Semi-Continuous $PM_{2.5}$ Nitrate and Sulfate Measurements at the Pittsburgh AQS Supersite

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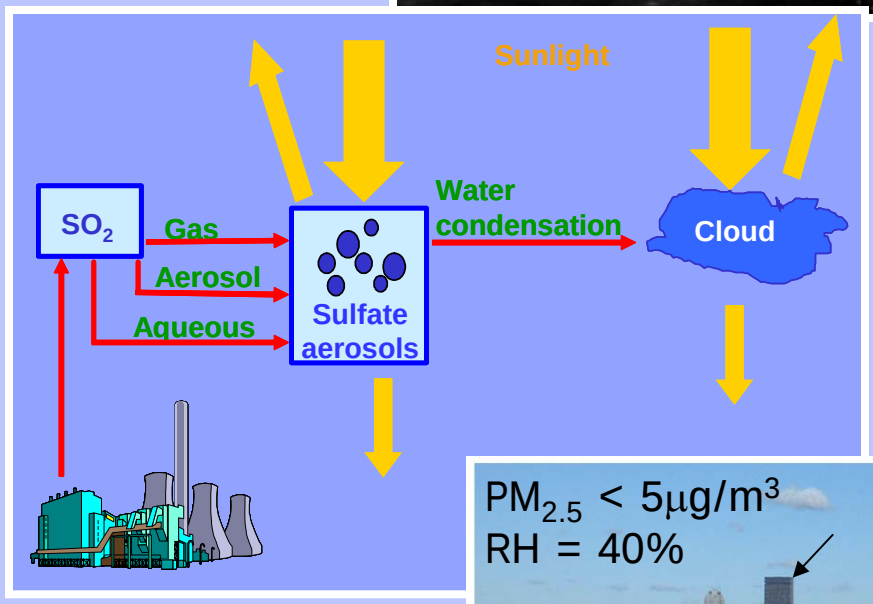
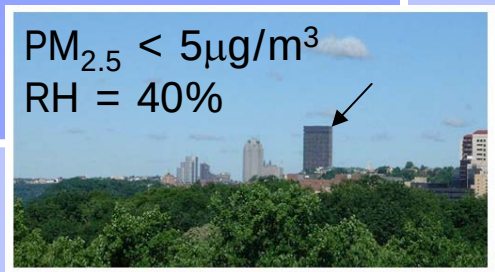
Presentation outline

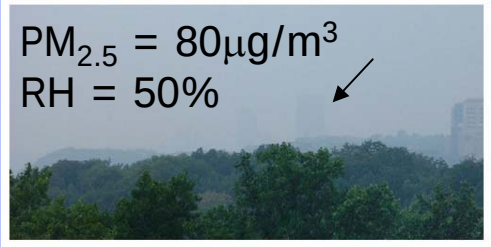
- Motivation
- Overview of Pittsburgh AQS Supersite
- Inorganic aerosol measurement methods
  - Focus on flash volatilization method
  - Quality control and data reduction approach
  - Evaluation of method performance
- Interesting trends in measurements
- Conclusions

Motivation

- Ambient aerosols can have negative impacts on:
  - Public and environmental health
  - Climate change
  - Visibility

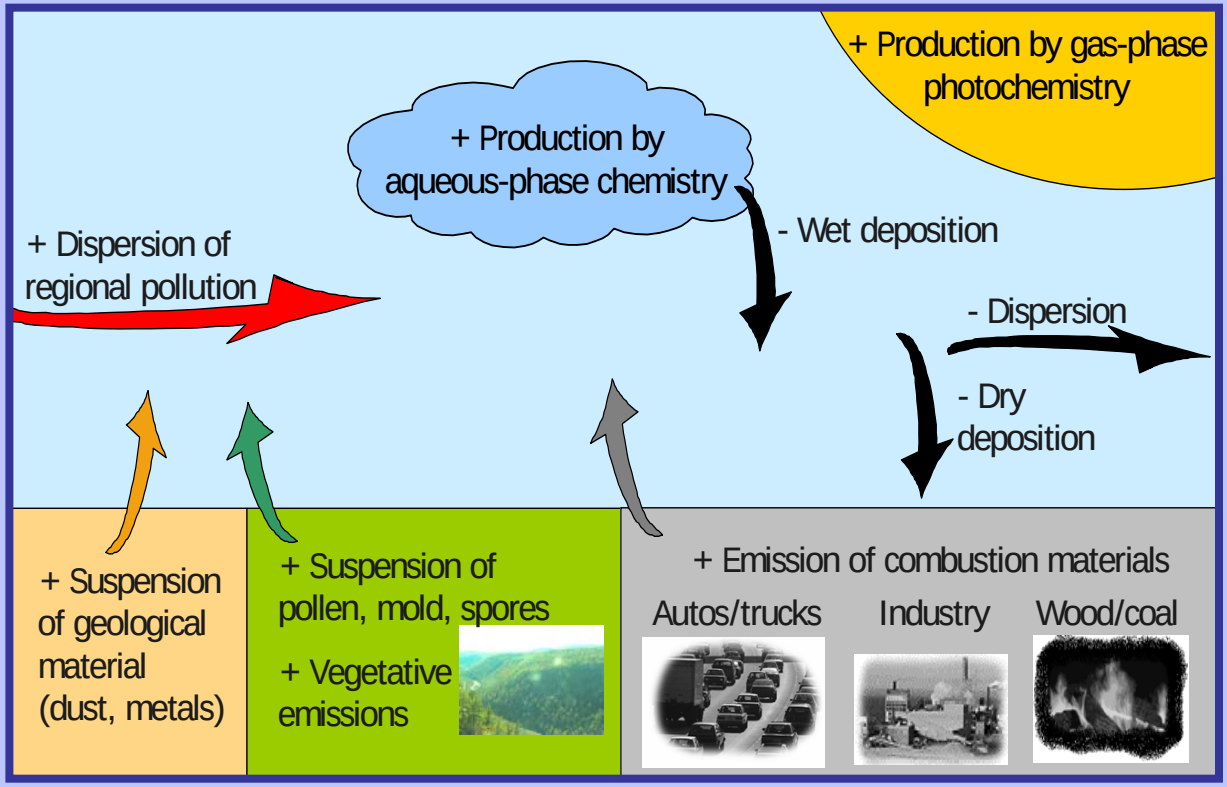






Motivation

- Ambient aerosols can originate from many sources
  - Local or regional
  - Primary or secondary



