



TriCities Ozone Precursor Study (T-COPS)

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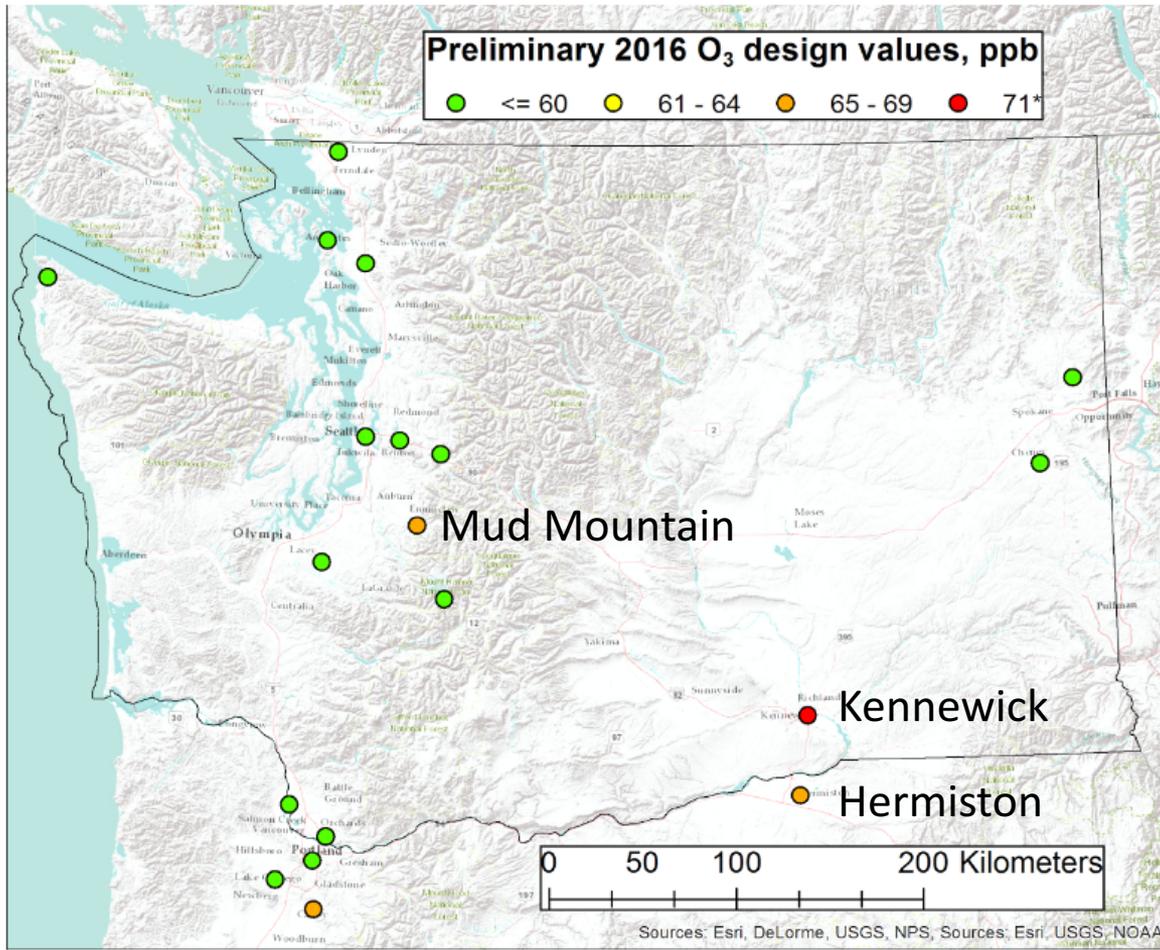
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Recent O₃ monitoring in Kennewick has shown elevated levels in summer.

Ozone NAAQS standard:
70 ppbv
Averaged 4th highest daily 8-hour maximum averaged over 3 years.

Kennewick ozone levels similar to Mud Mountain.

Why is there elevated ozone in Kennewick?

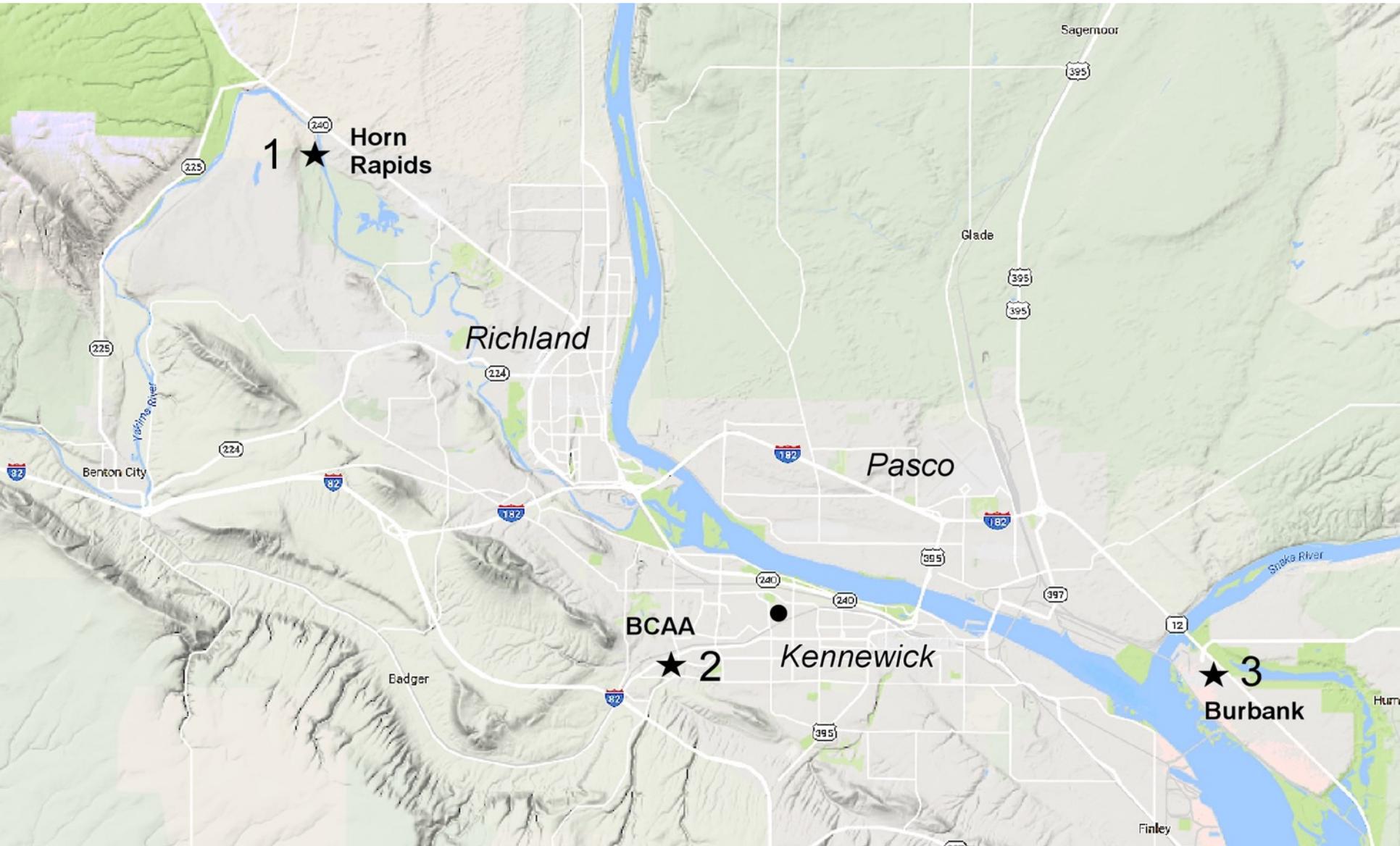
Ozone Design Values (ppbv)

Year	MM	Kennewick	Hermiston	Spokane
2013	57	--	62	61
2014	67	--	64	60
2015	74	75	70	62

T-COPS measurements sites

July 28 – August 19, 2016

3 fixed sites + mobile van (RJ Lee)



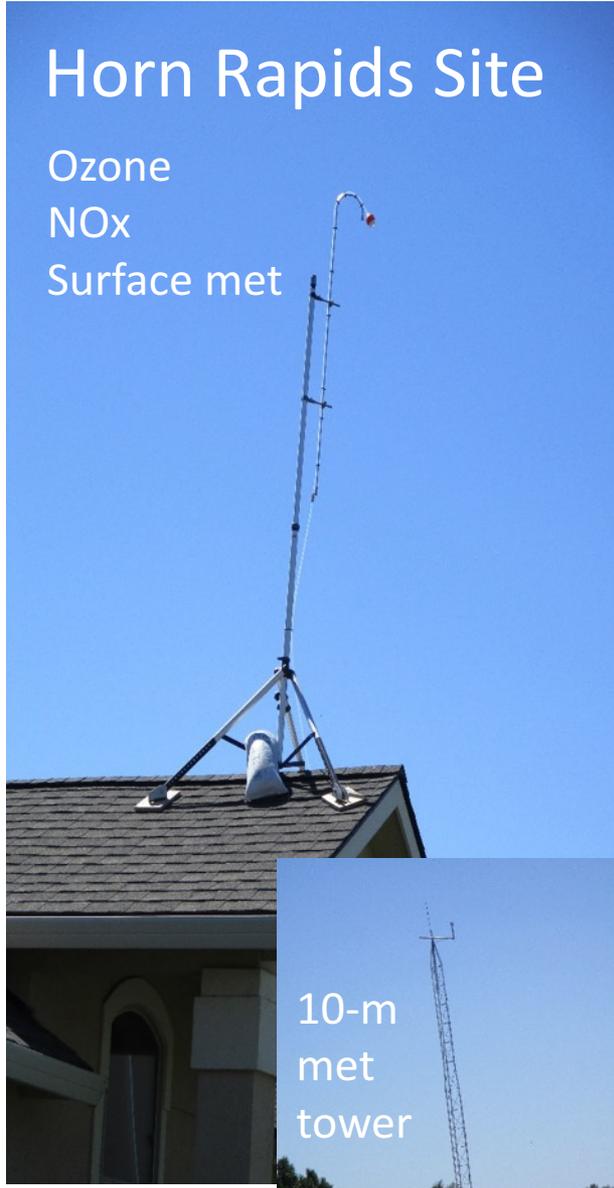
BCAA Site

MACL



Horn Rapids Site

Ozone
NOx
Surface met



10-m
met
tower

BCAA Site

Ozone
NOx
CO
Surface met
RJ Lee van (hydrocarbons)



