Nighttime Aerosol, Trace Gas and Boundary-Layer Measurement from the Texas 2000 Field Campaign

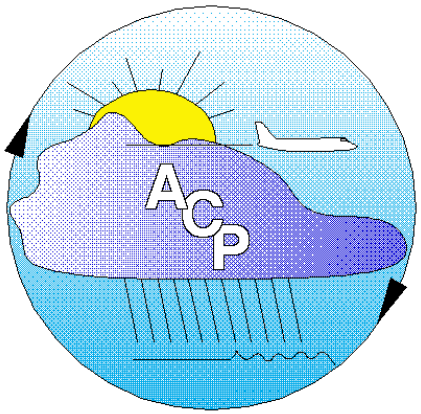
Preliminary Results from Pacific Northwest National Laboratory and Battelle

Carl Berkowitz

Atmospheric Sciences Program Meeting

Tuesday, February 13, 2001

Raleigh, North Carolina



Contributors/authors

- *Trace-gas Observations: Battelle*

  Chet Spicer*, Darrell Joseph, Raj Mangaraj, Jan Satola, Andrew Savage

- *Meteorology/PBL:*

  Chris Doran*, John Hubbe, Will Shaw

- *Time-tagged Particle Collection:*

  Jim Cowin*, Alex Laskin, Martin Iedema

- *TOFSIMS:*

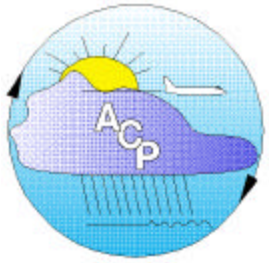
  Dan Gaspar*, Jim Cowin, Rob Disselkamp,Len Barrie

- *Membrane Introduction Ion Trap MS*:

  Mike Alexander*, Chris Aardahl

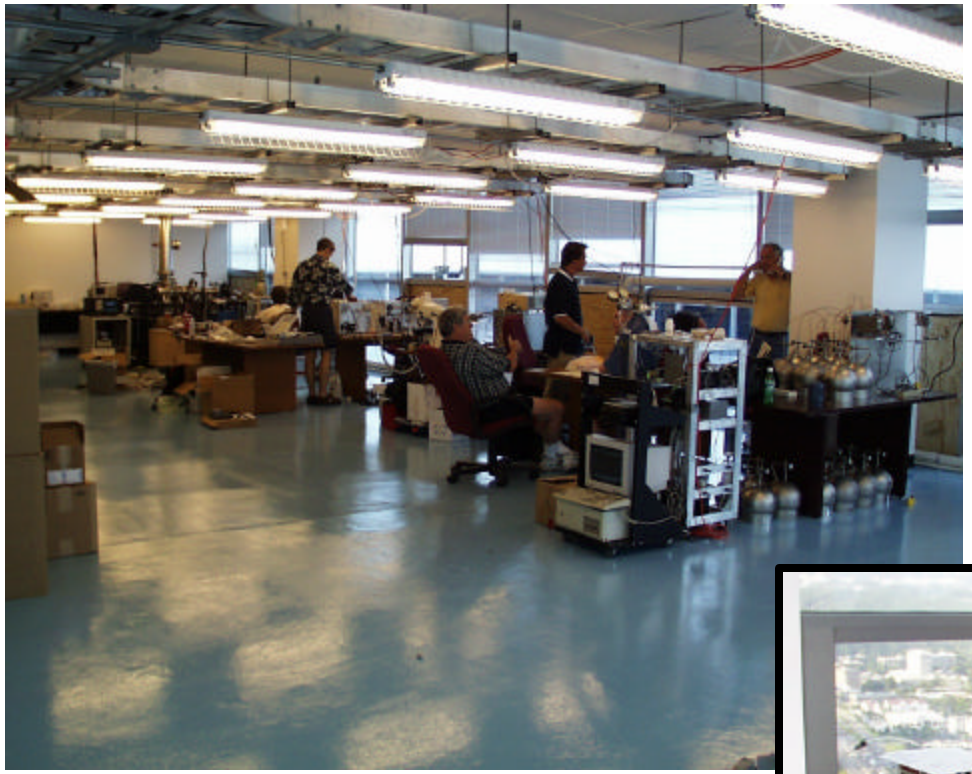
- *Surface chemistry: TNRCC*

  Jim Price*, Ken Rozacky



Motivation

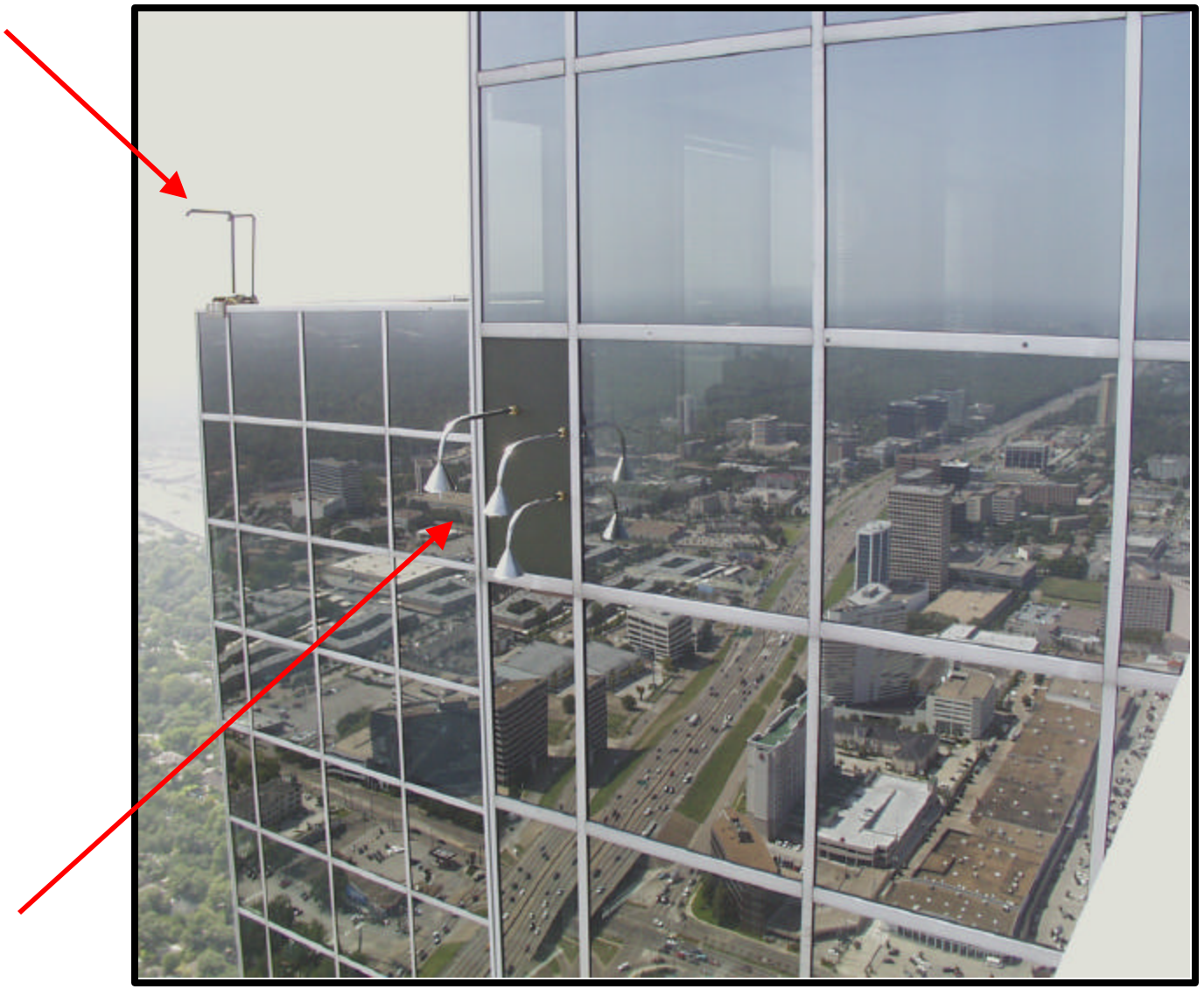
- No local sources.
  - measurements representative of average values for the greater Houston area.
- Sampling above and within mixed layer:
  - strong contrast in day/night chemical mix.
- Aloft, at night.
  - measurements of regional scale transport into/out of Houston area.
- West of major NOx/VOC sources of Houston;
  - will sample processed plume.



