Lewiston-Clarkston Valley Formaldehyde Study 2016-2017

Julie Simpson, Nez Perce Tribe
Tom Jobson, Washington State University
Rong Li, Idaho Department of Environmental Quality

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Community-Scale Air Toxics Study 2006-2007

Toxics Monitoring Around a Kraft Pulp and Paper Mill in Lewiston, Idaho

24 h samples; EPA's one in six day sampling schedule; 5/1/2006-4/30/2007

Particulate metals
PM10 Hi-Vol.
Quartz microfiber filters
EPA method IO-3.5

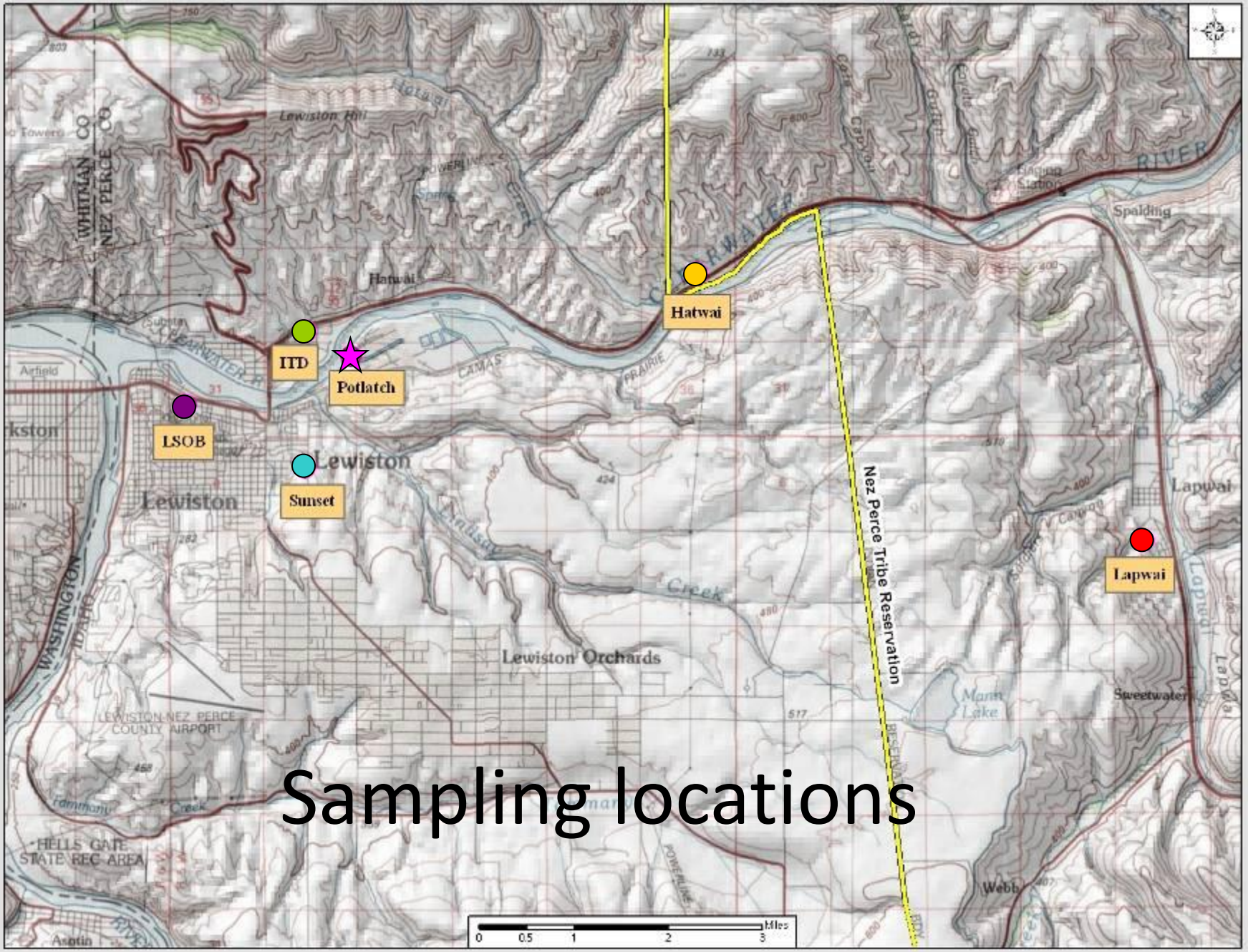
Arsenic, beryllium, cadmium, chromium, lead, manganese, nickel

Volatile Organic Compounds
ATEC 2200 sampler
canisters
EPA method TO-15

Benzene, carbon tetrachloride, chloroform, 1,3-butadiene, 1,2-dichloropropane, methylene chloride, tetrachloroethylene, trichlororethylene, vinyl chloride

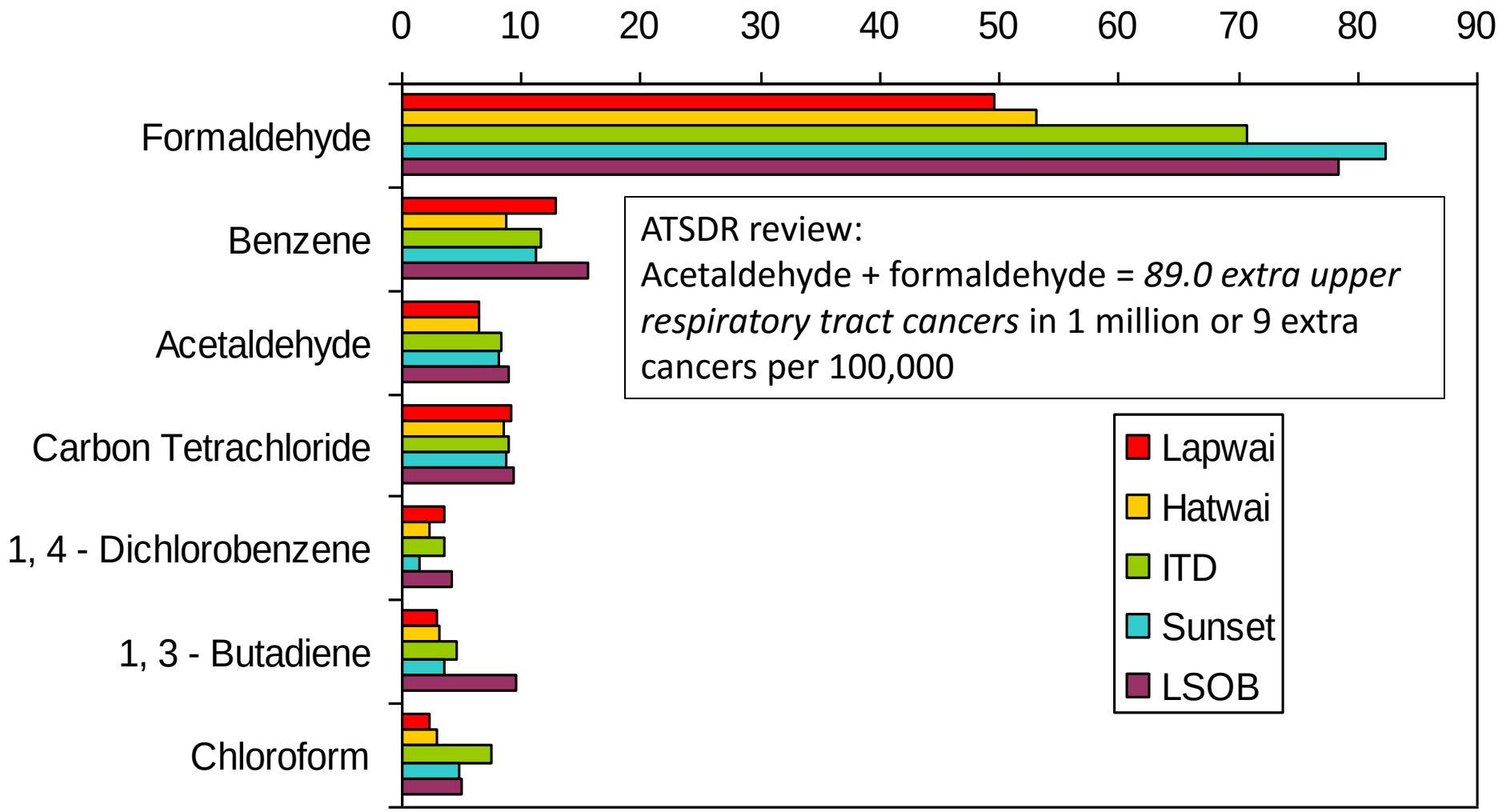
Carbonyls
ATEC 2200 sampler
DNPH cartridges
EPA method TO-11A

