YAWNS – Yakima Air Wintertime Nitrate Study

Tom Jobson, T.M. Vanreken, G.S. VanderSchelden, B.K. Lamb, C.L. Hering, H. Liu

Laboratory for Atmospheric Research, Washington State University

S.D. Kaspari

Dept. Geological Sciences, Central Washington University

R.S. Dhammapala

Washington State Dept. of Ecology

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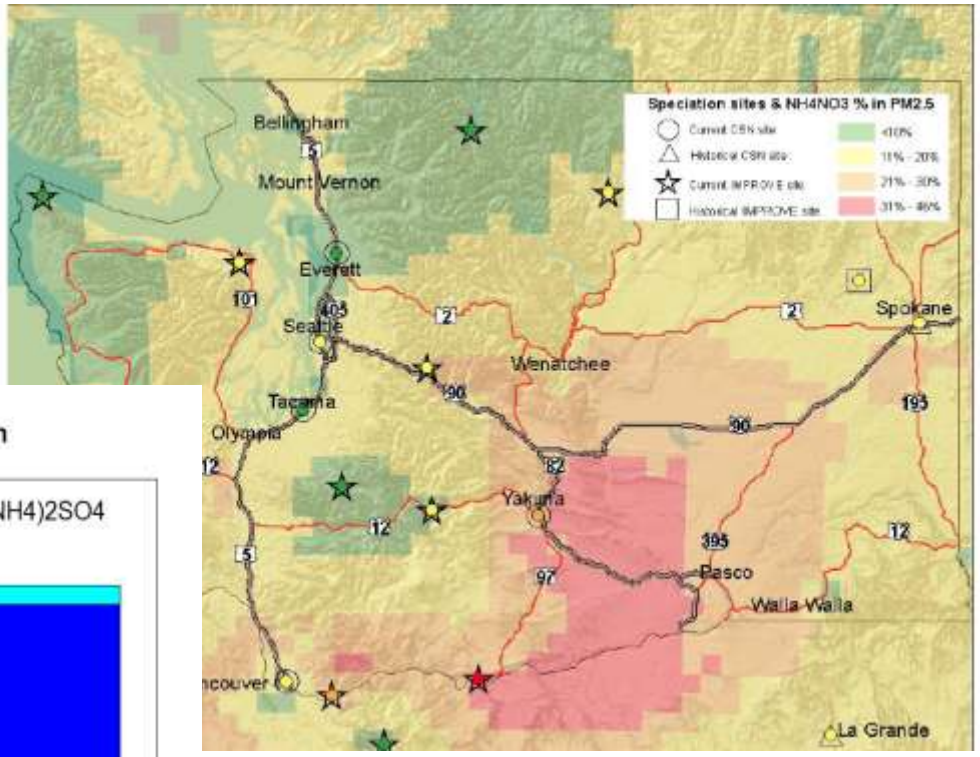
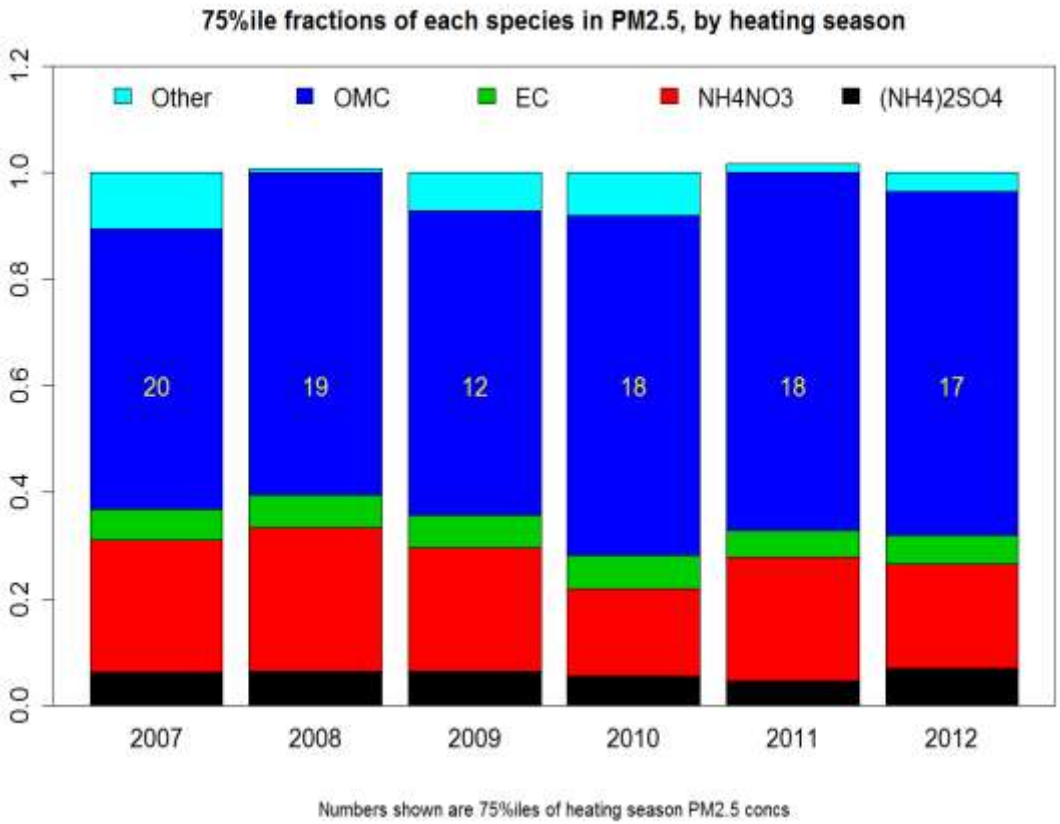
Motivation

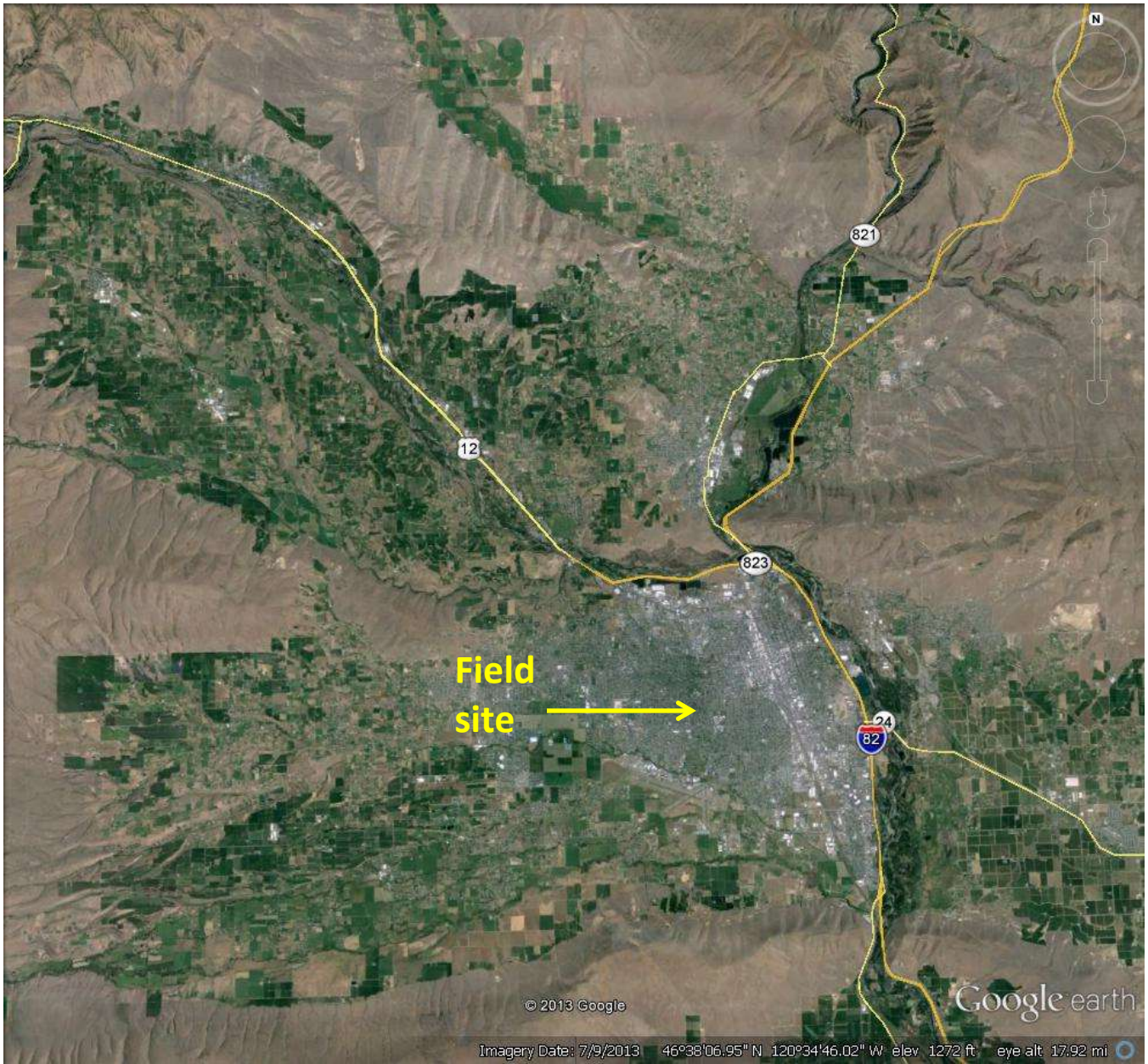
Why is nitrate such a large fraction of winter time $PM_{2.5}$ in Yakima?