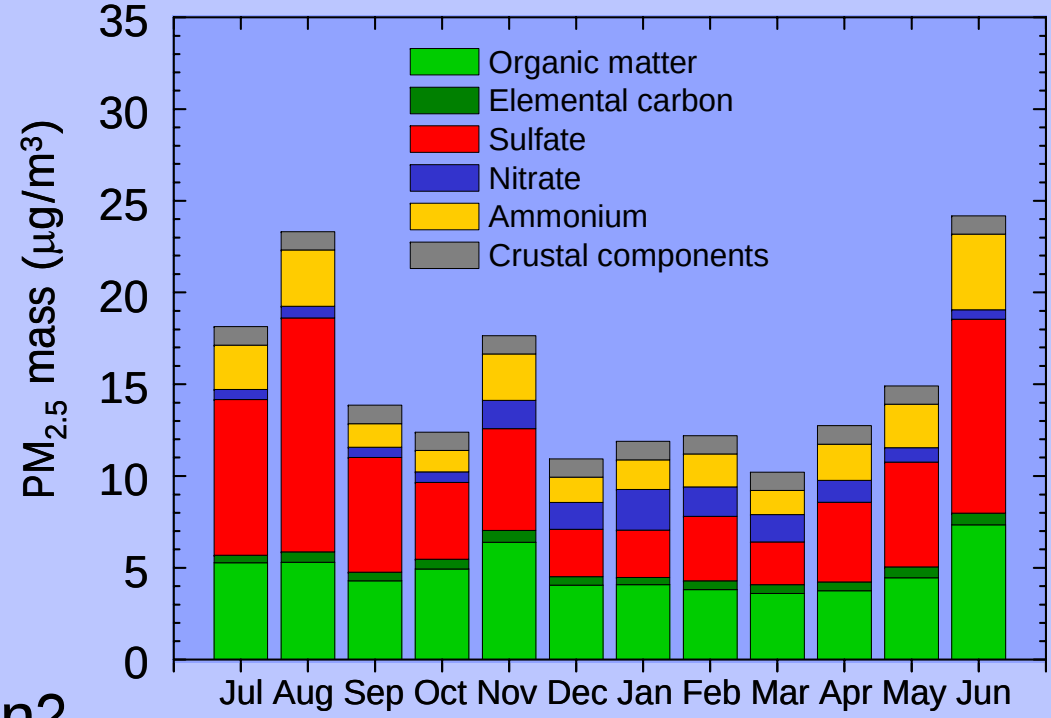
→ Need to understand pollutant behavior in order to identify critical sources.

Motivation

- Why inorganics?

  They are a major component of the Pittsburgh aerosol.

  - 30% sulfate
  - 7% nitrate
  - 13% ammonium

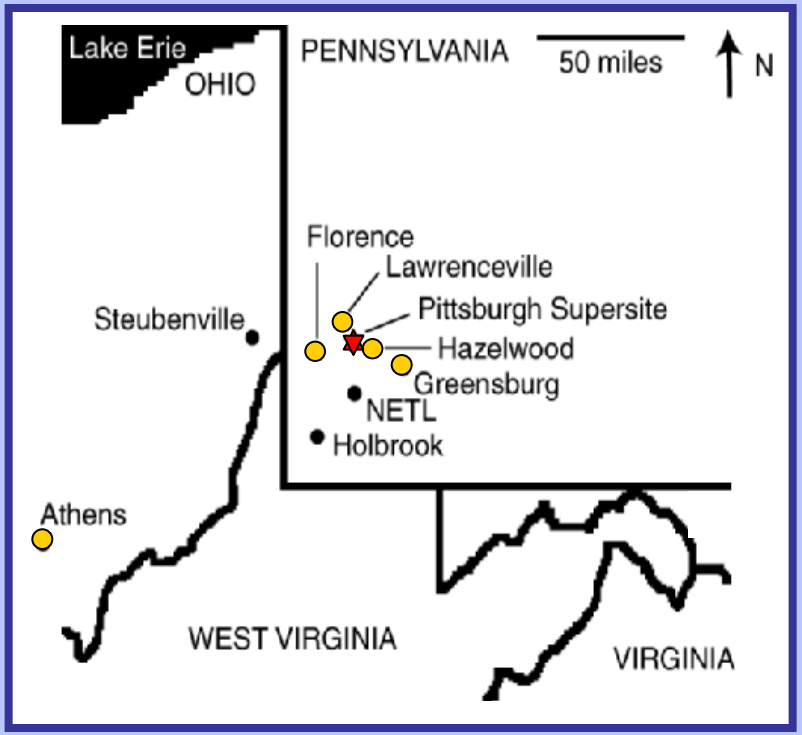


- Why flash volatilization?

  It is a new but relatively untested methods that agencies are turning to, to acquire the data needed to numerically assess SIPs.

Overview of PAQS Supersite

- Study period: July 1, 2001 - August 31, 2002
- Study locations:
  - Central site
  - 5 satellite sites
- Many measurements:
  - Aerosol characteristics
  - Gas concentrations
  - Meteorology



$PM_{2.5}$ nitrate and sulfate measurement overview

- Filter based method:
  - 24-hour average resolution
  - CMU Speciation sampler
- Steam based method:
  - 1 to 2-hour average resolution
  - Khlystov Steam sampler
- Flash volatilization method:
  - 10-min average resolution
  - Rupprecht and Patashnick 8400

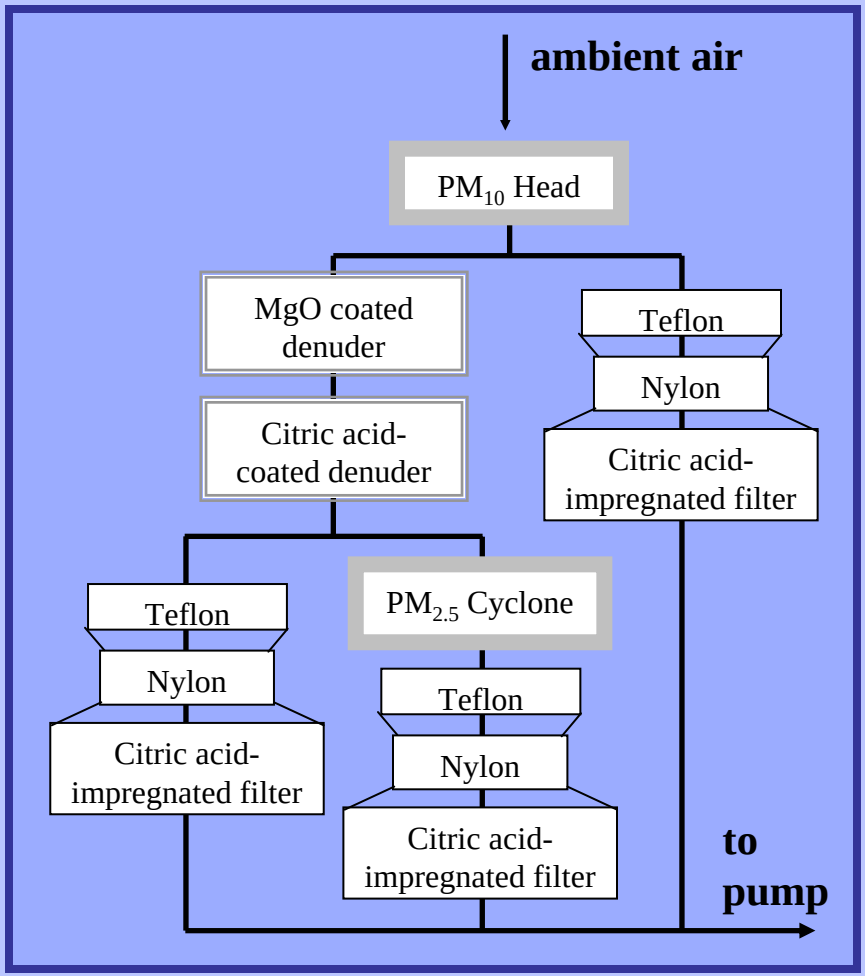
Filter based method

Approach

- Aerosols and gases are collected onto filters
- Filters are extracted and analyzed offline by IC for major inorganic ions

Resulting measurement

- 24-hr average concentration of inorganic ions (nitrate, sulfate, ammonium, etc.)
  - Gas plus aerosol (total)
  - Aerosol only