Formaldehyde, Acetaldehyde

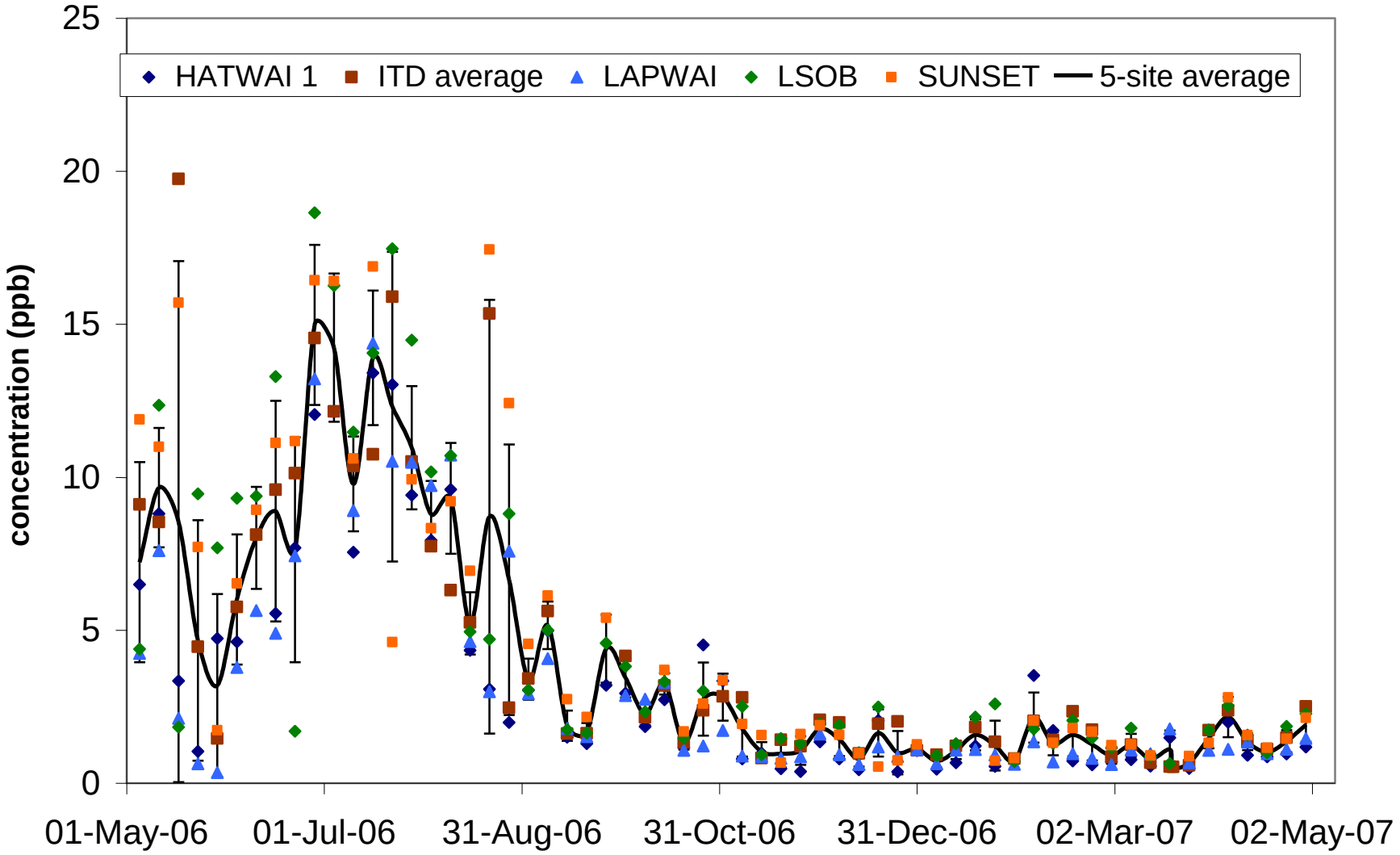

Hatwai
ITD
Potlatch
LSOB
Sunset
Lapwai
Lewiston
Lewiston Orchards
Nez Perce Tribe Reservation
Spalding
Sweetwater
Webb
Asotin
Sampling locations

