

Inter-Comparison of Formaldehyde Measurement Methods in the Lewiston-Clarkston Formaldehyde Study

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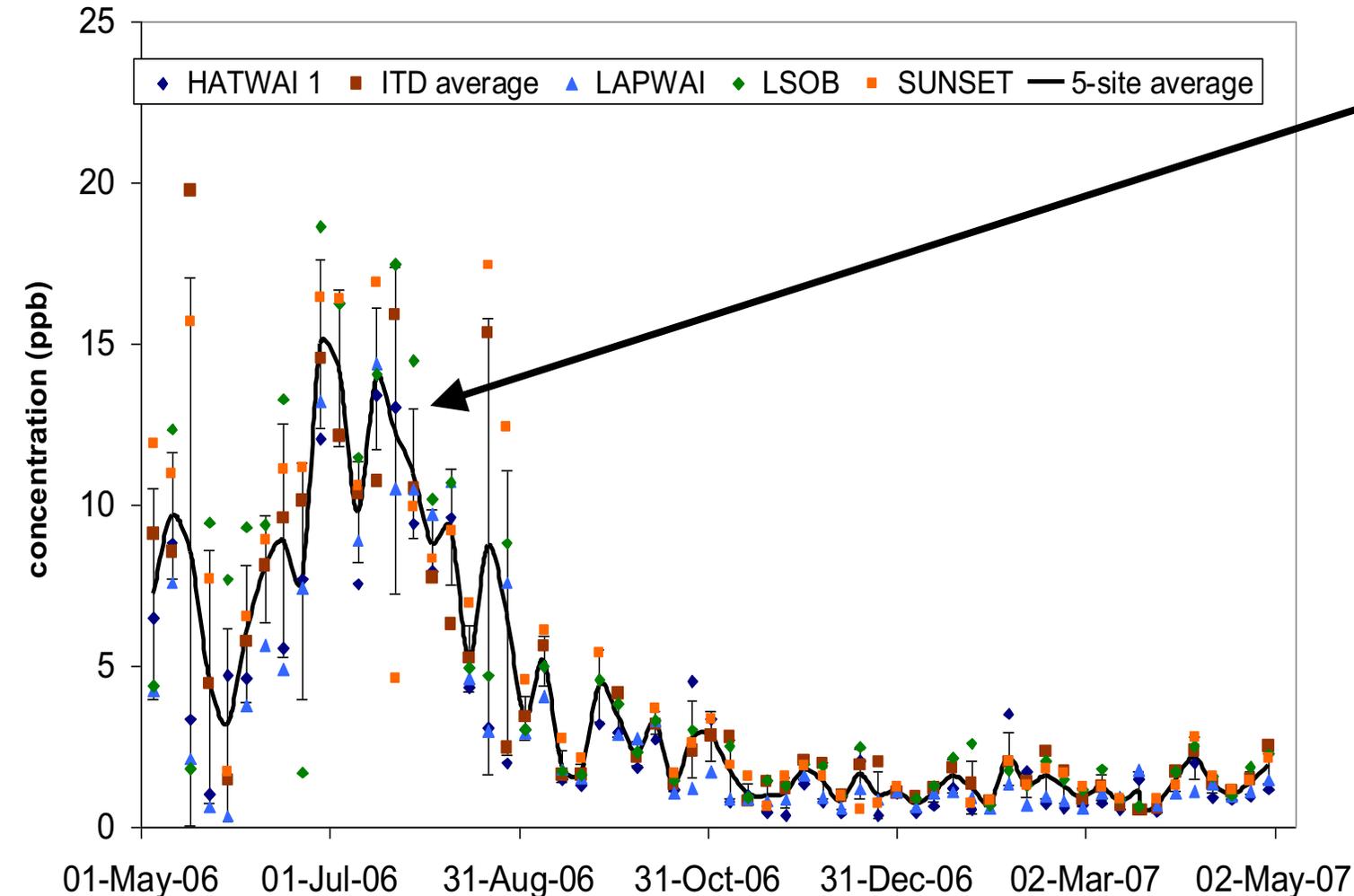
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Norwest AirQuest Meeting, Boise, ID, June 11, 2019

Lewiston-Clarkston Valley Formaldehyde Study summer 2016 / 2017

Motivation: High levels of formaldehyde and acetaldehyde measured summer from a 1 in 6 day DNPH based sampling study performed in **2006-2007**.



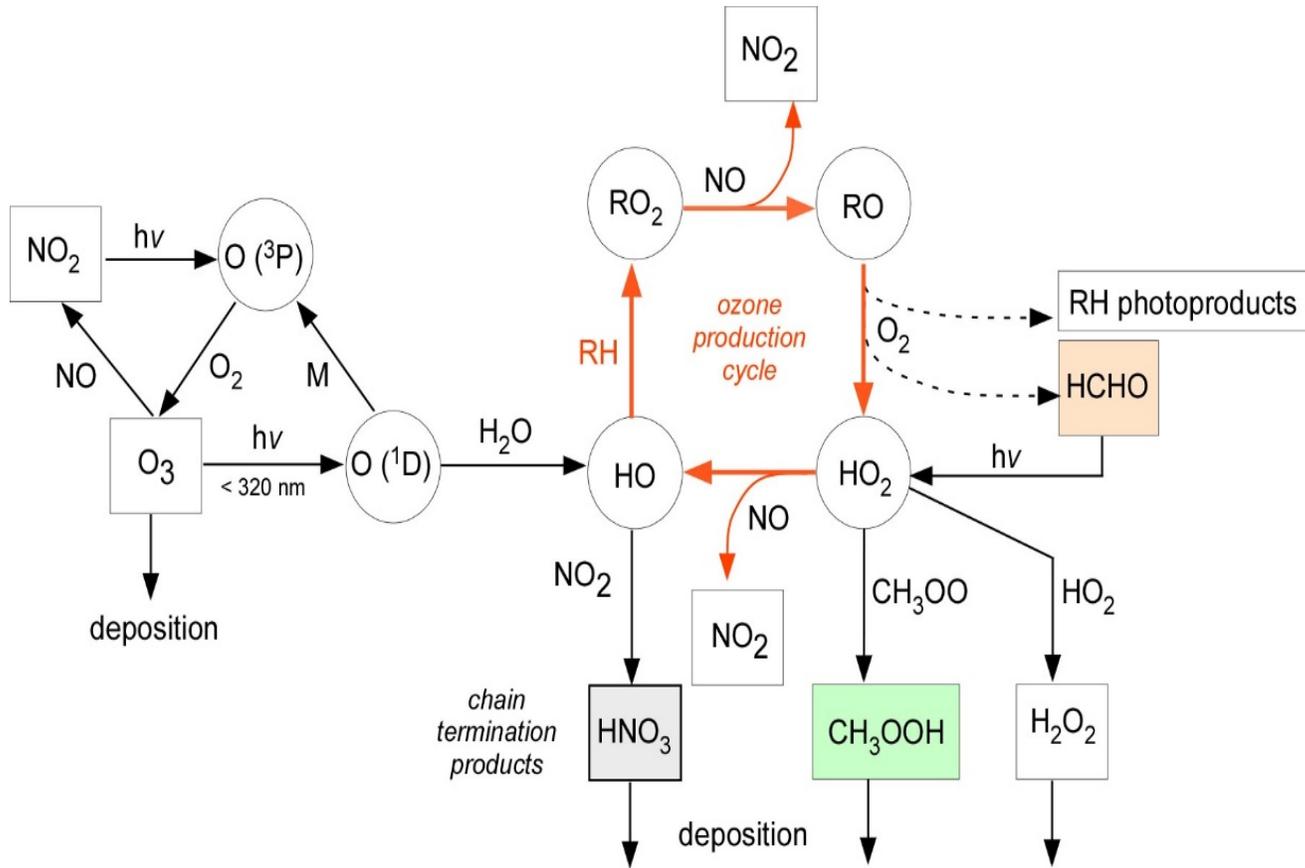
24-hr average HCHO > 10 ppbv in July / Aug at multiple sites in the valley. Unusually high levels for a small town (~50,000). Elevated cancer risk from Health Risk Assessment.

- High in summer because of secondary production?
- Influence of pulp and paper mill?

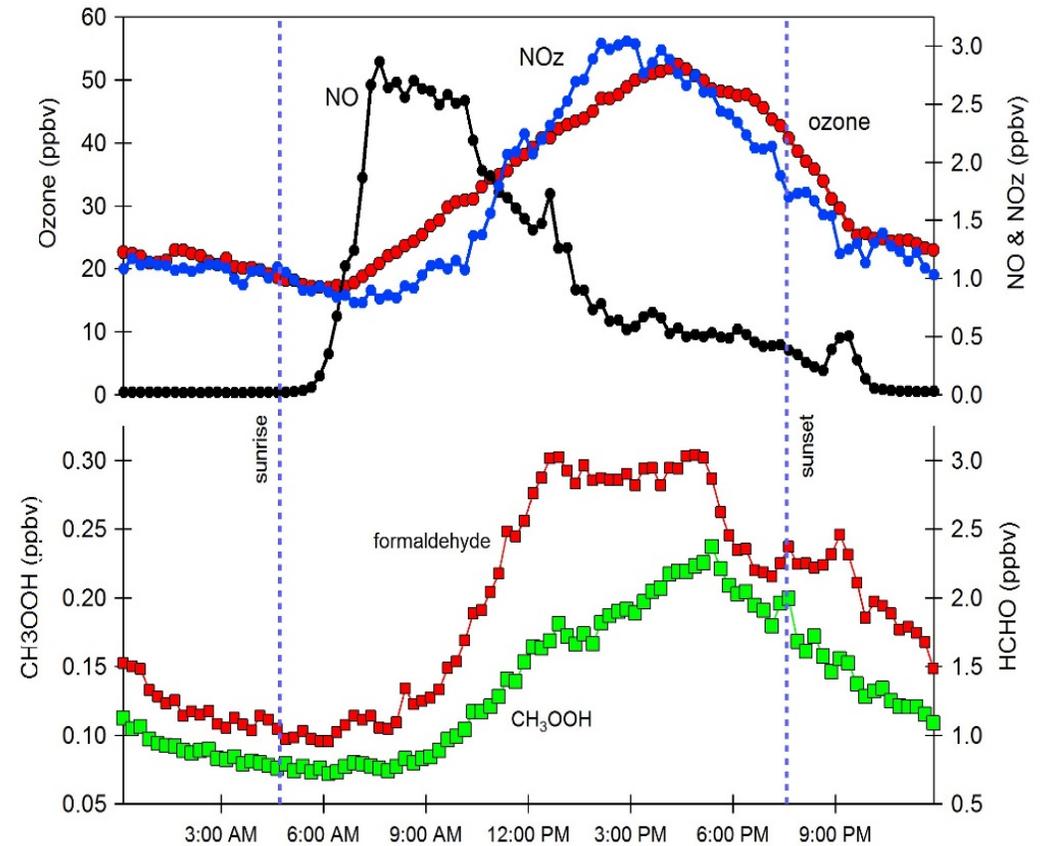
Identify sources of HCHO.

Secondary formaldehyde from oxidation of hydrocarbons (RH)

Hydrocarbon oxidation and ozone production

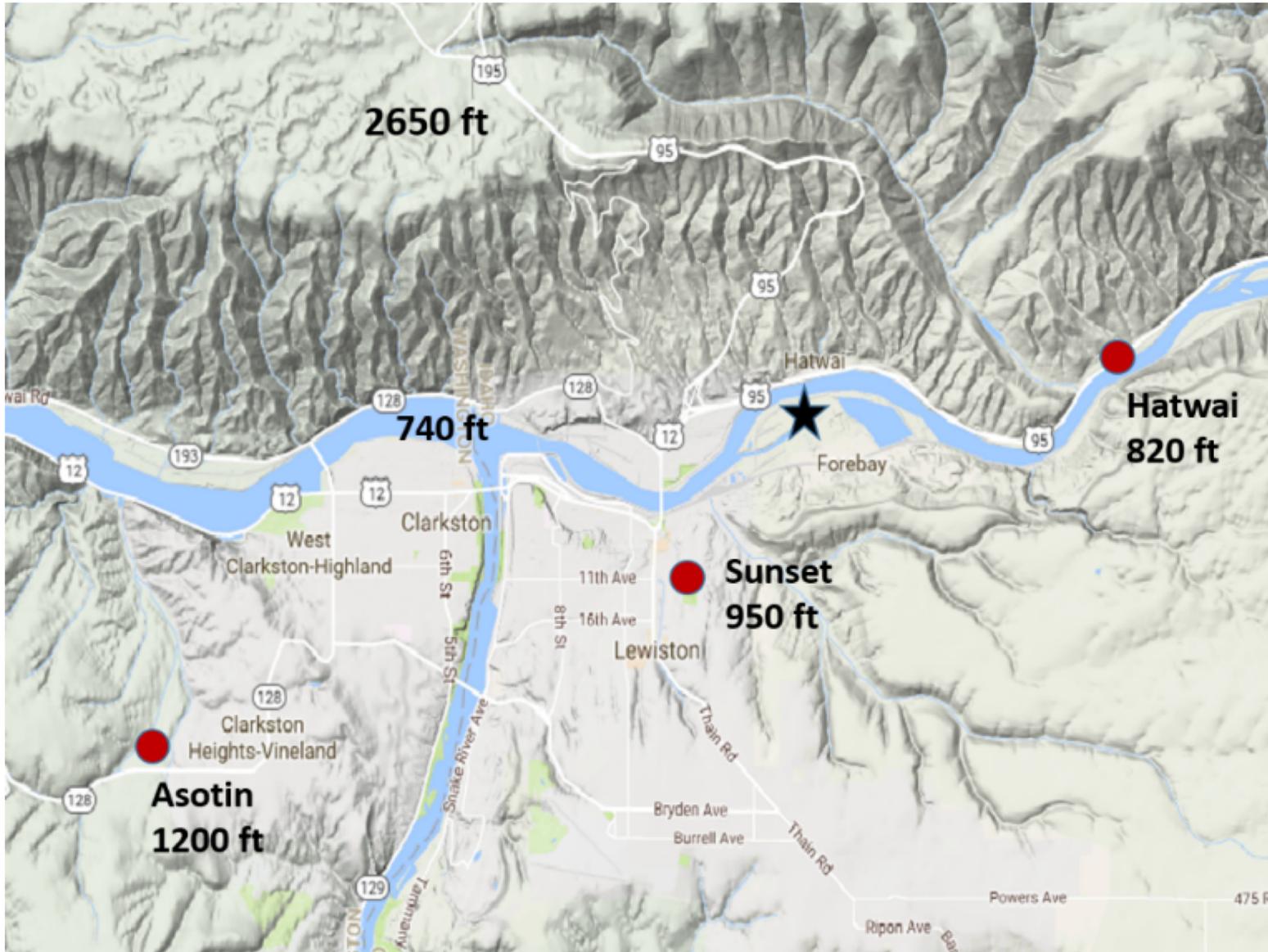


Example secondary formaldehyde at urban site



If secondary formaldehyde should display an afternoon maxima like ozone

Lewiston-Clarkston Valley



Locations sampling sites for 2016 and 2017 field study (4 weeks in summer)

1. Asotin (county landfill, WA)
Surface meteorology
Grab sampling (12-hr, DNPH / silica gel)

2. Sunset Park (Lewiston, ID)
Main site
Surface meteorology
Continuous measurements
Grab sampling (12-hr, DNPH / silica gel)

3. Hatwai (Nez Perce lands, ID)
Surface meteorology
Grab sampling (12-hr, DNPH / silica gel)

14 miles



SUNSET PARK SITE

Instrumented trailer (MACL)

surface meteorology (WXT-520)
NO, NO₂, NO_y (*Air Quality Design*)
SO₂, CO, NO_x, O₃, (Teledyne)
CO₂, H₂O (Licor)
PTR-MS (Ionicon Analytik)
*for VOCs including
formaldehyde and
acetaldehyde*

grab sampling for aldehydes
(12-hr : Day / Night samples)

Asotin Site



Hatwai Site



Aldehyde Measurement Methods

1. DNPH based sample collection and analysis

Adsorbent: DNPH coated silica gel cartridges (Waters Sep-Pak DNPH-Silica).
900 ccm flow for total over 12-hr for a sample volume ~ 650 L.

