Comparison Between Particulate Matter Sampled at Urban and Rural Locations in the San Joaquin Valley: Continuous Measurement of Single Particle Size and Composition

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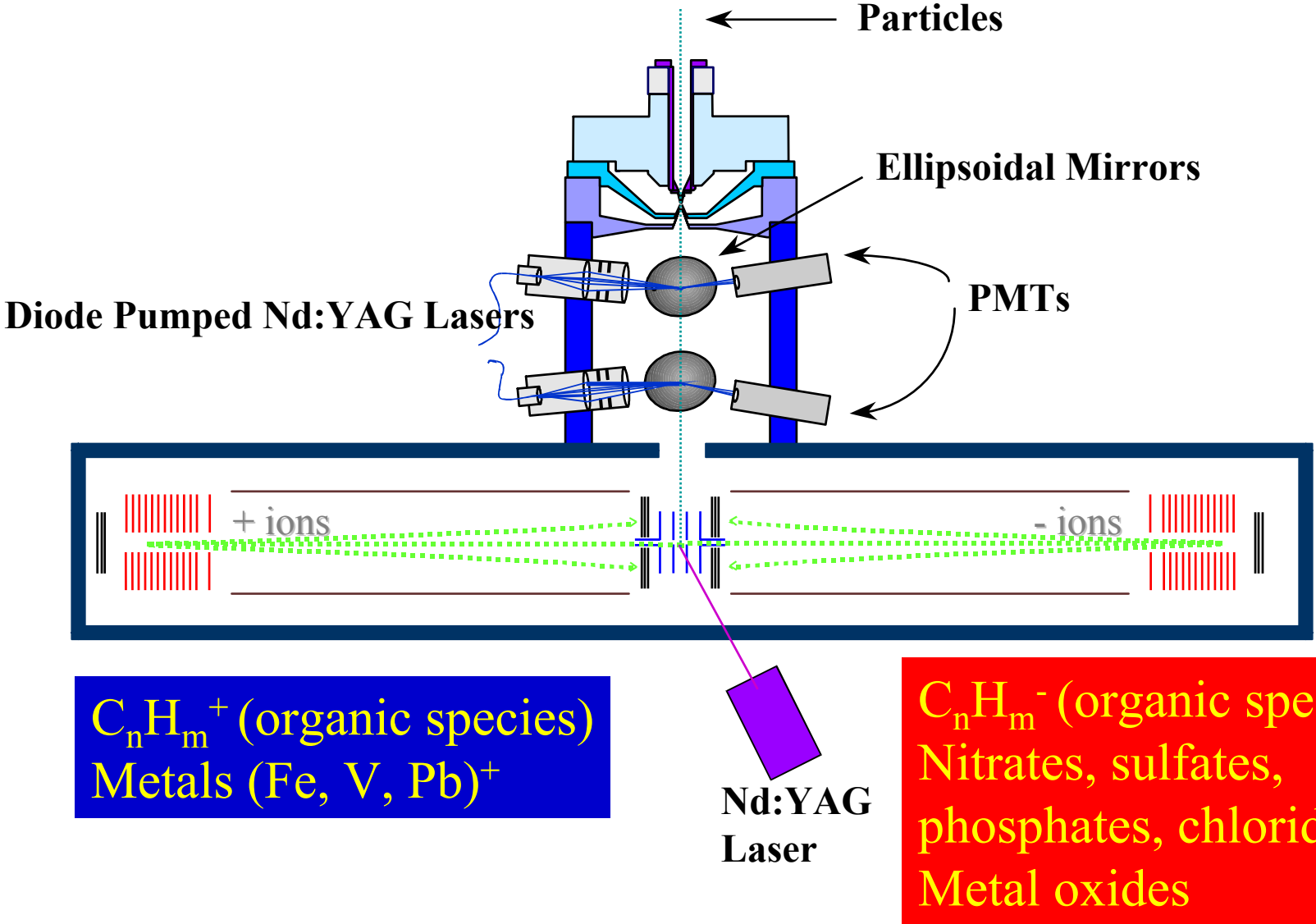
Goals of ATOFMS CRPAQS Studies

- Use ATOFMS at 2 locations (Fresno and Angiola) to measure the temporal variability of individual particle composition and size (30-60 minute temporal resolution).
- Determine composition differences in rural (Angiola) vs. urban (Fresno) locations.
- Determine major sources in the different regions
- Study effects of fog processing on particle composition

ATOFMS

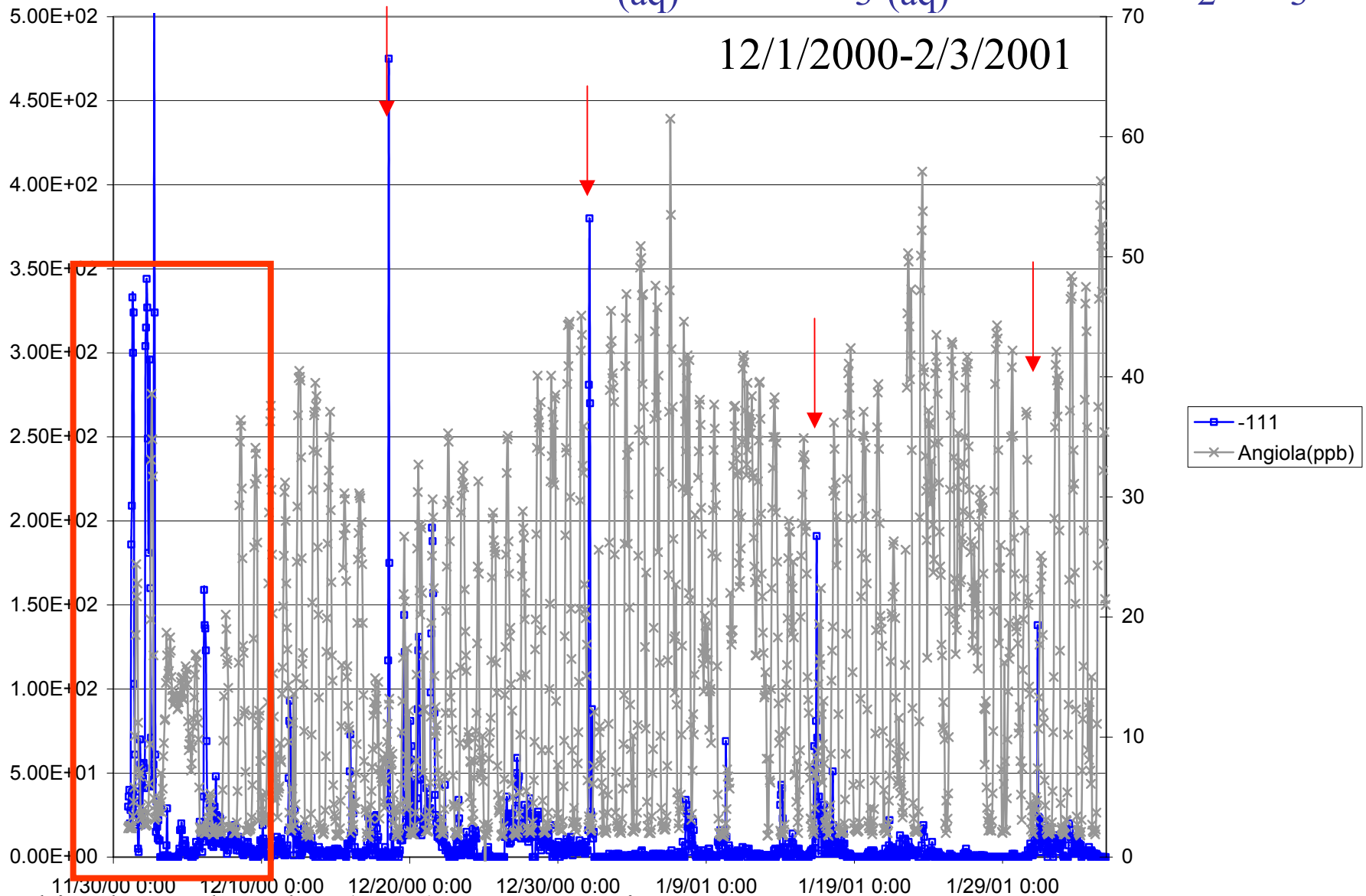


$C_nH_m^+$ (organic species)
Metals (Fe, V, Pb)$^+$

$C_nH_m^-$ (organic species)
Nitrates, sulfates, phosphates, chloride
Metal oxides

Ozone(g) versus HMS(particles)

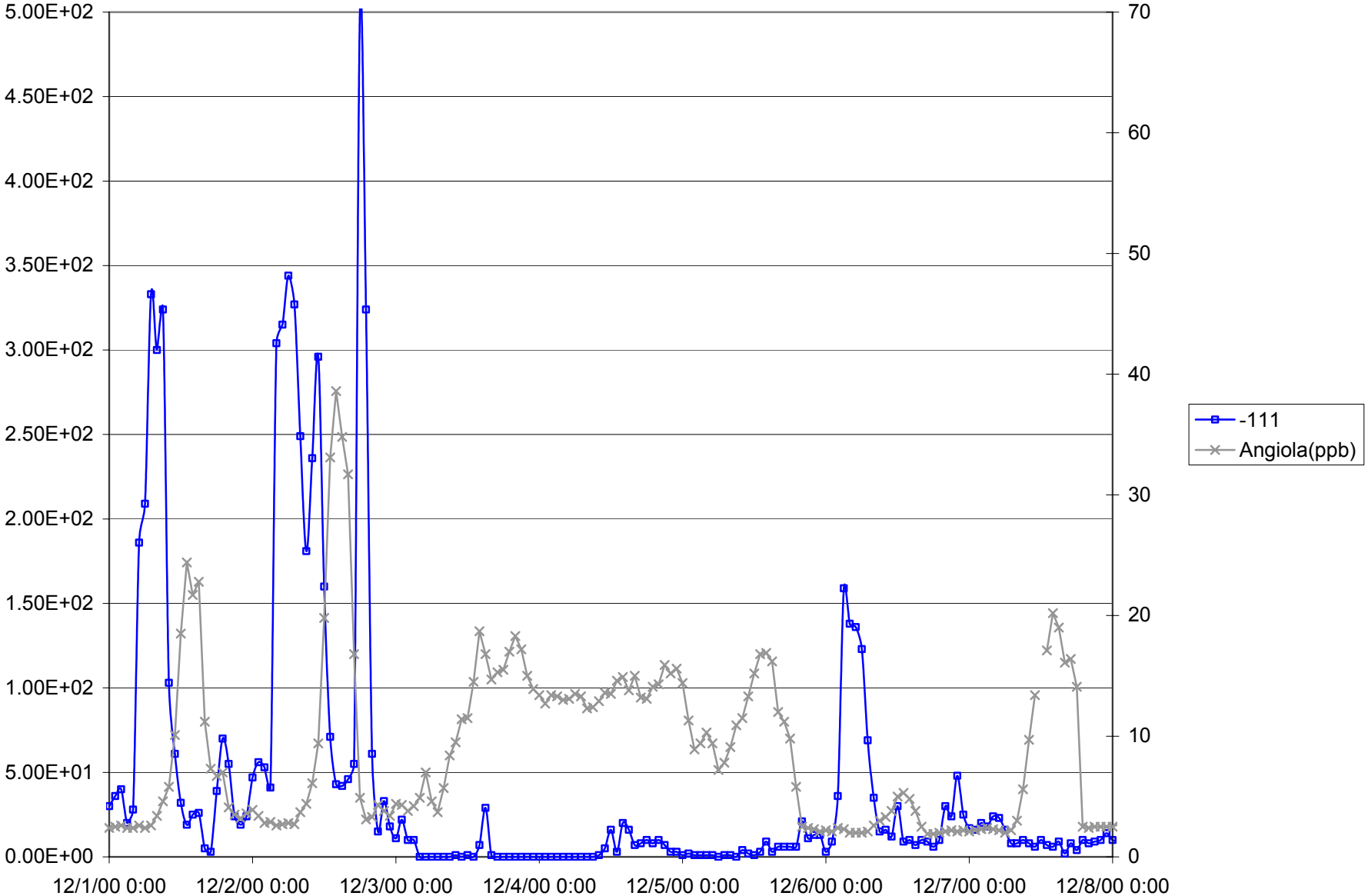
HMS formation: $HCHO_{(aq)} + HSO_3^-{}_{(aq)}$? $HOCH_2SO_3^-$



