Source Attribution Using Volatile Organic Compound Measurements to Assess Air Quality Impacts at Five National Parks in the Western US

Barkley C. Sive
Air Resources Division

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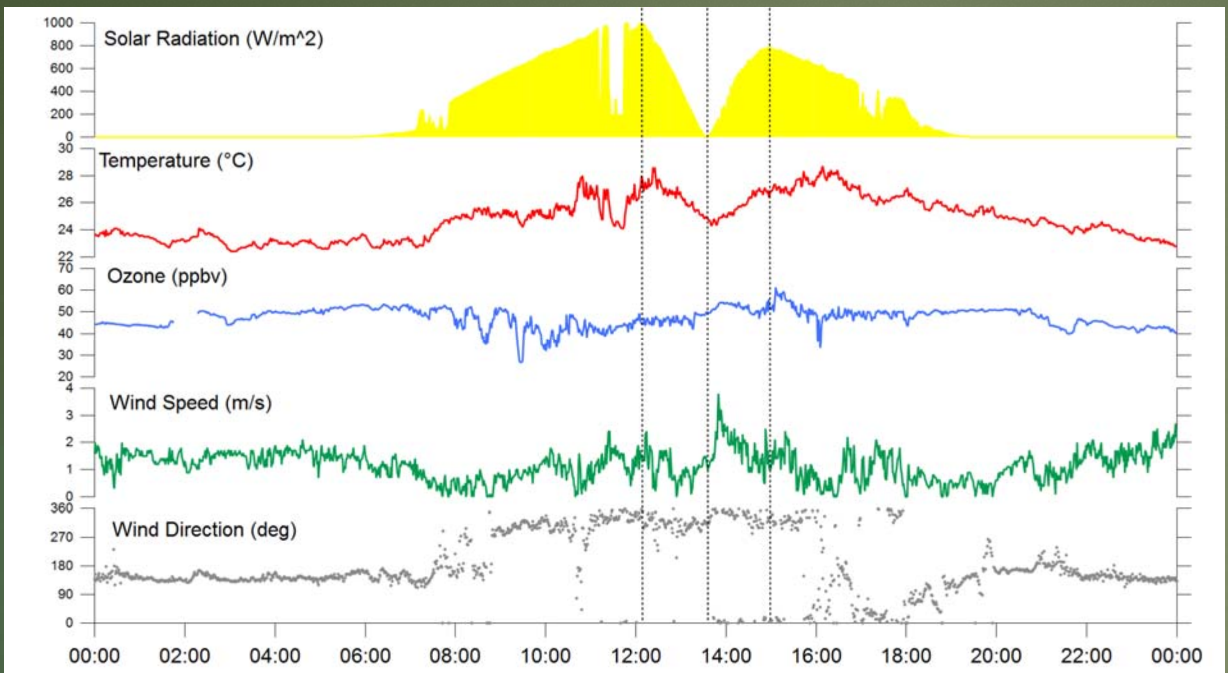
ECLIPSING!!!

GRSM-LR



August 21, 2017

FOLA

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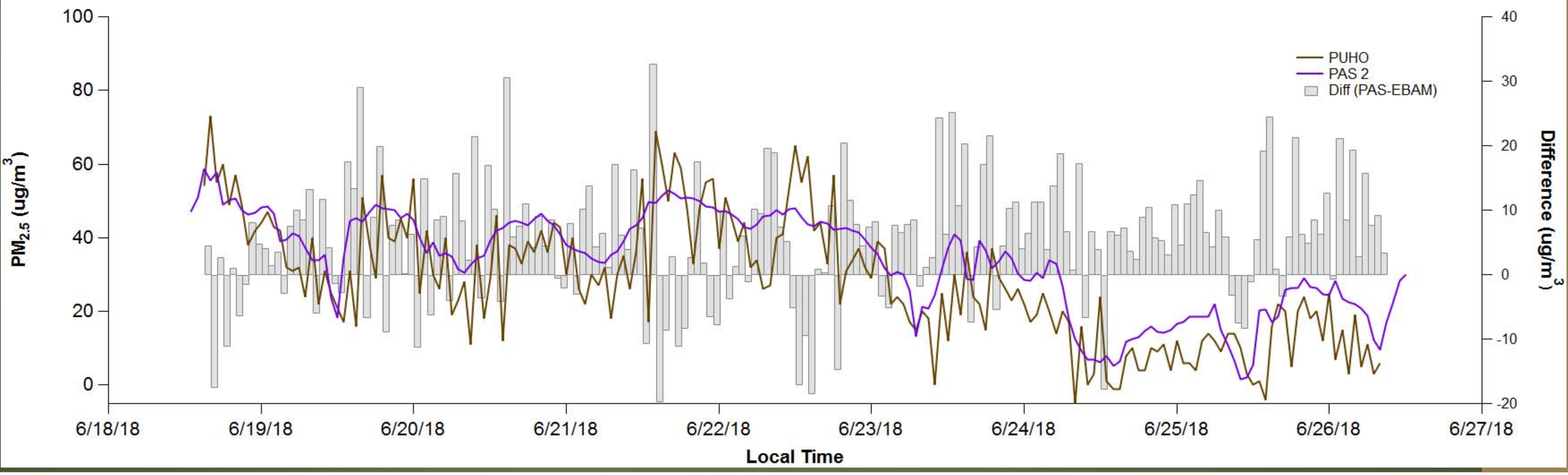
$PM_{2.5}$ Measurements at *Kaloko-Honokohau and Pu'uhonua o Honaunau* National Historical Parks

Barkley C. Sive

Air Resources Division

Comparison of E-BAM with PAS
June 14-26, 2018

PUHO E-BAM vs. ARD 002



Objective

Using Volatile Organic Compound (VOC) markers, determine primary sources impacting park air quality, with a focus on parks approaching/exceeding the ozone standard.

Currently 85 VOCs Quantified

Oil & Gas

NMHCs: light alkanes C2-C6, i-butane/n-butane, i-pentane/n-pentane

Biomass Burning

acetonitrile, methyl halides (CH_3Cl, CH_3Br, CH_3I), OVOCs (MeOH, acetone)

Urban

industrial: benzene, toluene, xylenes

solvent evaporation: halocarbons (CH_2Cl_2, C_2Cl_4, C_2HCl_3, $CHCl_3$, CH_3CCl_3)

Waste water treatment: $CHCl_3$, $CHBr_3$

Agriculture

crops: alkenes (hexenes, ethene, propene), DMS, $CHBr_2Cl$

animal husbandry: methanol, ethanol, acetaldehyde

Transportation

Fuel Evaporation: i-pentane/n-pentane

fuel combustion: ethyne, ethene, propene, benzene

exhaust: i-butane/n-butane, i-pentane/n-pentane, alkenes, ethyne

Biogenic/natural emissions:

isoprene, monoterpenes

Stratospheric Intrusion:

OCS, CFCs, HCFCs

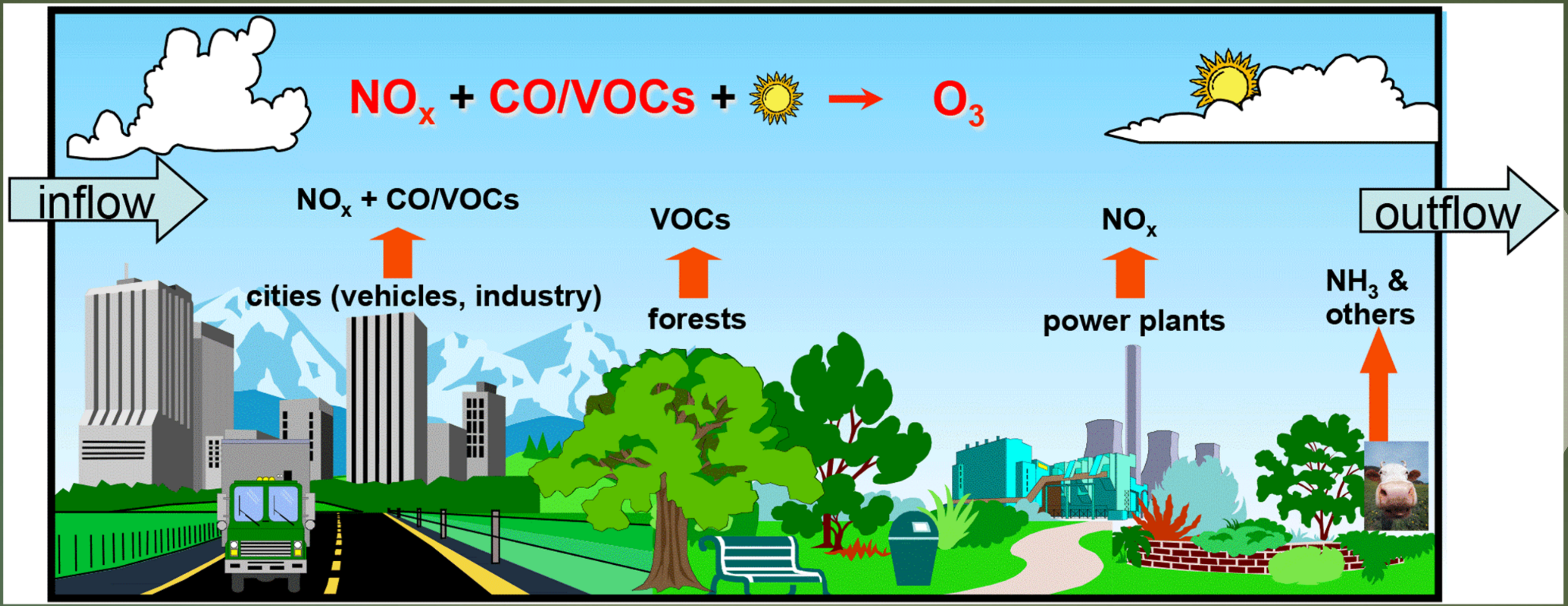
Ocean/Marine:

$MeONO_2$, CH_2Br_2, $CHBr_3$, CH_2ClI, DMS, OCS

Oxidation/photochemical processing:

$RONO_2$, OVOCs

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

Sampling Approach

Sampling Dates

First canisters in place: April 13, 2017
Last canister collection: September 14, 2017

Sample Collection

3 canisters collected per week

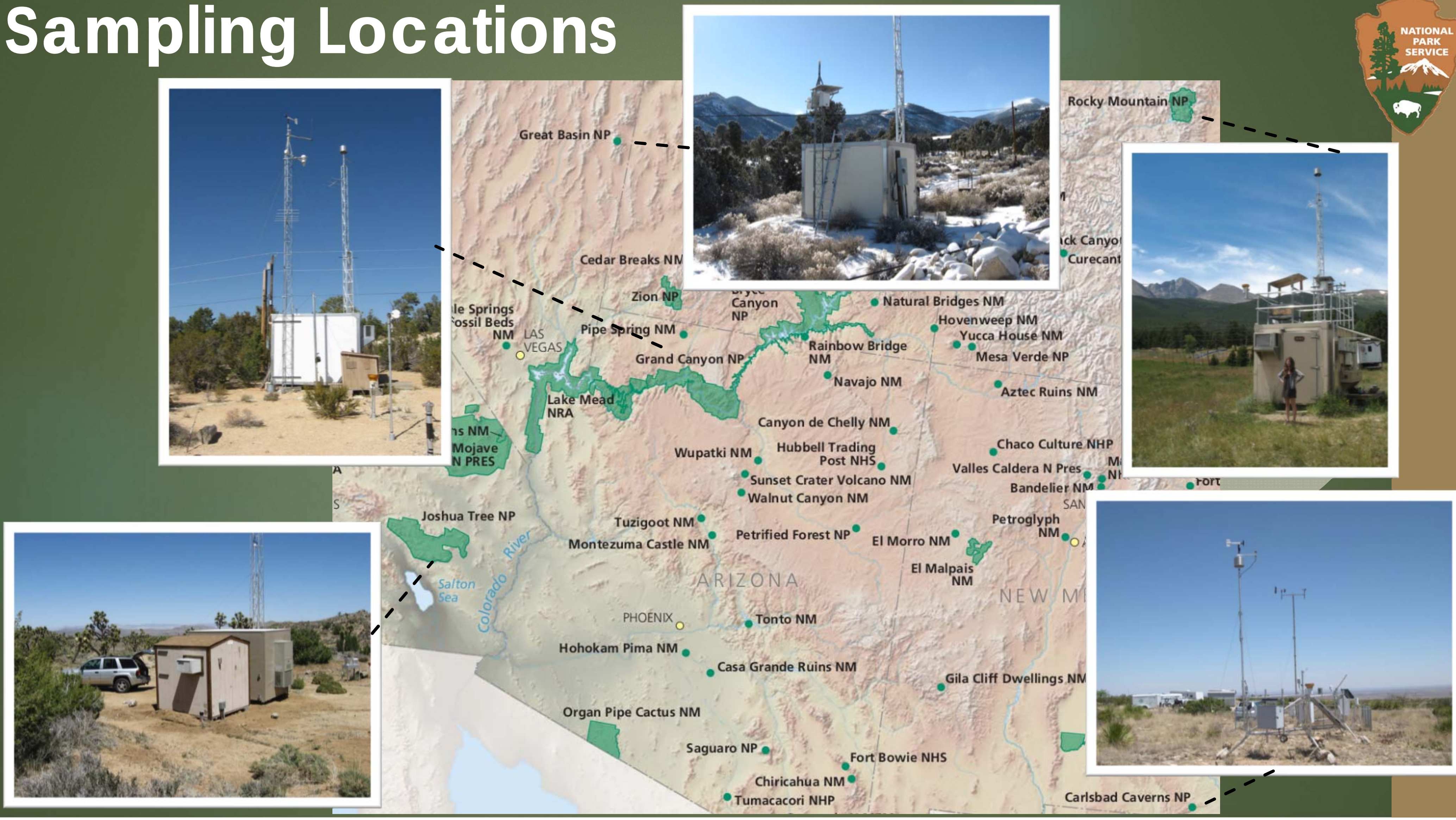
- Automated
- Collections on Wednesday, Saturday, Monday (3 PM local time)
- Canister Collection time: ~1 hour
  - Short enough to capture potential events without diluting high concentrations

Site Operators swap out canisters during weekly site visit (Tues)

Measurements

VOCs and CH_4 from canisters
O_3 and Met from GPMP
PM from IMPROVE
Deposition from CASTNET and NADP
Short term mobile CH_4 measurements; higher time resolution VOC grab samples
September 8-15, 2017
Includes GUMO and Bitter Lake (SACR)

Sampling Locations



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Measurement Summary

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Site	Cans Collected with validated data
CAVE	56*
GRBA	65
GRCA	61
JOTR-BR	66
JOTR-CC	23
ROMO	50
GUMO	5
SACR	5
Intensive	88
TOTAL	419