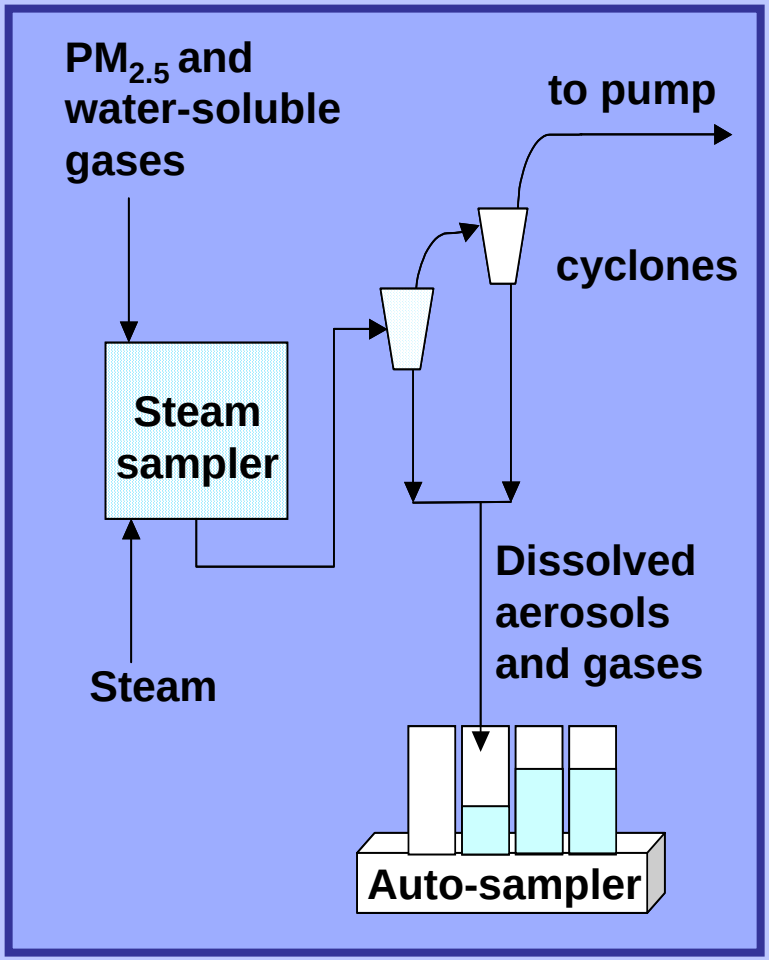
Steam based method

Approach ¤

- Steam solubilizes ambient aerosols and water-soluble gases
- Steam is condensed and collected into vials for offline IC analysis

Resulting measurement

- Gas plus aerosol (total) inorganic ion concentrations on 1-2 hr basis
- Lower sample times are possible by eliminating the extraction step



¤ Khlystov, Wyers, and Slanina (1995). The Steam-Jet Aerosol Collector. Atmos. Environ. 29:2229-2234.

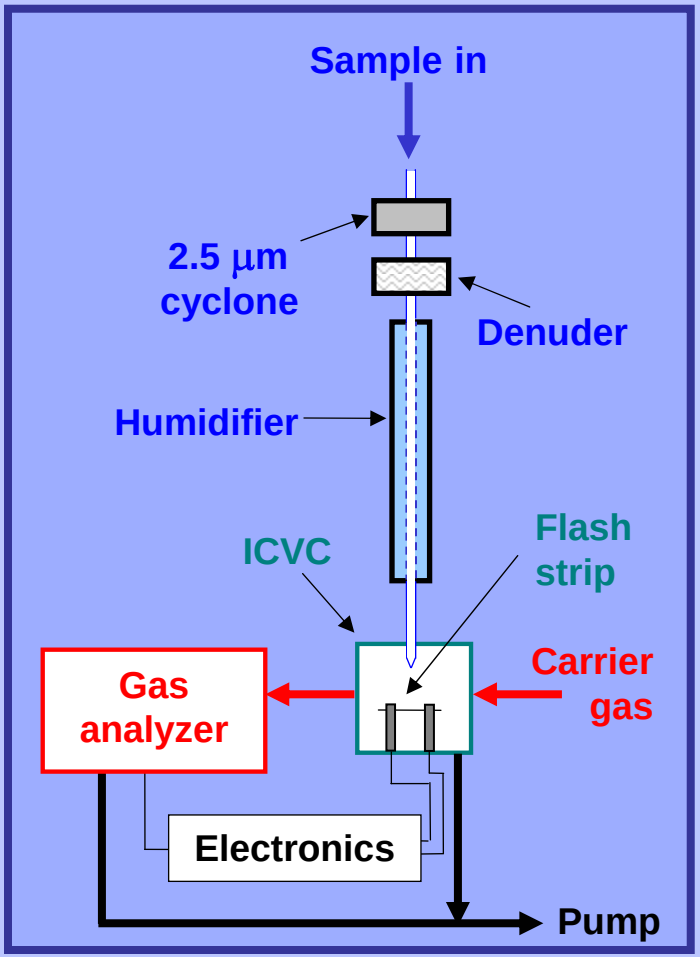
Flash volatilization method

Approach ¤ §

- Ambient air is pretreated, humidified, and impinged onto a metal flash strip
- ICVC is purged and aerosol is flash vaporized to NO_x or SO_2 gas
- Pulse of gas is measured using a high sensitivity gas analyzer

Resulting measurement

- Aerosol nitrate -or- aerosol sulfate on a 10-min basis



¤ Stolzenburg and Hering (2000). A new method for the automated measurement of atmospheric fine particle nitrate. EST 34:907-914.

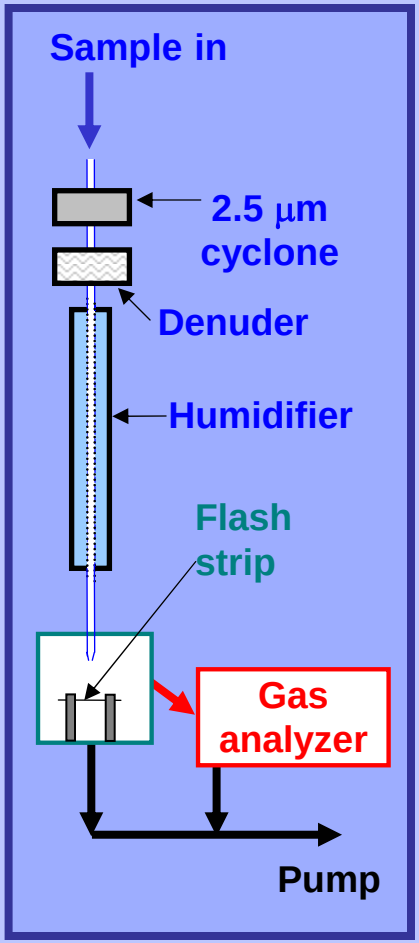
§ Roberts and Friedlander (1976). Analysis of sulfur in deposited aerosol particles by vaporization and flame photometric detection. AE 10:403-408.