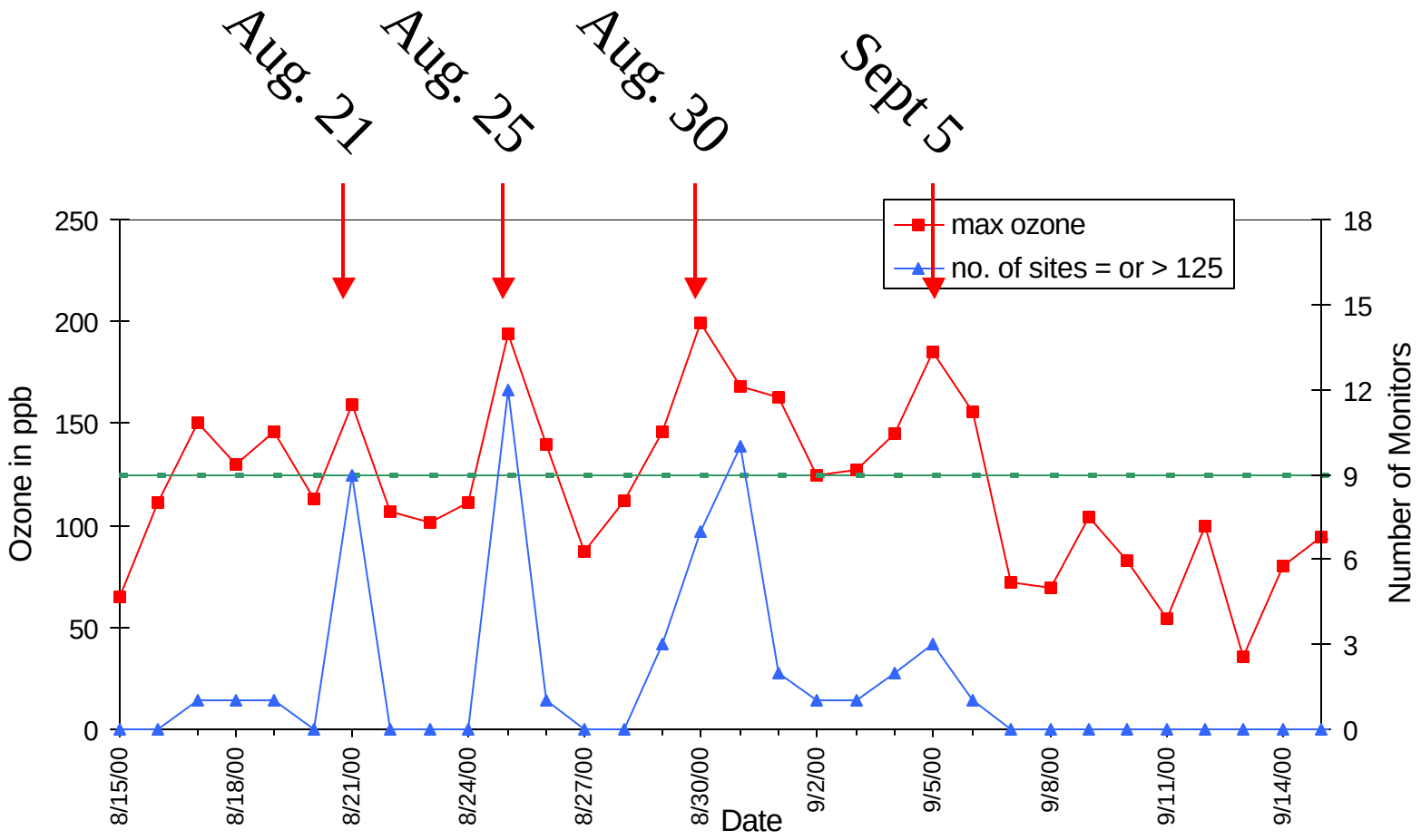
The “Aerosol” Room
Pacific N’west,
Brookhaven, SUNY
Argonne,UC/Davis