Whiteaker and Prather (2003) Atmos. Environ. 37 1033-1043

Ozone(g) versus HMS(particles)

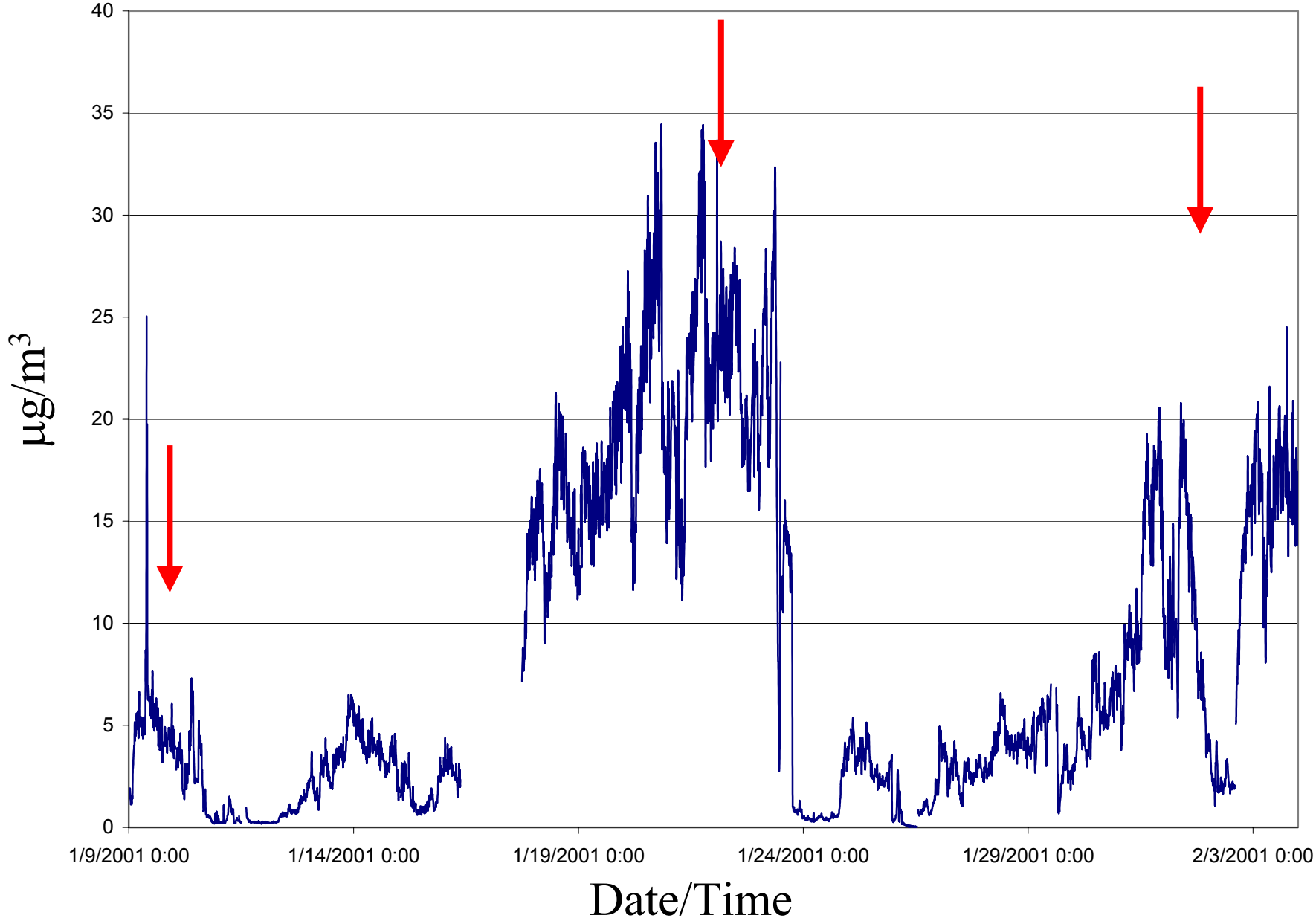
December 1, 2000-December 8, 2001



Motivation for SVOC measurements

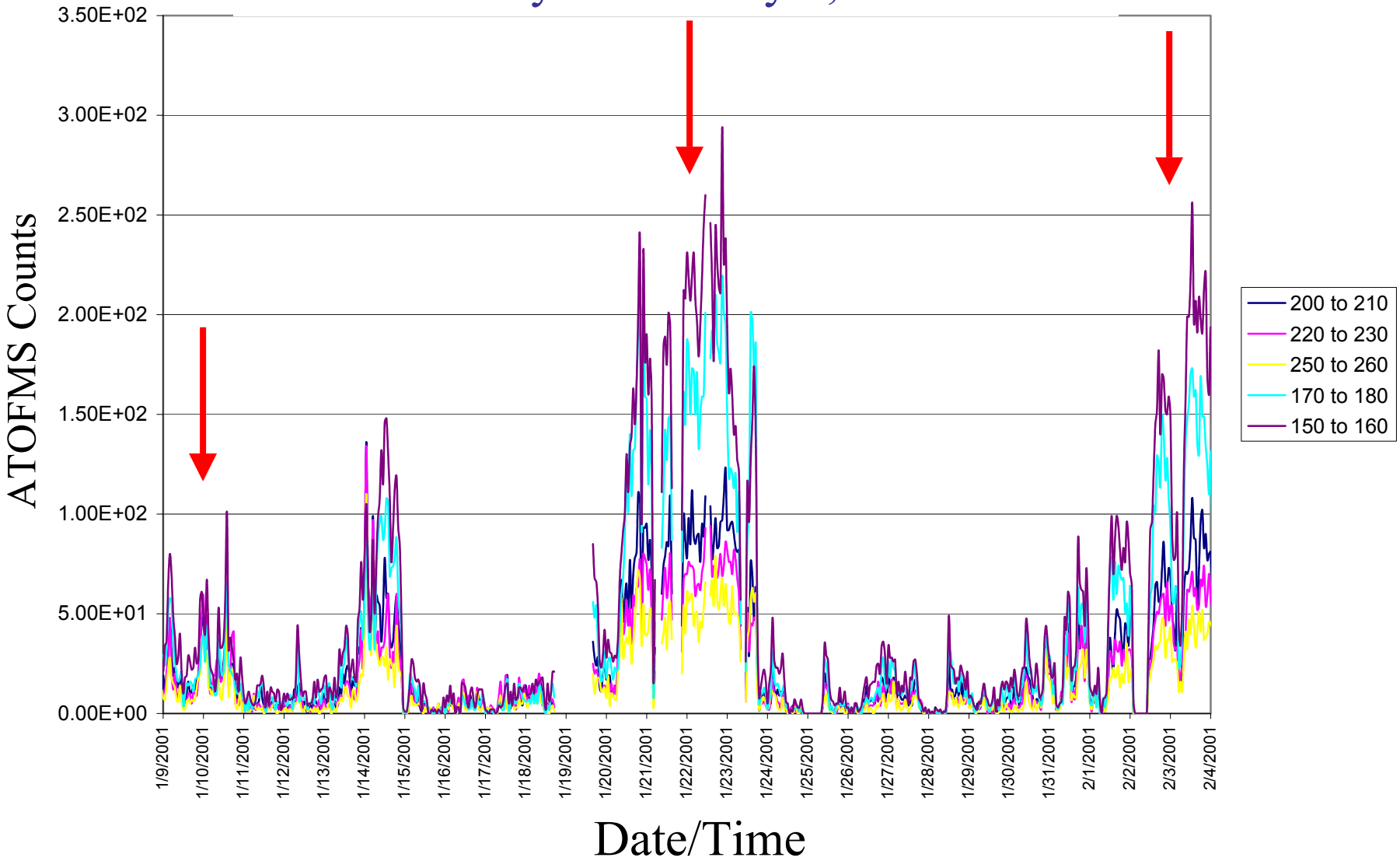
- High fraction of SVOC associated with PM in central California region
- ATOFMS measures nitrate, sulfate, carbon (EC vs. OC), metals, phosphates, etc.
  - Correlations established with $PM_{2.5}$, nitrate, sulfate, ammonium mass on long (MOUDI 4 hr.) and short (30 minute) timescales
- Can ATOFMS be used to measure temporal variability of semivolatile organic species?
  - Proposed as contributors to health effects
  - Many are aromatic, PAH, and derivitized (i.e. nitrated) species with known mutagenicity and carcinogenicity
  - ATOFMS highly sensitive to aromatic compounds (λ = 266 nm)

Nitrate Mass (Angiola, January 2001)



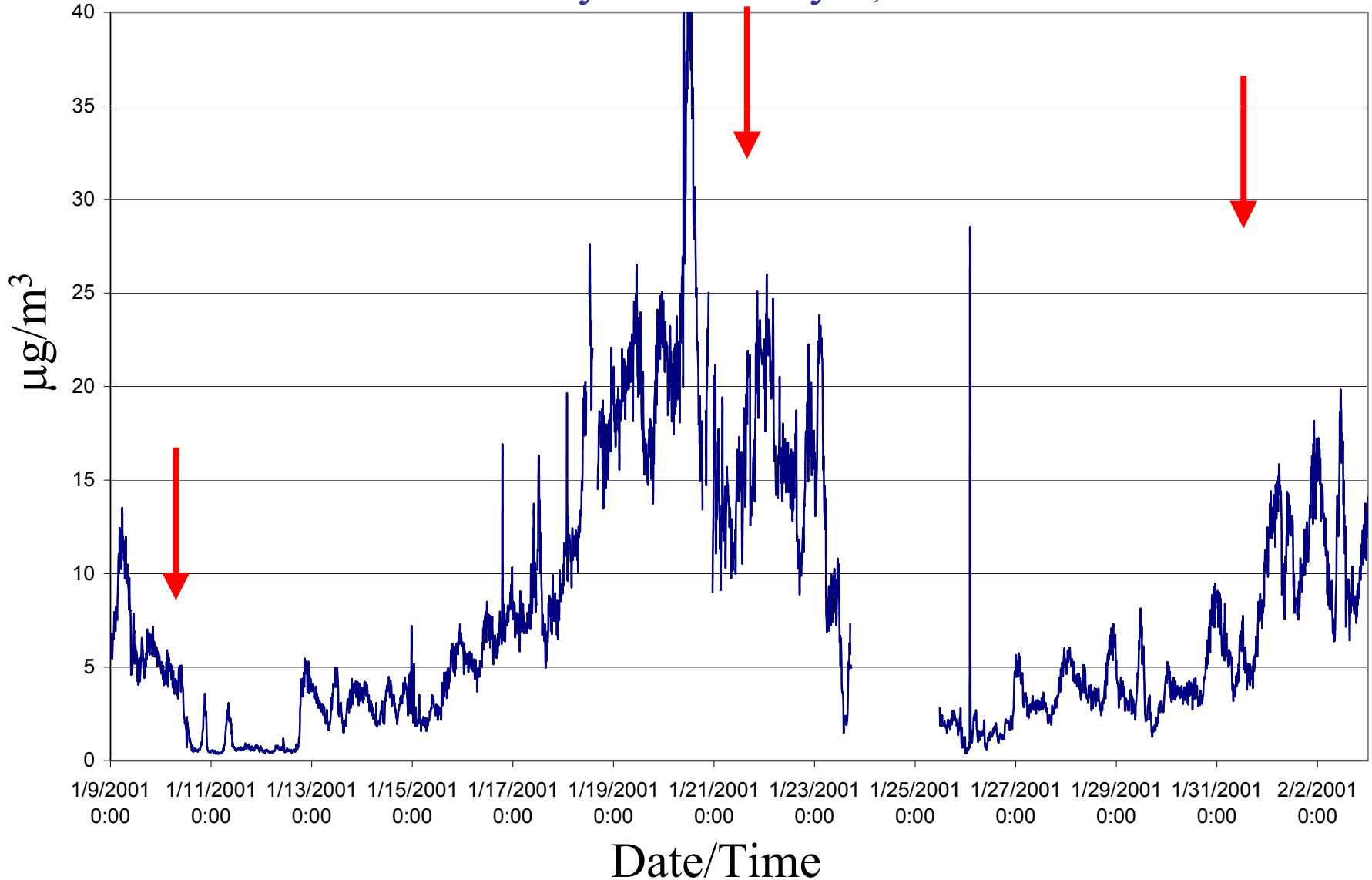
Data provided by Susanne Hering

Temporal Evolution (Angiola)
PAH and Aromatic Marker Ions
January 9-February 4, 2001