Relative Risk Rank

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



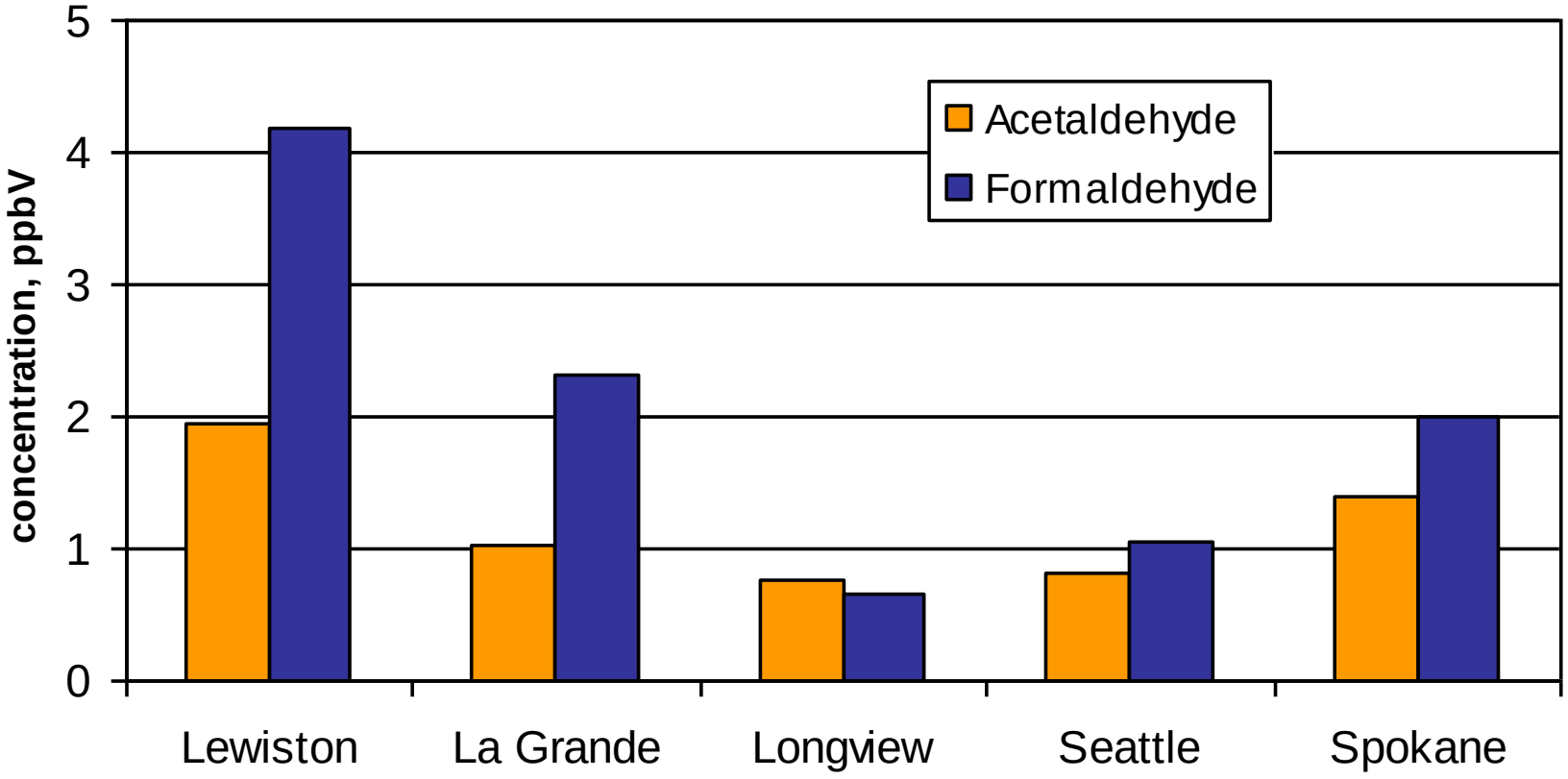
Formaldehyde Time Series

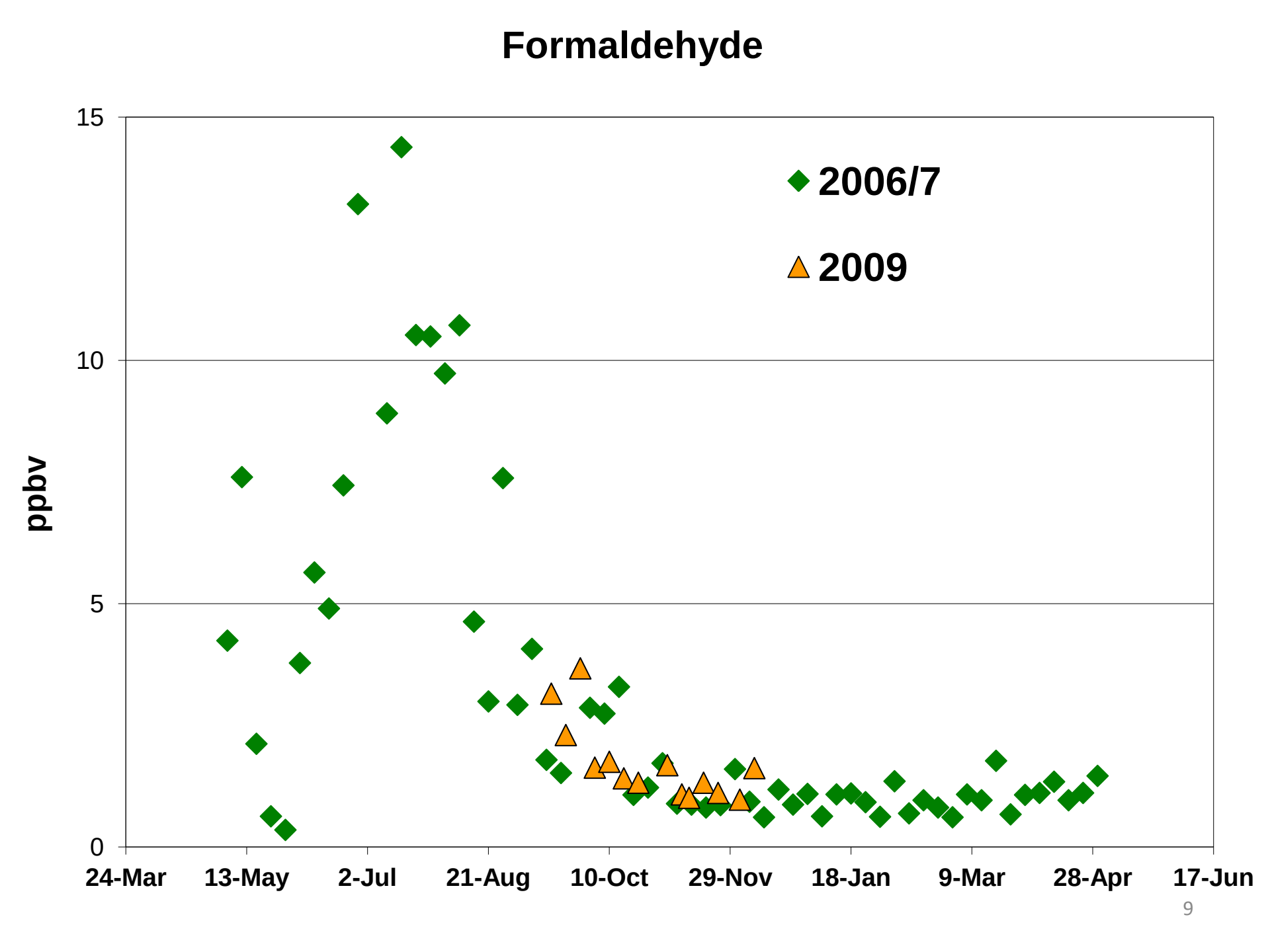


Regional Comparison

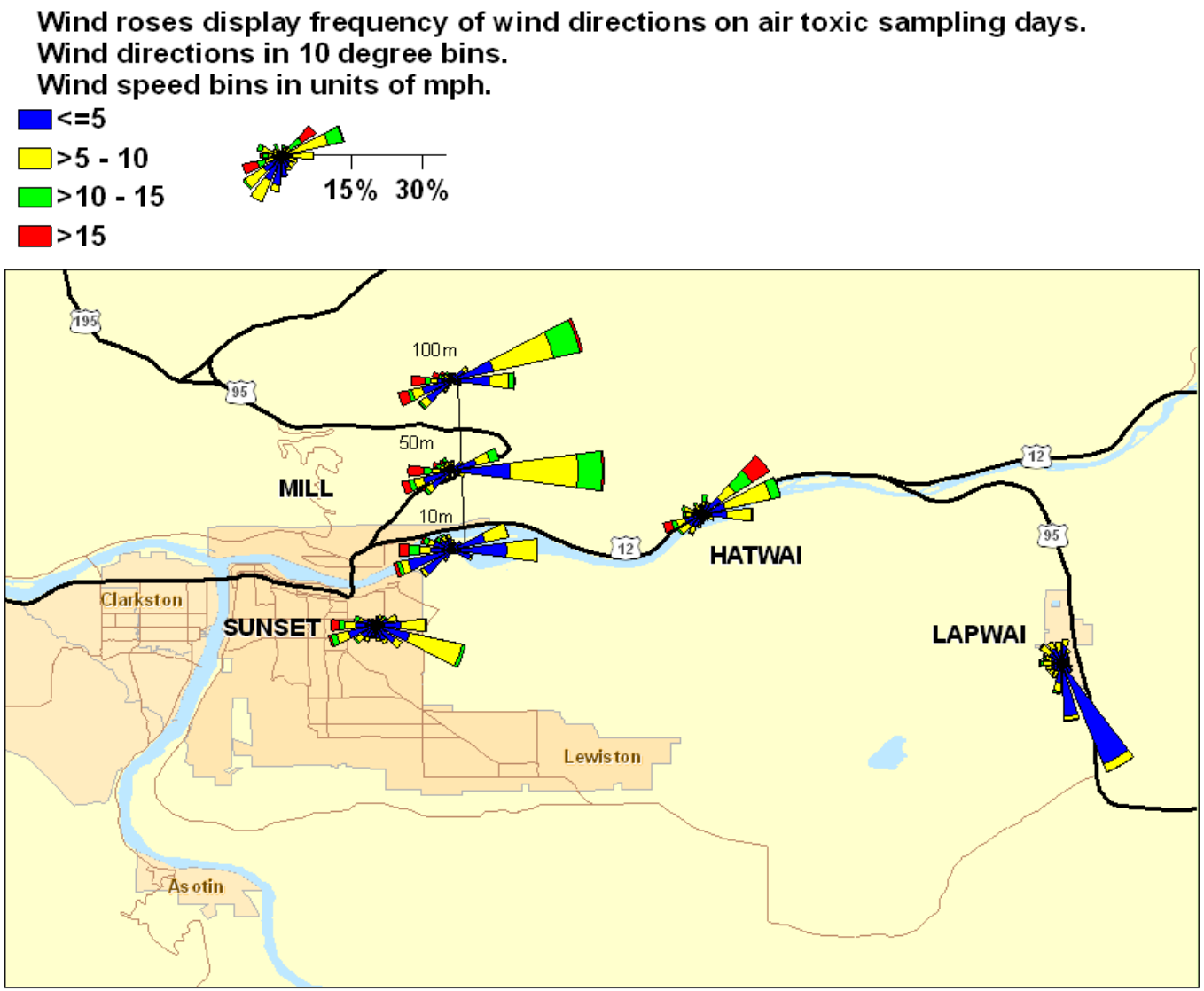
La Grande, OR May 2006-April 2007 rural NATTS site
Longview, WA May 2004-May 2005 Pulp & paper, urban setting
Seattle, WA 2005
Spokane, WA 2005