BCAA Site

WSU Mobile Atmospheric Chemistry Lab (MACL) instruments

Description	Data Label	Instrument	Units
carbon dioxide	CO2	Licro 840A	ppmv
water vapor	H2O	Licor 840A	‰ ; mmol mol ⁻¹
carbon monoxide	CO	Teledyne T300U	ppbv
ozone	O3	Teledyne T400	ppbv
sulfur dioxide	SO2	Teledyne T100U	ppbv
nitric oxide	NO	Teledyne T200U	ppbv
nitrogen oxides	NOx	Teledyne T200U	ppbv
nitrogen dioxide	NO2	Teledyne T200U	ppbv
pressure	Prs	WXT510	mbar
temperature	Temp	WXT510	°C
RH	RH	WXT510	percent
wind speed	WindSpd	WXT510	m/s
wind direction	WindDir	WXT510	deg from true North
VOCs	Formaldehyde, etc	PTR-MS	ppbv
nitric oxide (NO)	AQD_NO	Air Quality Design	ppbv
nitrogen dioxide (NO2)	AQD_NO2	Air Quality Design	ppbv
nitrogen oxides (NOx)	AQD_NOX	Air Quality Design	ppbv
nitric oxides (NOy)	AQD_NOy	Air Quality Design	ppbv

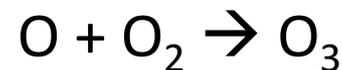
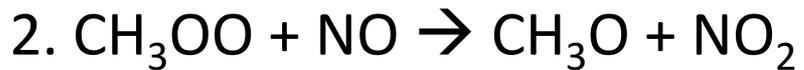
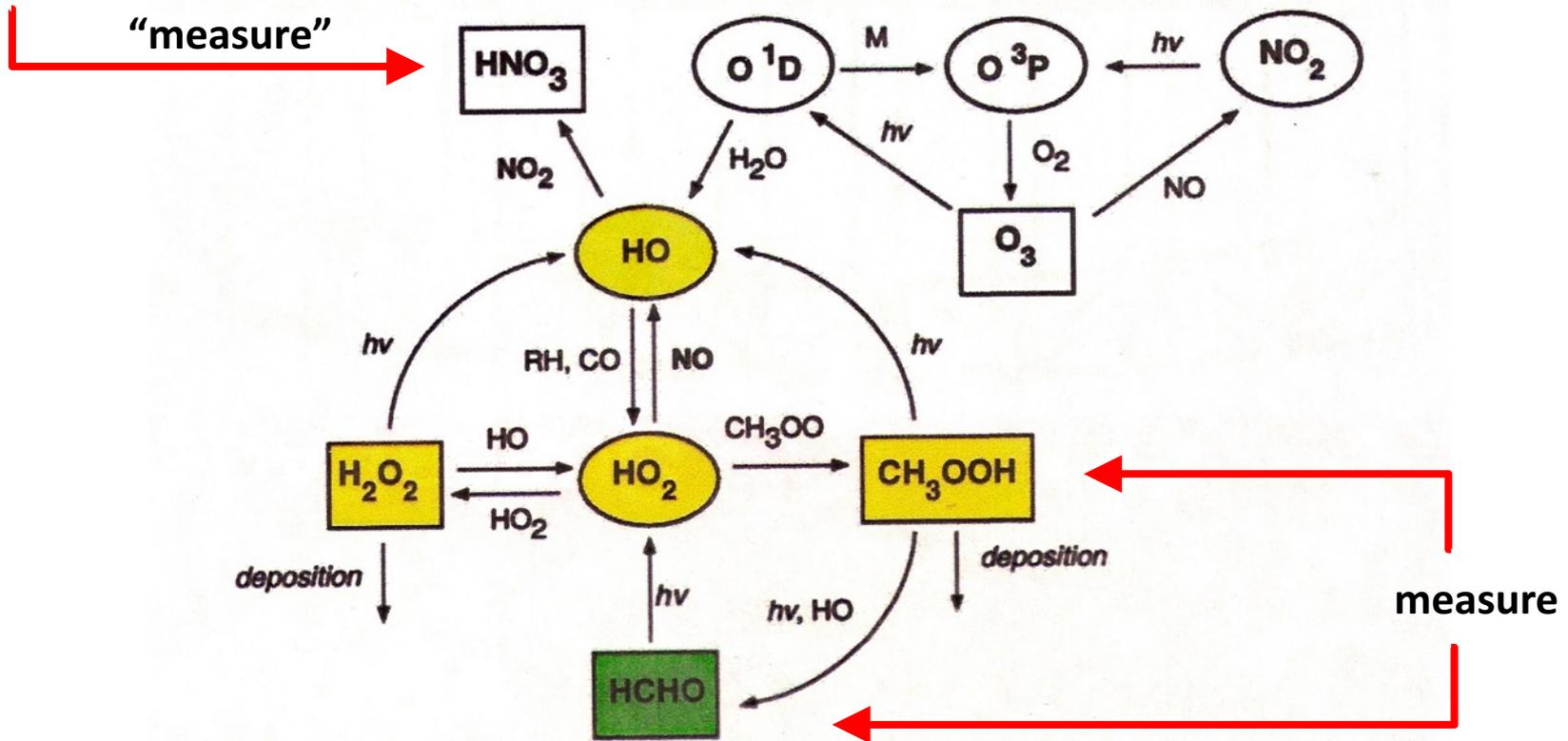
Data collected at 1-minute frequency

Proton Transfer Reaction – Mass Spectrometer (PTR-MS) Data

#	Description	label	Source tracer
1	formaldehyde	formaldehyde	
2	methanol	methanol	
3	hydrogen sulphide (H ₂ S)	H ₂ S	Pulp mill
4	acetonitrile	acetonitrile	smoke
5	acetaldehyde	acetaldehyde	
6	methyl hydroperoxide	MeOOH	Photoproduct
7	acetone + propanal	acetone	
8	isoprene	isoprene	trees
9	methyl vinyl ketone + methacrolein	MVK_MACR	Photoproduct
10	2-butanone + butanal	MEK	
11	benzene	benzene	
12	toluene	toluene	exhaust
13	C ₂ -alkylbenzenes	C ₂ -Benz	exhaust
14	C ₃ -alkylbenzenes	C ₃ -benz	exhaust
15	C ₄ -alkylbenzenes	C ₄ -Benz	exhaust
16	methylcyclohexane + other cycloalkanes	m97	Diesel exhaust?
17	alkanes > C ₁₂ (fragment ion)	m99	Diesel exhaust?
18	naphthalene	Naphthalene	exhaust
19	ethanol	EtOH	gasoline
20	monoterpenes (C ₁₀ H ₁₆)	monoterpenes	trees