Quality control for flash volatilization method

Need for extensive quality control

- An electronic instrument
- Instrument relies on a careful balance of flows
- Aerosol species are not measured directly
- Collected aerosols cannot be archived

Check	Frequency
Response to filtered air	Biweekly
Response to aqueous standards	Biweekly
Response to gas standards	Daily/every 4 days
Drift in sample flow meter calibration	Bimonthly
Drift in gas analyzer vacuum *	Every 10 mins



Data reduction of raw flash volatilization measurements

$$C_i^* = 1000 \bullet \frac{\left(\int C_{s,i}\,dt - \int C_{b,i}\,dt\right)}{t_{s,i} \bullet ef_{c,i}} \bullet \frac{MW_i}{V} \bullet \frac{Q_{c,i}}{Q_{s,i}}$$

- Typical reduction:

  Accounts for filter blank and aqueous calibrations

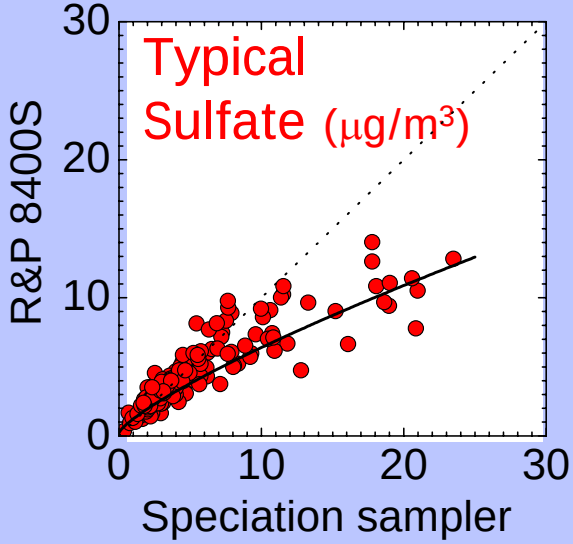
$$C_i = \left(C_i^* - C_{o,i}\right) \bullet \frac{ef_{c,i}}{ef_{c,i}^{'}}$$

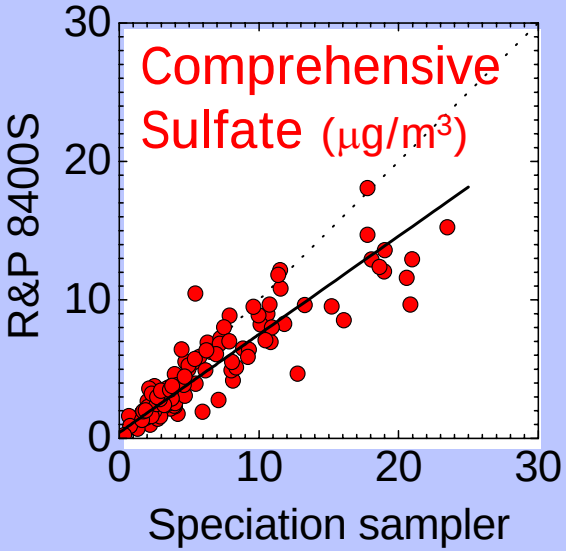
- Comprehensive reduction:

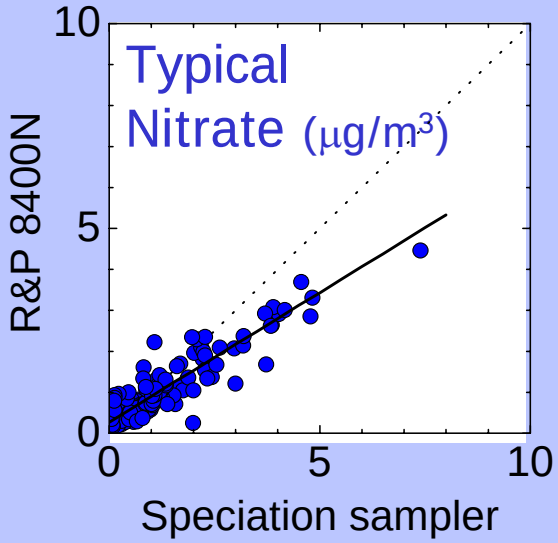
  Also accounts for gas analyzer and flow meter performance

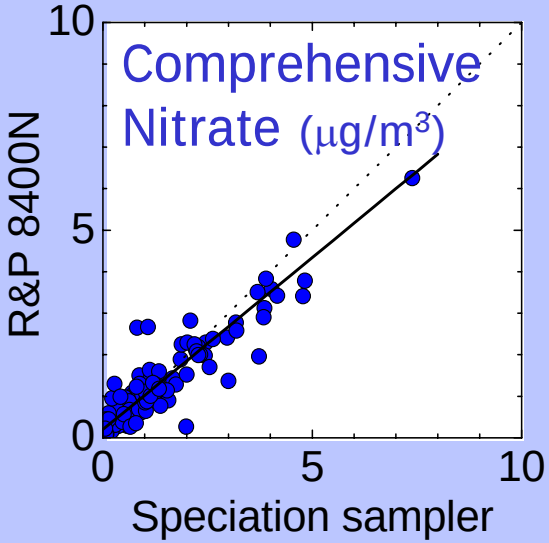
$$C_i = \left(C_i^* - C_{o,i}\right) \bullet \frac{ef_{c,i}}{ef_{c,i}^{'}} \bullet \frac{1}{ef_{ga,i}} \bullet \frac{Q_{s,i}}{Q_{s,i}^{'}} \bullet \left[1 + 0.13 \bullet \left(V_i - 5.0\right)\right]$$

Result of data reduction schemes









Typical

Resulted in nonlinear underestimates of true concentration

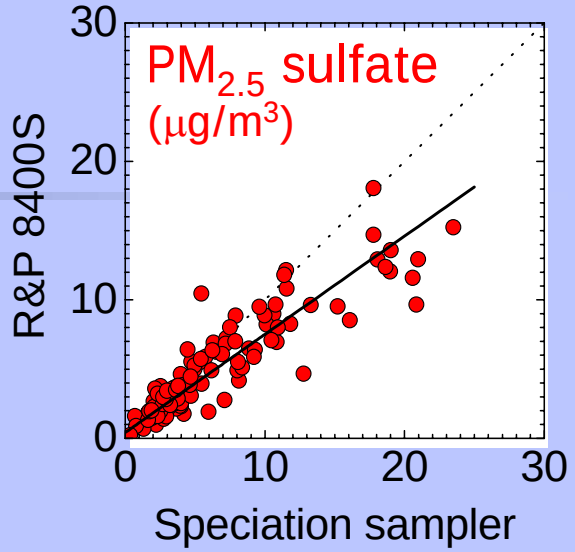
Comprehensive

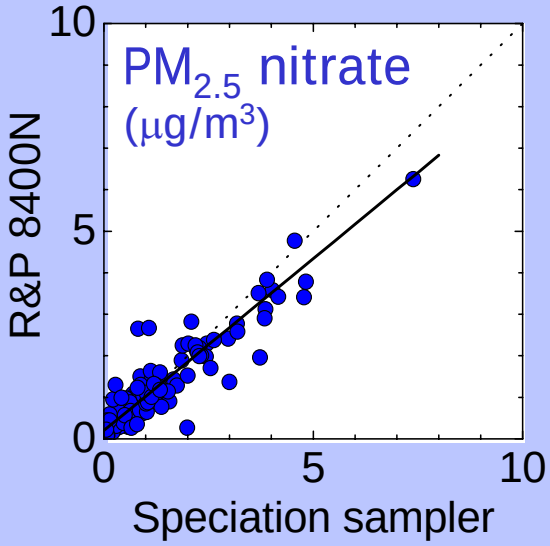
Time consuming, but resulted in better agreement and minimized nonlinearity

But, still a bias ...

