

# **Real-Time PM<sub>2.5</sub> and Speciation Measurements: Needs, Practical Approaches, and Methods Issues**

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**Northeast States for Coordinated Air Use Management  
Boston, MA**



**EPA PM Model Performance Workshop  
February 10-11, RTP NC**

## **Introduction**

Many new methods for real-time ambient aerosol measurements have been developed in the last 5-7 years

- response to the new pm<sub>2.5</sub> standard and related health studies
- need for better understanding of aerosol formation and transport

### Goals of this presentation:

Summarize needs & applications for “highly time-resolved” aerosol data

Review existing commercial or widely used non-commercial methods

Discuss data quality needs and limitations

## What is the value and application for modeling use?

Traditional “integrated” sampling provides 24-hour mean aerosol data

Usually every 3<sup>rd</sup> or 6<sup>th</sup> day sampling (occasionally every day)

**BUT** -- Formation and transport processes (meteorology, vertical mixing, photochemistry) can occur on time-scales of a few hours or less

24-hour duration integrated samples often “smear” different regimes

-- difficult to observe and understand sub-daily processes

Sample durations of 3-hours or less provide **awesome** insight!

Invaluable for aerosol model development and evaluation

15-60 minute data can be used for “spatial scale” FDFT analysis

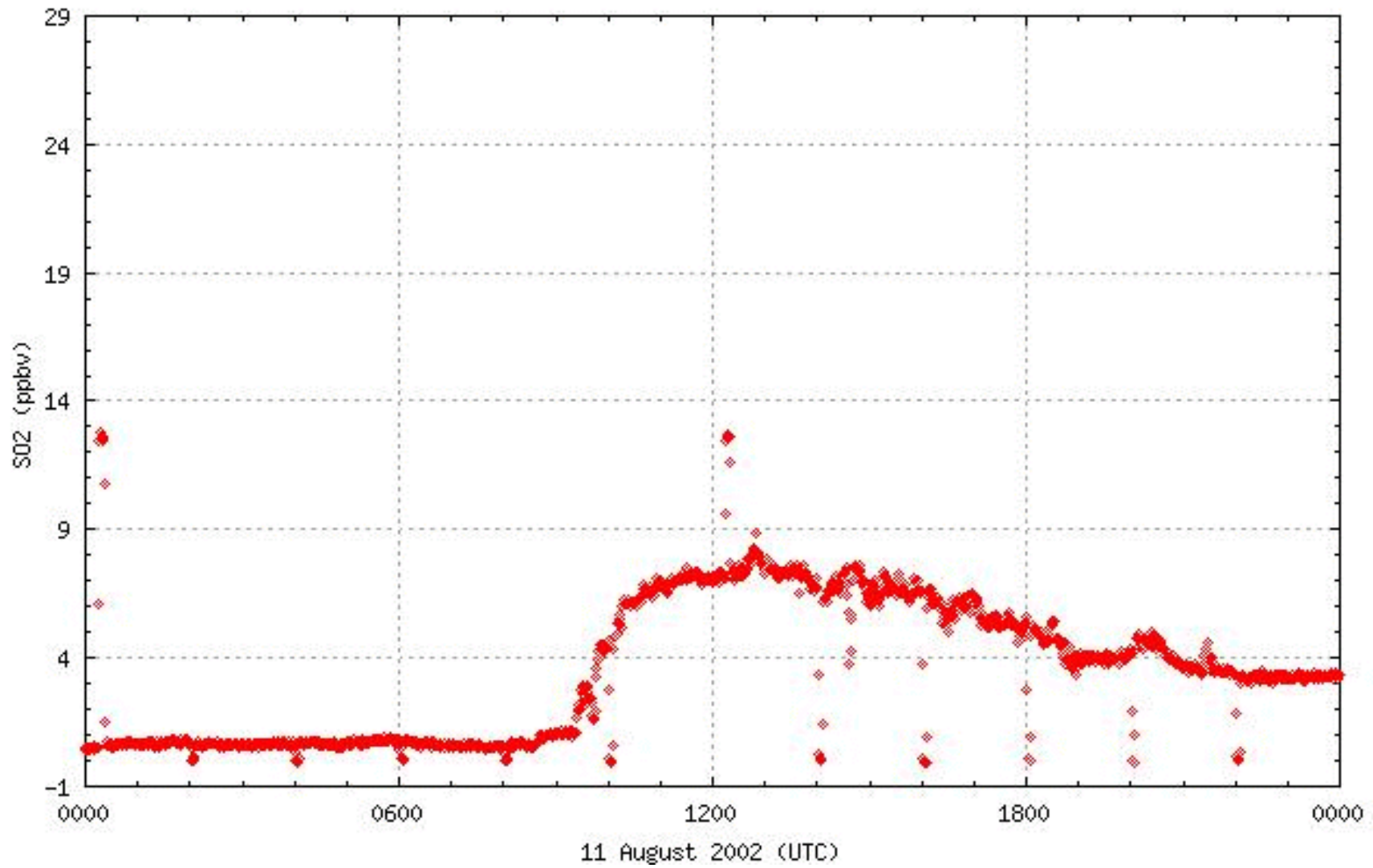
Forecast model use: real-time data are available as a “nowcast”