Carbonyls


concentration, ppbV
0
1
2
3
4
5
Acetaldehyde
Formaldehyde
Lewiston
La Grande
Longview
Seattle
Spokane


Formaldehyde
15
10
5
0
ppbv
2006/7
2009
24-Mar
13-May
2-Jul
21-Aug
10-Oct
29-Nov
18-Jan
9-Mar
28-Apr
17-Jun

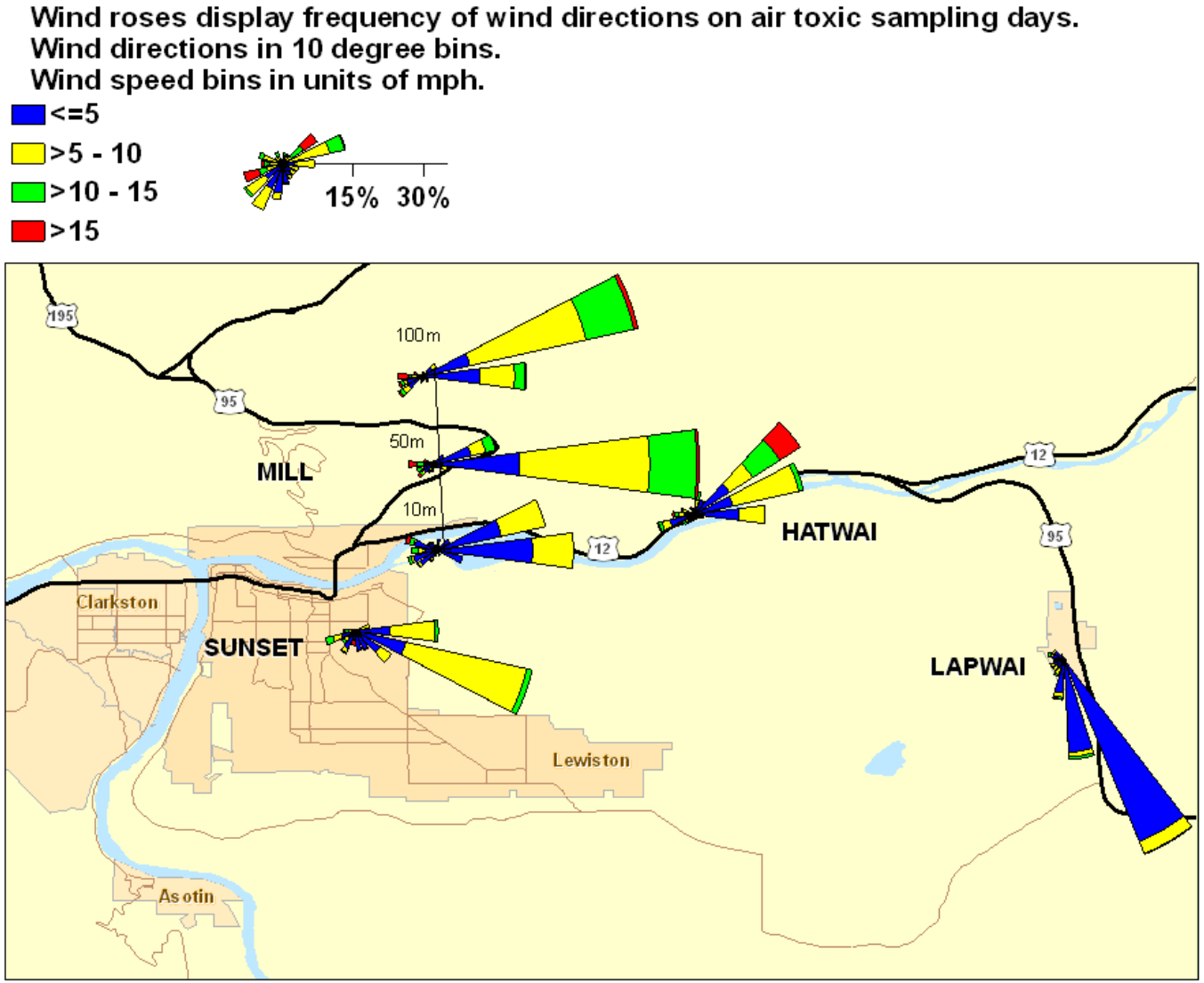
24-hr Wind Roses Map



Winds are aligned along valleys. Topography is channeling the winds up and down the river valleys.

Most winds are low (<10 mph).

Nighttime Wind Roses (9 p.m. to 5 a.m.)



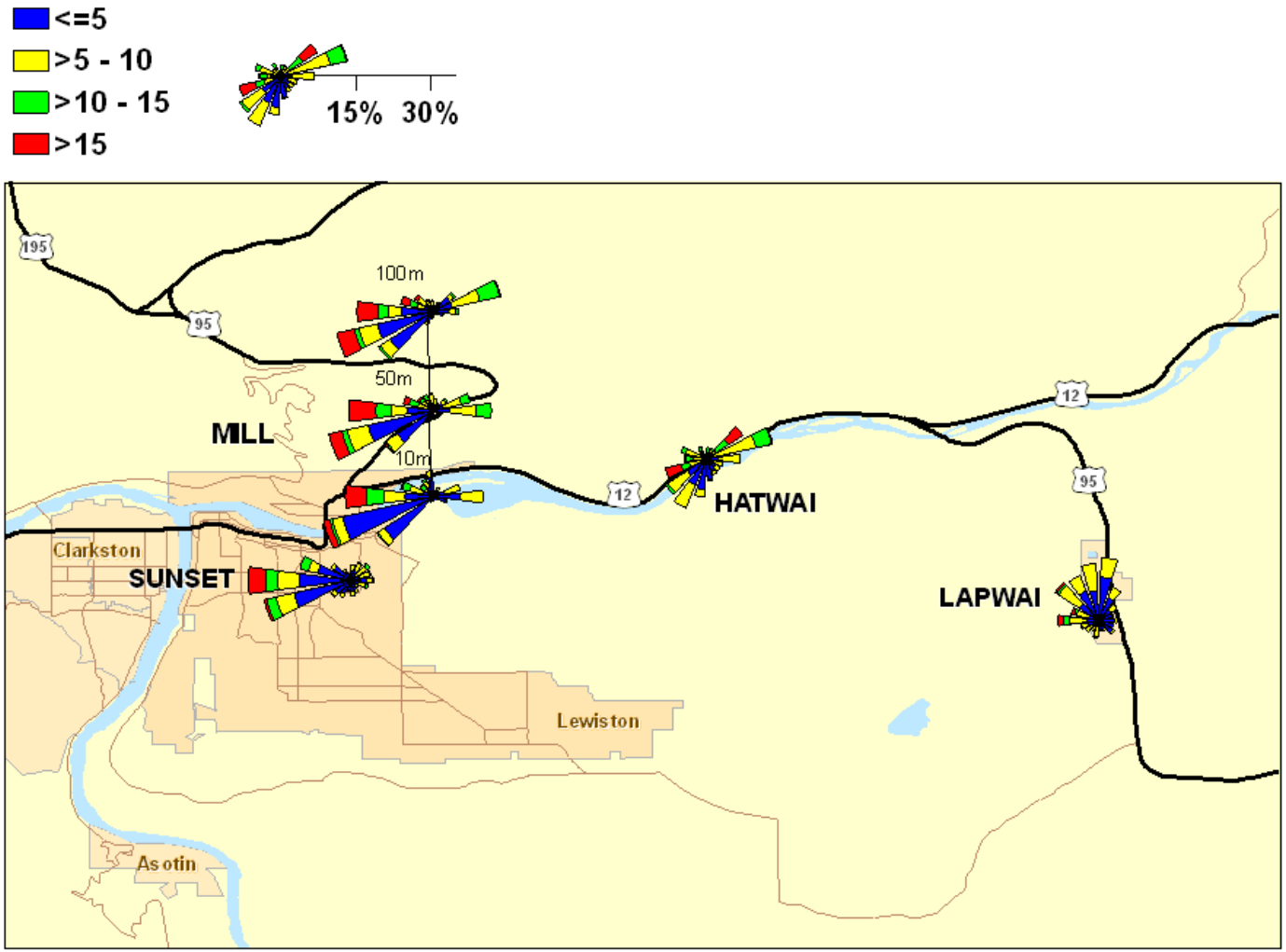
Nighttime winds are from the east (south for Lapwai).