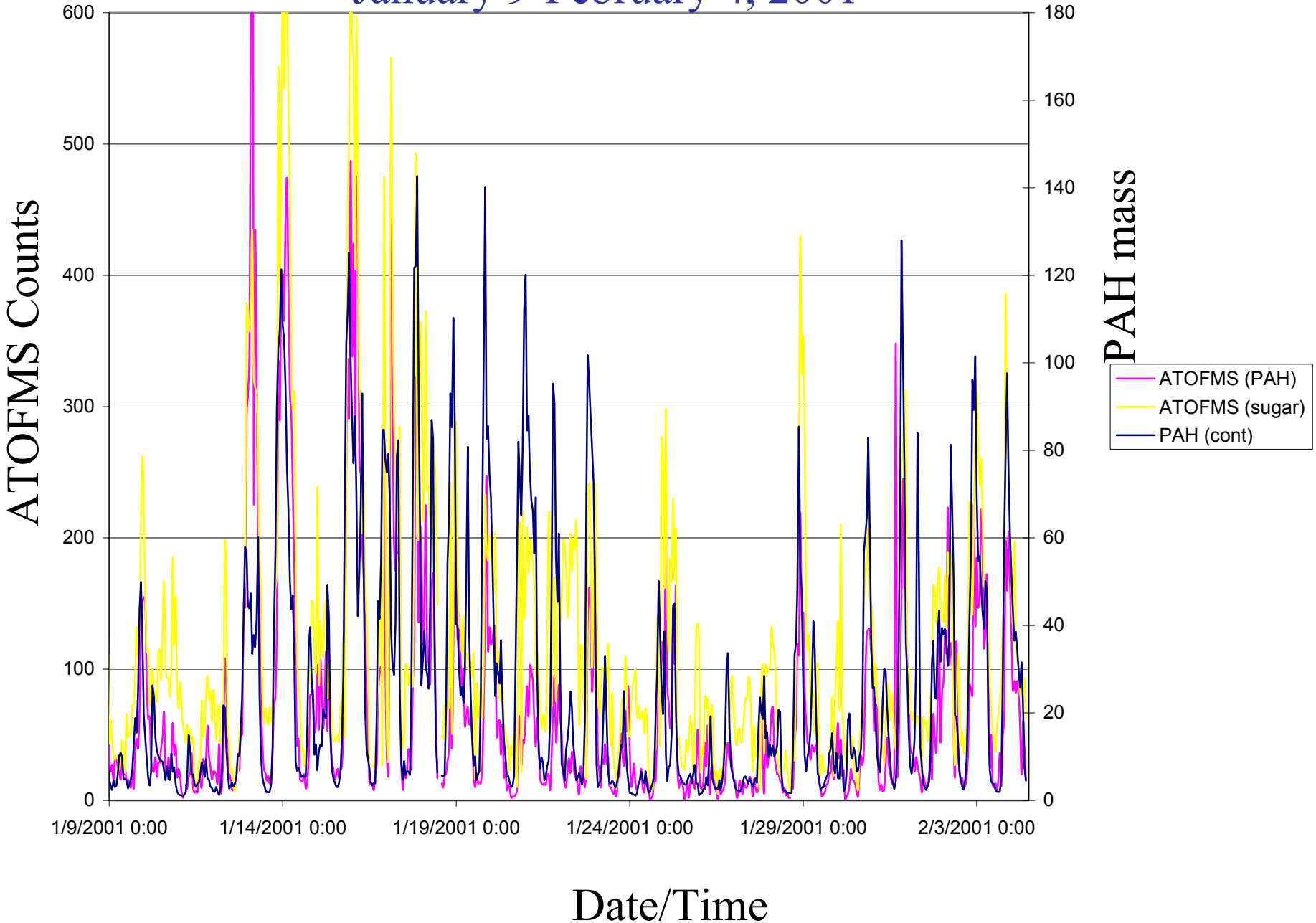
Nitrate Mass (Fresno)

January 9-February 4, 2001



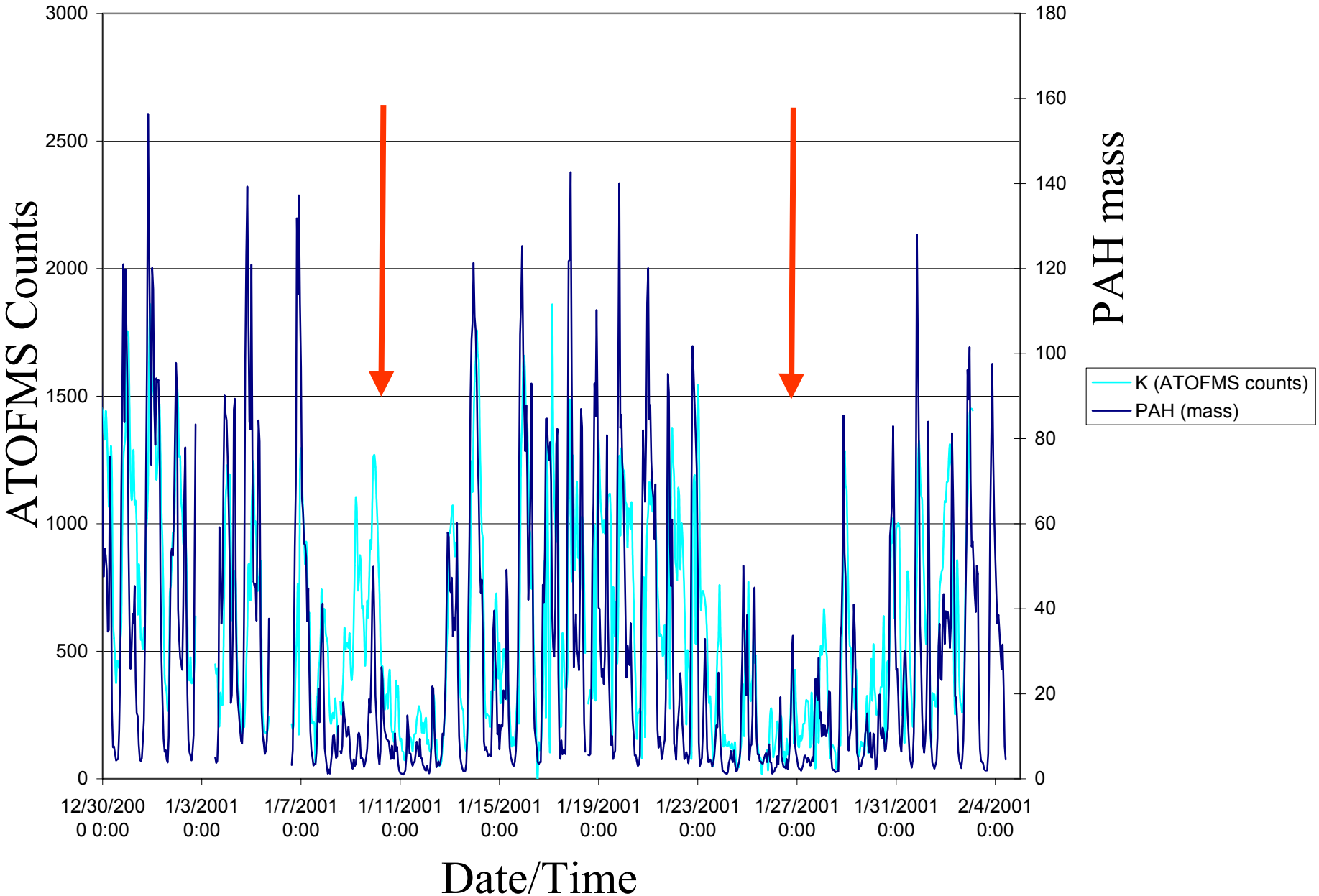
Data provided by Susanne Hering

PAH mass (PAS), # of PAH, # of Biomass (-45) particles (ATOFMS)
January 9-February 4, 2001



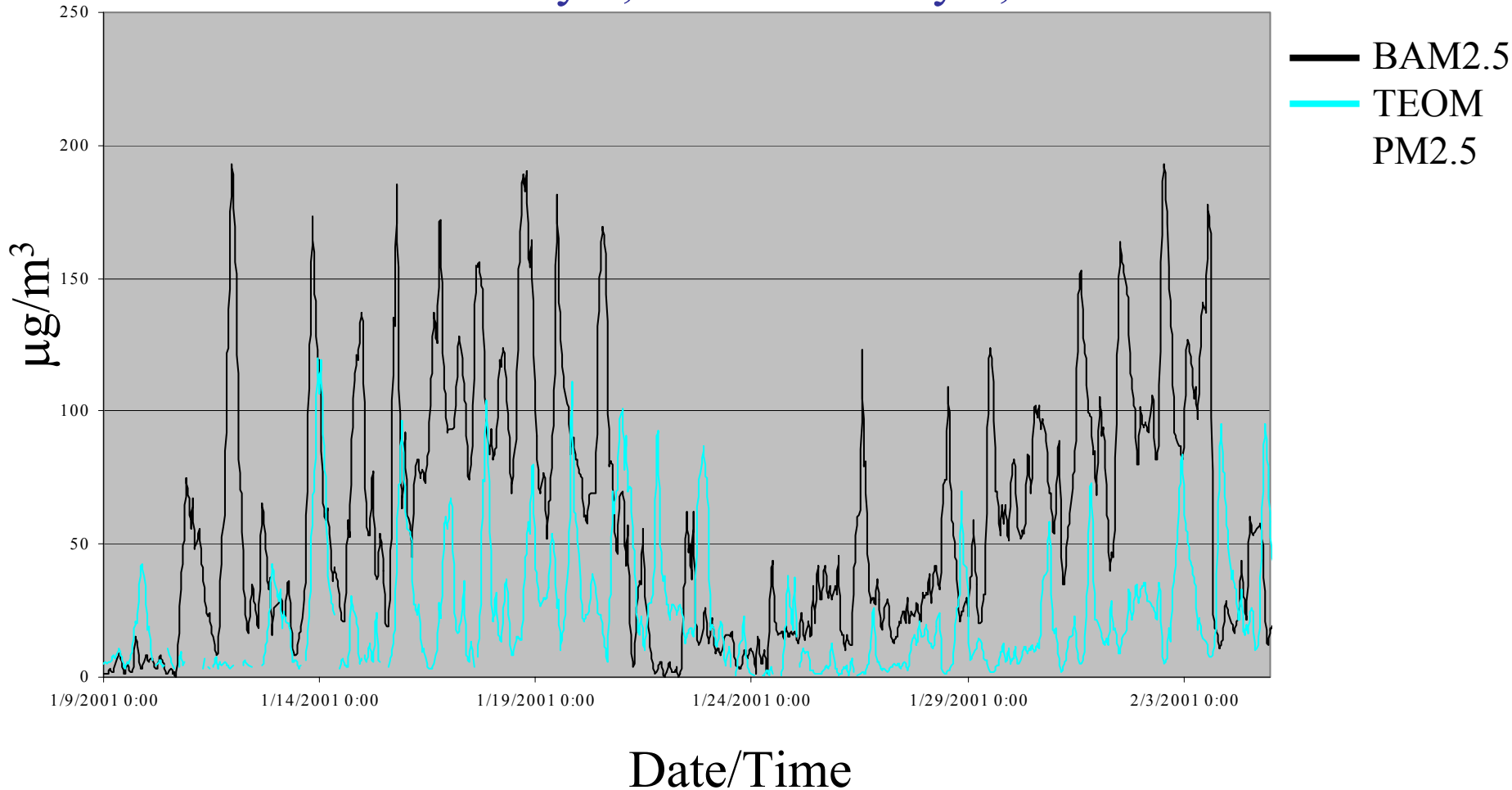
PAH mass (PAS) vs. # of Biomass (K) particles