Samples: shipped everyday by FedEx cold paks to ERG for analysis

Analysis at ERG: TO-11A [Waters HPLC – UV/VIS ; Agilent Zorbax ODS reverse phase column]

Two types of automated samplers were used (9 samplers were used in the study):

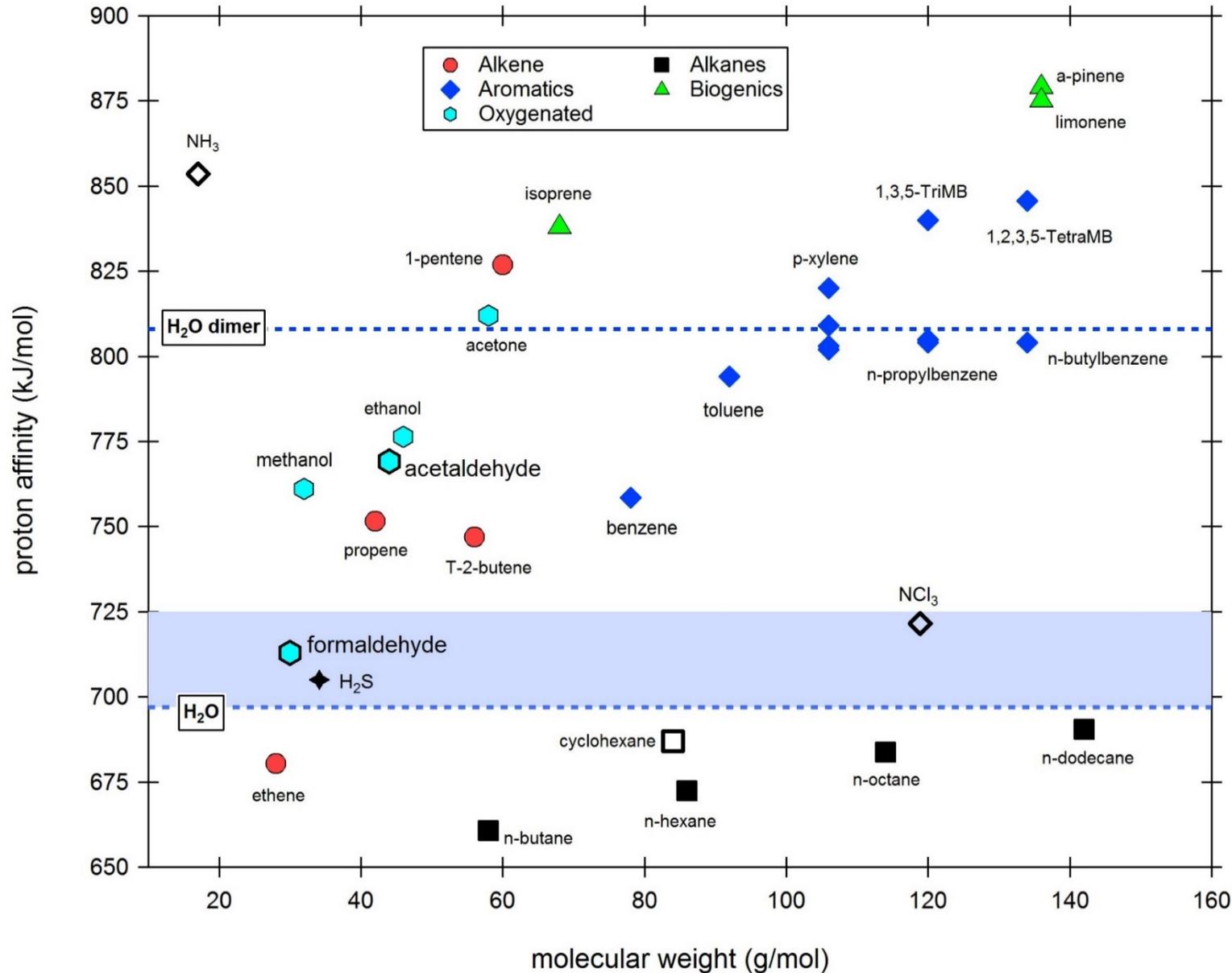
1. TAMS samplers - Tribal Air Monitoring Support
2. ATEC brand samplers (model 2200 Air Toxic Samplers, Atmospheric Technologies, Malibu, CA).

O₃ scrubbers were re-coated with potassium iodide before the study.

TAMS samplers: O₃ scrubbers were between 65 °C and 75 °C.

ATEC samplers: O₃ scrubber temperature was maintained at 50 °C.

2. Proton Transfer Reaction Mass Spectrometry



The PTR-MS has low response to formaldehyde; water vapor dependent.



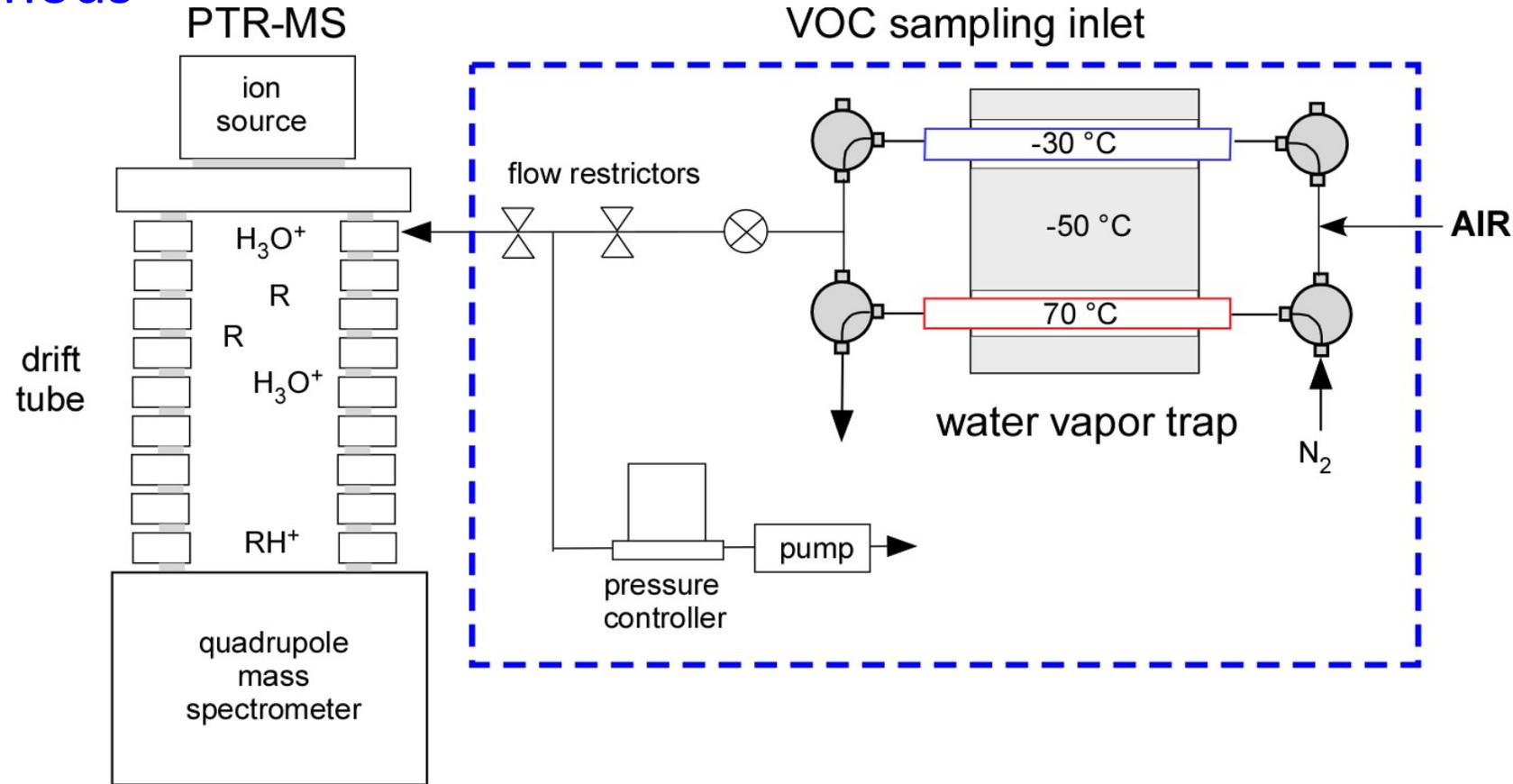
Slower proton transfer reaction

remove water vapor from air sample

PTR-MS Measurement Methods

drift tube conditions
 $P_{\text{drift}} = 2.0 \text{ mbar}$
 $T_{\text{drift}} = 60 \text{ }^\circ\text{C}$
 $U_{\text{drift}} = 320 \text{ volts}$

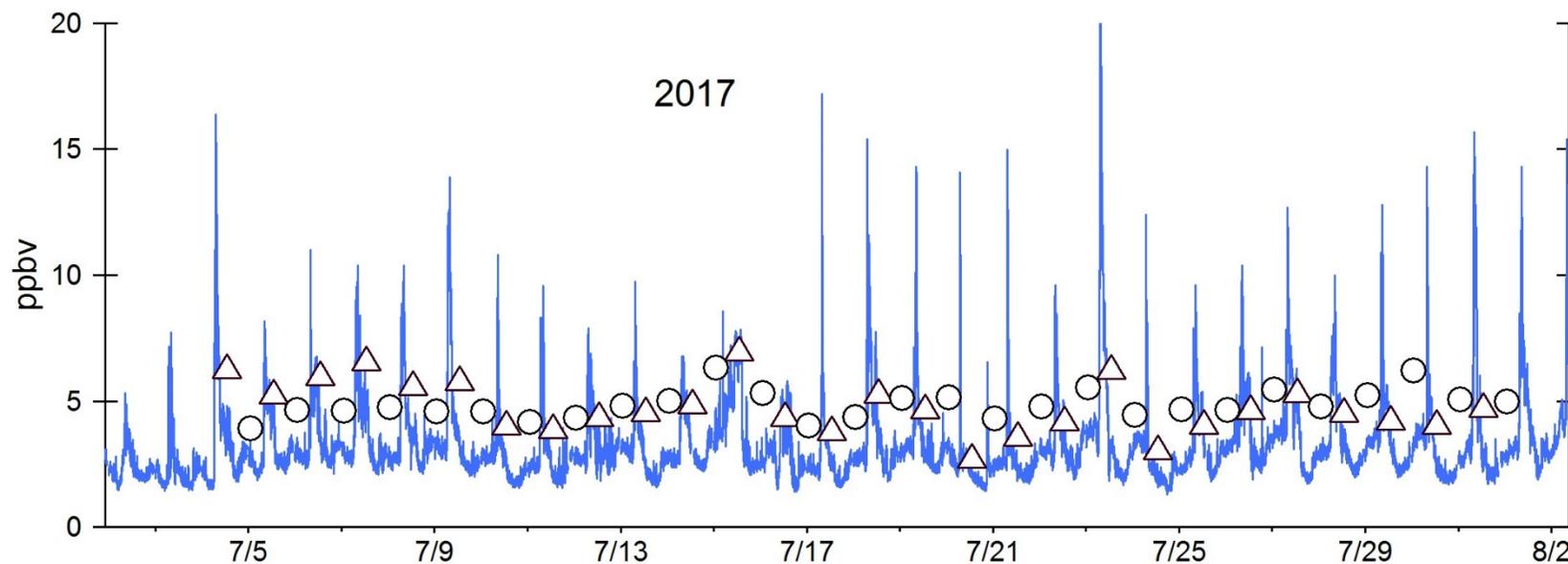
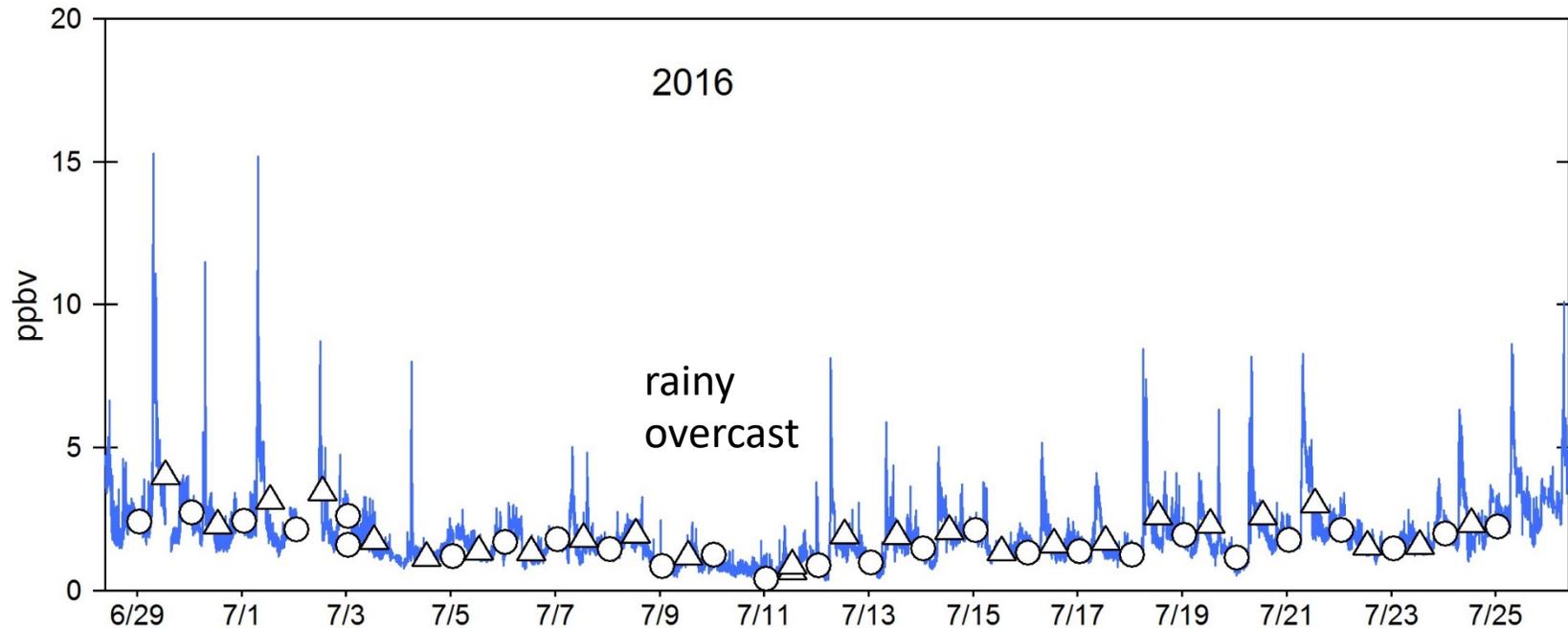
operation at
80 Td