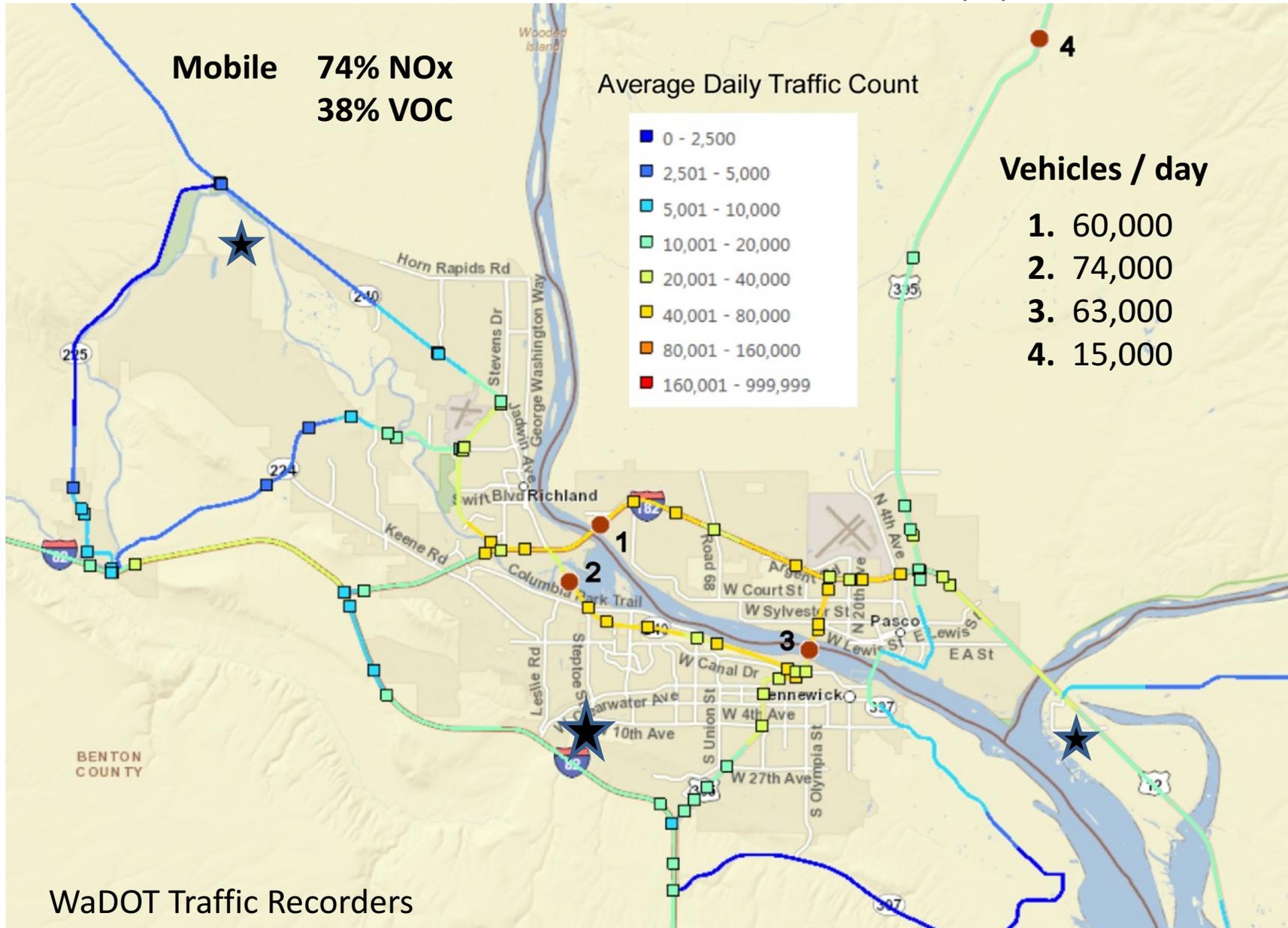
$\text{NO}_y\text{-NO}_x = \text{NO}_z$

$\text{NO}_z = \text{HNO}_3 + \text{PAN} + \text{RONO}_2 + \dots$



Automobile Traffic

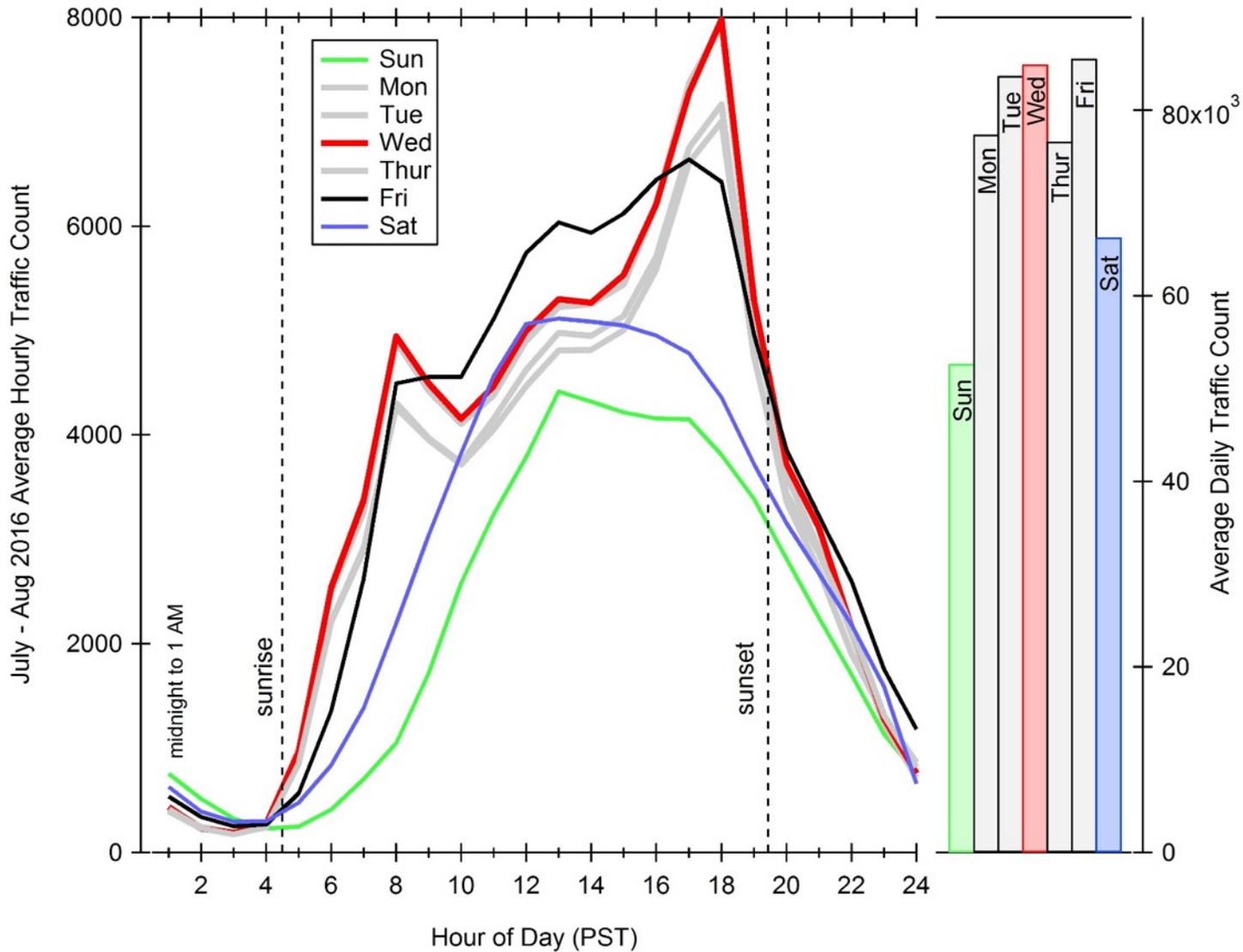
TriCities population = 232,740



WADOT Traffic Recorders

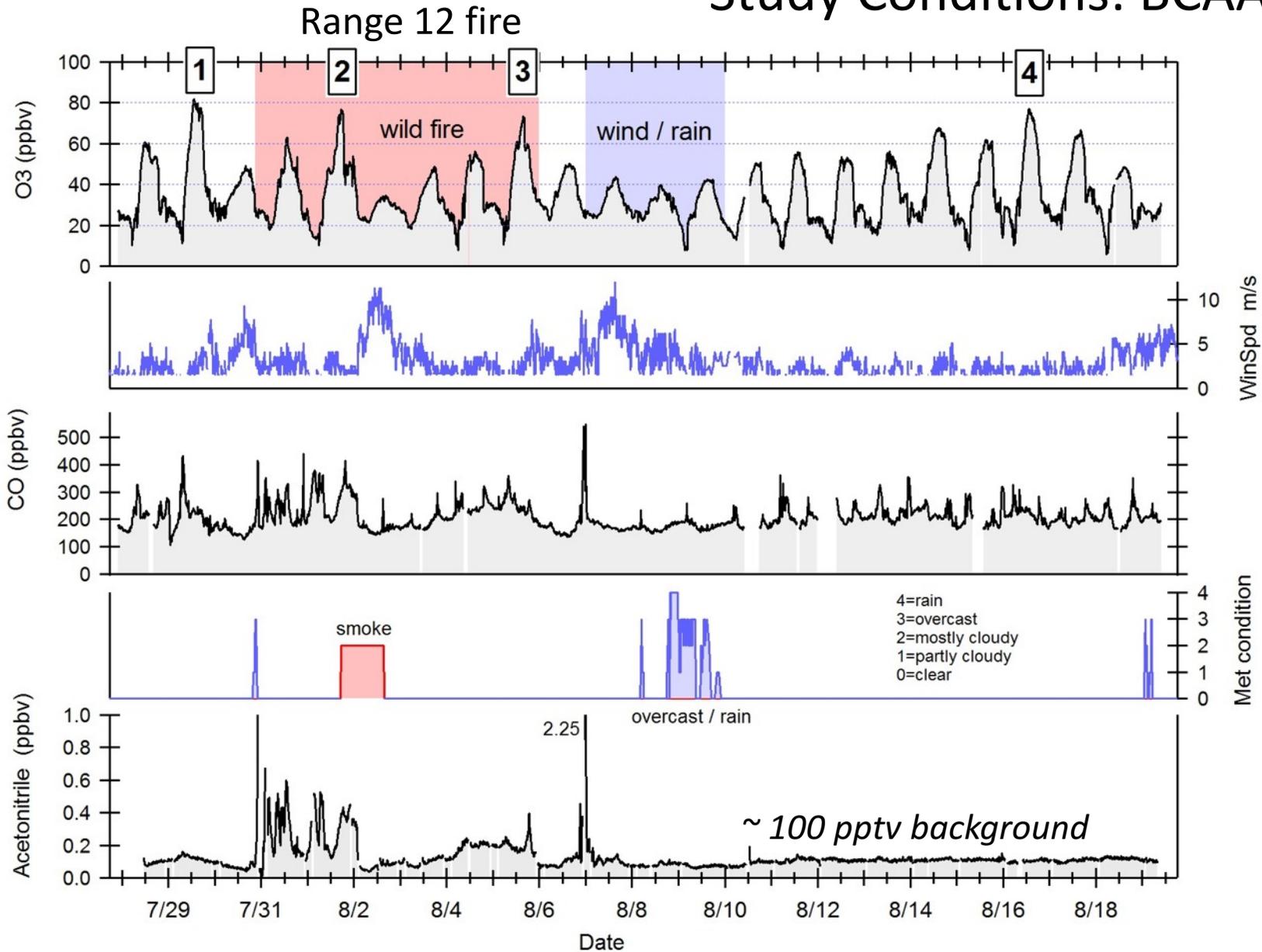
Sites are outside of high traffic loop (I-182 / 240 / 395)

July-Aug, 2016 at automated traffic recorder site R062W (SR-240)

