

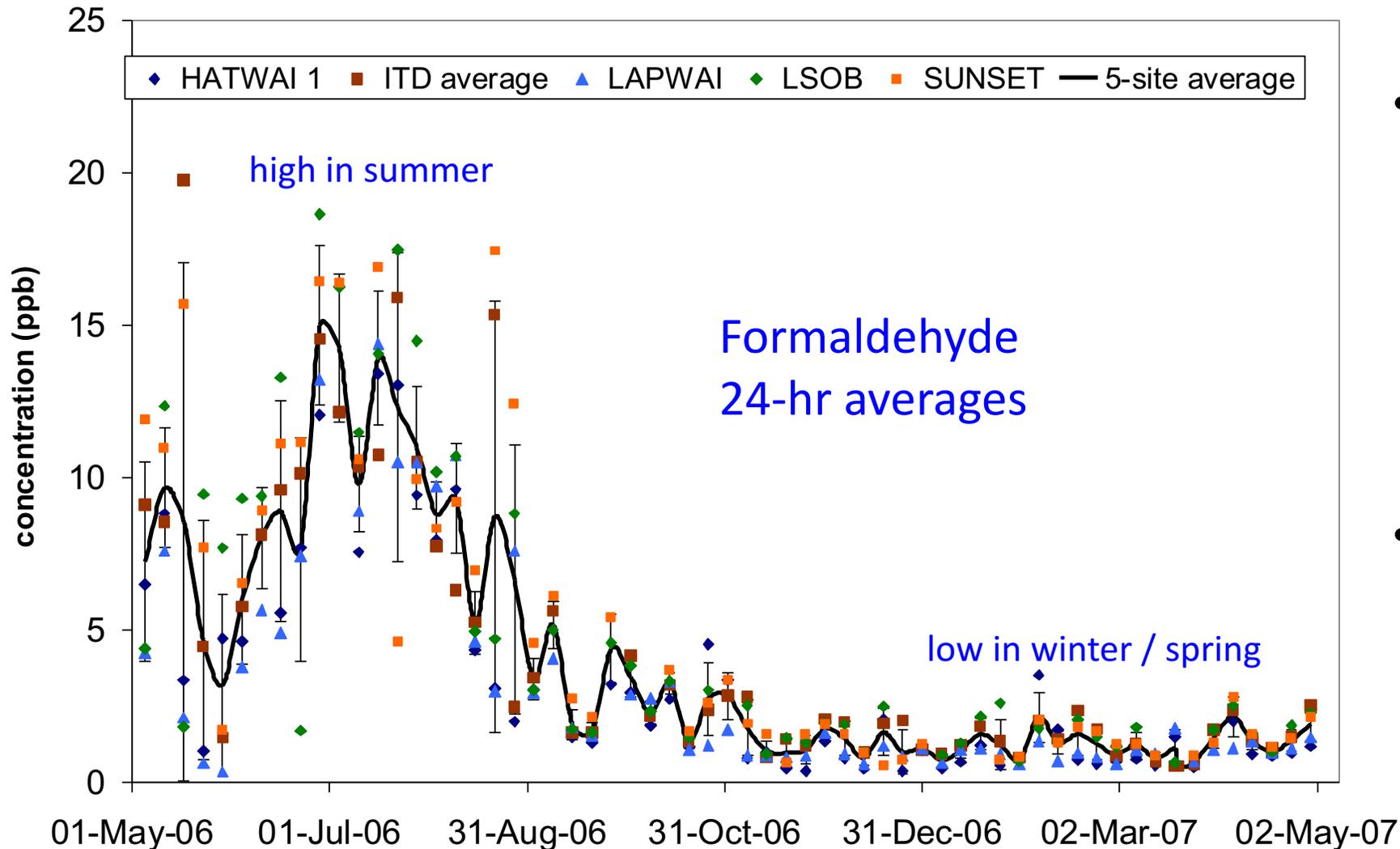
Lewiston-Clarkston Valley Formaldehyde Study Summer 2016 Summary

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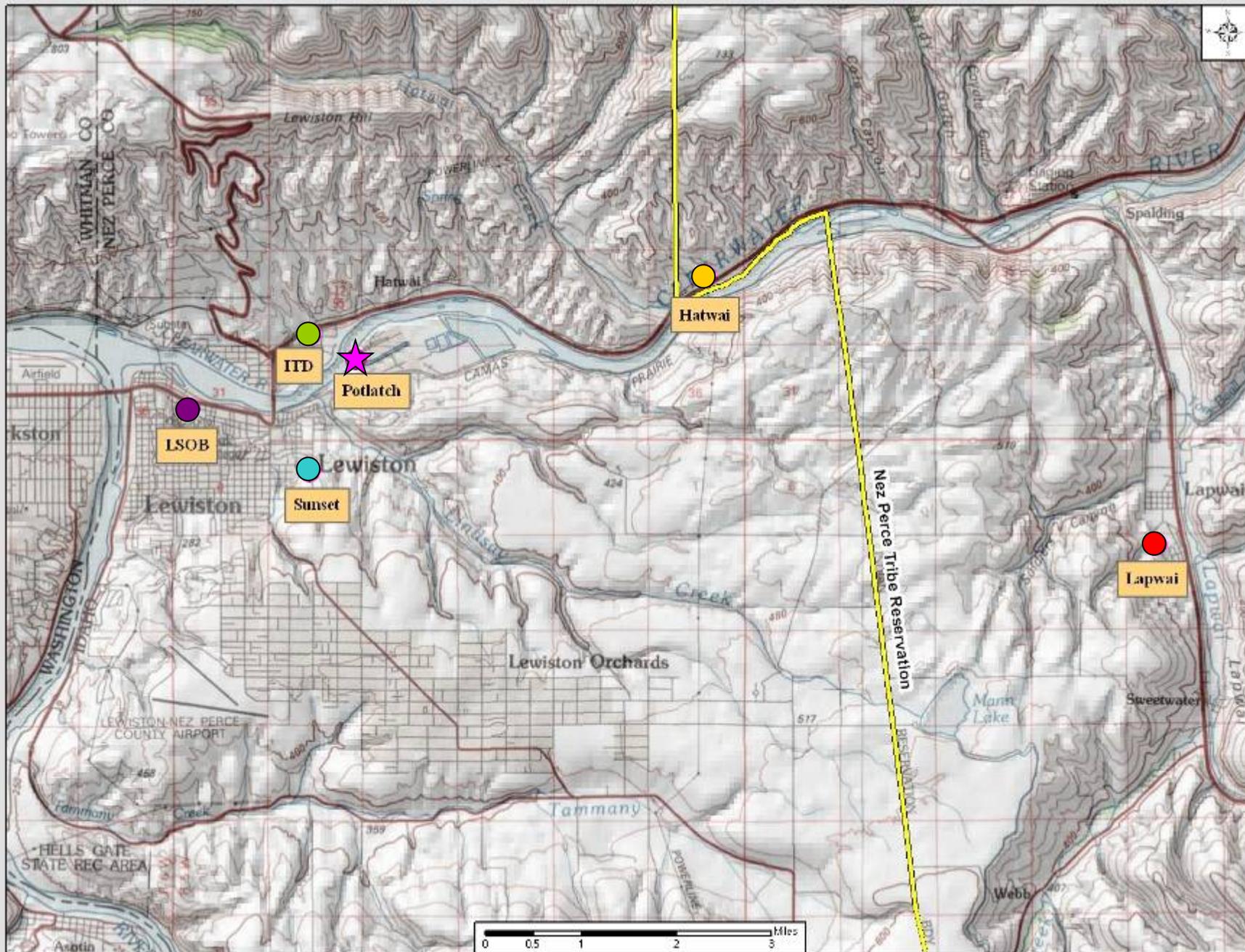
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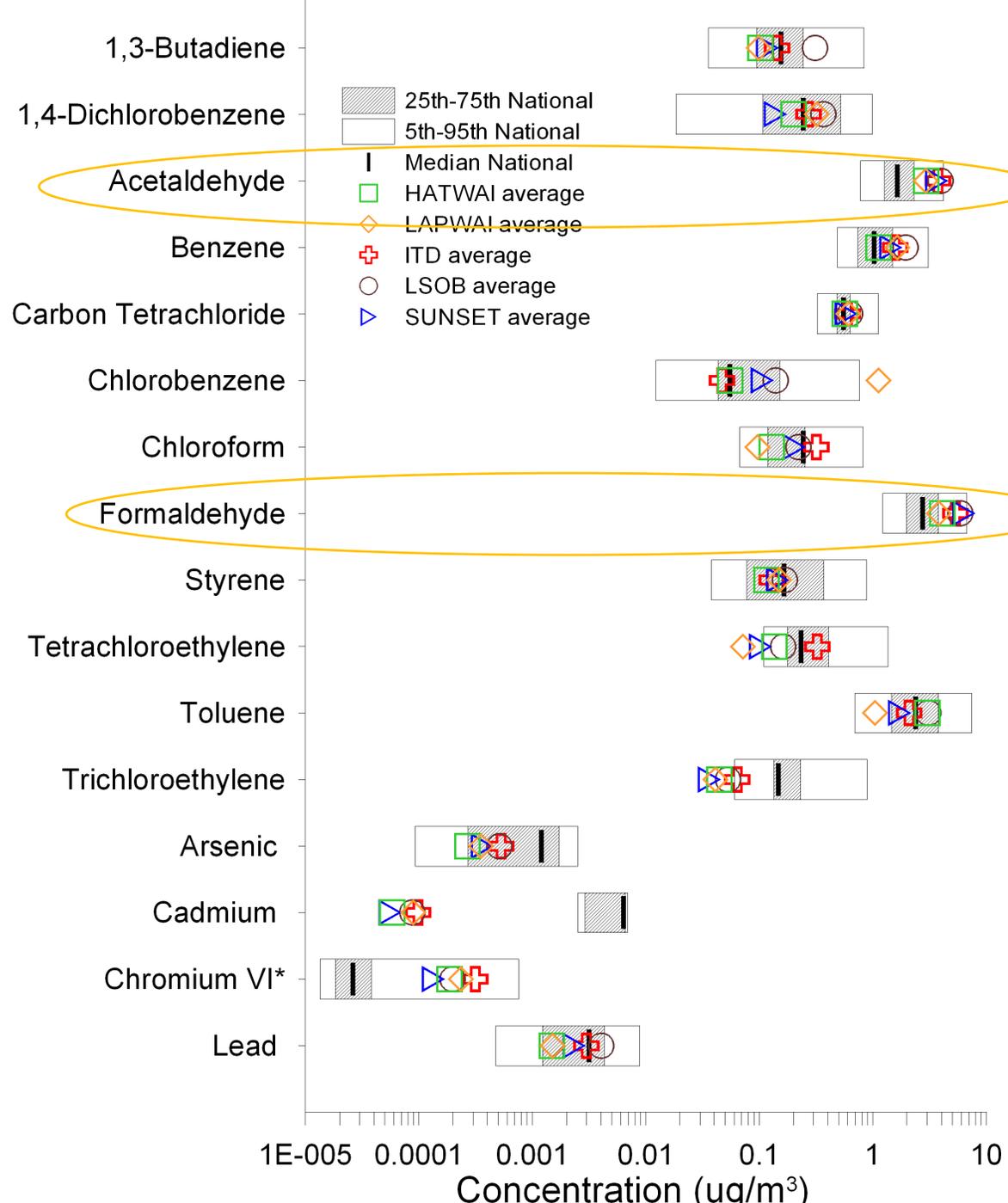
Study funded by an *EPA Community Scale Air Toxics Monitoring* grant to the Nez Perce Tribe. Motivated by results from 2006-2007 study.