To reduce back reaction and increase formaldehyde response factor the sample is **dehumidified to a dew point of $-30 \text{ }^\circ\text{C}$** . Condition trap for 15 minutes before sampling.

Allows for **PTR-MS operation at 80 Td** which dramatically reduces *dissociative* proton transfer reactions (*ie. eliminates ethylbenzene interference on benzene*) and increases response factors.

Sunset Park **Formaldehyde** Time Series



PTR-MS data

DNP 12-hr sample

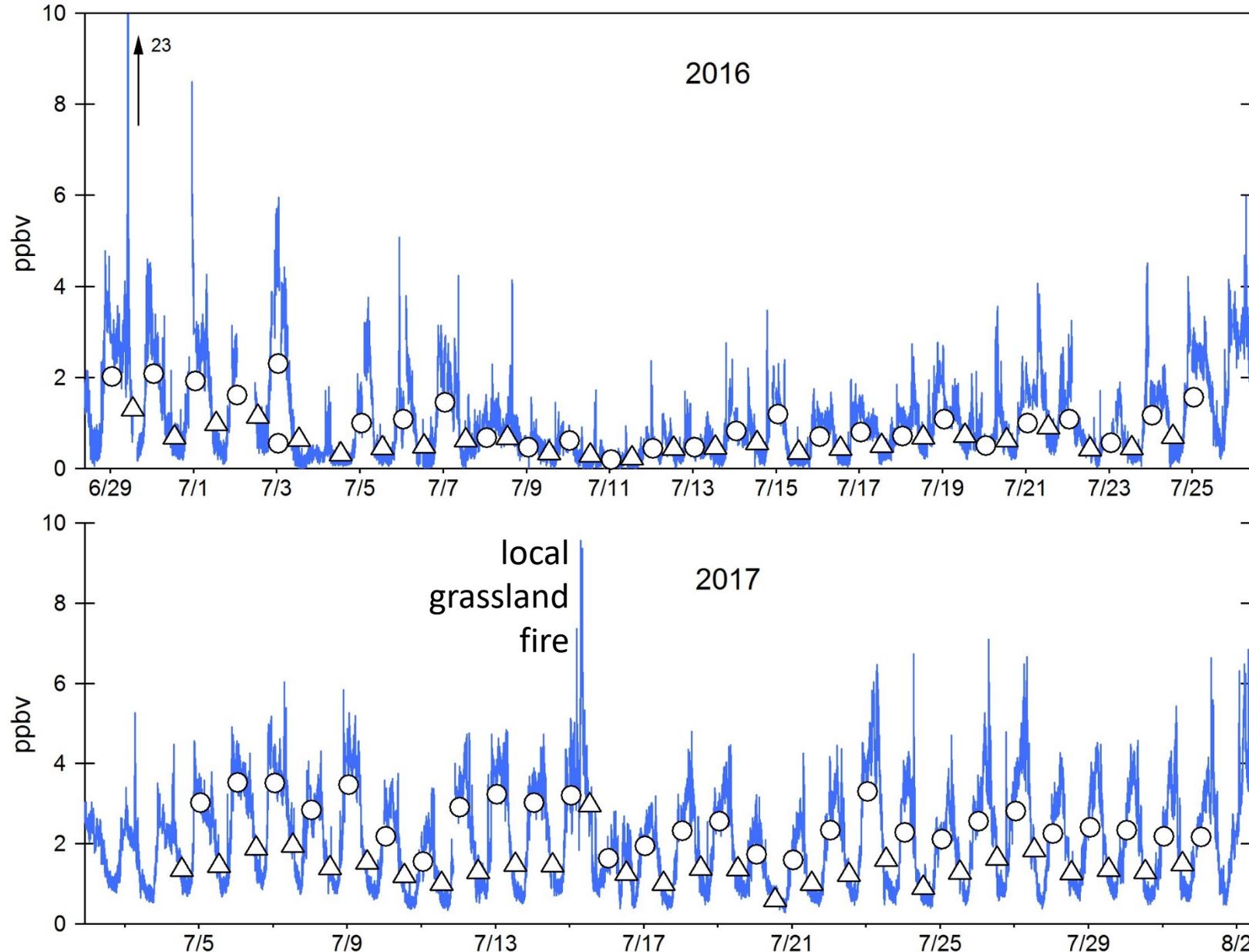
TAMS #2 night (○)

TAMS #4 day (△)

Daily occurrence of high formaldehyde in the early morning - max 19 ppbv.

2017 was sunnier and much warmer than 2016.

Sunset Park **Acetaldehyde** Time Series



PTR-MS data

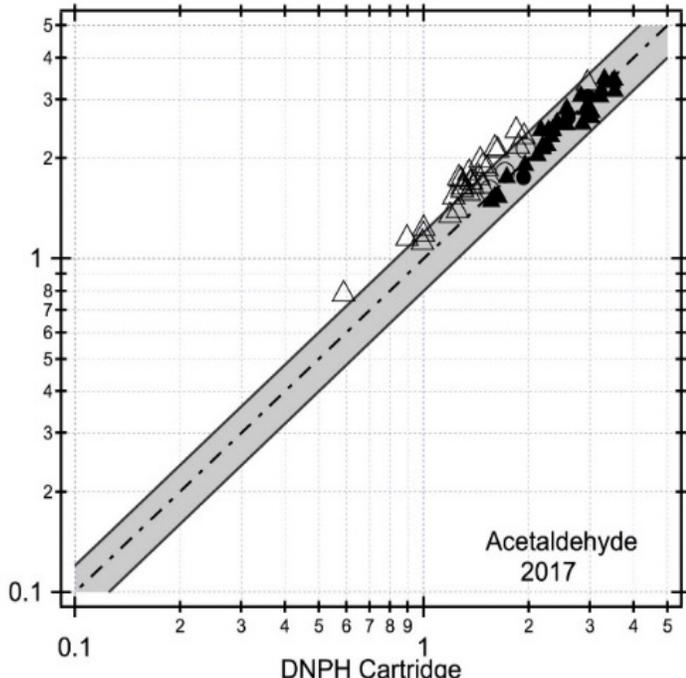
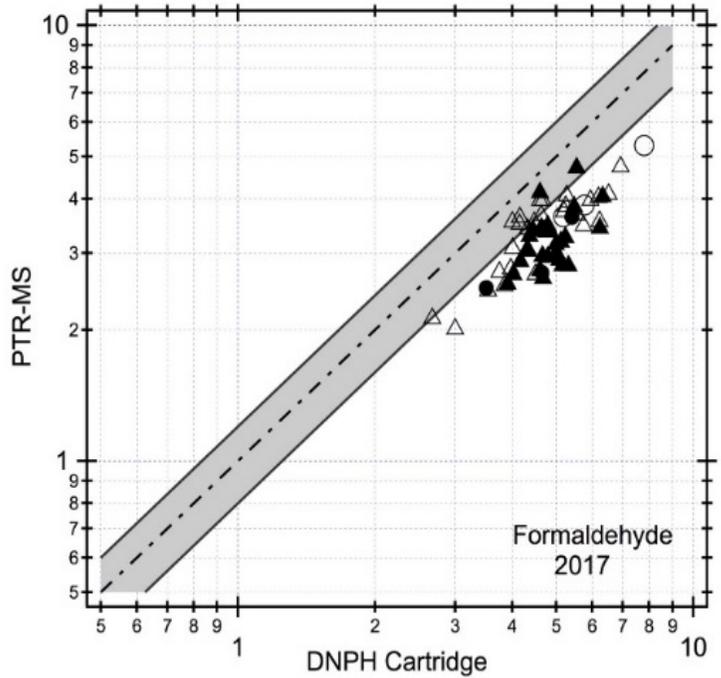
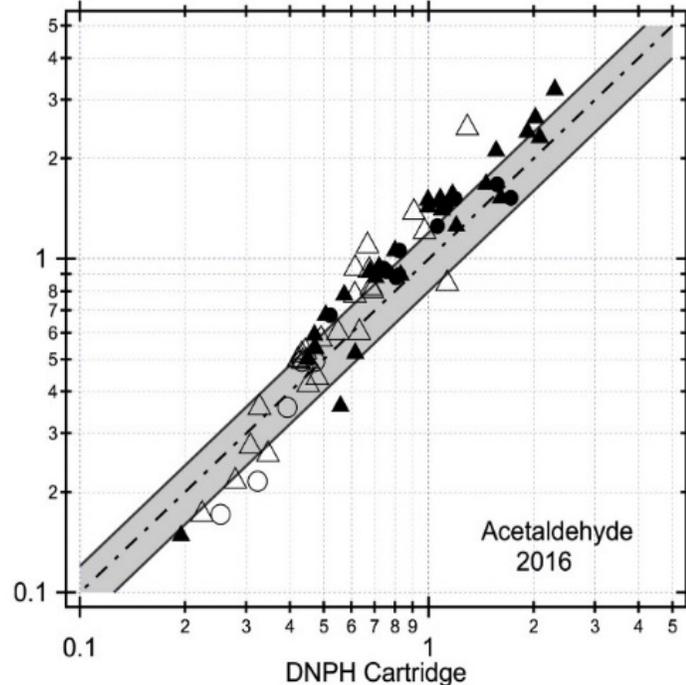
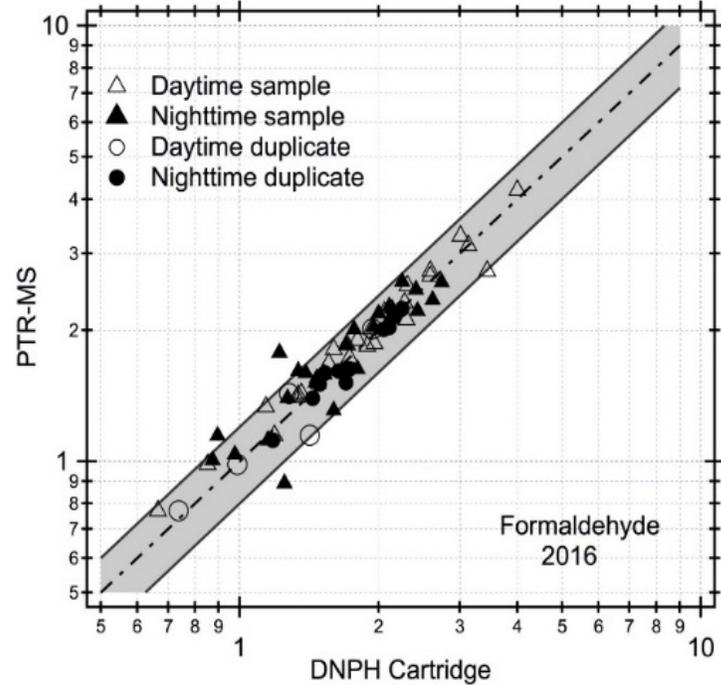
DNP-H 12-hr sample

TAMS #2 night (○)

TAMS #4 day (△)

Acetaldehyde ~3x more abundant at night!

Meteorological modulation drives formaldehyde and acetaldehyde variability.