~30% contribution in winter time

Study Area: Yakima, WA



Yakima, WA

Population = 91,000

wintertime air stagnation events common

Regional **NH_3** emissions high from agriculture emissions (diary farms, feed lots)

Interstate **I-82** runs through the Yakima Valley

Yakima Wintertime Nitrate Study (YAWNS)

3 weeks in winter : Jan 5, 2013 – Jan 26, 2013

Measured:
VOCs by PTR-MS
NO, NO_2, NOy
CO, CO_2, O_3

Particle size distribution

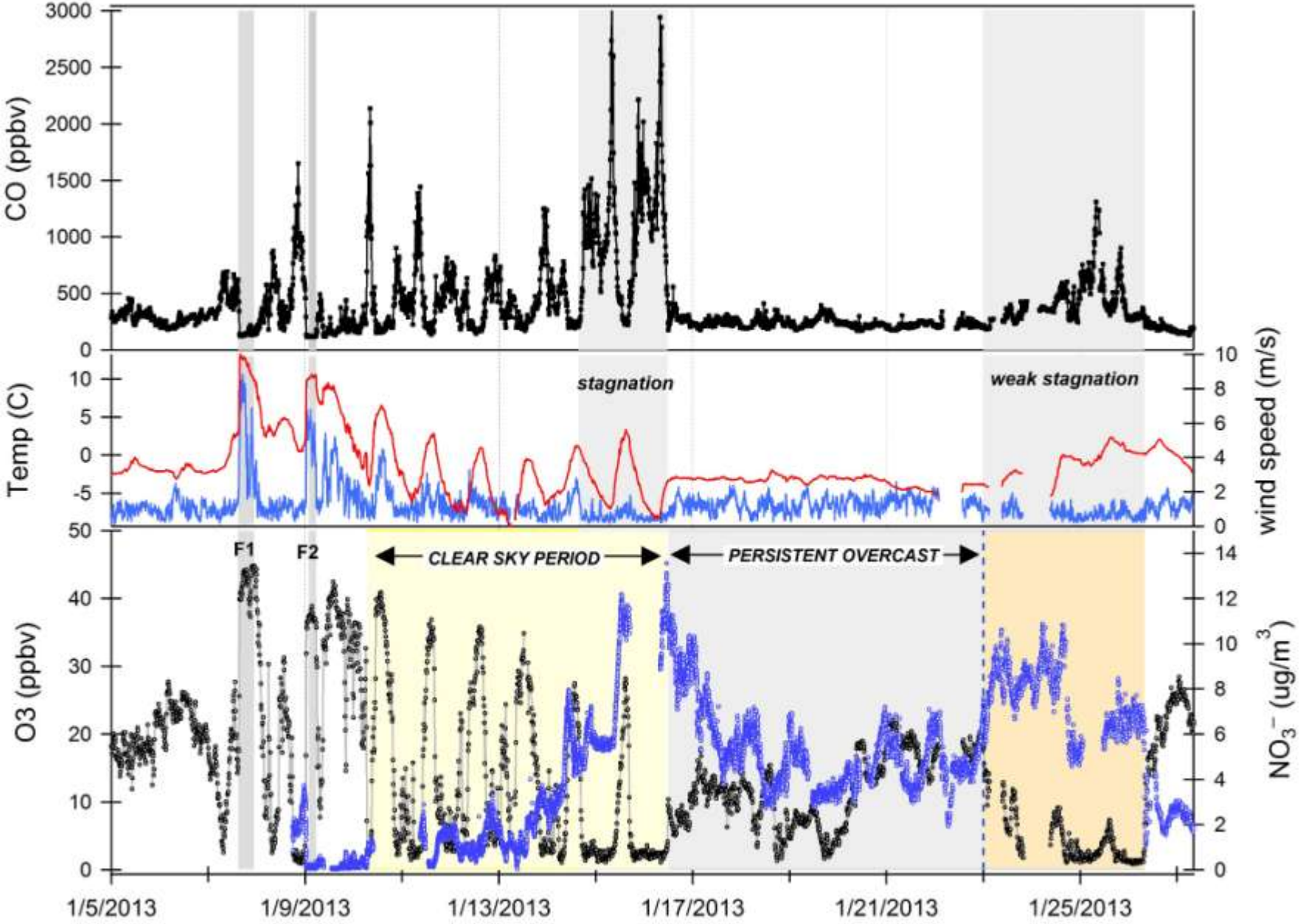
Particle chemical composition by AMS

Black carbon by single particle soot photometer (SP2)

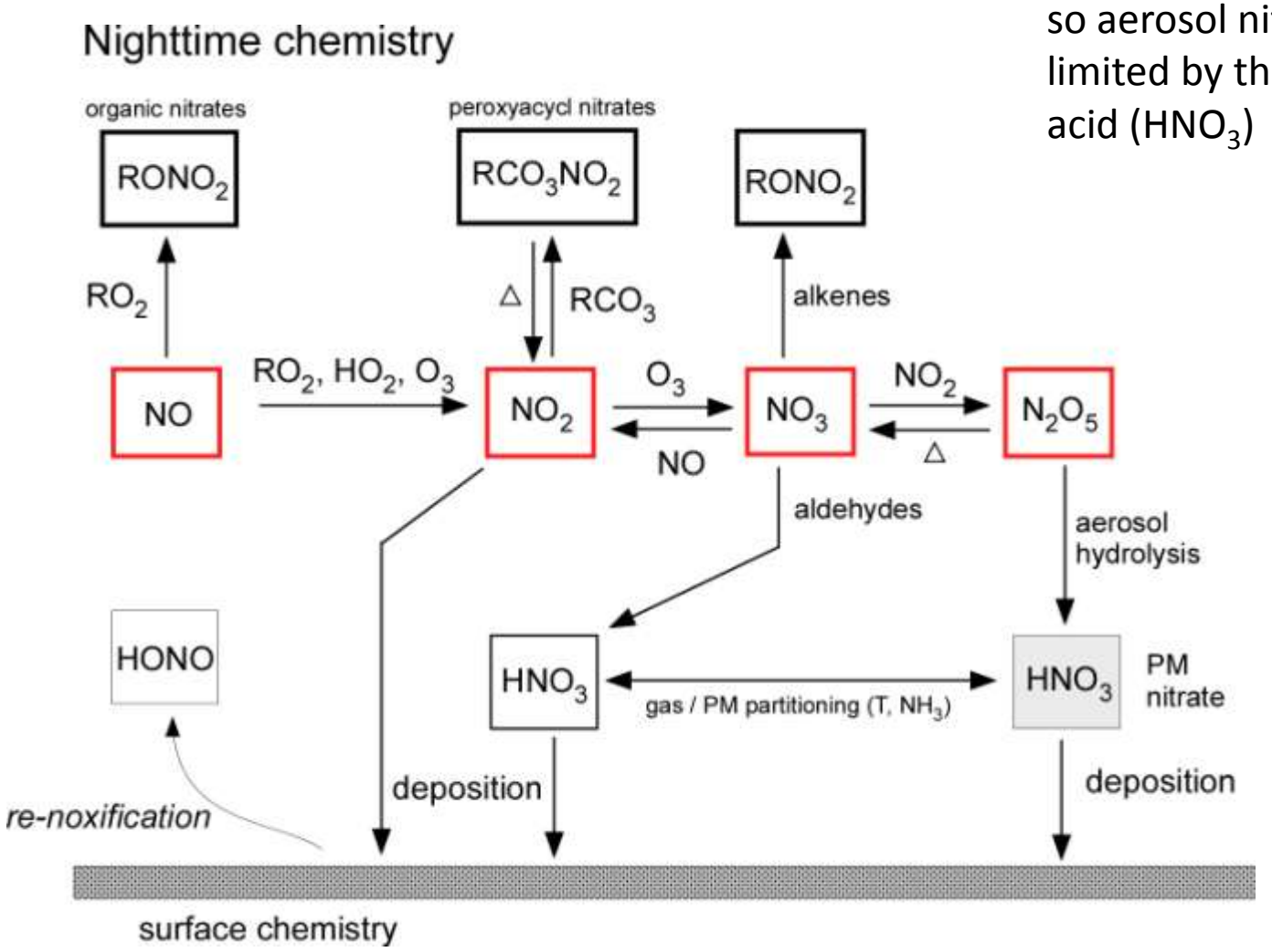
Surface meteorology

PBL height by celiometer

YAWNS data – not so boring!