Integrated samples: wait days to months

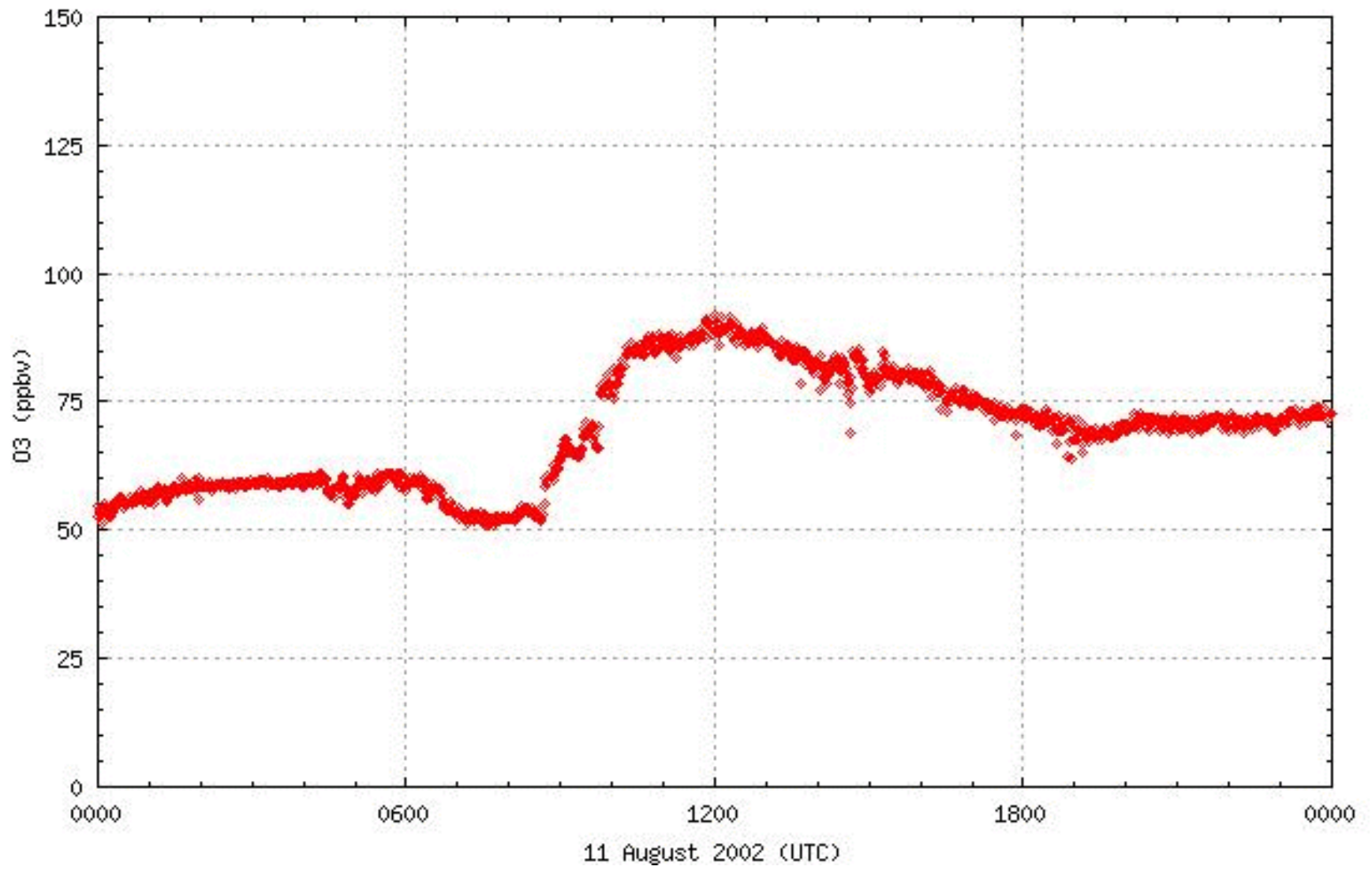
Examples of hourly S data demonstrate the additional information that can be obtained that is often lost with daily sampling: Example from Mt. Washington NH August 2002.