12-hr averaged PTR-MS data vs. DNPH sample

shaded area $\pm 20\%$ about 1:1 line

Linear regression results

	slope	intercept	r^2
Form 2016	0.92 ± 0.03	0.17 ± 0.06	0.92
Form 2017	0.56 ± 0.09	0.64 ± 0.43	0.40
Acet 2016	1.28 ± 0.05	0.06 ± 0.05	0.90
Acet 2017	0.83 ± 0.03	0.48 ± 0.07	0.92

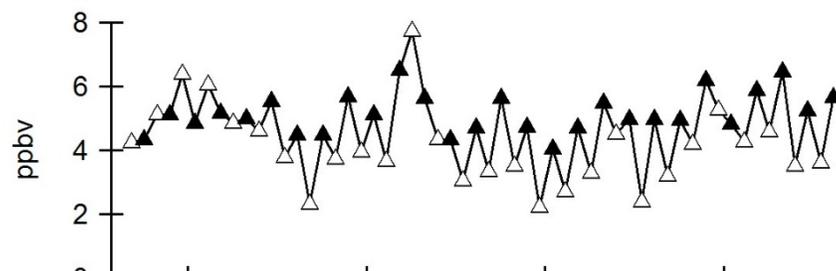
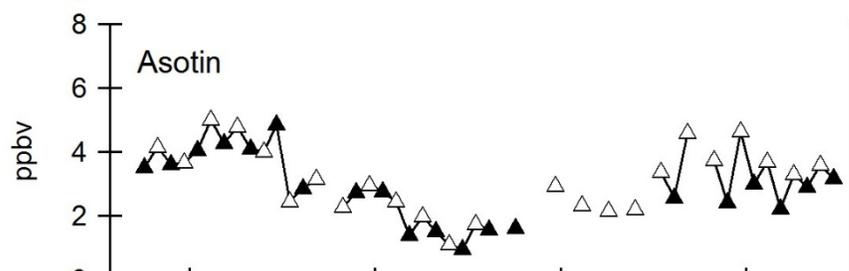
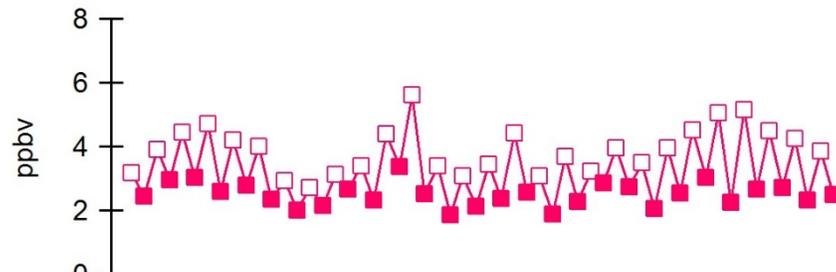
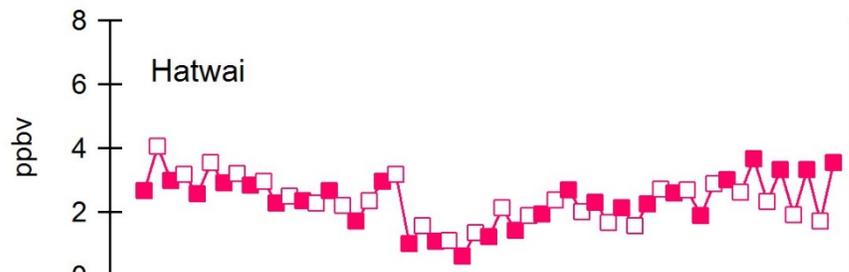
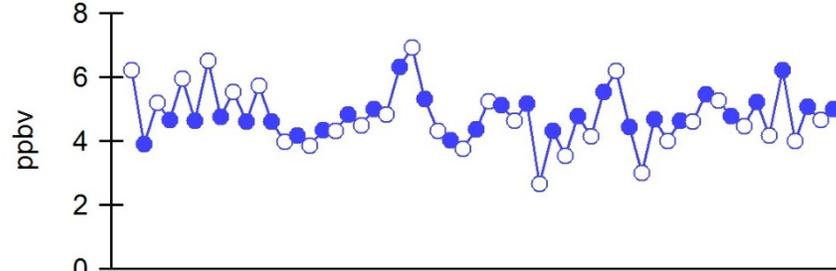
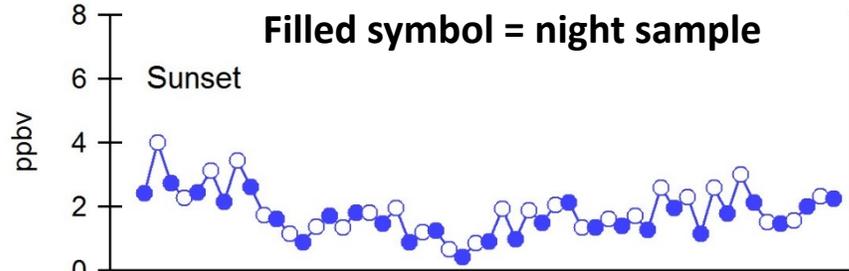
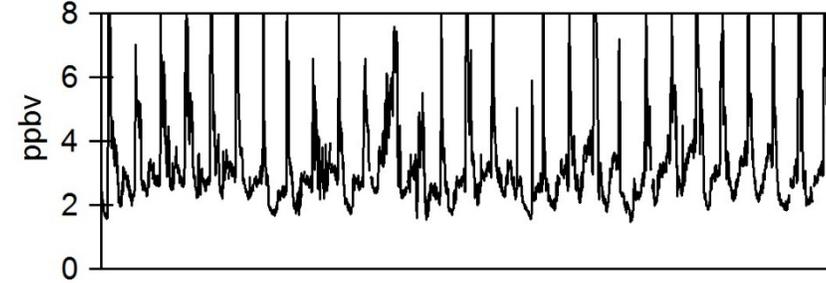
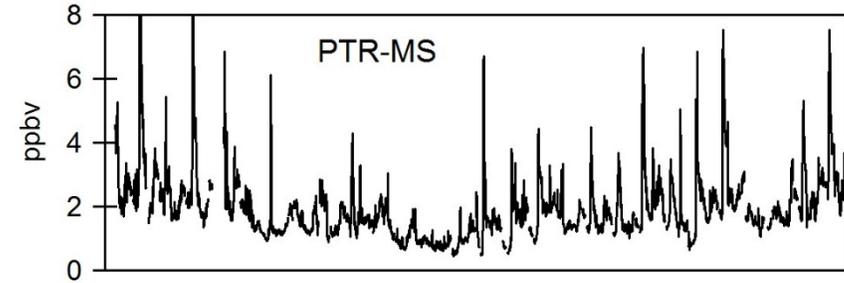
Agreement generally good.
Issue with HCHO in 2017

2016

Formaldehyde

2017

Day-Night Differences at Satellites Sites



7/1/2016 7/8/2016 7/15/2016 7/22/2016

7/7/2017 7/14/2017 7/21/2017 7/28/2017

July 2006 > 12 ppbv
average all sites

Higher day time in 2017:
photochemical HCHO?

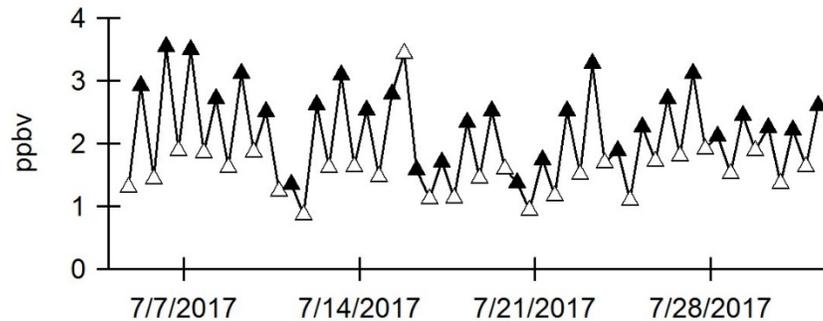
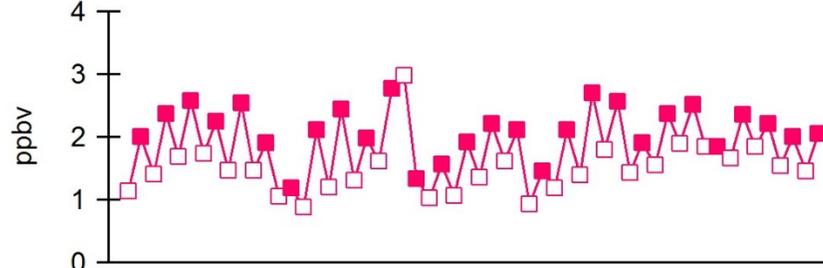
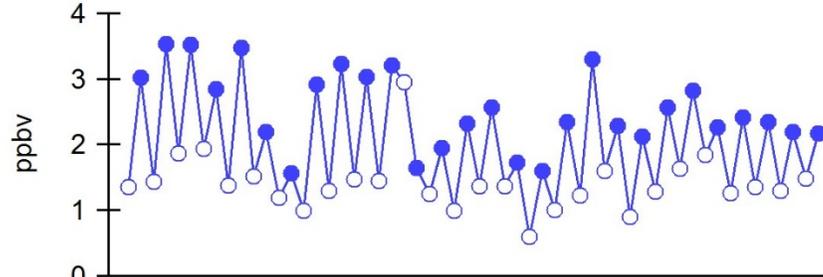
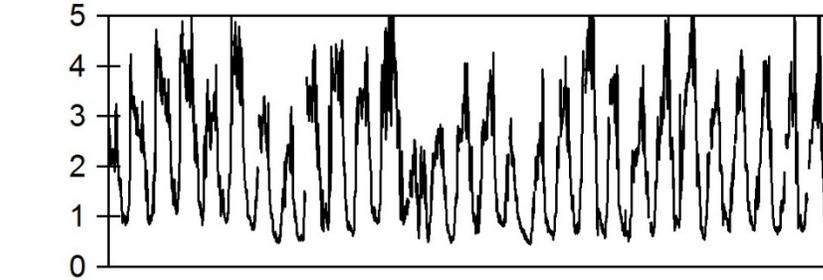
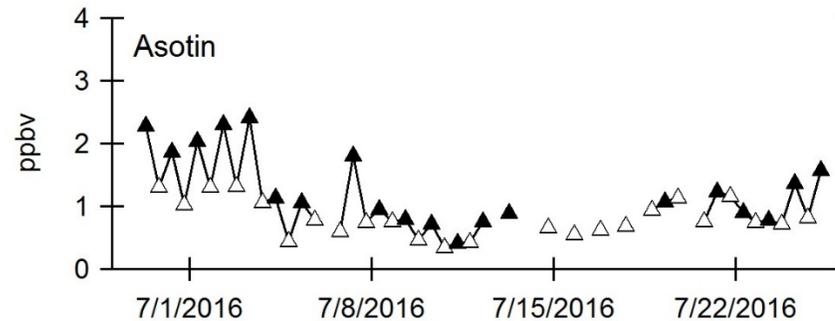
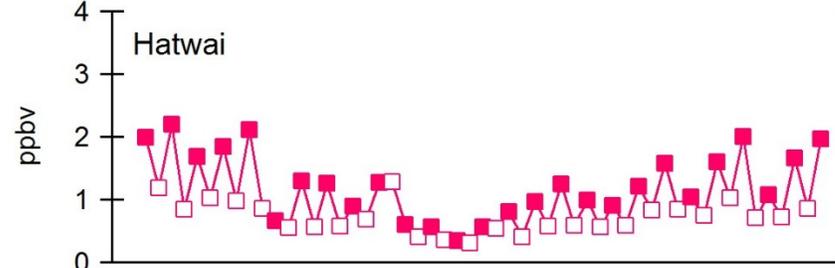
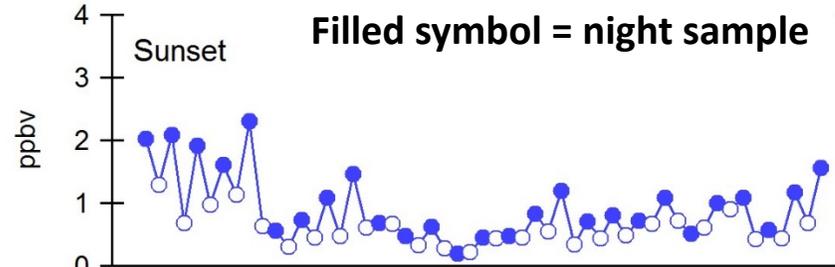
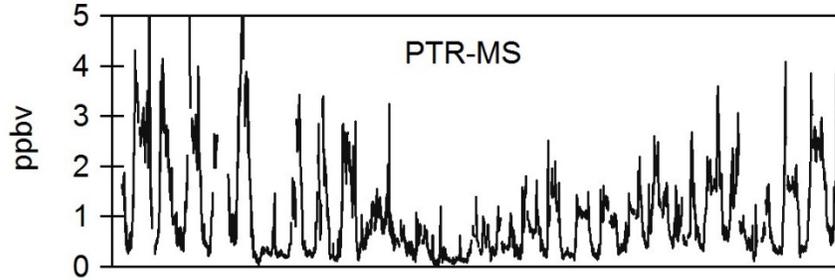
Higher night time in
2017

2016

Acetaldehyde

2017

Day-Night
Differences at
Satellites Sites



July 2006 > 6 ppbv
average all sites

Higher at night
typical for all
sites.

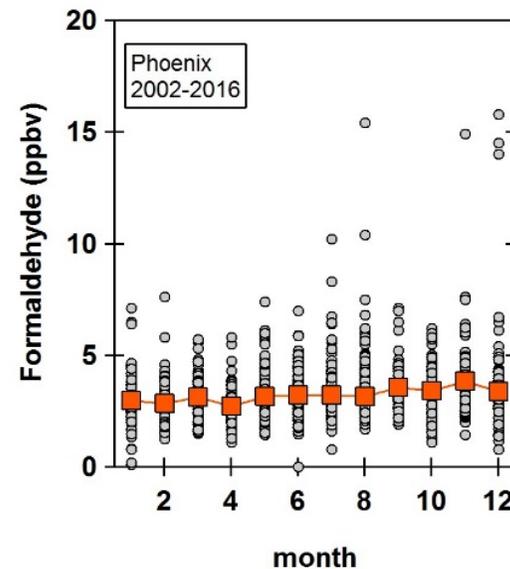
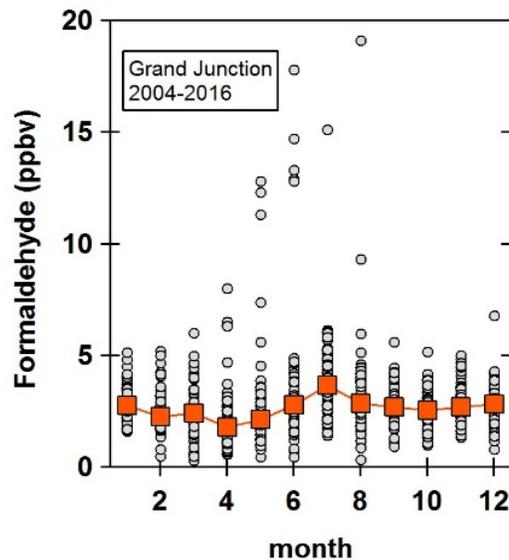
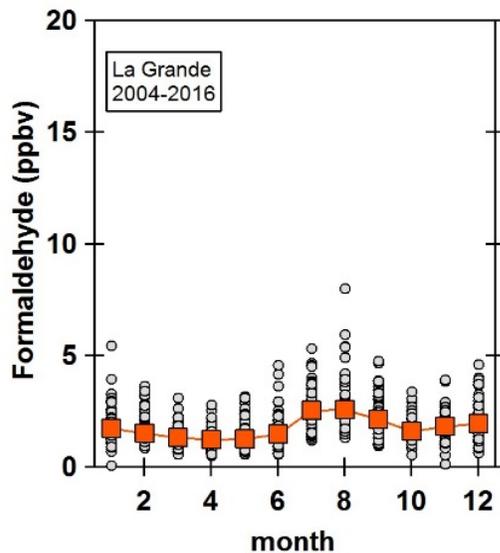
Surface emissions
from vegetation?