- 2006-2007 community air toxics study measured high concentrations of formaldehyde at several L-C valley locations in summer.
- 10-20 ppbv range for 24-hr average in summer months



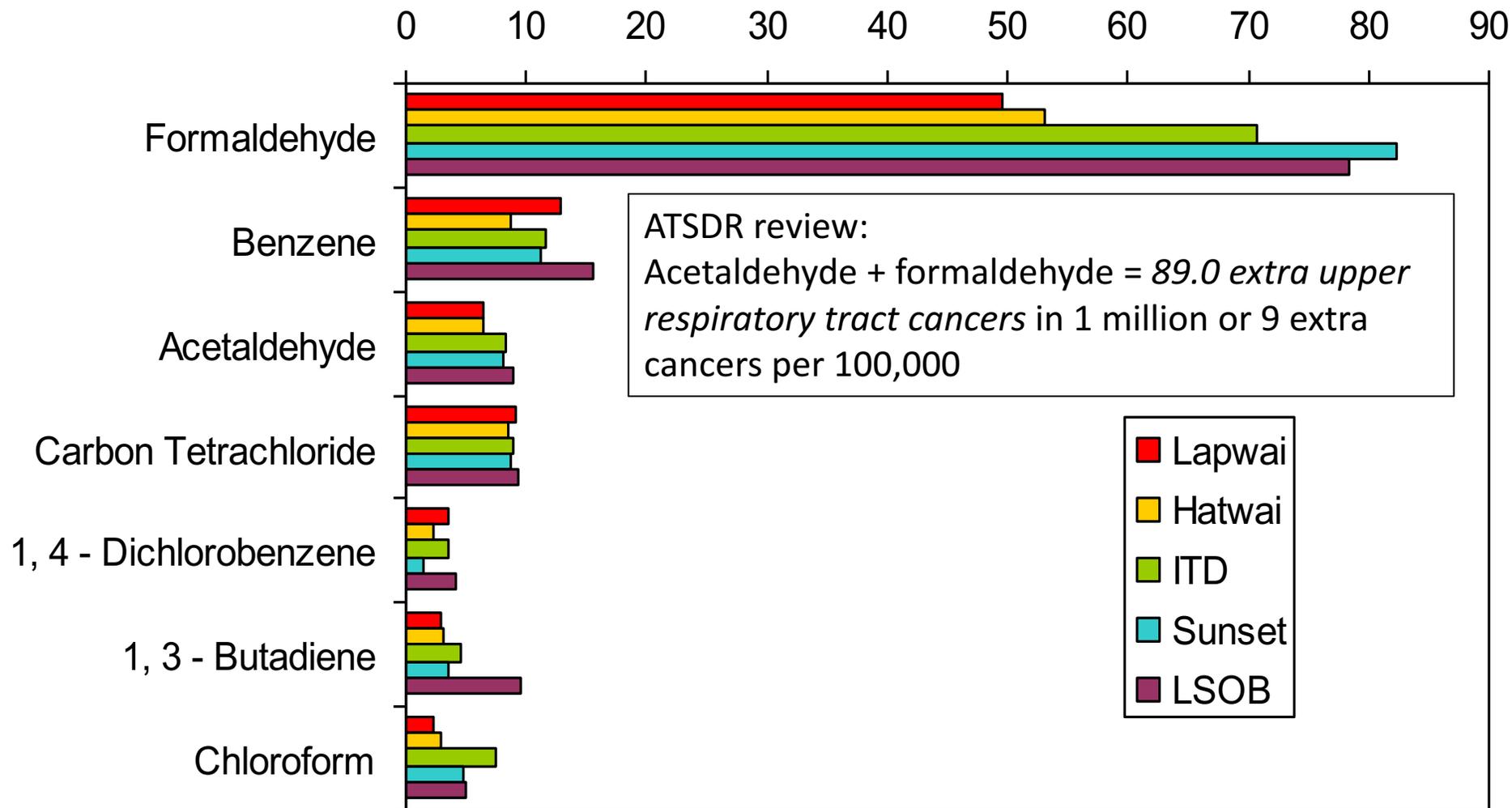
2006-2007
Study domain
and sampling
locations



All have high formaldehyde, acetaldehyde, benzene, and estimated chromium VI.

Relative Risk Rank 2006-2007 data

EPA Regional Screening Table/Calculator <http://epa-prgs.ornl.gov/chemicals/index.shtml>



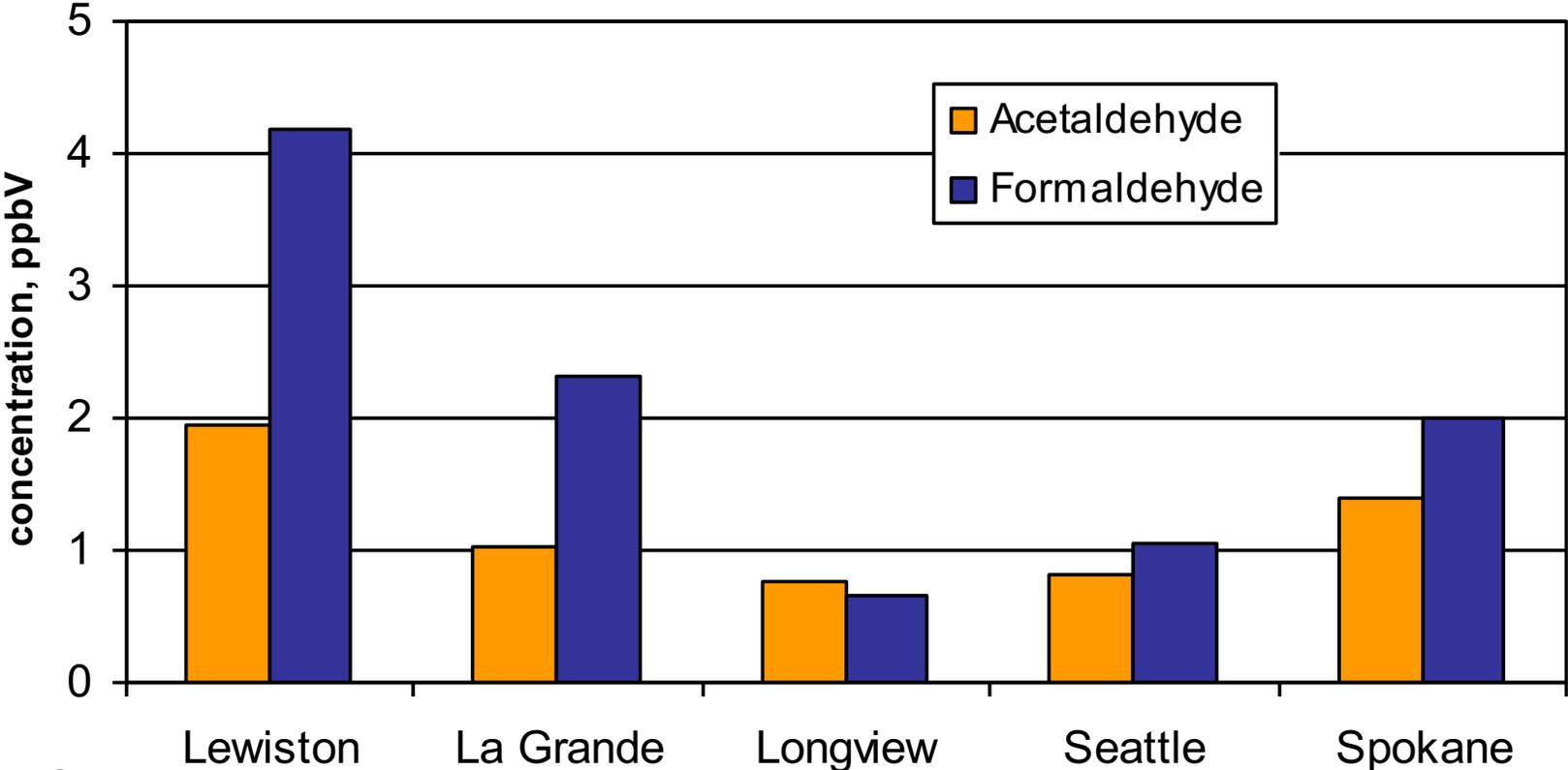
Purpose of the current study is to identify sources of formaldehyde in the L-C Valley.

1. primary sources

- i. direct emissions from vehicles*
- ii. direct emission form industry*

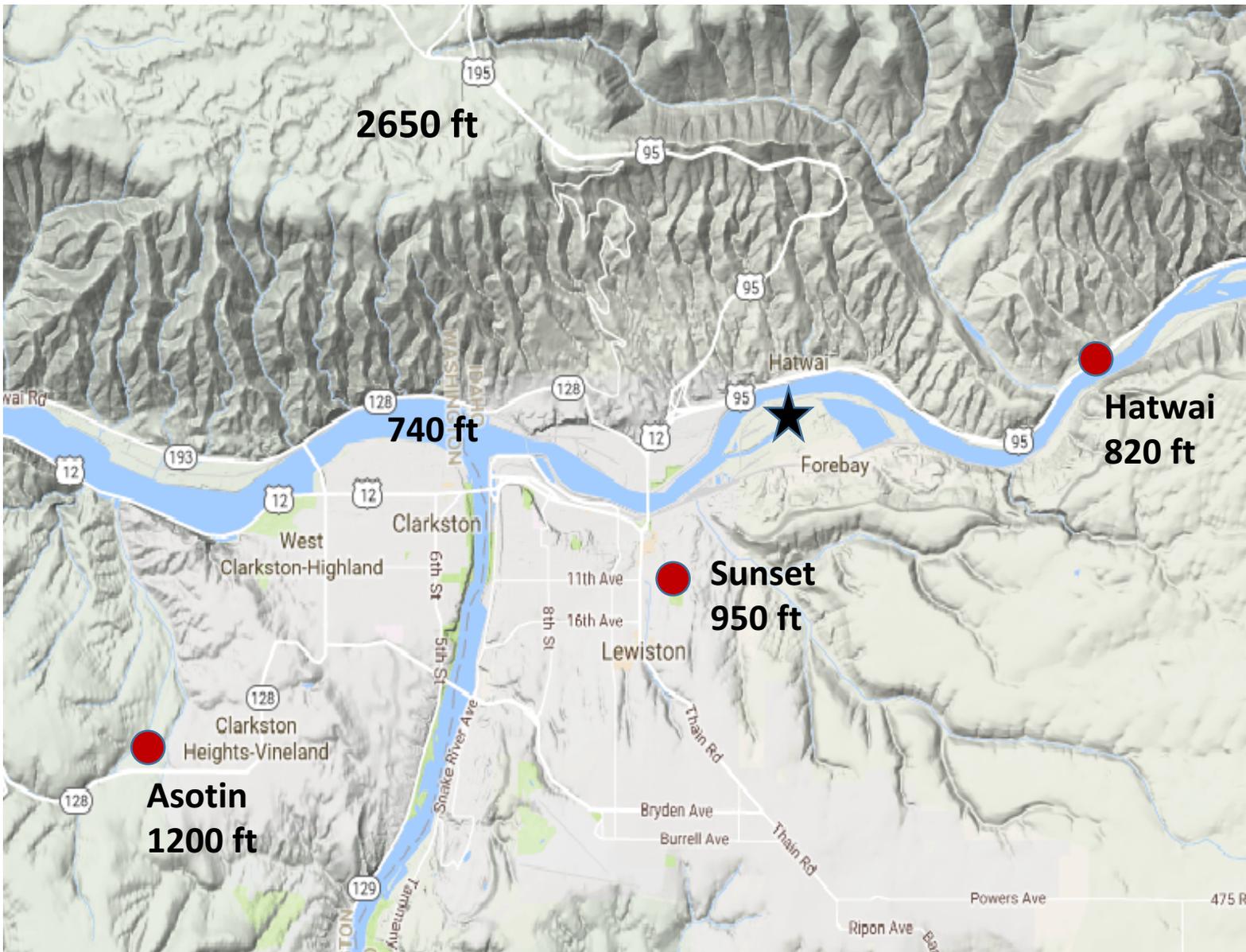
2. secondary sources

photochemical production from organic precursors (i.e. methanol?)



Average formaldehyde concentration in L-C valley higher than other locations.

What is different about the L-C Valley?