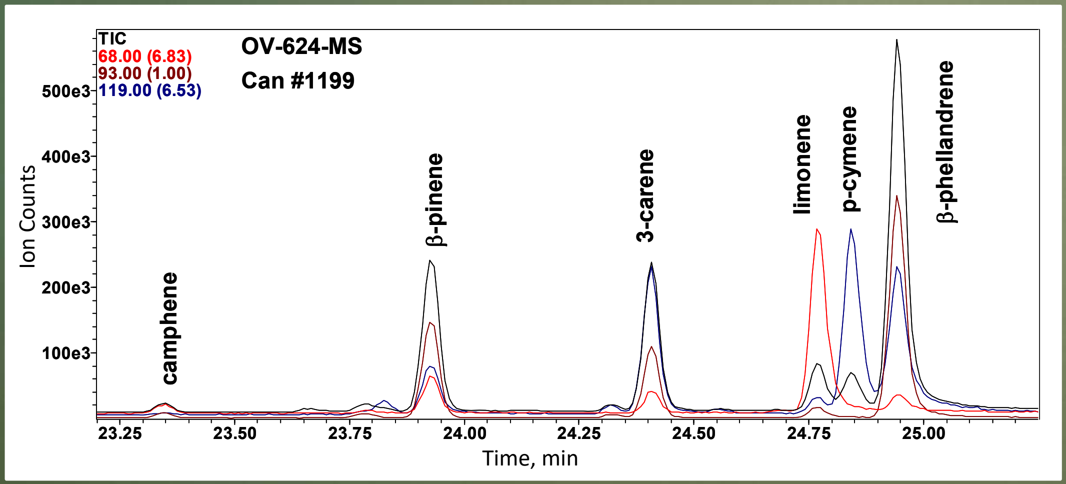
*malfunctioning valve

85 VOCs characterized

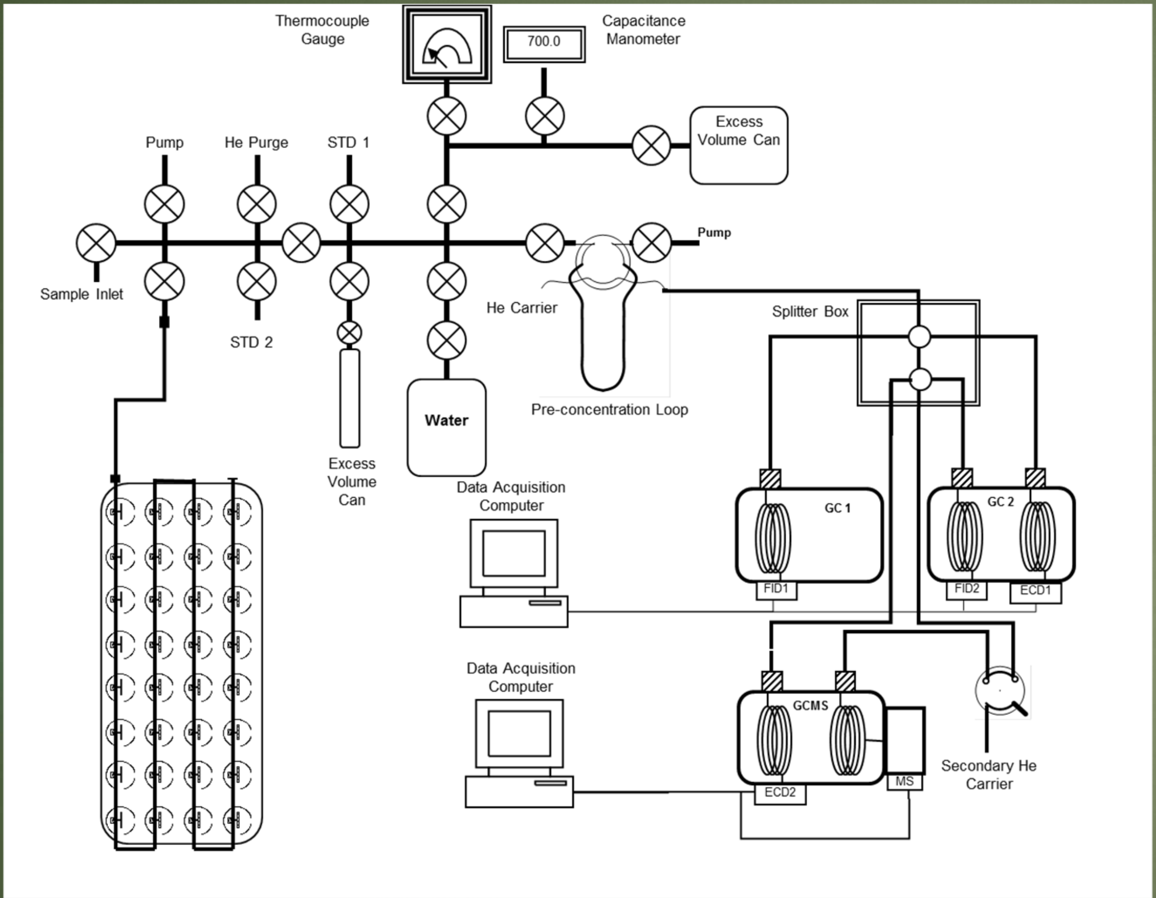
Canister VOC Measurements

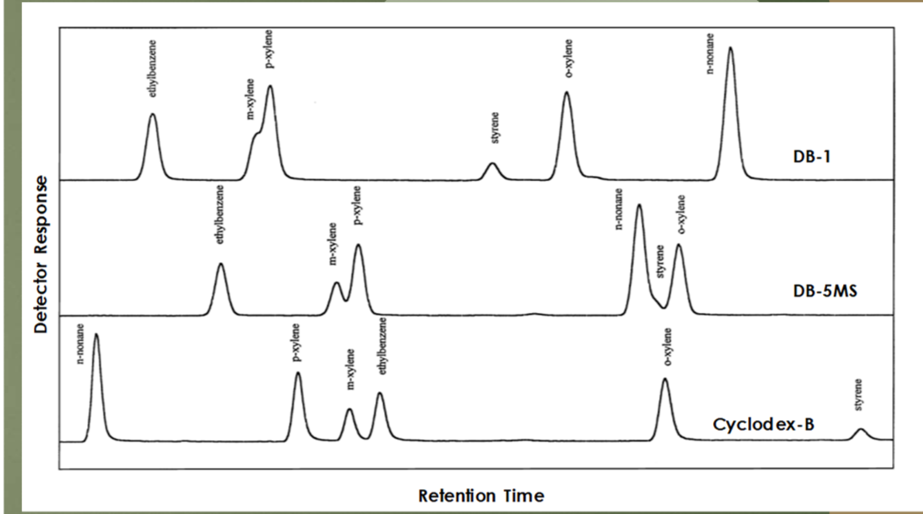
5 Channel GC-FID-ECD-MS System

- *C_2-C_{10} NMHCs*
- *C_1-C_2 Halocarbons*
- *C_1-C_5 Alkyl Nitrates*
- *OCS, CS_2, DMS, selected OVOCs*



Canister VOC Measurements

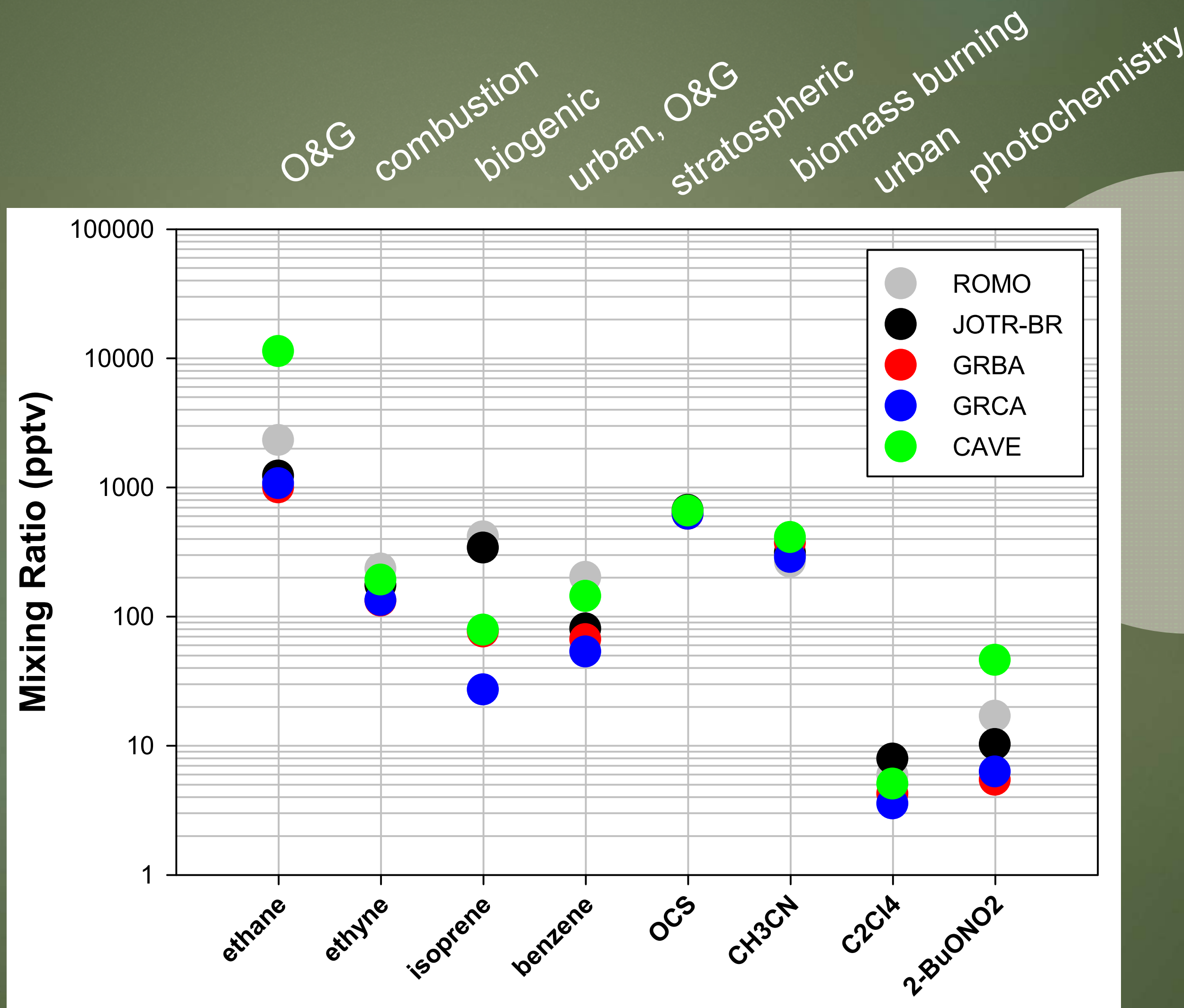




Typical Compound Archive List (92 gases)

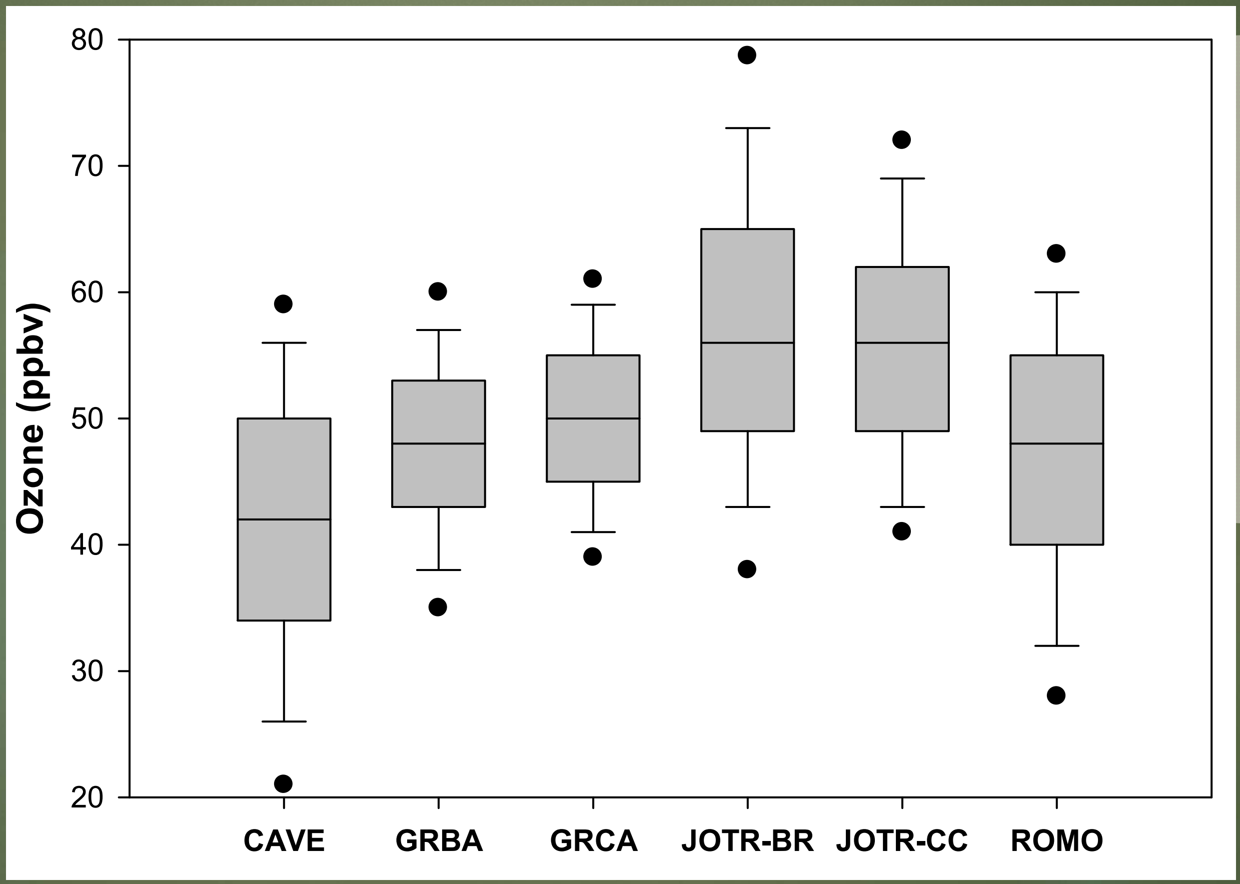
ethane	2-me-1-butene	cychexane	alpha-pinene	CH3I
propane	2-me-2-butene	mecychexane	camphene	CH2Cl2
i-butane	1-hexene	benzene	beta-pinene	CHCl3
n-butane	cis-3-hexene	toluene	3-carene	C2HCl3
i-pentane	trans-2-hexene	ethylbenze	d-limonene	C2Cl4
n-pentane	cis-2-hexene	m+p-xylene	p-cymene	CH2Br2
n-hexane	neopentane	o-xylene	g-terpinene	CHBr3
n-heptane	23-dimethylbutane	styrene		
n-octane	22-dimethylbutane	iso-propylbenzene	COS	DMS
n-nonane	2-mepentane	n-propylbenzene		
n-decane	3-mepentane	m-ethyltoluene	MeONO2	methanol
ethene	24-dimethylpentane	p-ethyltoluene	EtONO2	ethanol
ethyne	23-dimethylpentane	o-ethyltoluene	2-PrONO2	acetaldehyde
propene	2-methylhexane	135-trimethylbenzene	1-PrONO2	acetone
1-butene	224-trimethylpentane	124-trimethylbenzene	2-BuONO2	MEK
t-2-butene	234-trimethylpentane	123-trimethylbenzene	3-PenONO2	MBO
c-2-butene	2-methylheptane	13-diethylbenzene	2-PenONO2	MVK
1-pentene	3-methylheptane	14-diethylbenzene		MACR
t-2-pentene	cyclopentane	12-diethylbenzene		acetonitrile
c-2-pentene	mecycpentane	isoprene		

