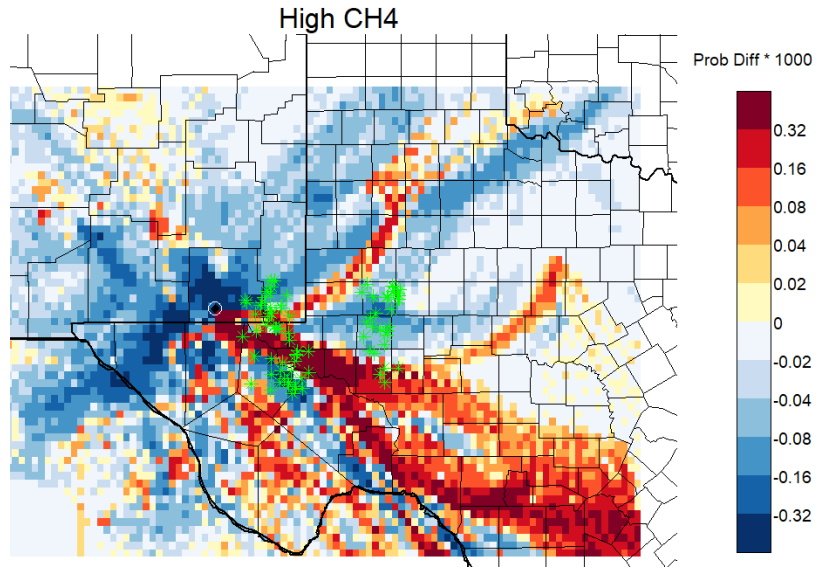
Lowest 10% ozone = 48 ppb



- High ozone corresponds to flow from the E and SE
- Associated with active drill rigs

- Low ozone corresponds to flow from the W and NW

# High Residence Time Analysis





# 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, secondary oxidized N, etc.) were transported from SE
- $PM_{2.5} \sim 10 \mu\text{g}/\text{m}^3$ , ranging from 2 to  $15 \mu\text{g}/\text{m}^3$
- Appears  $\sim 50\%$  of the  $PM_{2.5}$  mass is water-soluble (includes WSOC)
- PPN/PAN ratio is very high compared to other U.S. observations ( $\sim 0.25$ ) is associated with elevated  $CH_4$

**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.



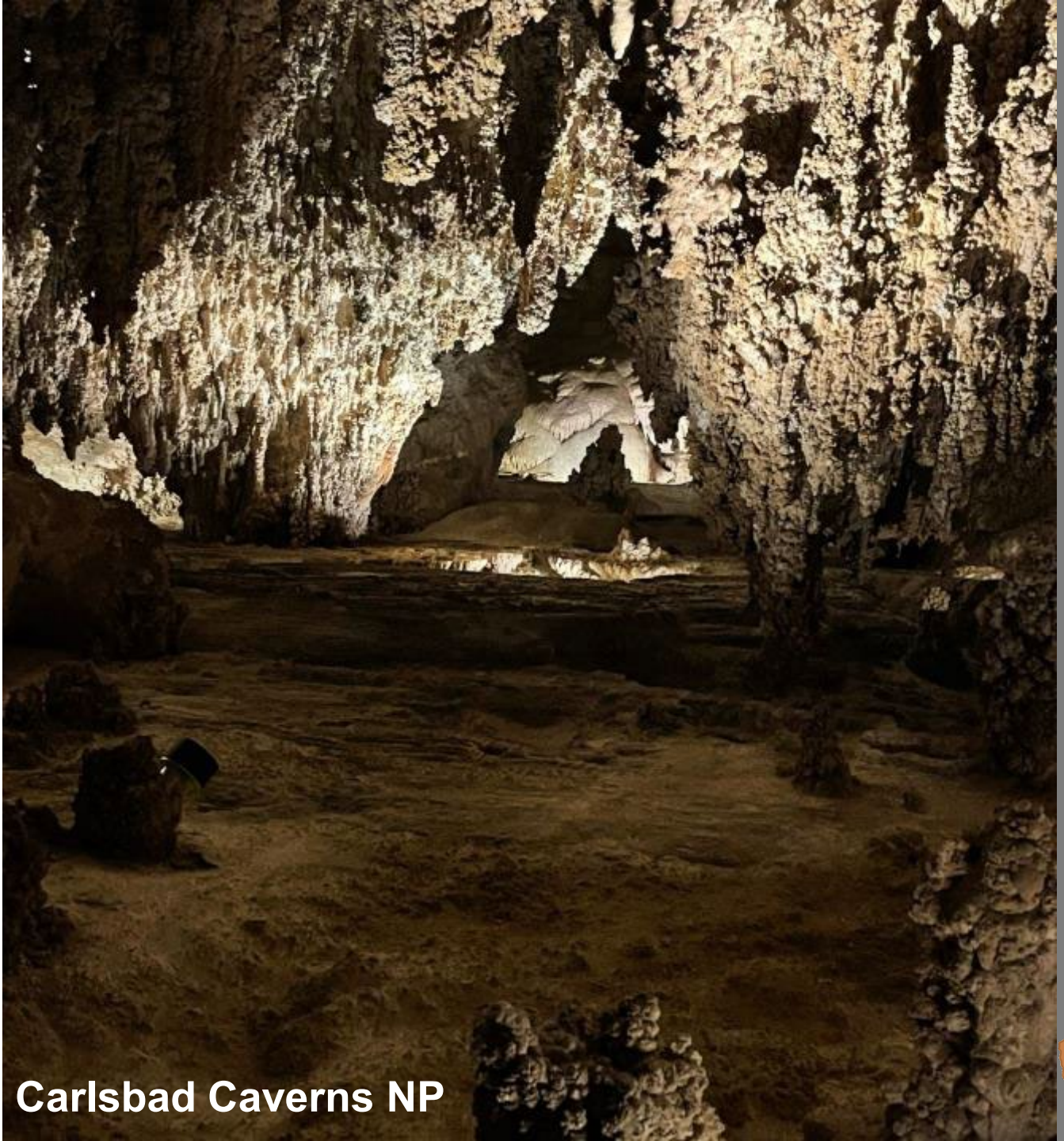
# Learn More

## ▶ [nps.gov/air](https://nps.gov/air)

- ▶ Live Data
  - ▶ Ozone & Meteorology
  - ▶ Webcams
- ▶ Conditions & Trends
  - ▶ National Data
  - ▶ By Park

## ▶ [epa.gov/castnet](https://epa.gov/castnet)

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Carlsbad Caverns NP