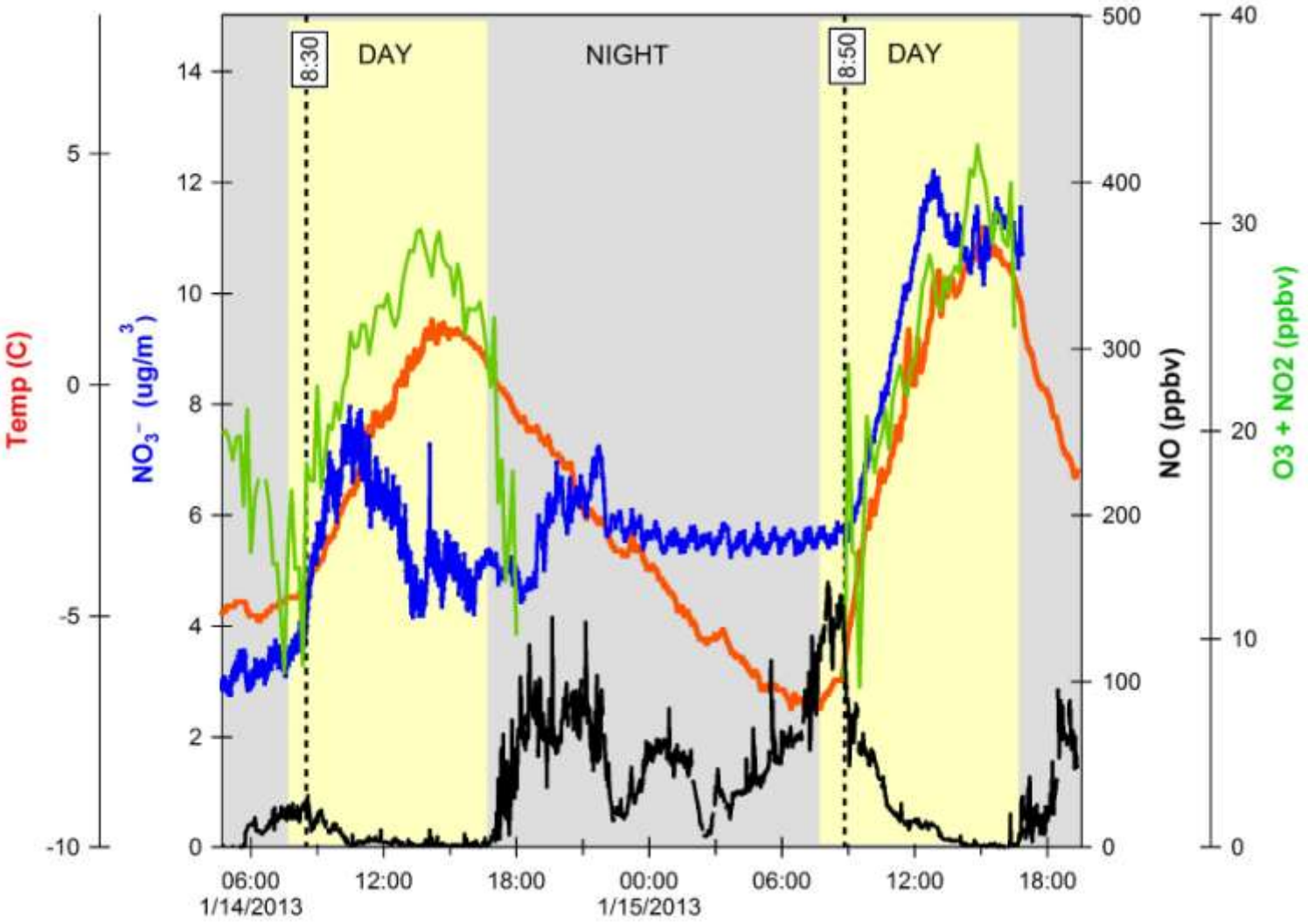
NO_3 Formation Chemistry at Night



Yakima airshed has excess ammonia, so aerosol nitrate formation is limited by the availability of nitric acid (HNO_3)

The NO concentration is key – too high a concentration then NO_3 concentrations are low and nitrate production will be limited.