Systematic bias

- Incomplete collection?
  - At high concentration
  - Of high volatility species
- Incomplete reduction of aerosols?
  - Different anions or form of salts
  - Different aerosol phase
  - Presence of non-inorganic species
- Other variables in gas analyzer performance?
  - Different calibration conditions
  - Slow response at high concentrations



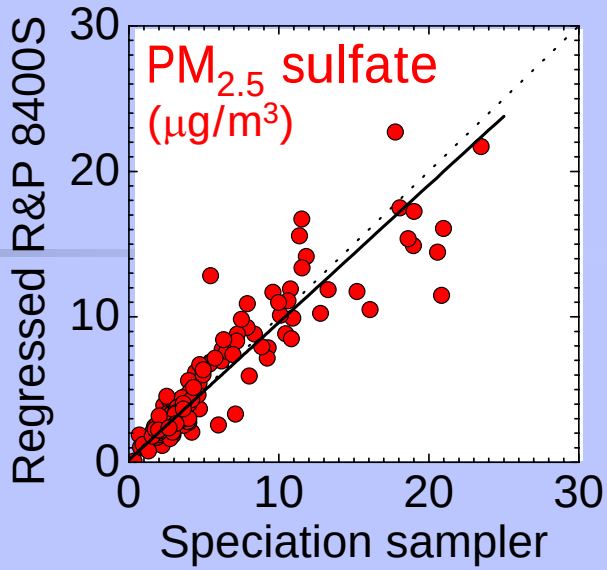


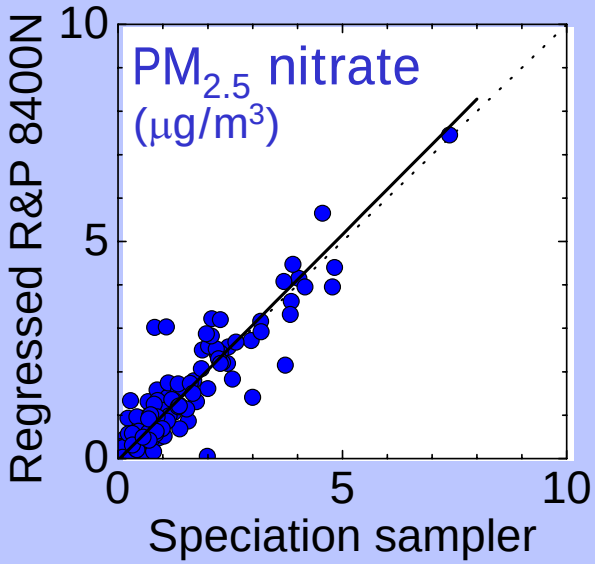
Reducing the bias by calibration

Identify outliers using Robust Huber's method

Calibrate using major axis regression against speciation sampler measurements

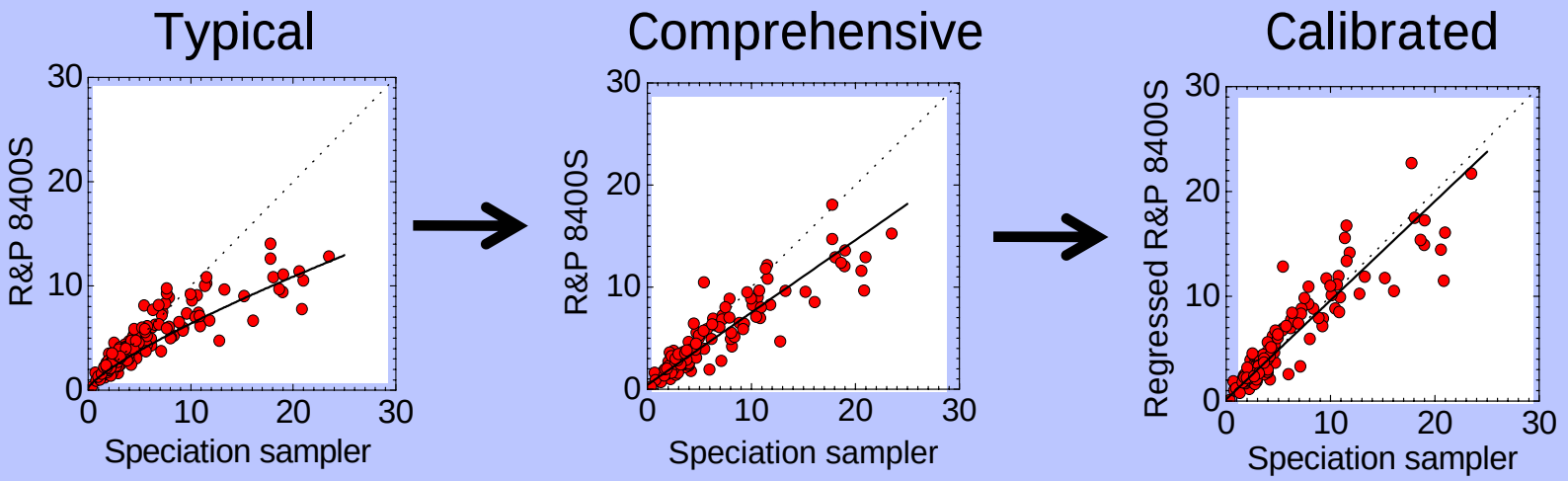
→ Combine accuracy with temporal resolution





Data processing summary

	Sulfate (below)	Nitrate
Recommended reduction	$y = x^{0.79}+0.23$	y = 0.63x+0.27
Comprehensive reduction	y = 0.71x+0.42	y = 0.83x+0.2
Reduced and calibrated	y = 0.94x+0.17	y = 1.04x-0.04
Data capture	> 90% (* 11/2001)	> 80% (* 08/2002)



Interesting trends in measurements ...

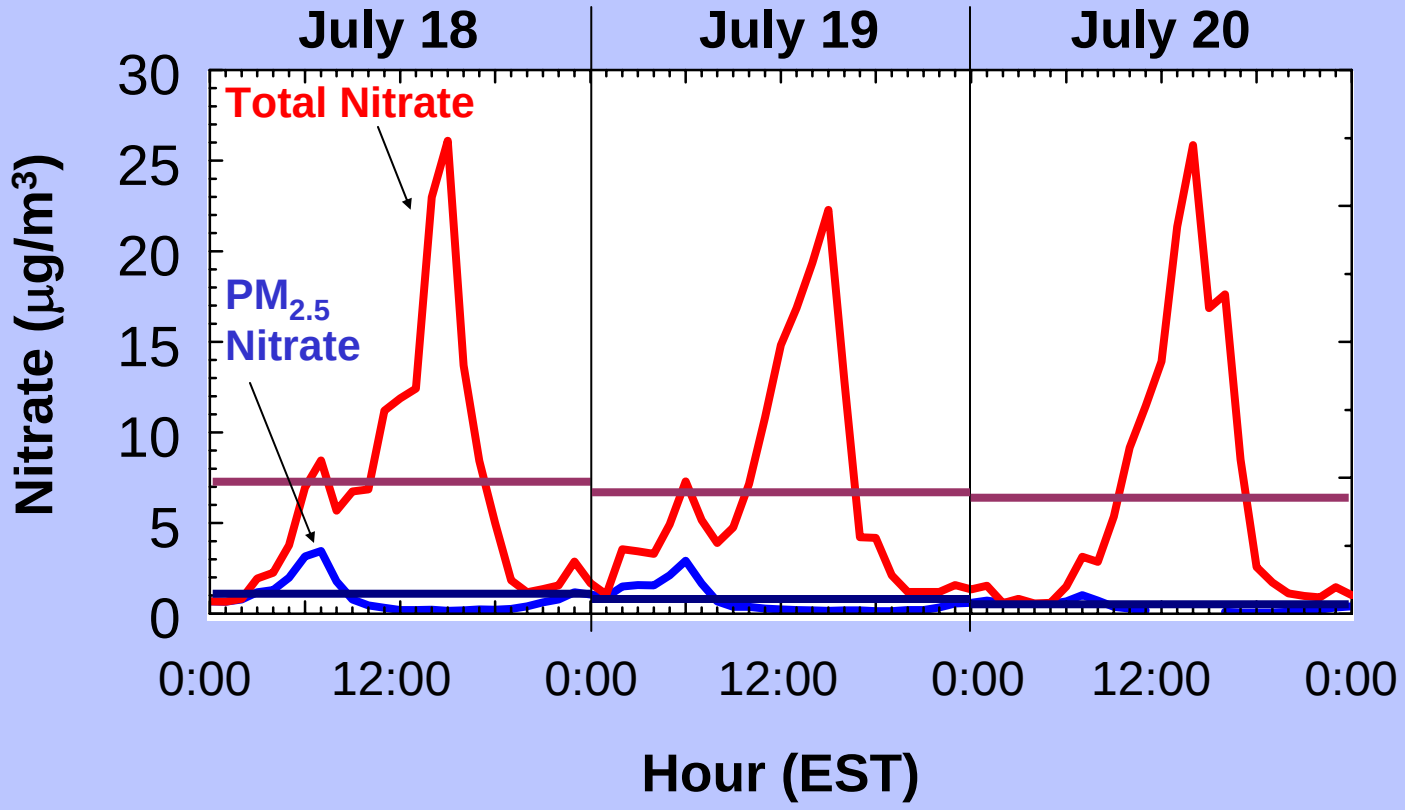
Question:

What do we lose by only making 24-hour (conventional) measurements?

Answer:

Information that helps us to understand particle chemistry and behavior and identify contributing sources.

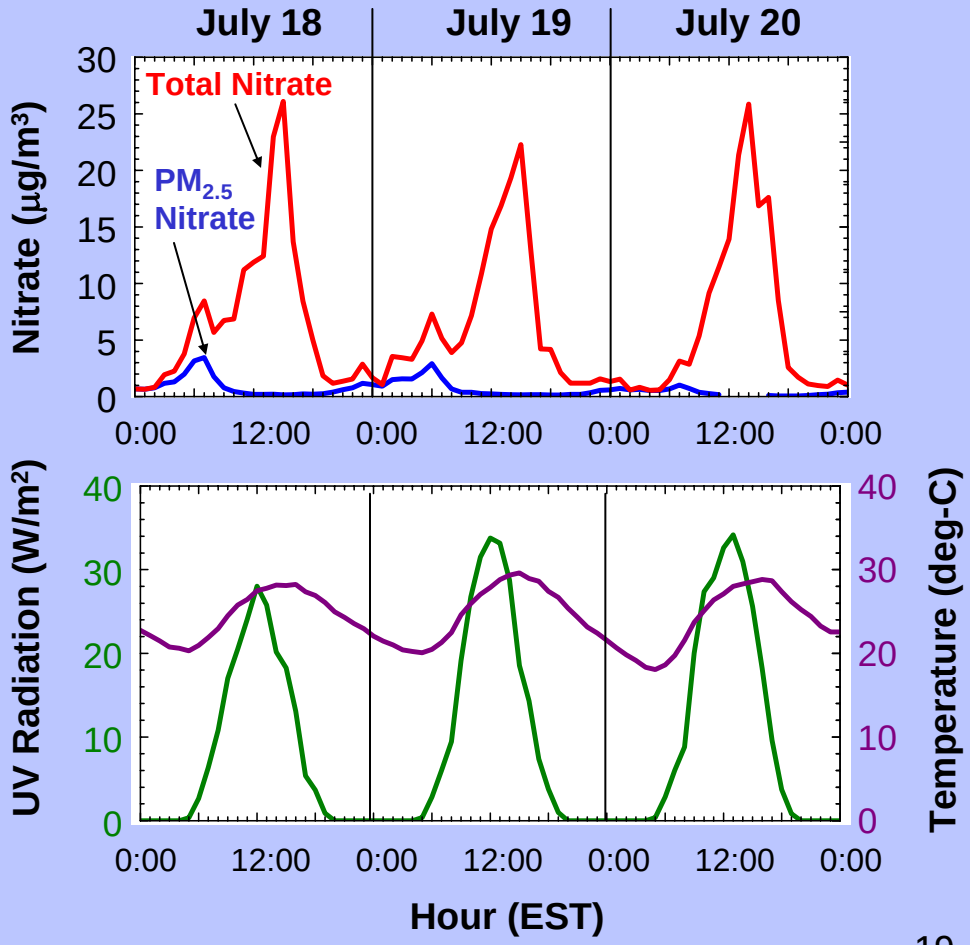
Variations in nitrate are lost by conventional methods



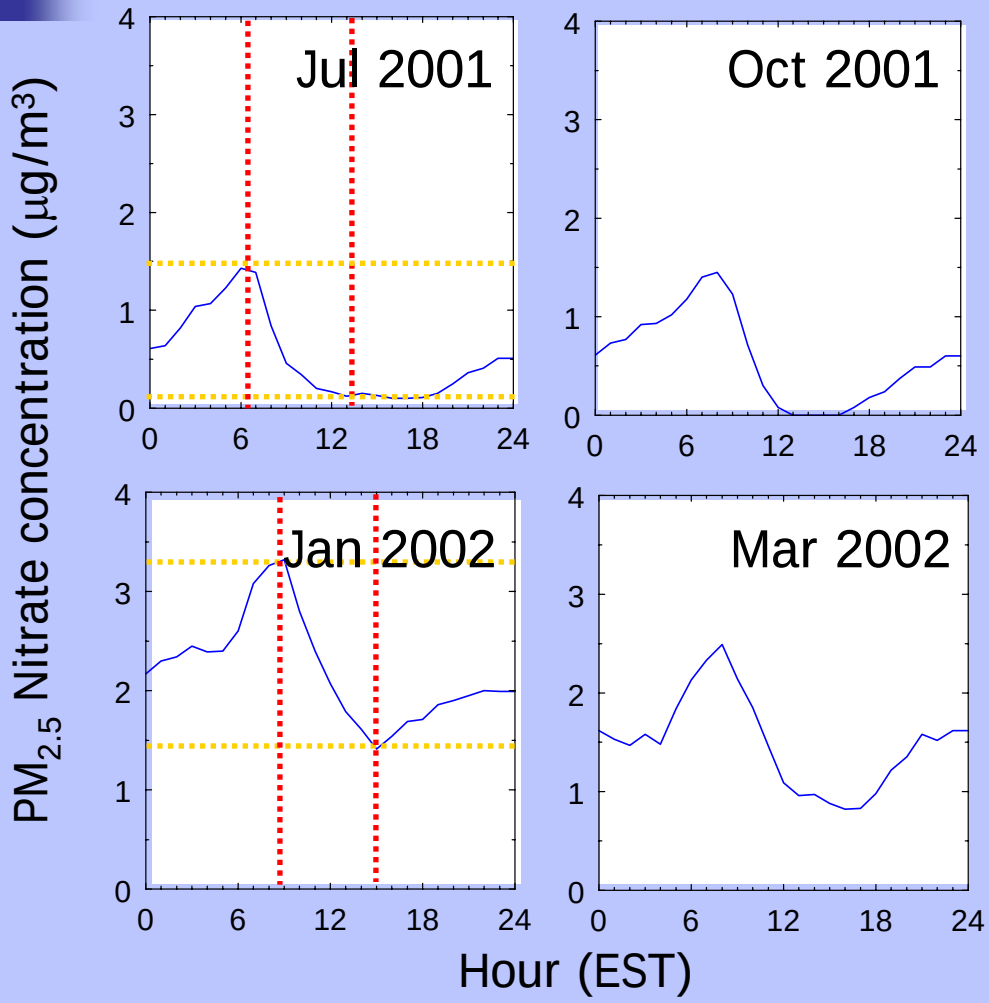
Diurnal pattern in nitrate driven by meteorology