January 9-February 4, 2001

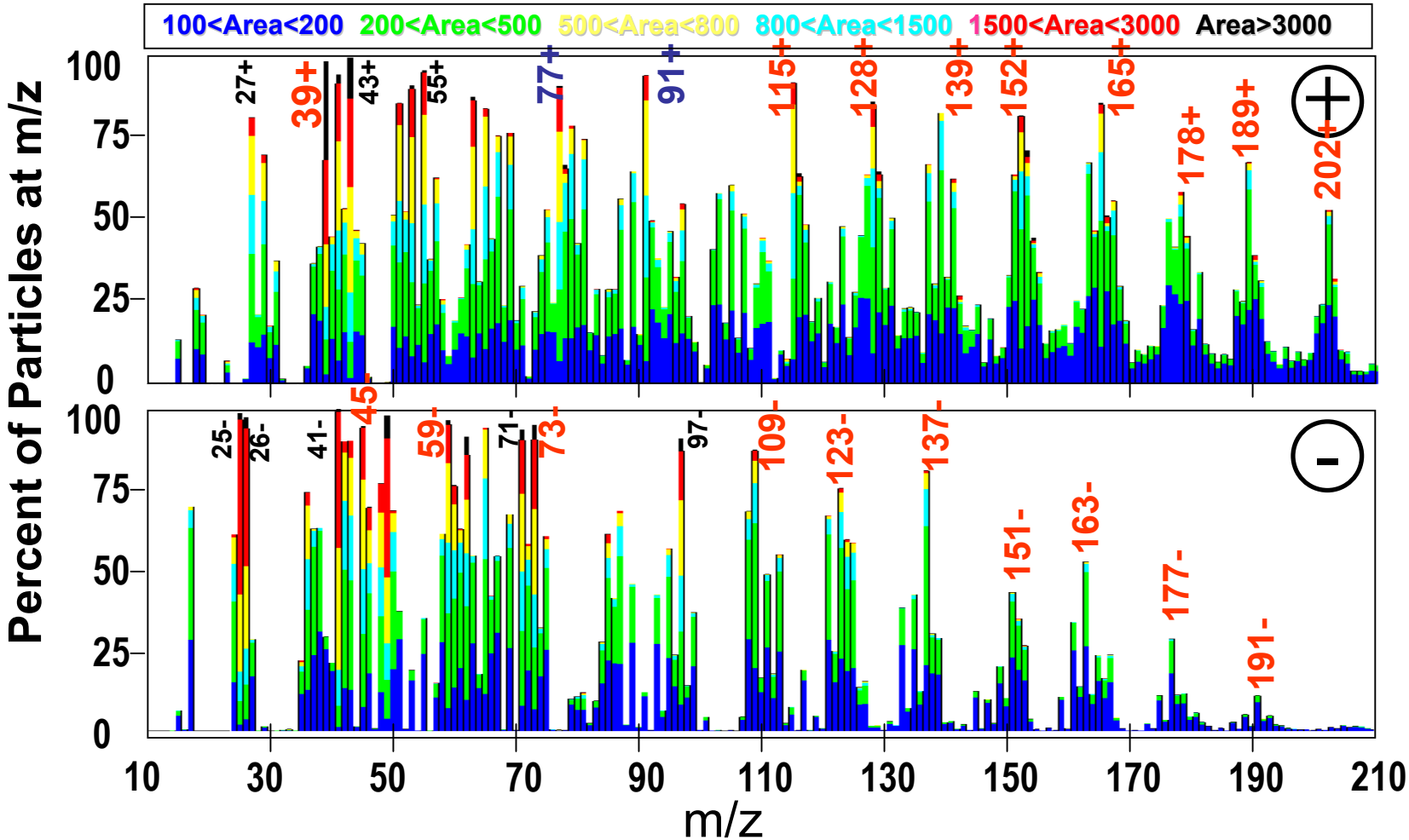


Semivolatile Species (Fresno)
BAM vs. TEOM

January 9, 2001-February 4, 2001

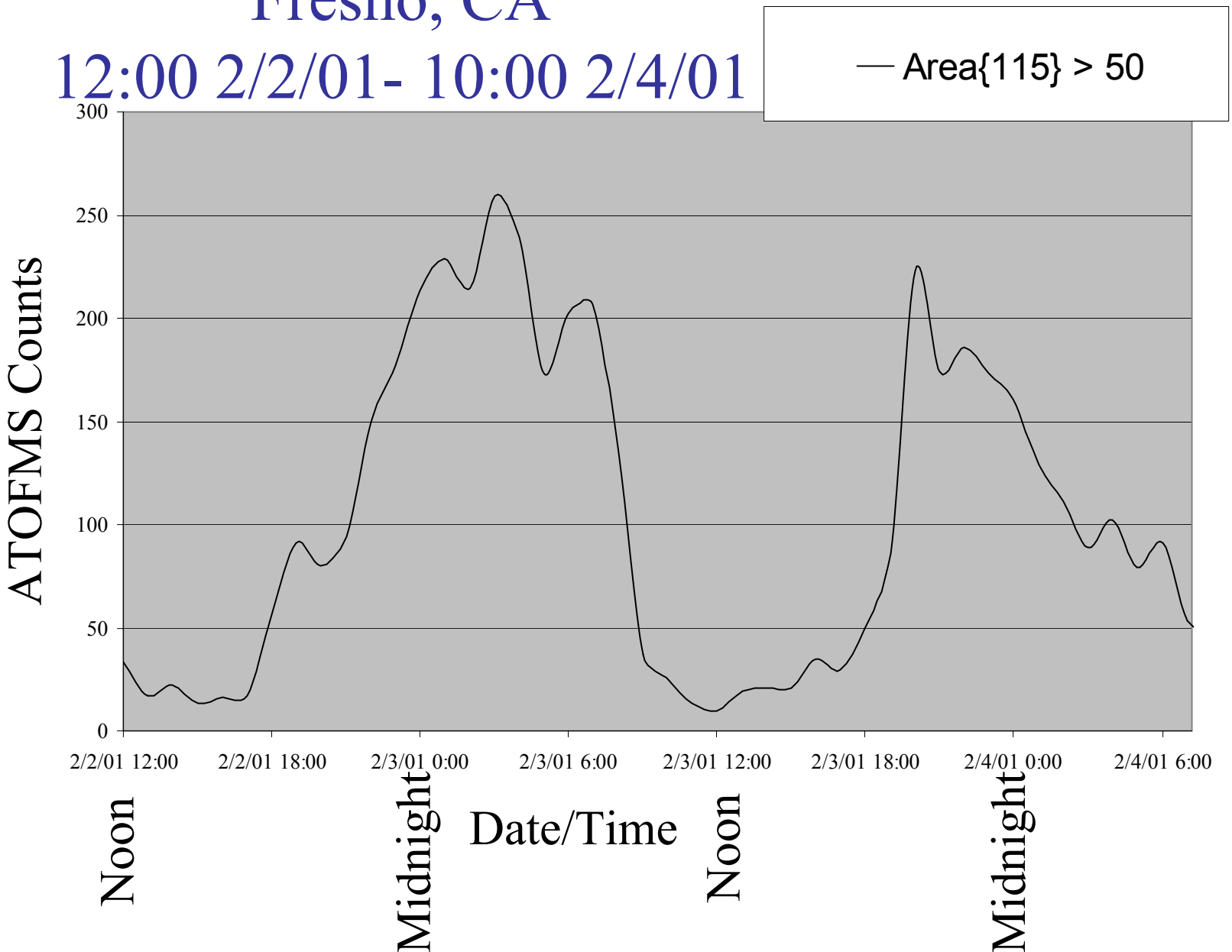


Fresno Semivolatile OC Particles Digital Histogram Spectra

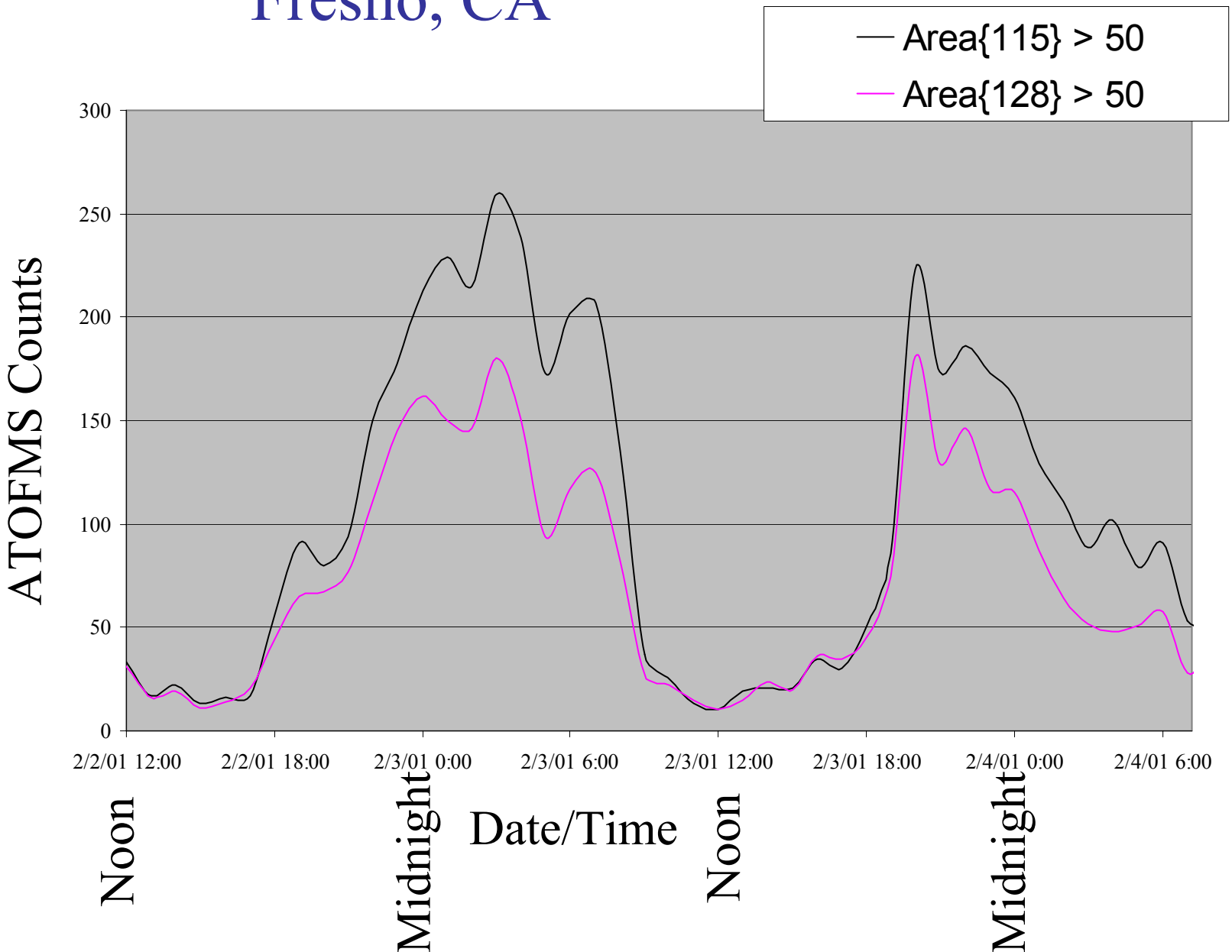


~100% have K^+-biomass core (both sub- and super-µm particle sizes)