Wind speeds are low.

Overall, winds flow upslope during the day and downslope during the night. This is classic drainage flow.

Daytime Wind Roses (9 a.m. to 5 p.m.)

Wind roses display frequency of wind directions on air toxic sampling days.
Wind directions in 10 degree bins.
Wind speed bins in units of mph.

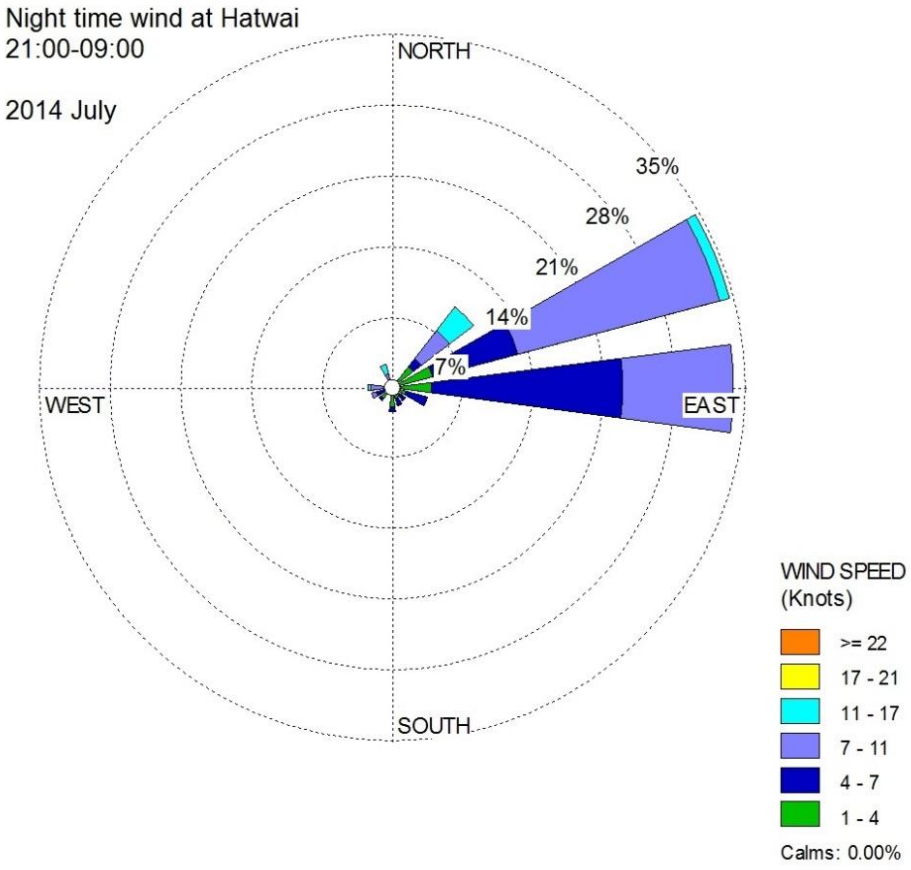


Daytime winds are predominantly from the west along the Snake River and from the north in Lapwai.

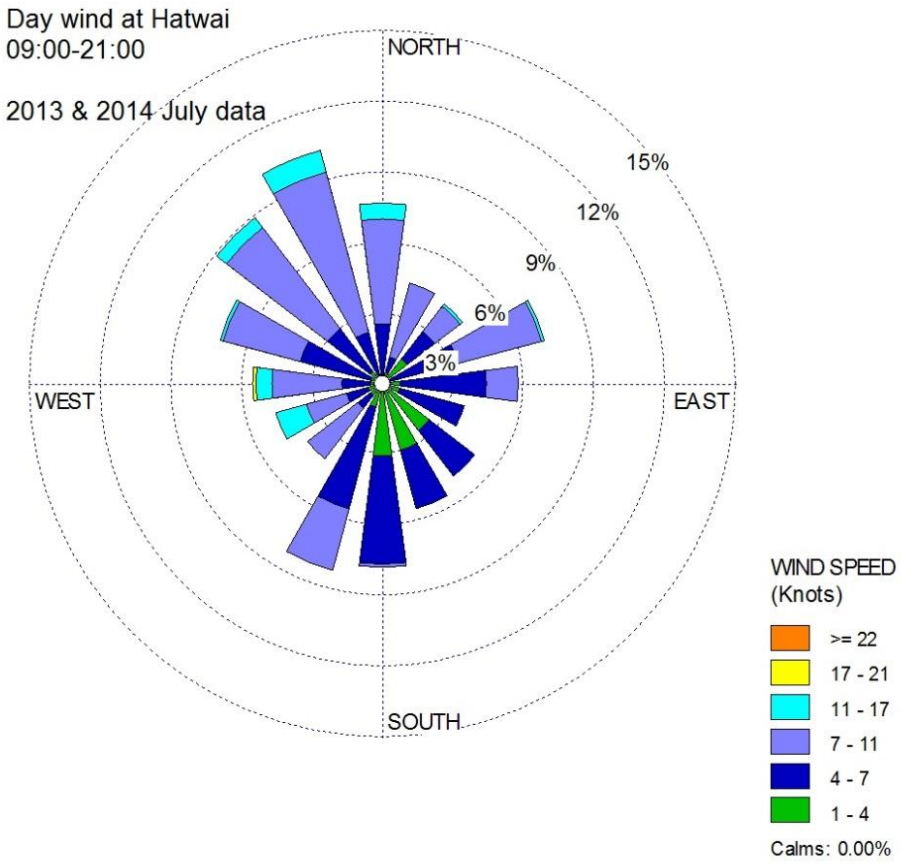
Wind speeds are more likely to be high in the daytime.