Formaldehyde

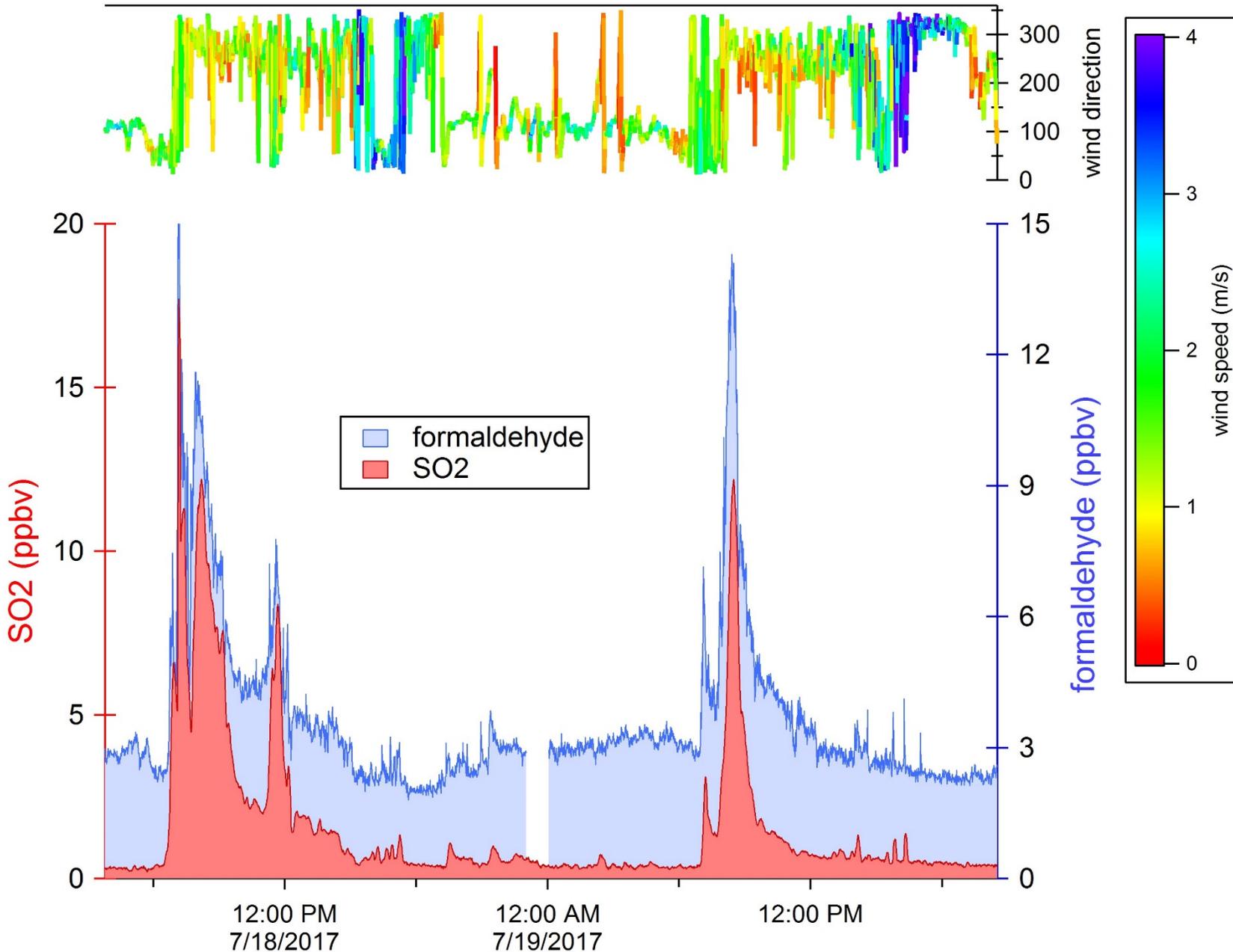
Year	Asotin	Hatwai	Sunset Park	Site Average	Sunset Park (PTR-MS)
2016	2.97 ± 1.00	2.35 ± 0.75	1.71 ± 0.66	2.35 ± 0.95	1.97 ± 1.09
2017	4.63 ± 1.11	3.19 ± 0.91	4.64 ± 1.00	4.20 ± 1.20	3.28 ± 1.67

Acetaldehyde

Year	Asotin	Hatwai	Sunset Park	Site Average	Sunset Park (PTR-MS)
2016	1.20 ± 0.77	0.99 ± 0.50	0.82 ± 0.48	0.94 ± 0.51	1.03 ± 1.01
2017	2.02 ± 0.70	1.79 ± 0.51	2.03 ± 0.71	1.93 ± 0.68	2.10 ± 1.21



Formaldehyde data from selected NATTS sites.



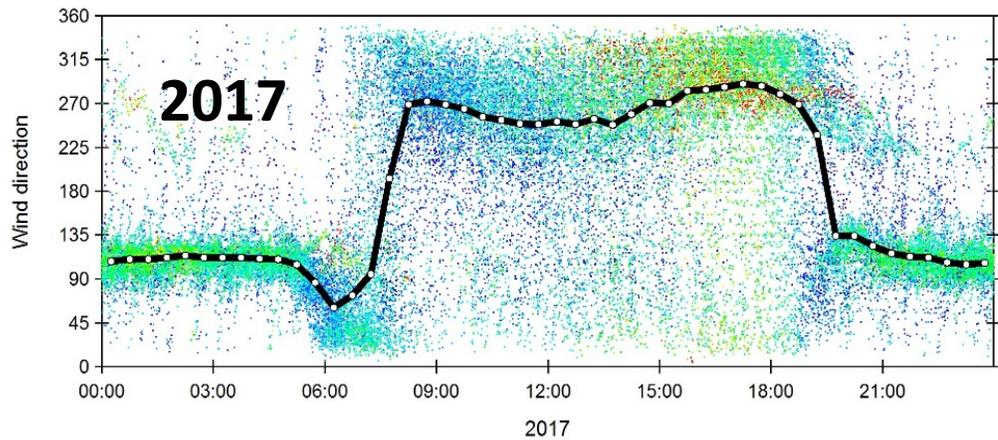
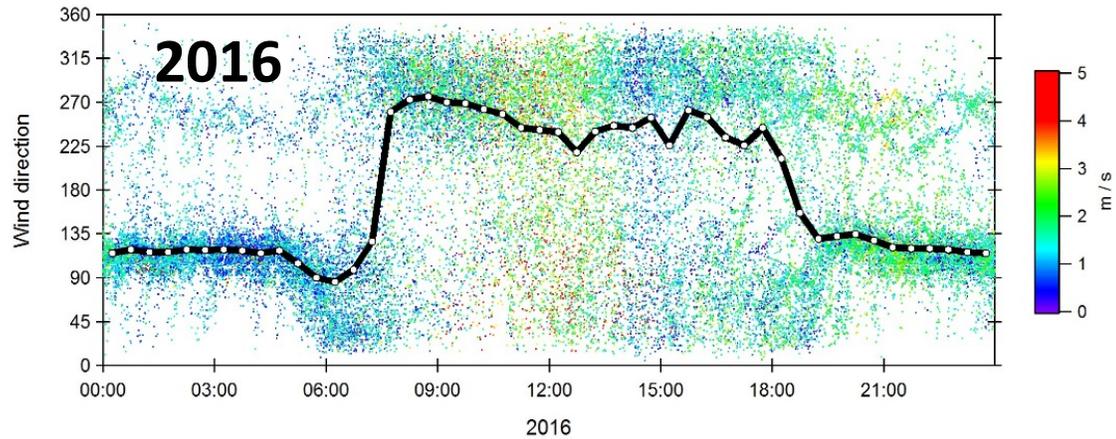
Formaldehyde well correlated in time with SO₂.

Morning peaks associated with light wind speeds and change in wind direction.

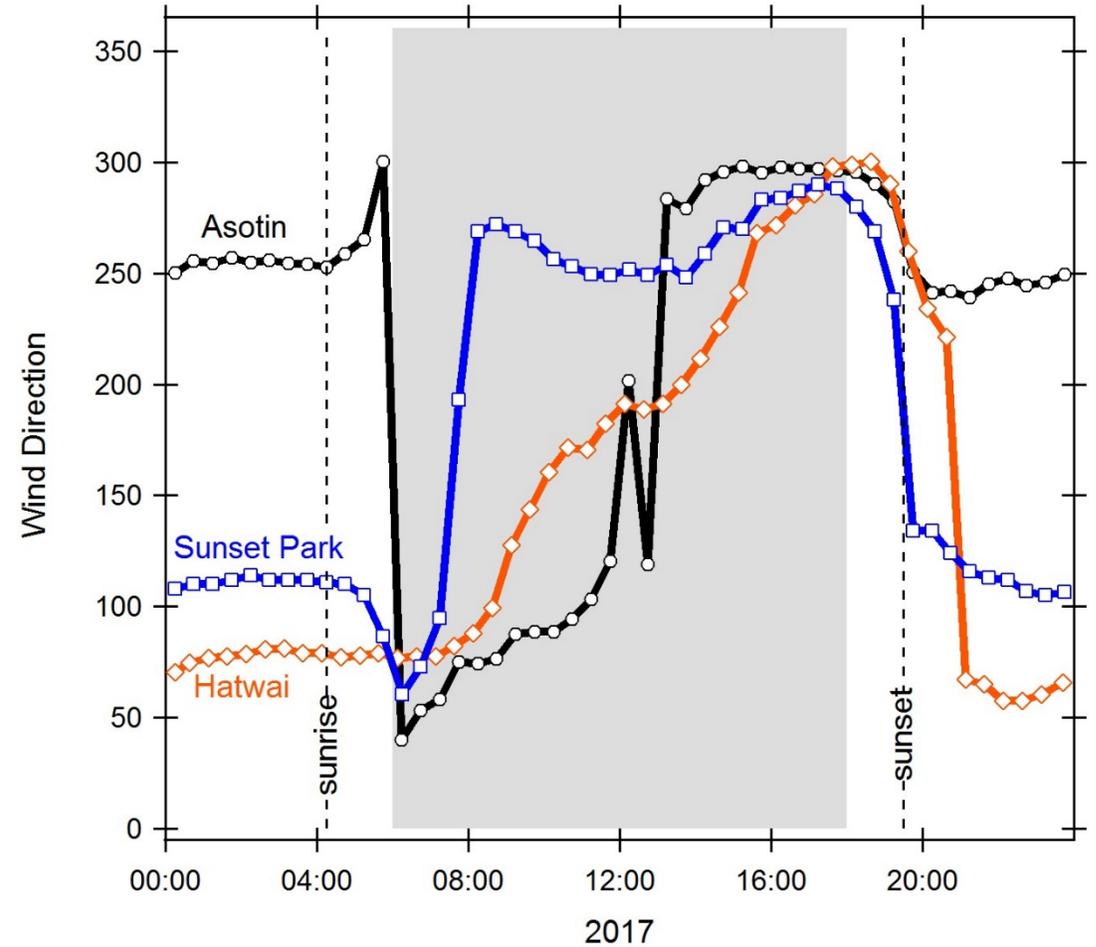
Sampling pulp mill emissions.

Sunset Park Data

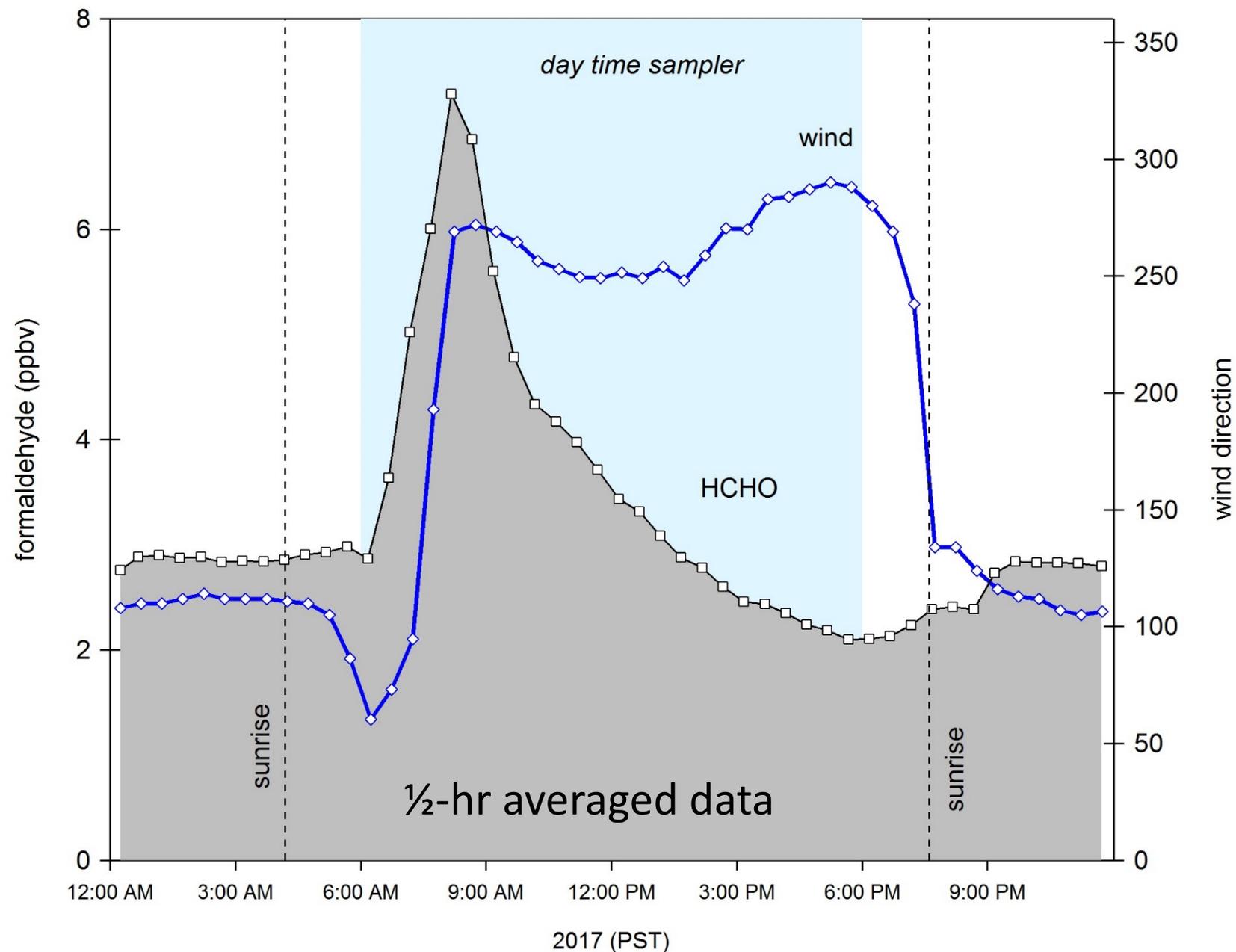
Regular wind pattern



2017 All Sites



Time of Day Formaldehyde Variation



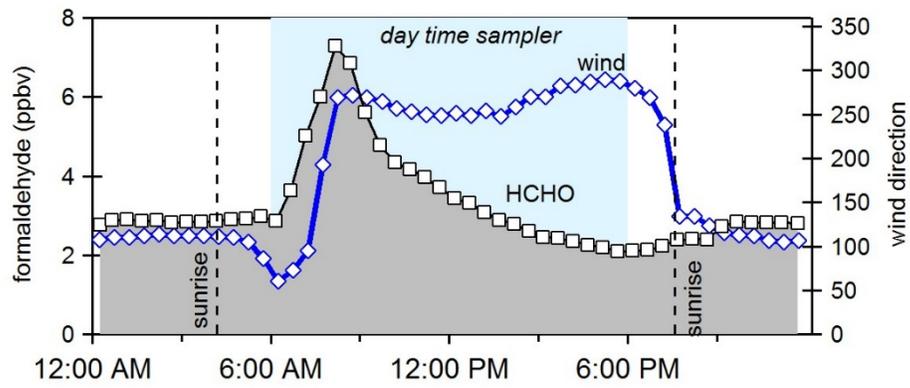
Morning *fumigation* of surface from pulp mill effluent as stable nocturnal boundary layer breaks up – mixing down of pollutants from above creates a morning peak ~ 8:00 PST.