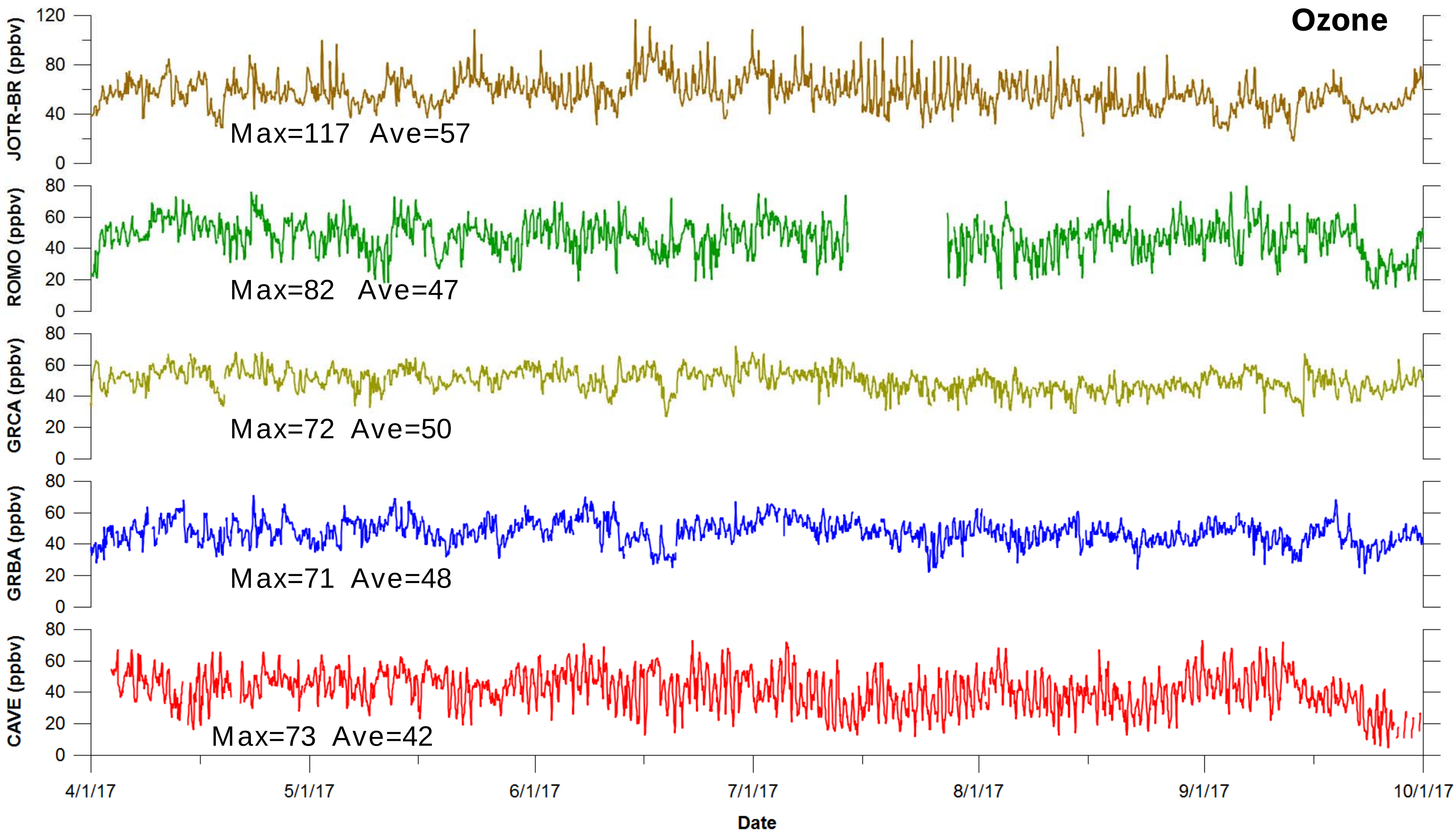
Average Mixing Ratios: Specific Source Markers



Ozone distributions during the study

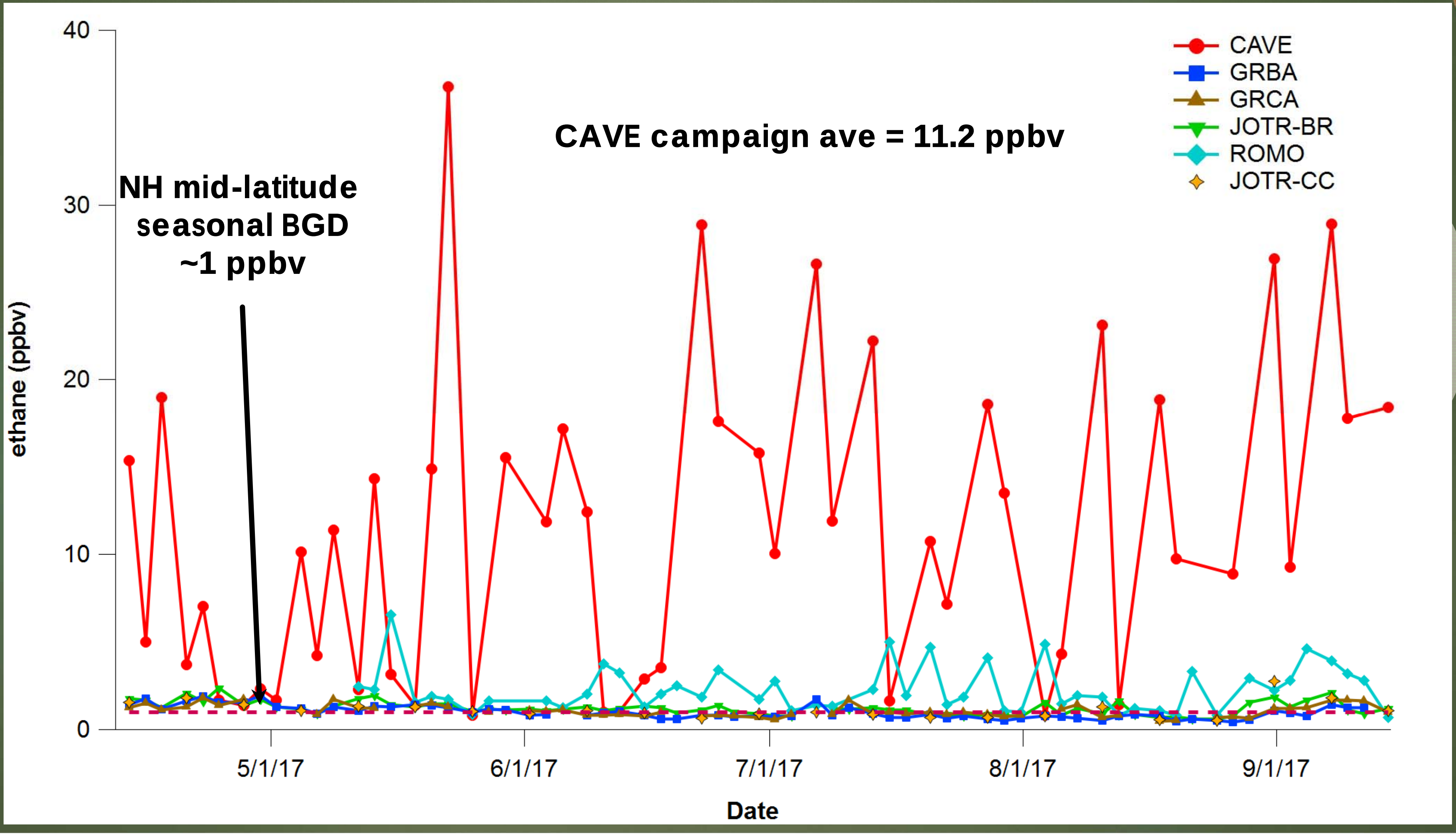
- Only during VOC measurement period (April-Sept 2017)



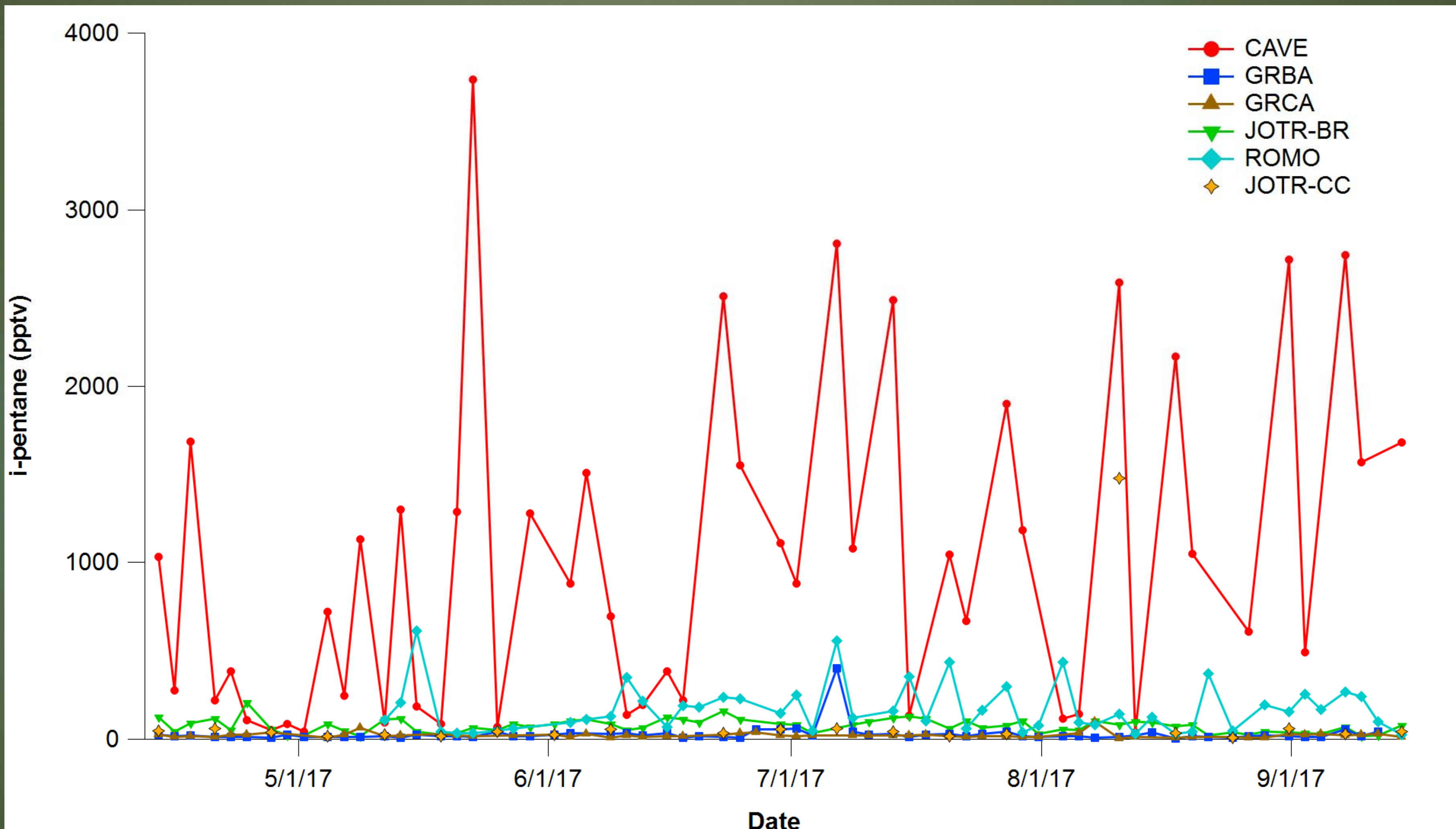


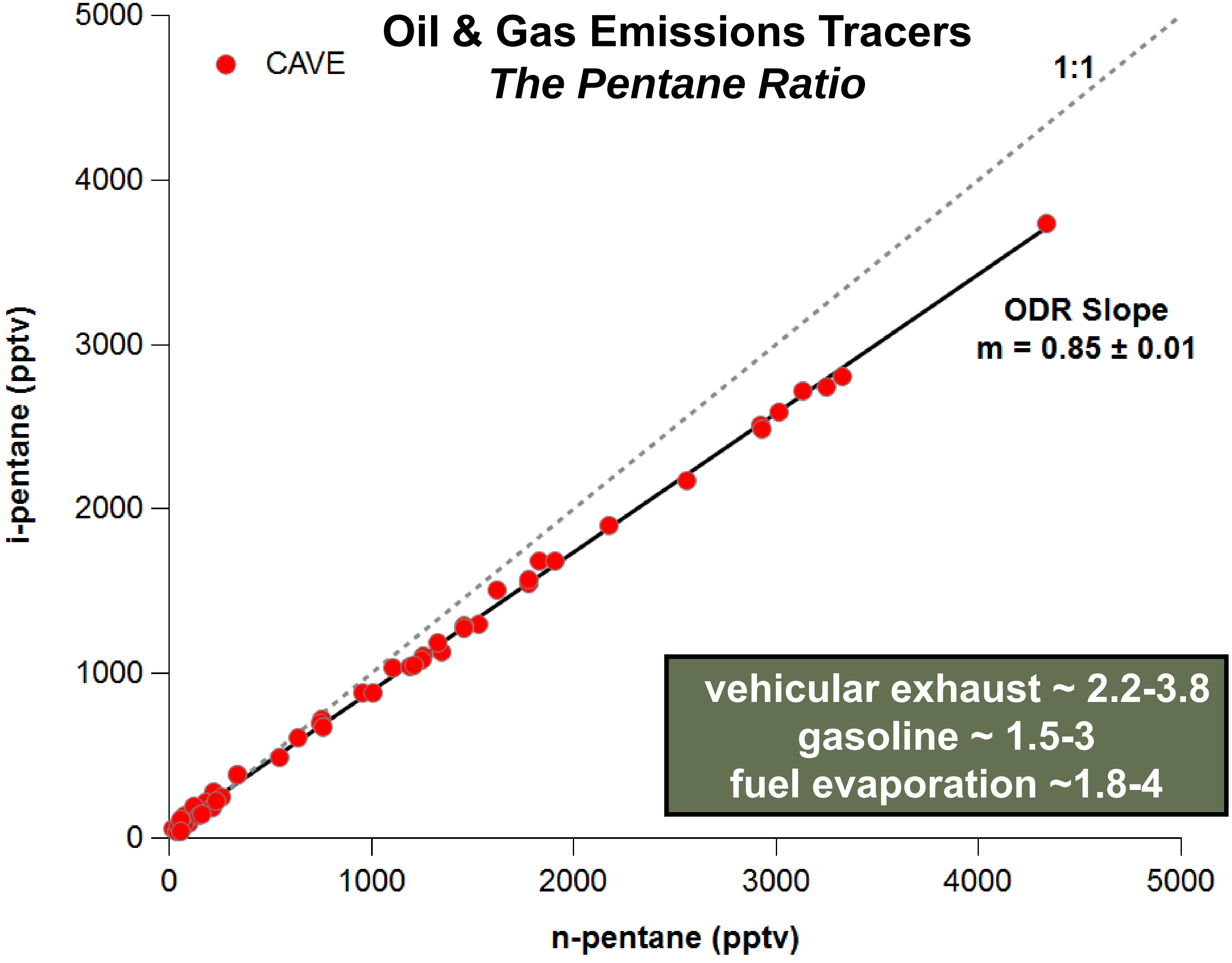
Ozone
JOTR-BR (ppbv)
Max=117 Ave=57
ROMO (ppbv)
Max=82 Ave=47
GRCA (ppbv)
Max=72 Ave=50
GRBA (ppbv)
Max=71 Ave=48
CAVE (ppbv)
Max=73 Ave=42
4/1/17
5/1/17
6/1/17
7/1/17
8/1/17
9/1/17
10/1/17
Date