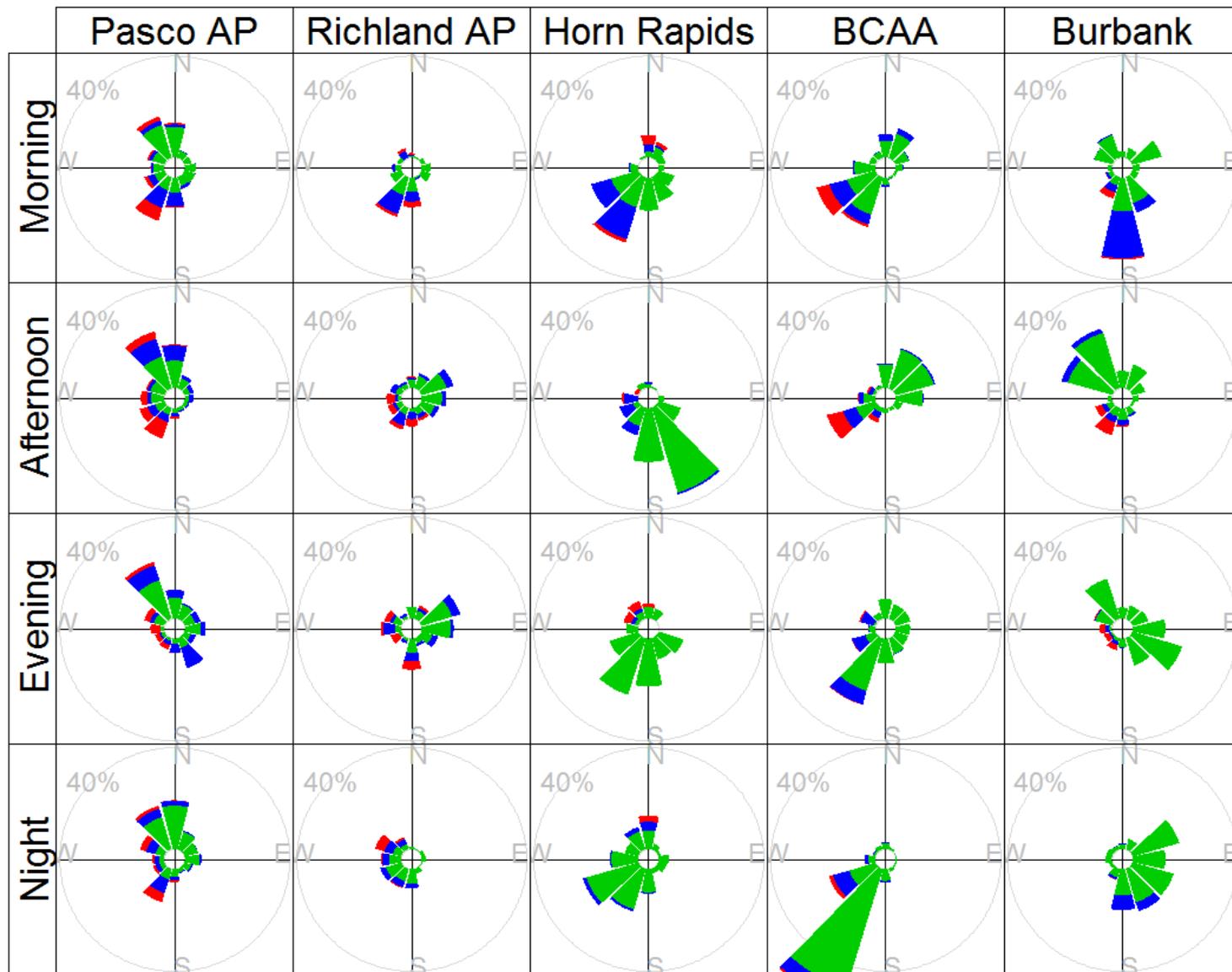


Weekday morning rush hour traffic volume ~ 4500 vehicles / hour

Study Conditions: BCAA data



Four BCAA O₃ events > 70 ppbv: (1) Columbia Cup Weekend, (2,3) wild fire period, (4) Aug 16