Lowest formaldehyde occurs in the late afternoon – PBL expands till late in the afternoon.

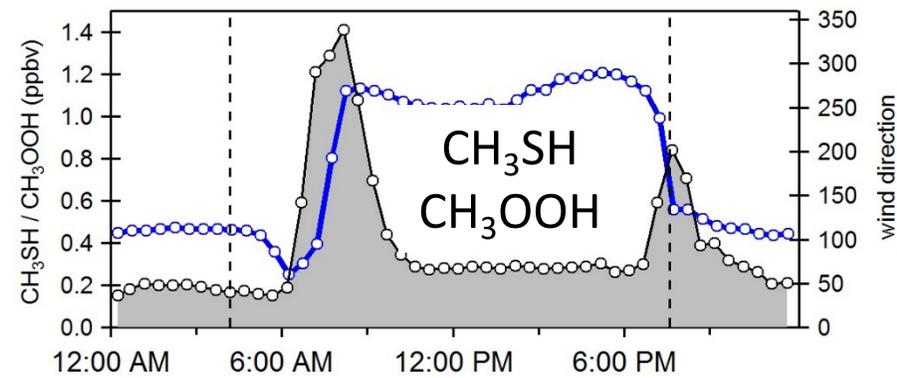
PTR-MS:

Day avg = 3.8 ± 1.5

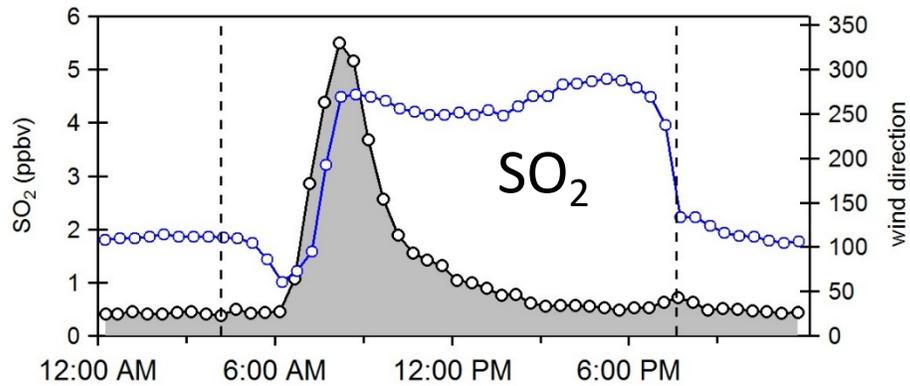
Night avg = 2.7 ± 0.2



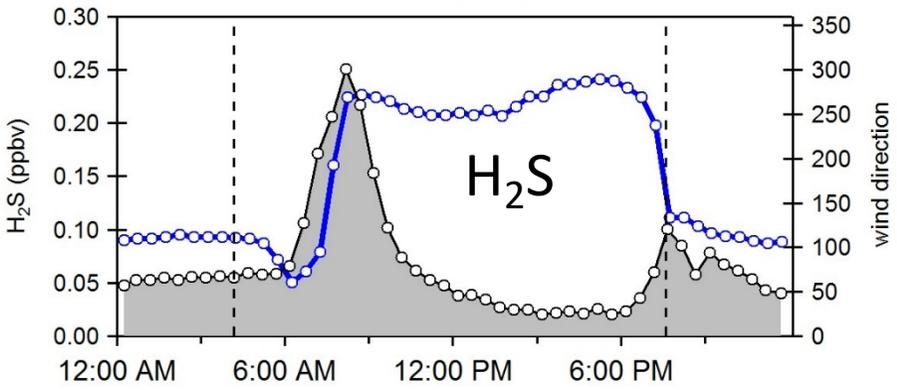
2017 (PST)



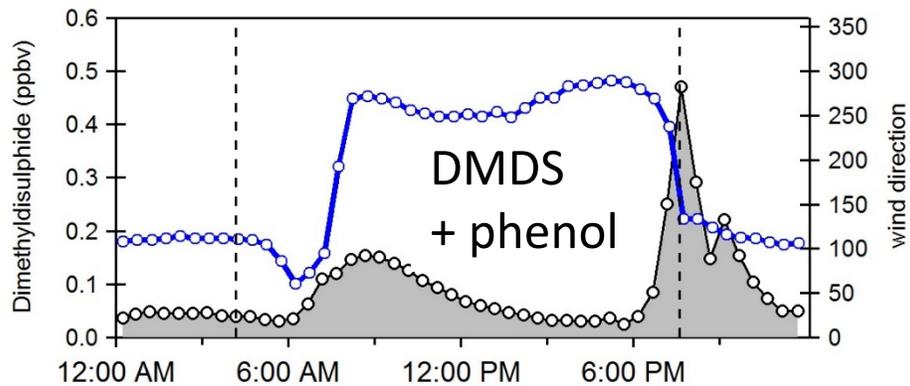
2017 (PST)



2017 (PST)



2017 (PST)

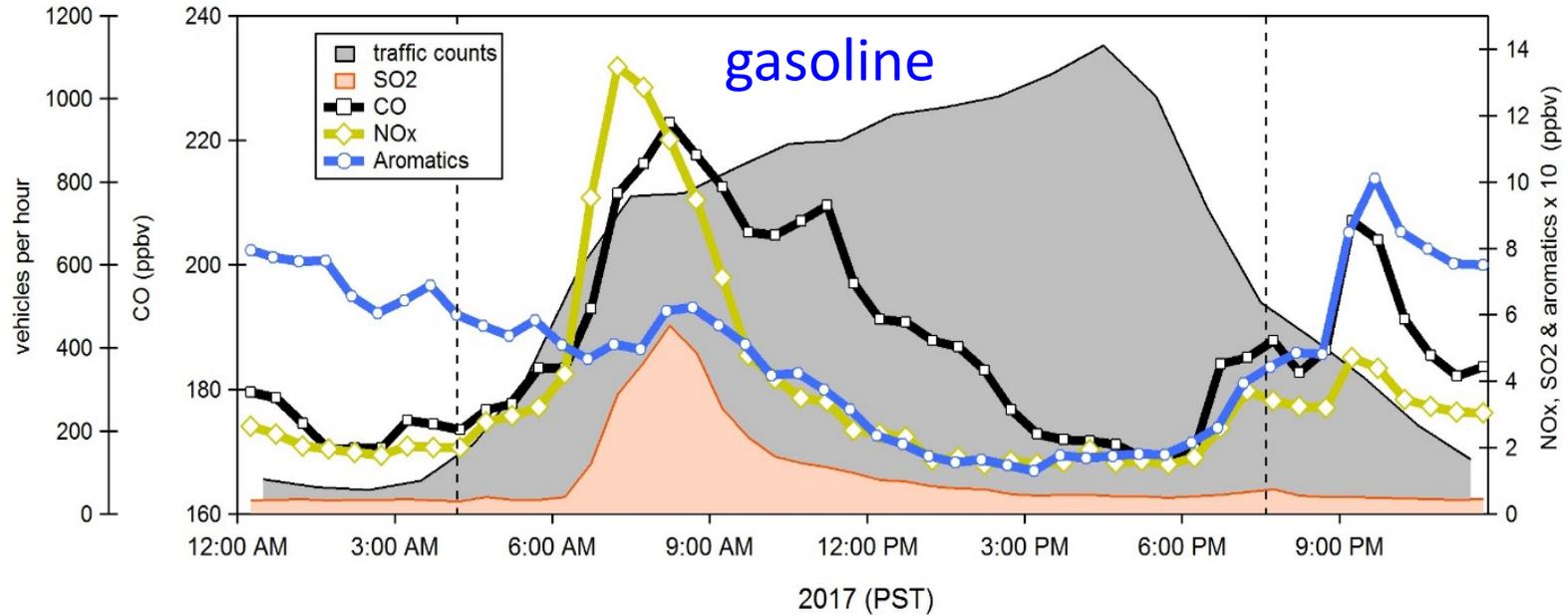


2017 (PST)

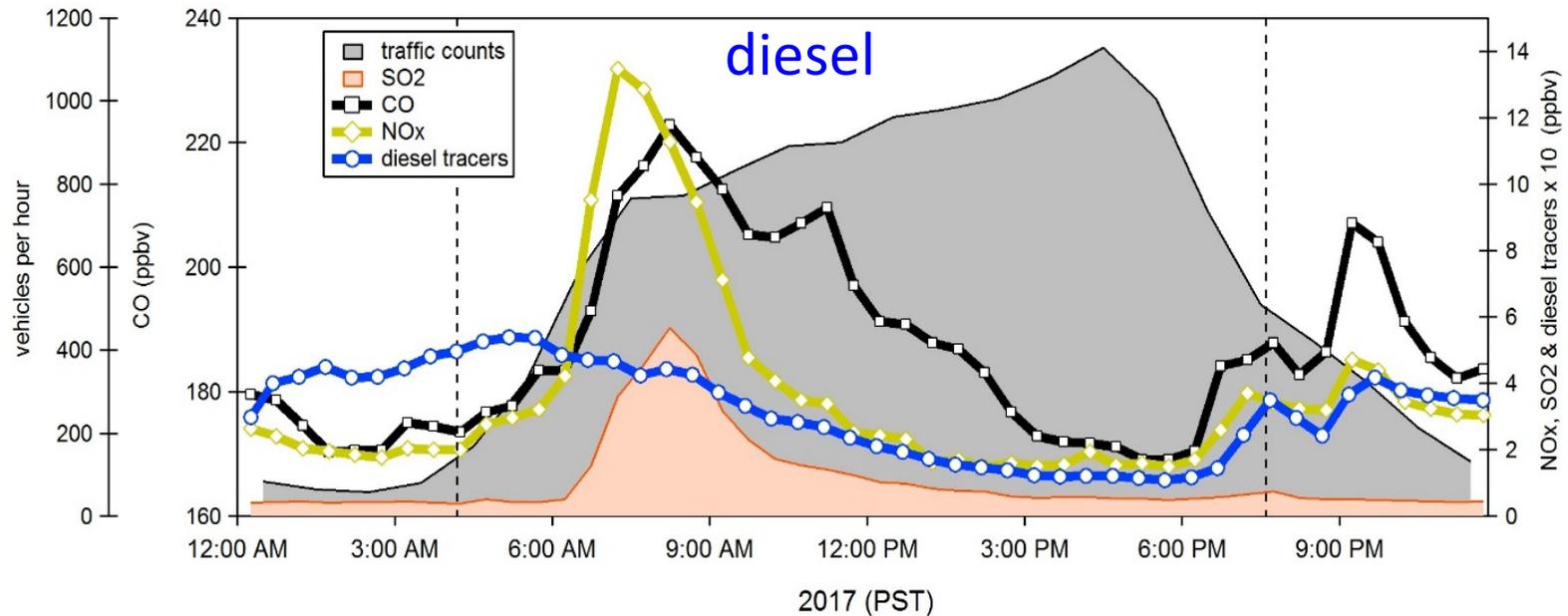
All S-compounds display a morning peak. Some compounds had an evening peak.

Formaldehyde well correlated with SO₂ but not reduced sulfur compounds.