Three sites for 2016-2017 study:

1. Asotin Landfill site
 Surface met station
 12-hr VOC sampling (each day / night)
 12-hr carbonyl sampling (each day / night)

2. Sunset Park (June 27 – July 26)
 Surface met station
 MACL instruments
 12-hr VOC sampling (each day / night)
 12-hr carbonyl sampling (each day / night)

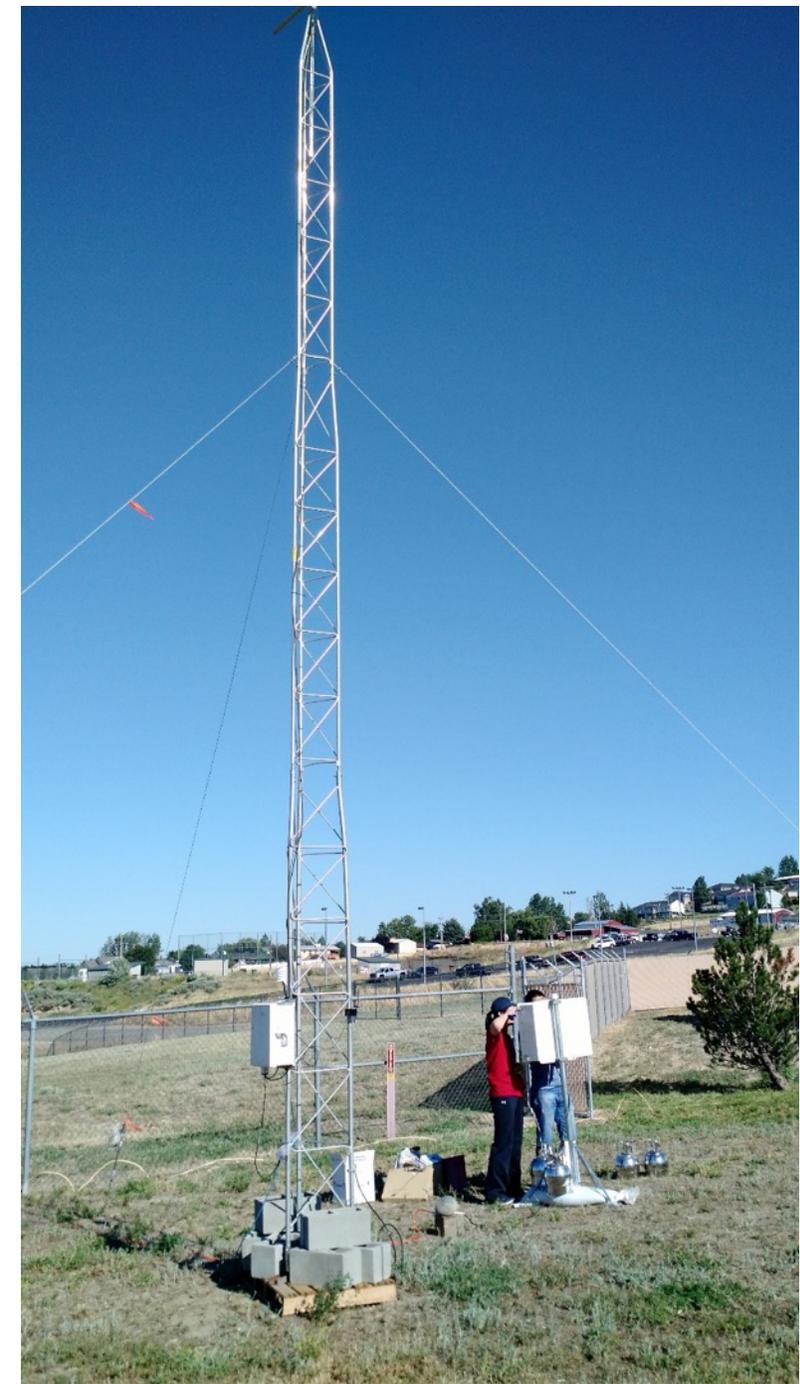
3. Hatwai
 Surface met station
 12-hr VOC sampling (each day / night)
 12-hr carbonyl sampling (each day / night)

★ Pulp mill

Asotin Site



ATEC 2200
Sampler
Day 7 AM – 7 PM
Night 7 PM – 7 AM



Hatwai Site



Alkanes	Aromatics	Industrial tracers	Biogenics
Hexane	Benzene	Dichloromethane	Isoprene
2-methylpentane	Toluene	1,1,1-trichloroethane	α -pinene
3-methylpentane	Ethylbenzene	Chloroform	β -pinene
Heptane	m,p-xylene	Trichloroethylene	Limonene
2-methylhexane	o-xylene	Tetrachloroethylene	Myrcene
Octane	Isopropylbenzene	Chloromethane	α -phellandrene
2,2,4-trimethylpentane	Styrene	Carbon Tetrachloride	3-carene
2,3,4-trimethylpentane	2-ethyltoluene	1,2-dichloroethane	Camphene
Nonane	3-ethyltoluene	<i>Carbon disulfide</i>	
Decane	4-ethyltoluene	<i>Dimethyl disulfide</i>	
Methyl-cyclopentane	1,2,3-trimethylbenzene		
	1,2,4-trimethylbenzene		
	1,3,5-trimethylbenzene		
	n-butylbenzene		
	i-butylbenzene		

WSU target compounds for GC-MS analysis of canisters

Canister Data : 12-hr integrated sample

Canister Collection Summary

Site	Total	Day	Night	Duplicates	Blank
SUNSET	52	25 (3D)	27 (3D)	6	11
HATWAI	53	26	27	0	0
ASOTIN	45	24	21	0	0

Total 150

Samples were collected from night of June 28, 2016 to night of July 25, 2016

DAY sample = 7 AM to 7 PM

NIGHT sample = 7 PM to 7 AM next morning

Canister Analysis

Entech 7200 preconcentrator

Agilent GC-MS/FID

separation on HP-624 column, MS detection

light hydrocarbons on Al₂O₃/KCl column, FID detection

Sunset Park site



Sunset Site Instrumentation

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)	H2S	Pulp mill
4	acetonitrile	acetonitrile	Wild fire smoke
5	acetaldehyde	acetaldehyde	
6	methyl hydroperoxide	MeOOH	Photoproduct
7	acetone + propanal	acetone	
8	isoprene	isoprene	Biogenic
9	methyl vinyl ketone + methacrolein	MVK_MACR	Photoproduct
10	2-butanone + butanal	MEK	
11	benzene	benzene	
12	toluene	toluene	
13	dimethyldisulfide (CH ₃ SSCH ₃)	DMDS	Pulp mill
14	methylcyclohexane + other cycloalkanes	m97	Diesel exhaust?
15	alkanes > C12 (fragment ion)	m99	Diesel exhaust?
16	sum of xylenes isomers + ethylbenzene	C2Benz	exhaust
17	sum of trimethylbenzene, ethyltoluene, etc	C3benz	exhaust
18	naphthalene	Naphthalene	
19	sum of tetramethylbenzene, diethylbenzene, propyltoluene, and butylbenzene isomers	C4Benz	exhaust
20	monoterpenes (C ₁₀ H ₁₆)	monoterpenes	Biogenic +



Master list submitted for analysis has 20 compounds. **Time interval between data points ~ 50 seconds.**

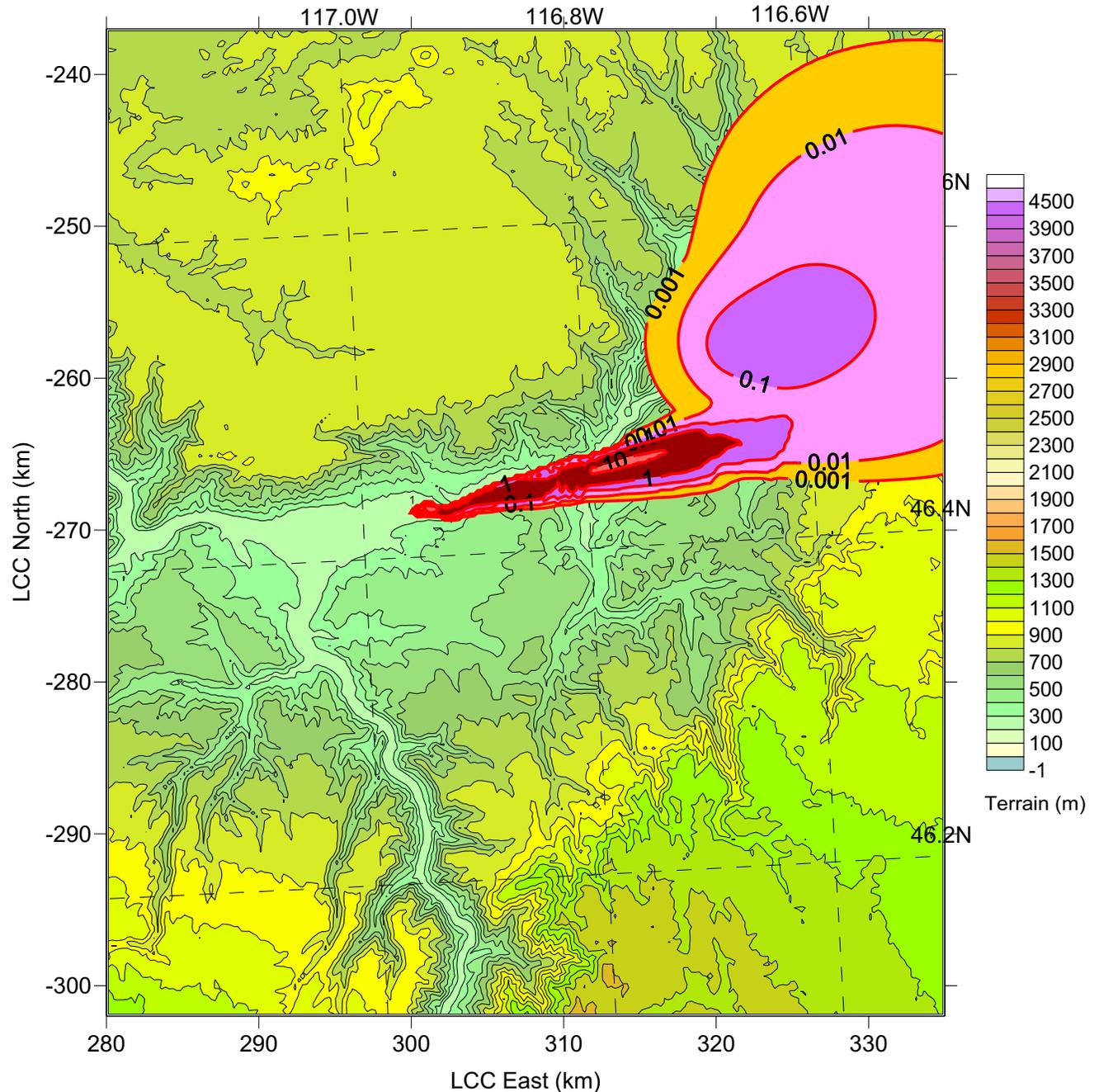
Some compounds are not routine measurements for this technique:

MeOOH
m97
m99
H₂S
DMDS

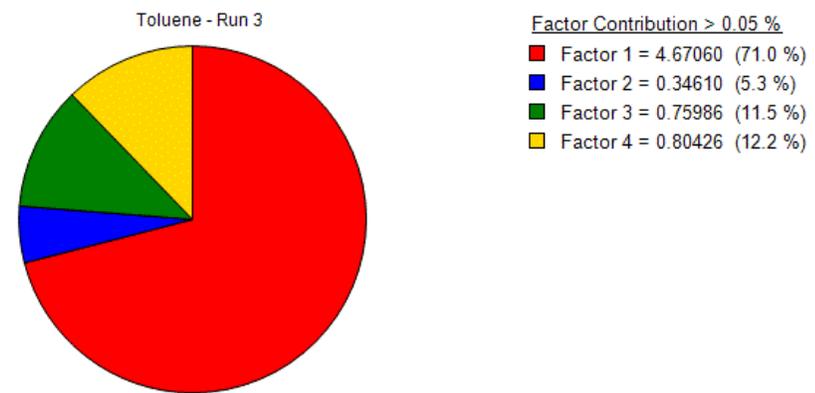
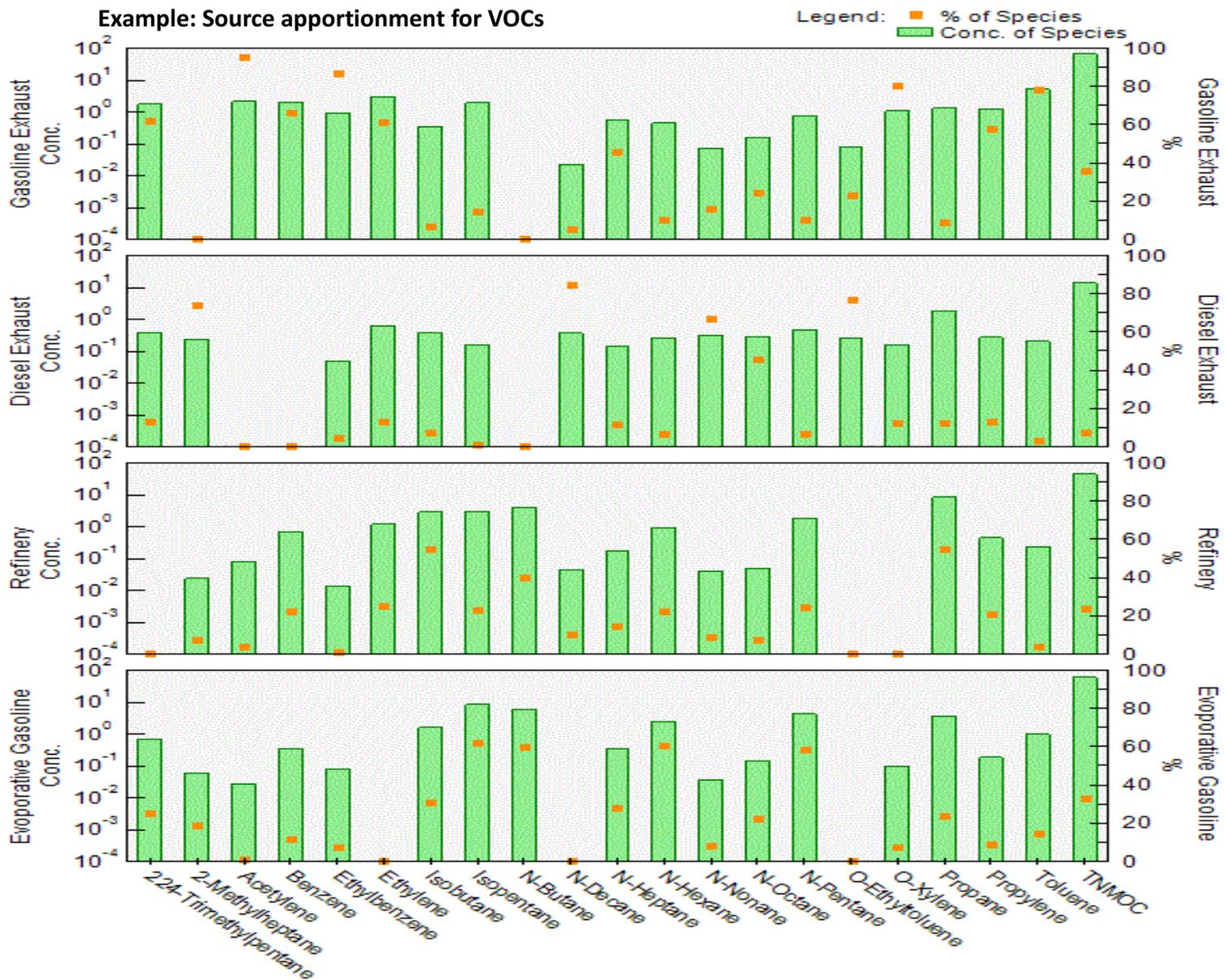
IDEQ Group