The “Trace-gas” Room
Battelle, Pacific N’west,
Georgia Tech.,TNRCC

Outside View of Sampling Lines



High One Hour Houston-Galveston Area Ozone

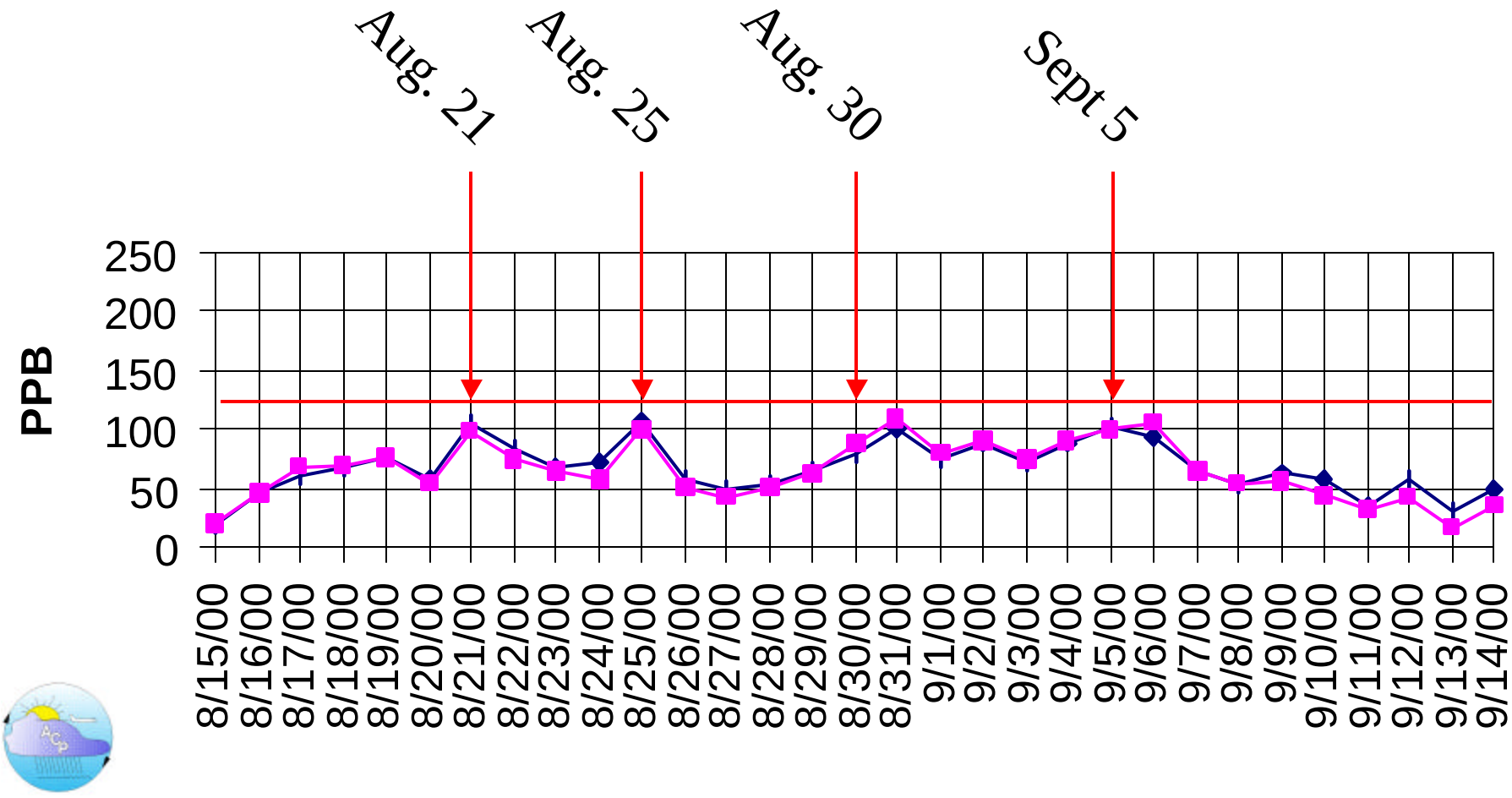


Summary Statistics

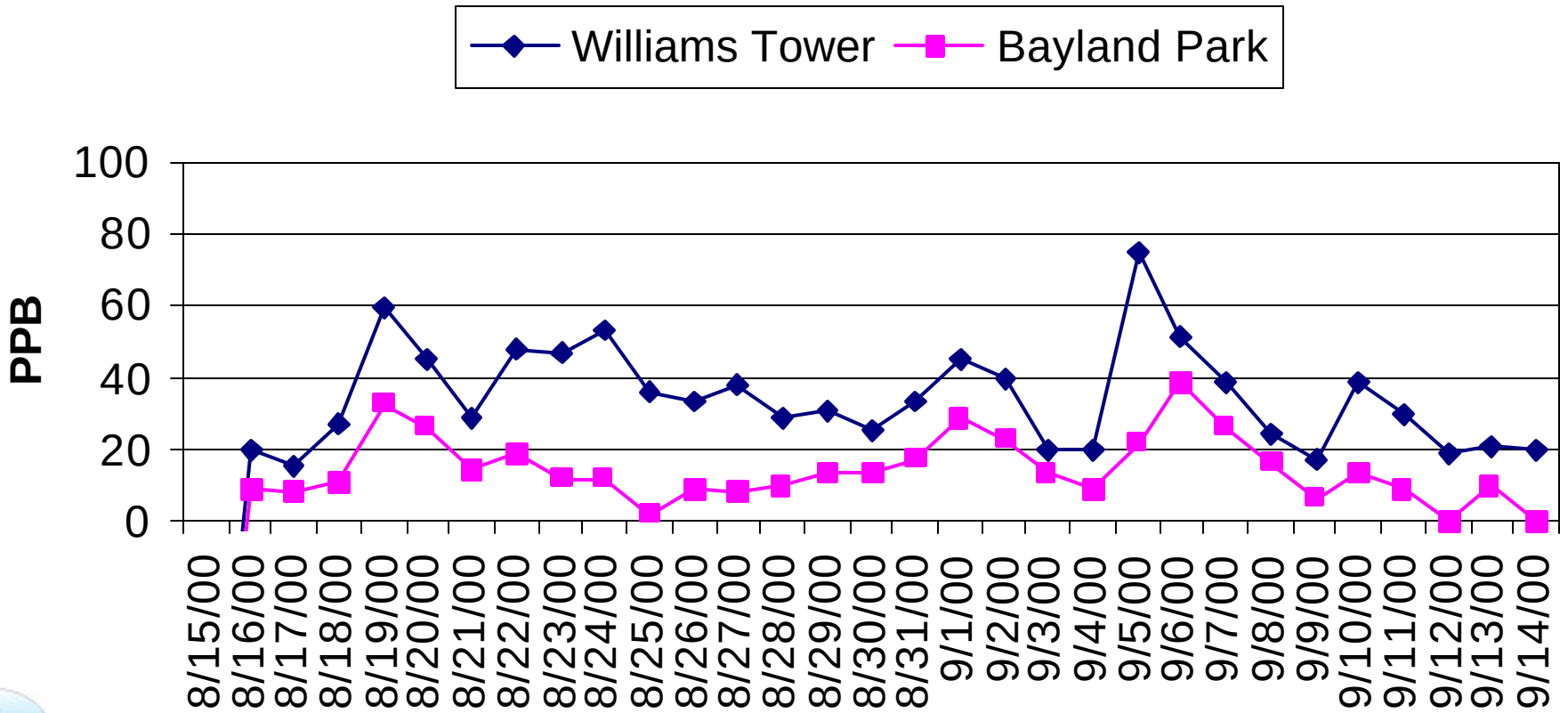
ozone mixing ratio, aloft and at surface

Williams Tower (830 ft AGL)	Bayland Park (surface site)
• Mean Value (day + night) = 47ppb	• Mean Value (day + night) = 34ppb
• Max = 205ppb	• Max = 164ppb
• Mean Value, afternoon = 69ppb	• Mean Value, afternoon = 67ppb
• Mean Value, pre-dawn = 36ppb	• Mean Value, pre-dawn = 14ppb