Temporal Distributions of VOCs

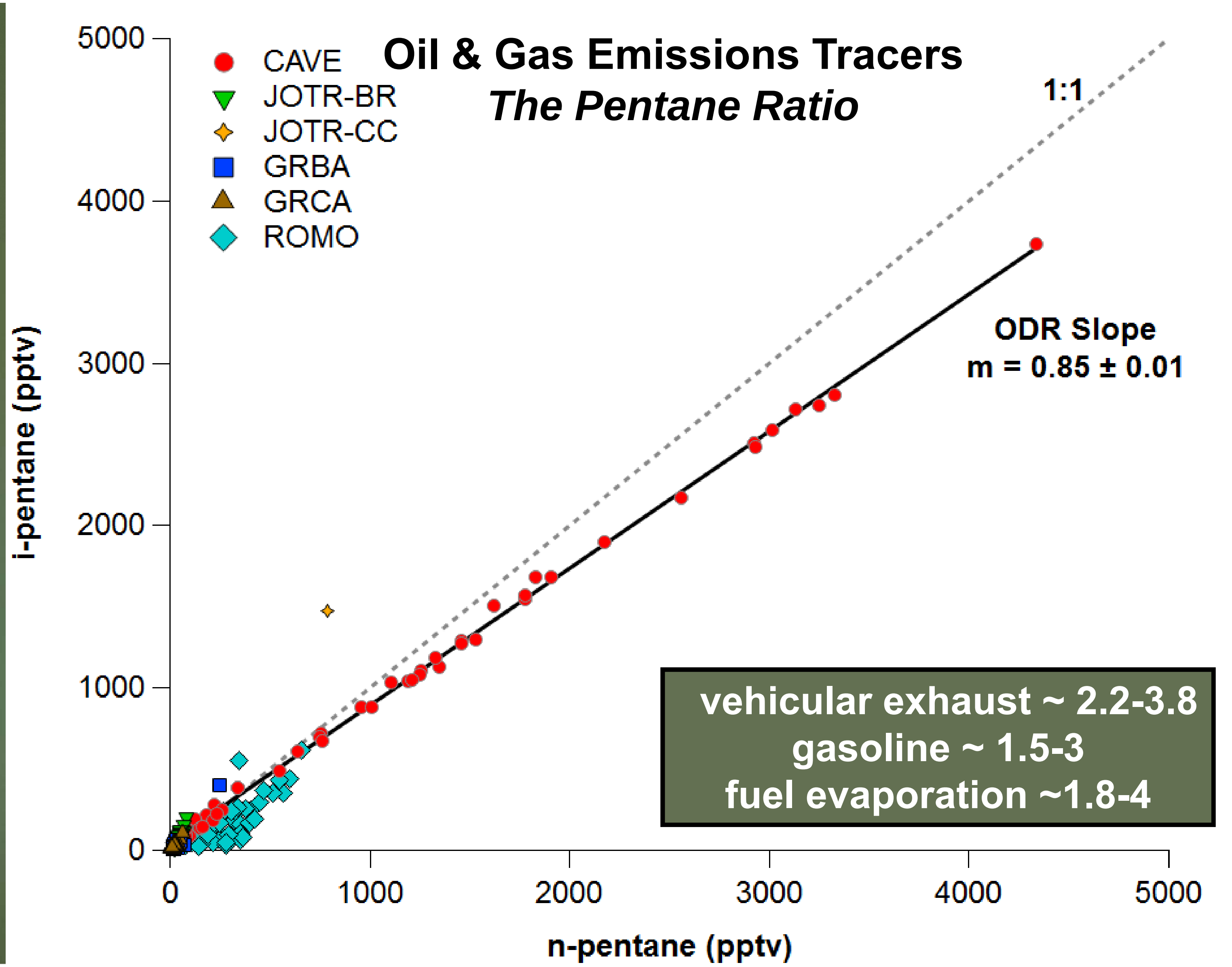


Temporal Distributions of VOCs





Oil & Gas Emissions Tracers
The Pentane Ratio
CAVE
1:1
ODR Slope
m = 0.85 ± 0.01
vehicular exhaust ~ 2.2-3.8
gasoline ~ 1.5-3
fuel evaporation ~1.8-4
i-pentane (pptv)
n-pentane (pptv)
0
1000
2000
3000
4000
5000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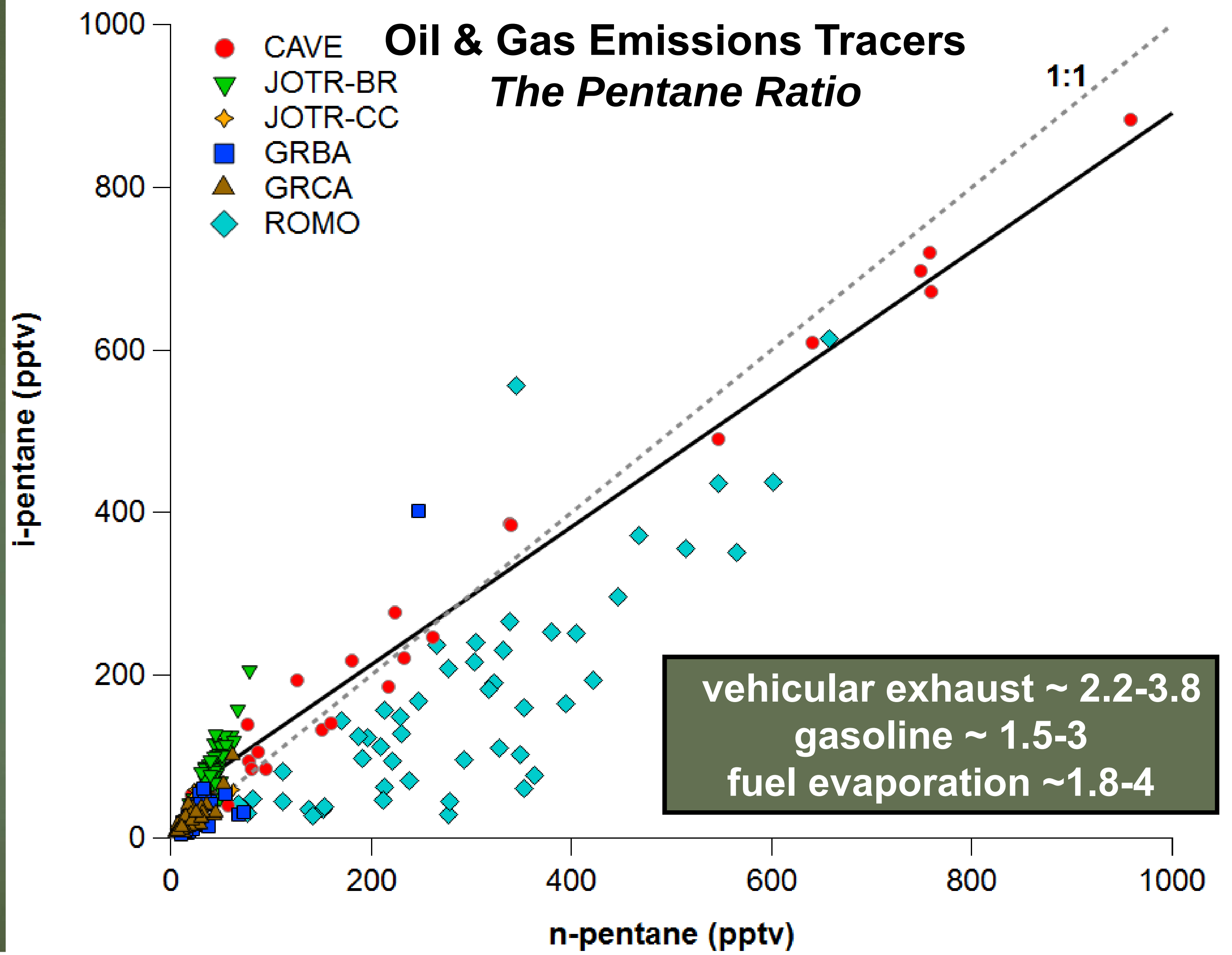
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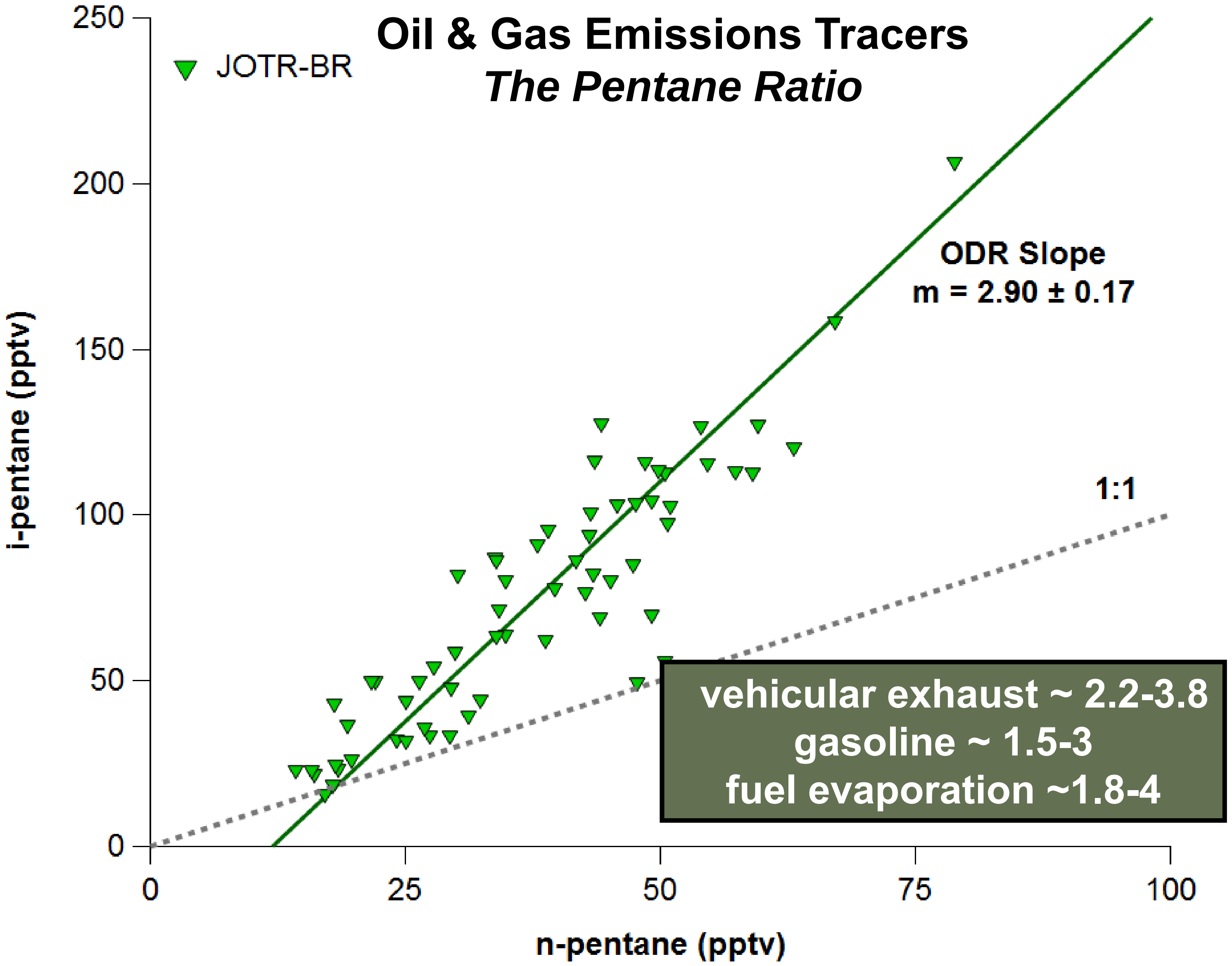
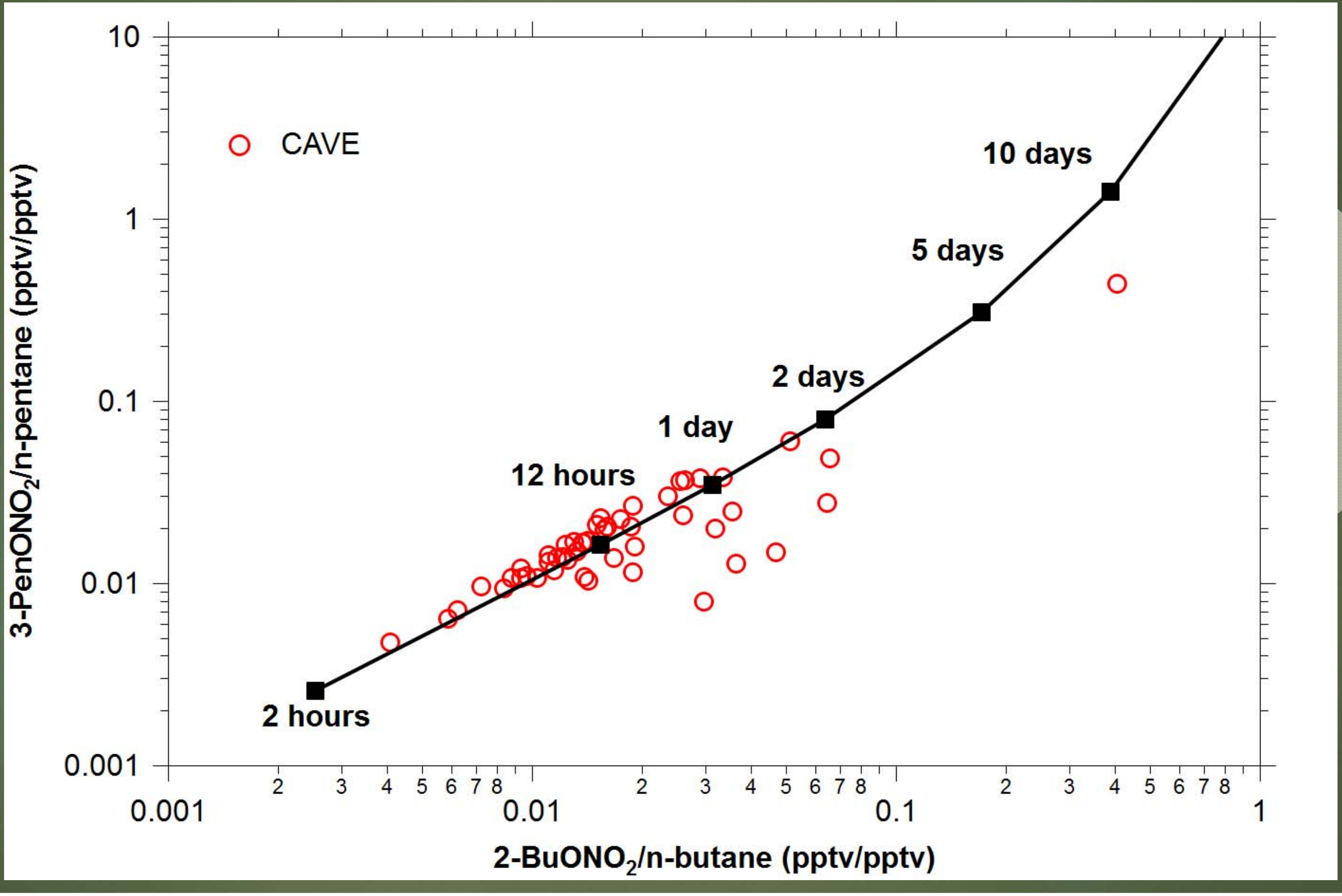
800
1000