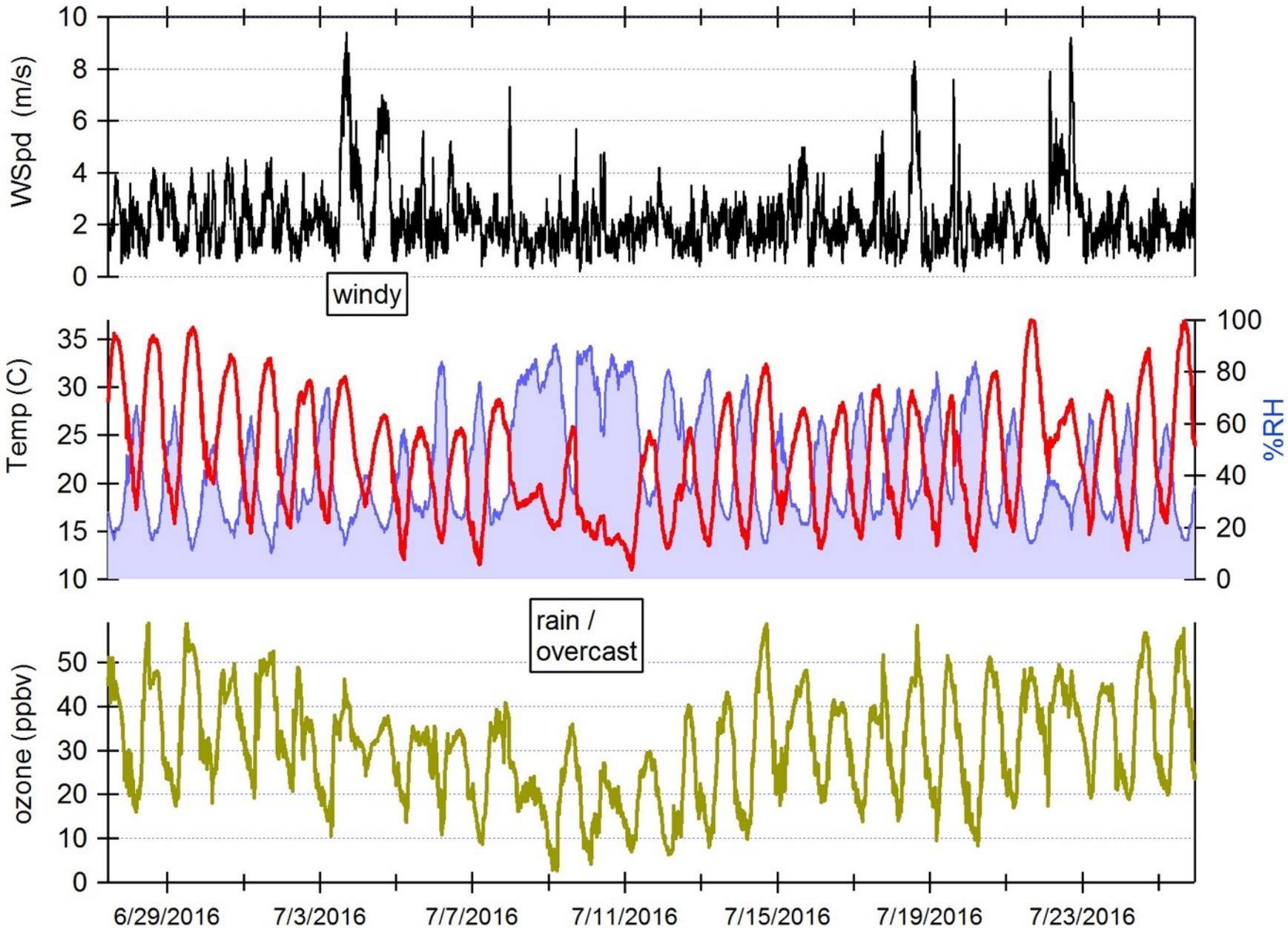
1. Dispersion Modeling:
WRF-CALPUFF system
Will provide insight on pulp mill effluent dispersion within the valley system

2. Perform source apportionment analysis on measurement data using Positive Matrix Factorization
→ *source of formaldehyde?*



Example: Source apportionment for VOCs





Sunset Park Data Study Conditions

Clear and sunny conditions prevailed.

Avg afternoon temp
29 °C. Max 38 °C.

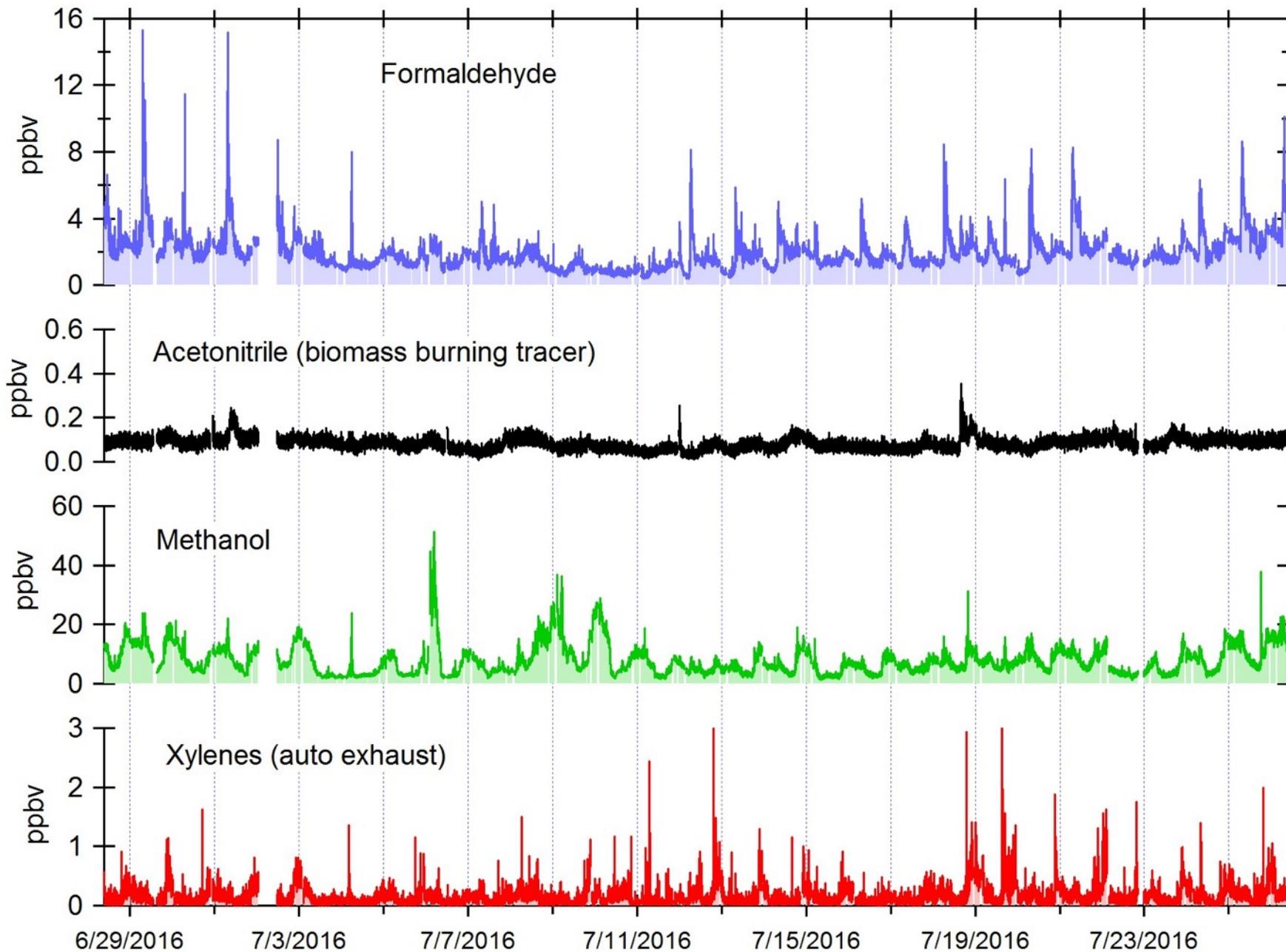
O₃ as high as 60 ppbv

Sunset Park VOCs

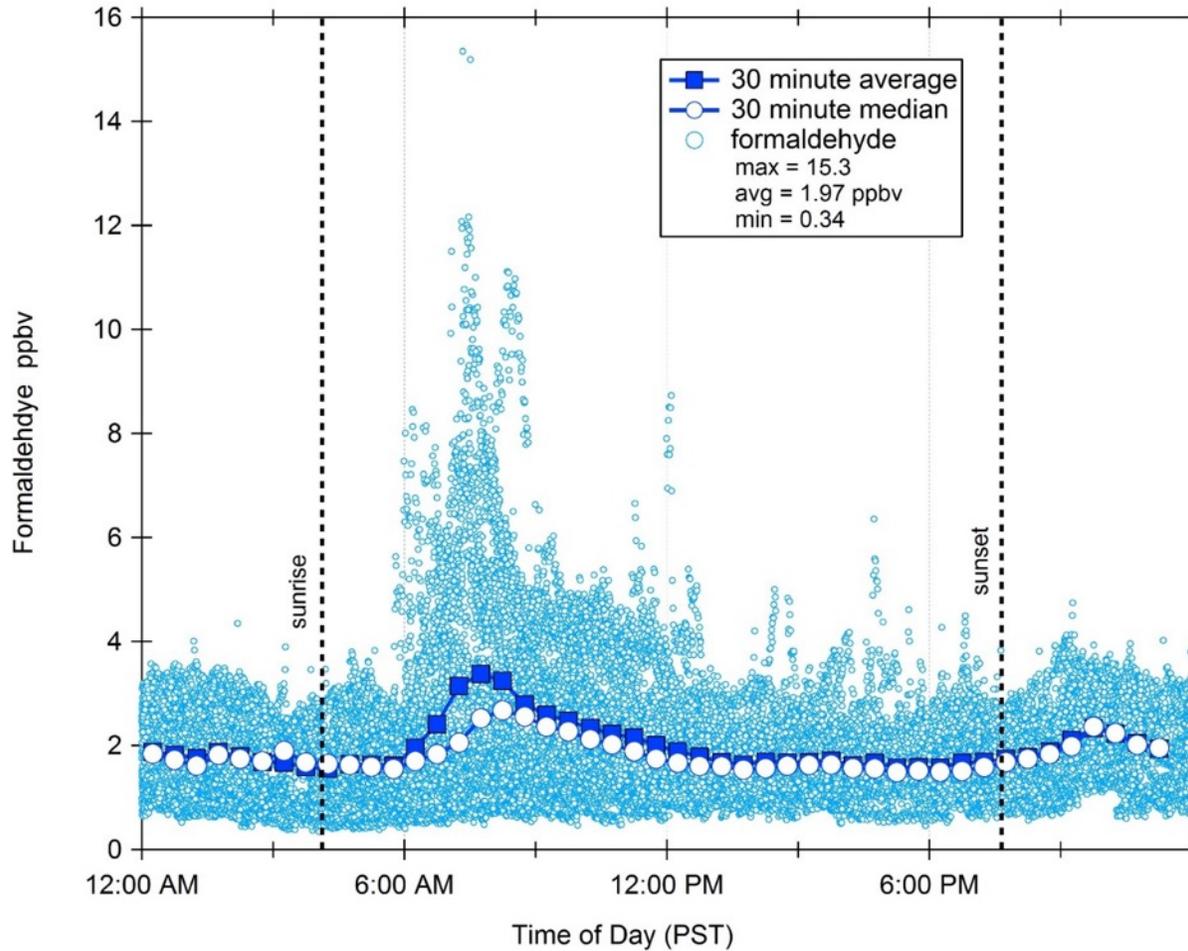
PTR-MS formaldehyde (HCHO) data show short term peaks in the time series.