Partitioning of nitrate between phases:

- Most dramatic during summer
- Pattern observed nearly daily but to varying degrees

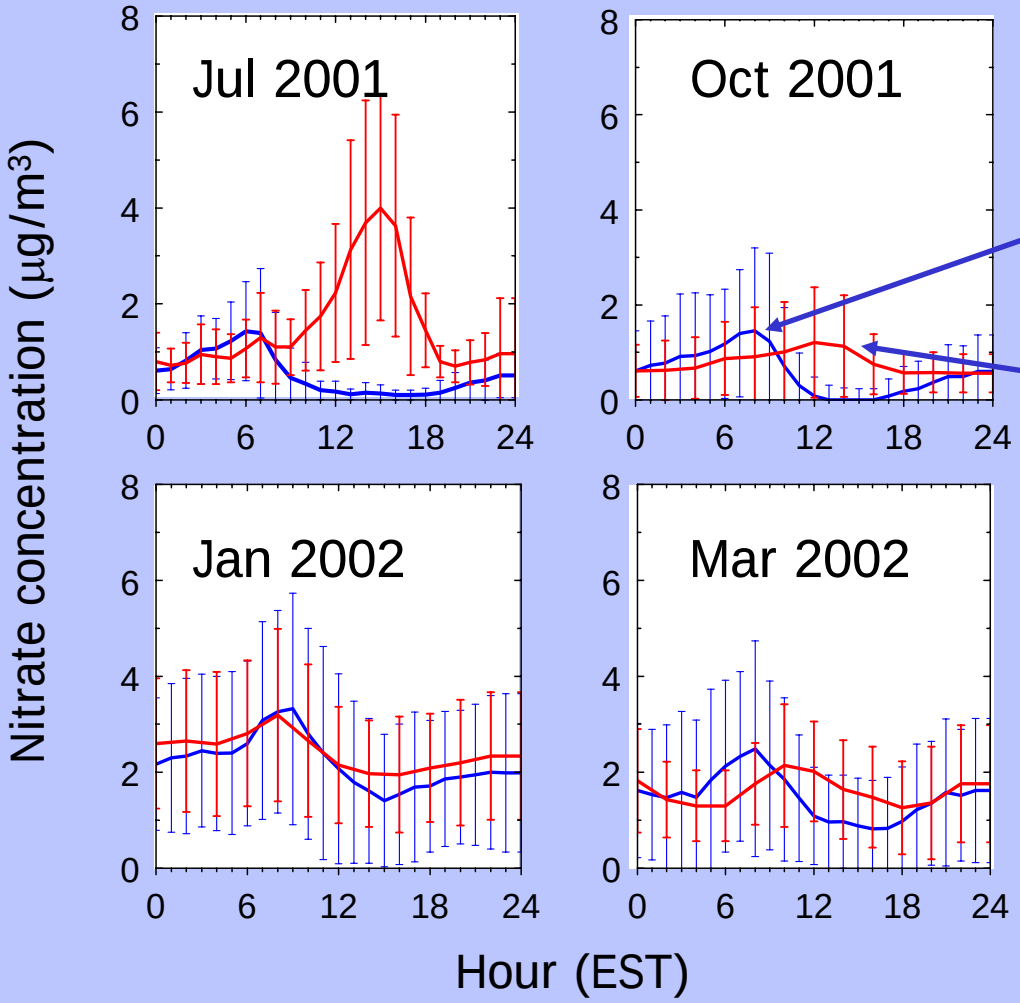


Consistencies in diurnal pattern of $PM_{2.5}$ nitrate



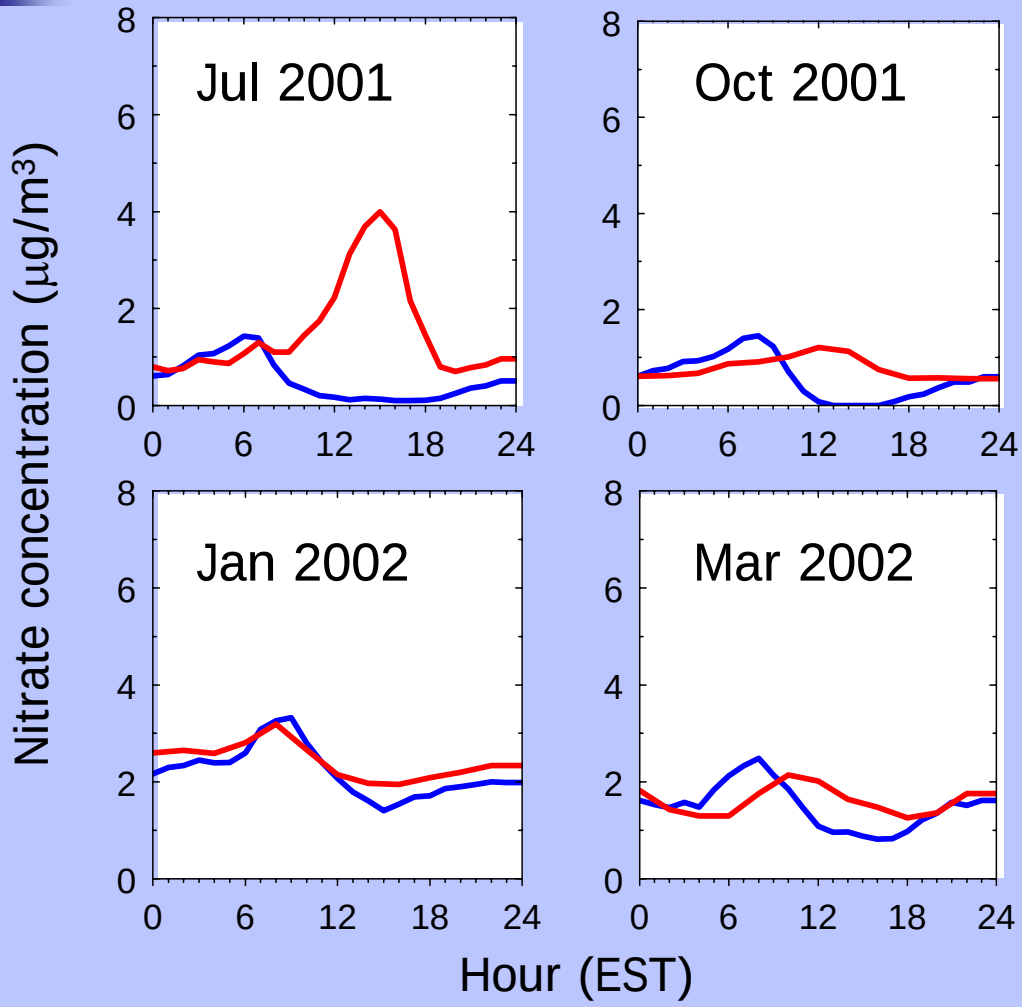
- Similarities in shape across season (80%-90% of profiles agree)
- Differences in specific features