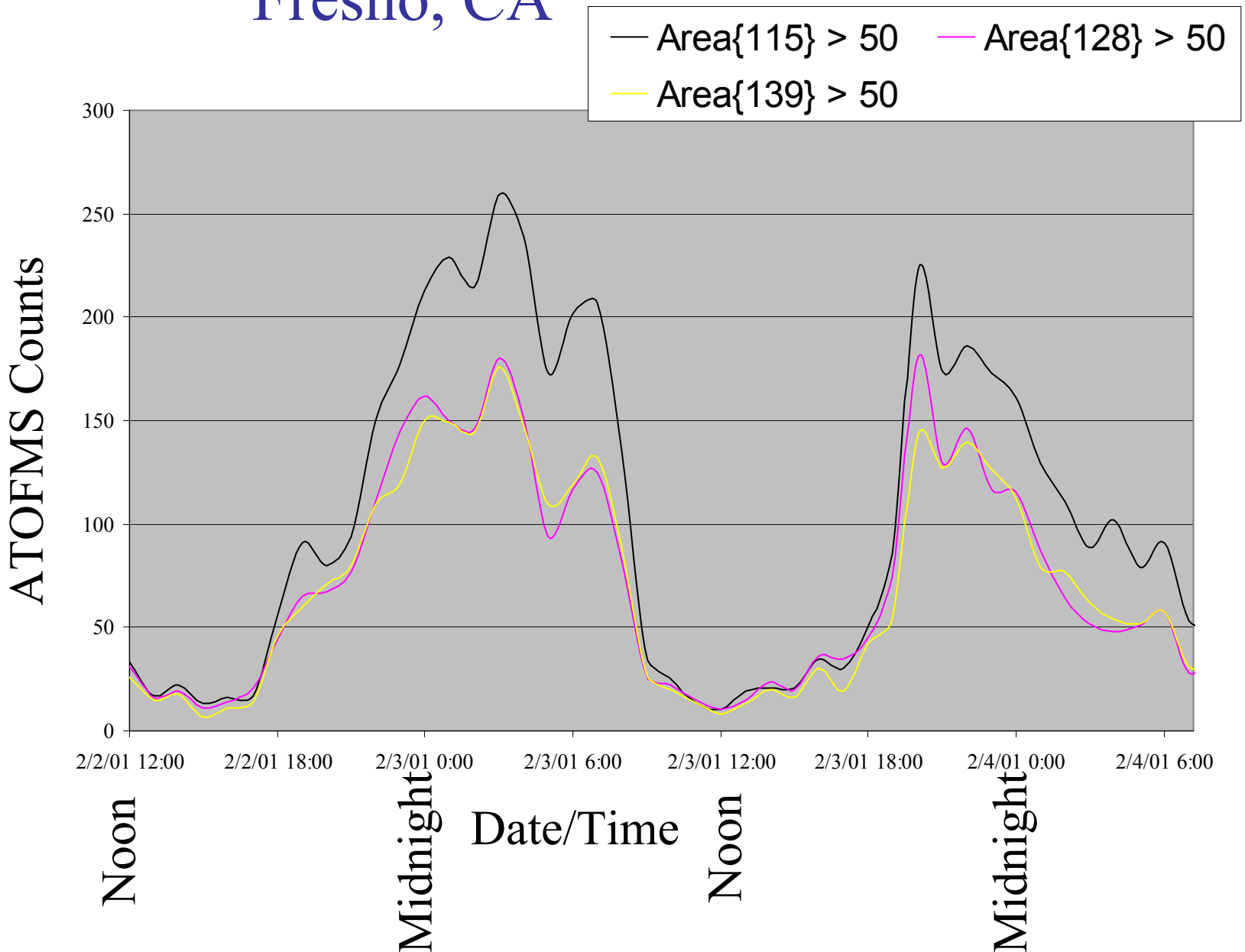
Temporal Evolution of Positive Ions
Fresno, CA
12:00 2/2/01- 10:00 2/4/01



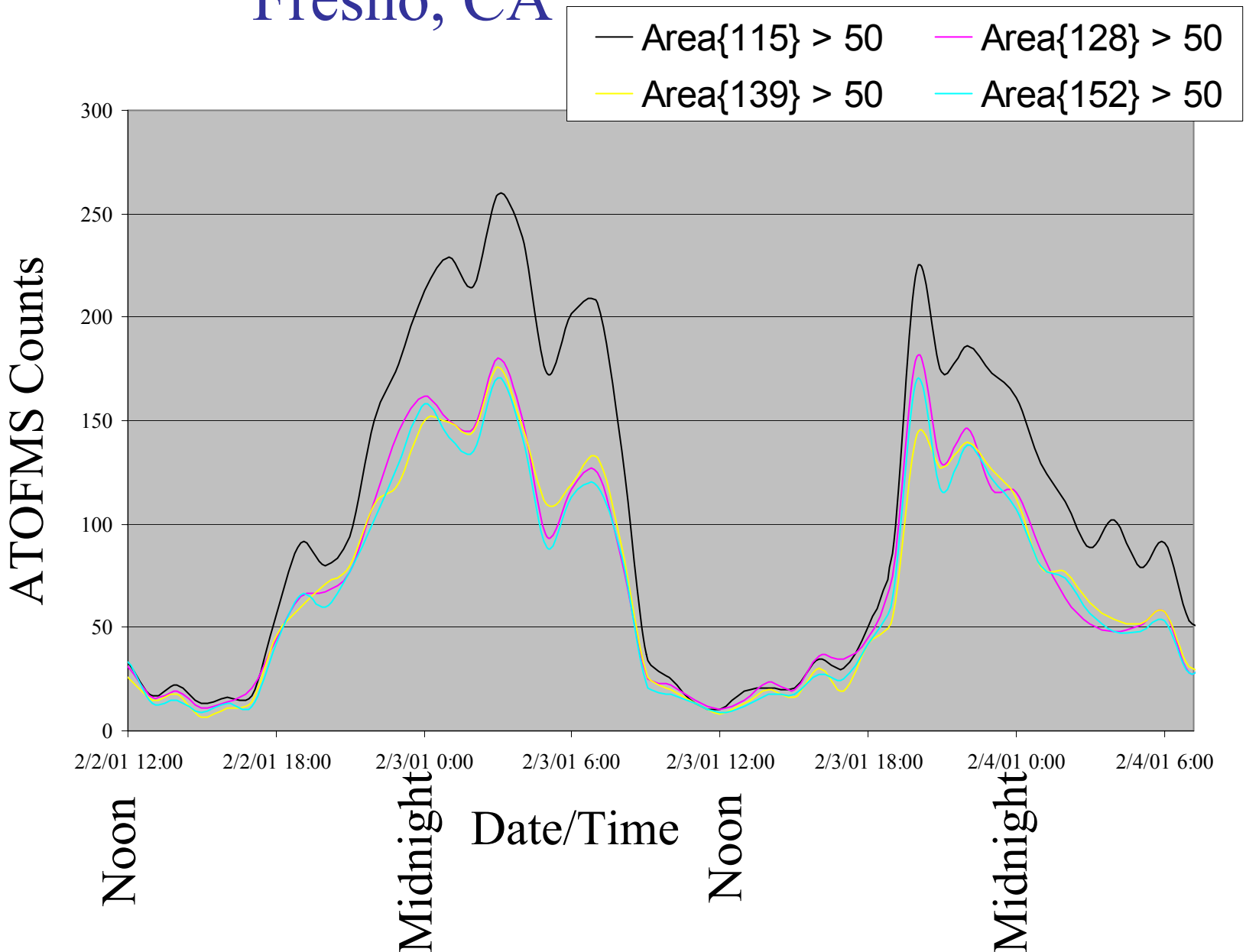
Temporal Evolution of Positive Ions
Fresno, CA



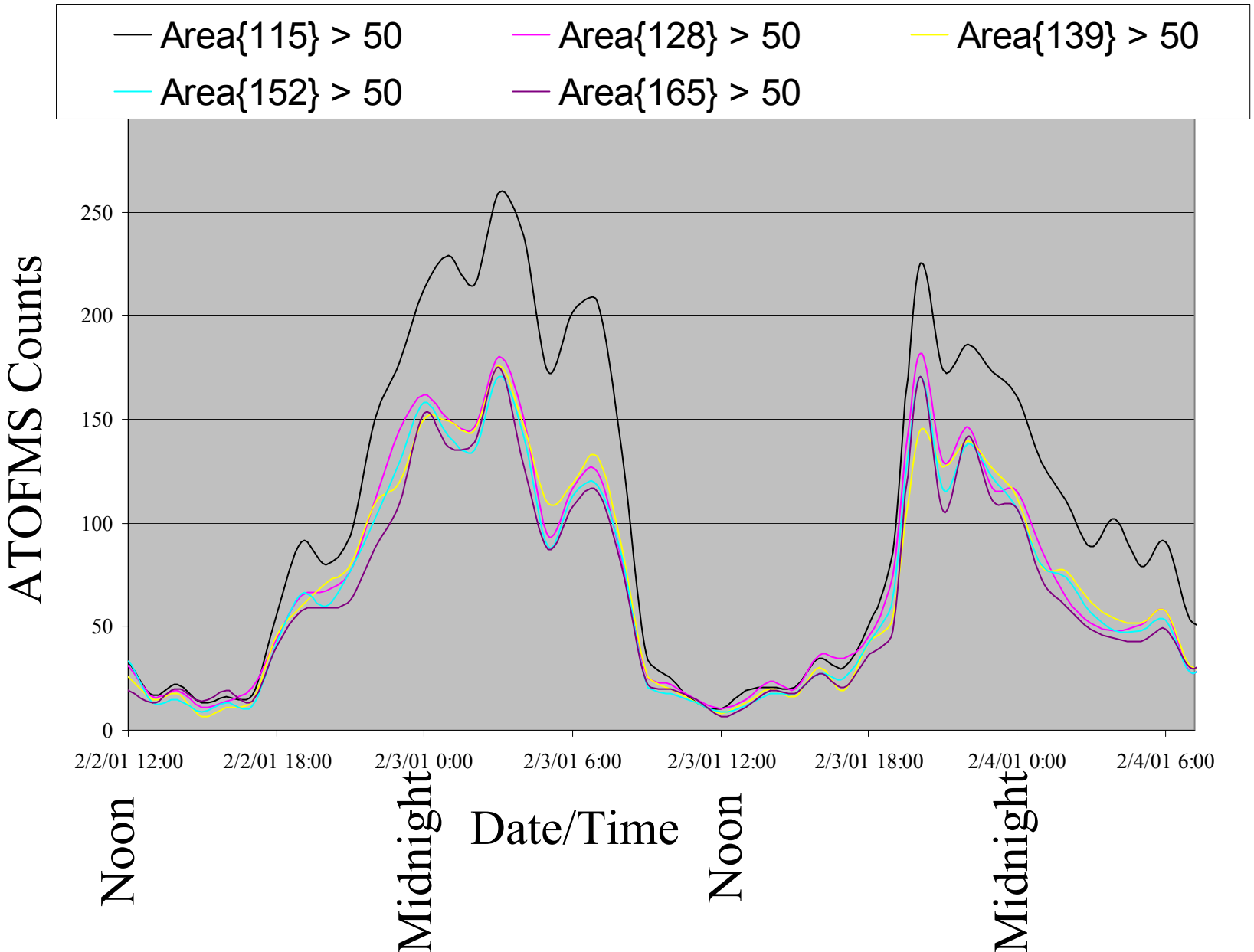
Temporal Evolution of Positive Ions
Fresno, CA