Light winds
variable Wdir

BCAA site
experiences
drainage
flow at night



0 to 3

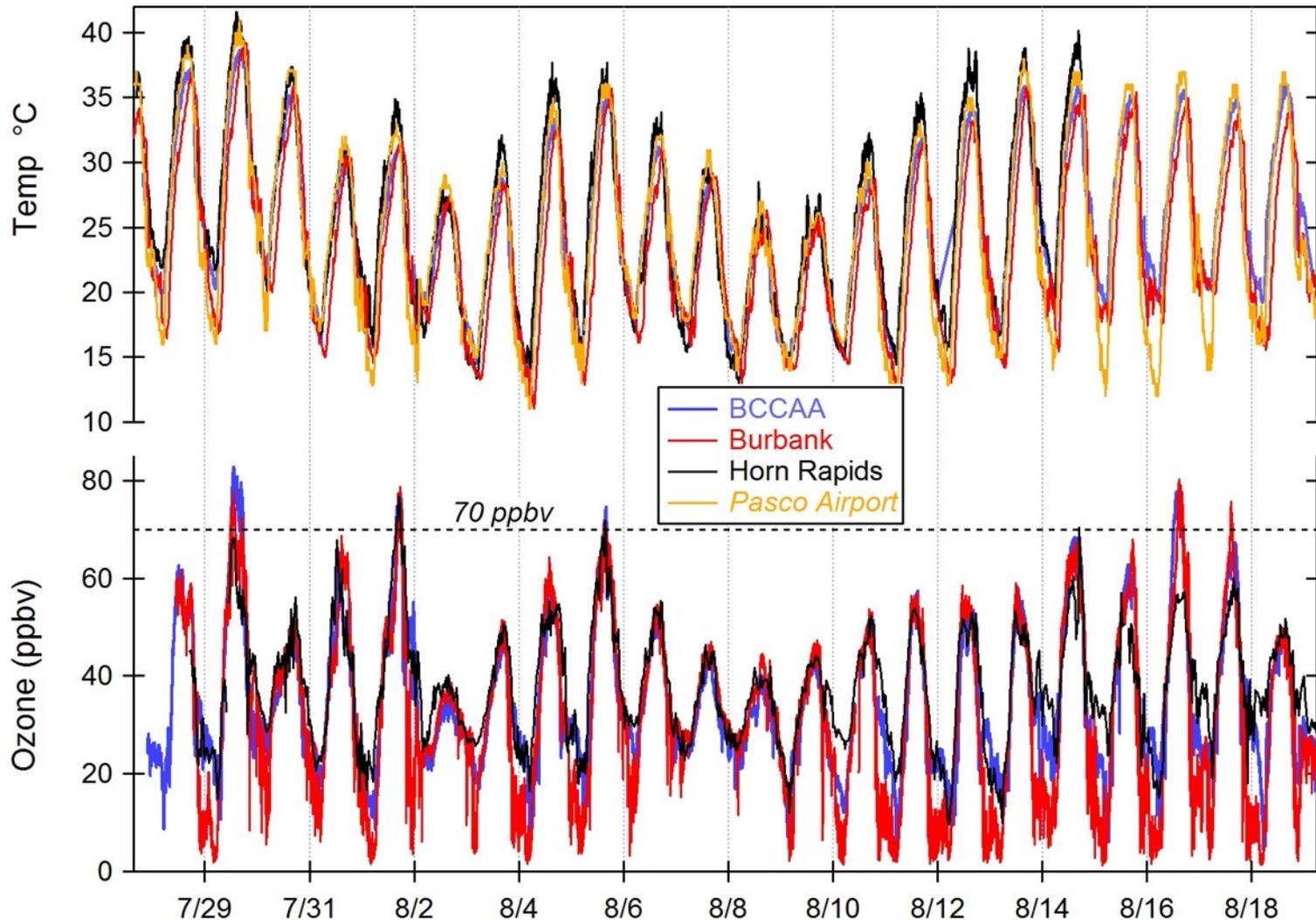
3 to 5

5 to 10

Wind speeds, m/s

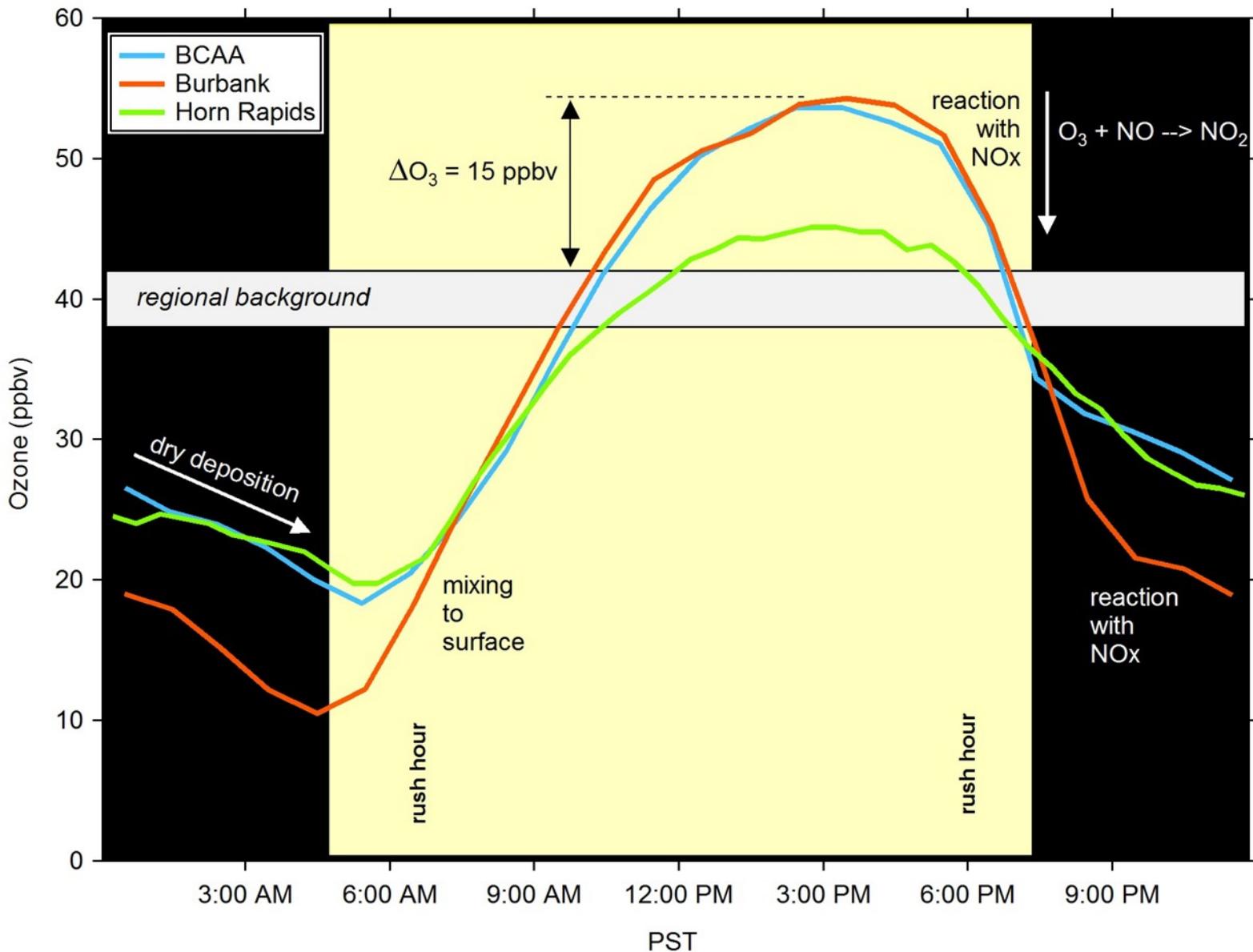
Ozone spatial gradients

1. Ozone similar between sites during wild fire period --> transported O_3 or precursors?
2. Horn Rapids typically < BCAA afternoon values
3. Burbank often > BCAA afternoon values



Burbank
"hot spot"

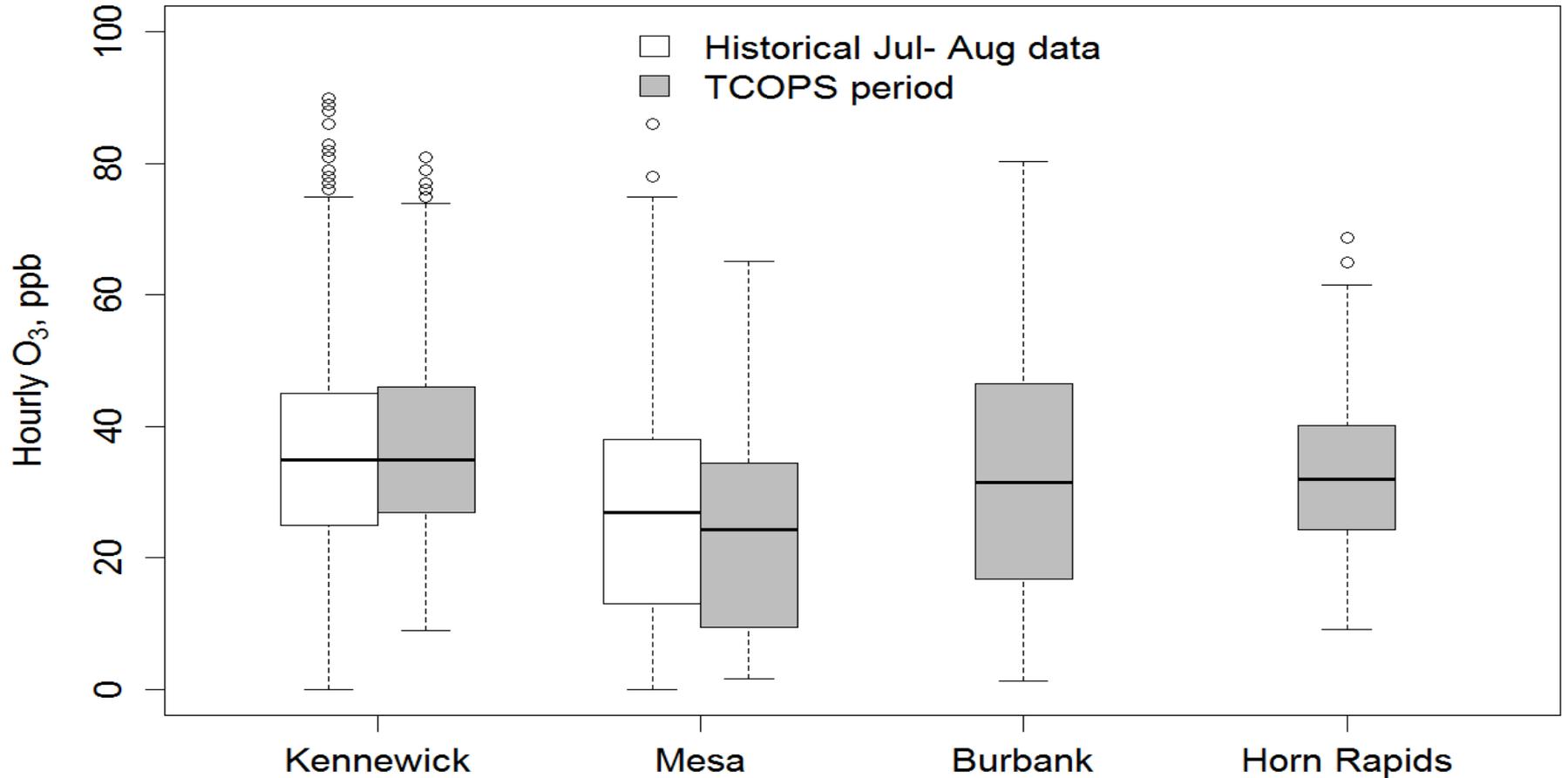
Comparison of O₃ diel variability (1/2 hr averages)



On a typical day airshed makes 15 ppbv O₃.

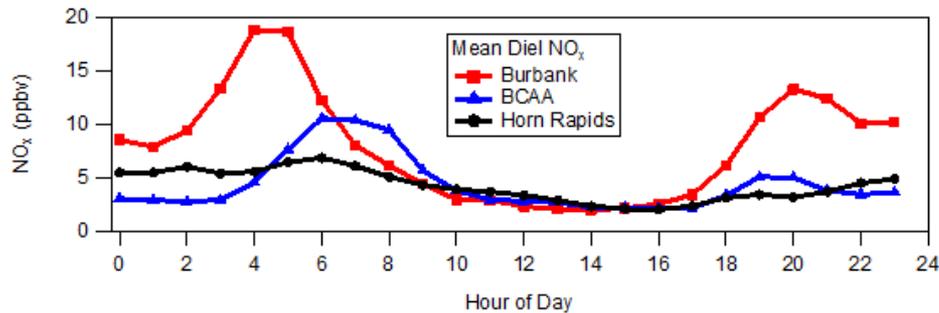
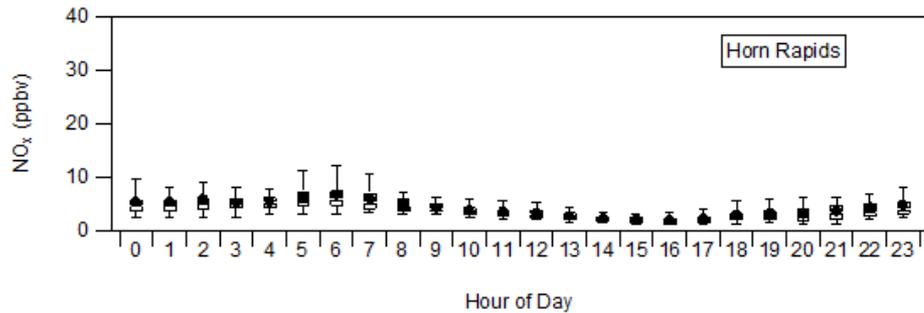
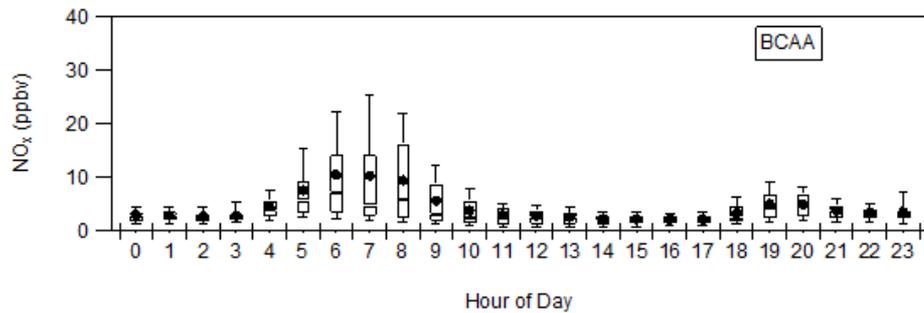
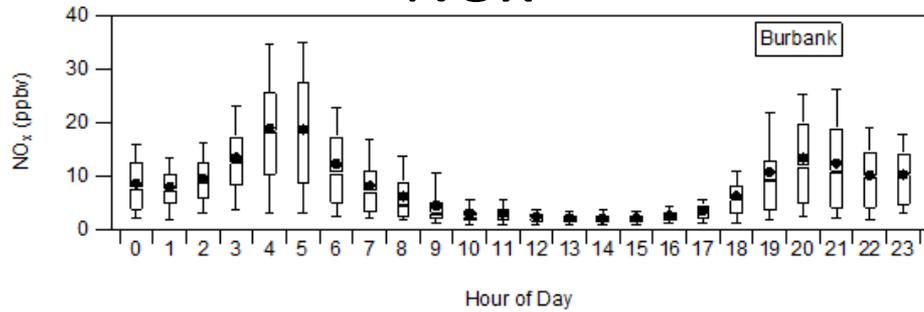
On "bad" days airshed makes up to 30 to 40 ppbv O₃.