Ozone:
mean afternoon values
(12PM to 6PM LST)
aloft ≈ surface

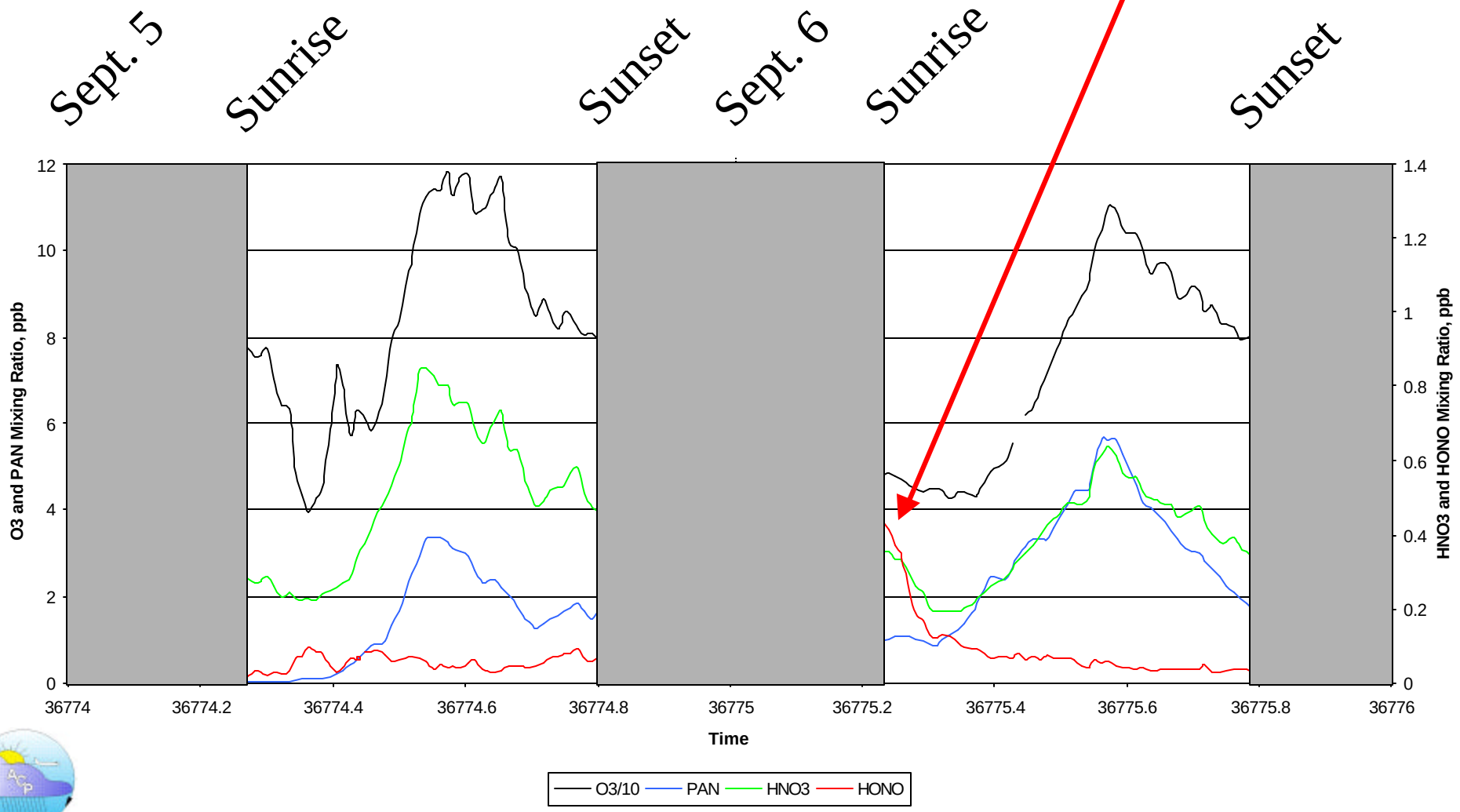


Ozone:
mean pre-dawn values
aloft ≈ surface + 22pb



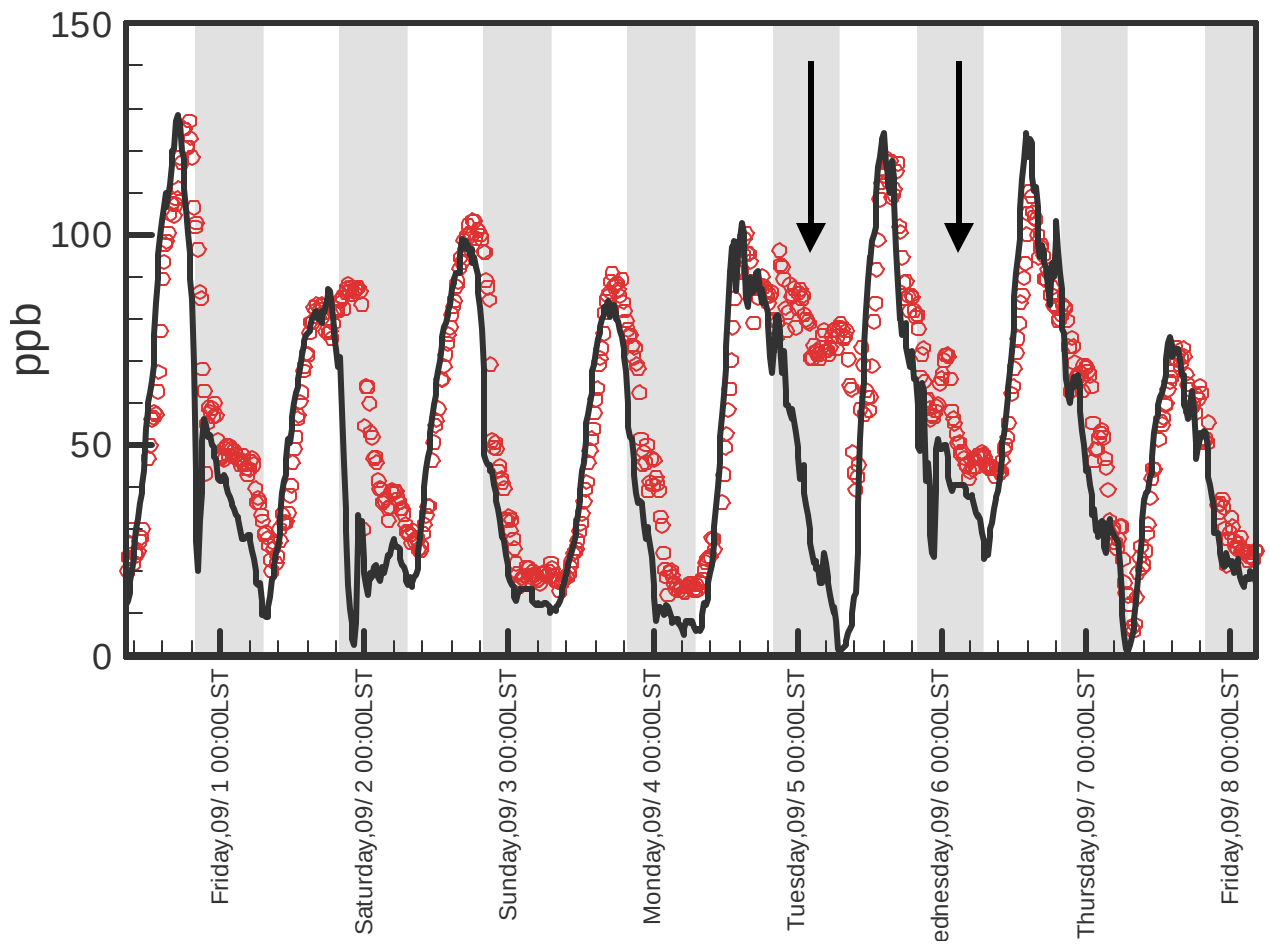
Greatest HONO usually observed pre-dawn, ~ 1/2 ppb.

(O3/10, PAN, HNO3, HONO)



Frequently a well defined chemical signature of Convective Boundary Layer

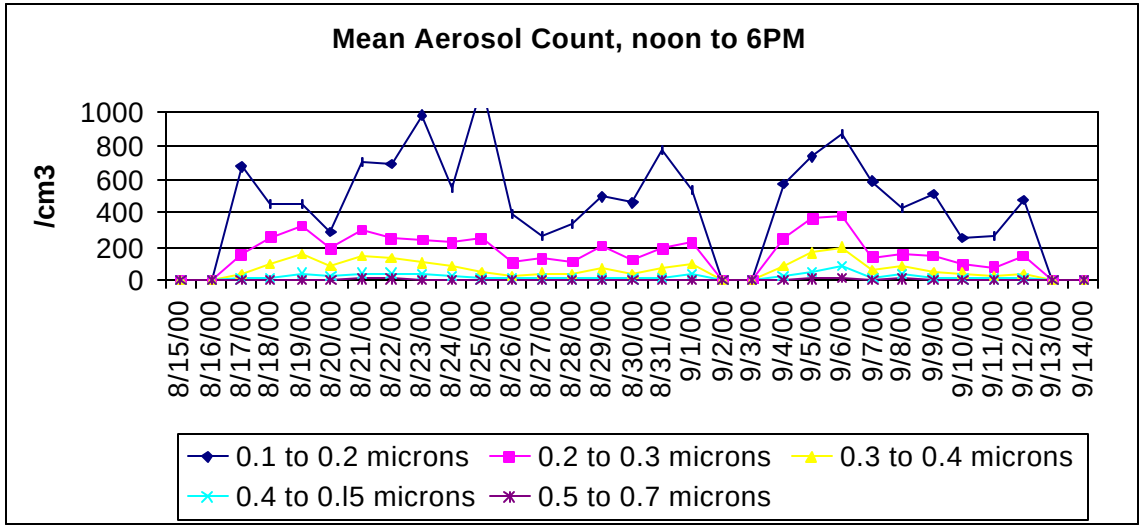
Williams Tower (o) & Bayland Park (---)

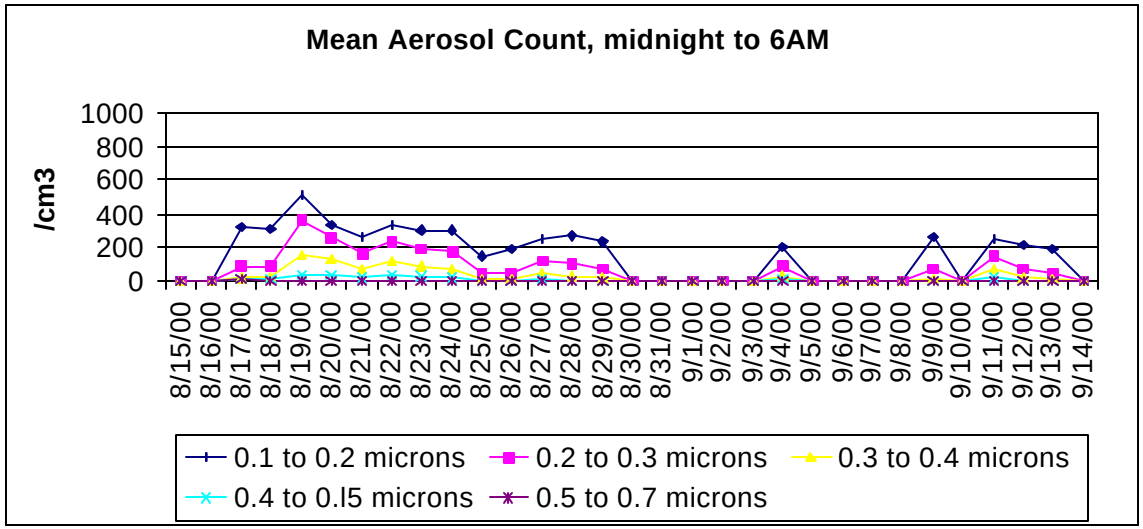


Subtle variations in thermal stability associated with observed decoupling

- August 19th: Weakly stable all the way up, with slightly stronger stability within bottom 25 meters.
- August 25th: More stable than on the 19th above 65 m, and neutral below 65 m.
- September 6th: roughly neutral, or weakly stable, throughout the layer.