Motor Vehicle Traffic Tracers

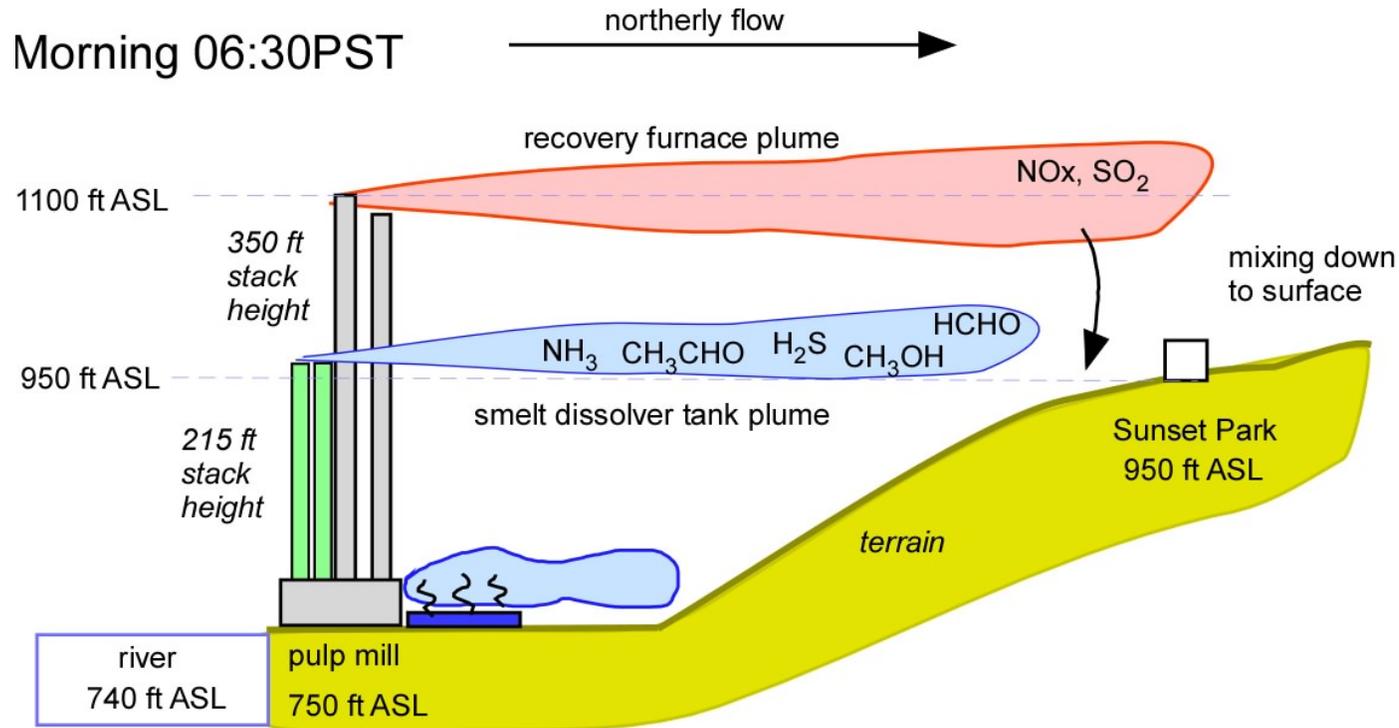


No obvious impact of vehicle emissions on early morning concentrations of VOCs.



Pulp mill emissions obscure morning rush hour signature.

Pulp Mill Sources



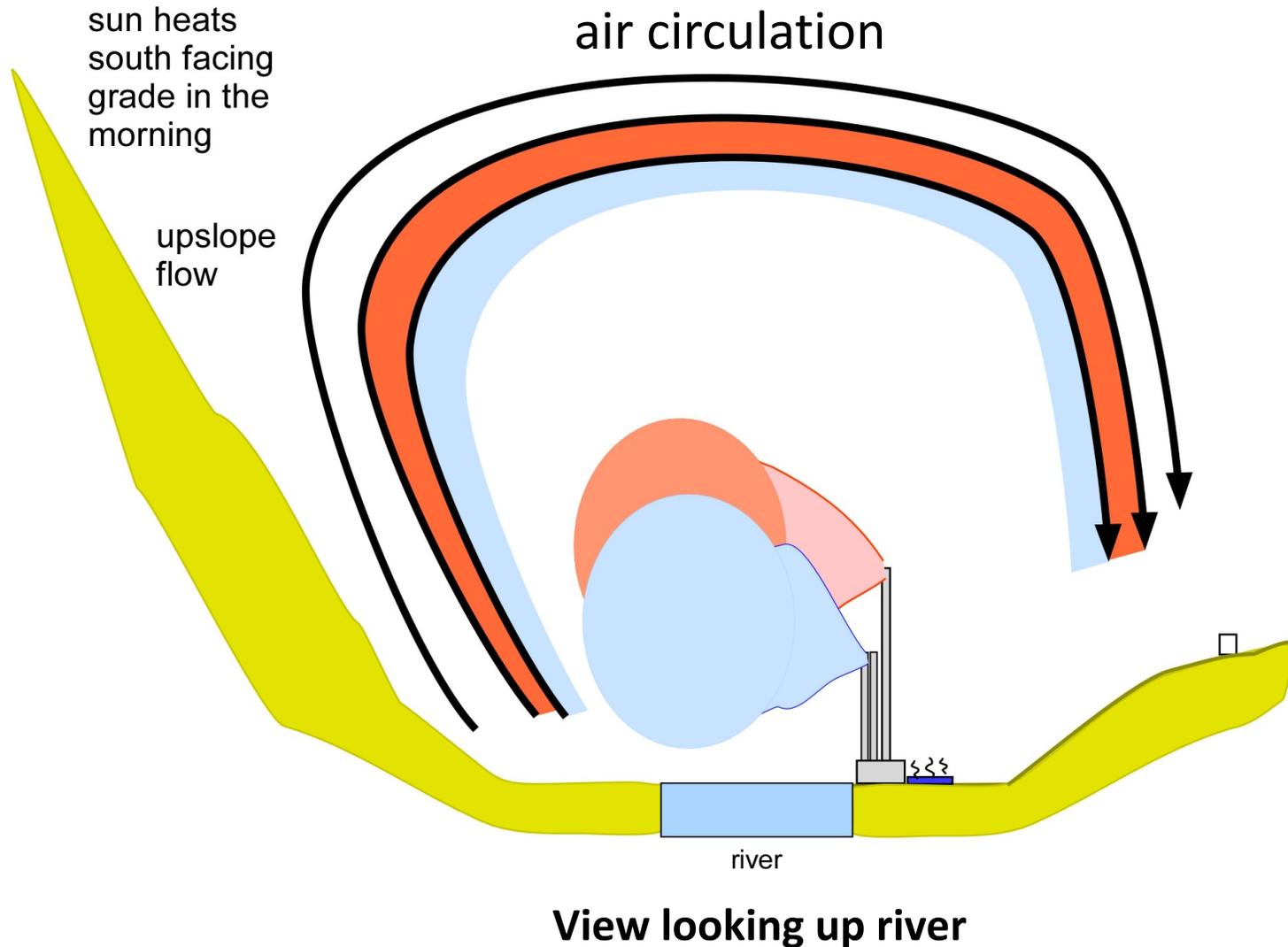
2014 Emissions Inventory of Lewiston Clear Water pulp mill

- 1. Recovery furnace plume** (burns black liquor) – largest source of NO_x and SO₂
- 2. Smelt dissolver tank** – major source of HCHO & CH₃CHO, H₂S, methanol, ...

Formaldehyde and SO₂ emitted from different stacks

Valley wind circulation in the morning

Bader, D.C., C.D. Whiteman, Numerical simulation of cross-valley plume dispersion during the morning transition period, *J. Applied Meteorology*, 28, 652-664, 1989.



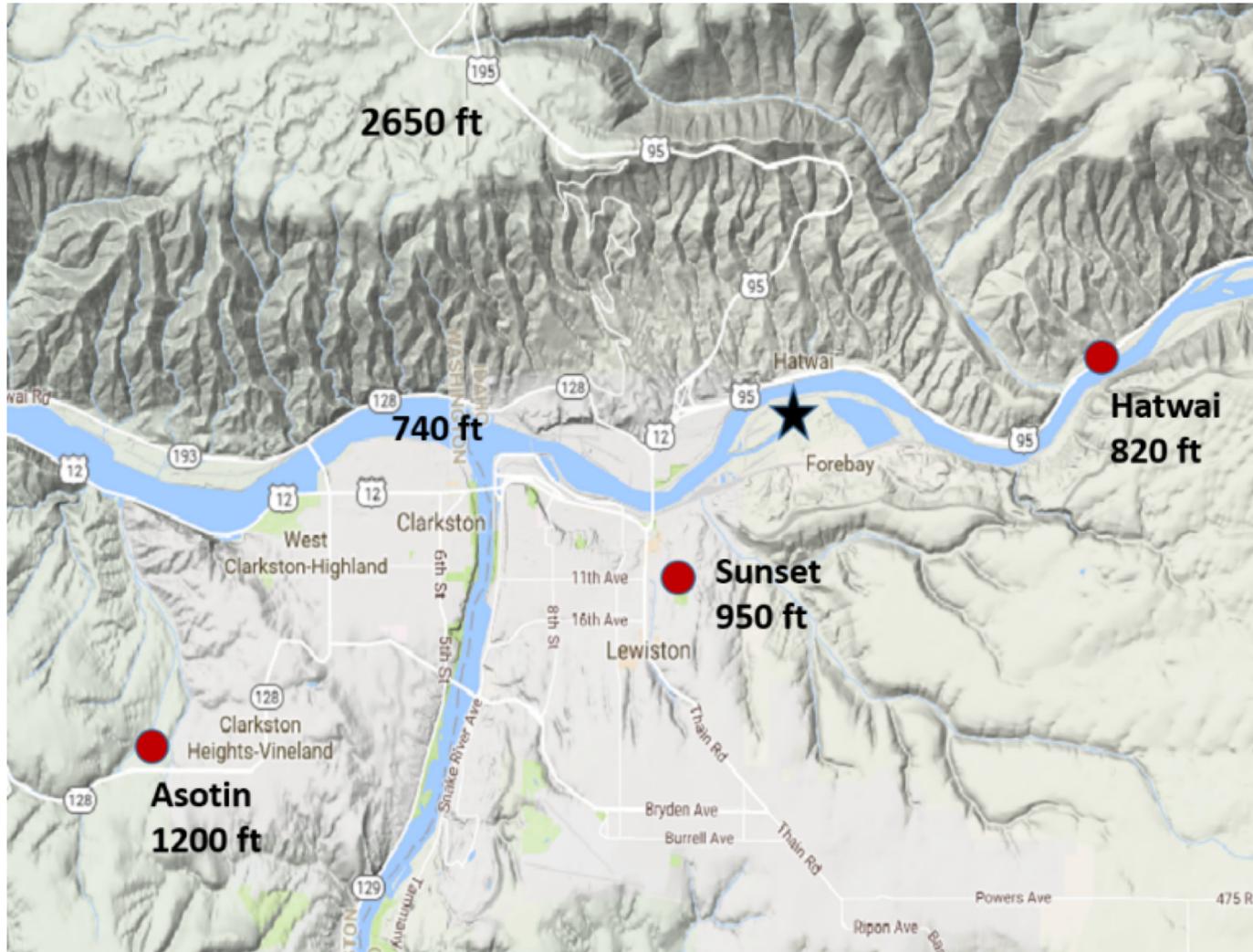
Erosion of stable nocturnal boundary layer by mid-valley subsidence

At night pulp mill plume flows down river under drainage flow conditions.

In the morning, heating the Lewiston grade causes upslope flow and subsidence of plume to central portion of the valley.

Mechanism for dispersing plume in the morning.

Lewiston-Clarkston Valley



14 miles

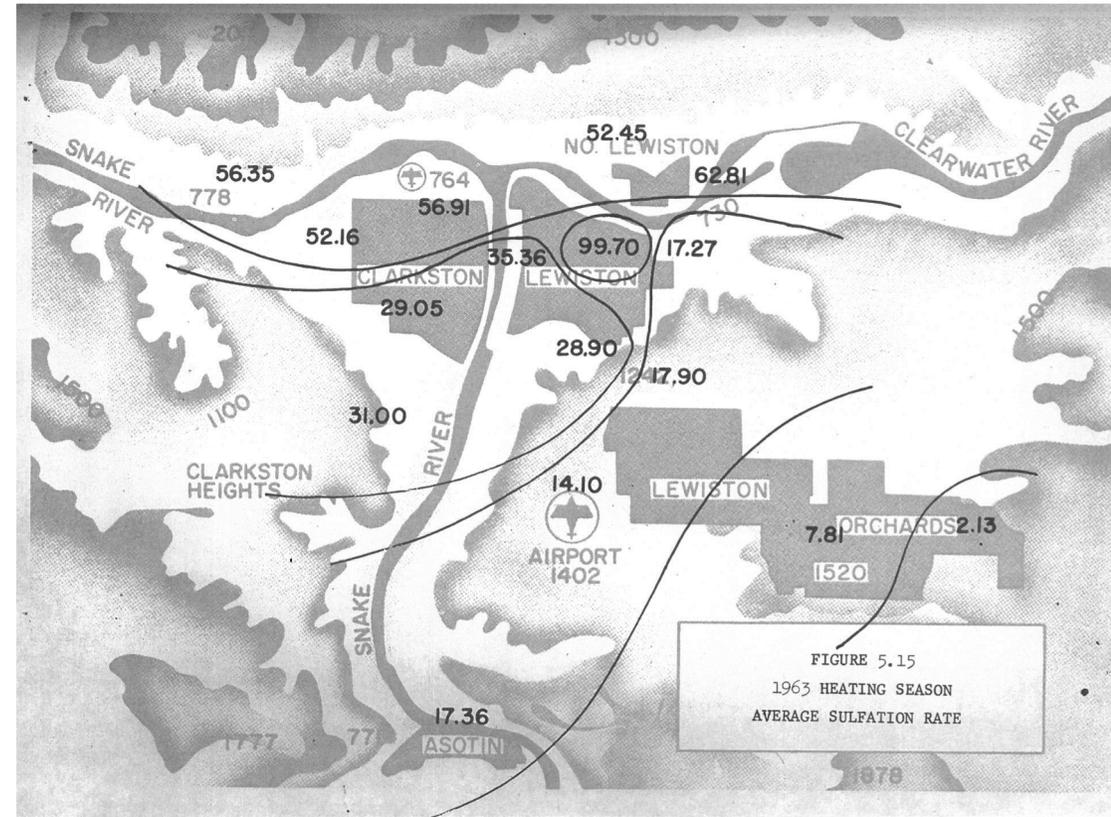
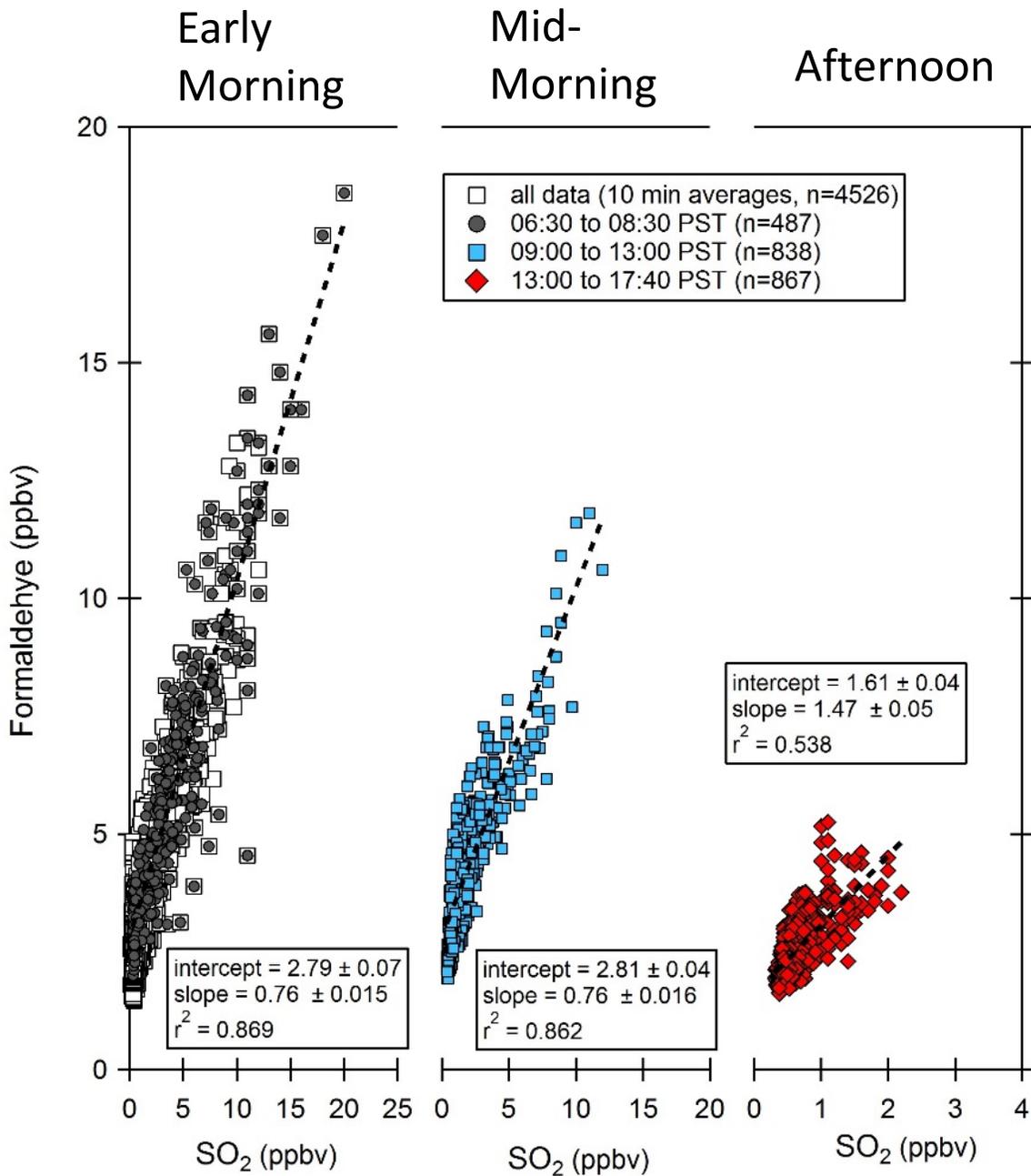