Representativeness of ozone data during TCOPS period



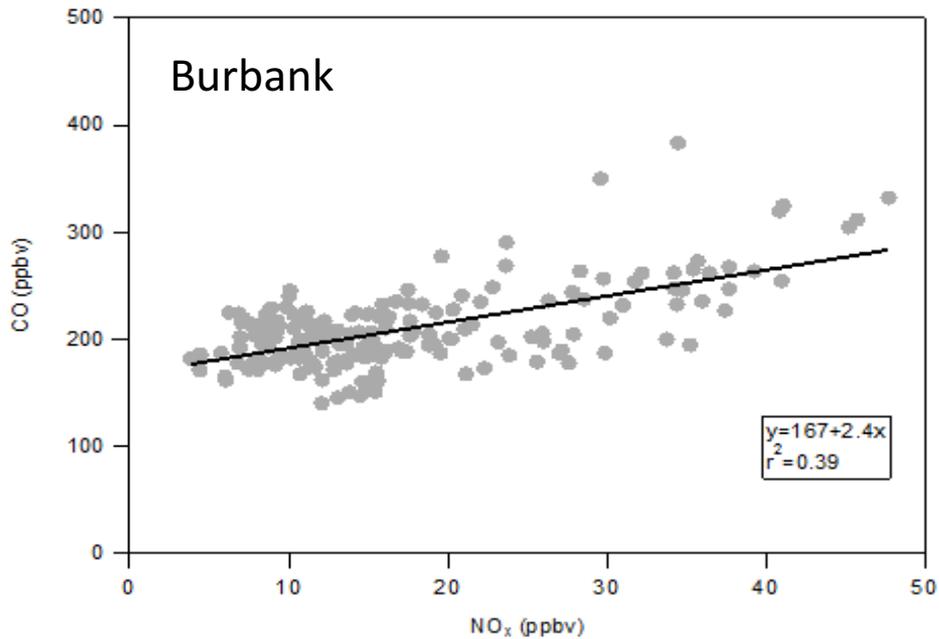
Nothing unusual about T-COPS levels of ozone compared to what had been measured at Kennewick in previous years (Metaline site and BCAA site)

NO_x



Burbank had much higher levels of NO_x at night...

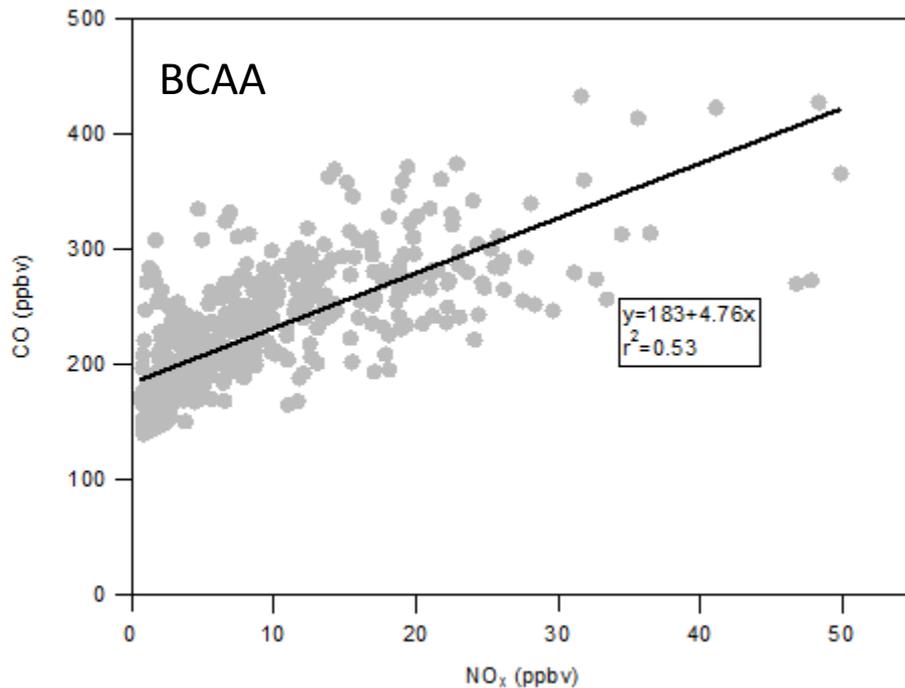
and displayed early morning max of ~ 20 ppbv at 4-5 AM compared to BCAA's ~ 10 ppbv at 6-7 AM.



Morning CO-to-NO_x molar ratios

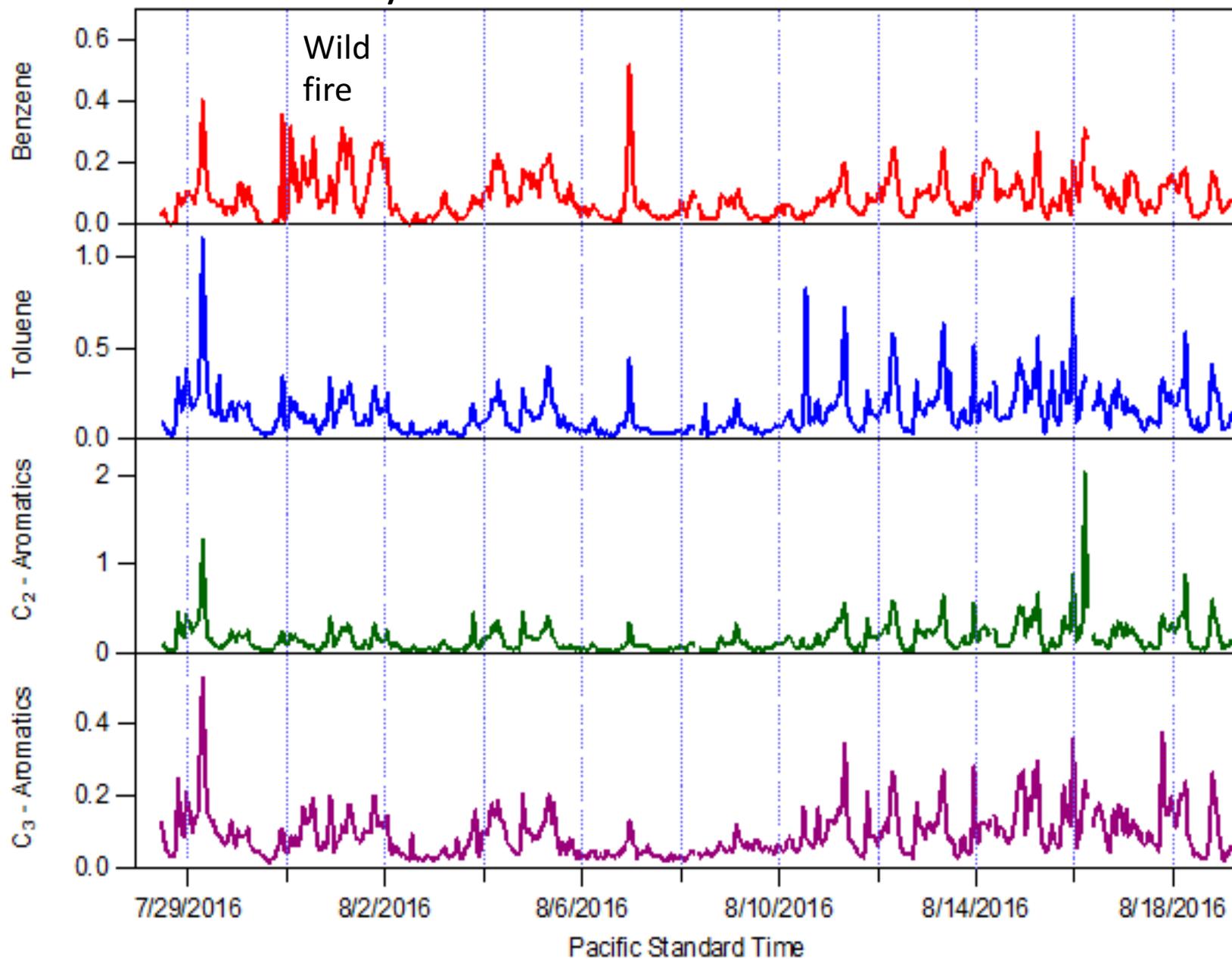
Ratio = 2.4
 low for spark ignition traffic
Diesel trucks?
Influence of point sources?