0.1 to 0.2 micron aerosols predominate during day; less significant domination at night.





Observations courtesy of Alex Laskin/PNNL

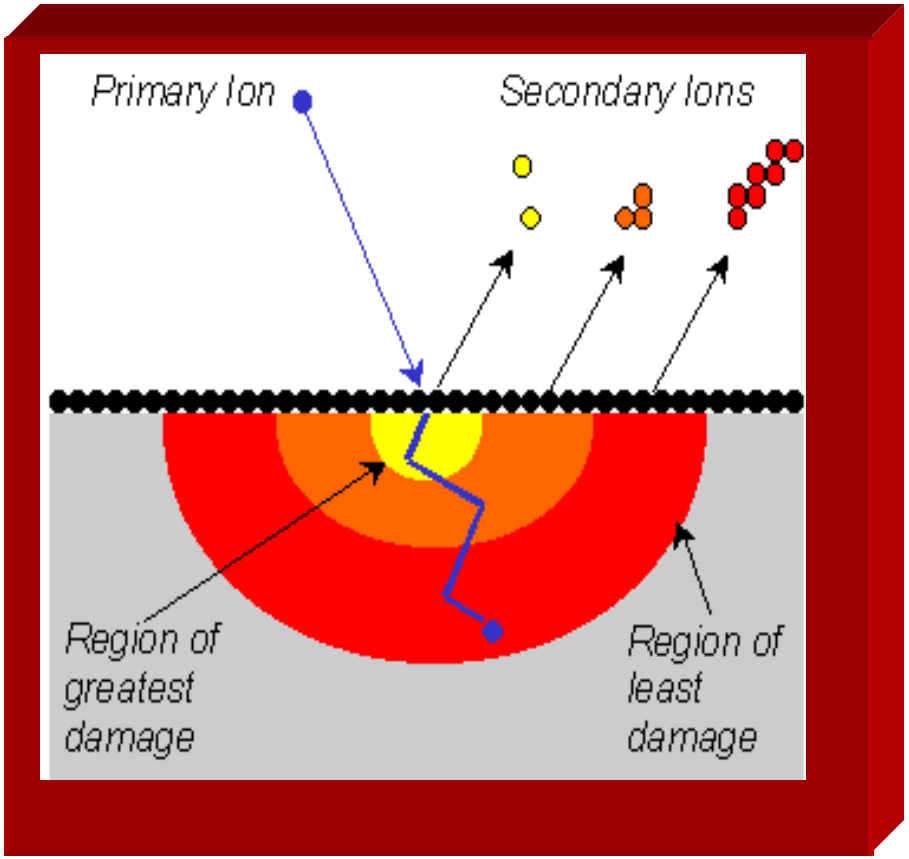
TOFSIMS (Time of Flight Secondary Ion Mass Spectrometry)

Imaging 3D analysis of single particles (Dan Gaspar)

Rastered primary ion beam impacts surface, ejects pieces of surface molecules (secondary ions), mass-selected by Time-of Flight

Spatial Resolution: 0.2 μ
Mass Resolution: 0.002 amu

Can Depth Profile Particles

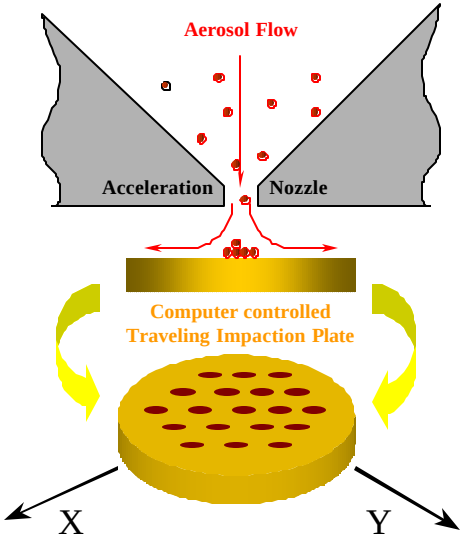


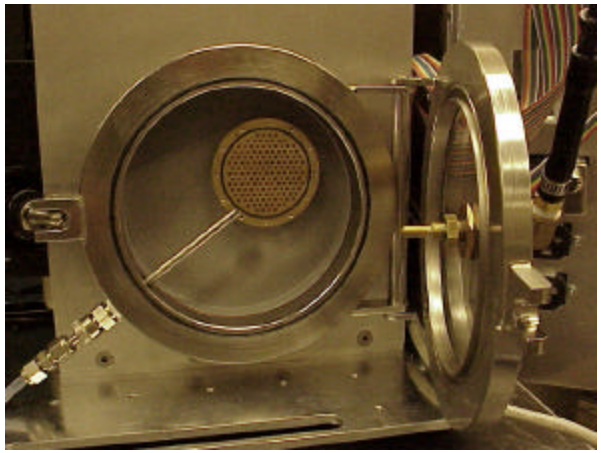
Drawing courtesy of Physical Electronics