High HCHO (6 – 15 ppbv) sometimes observed in the morning.

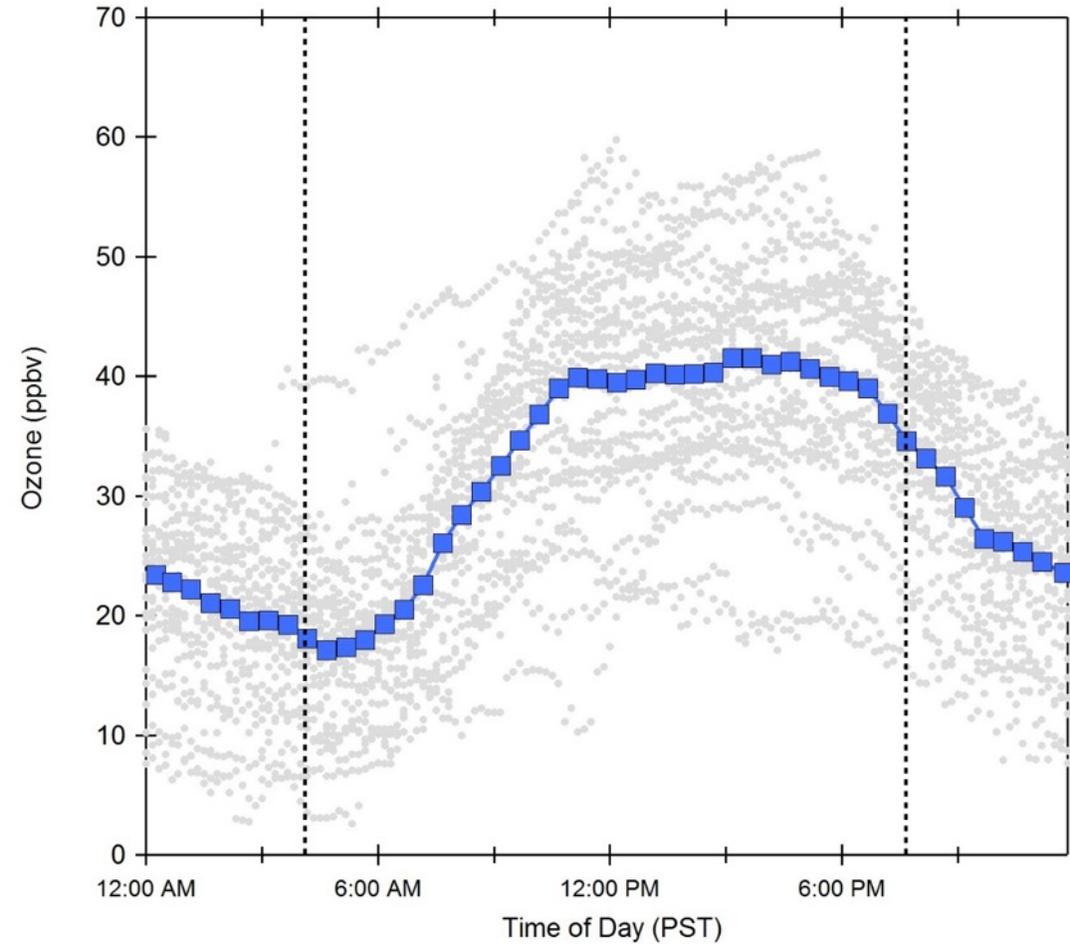
Overall HCHO mixing ratios lower than observed in 2006-2007 study.



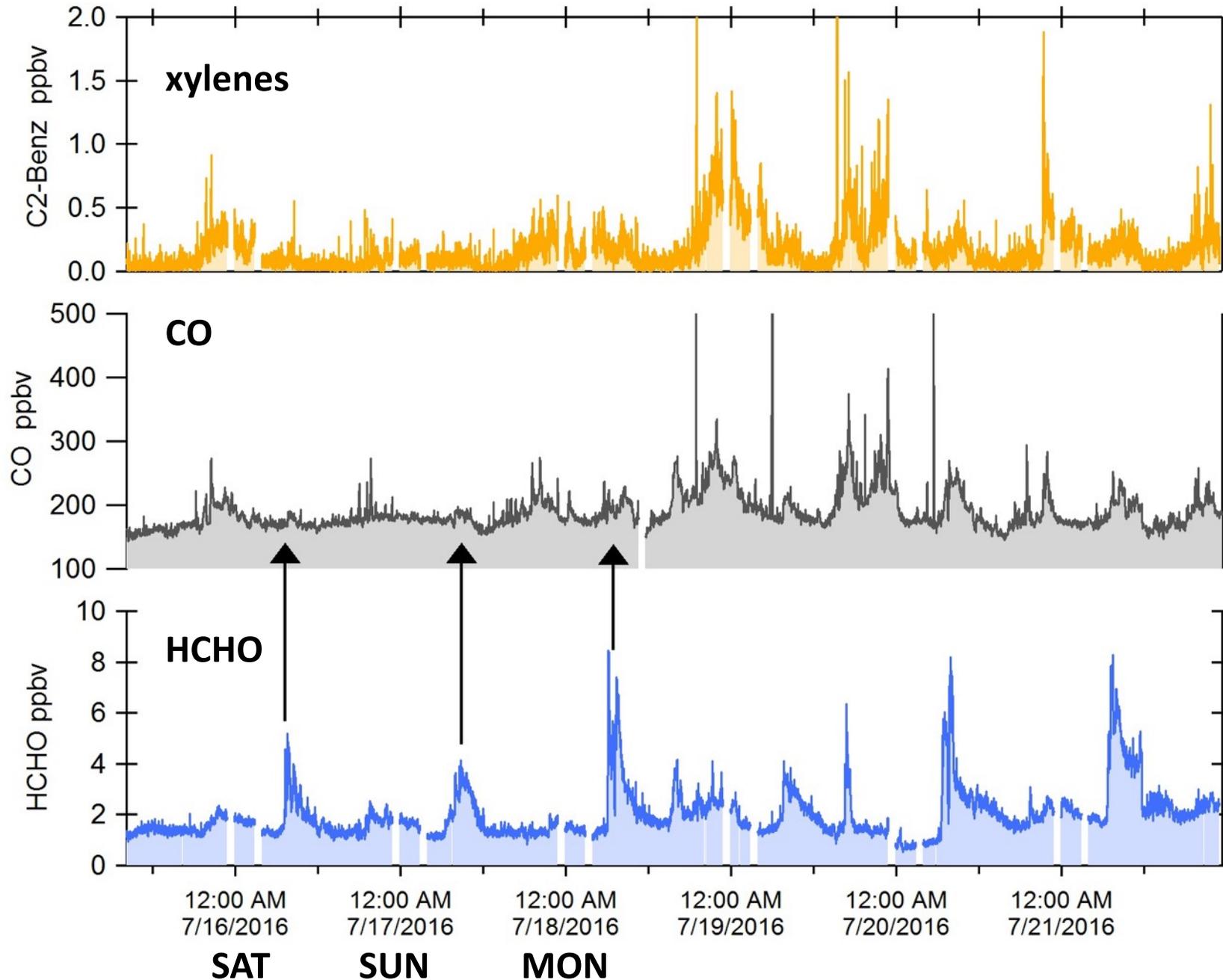
Sunset Park Formaldehyde (1 min data)



Ozone



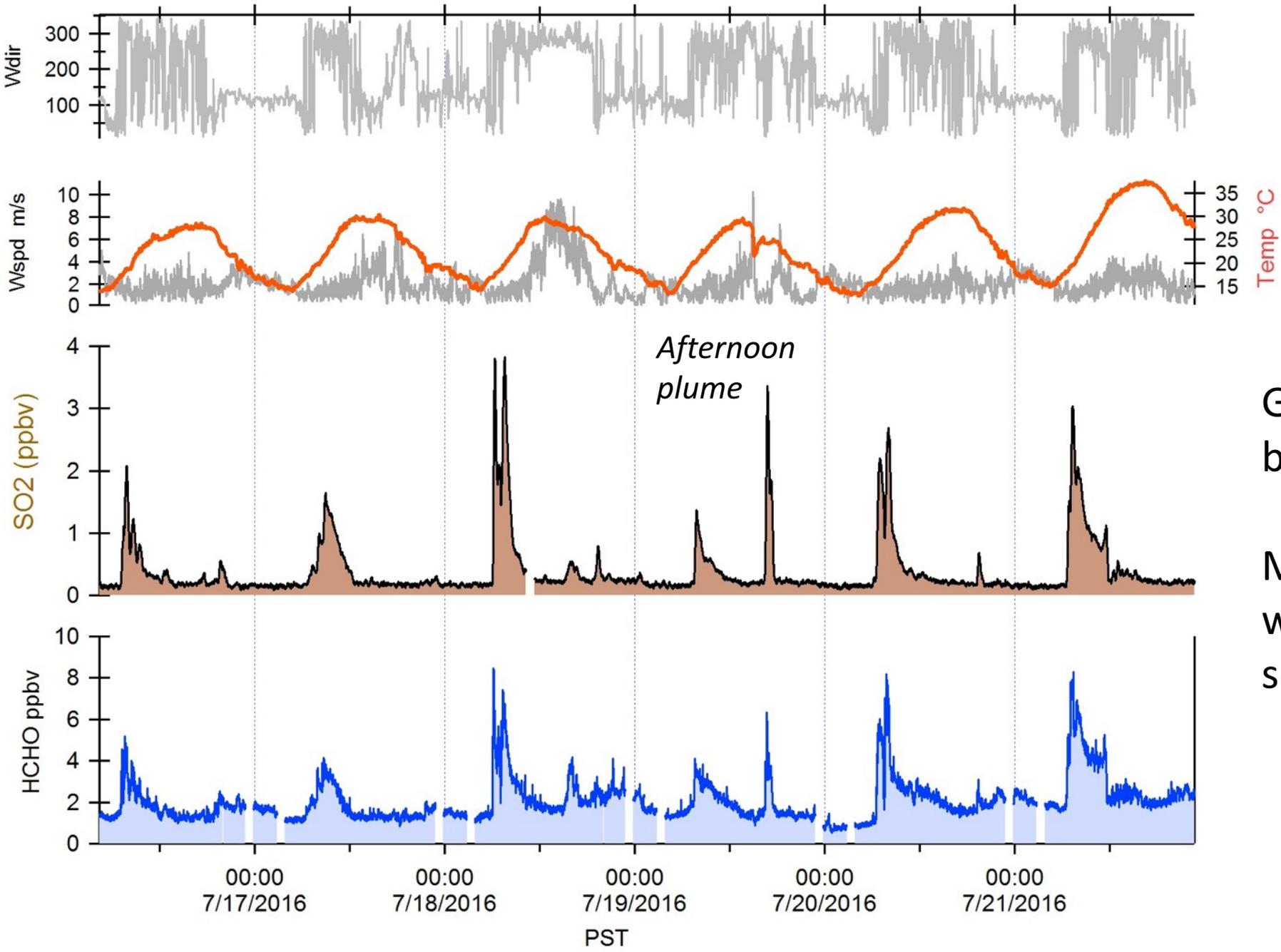
Morning peak (7-8 am PST) → not photochemical