Burbank is different

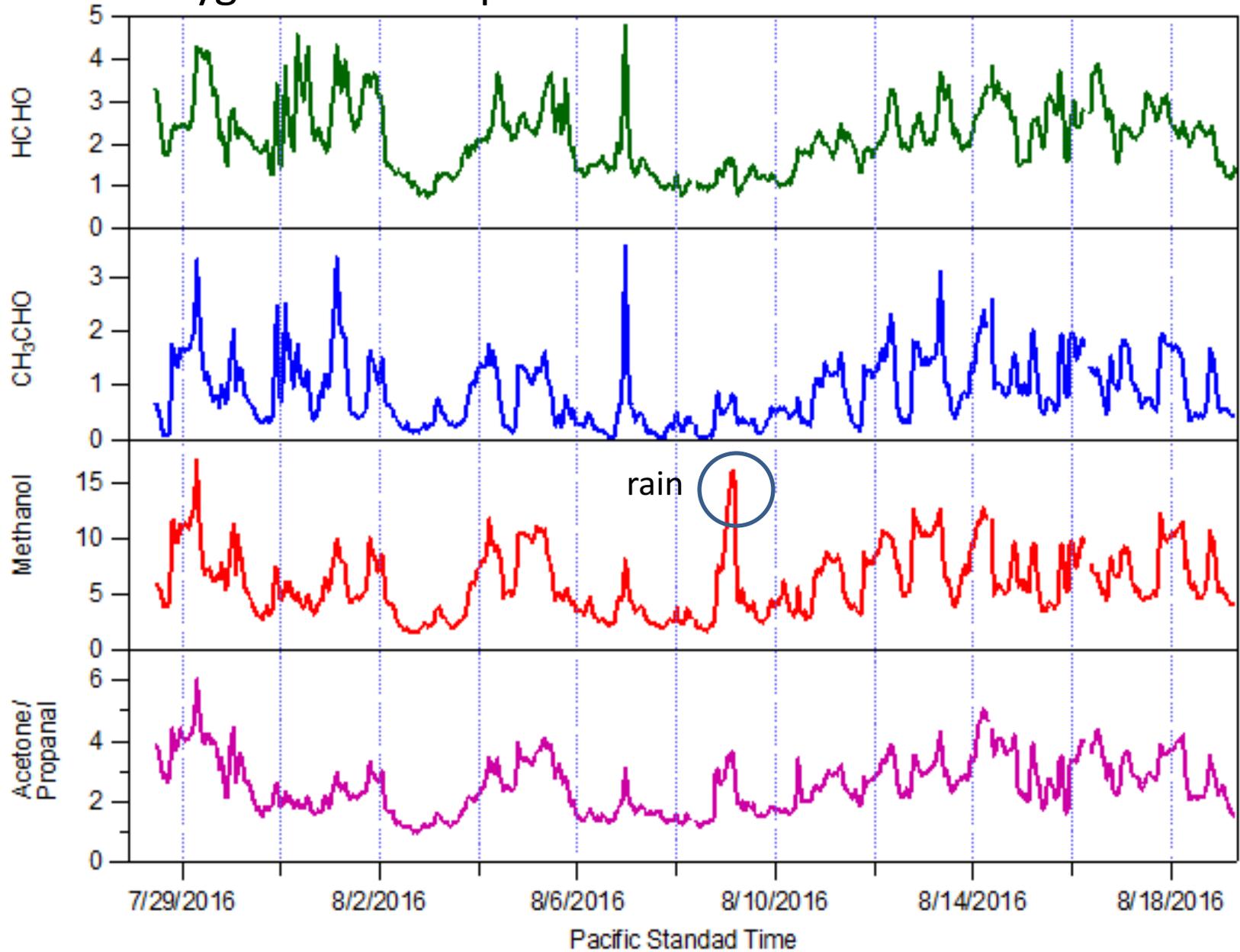


Ratio = 4.8
 reasonable for spark ignition traffic

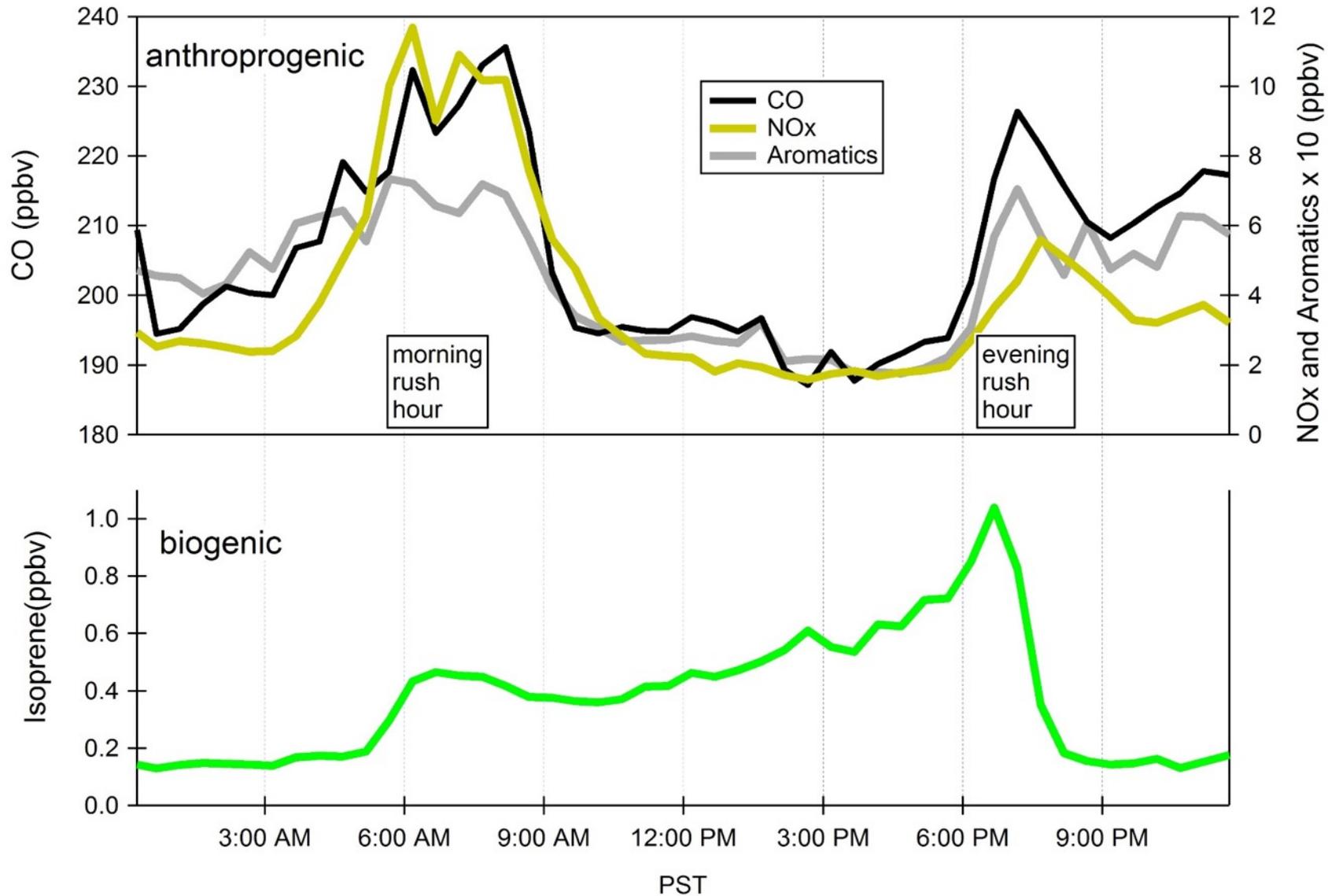
Aromatic Hydrocarbons



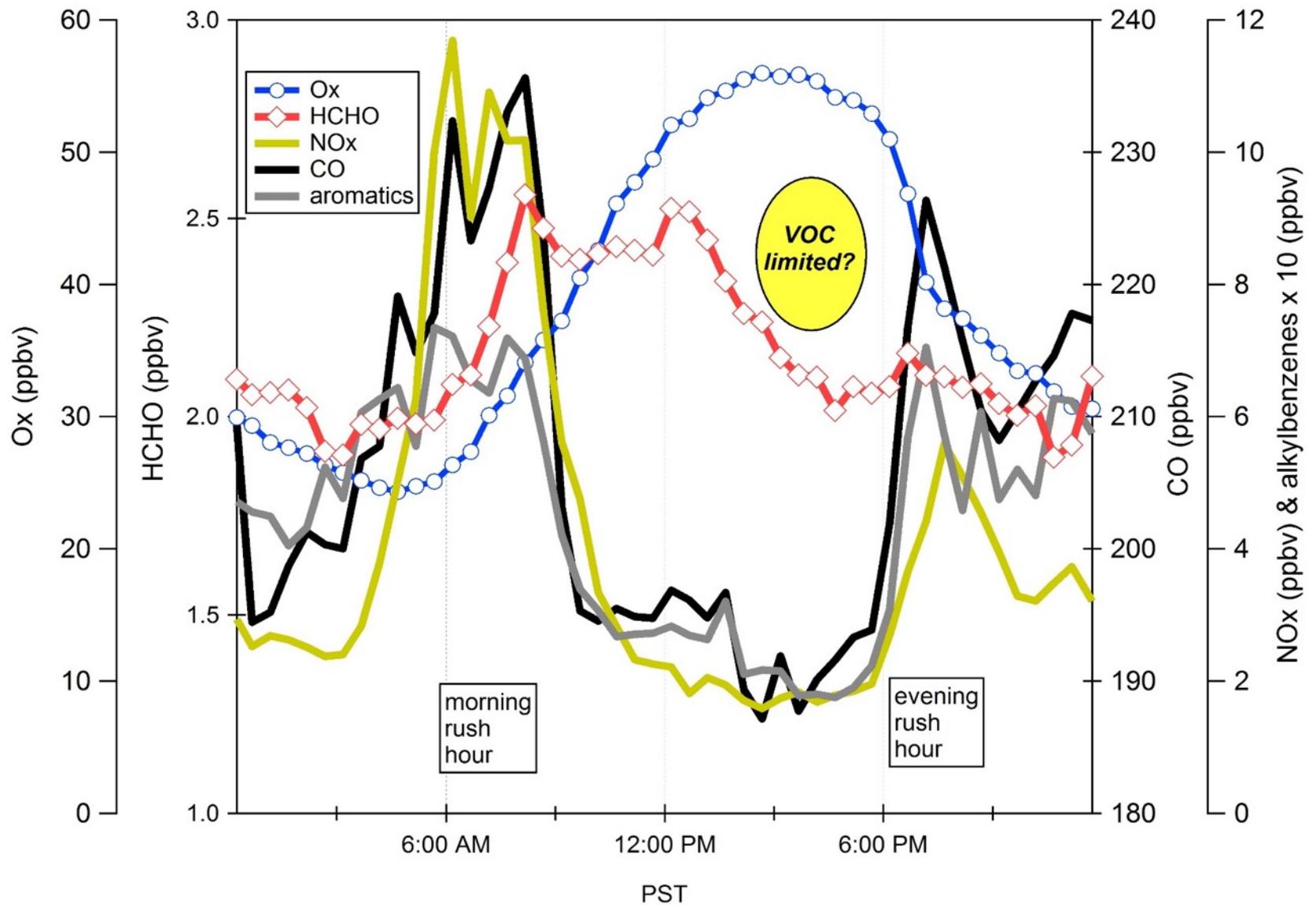
Oxygenated Compounds



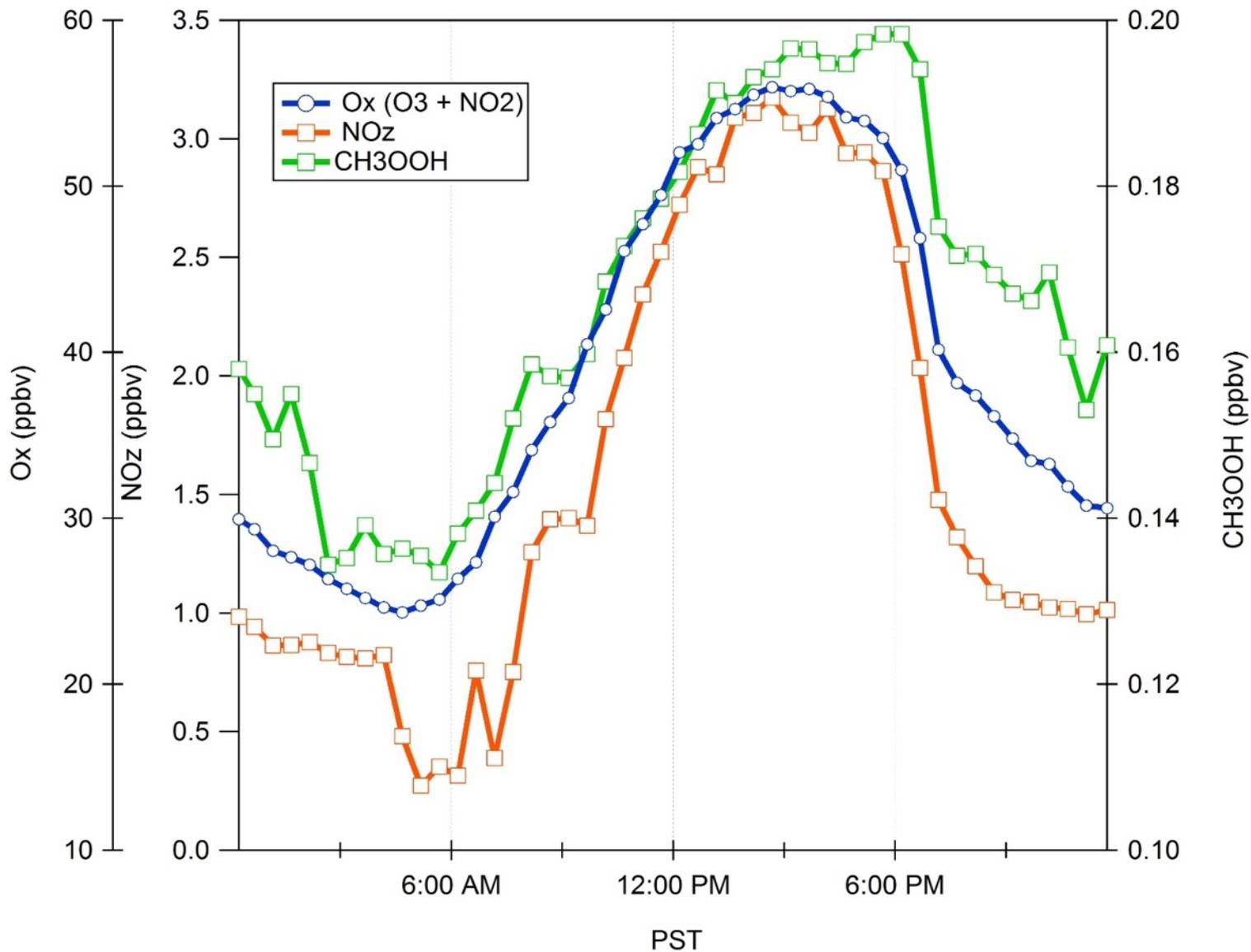
Diel Variation of Ozone Precursors



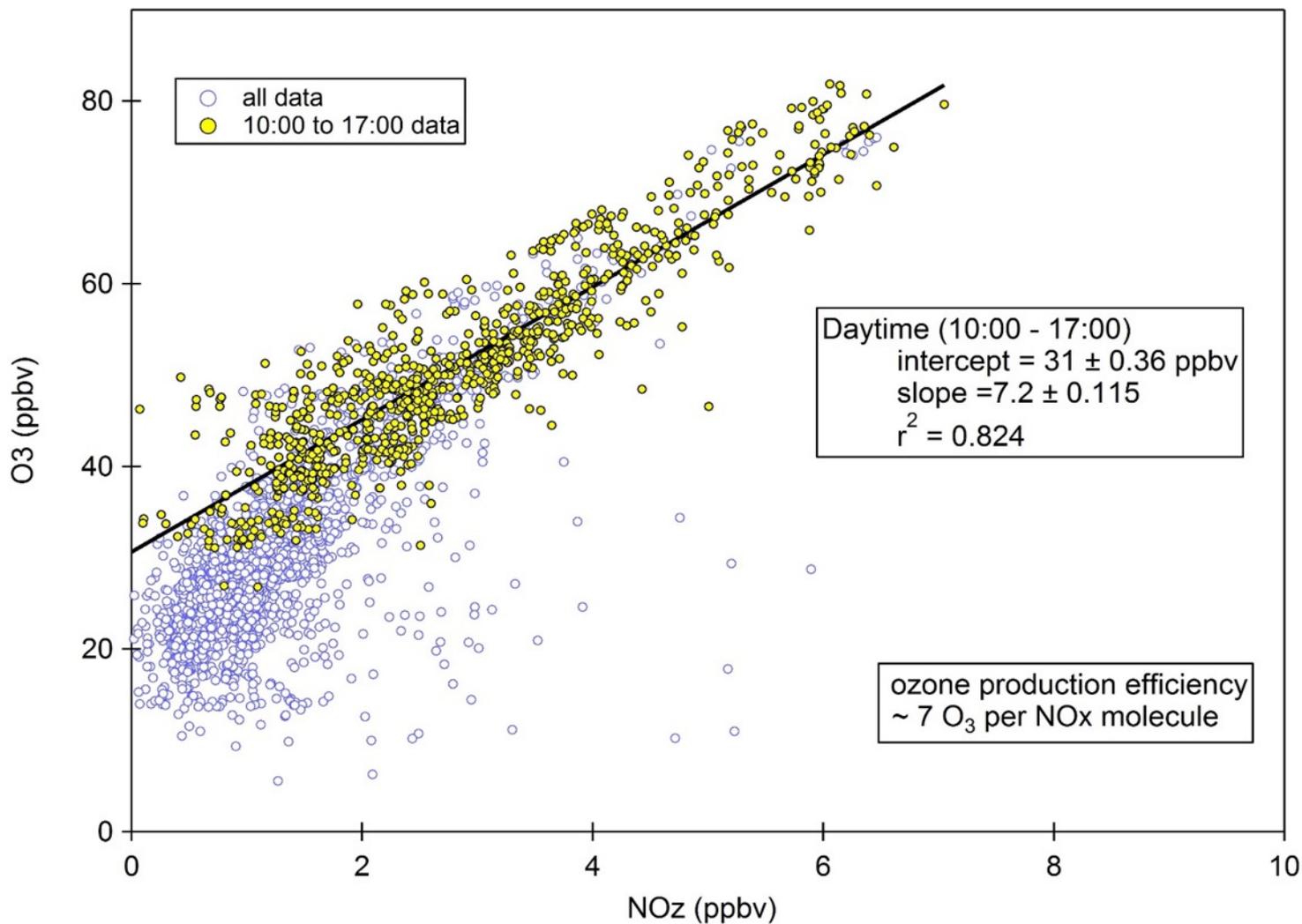
Diel Variation of Precursors and Photoproducts



Ox and Chain Termination Products



Ozone Production Efficiency (OPE)



Compare to

New York : 2-4

Phoenix : 3

Nashville : 3-6

Beijing : 5

Higher OPE

occurs at

lower NO_x

mixing ratios.

Ozone vs NO_z

Afternoon Period	O ₃ / NO _z		
	Intercept	Slope	r ²
Whole Campaign	31	7.2	0.82
Boat Race Day (7/29)	23	9.5	0.89
Wild Fire (7/31 - 8/1 & 8/4 - 8/6)	30	7.2	0.79
End of Camp. (8/10 - 8/18)	33	6.5	0.79

Summary & Conclusions

- Burbank “hot spot”
 - Highest NO_x mixing ratios
 - Often highest afternoon ozone
- O₃ precursor variation (aromatics, CO, NO_x) and abundance consistent with traffic emissions
- Ozone production efficiency from NO is 7.2 (range 6.5 – 9.5)
- CH₃OOH / NO_z ratio low
 - Airshed appears VOC limited