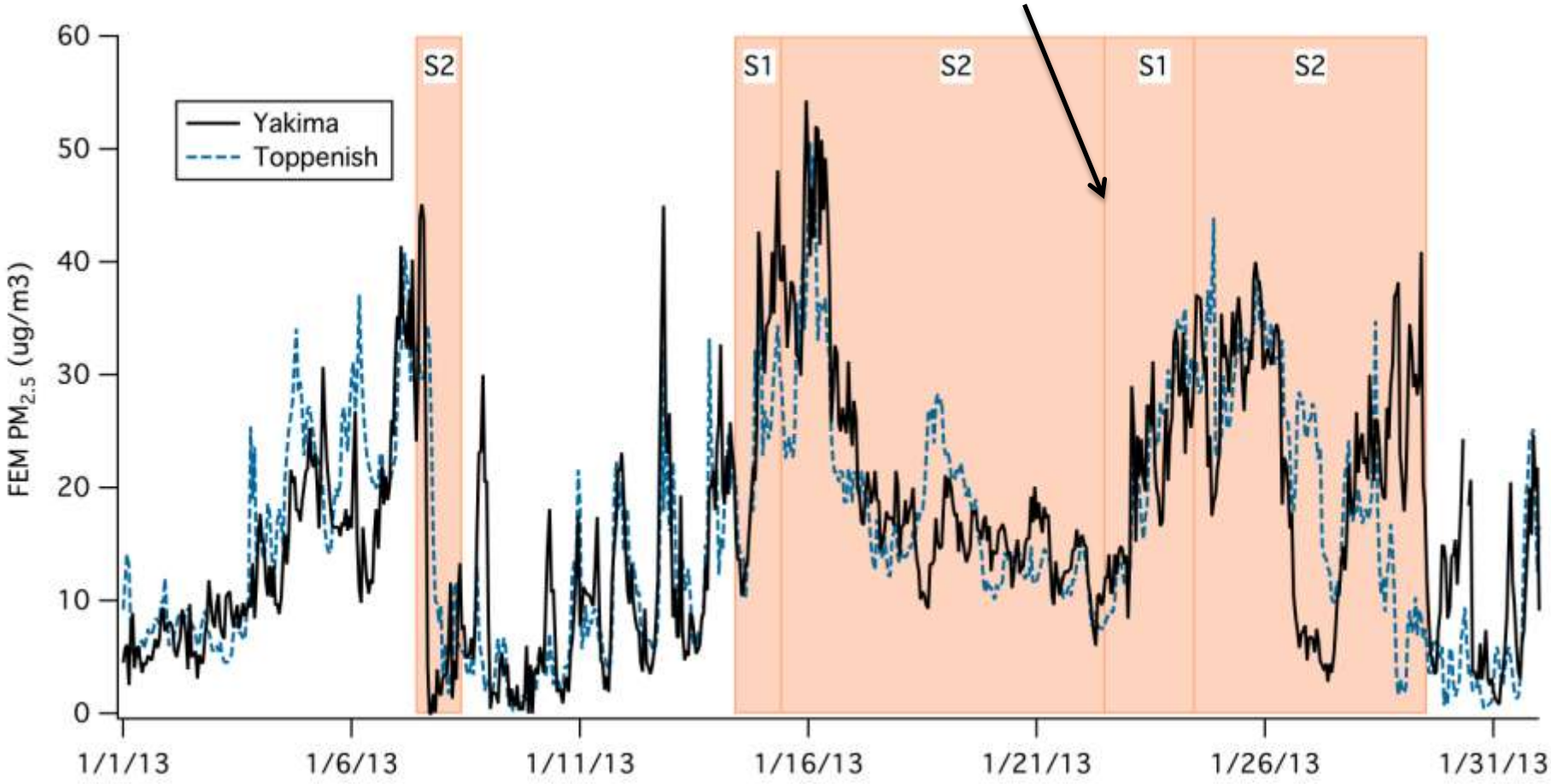
Clear Sky Nitrate Formation



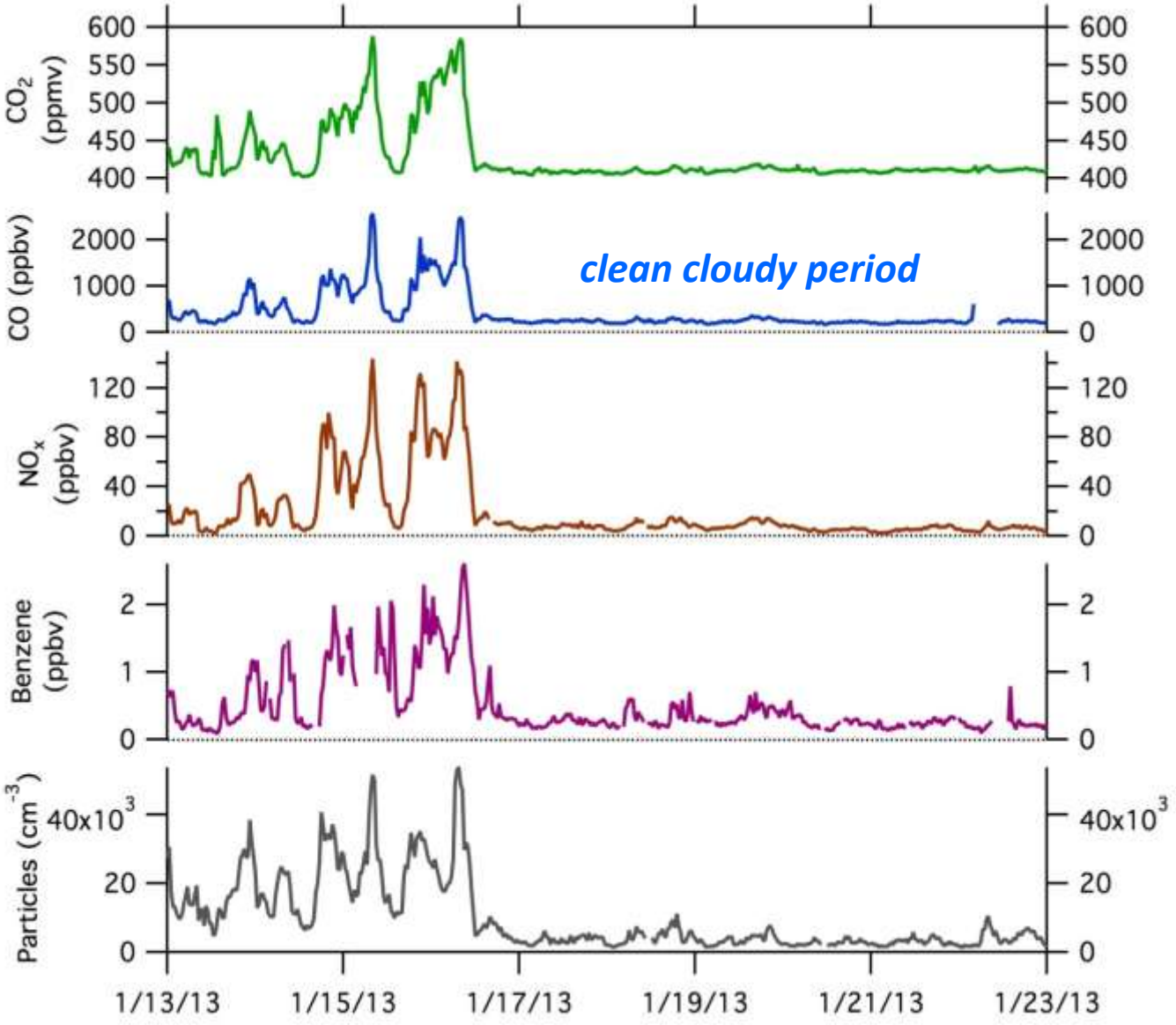
Rapid increase in PM Nitrate after sunrise, is this evidence of elevated nitrate in residual layer?

Persistent Overcast Period: Jan 16, noon – Jan 23

From press release: "*YRCAA affirms that, based on air quality readings through this air stagnation episode, public compliance has been exceptional through this current Stage 2 Burn Ban, enabling YRCAA to now reduce the Burn Ban to a Stage 1 Burn Ban, for those that have a great need to use wood and pellet stoves to heat their homes.*"

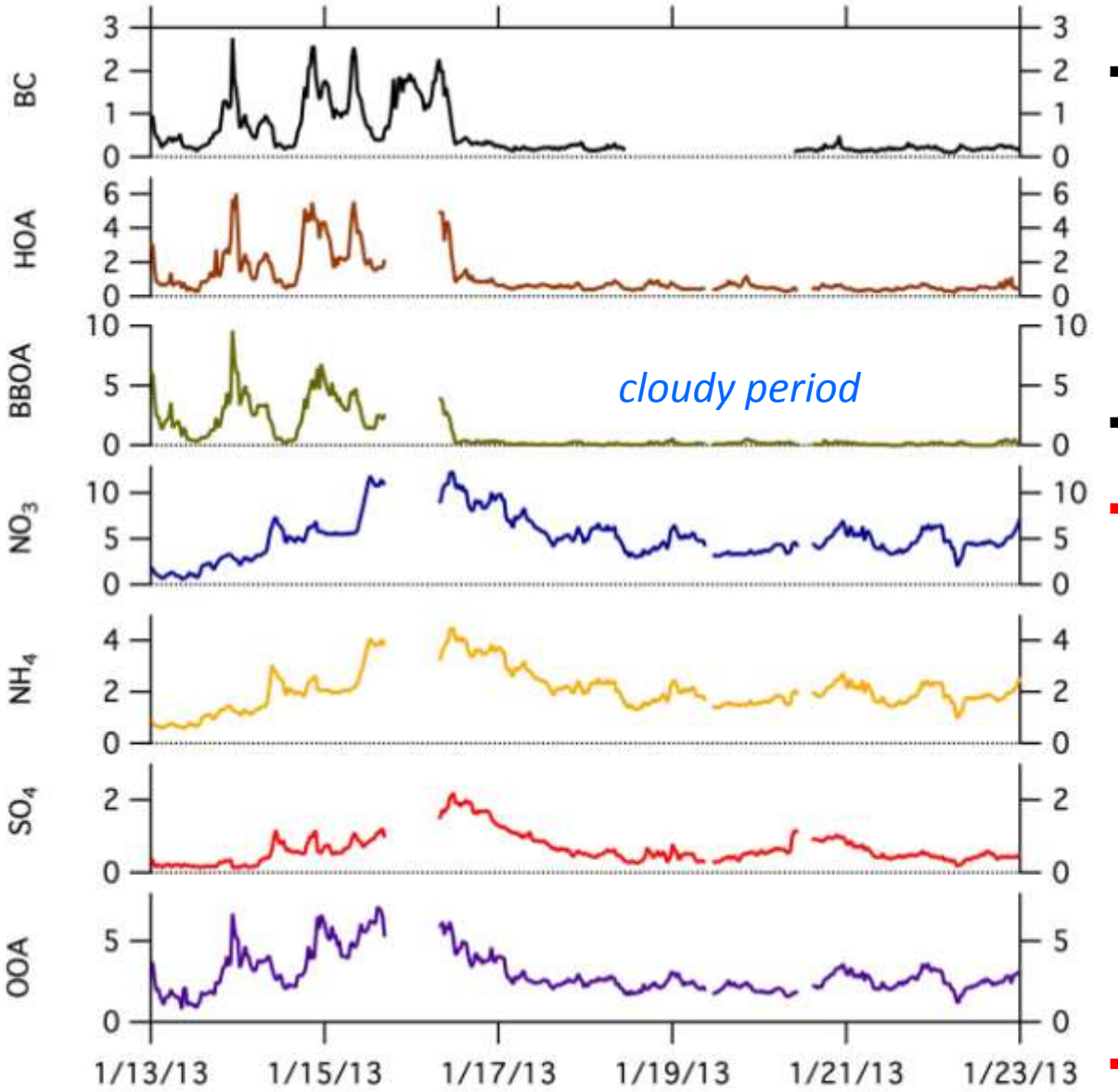


The Persistent Cloudy Period



The cloudy period with elevated PM mass was remarkably clean (low concentrations of primary pollutants)