Formaldehyde
correspondence with
vehicle exhaust
tracers

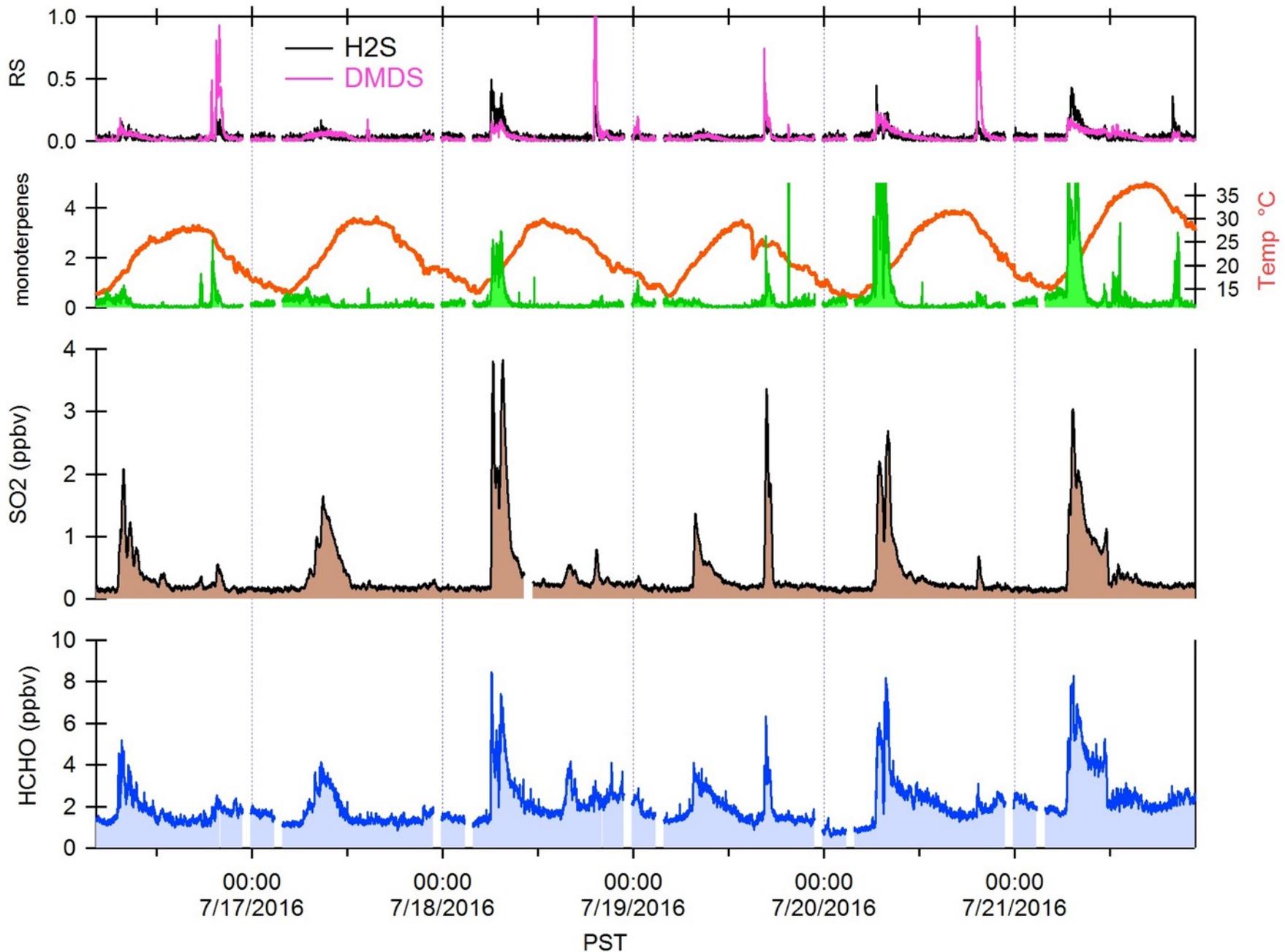
Morning HCHO peaks
often not associated
with elevated CO or
vehicle exhaust tracers.

Suggests non-traffic
source.



Good correspondence between HCHO and SO₂

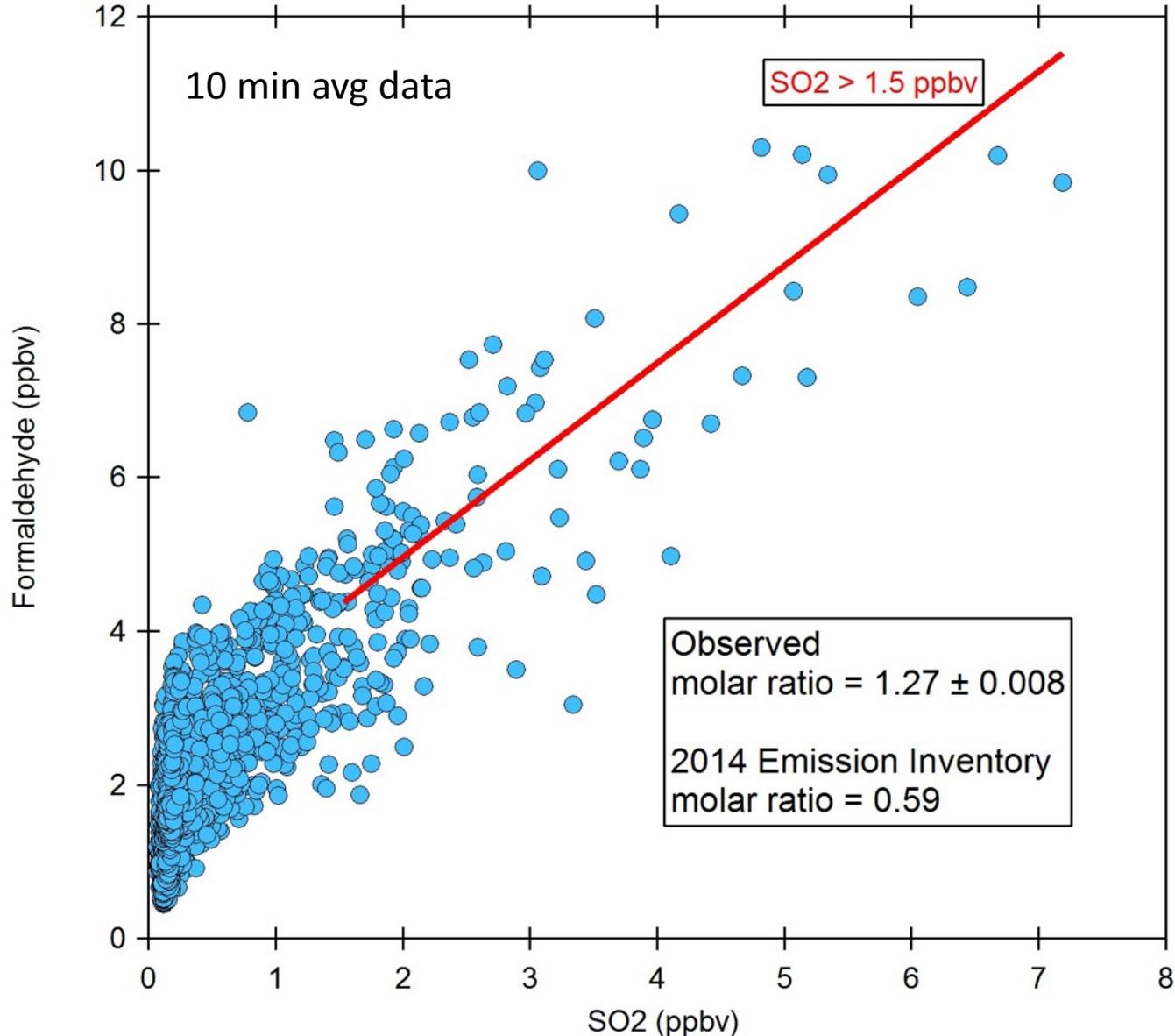
Morning peaks – light winds from northerly sector



HCHO events often associated with elevated SO₂, monoterpene, H₂S and DMDS mixing ratios.

Suggests emission location from the paper and lumber mill area.

Correlation between formaldehyde and sulfur dioxide at Sunset Park

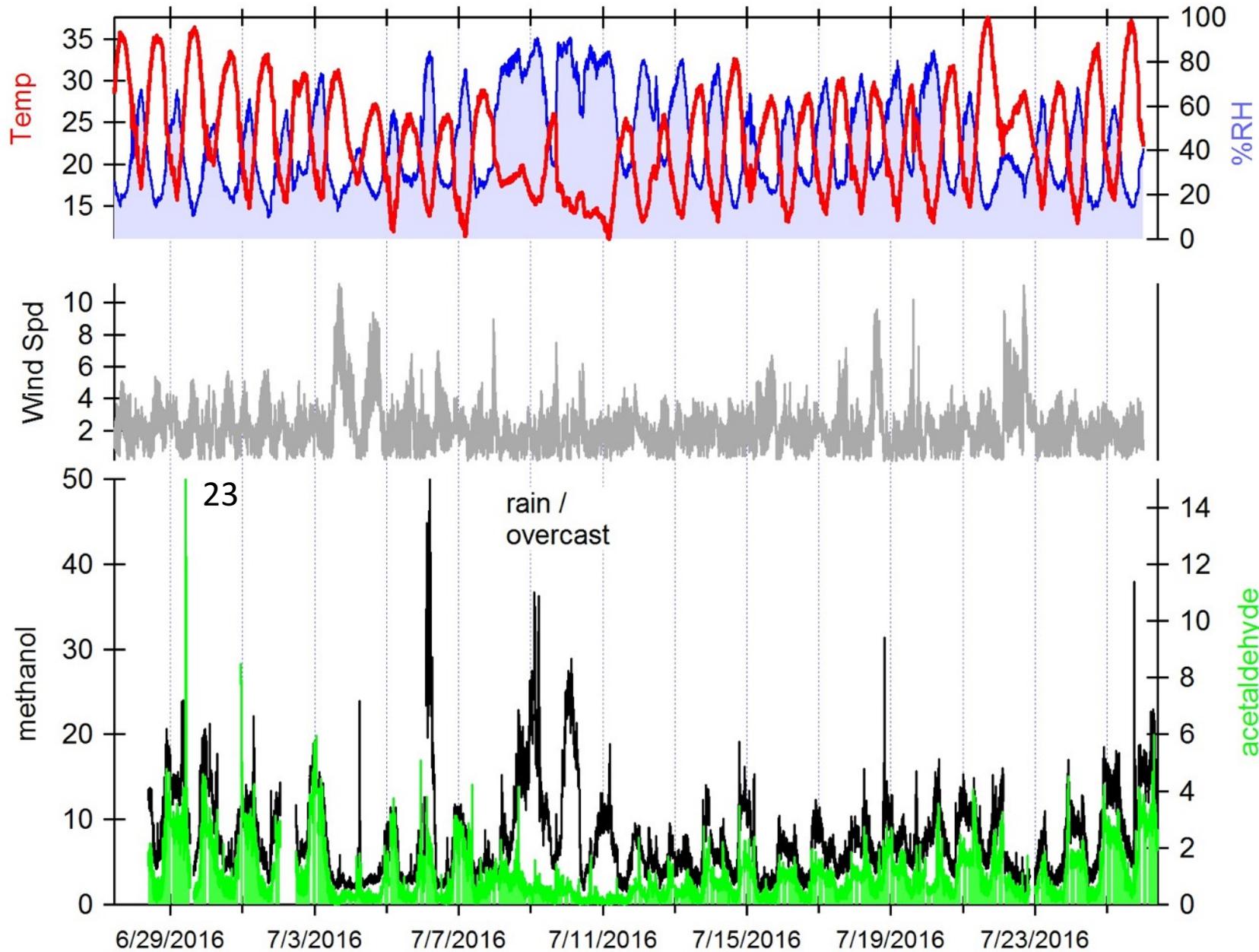


High SO₂ mixing ratios suggest industrial source as opposed to vehicles.

Correlation suggests common source location (*but it is scattered*)

Why morning peaks?