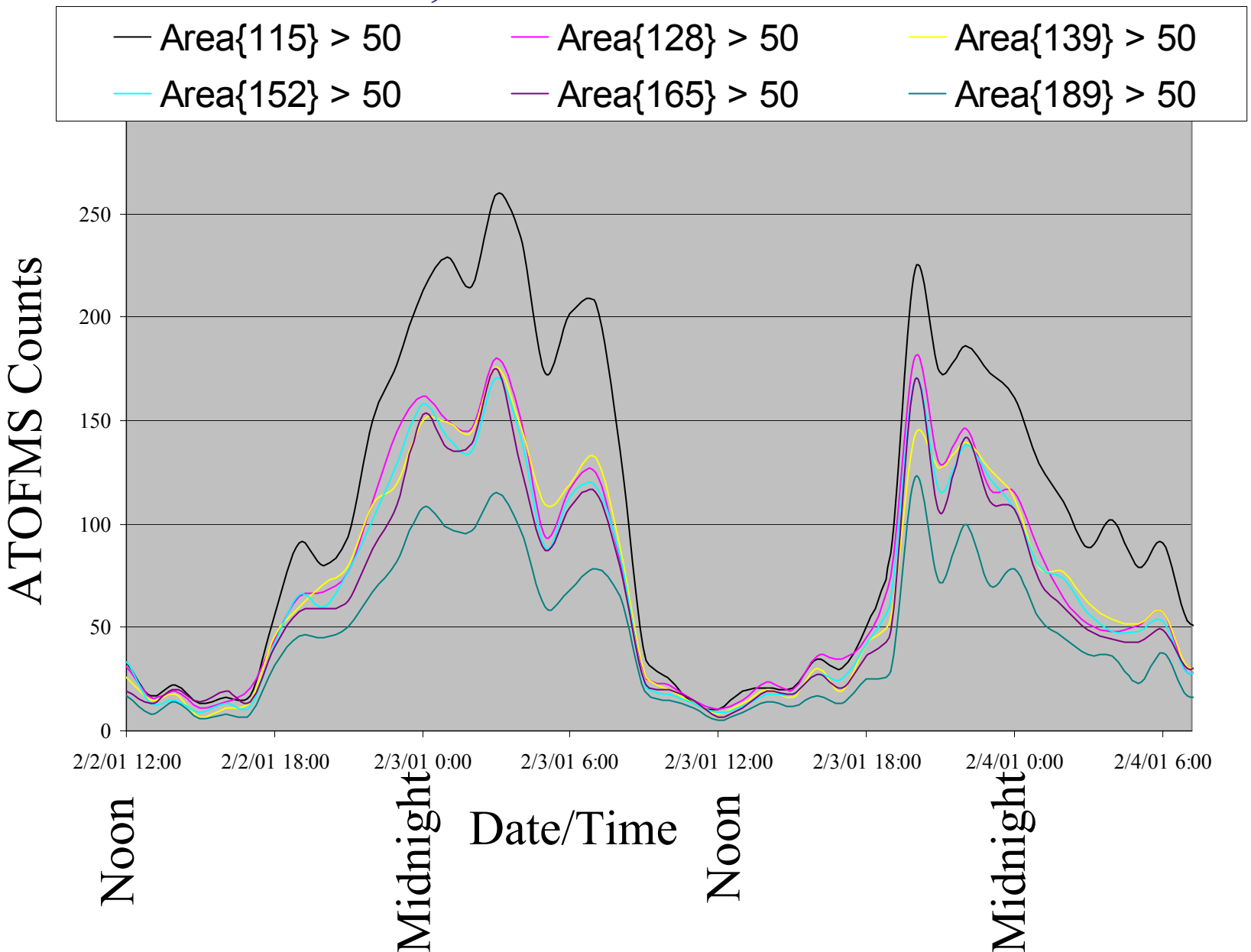
Temporal Evolution of Positive Ions
Fresno, CA



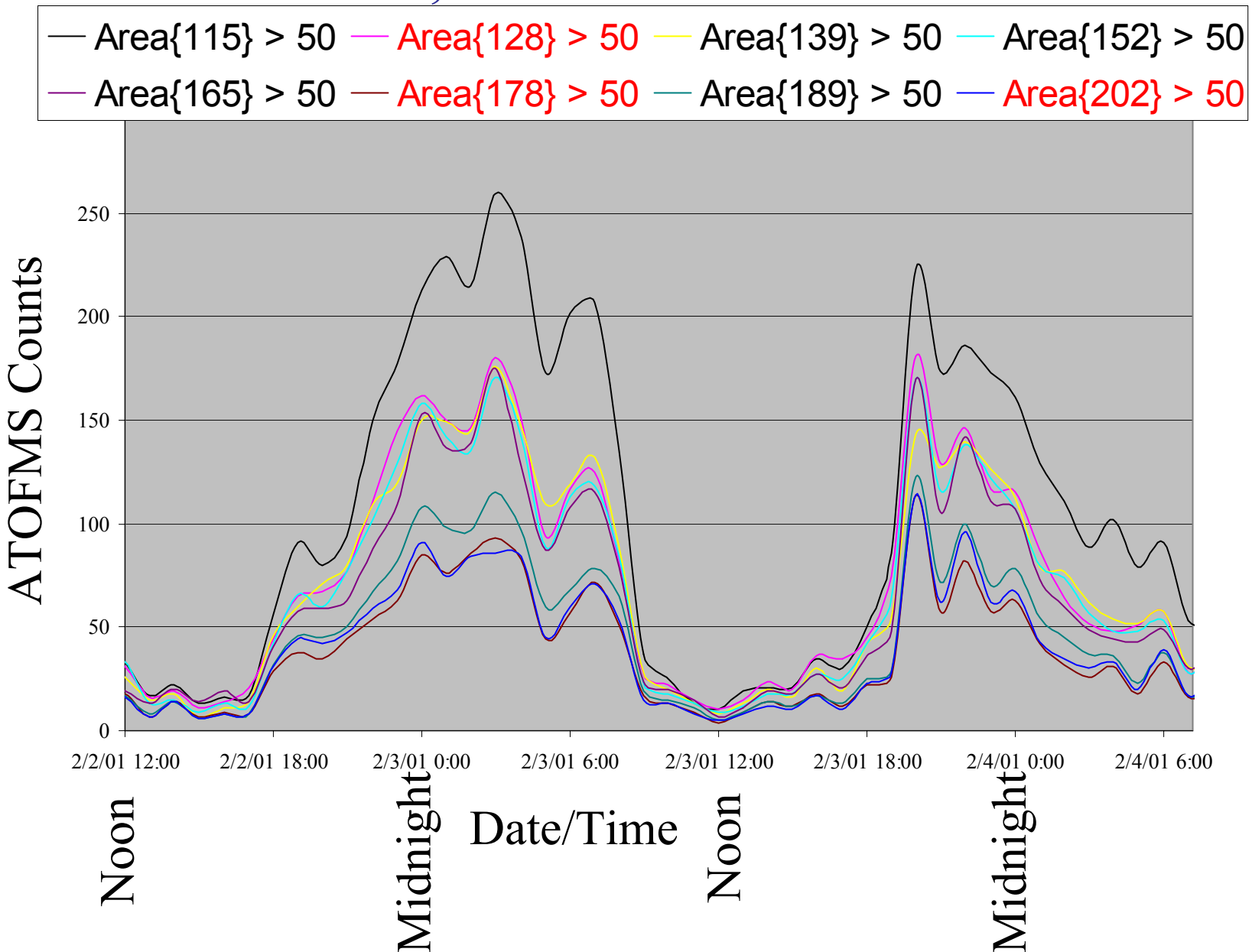
Temporal Evolution of Positive Ions
Fresno, CA



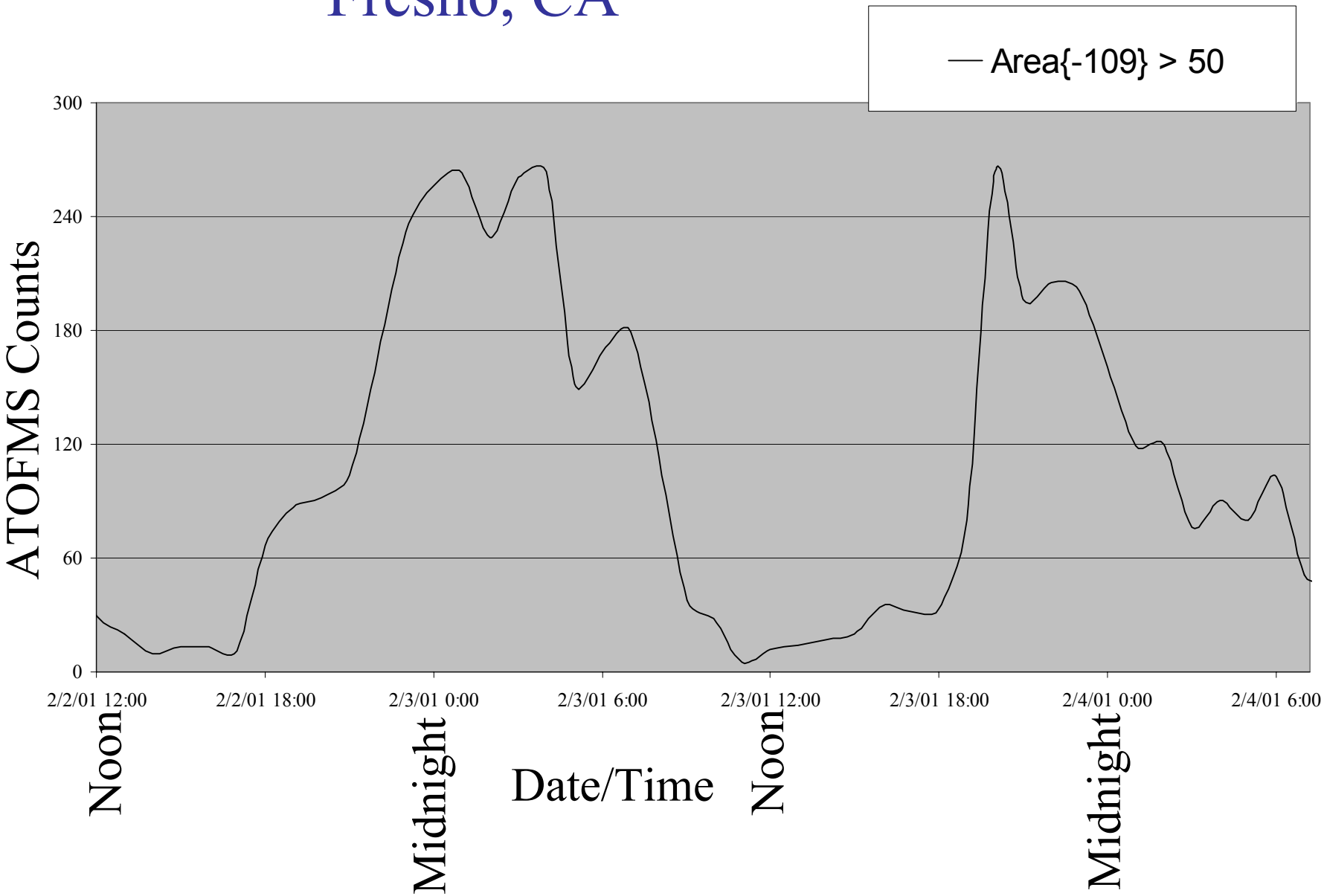
Temporal Evolution of Positive Ions
Fresno, CA