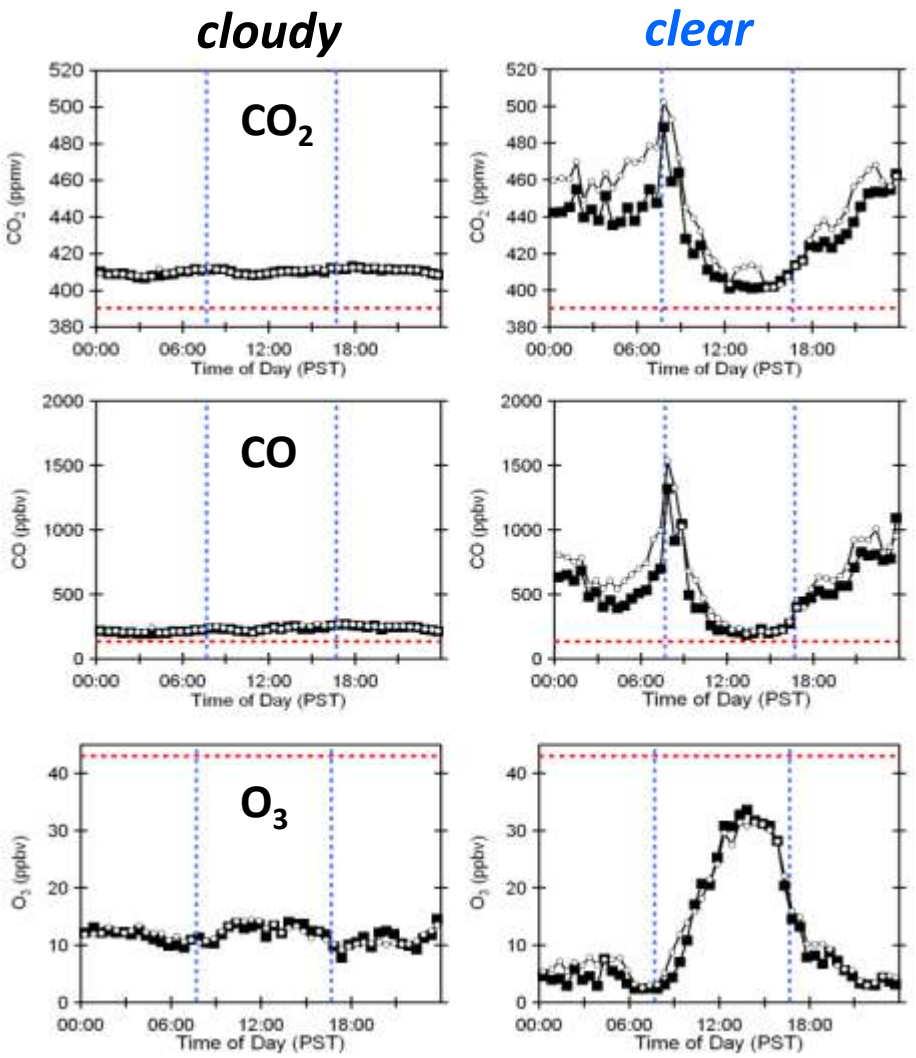
The Persistent Cloudy Period: PM composition (µg/m^3)



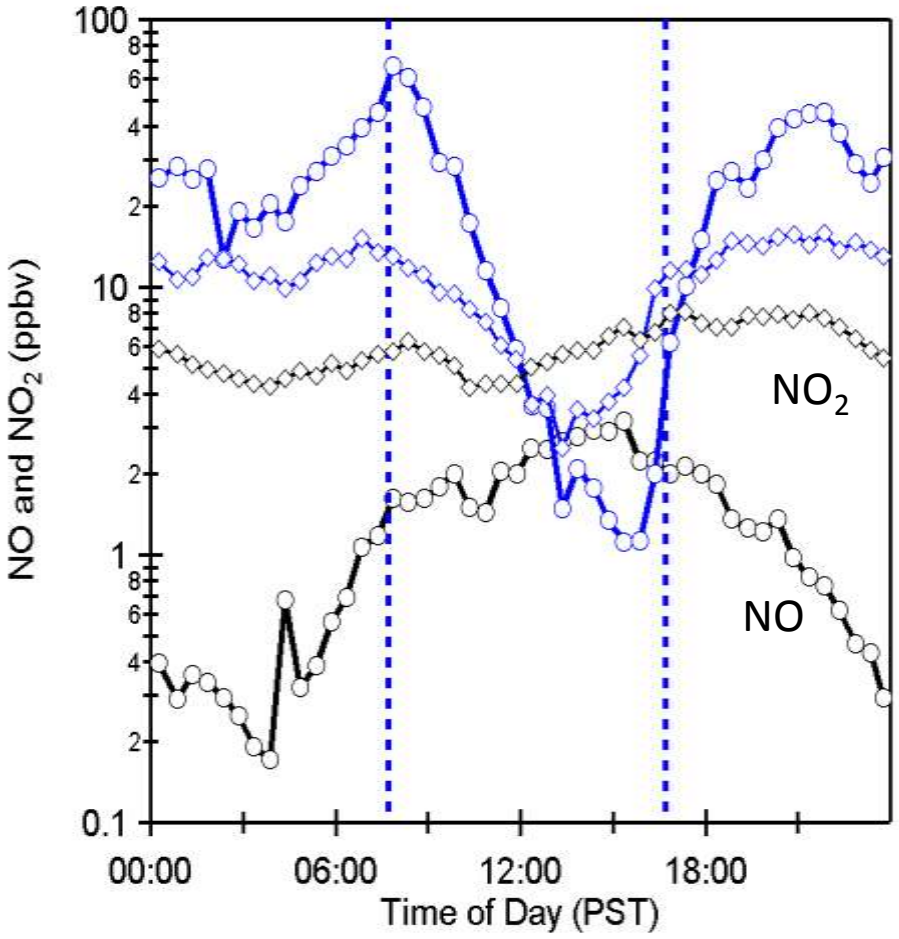
Low concentrations of *primary compounds*

Elevated concentrations of *secondary compounds* (produced by atmospheric chemistry reactions)

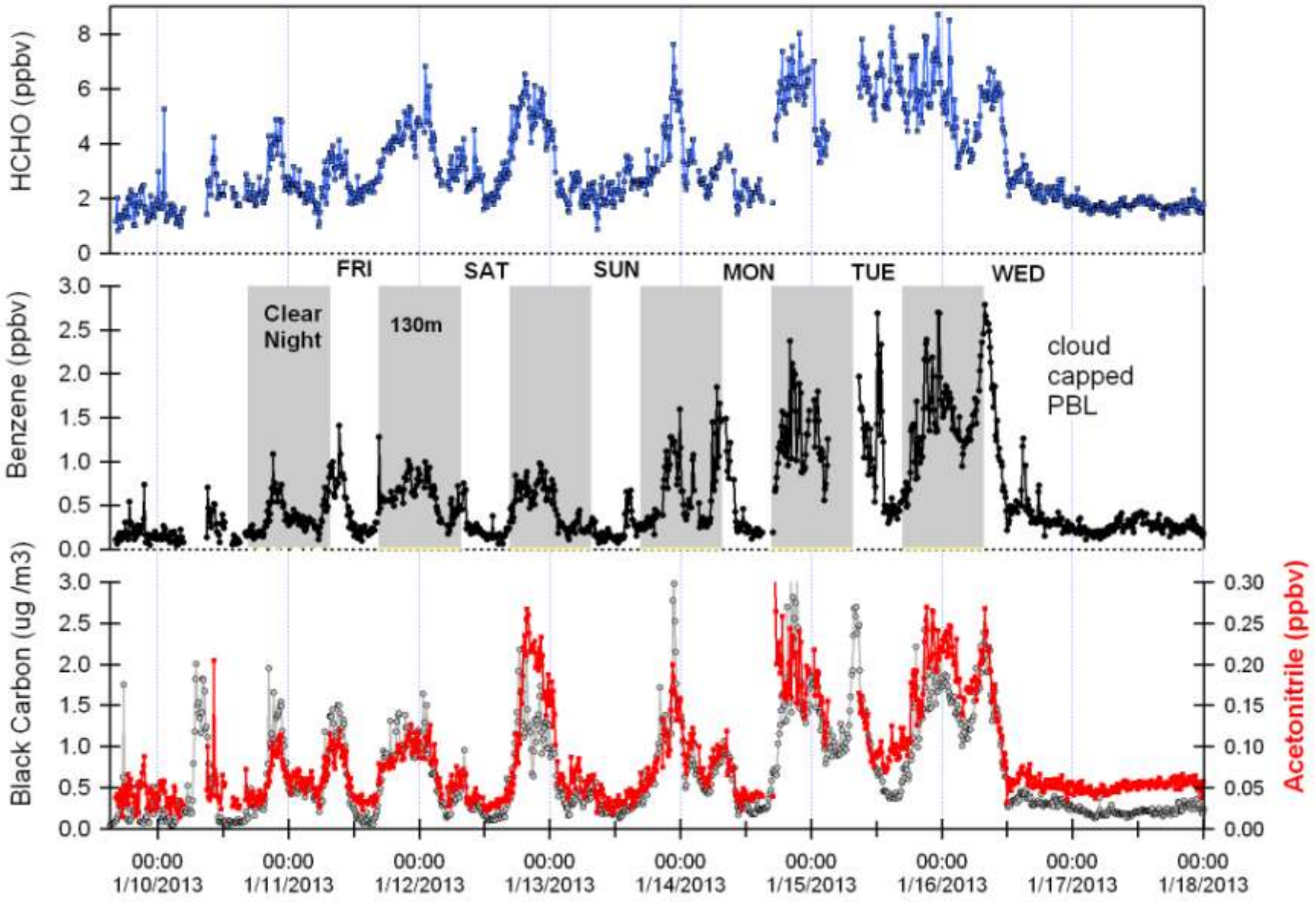
Diel Variation : Contrast Clear Sky and Cloudy Period