FIGURE 5.15
1963 HEATING SEASON
AVERAGE SULFATION RATE

Data from 1963 on S-compounds



Formaldehyde Correlation with SO₂

*Early and mid-morning ratio similar
HCHO-to-SO₂ molar ratio = 0.76 ± 0.02*

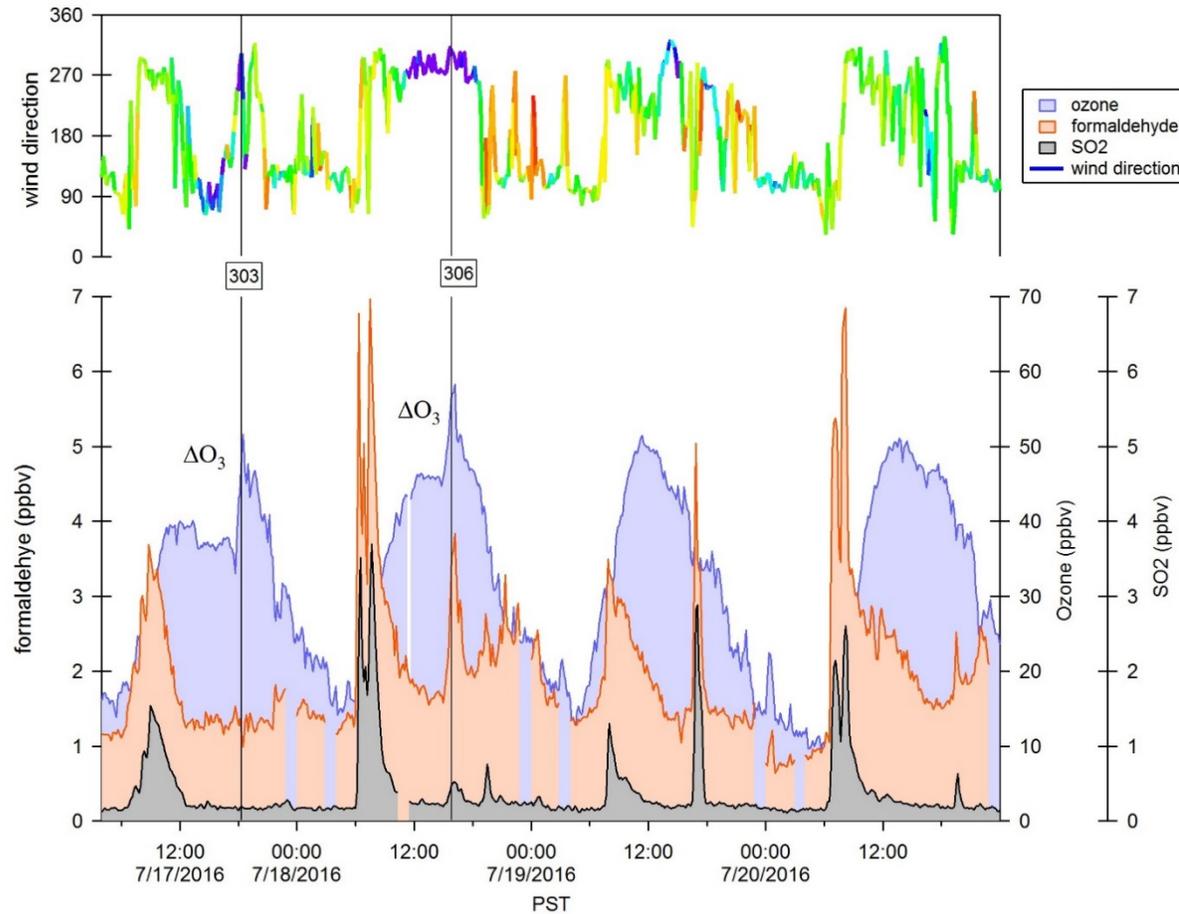
2014 Emissions Inventory = 0.40

*Observed ratio twice as much as listed in
2014 EI for this facility.*

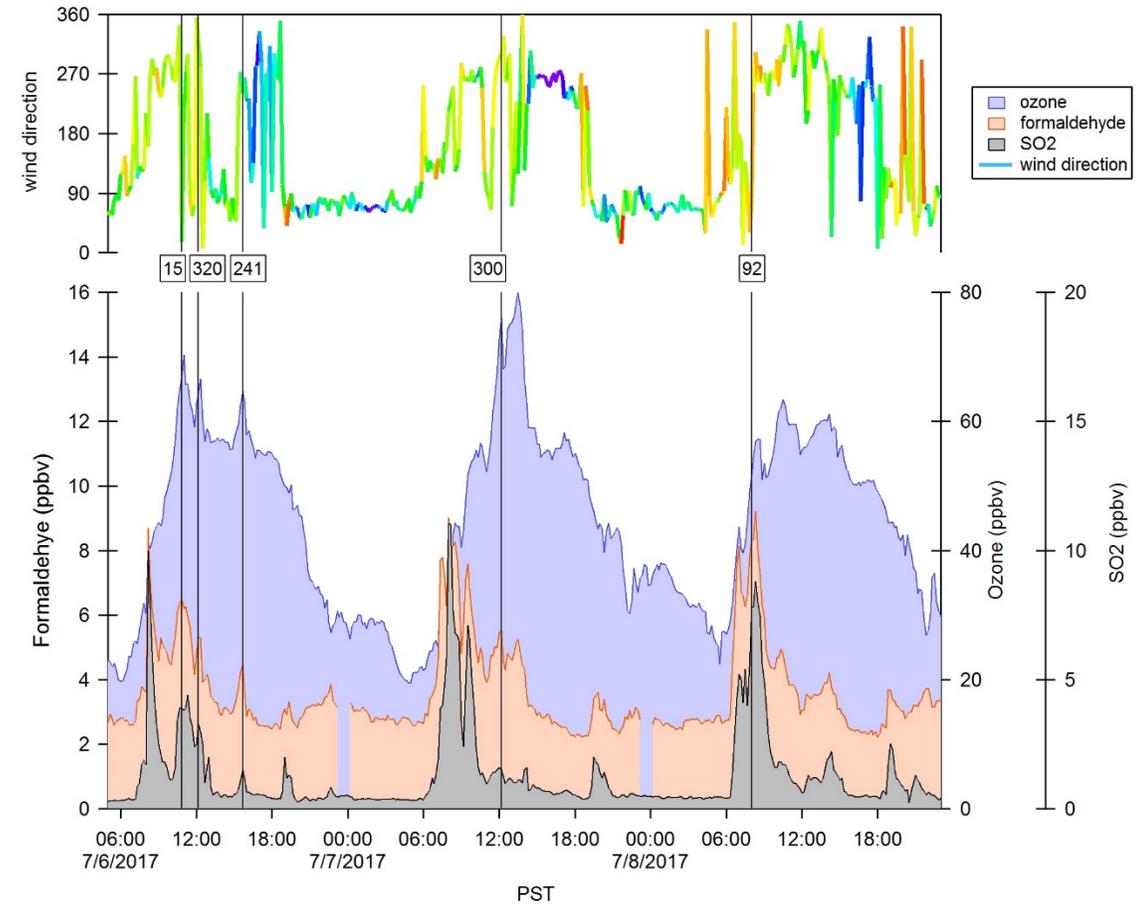
Ozone

Afternoon ozone highly variable suggesting gradients in the valley
Plume mill plume making ozone?

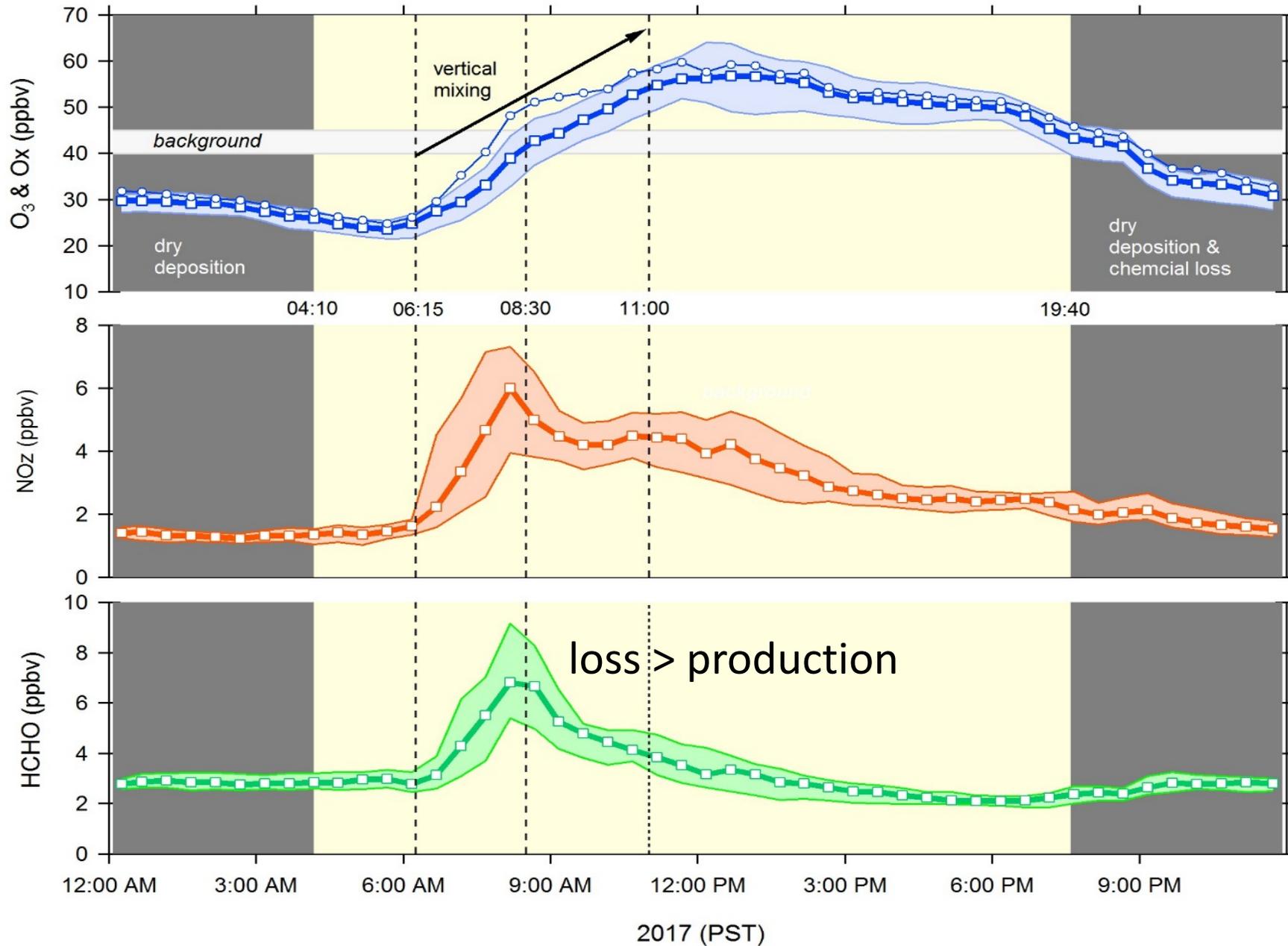
2016



2017



2017 Secondary Pollutants



Potential NH₃ interference in the morning?

CONCLUSIONS

1. Average formaldehyde levels much lower than observed in summer 2006. Average levels ~ typical of western small town NATTS sites.
2. High levels of formaldehyde observed in the morning ~ 08:00 PST associated with pulp mill emissions (SO₂, mercaptans).
3. Acetaldehyde also lower than in summer 2006. Highest at night – implies surface emission source.
4. PTR-MS measurements of formaldehyde and acetaldehyde generally in good agreement with DNPH (within 20%) with exception of 2017 formaldehyde data. Reason for difference not determined.
5. No strong evidence of LC-Valley airshed production of secondary formaldehyde. Formaldehyde may be produced in the pulp mill plume as it travels up valley during the day to Hatwai and Nez Perce tribal lands.

ACKNOWLEDGEMENTS

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