Consistencies in diurnal partitioning of nitrate



- Aerosol NO_3^- measurements
- Gas + aerosol (Total NO_3^-) measurements
- Standard deviation of measurements

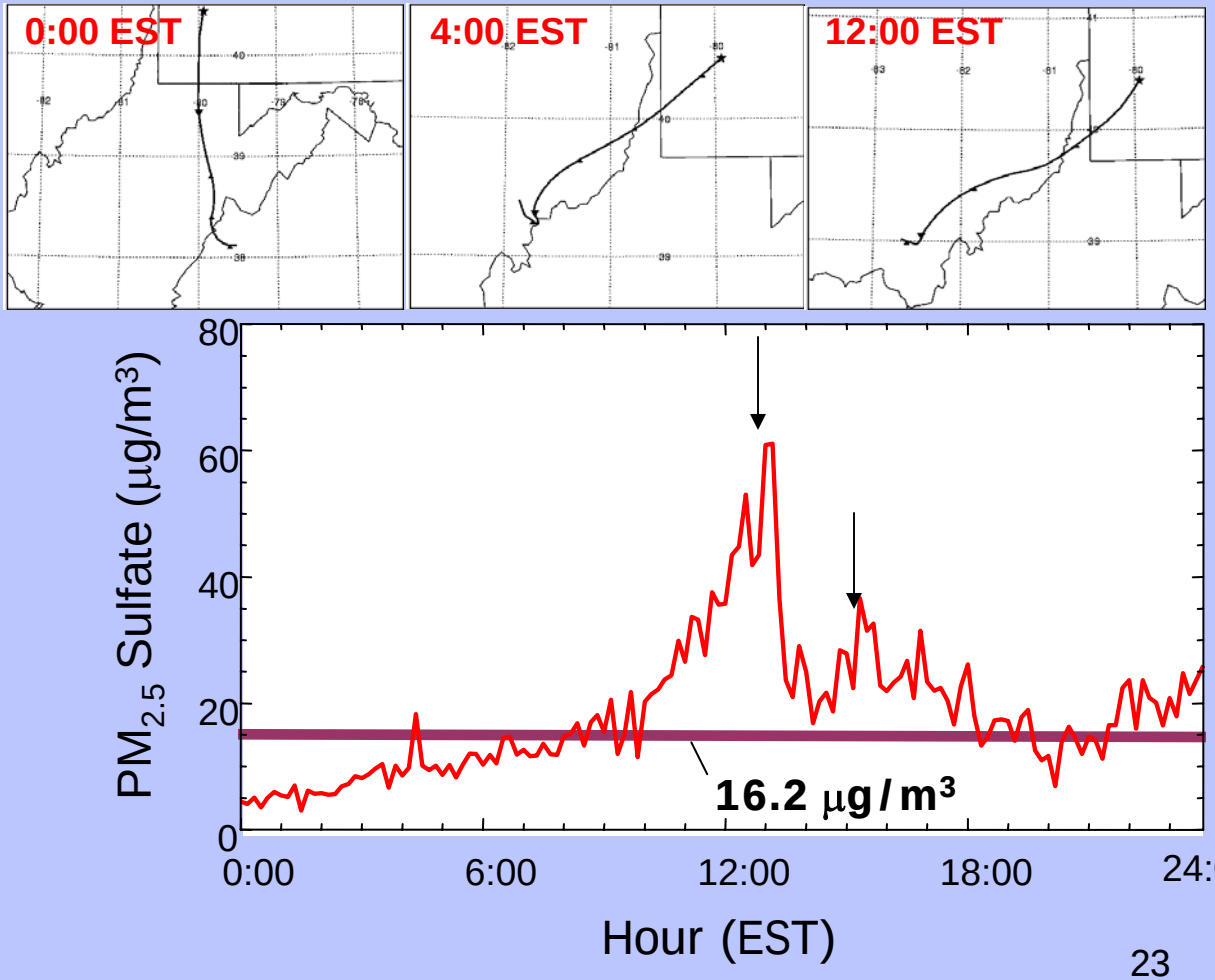
Consistencies in diurnal partitioning of nitrate



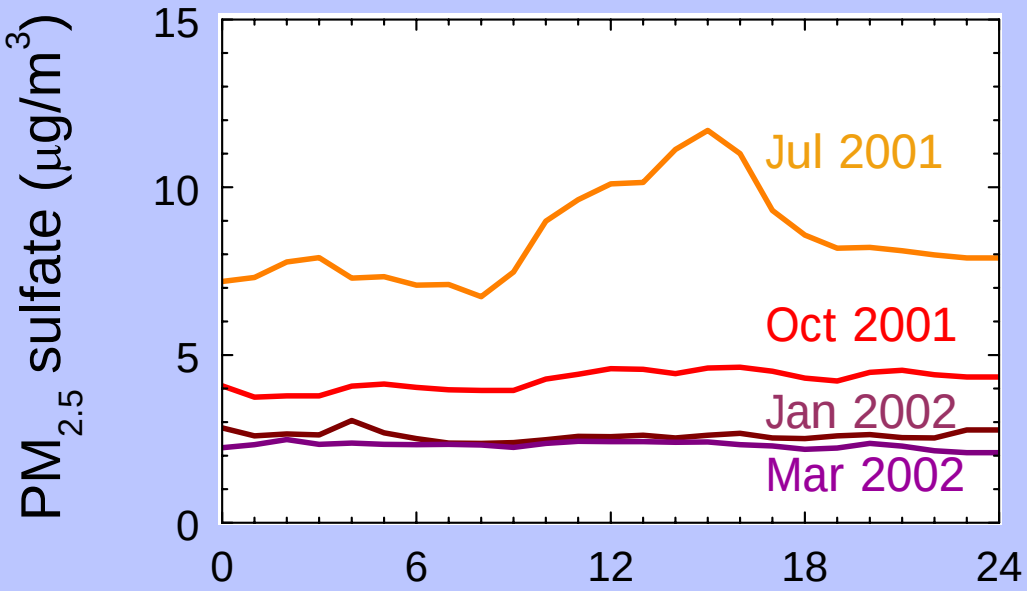
- Consistencies are observed
- Majority of NO_3^-
  - Gas phase in summer
  - Aerosol phase in winter
  - Intermediate partitioning in fall and spring

Variations in sulfate are also lost by conventional methods

- 7/26/02
- Increase as winds shift direction
- Decrease after a front passed, wind speeds decreased, and some rain fell



Inconsistent diurnal pattern in $PM_{2.5}$ sulfate



Consistent diurnal variation was observed in the summer (70% of profiles agree)

Conclusions

- High time resolution aerosol measurements are needed but still have issues. Commercialized versions of the flash volatilization method demonstrate poorer performance than the prototype instruments.
- Measurements made using the R&P nitrate and sulfate instruments require extensive data reduction AND regression to achieve temporal resolution AND accuracy.
- But, by expending this effort, we obtained resolved measurements that were used to learn about nitrate partitioning and used to track plumes affecting the local air quality.

Contributors

- Funding for the PAQS Supersite
  - US Environmental Protection Agency
  - US Department of Energy National Energy and Technology Laboratory

- Collaborators
  - Carnegie Mellon University: Spyros Pandis, Cliff Davidson, Satoshi Takahama, and Andrey Khlystov
  - Aerosol Dynamics Inc: Susanne Hering and Brent Kirby

Questions?