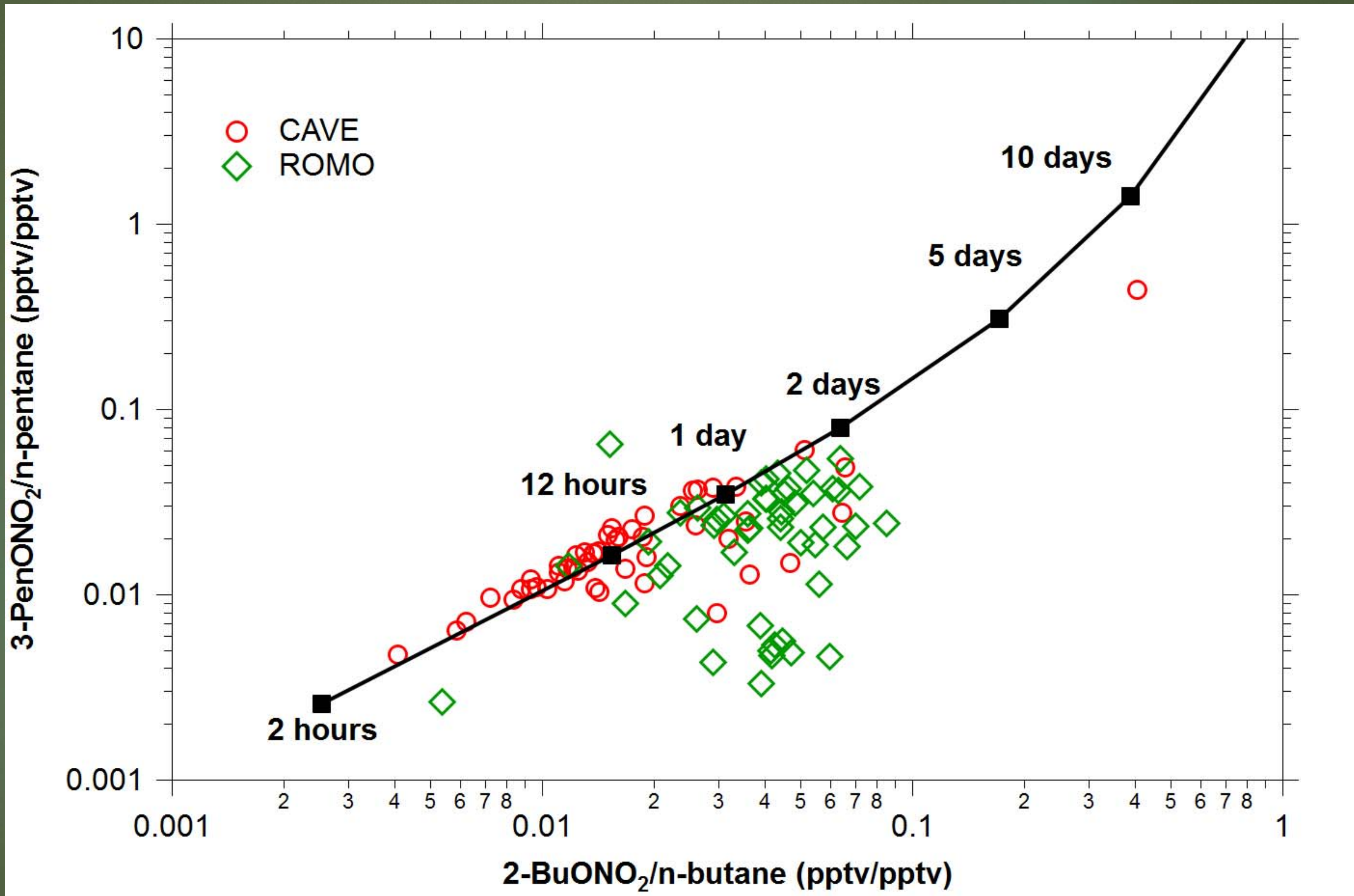


Oil & Gas Emissions Tracers
The Pentane Ratio
JOTR-BR
ODR Slope
m = 2.90 ± 0.17
1:1
vehicular exhaust ~ 2.2-3.8
gasoline ~ 1.5-3
fuel evaporation ~1.8-4
i-pentane (pptv)
n-pentane (pptv)
0
50
100
150
200
250
0
25
50
75
100

Photochemical Age using Alkyl Nitrates



Photochemical Age using Alkyl Nitrates



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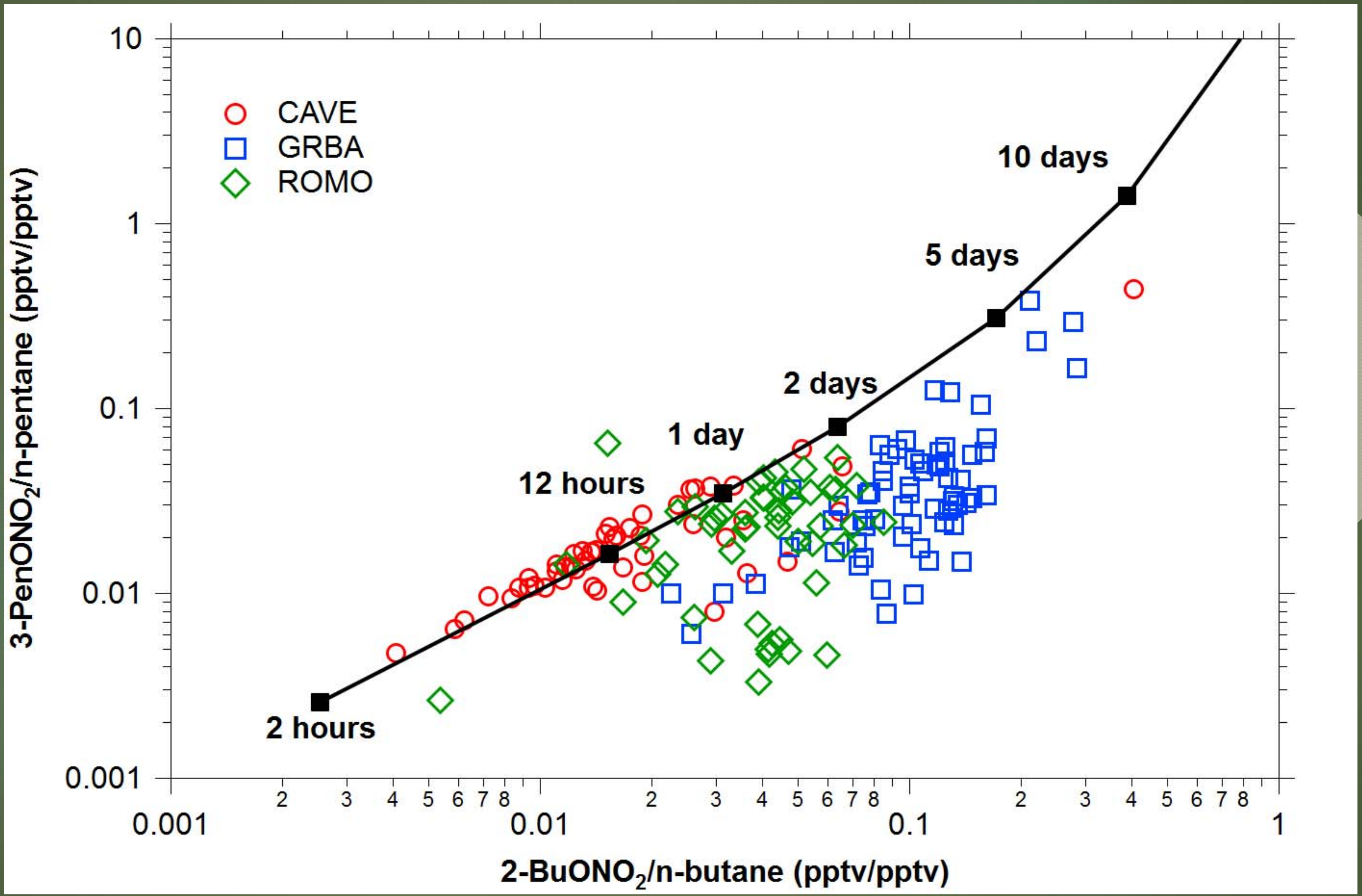

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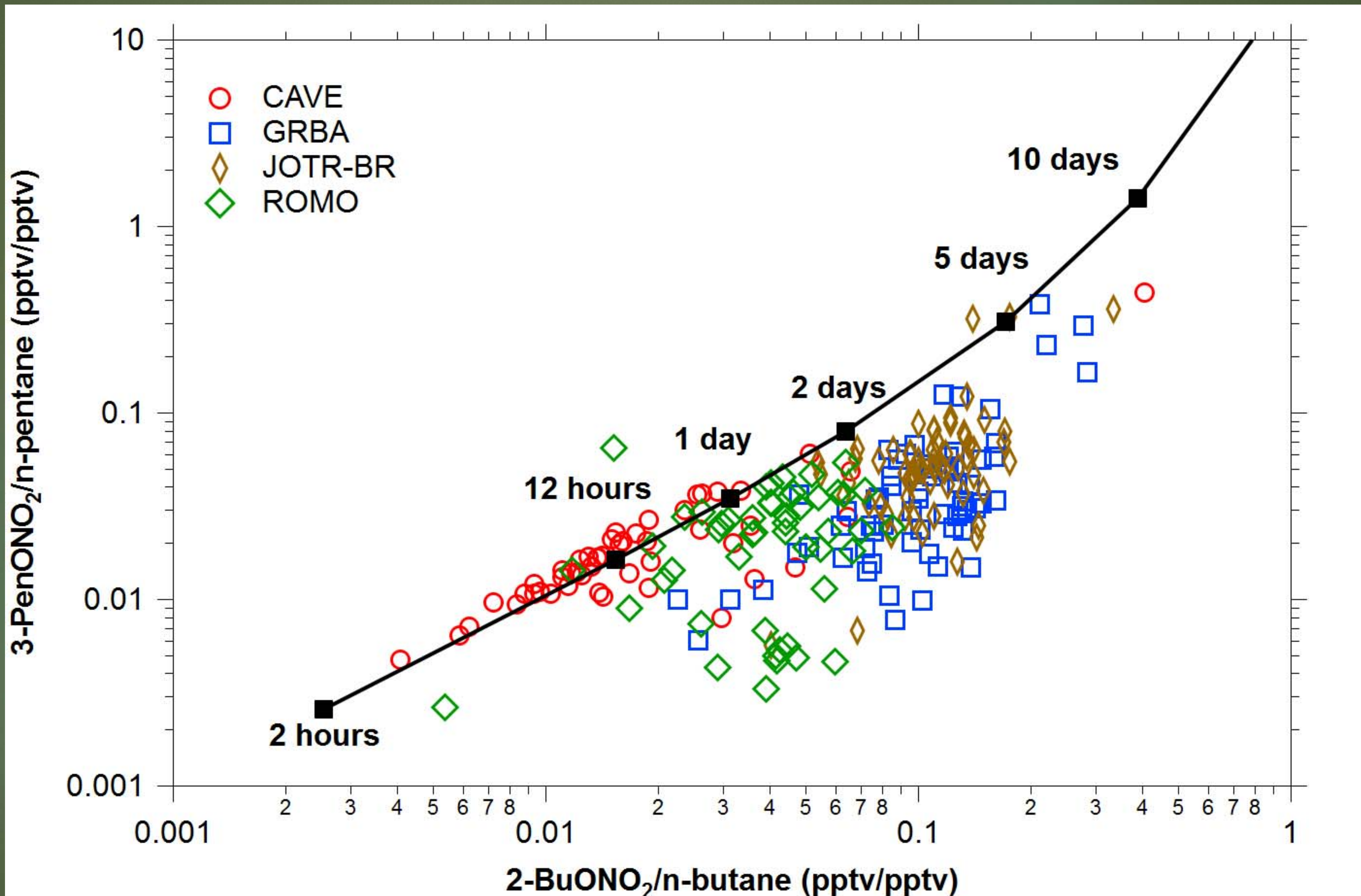

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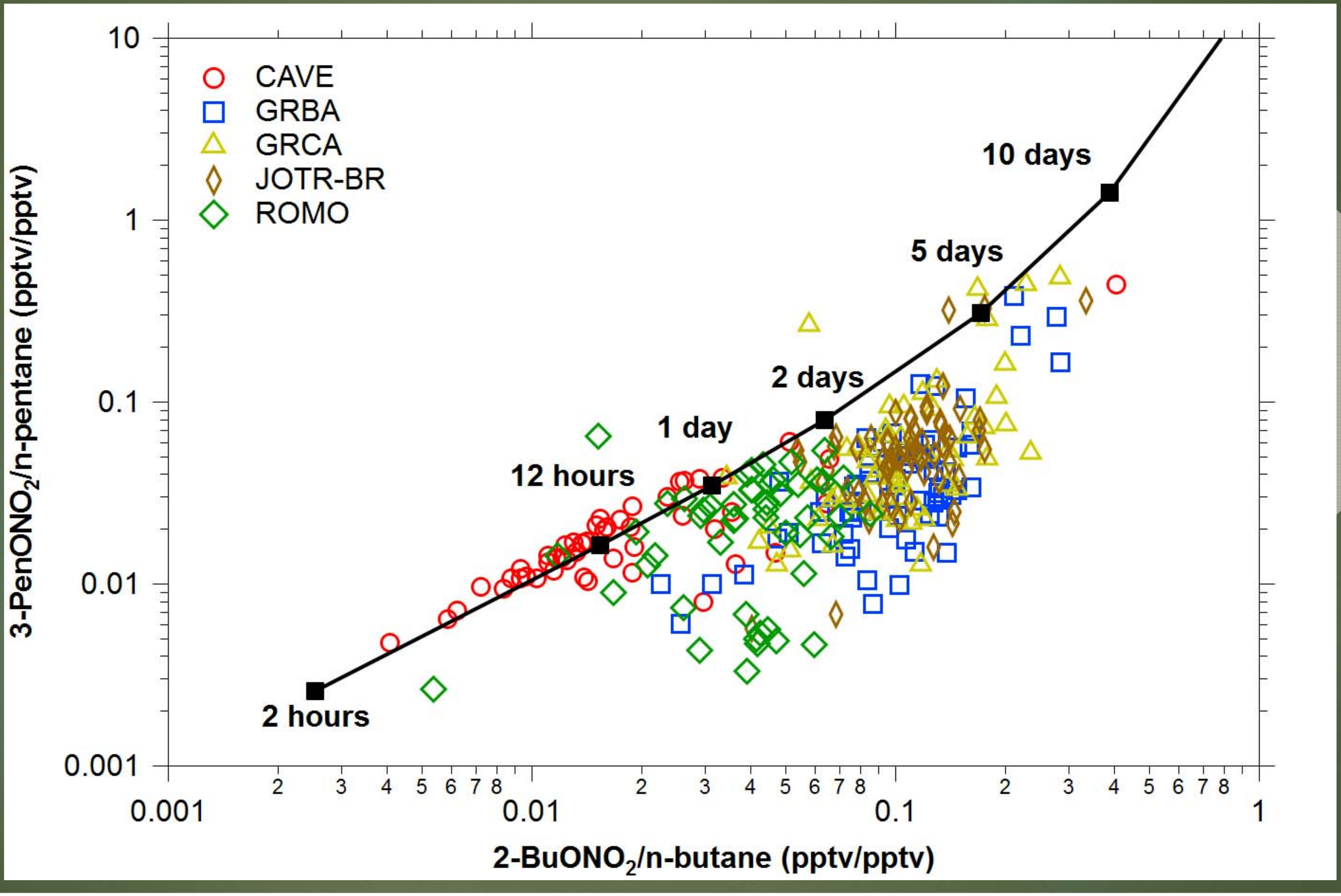