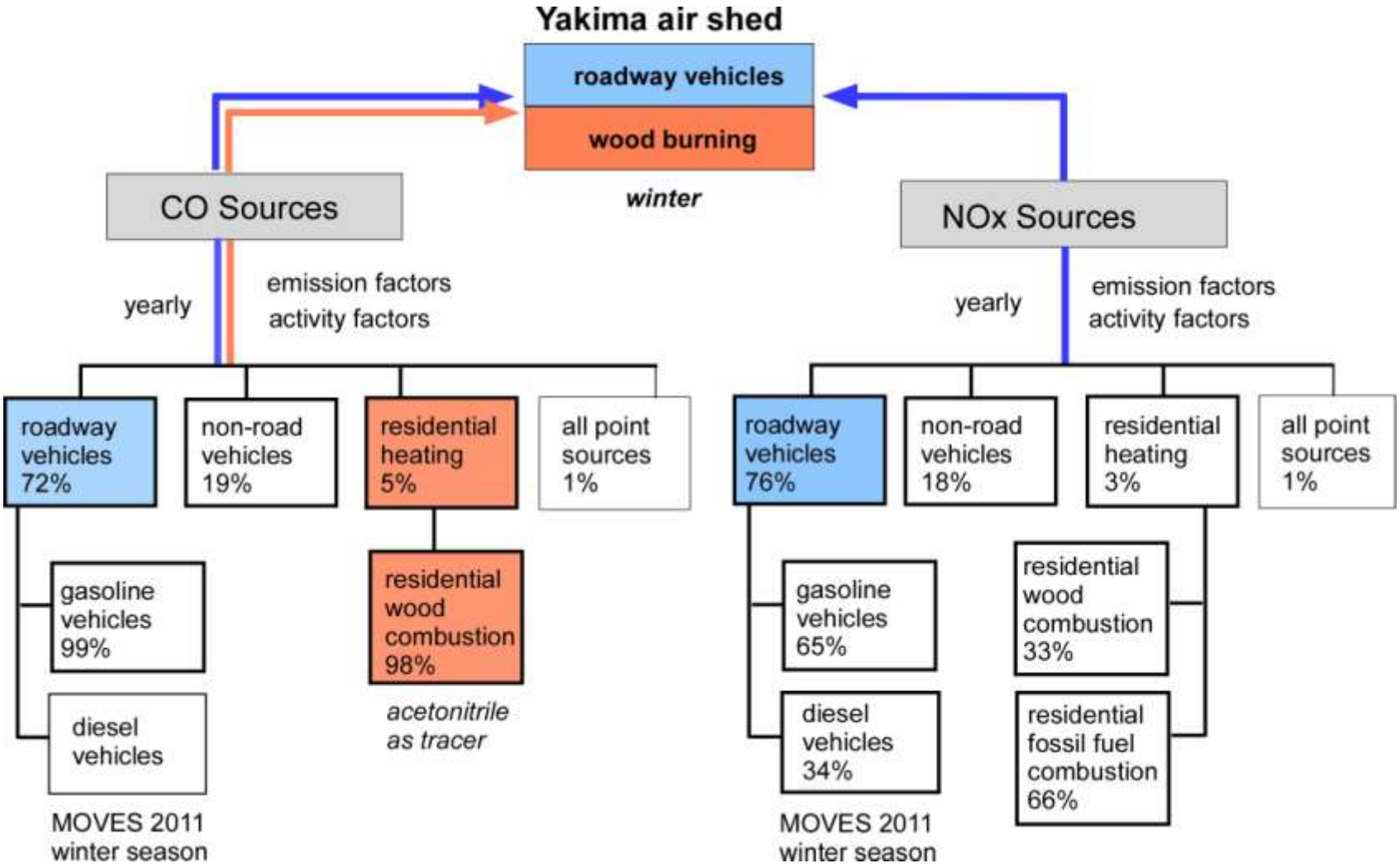
NO mixing ratios (circles) much lower during cloudy period



Acetonitrile (CH_3CN) **:** Wood Burning Tracer



Sources: Yakima County Inventory



Combustion sources are also major sources of PM & VOCs

Simple EI of small town enables better source characterization

Chemical Mass Balance Model

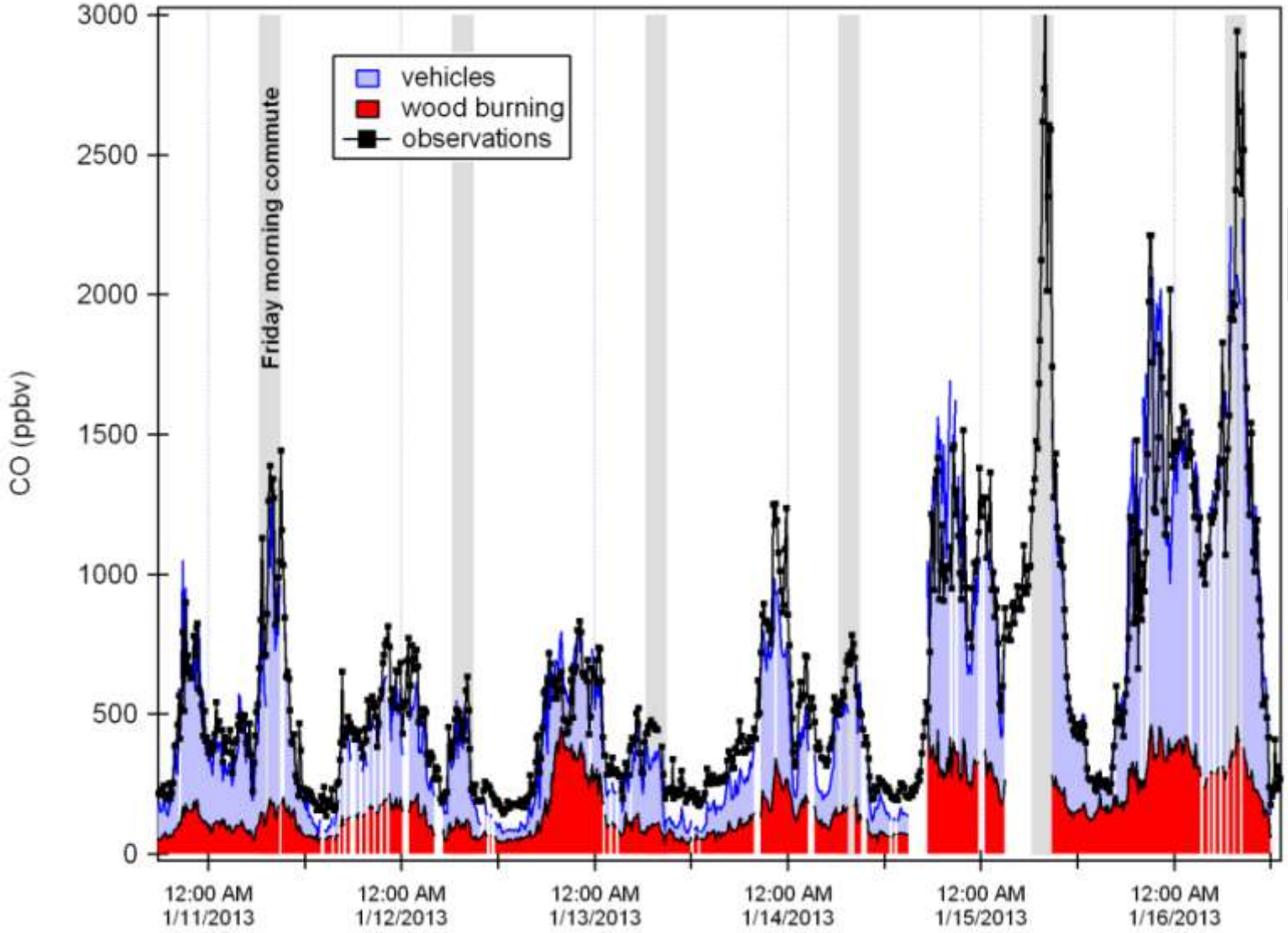
- Use **Acetonitrile** as a tracer for residential wood combustion emissions
- Use **NO_x** as a tracer for fossil fuel combustion emissions (dominated by roadway vehicles)
- Apply a bivariate model to account for other primary pollutant (**P**) concentrations assuming pollutants are conserved:

$$\Delta P = ER_w * [\Delta CH_3CN] + ER_{FF} * [\Delta NO_x]$$

  - ER_w =wood combustion molar emission ratio **P** / CH_3CN
  - ER_{FF} =fossil fuel combustion molar emission ratio **P** / NO_x