July Wind Rose - Hatwai

Night – 9pm until 9am

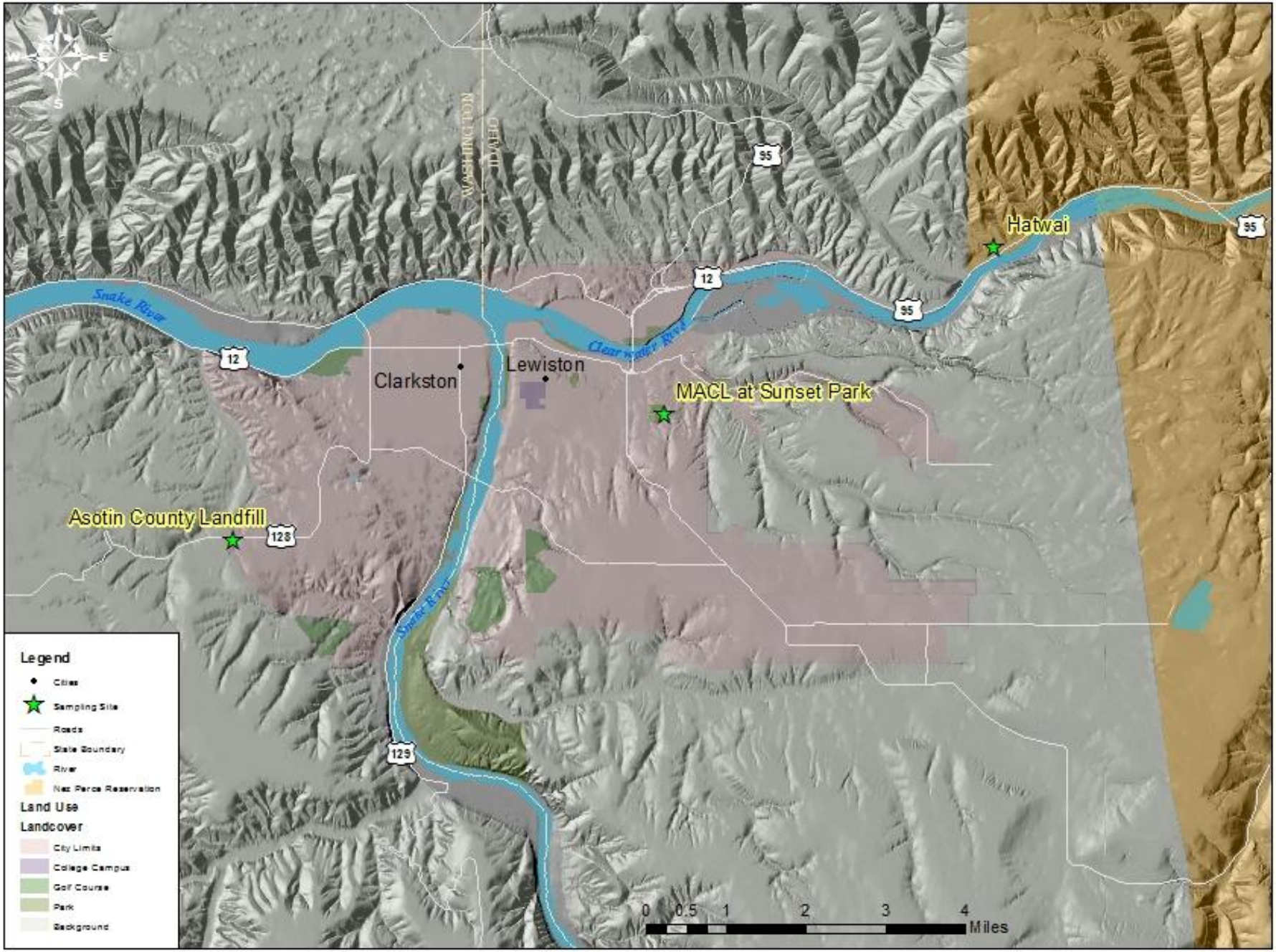


Day – 9am until 9pm



This study

- Three sites: upriver/downriver/intensive site
- Two years
- Four-week period each summer (July)


Hatwai
Snake River
Clearwater River
Clarkston
Lewiston
MACL at Sunset Park
Asotin County Landfill
Snake River
95
12
128
129
Legend
Cities
Sampling Site
Roads
State Boundary
River
Nez Perce Reservation
Land Use
Landcover
City Limits
College Campus
Golf Course
Park
Background
0 0.5 1 2 3 4
Miles

Upriver/Downriver sites

- 12h integrated sampling – DNPH cartridges, 6L SUMMA canisters (ATECs)
- Surface meteorology

Intensive site

- 12h integrated sampling – DNPH cartridges, 6L SUMMA canisters (SAT Equipment)

VOC canister with timer

Carbonyl sampler

Intensive site: Sunset Heights Park

- WSU mobile atmospheric chemistry lab (MACL)

  Continuous measurements

  – Selected VOCs by PTR-MS (i.e formaldehyde)

  – NO, NO_2, NOy, CO, SO_2, CO_2, O_3

  – Surface meteorology

  – Ceilometer

Trace organic gases species to be measured by PTR-MS.

m/z	Compound	Notes
Oxygenated species		
31	formaldehyde	**Primary emissions / photoproduct**
33	methanol	**pulp mill emission tracer**
45	acetaldehyde	**Primary emissions / photoproduct**
49	methyl hydroperoxide	**photoproduct**
59	acetone + propanal	**solvents + photoproducts**
71	MVK + MACR	**isoprene photoproducts**
73	2-butanone	**solvents**
Aromatic compounds		
79	benzene	**vehicle emissions**
93	toluene	**vehicle emissions**
105	styrene	**industrial**
107	C_2 benzenes (C_8H_{10})	**vehicle emissions**
121	C_3 benzenes (C_9H_{12})	**vehicle emissions**
135	C_4 benzenes ($C_{10}H_{14}$)	**vehicle emissions**
Biogenic emissions		
69	isoprene	**biogenic emission**
137	monoterpenes	**biogenic emission**
139	nopinone	**b-pinene oxidation product**
Industrial tracers		
35	H_2S	**potential pulp mill tracer**
Biomass burning tracers		
42	**acetonitrile**	**biomass burning tracer**

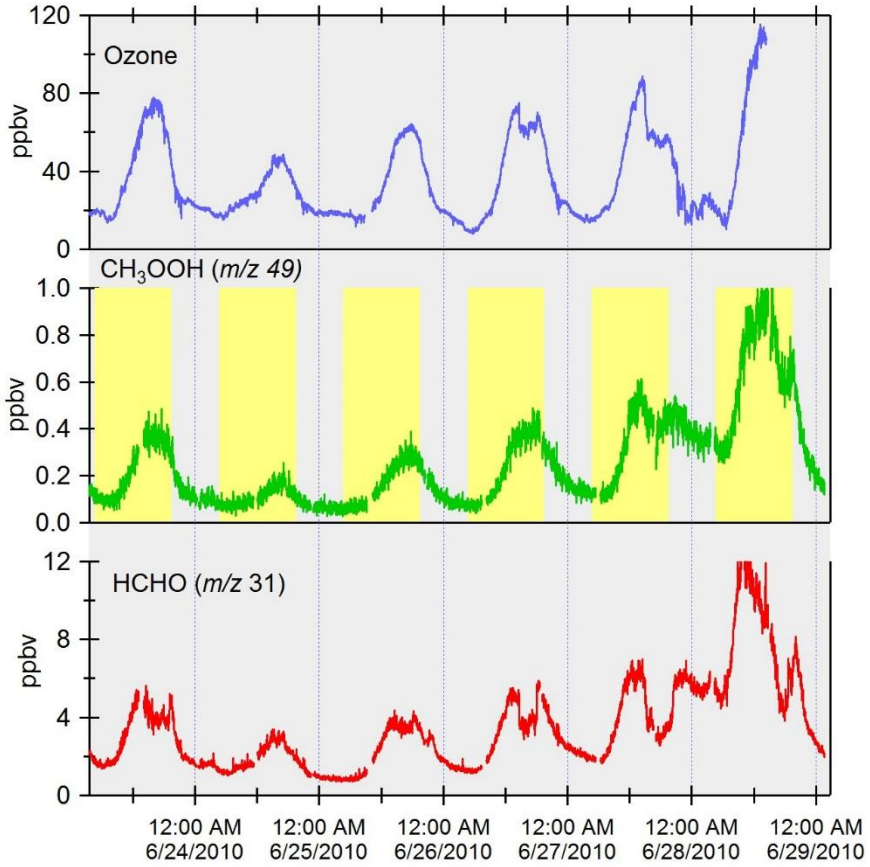
Scan through list once per minute. Data collection rate allows for comparison with meteorological variables (WD distribution plots) and to measure diel variability, and tracer relationships.

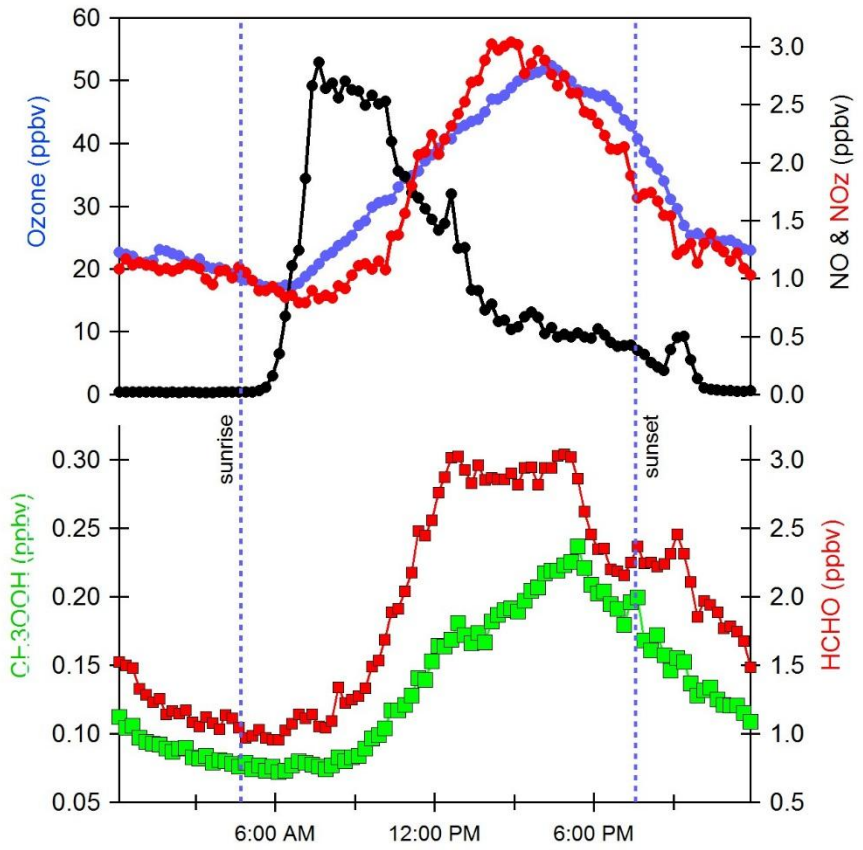
Potential secondary origin of HCHO from photochemical oxidation of organics