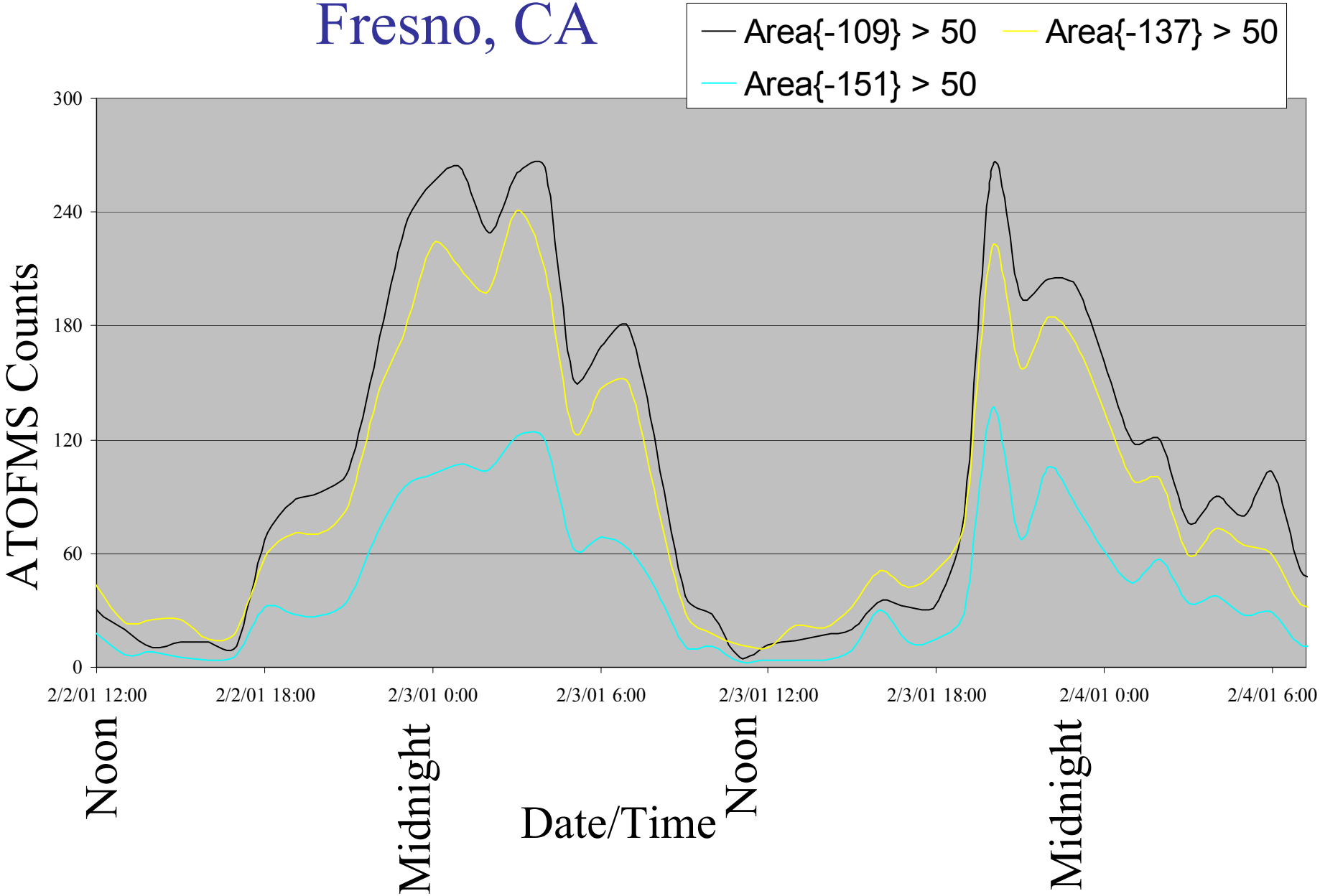
Temporal Evolution of Positive Ions
Fresno, CA



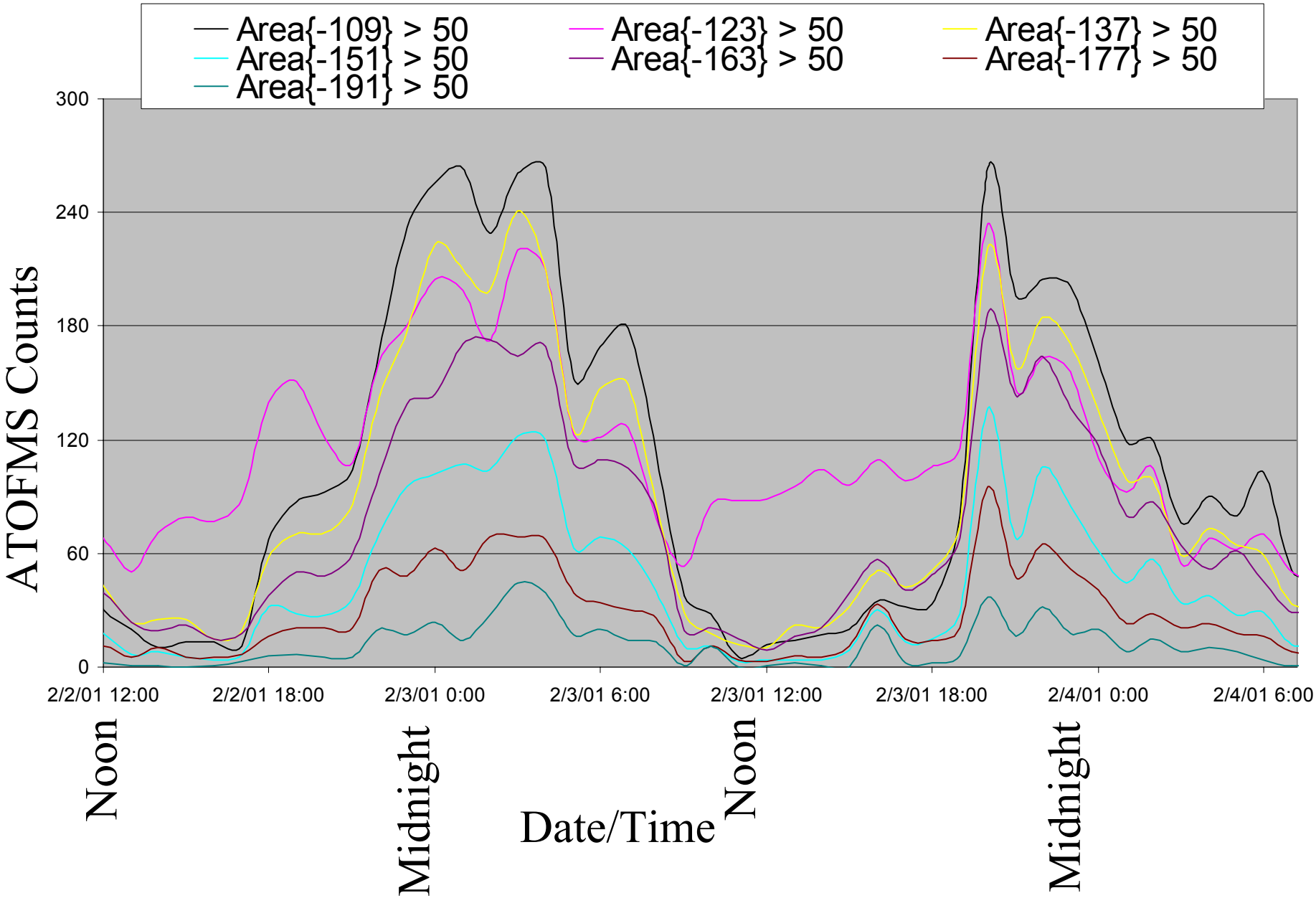
Temporal Evolution of Negative Ions
Fresno, CA



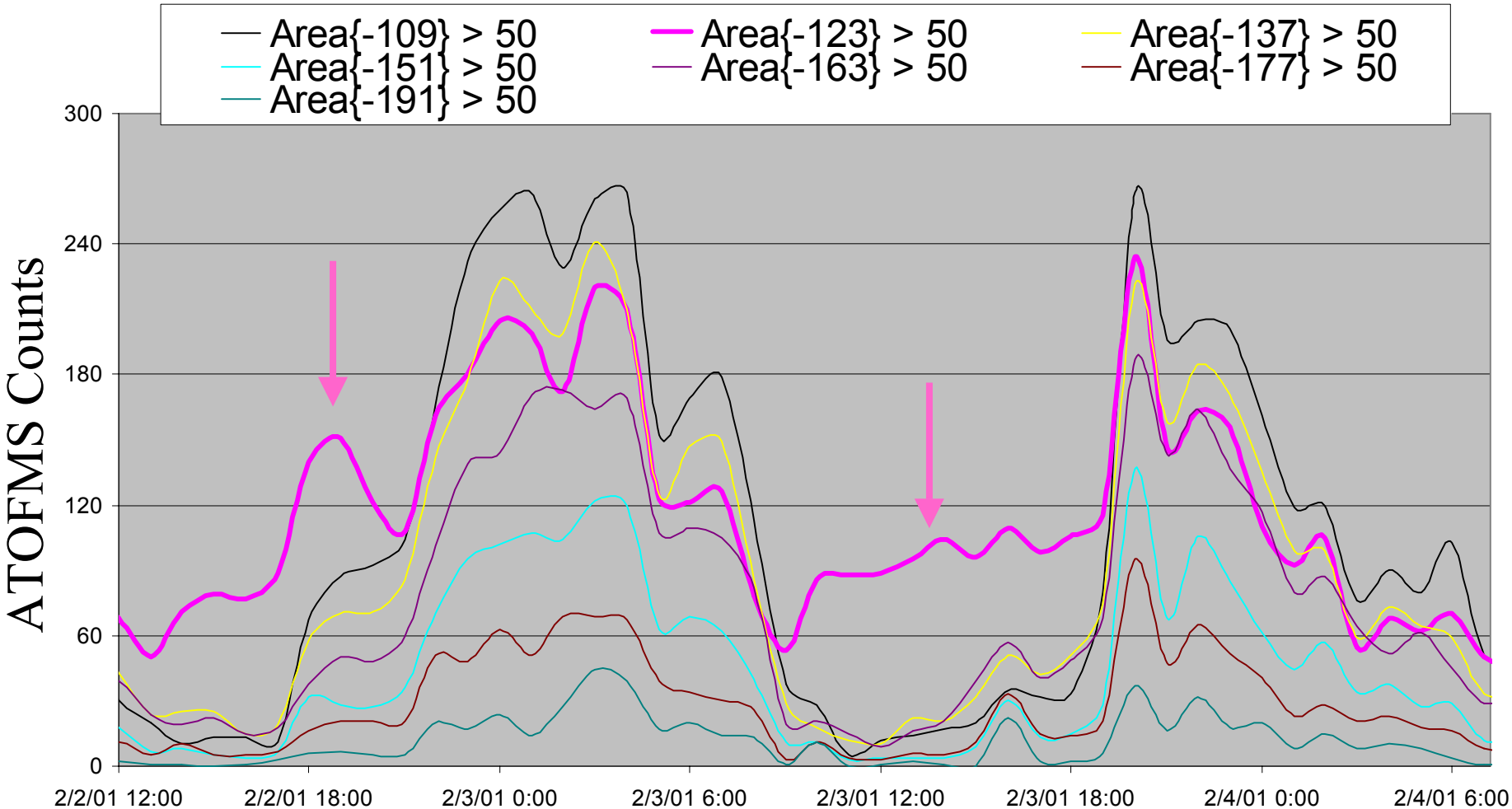
Temporal Evolution of Negative Ions
Fresno, CA



Temporal Evolution of Negative Ions (Fresno, CA)