Optimize linear fit (slope and r^2) between predicted ΔP and measured

1. Carbon Monoxide Attribution



Good fit of model to observations

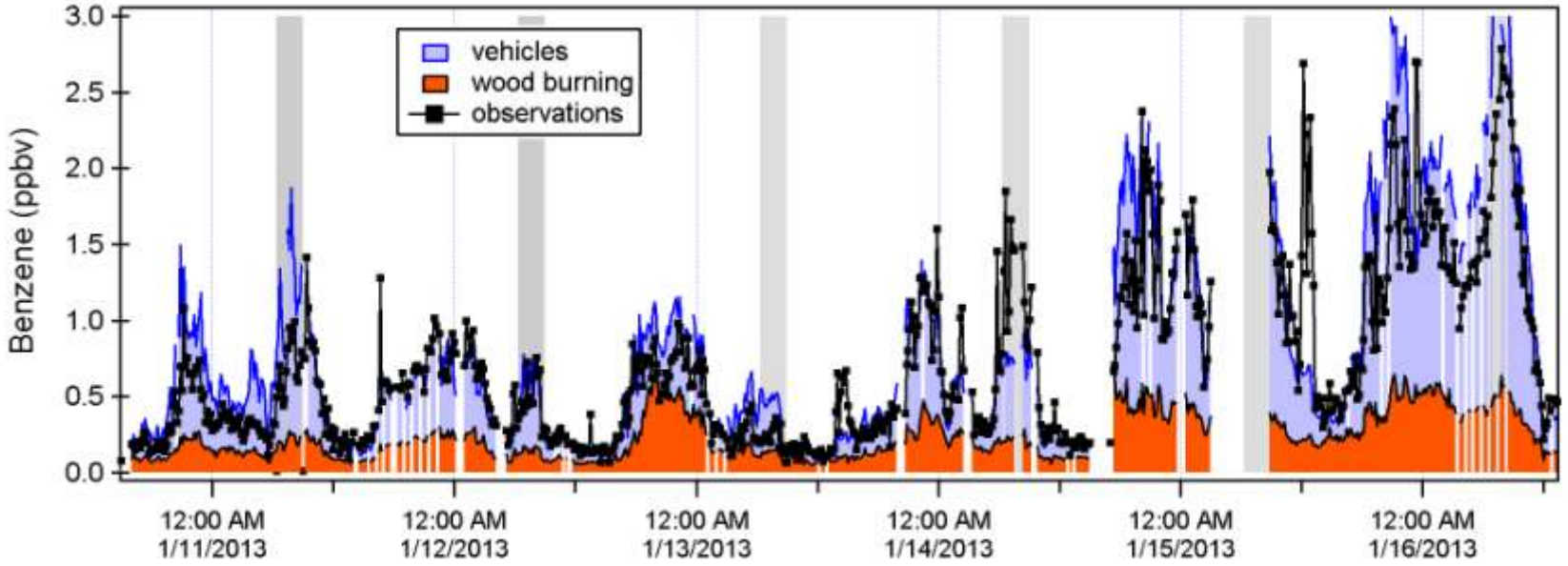
Rush hour evident

Period Average Contributions

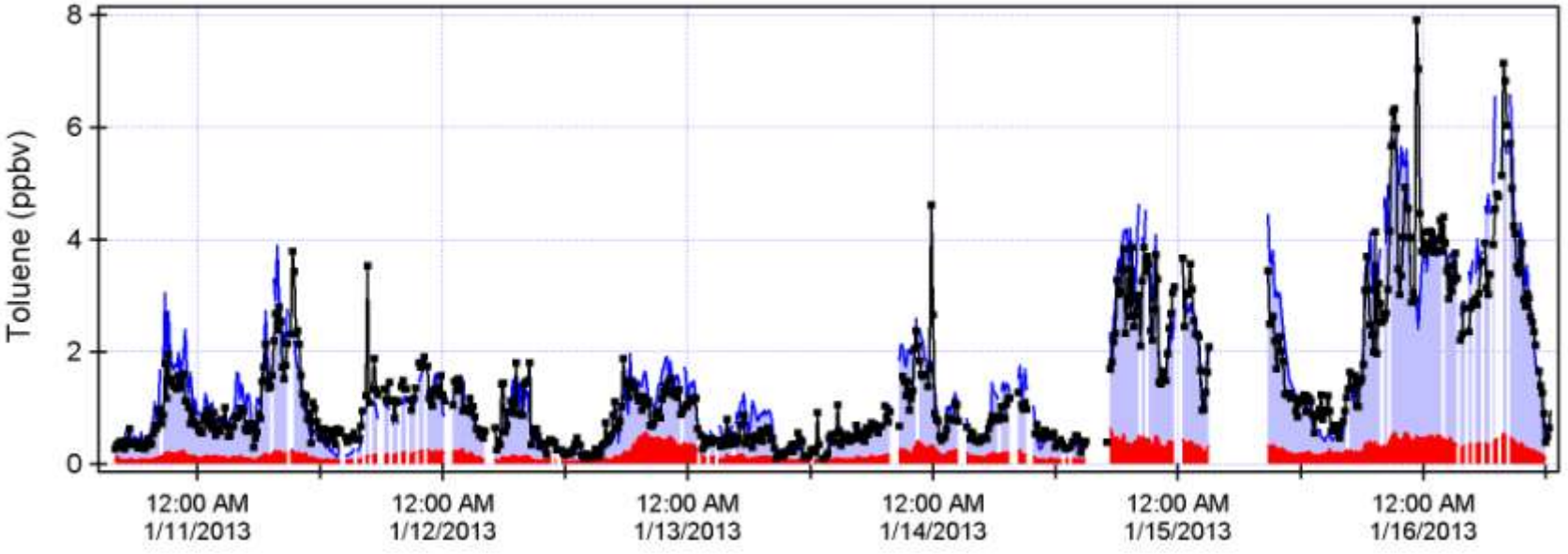
Vehicle exhaust contribution 54%

Wood burning contribution 46%

2. Benzene & Toluene Attribution

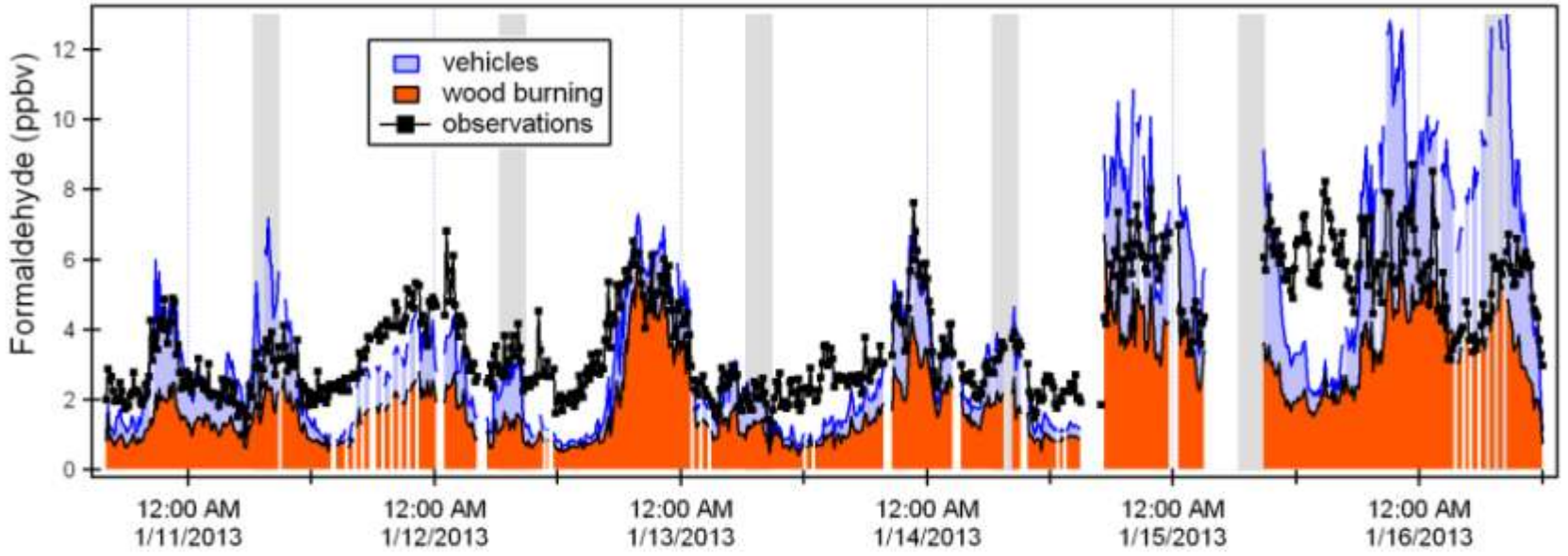


61%
39%

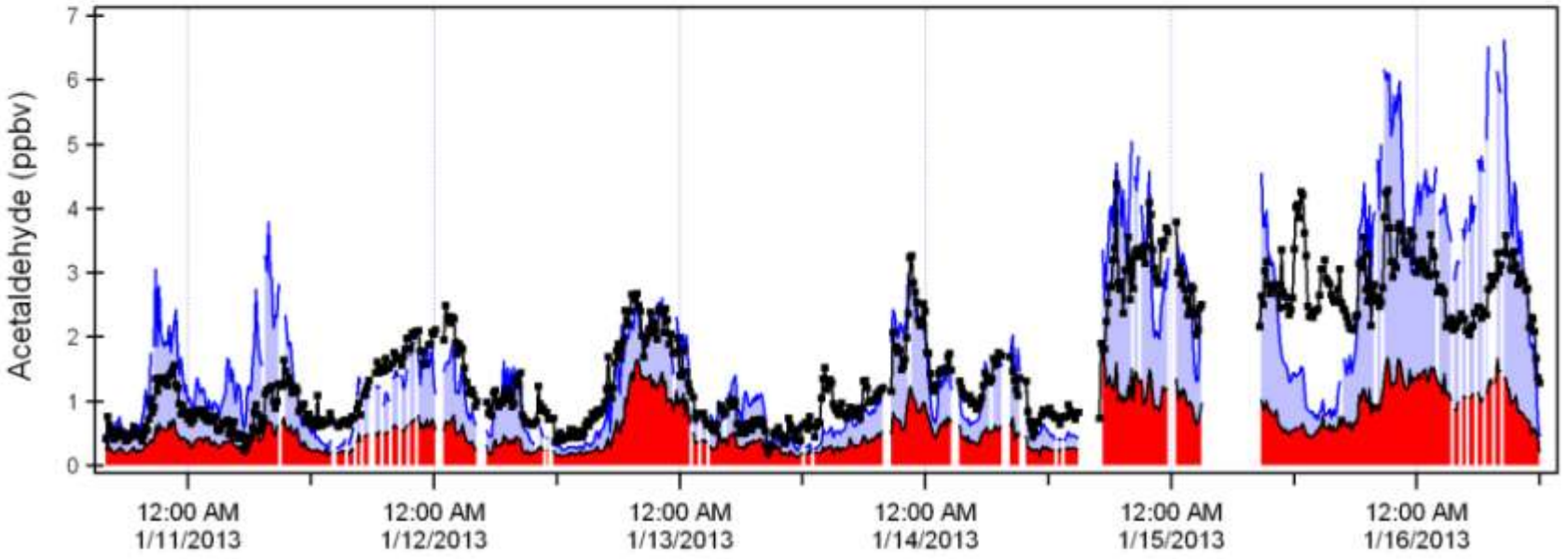


72%
28%

3. Formaldehyde & Acetaldehyde Attribution

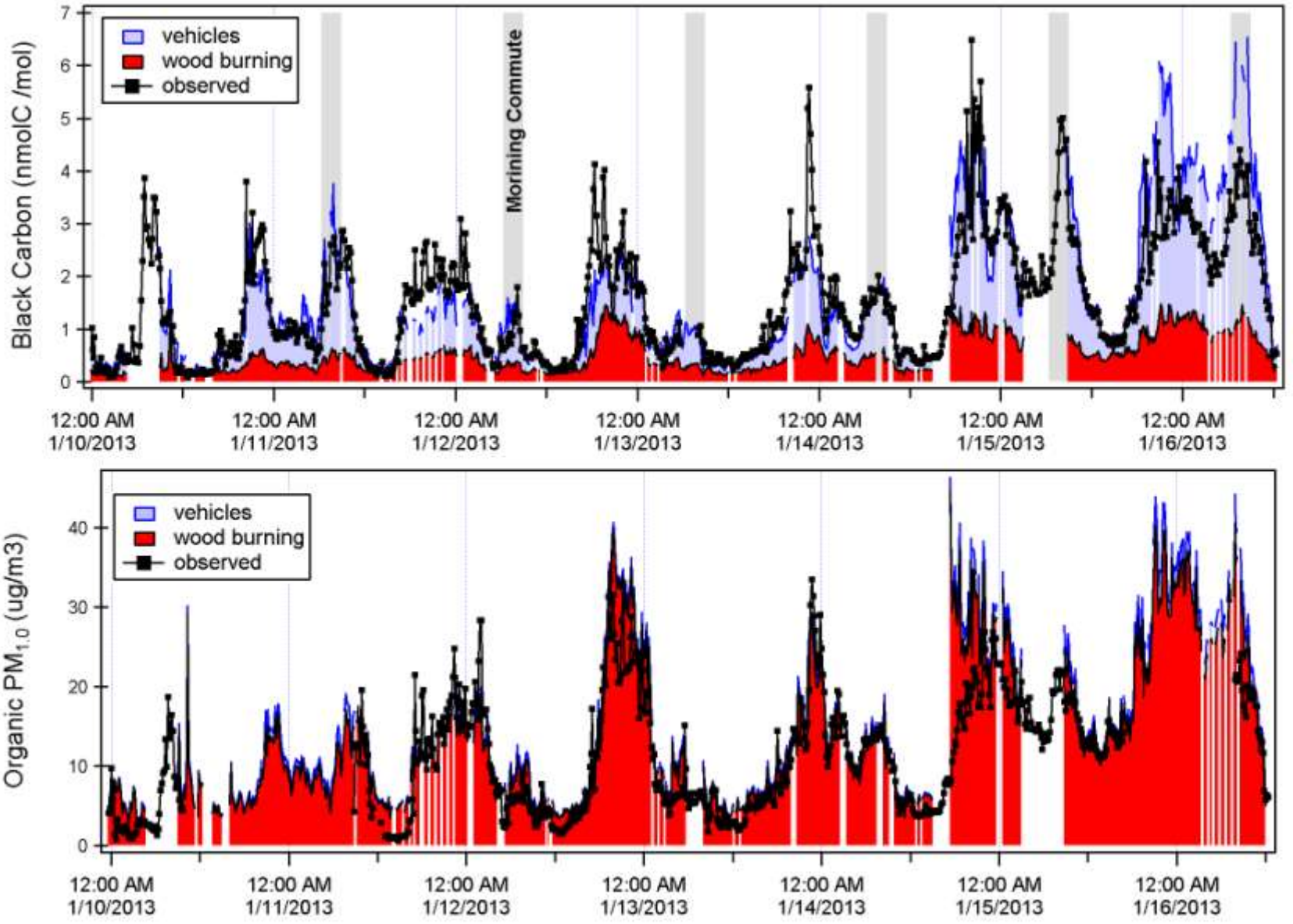


31%
69%



52%
48%

4. Black Carbon & Organic $PM_{1.0}$ Attribution



40%
60%

0%
100%

Comparison to On-Road Emissions Inventory

Compare **ER_{FF}** to Motor Vehicle Emissions Simulator (MOVES) predicted emissions

	ER_{FF}	MOVES	Diesel	Gasoline
CO / NOx	**12.2**	**10.5**	0.32	15.8
BC / NOx	**0.029**	0.040	0.082	0.019
HCHO / NOx	**0.053**	0.0074	0.0063	0.0080
CH_3CHO / NOx	**0.034**	0.0054	0.0019	0.0072
Benzene / NOx	**0.018**	0.0073	0.0002	0.012
Toluene / NOx	**0.039**	0.019	0.0002	0.029

Aldehyde emission ratios underestimated by a factor of 6-7

Aromatic emission ratios underestimated by a factor of ~2

Summary

- High concentrations of aerosol and trace gas pollutants were seen during clear-sky stagnation conditions.
- Under overcast conditions, concentrations of primary pollutants decreased dramatically, but particulate nitrate and other secondary species remained at relatively high levels.
- Observed behavior could be explained by shifts in the nitrogen chemistry (NO_3 radical chemistry at night) due to better PBL mixing.
- Simple CMB model suggests residential wood burning dominate source of formaldehyde (70%) and black carbon (60%).