Courtesy Jim Cowin/PNNL

Automated Time-Resolved Collector of Field Aerosols

- 3000 individual samples with the time resolution of 10 minutes

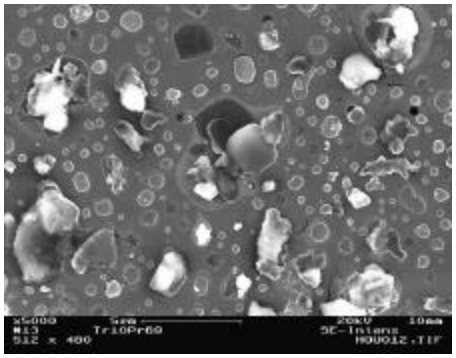


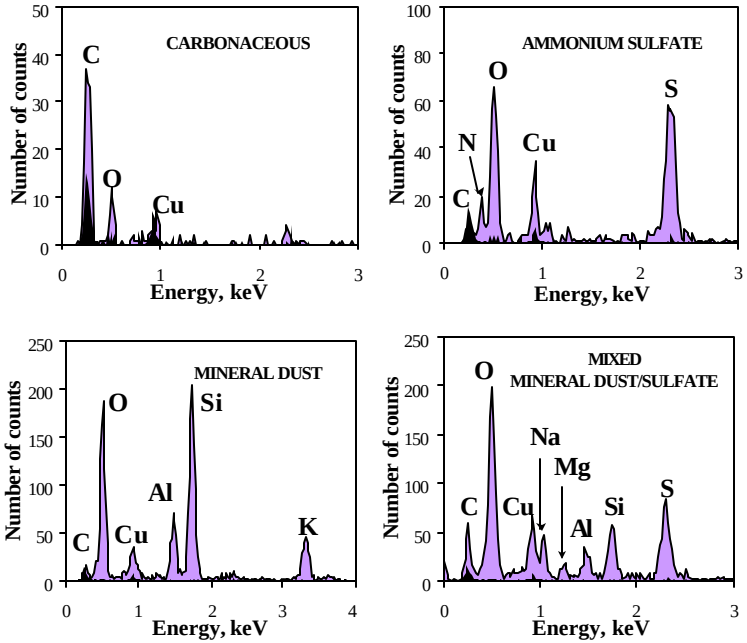


Courtesy Alex Laskin/PNNL

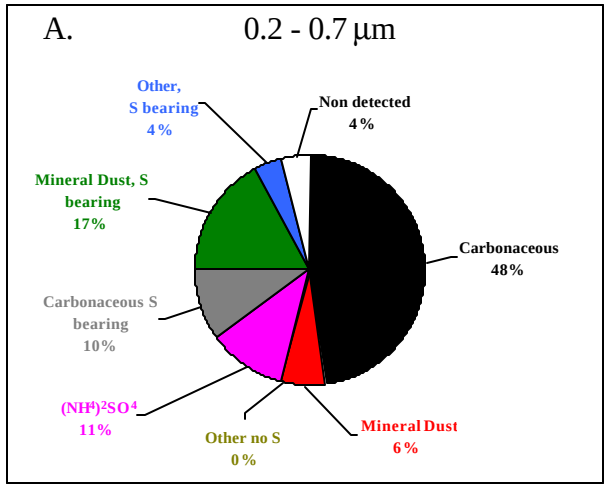
Automated SEM/EDX Single Particle Laboratory Analysis

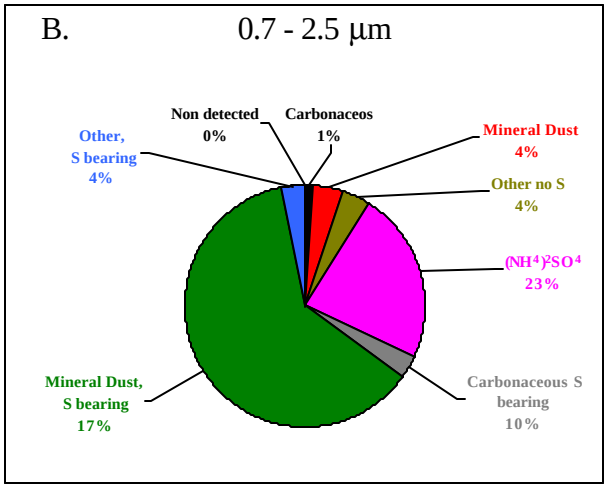
- analysis down to 0.1mm particles
- analysis speed of 2000 particles/hour
- quantitative detection of low-Z elements: C, O, N



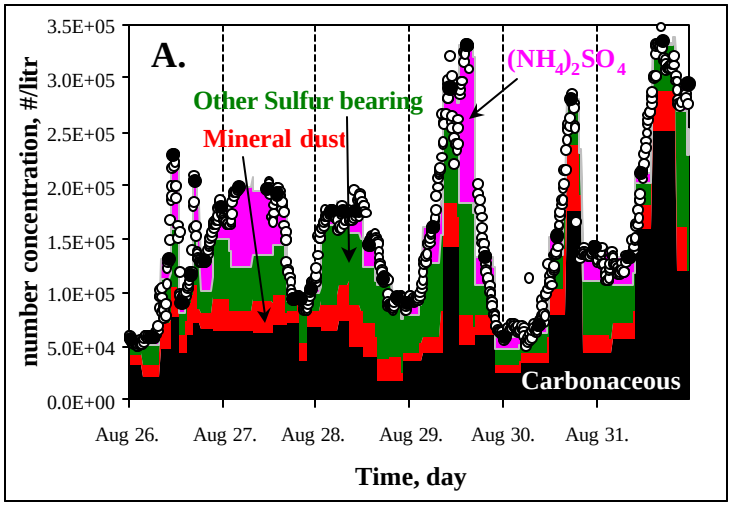


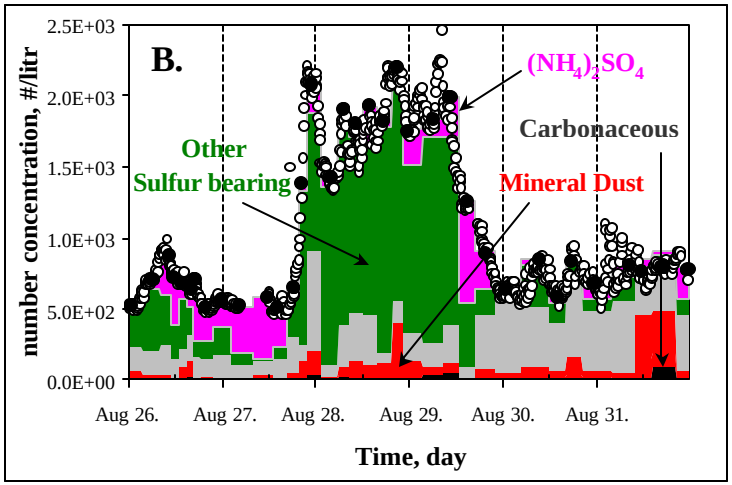
Particle-type Classification of Representative Aerosol Samples





Time-Resolved Particle-Type Characterization of Aerosols





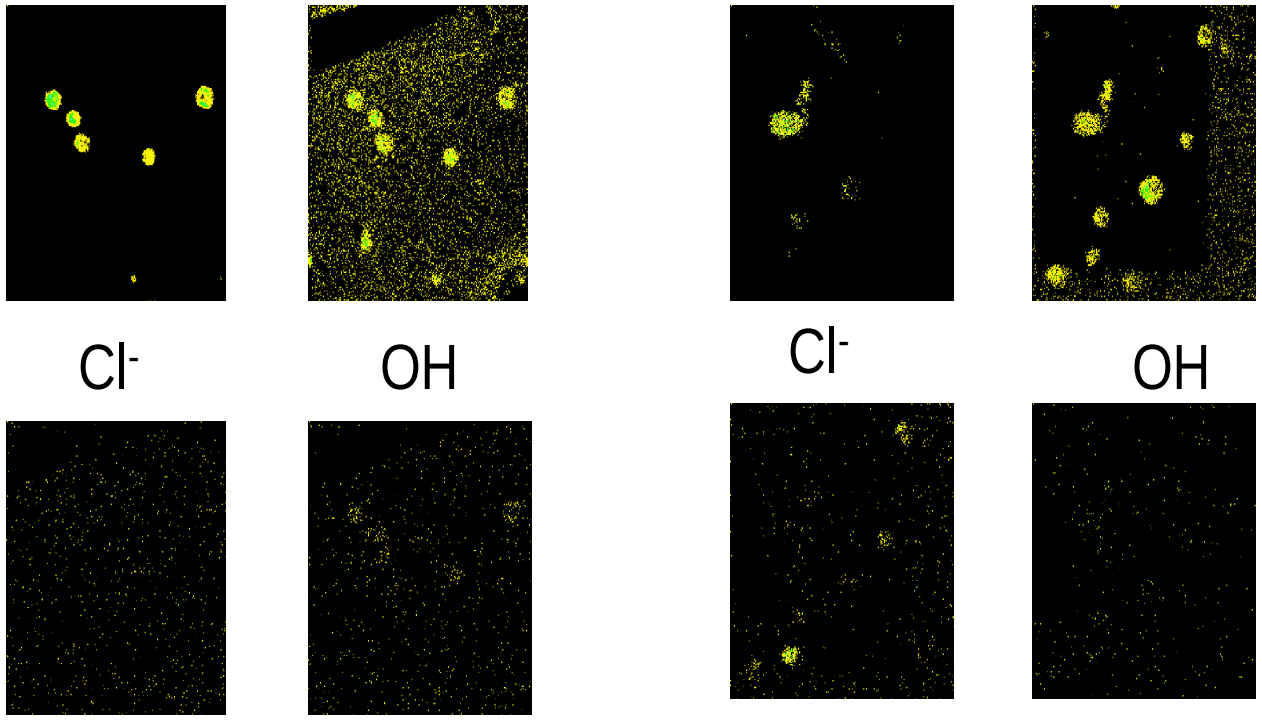
Courtesy Alex Laskin/PNNL

Changes in aerosol composition, day/night (TOF secondary aerosol MS)

Night-time Aug 17

Day-time Aug 17

10 microns



Cl^- OH Cl^- OH

NO_3^- ClO^- NO_3^- ClO^-

Courtesy Jim Cowin/PNNL

Salt particles: Much Cl, OH, No nitrate, Some hypochlorite(!)