(SO<sub>2</sub>, O<sub>3</sub> courtesy AIRMAP/UNH)

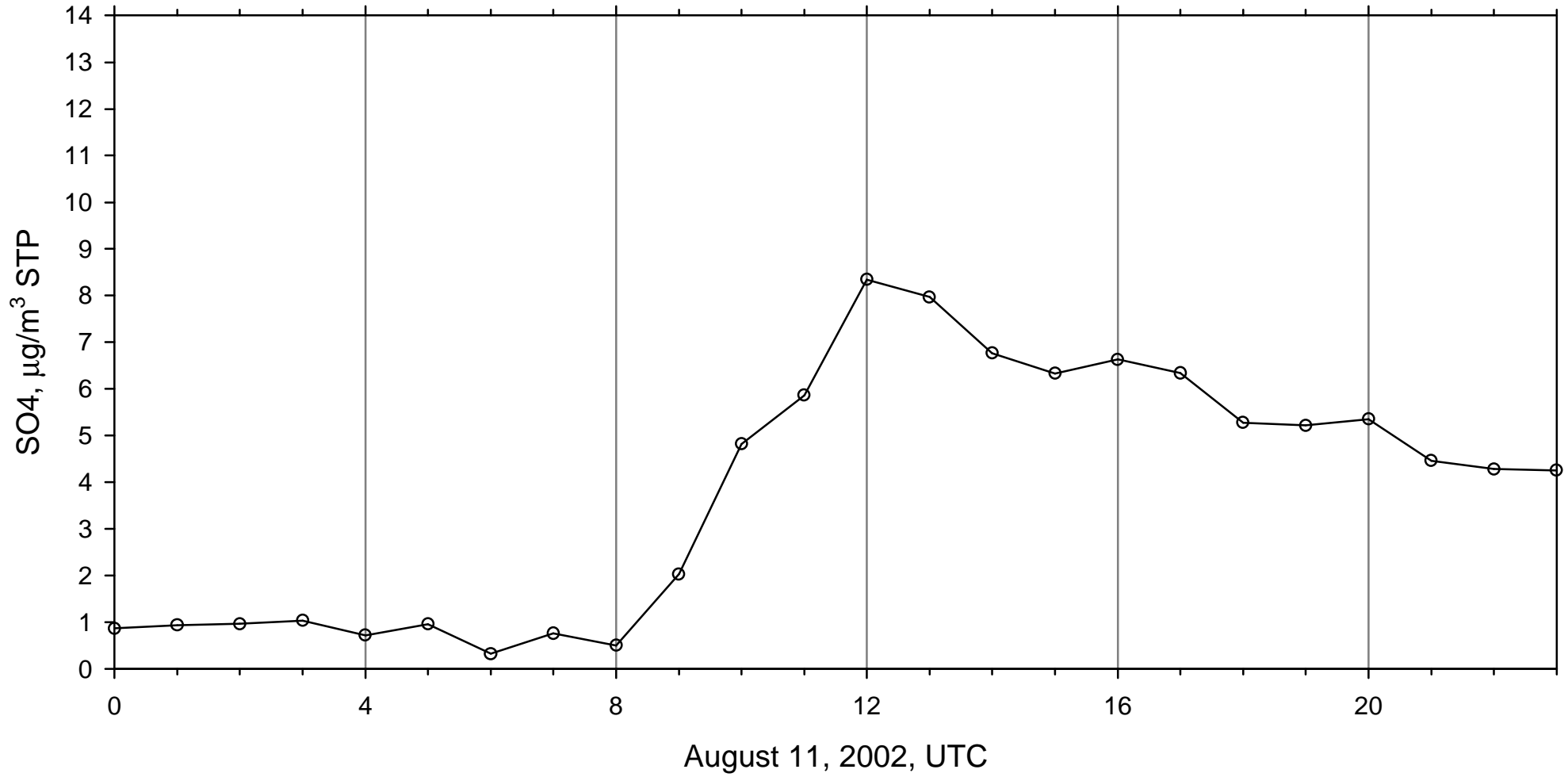
Mt. Washington Observatory S02 - (Note: High values are calibrations)