Perhaps methanol oxidation: $CH_3OH + HO \rightarrow CH_2OH + H_2O$

$CH_2OH + O_2 \rightarrow HCHO + HO$

Example PTR-MS data of HCHO and CH_3OOH (Sacramento, CA)





Positive Matrix Factorization (PMF)

- Mathematical receptor model
- Goal: Identify sources of air pollutants (e.g. Formaldehyde & others)

How does the model work?
Separate signals in air quality data

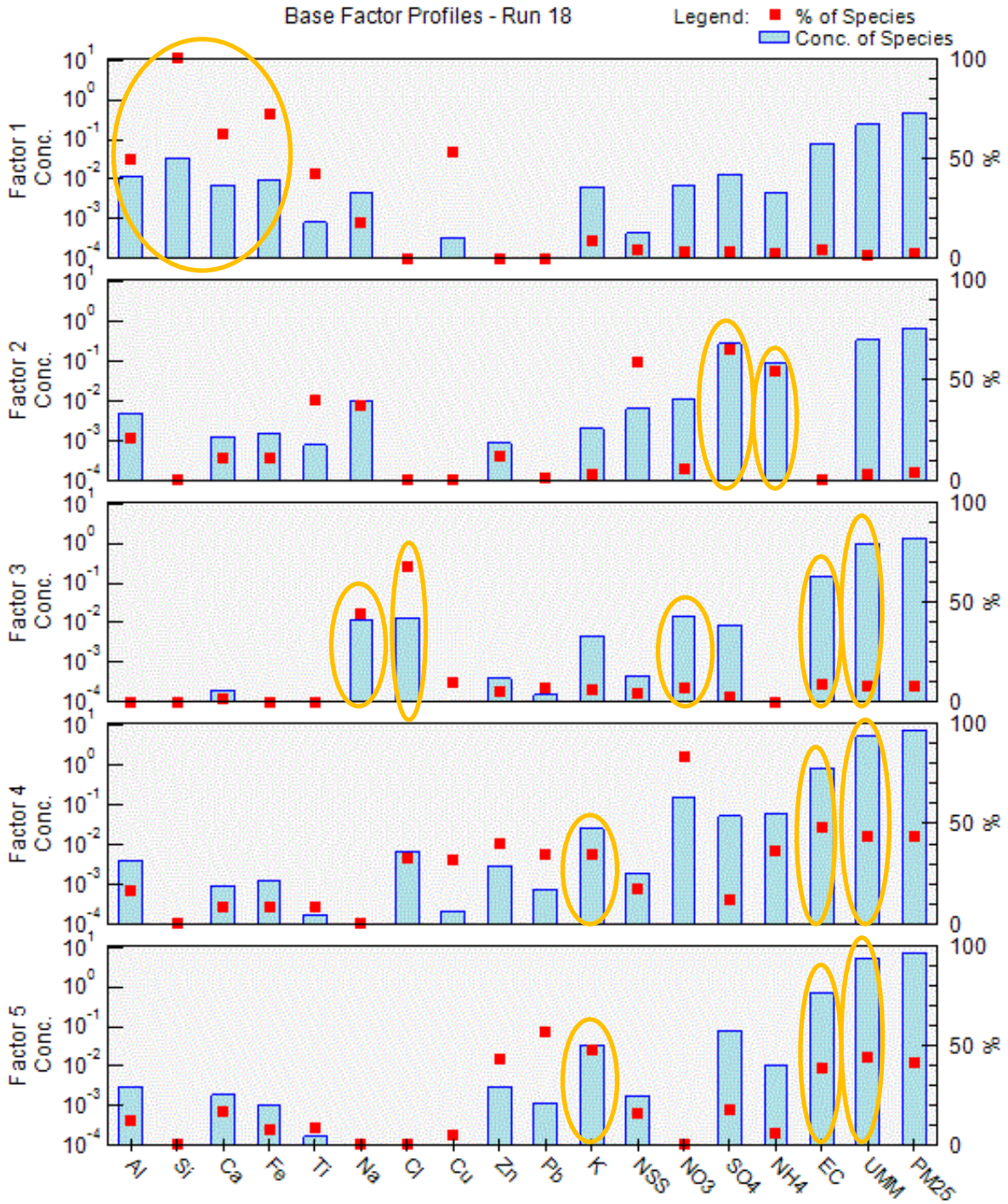
Examples:
- PMF modeling for $PM_{2.5}$ in Pinehurst
- Source apportionment of VOCs

July 2016
July 2017

- Preliminary thoughts for PMF modeling in this study

Input data: species concentrations and uncertainties of measurements

The model calculates source profiles or fingerprints (factors), and source contributions