Processed salt: Little Cl, much OH, Some nitrate, No hypochlorite

Chlorine Depletion from Sea Salt Particles ?

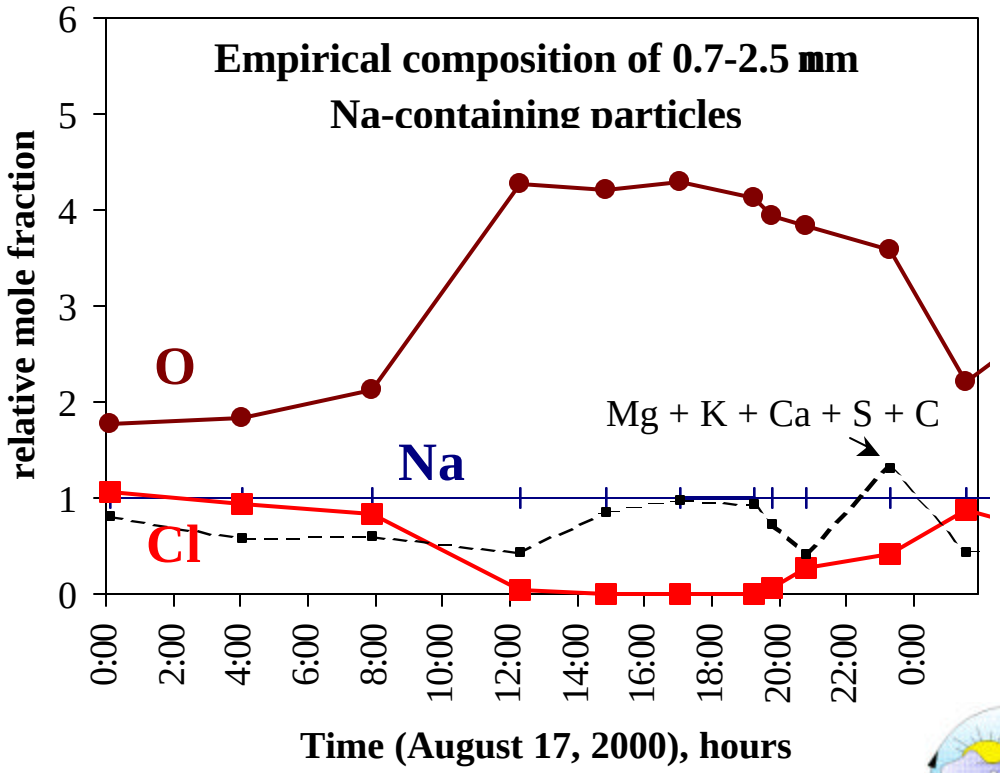
August 17, 2000

- steady wind from Mexican Gulf

- 50-70% of 0.7-2.5 mm particles are Na-containing particles

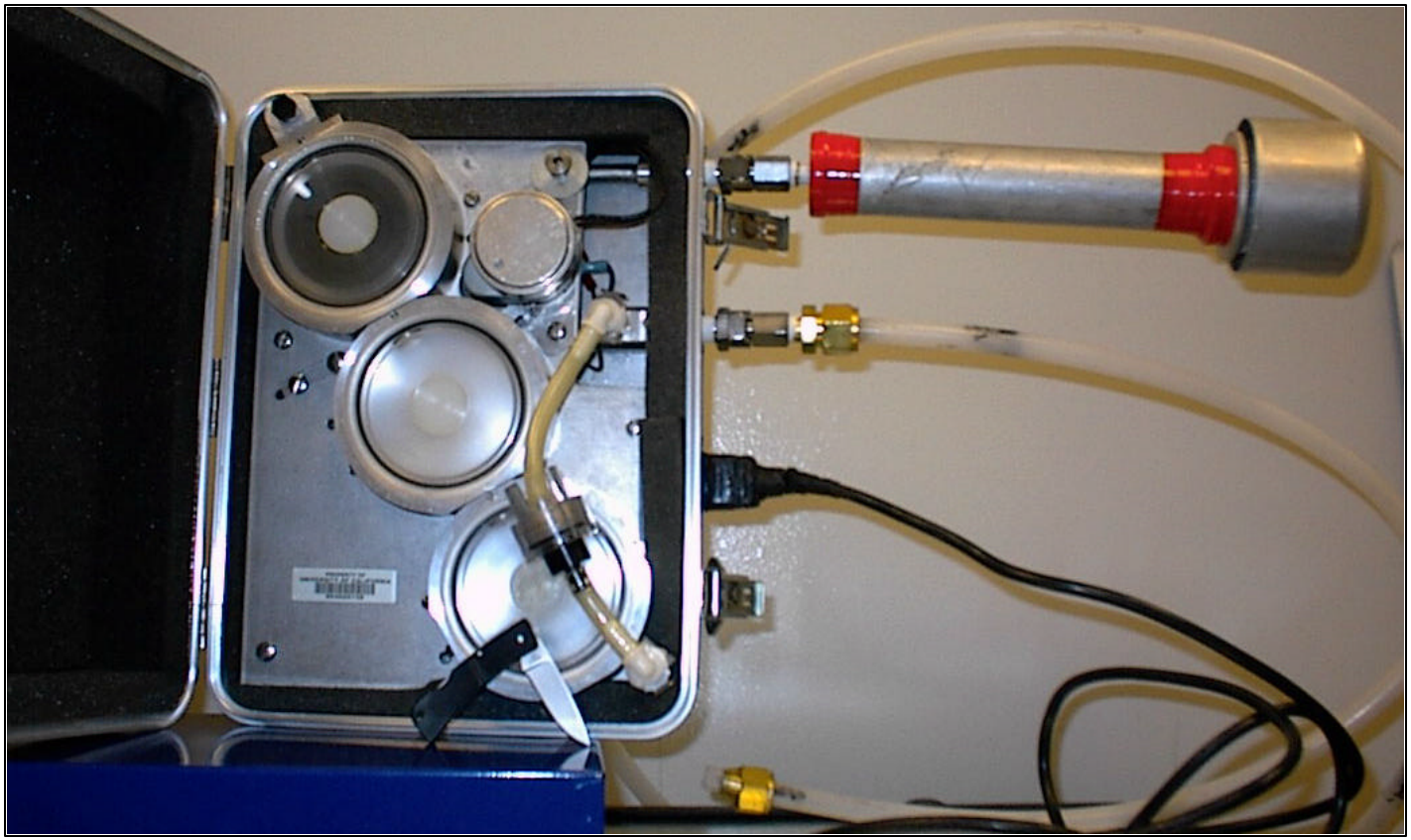
- absolute conversion of NaCl to $NaNO_3$ after the sunrise