- *Does meteorology play a role - mixing down to surface from stack emission at night into the residual layer?*



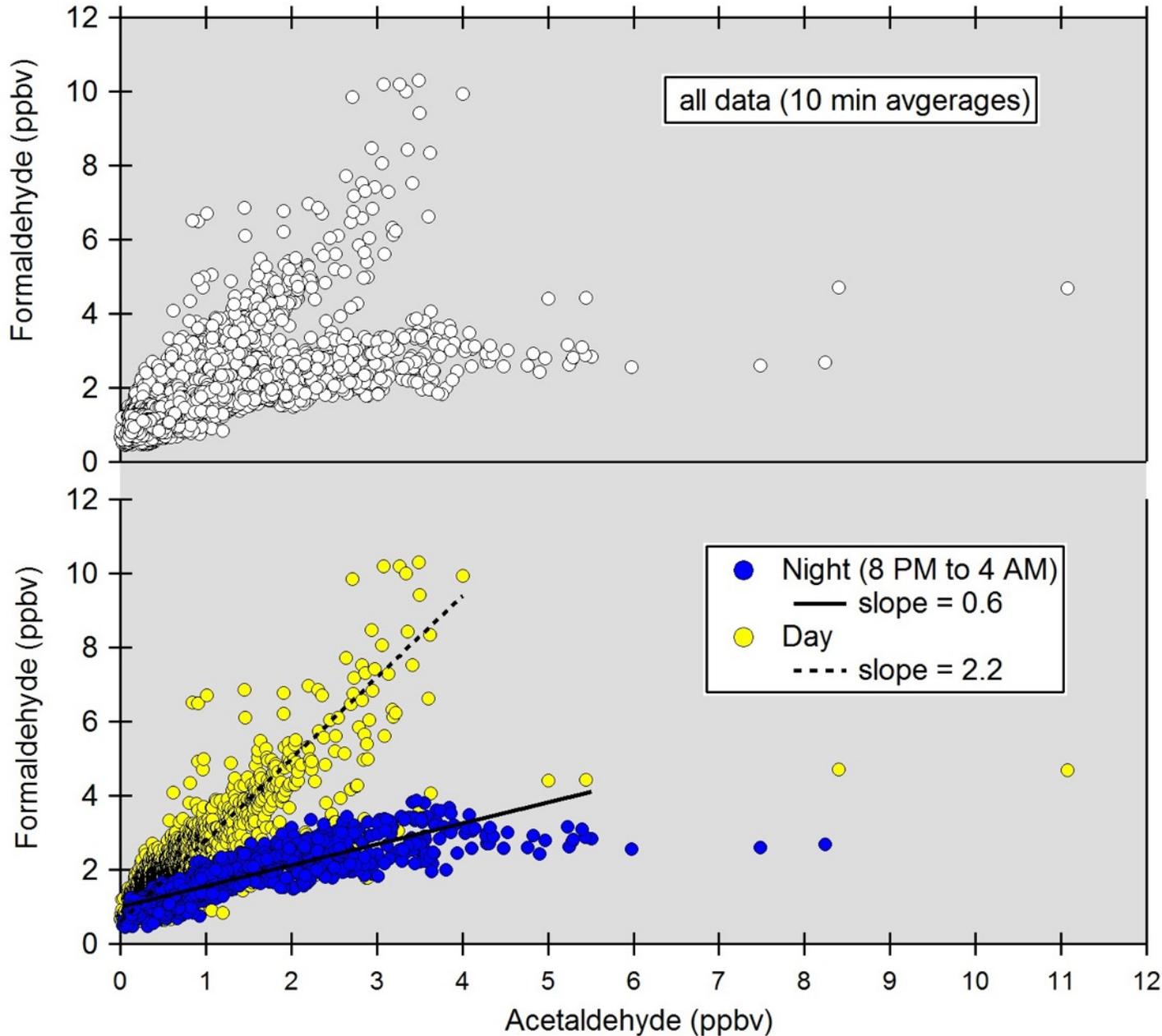
Acetaldehyde

Acetaldehyde and methanol displayed same diel behavior (higher at night).

Acetaldehyde sources appear to be somewhat different than formaldehyde sources.

Highest methanol abundance observed during rainy periods (?)

Formaldehyde vs. Acetaldehyde



Formaldehyde vs acetaldehyde relationship different between day and night.

Day ~ 2:2

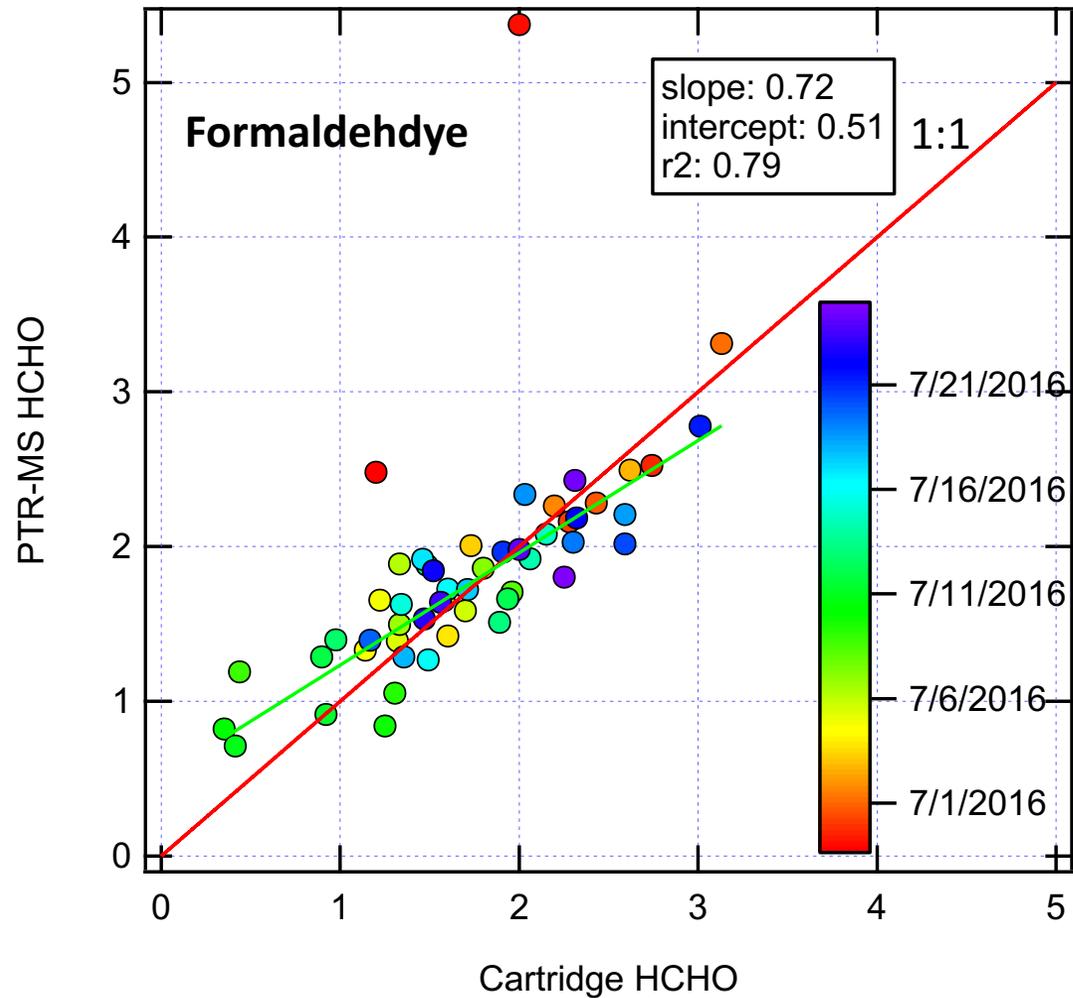
Night ~ 0.6

Average

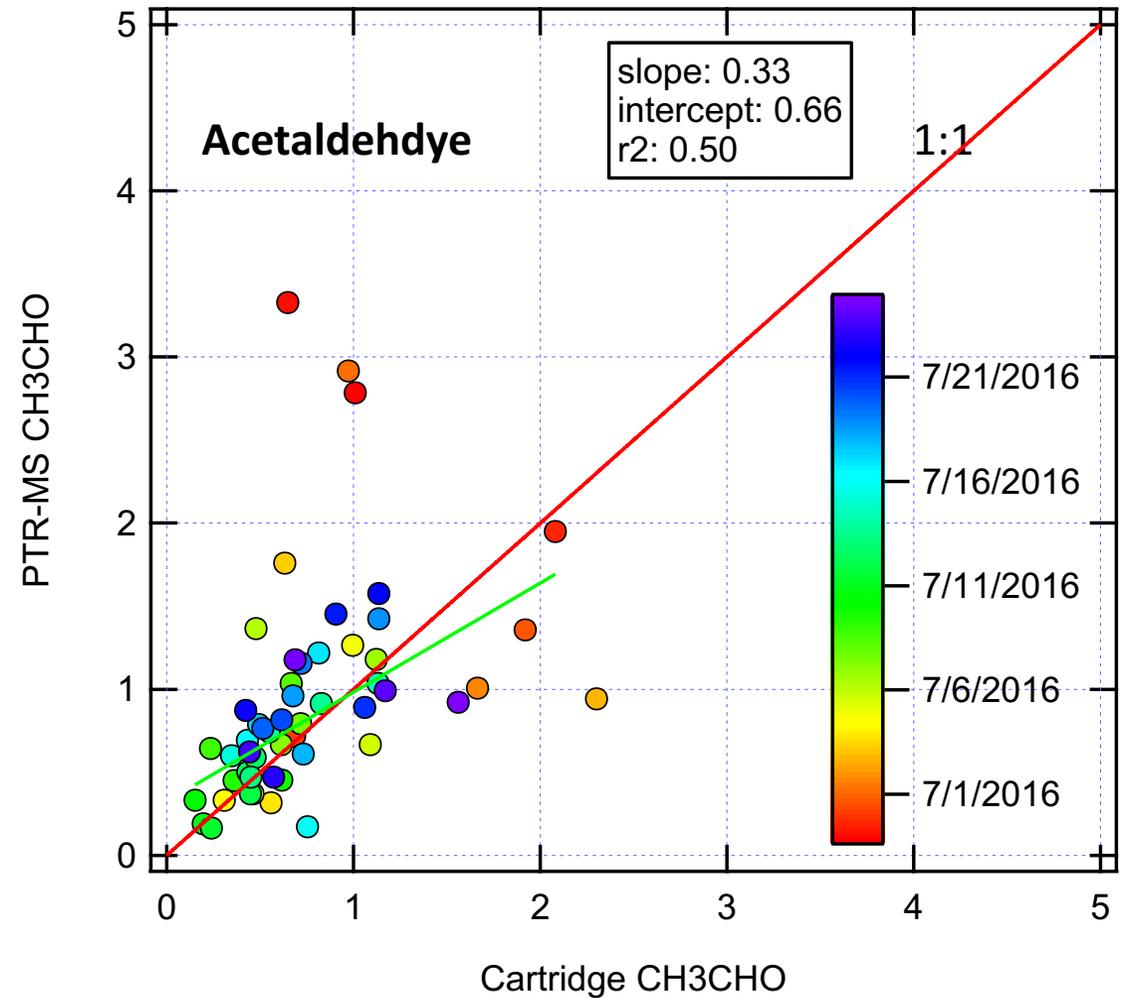
Formaldehyde	1.9 ± 1.0 ppbv
Acetaldehyde	1.0 ± 1.0 ppbv

ERG Formaldehyde Data

PTR-MS measurements vs DNPH cartridge analysis for aldehydes mixing ratios (12-hr averages)