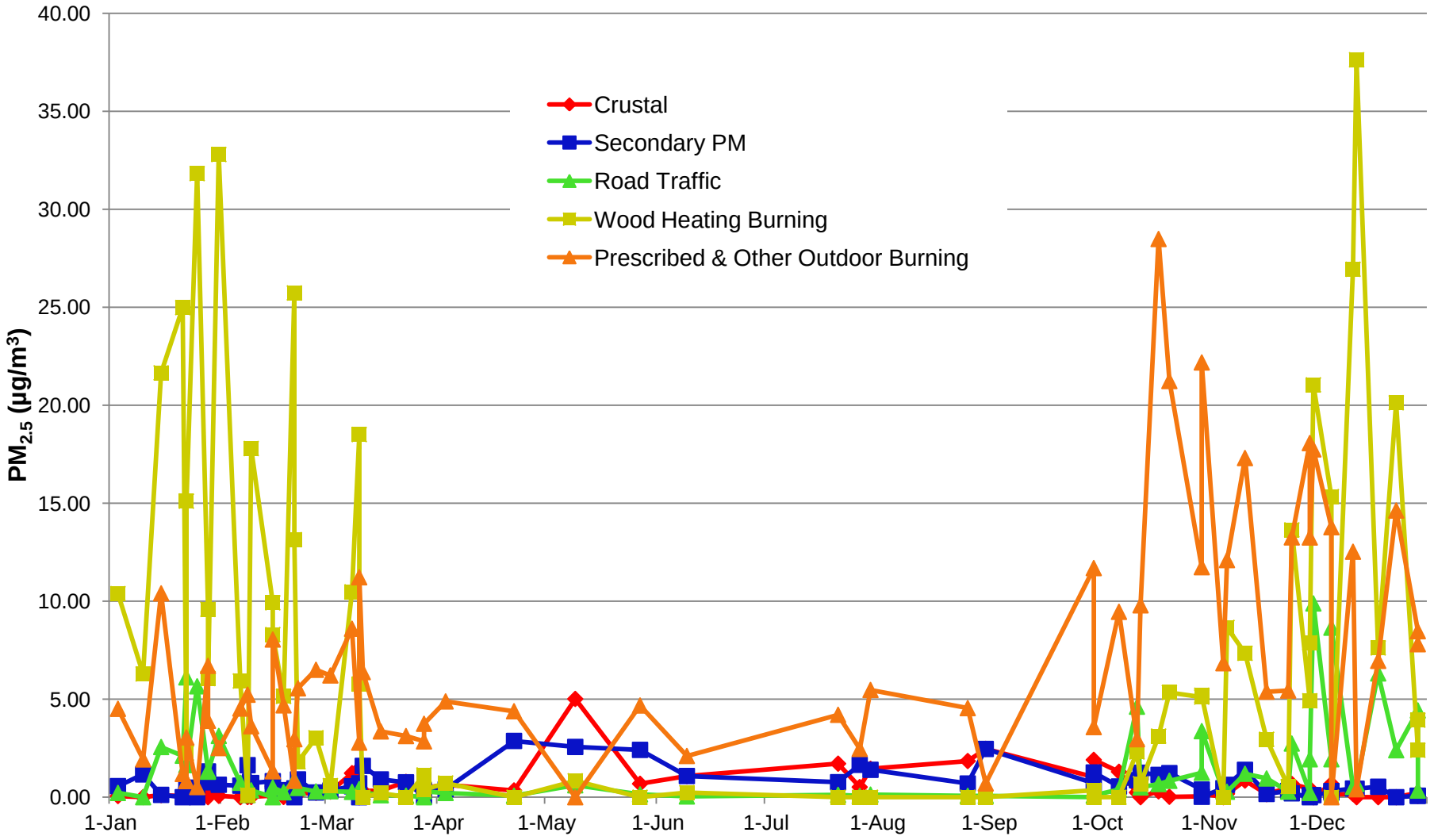
Crustal

Secondary Sources:
Sulfate, Ammonium, Nitrate, …

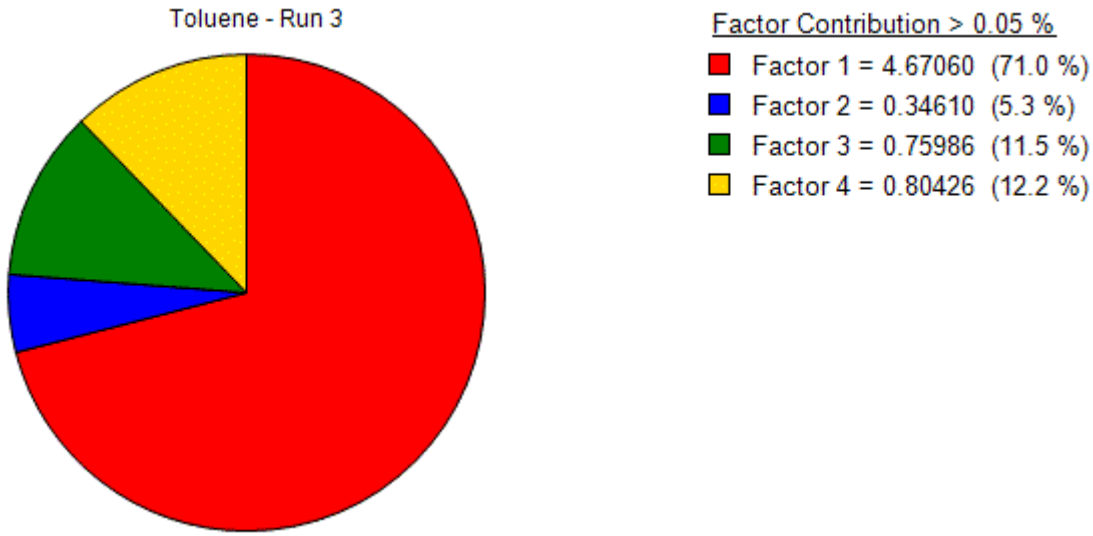
Road Traffic PM: road salt, diesel and gasoline engines

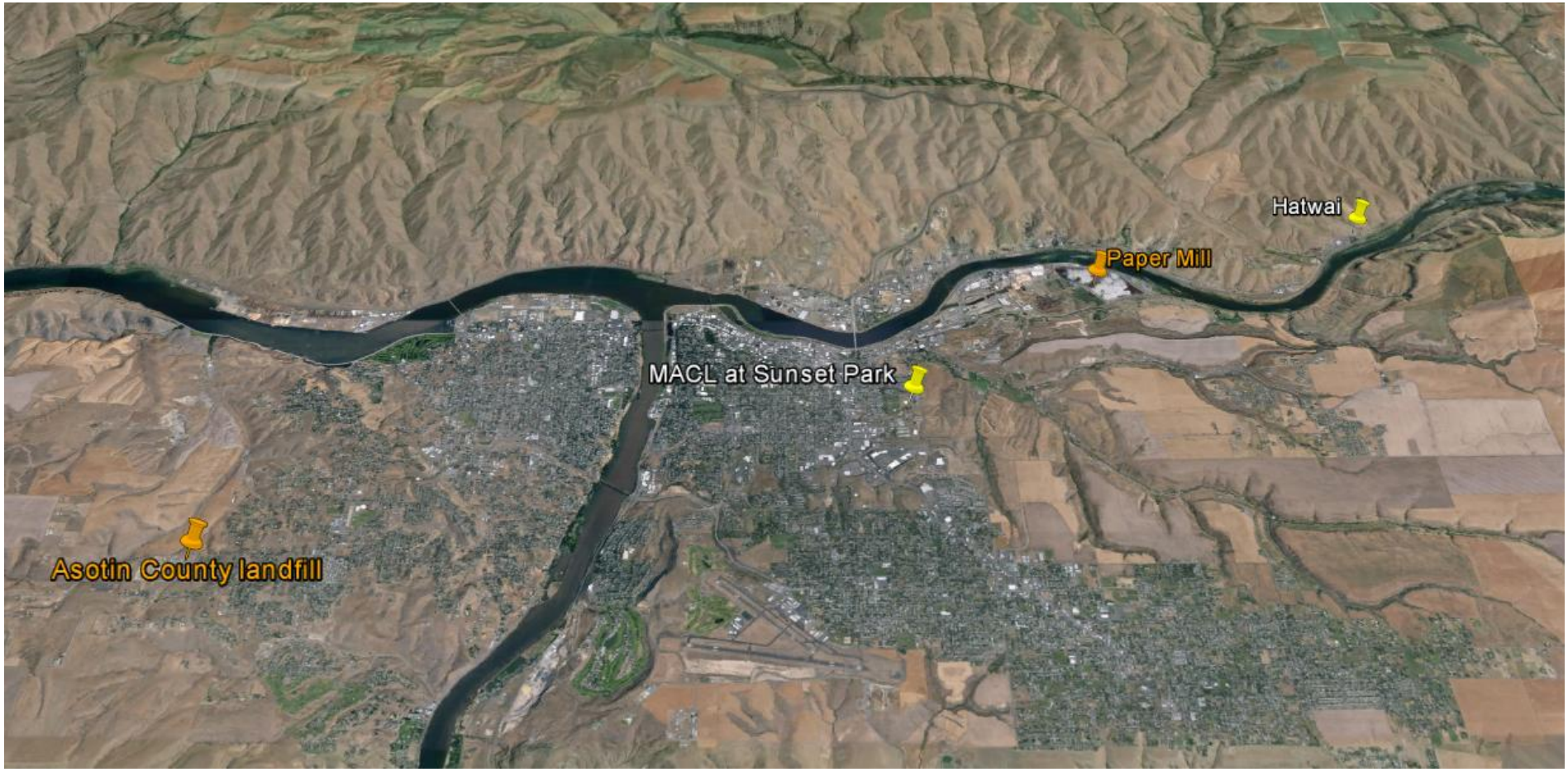
Biomass Burning

Biomass Burning


40.00
35.00
30.00
25.00
20.00
15.00
10.00
5.00
0.00
PM2.5 (µg/m3)
1-Jan
1-Feb
1-Mar
1-Apr
1-May
1-Jun
1-Jul
1-Aug
1-Sep
1-Oct
1-Nov
1-Dec
Crustal
Secondary PM
Road Traffic
Wood Heating Burning
Prescribed & Other Outdoor Burning

Example: Source apportionment for VOCs


Toluene - Run 3
Factor Contribution > 0.05 %
Factor 1 = 4.67060 (71.0 %)
Factor 2 = 0.34610 (5.3 %)
Factor 3 = 0.75986 (11.5 %)
Factor 4 = 0.80426 (12.2 %)



Thoughts for PMF modeling:

- For each site
- Different temporal resolution:
  - 1-min data
  - 1-hour data
  - 12-hour data

Questions?