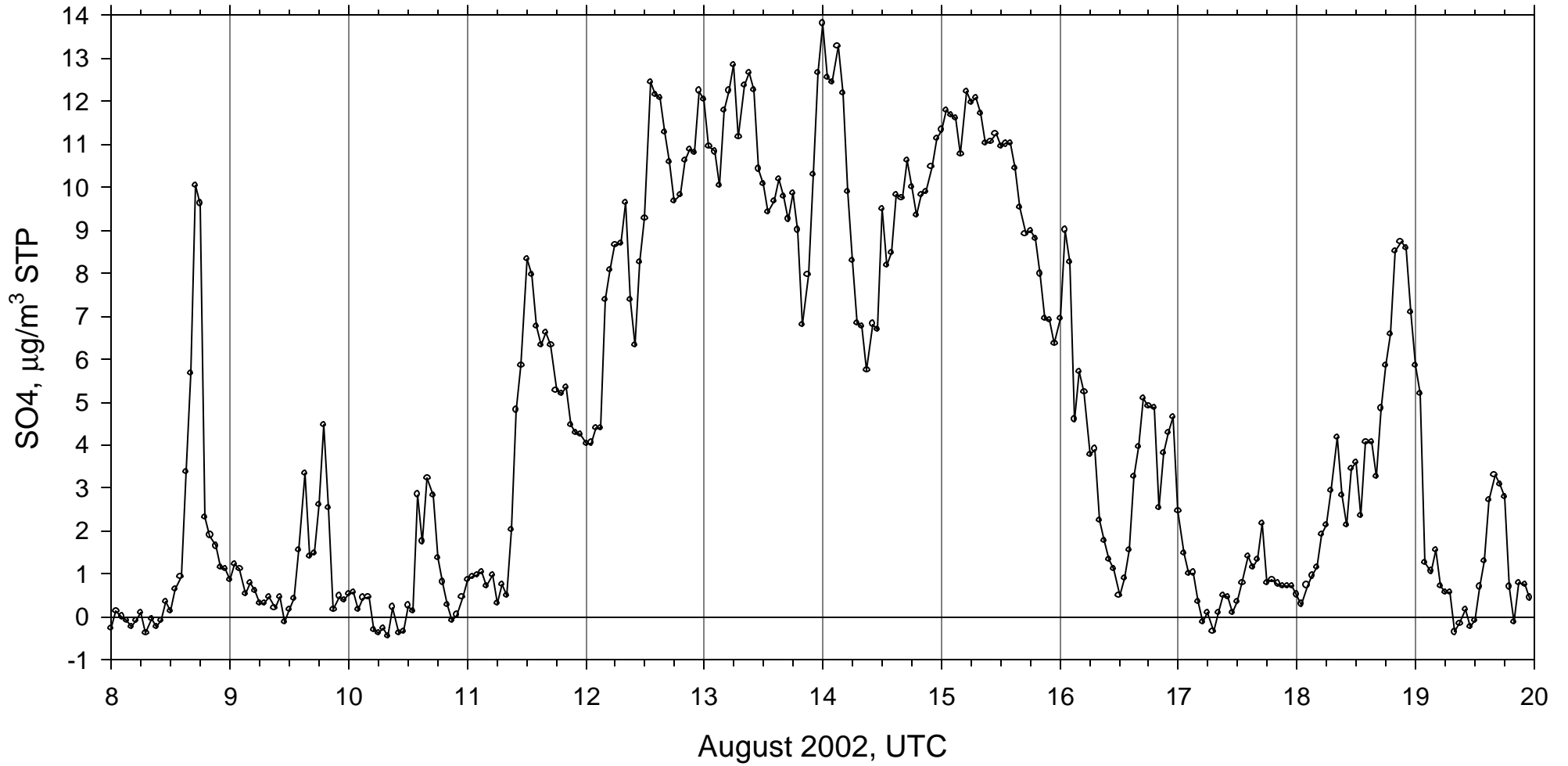
Mt. Washington Observatory 03



HSPH/NESCAUM Sulfate, 1-hour means  
Mt. Washington, NH Summit Site



HSPH/NESCAUM Sulfate, 1-hour means  
Mt. Washington, NH Summit Site



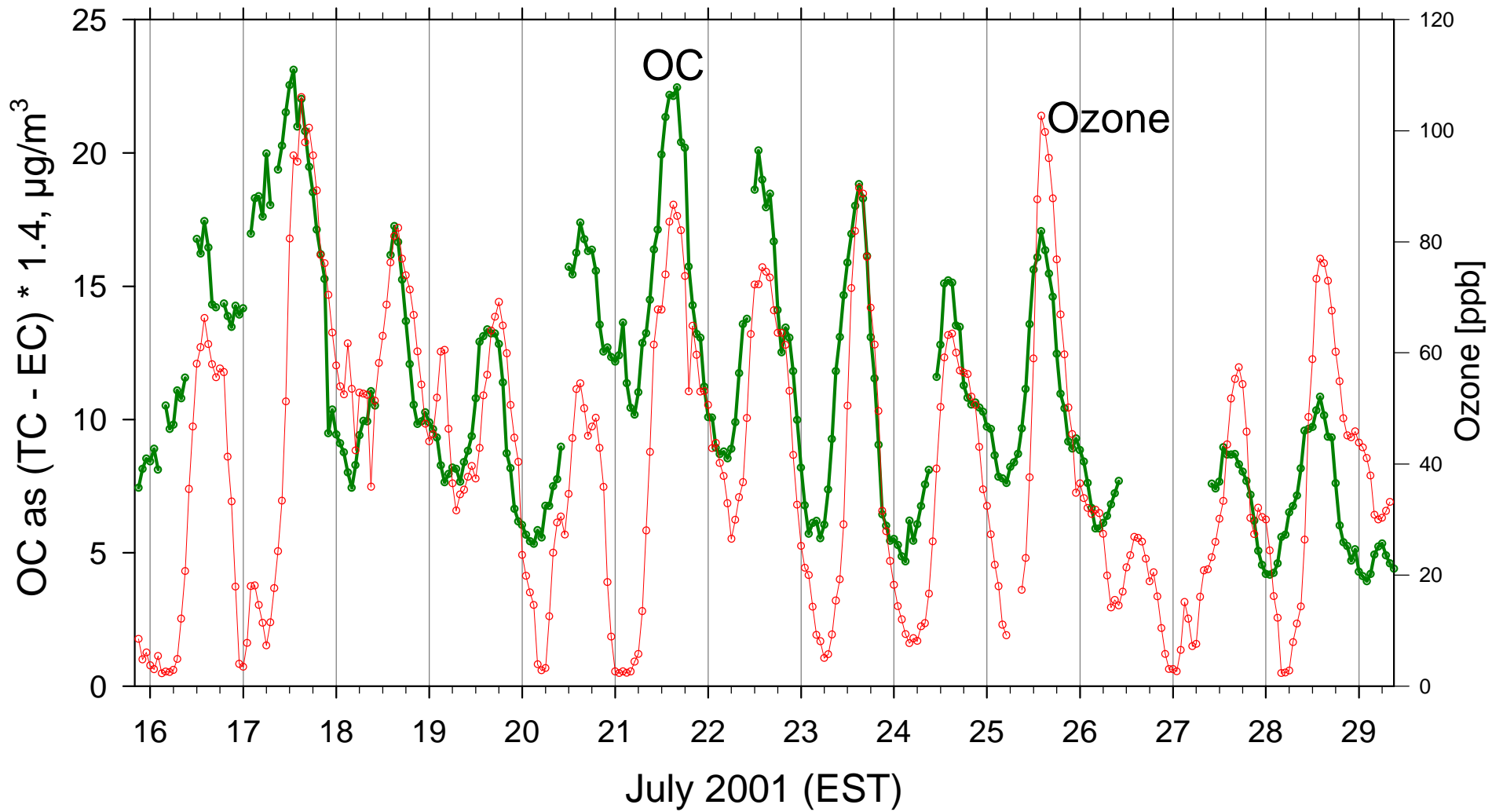
Examples of hourly carbon data demonstrate the additional information that can be obtained that is often lost with daily sampling:

Philadelphia OC and Ozone peak at the same time of day every day during summer - indicative of a secondary regional OC component.