- termination of the process after the sunset



Courtesy Alex Laskin/PNNL

3-stage rotating drum cascade impactor

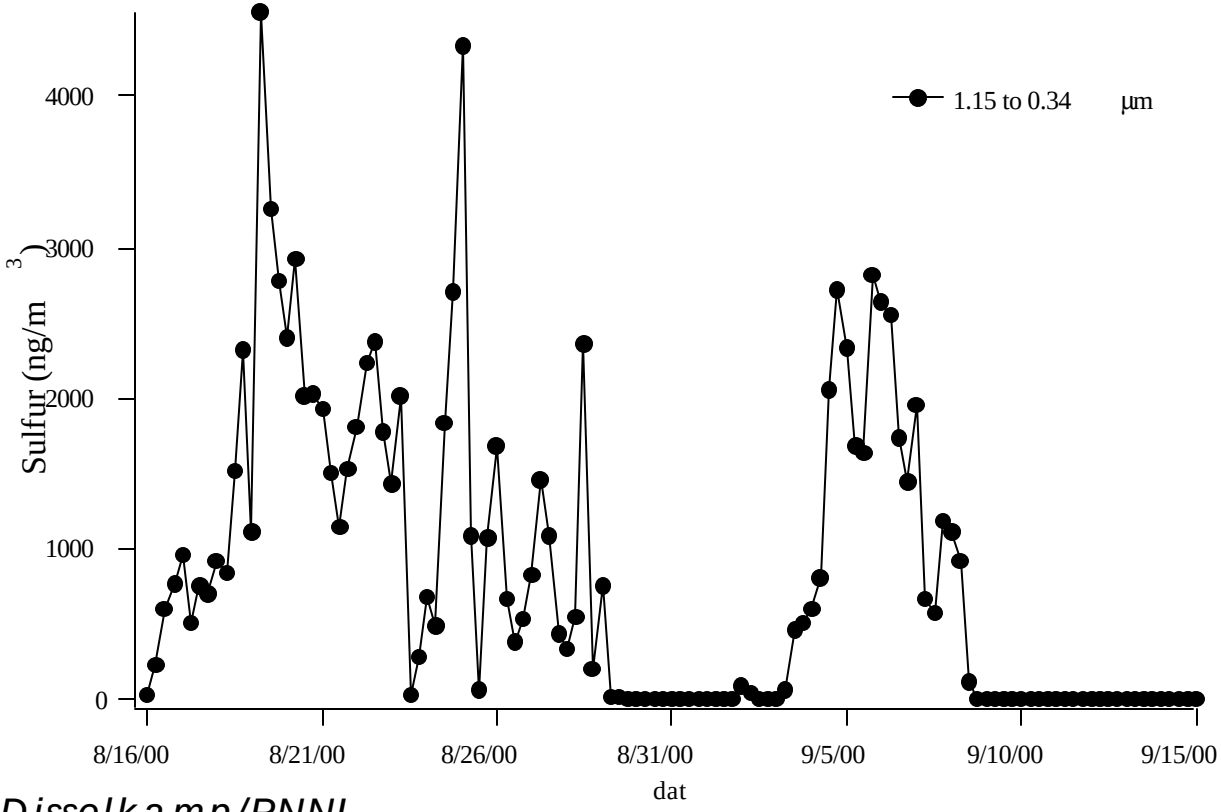


PIXIE/PESA/STIM analysis of deposited aerosol yields
elemental (Na-Ga), hydrogen, and total aerosol loading in atmosphere

Courtesy Rob Disselkamp/PNNL

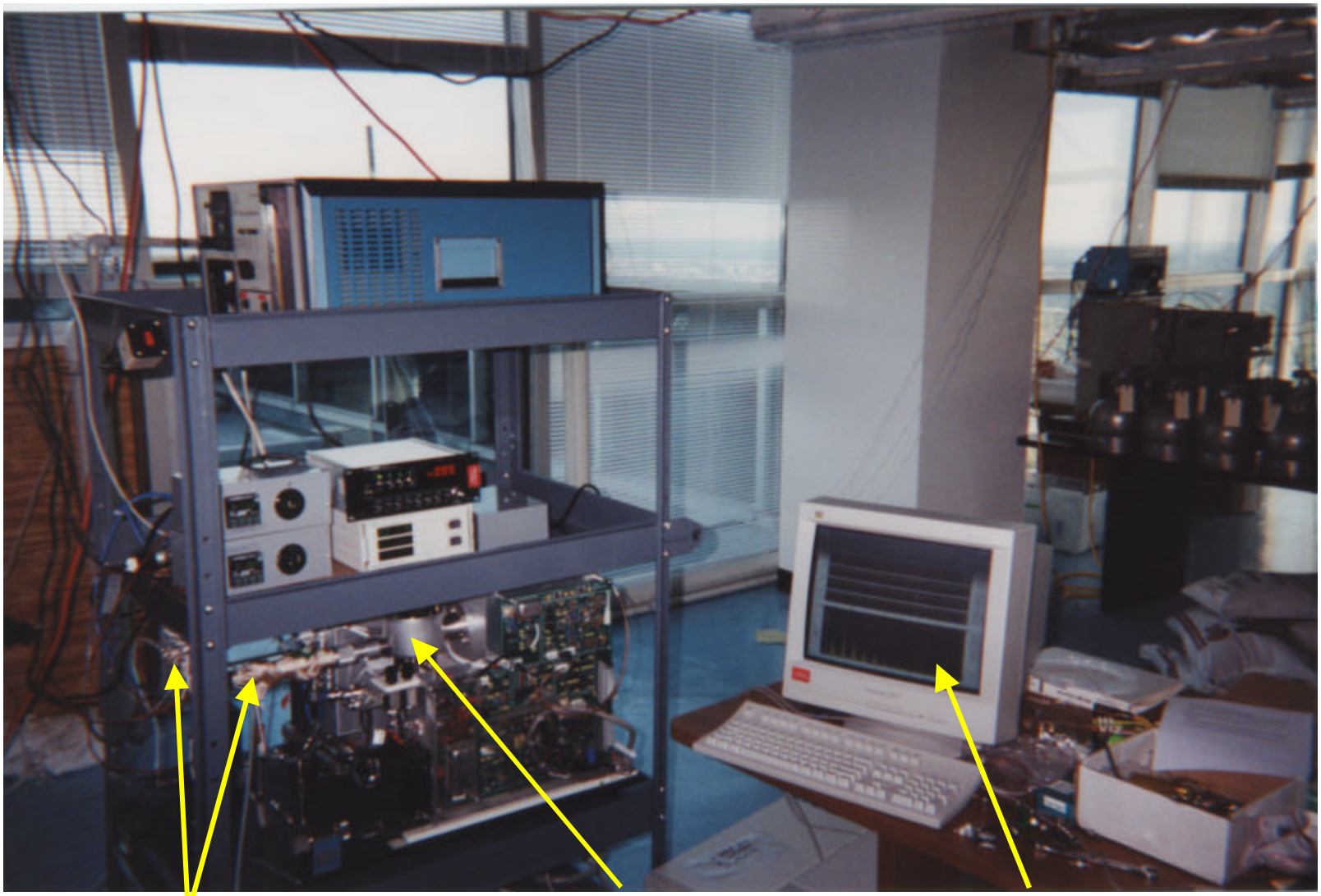
Trends and diurnal variation observed in sulfur loading

(3-stage rotating drum cascade impactor PIXIE/PESA/STIM analysis of deposited aerosol)



Courtesy Rob Disselkamp/PNNL

Membrane Introduction Ion Trap Mass Spectrometer



Membrane Introduction Interface

Ion Trap Mass Spec.

Real-time Data Output

Courtesy Mike Alexander/PNNL

Still to Come…Aerosol Sampling with Simultaneous VOC Measurements

- Aerosols ≤2.5 microns collected on Quartz and Teflon filters (4 hour integrated samples).
- Simultaneous real-time VOC monitor using Membrane Introduction Ion Trap Mass spectrometer.
- Aerosol Filter samples being analyzed for semi- and involatile organic compounds.
- Analysis in Progress (VOC data).
  - VOC observations being correlated with aerosol data.

Courtesy Mike Alexander/PNNL

Near*-term goals at PNNL for TX2000 observations:*

1. Chemical Characterization of aerosols.

- relation of organic gas phase species and aerosol composition.
- To statistically characterize the diurnal cycle in size-segregated aerosol composition.
- Evidence of interactions of aerosol compounds with gas phase species.
- Use analytical results to develop aerosol chemistry modules for incorporation into air quality models.

2. PBL/Chemistry Observations.

- Growth of mixed layer: observations vs. model, under various synoptic conditions, and effect on trace gas species.
- Feedback mechanisms between aerosols/radiation/meteorology.
- Evidence of bay/sea breeze recirculation on pollutant distribution (day and night, surface and aloft).

3. Trace-gas measurements.

- NOy budget at night vs day.
- Chemical evidence of long range transport: consistency with meteorology.