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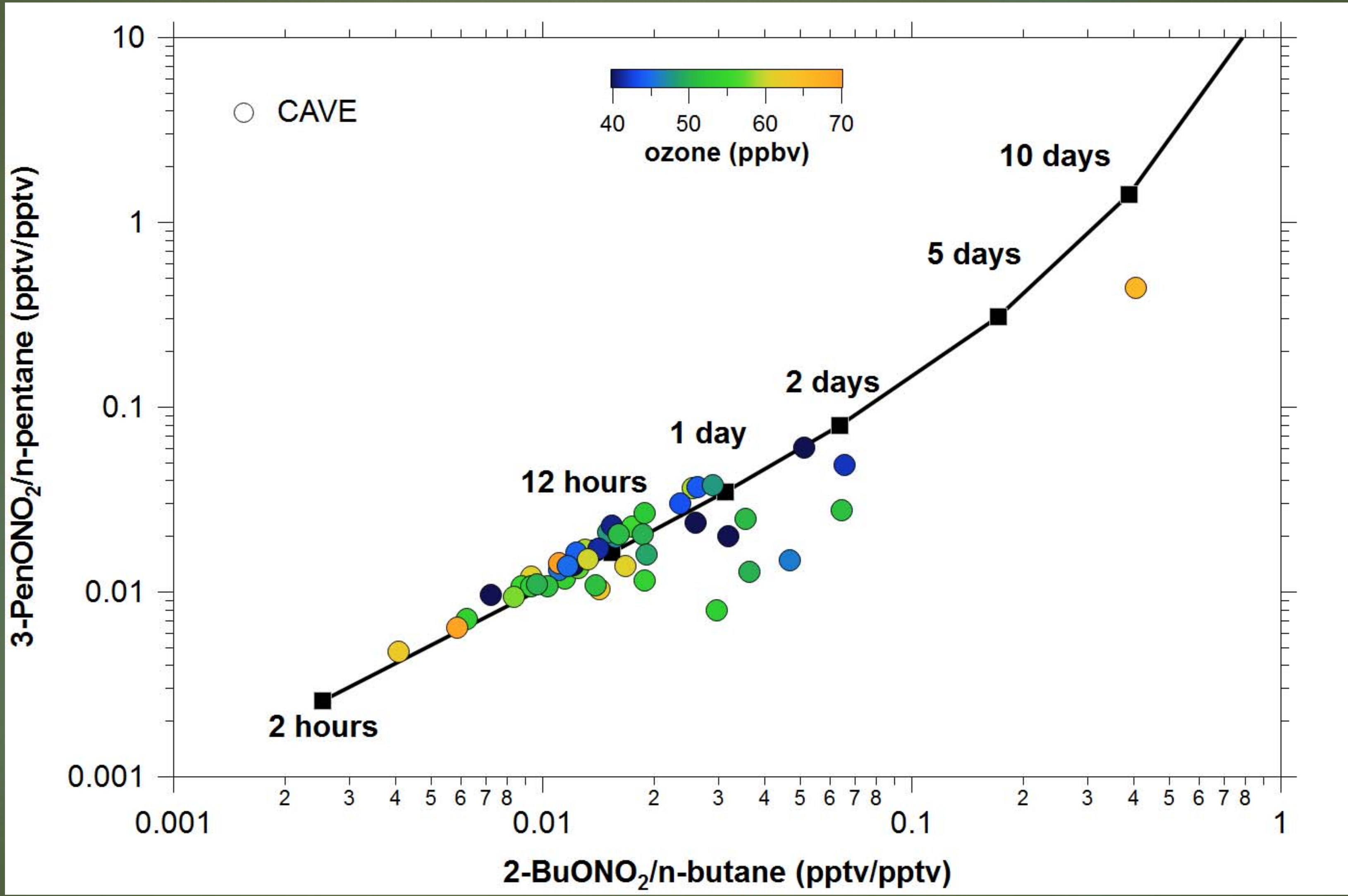

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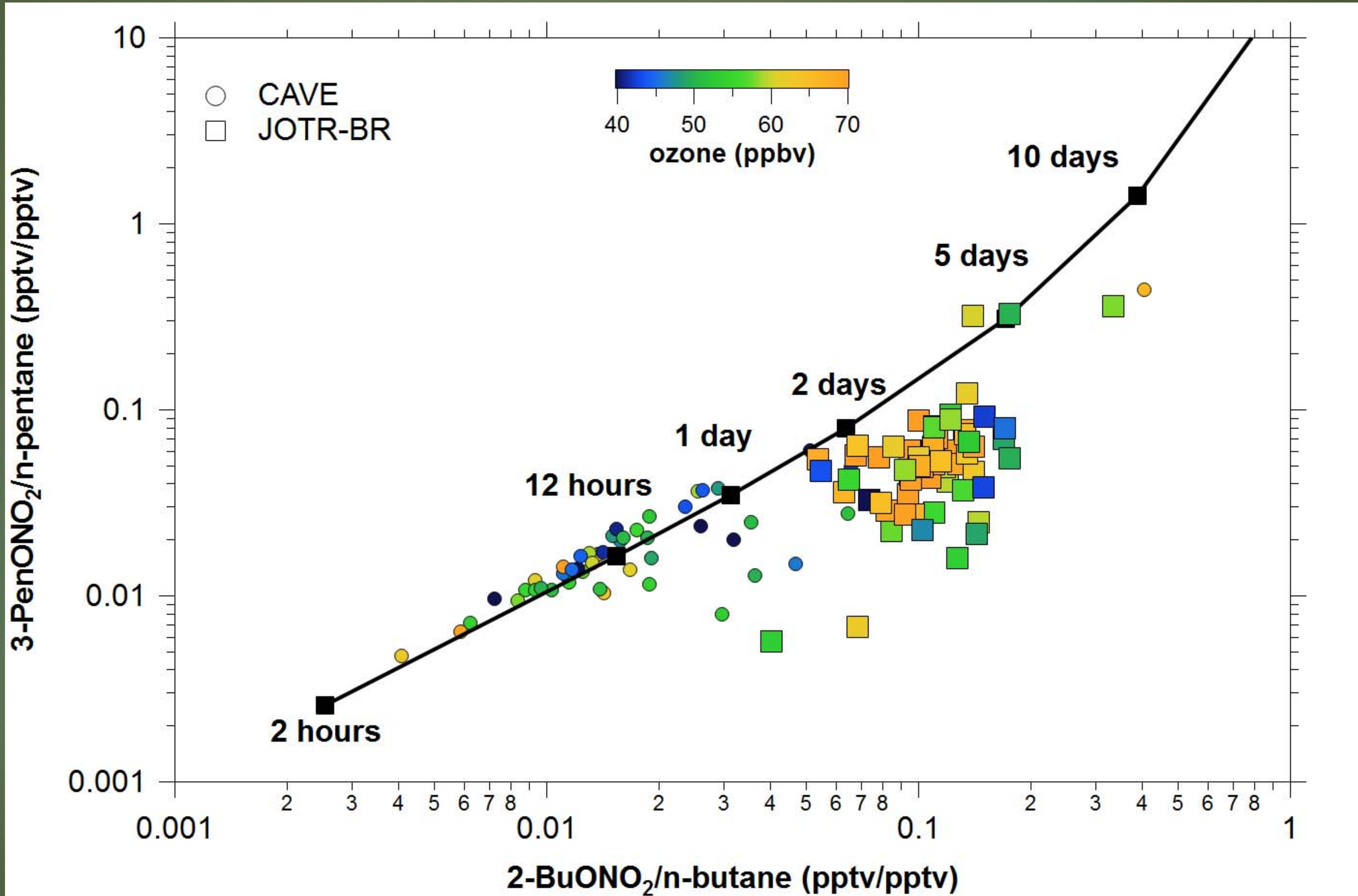
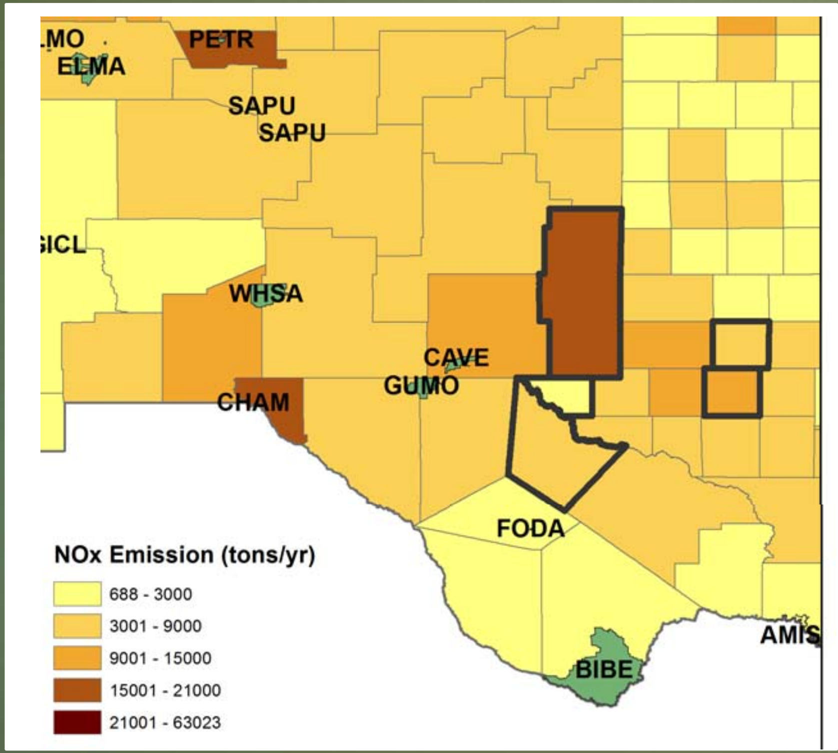


Oil and Gas in the Permian Basin

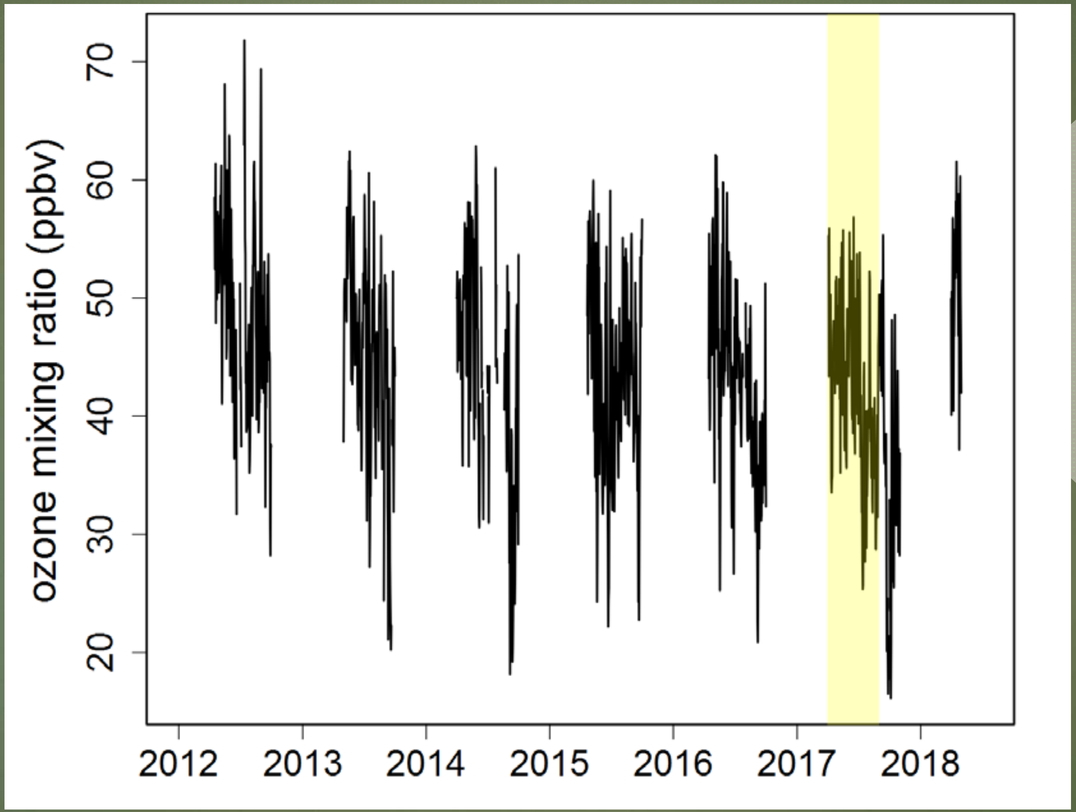
NO_x emissions by county



EIA:

- Permian Basin > 75,000 square miles in W Texas and SE New Mexico.
- More than half of the rigs added in the Permian are in just five counties: **Reeves, Loving, Midland, and Martin counties in TX and Lea County in NM.**

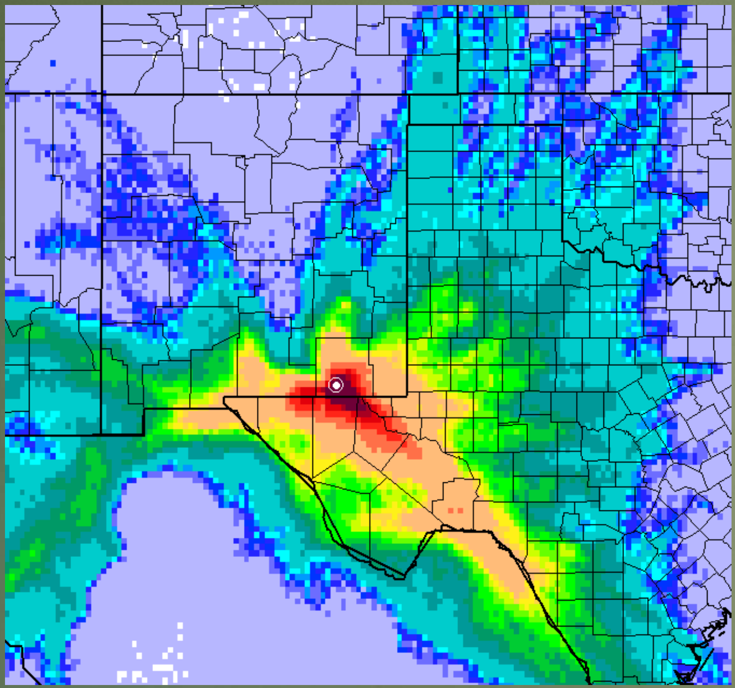
Long Term Ozone Measurements at Carlsbad Caverns National Park



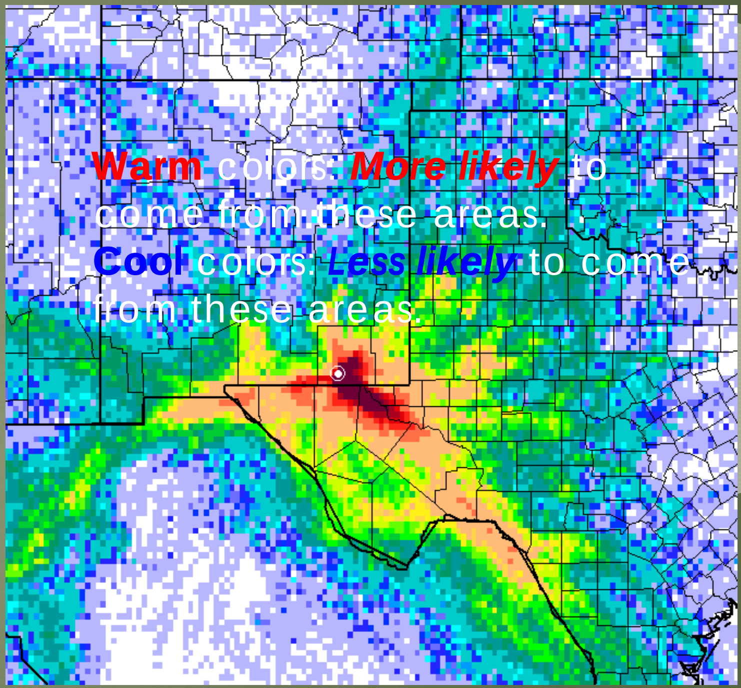
VOC study was done during a relatively low ozone year (daily averages).

Carlsbad Caverns National Park

April-Sept 2017. All Hours.