Good correspondence

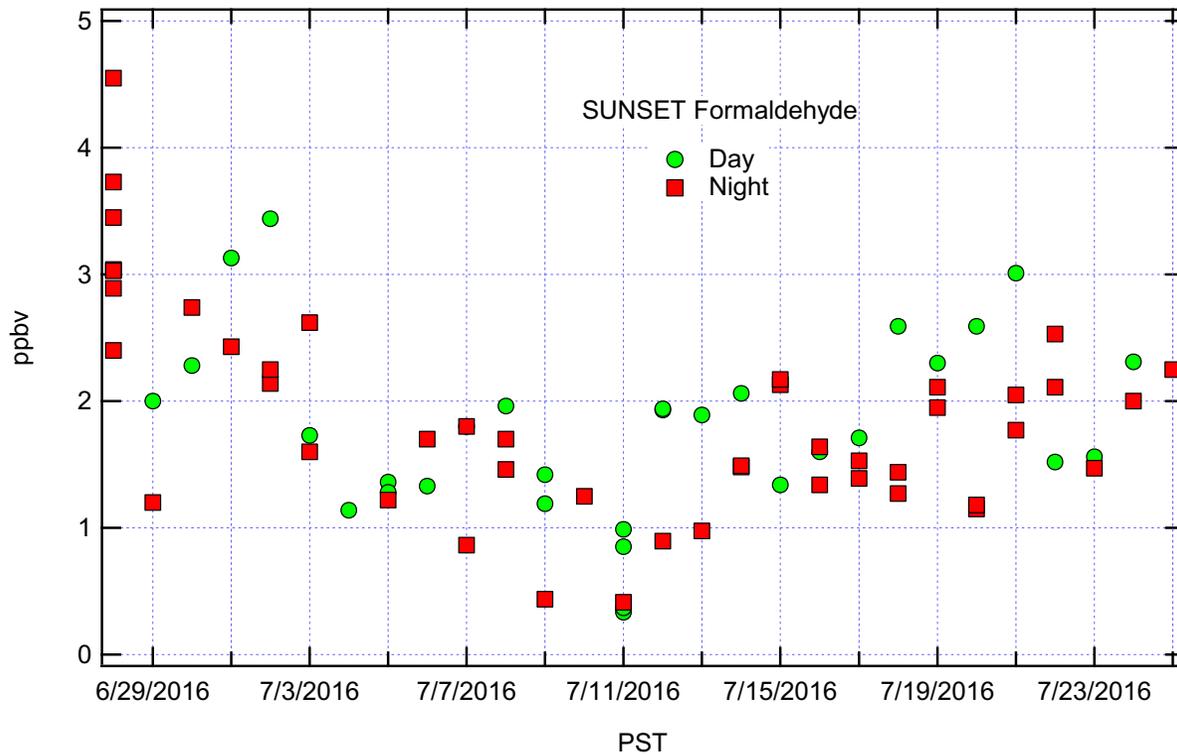


More scatter

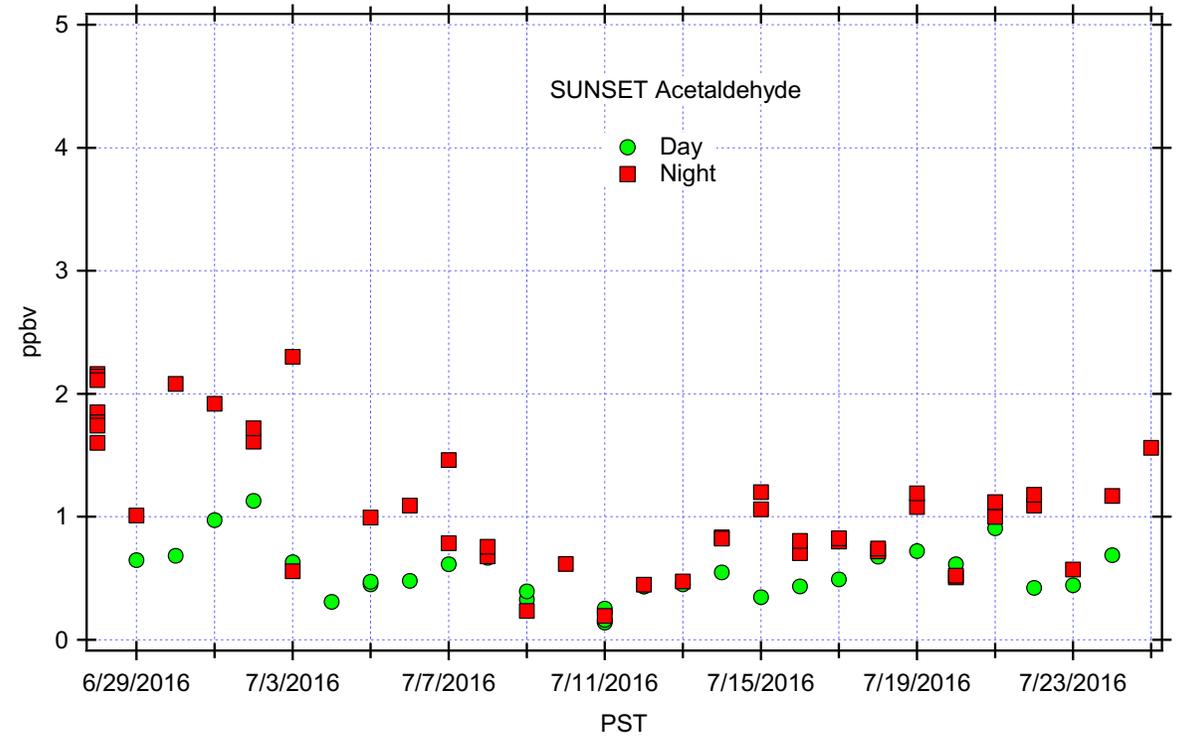
Spatial Gradient in L-C Valley

12-hr DNPH based samplers for Formaldehyde and Acetaldehyde

Sunset Park site

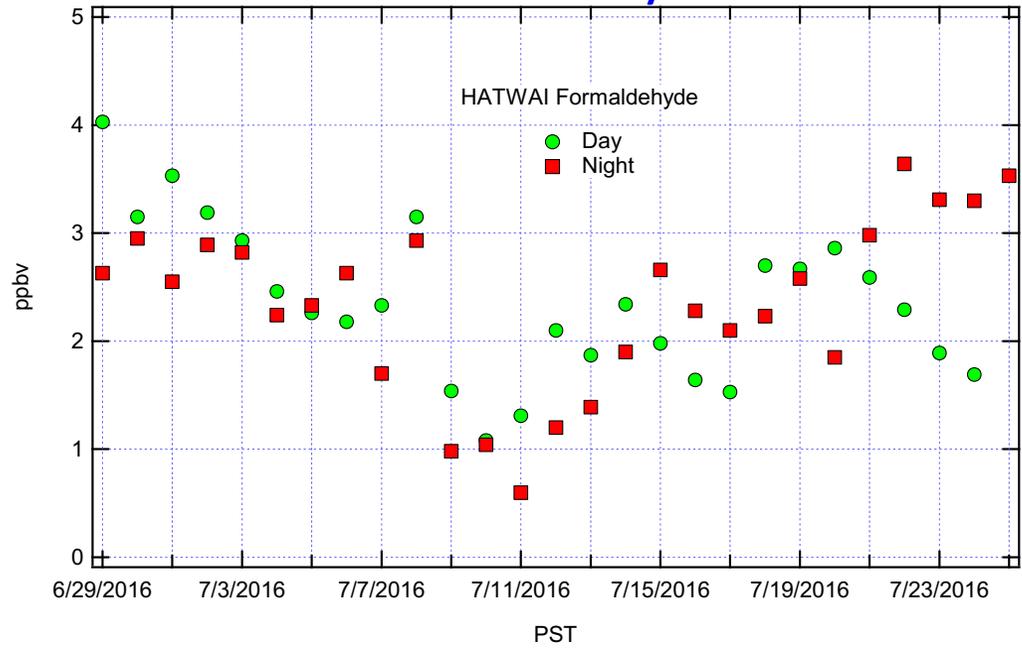


Day HCHO similar to night HCHO

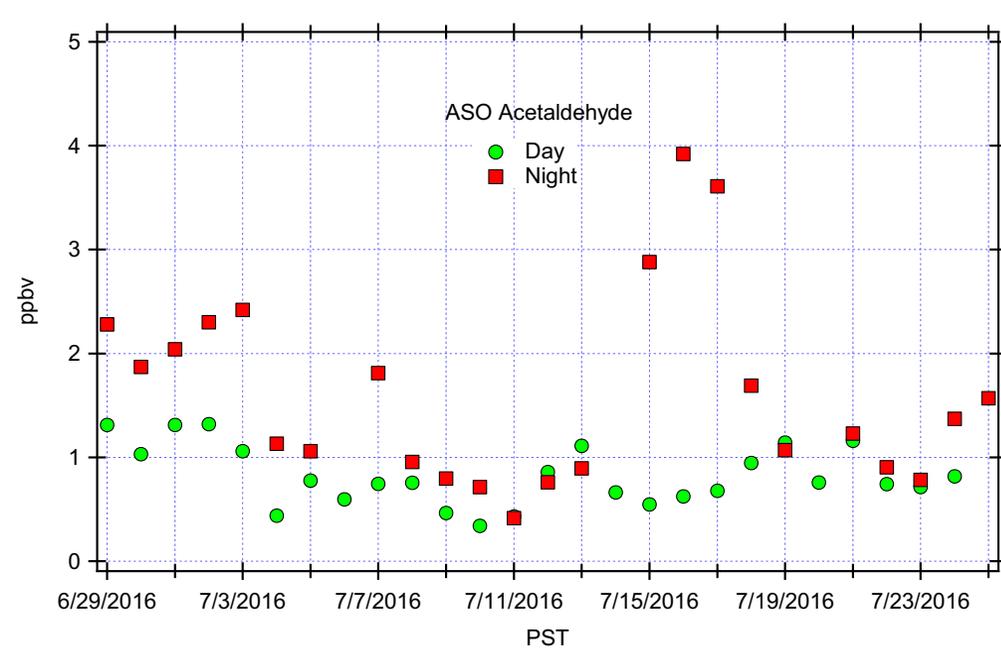
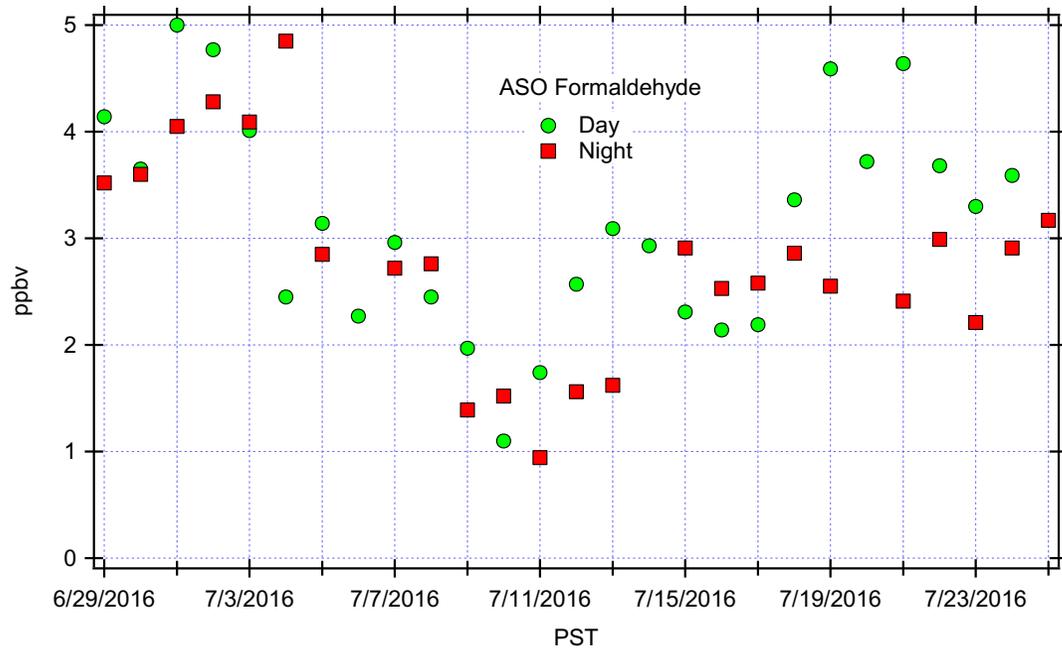
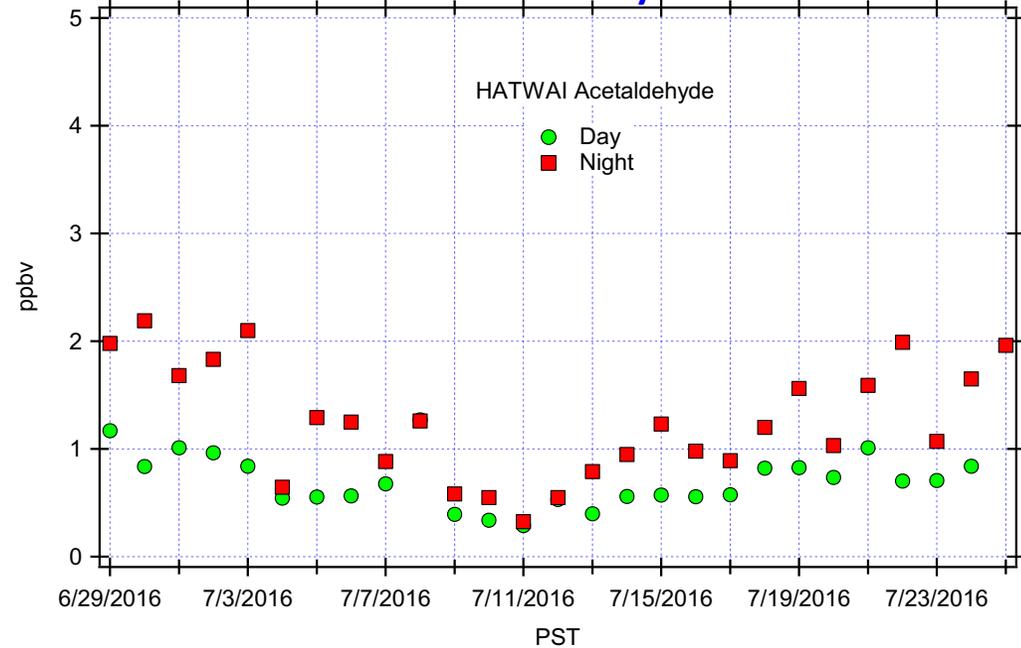


Night acetaldehyde data > day data

Formaldehyde



Acetaldehyde



Formaldehyde and Acetaldehyde Result Summary for All Sites

Site	Average (ppbv)	Standard Deviation	Number of Analysis
Sunset HCHO	2.02	0.93	86
Sunset CH3CHO	1.00	0.64	86
Hatwai HCHO	2.35	0.75	53
Hatwai CH3CHO	0.99	0.50	53
Asotin HCHO	2.97	1.00	50
Asotin CH3CHO	1.20	0.77	50

Mixing ratio of formaldehyde is generally higher (~2 x) than that of acetaldehyde for all the sites.

There is not much difference among the sites, for both formaldehyde and acetaldehyde.

Summary

- Highest levels of HCHO observed at Sunset in the morning after sunrise
short term events up to 15 ppbv
average HCHO ~ 2-3 ppbv across all sites
no significant day / night differences → no strong evidence of photochemical HCHO
- Formaldehyde events correlated with elevated SO₂ (H₂S, DMDS, monoterpenes).
- Formaldehyde concentrations significantly lower than in summer 2006 (2-3 ppbv compared to 10-15 ppbv).
- Have there been emissions changes at the pulp mill (or other industries) that would explain lower formaldehyde? Is this an L-C valley success story?