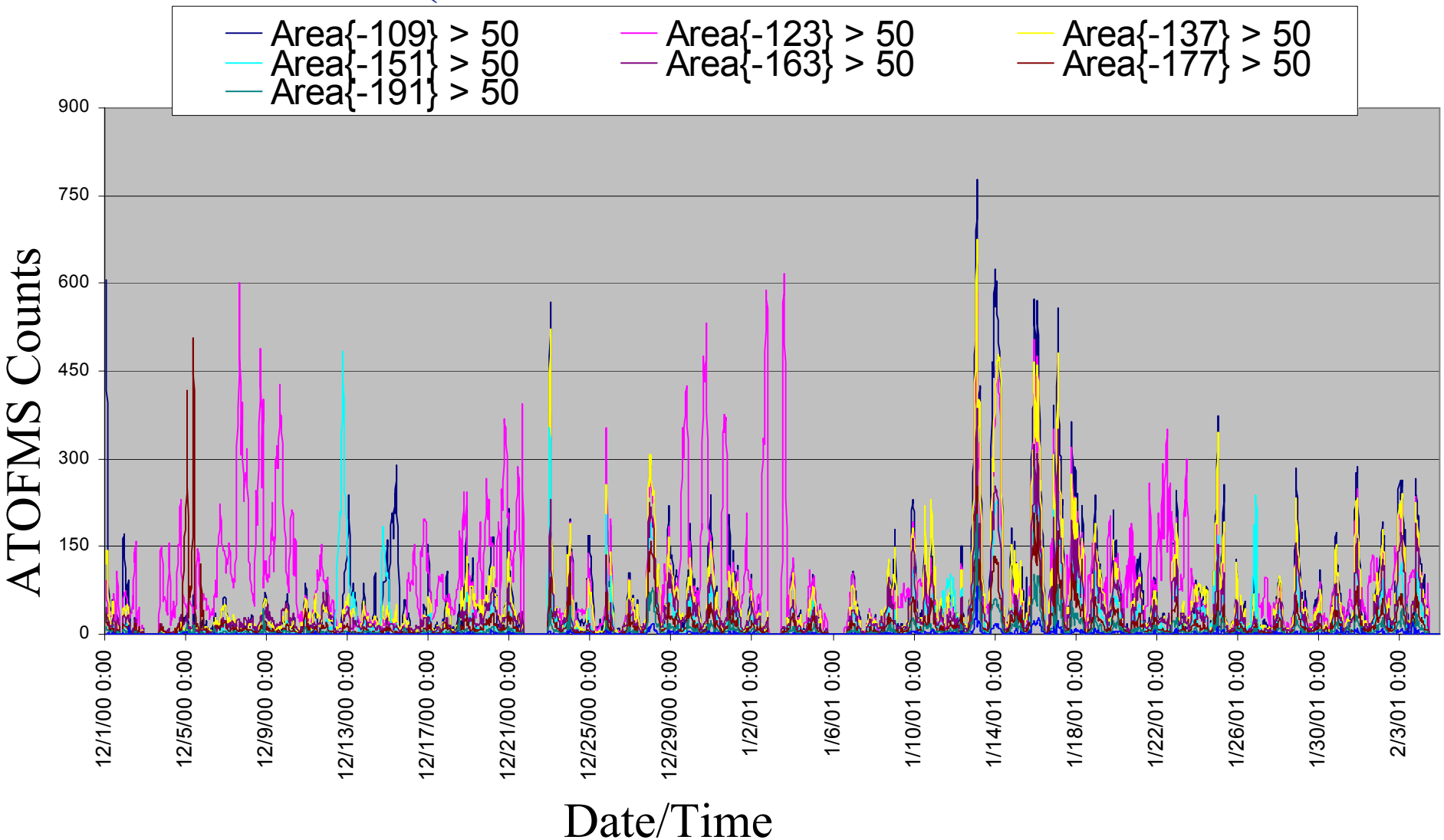


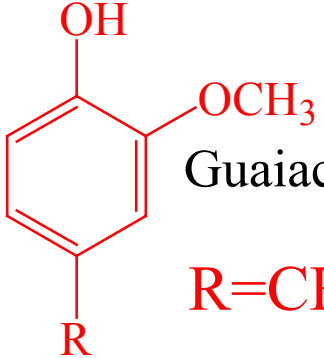
Temporal Evolution of Negative Ions
Fresno, CA



Gas-to-particle partit ght
Primary emissions during day or SOA formation?)

Temporal Evolution of Negative Ions
Fresno, CA (12/1/00-2/4/2001





Guaiacol (methoxy phenols)

$R=CH_3, C_2H_5$

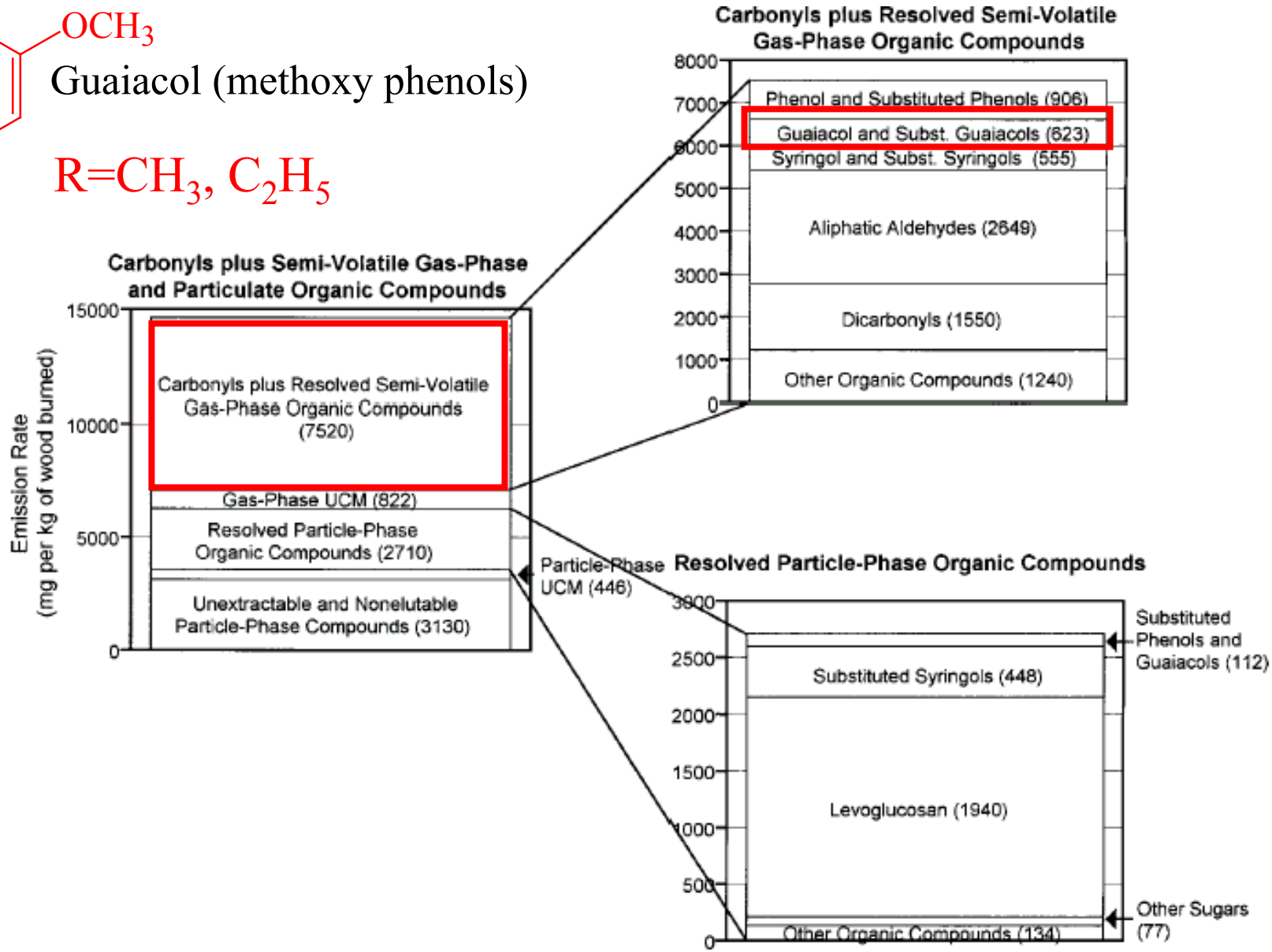
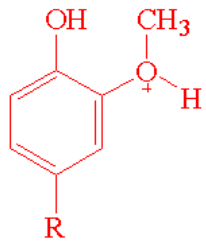


FIGURE 3. Mass balance on the carbonyl, semivolatile, and particulate organic compounds emitted from the fireplace combustion of eucalyptus wood.

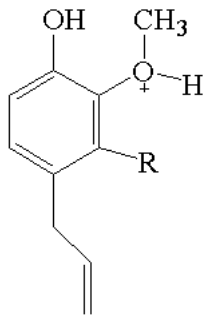
Schauer, Kleeman, Cass, Simoneit (2001), Environ. Sci. Technol. 35, 1716-1728.

ATOFMS Biomass Markers

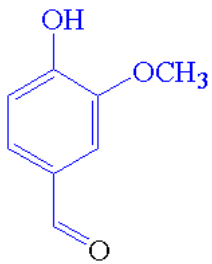
Positive Ions



substituted Guaiacol
R= methyl (m/z 139)

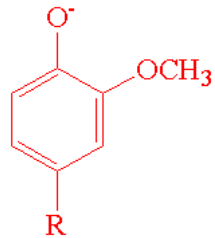


Eugenol $(M+H)^+$
R=H (m/z = 165)

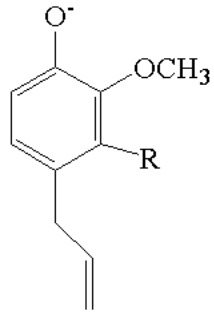


Vanillan $(M)^+$ = m/z 152

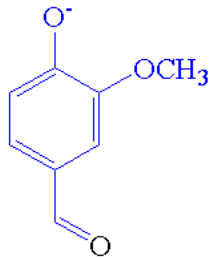
Negative Ions



Guaiacol $(M-H)^-$
R = H (m/z = -123)
R = methyl (m/z = -137)
R = ethyl (m/z = -151)



Eugenol $(M-H)^-$
R=H (m/z = -163)
R= methyl (m/z = -177)
R= ethyl (m/z -191)



Vanillan $(M-H)^-$ = m/z -151

**Most likely assignments based on Schauer et al. (2001) and Silva et al. (2000).

Conclusions

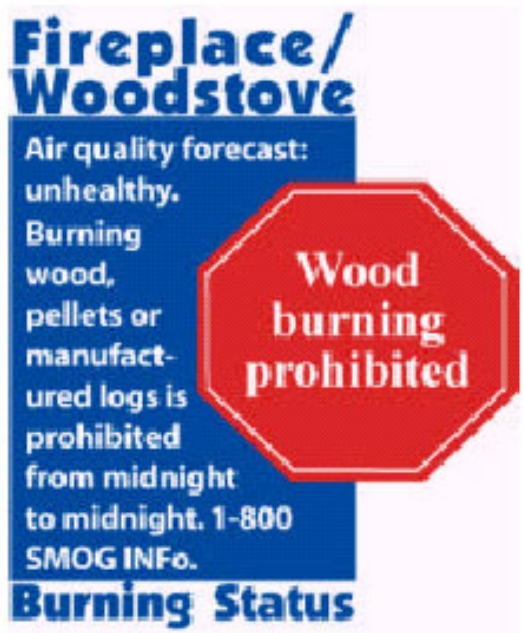
- HMS(particles) anti-correlated with ozone measurements
- Correlation observed between K^+ (core), m/z -45 (sugars + levoglucosan), PAH, and semivolatile aromatic species
- During stagnation (fog) episodes, build-up of K^+/biomass particles coupled with nitrates, sulfates, and SVOC (more EC observed in rural area)
- Major SVOC ion peaks compared to off-line chemical analysis results (Schaer and Cass) suggest methoxy phenols as major components of SVOC
- Particles more internally mixed in rural location (i.e. aged with significant SOA), whereas in urban location sources are still (for the most part) apparent

Future Plans

- Finish quantitation of ATOFMS data upon comparison with MOUDI data (see poster)
- Quantify ATOFMS data at higher time resolution using semi-continuous PM data (EC, OC, sulfate, nitrate)
- Scale ATOFMS counts using SMPS/APS
- Continue comparison with other gas, particle, and meteorological data
- Perform source apportionment using single particle signatures to assess relative impact of biomass burning (relative to other local sources)
- Long term goal: compare ATOFMS quantitative data with model/s (i.e. source oriented external mixture model with M. Kleeman)

Acknowledgements

- California Air Resources Board
- U.S. EPA

- Data collection: Jeff Whiteaker, Keith Coffee, George Kharrailah, Dave Suess
- Data analysis and quant. work: Sharon Qin, Steve Toner, Dr. Prakash Bhave, Prof. Jon Allen
- The entire Prather group

Central California: Effective November 1, 2003