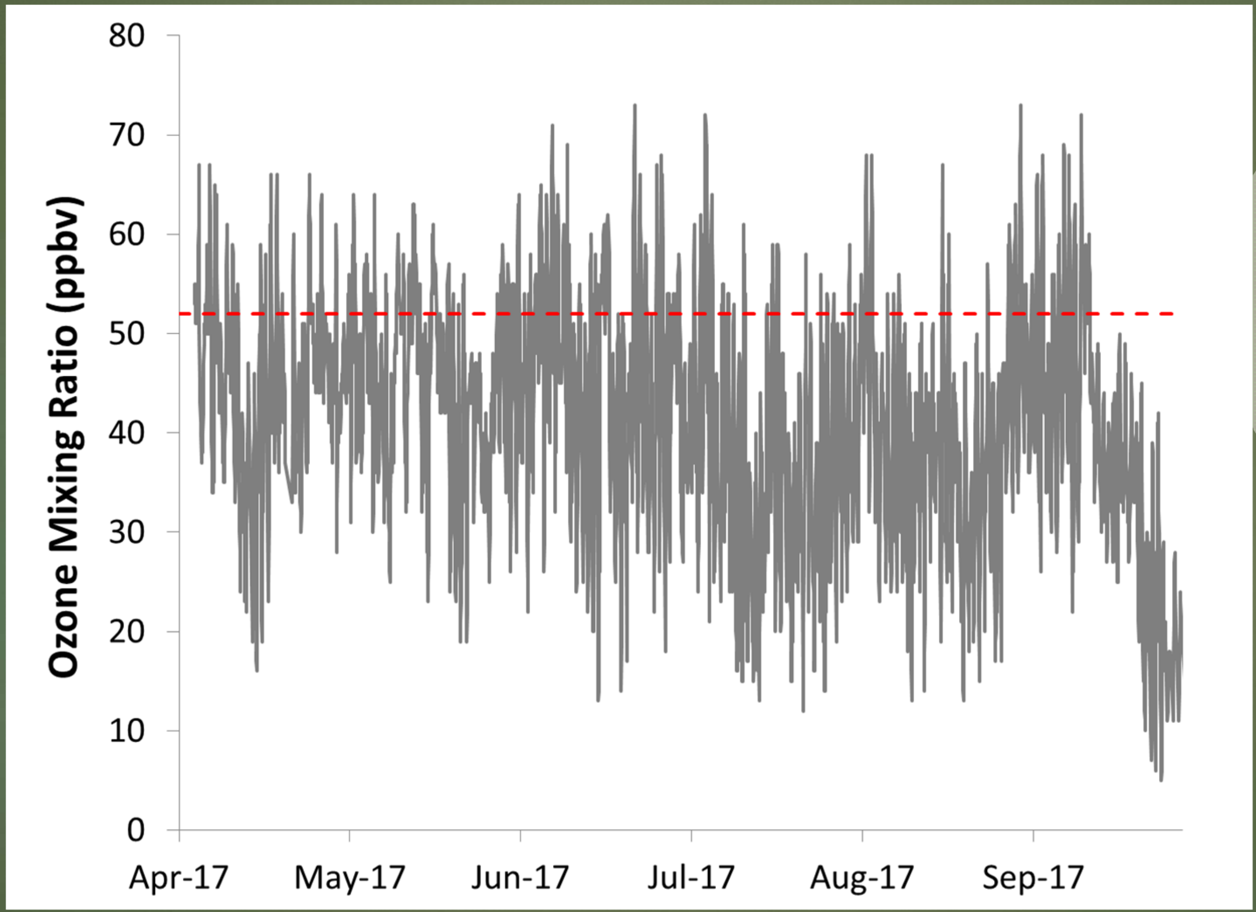
April-Sept 2017. Hours 15-16 Local.



Back Trajectories

- 2-day Overall Residence Time
- Air masses came primarily from west (El Paso) and southeast (O&G).

Carlsbad Caverns Ozone

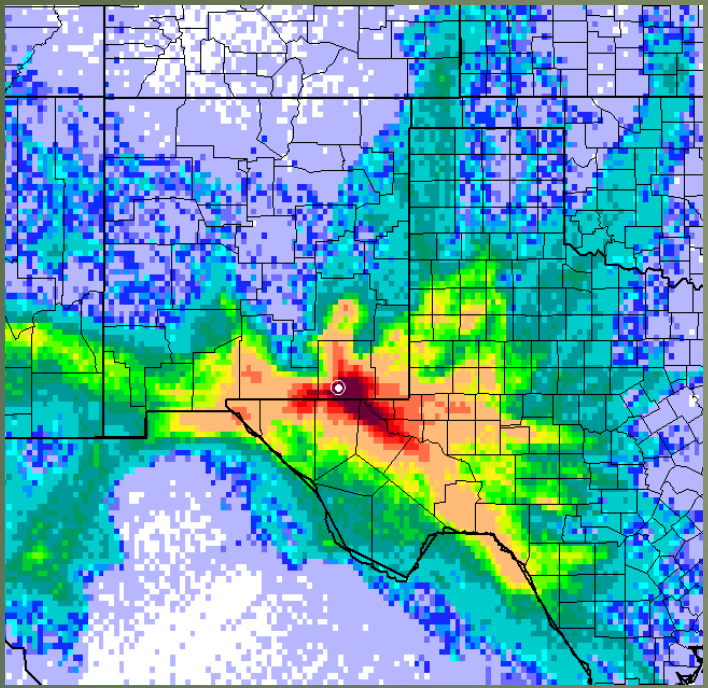


Where do air masses come from for these highest ozone values?

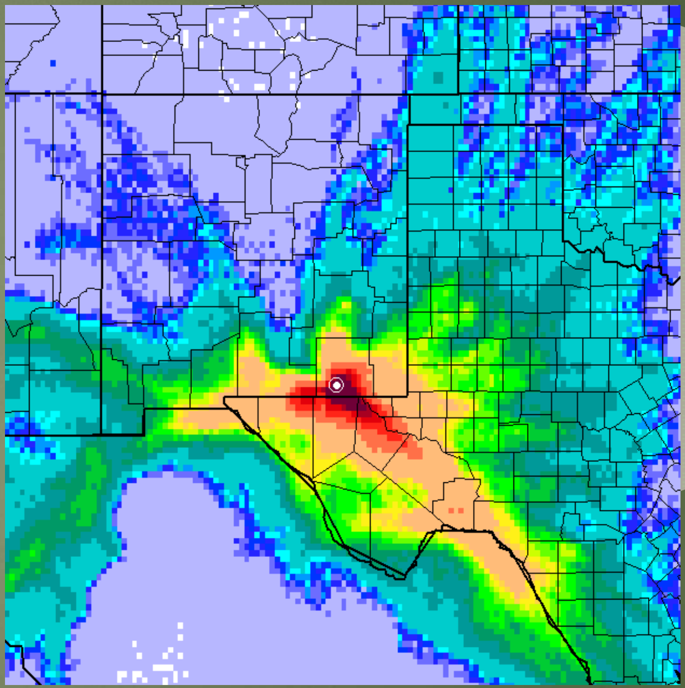
80th% value:

High Residence Time Analysis

High Concentration Residence Time (HRT)

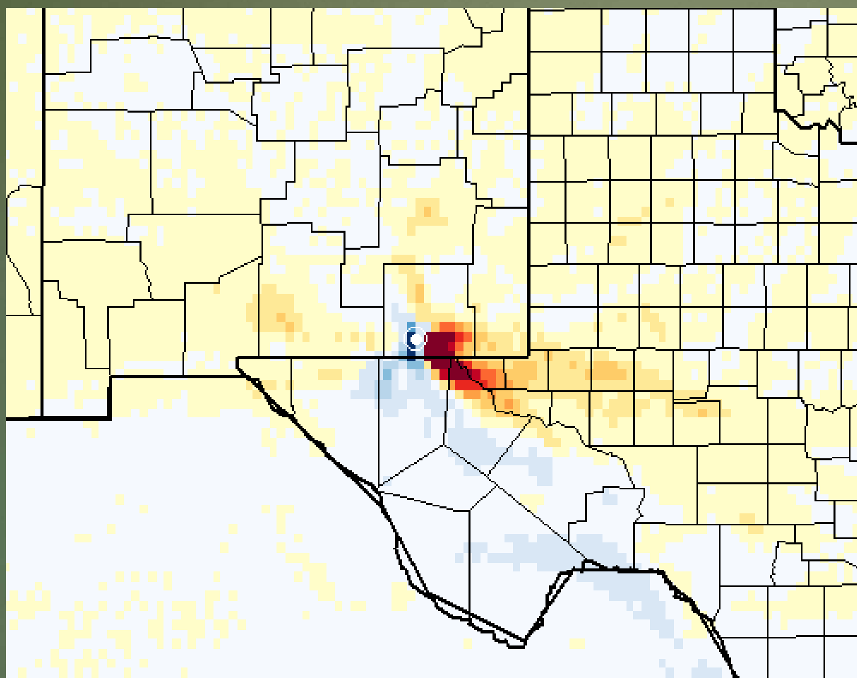


Overall Residence Time (ORT)



Ozone Top 20% of Apr-Sep all hours (above 52 ppb)

HRT – ORT for ozone all hours



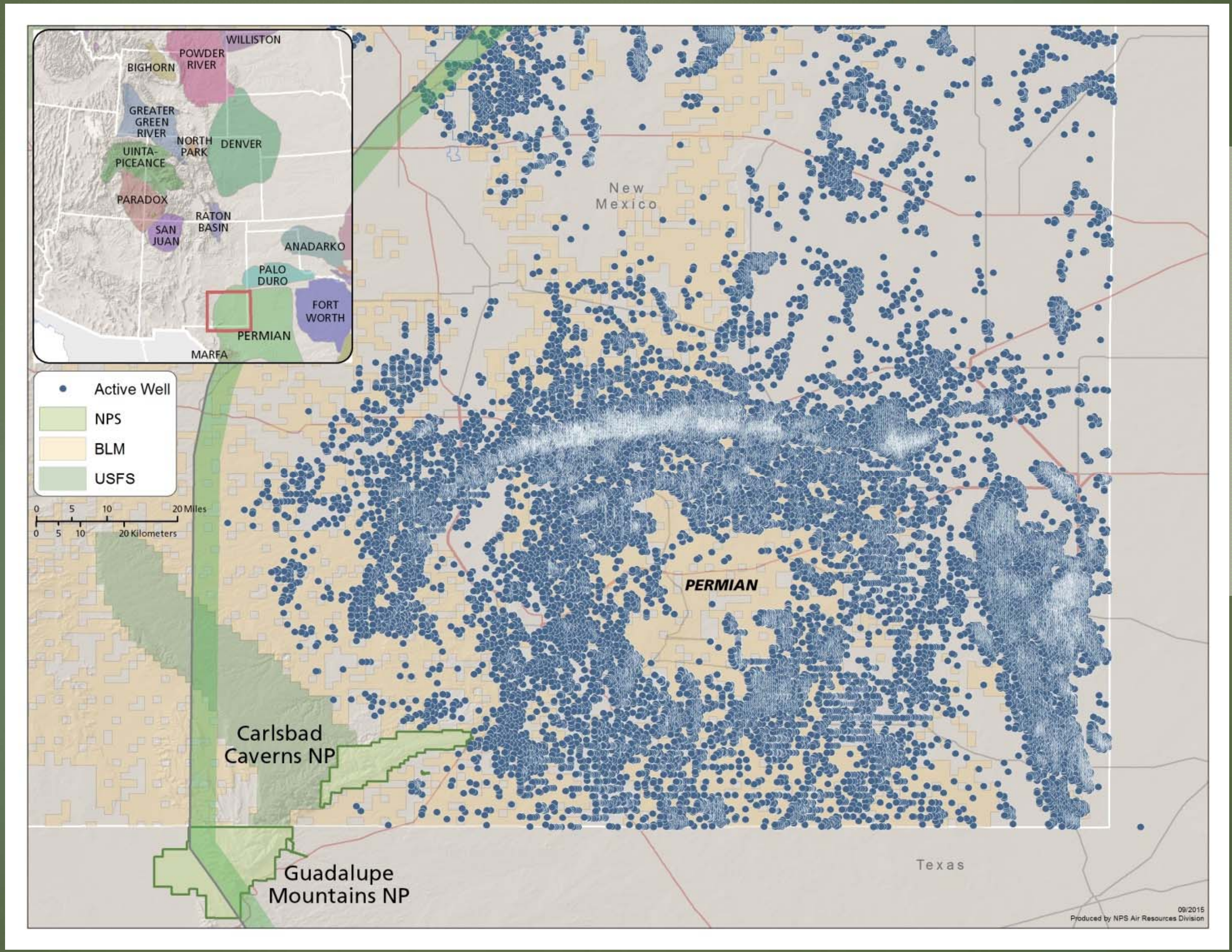
April – September, 2017

Warm colors: ***More likely*** to come from these areas during high concentrations than during average conditions.

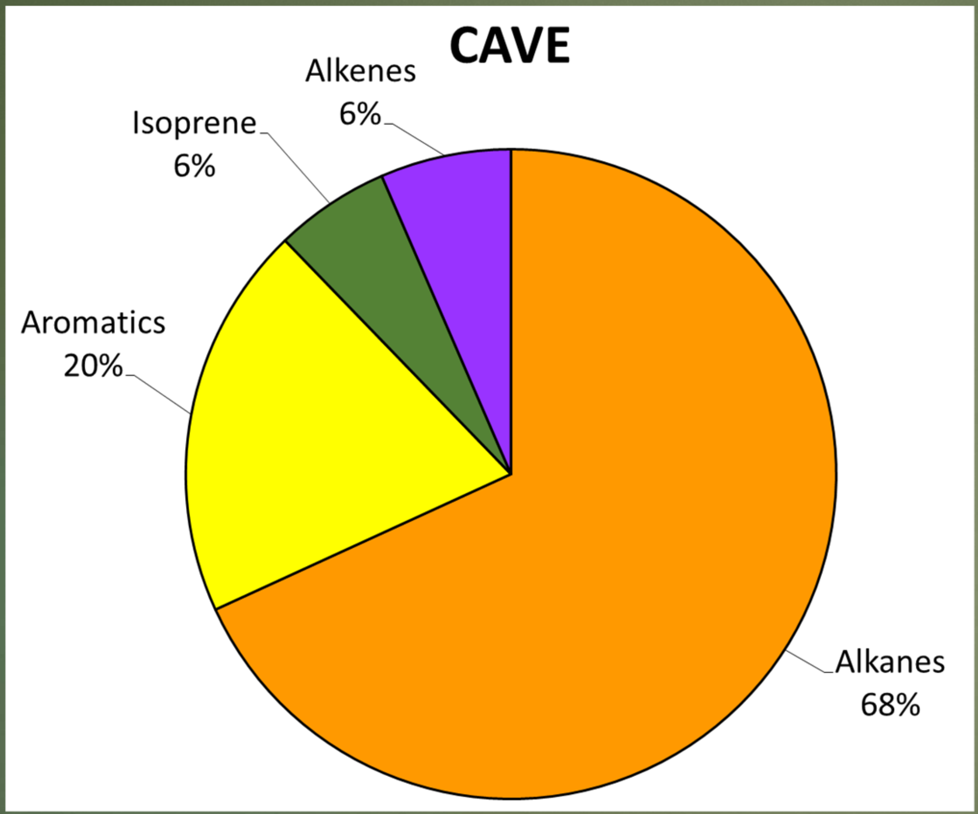
Cool colors: ***Less likely*** to come from these areas during high concentrations than during average conditions.

More likely to come from oil and gas region during high ozone periods.

Wells Near CAVE



CAVE OH reactivity during highest ozone periods

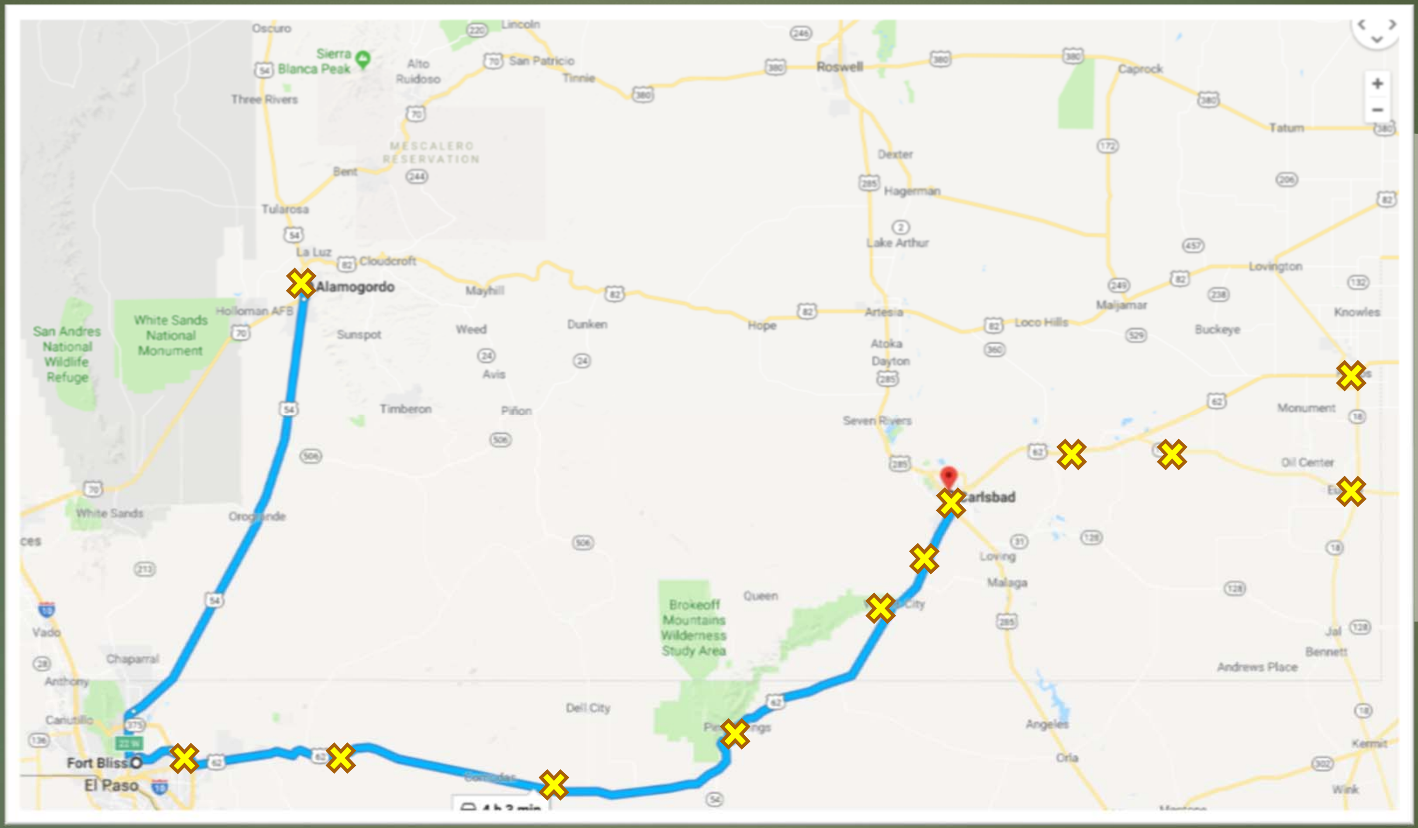


- Despite slow reaction rates, alkanes (O&G) are most important for OH reactivity.
- Aromatics (Urban + O&G)

OH reactivity helps to identify compounds that are likely to contribute to O_3 production.

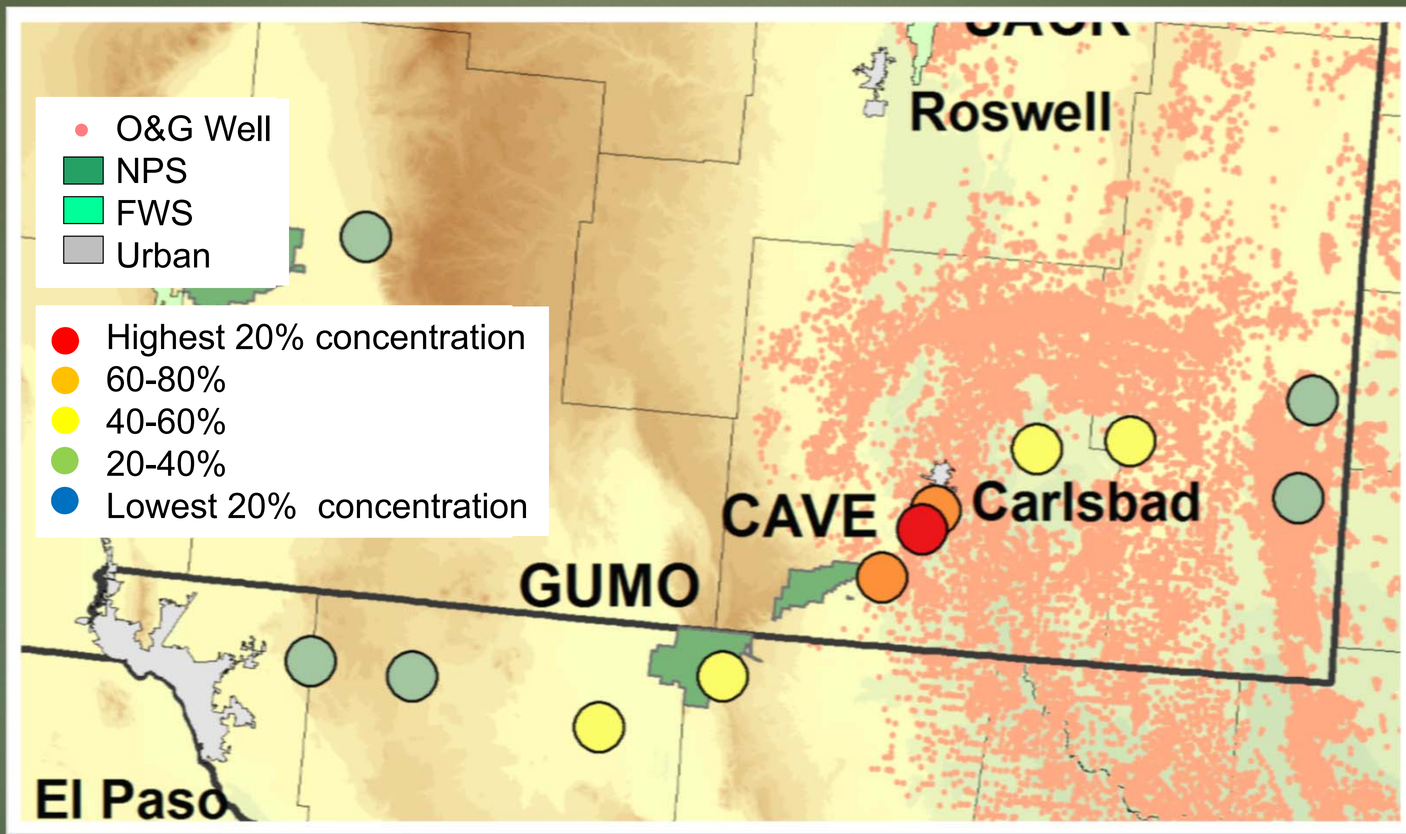
September 2017 Intensive Sampling

Sampling Approach



Mobile Lab Sampling
Canister Collection Locations

Ethane Concentrations



September 8

- Highest 20% concentration
- 60-80%
- 40-60%
- 20-40%
- Lowest 20% concentration

- O&G Well
- NPS
- FWS
- Urban

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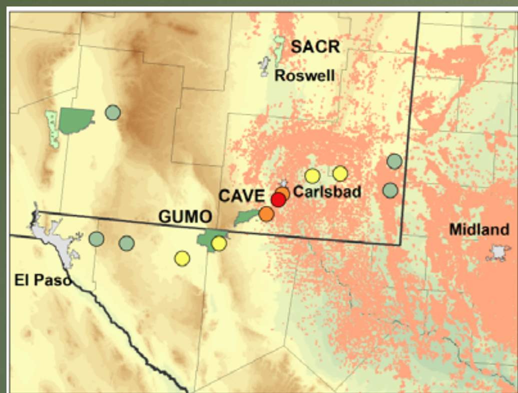
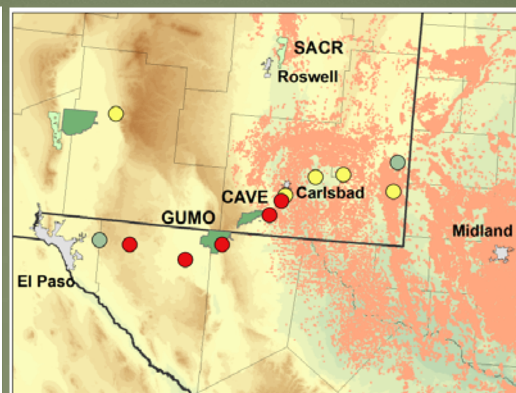
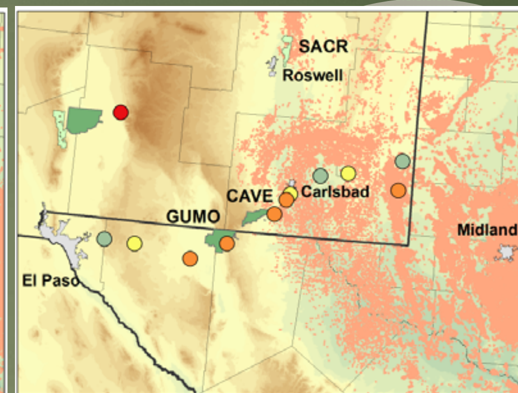
Ethane (O&G)



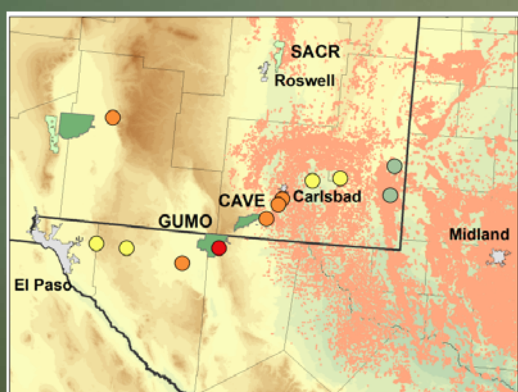
C_2Cl_4 (Urban, solvent)



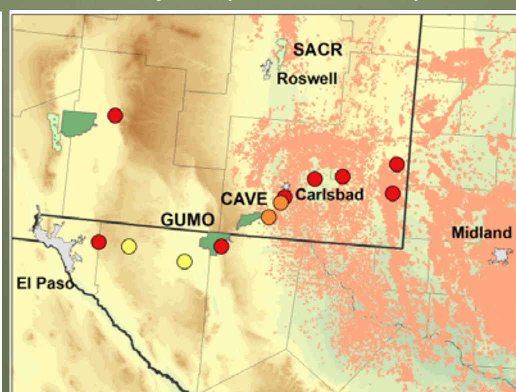
Benzene (Industrial, combustion, O&G)



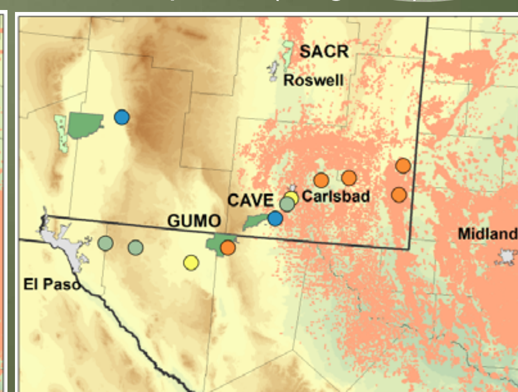
2-$BuONO_2$ (photochemical product of O&G)



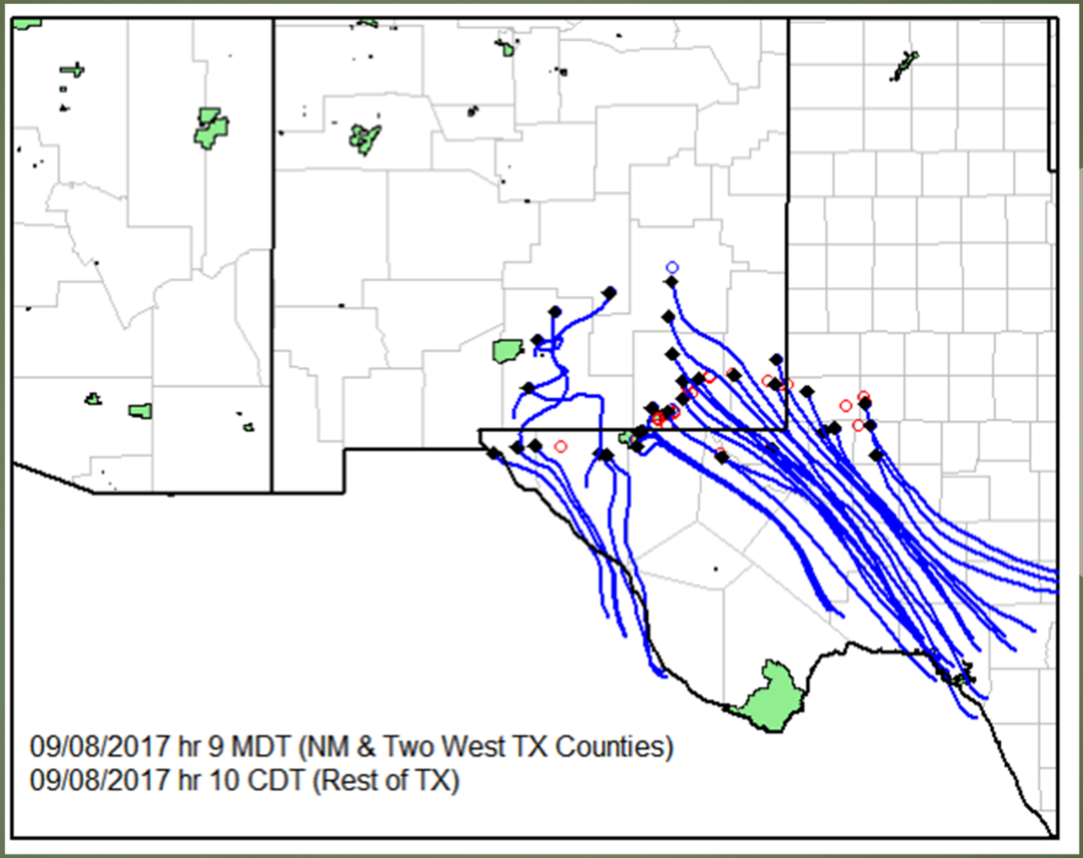
Ethyne (combustion)



Isoprene (biogenic)



September 8



Flow Primarily from the Southeast. Eastern Sites: O&G influenced. West of GUMO: Less O&G influence.

Summary

- CAVE had the highest levels of VOCs among 5 parks throughout the summer.
- VOCs in the region are dominated by oil and gas emissions from the Permian Basin.
- Despite the high levels of VOCs, ozone was relatively low in 2017.
  - Likely due to low levels of NO_x.
- High levels of VOCs were observed at CAVE, GUMO and SACR during intensive.
  - Concentrations driven by meteorology.
- Need real-time 24 hour VOC and NO_x measurements to better:
  - Understand the full impact of oil and gas emissions on the parks;
  - Characterize ozone formation in the region.
- Long-term VOC measurements needed at GUMO and SACR to better characterize full extent of oil and gas impacts.