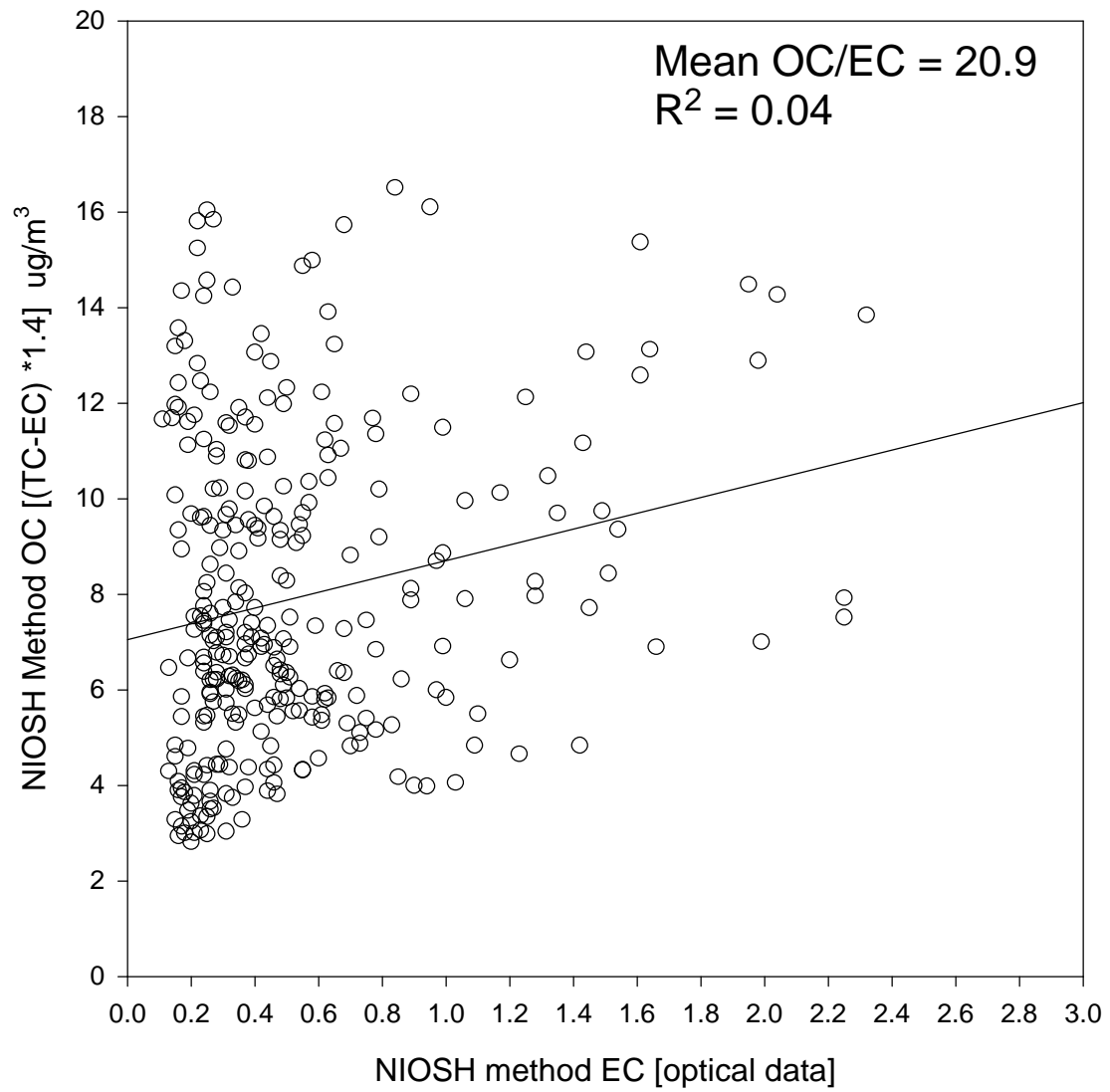
Phila hourly EC and OC are completely decoupled – EC is a local ground-level source [tailpipe].

BC from multiple Boston area sites show traffic influence in urban areas but not outside of the urban area.

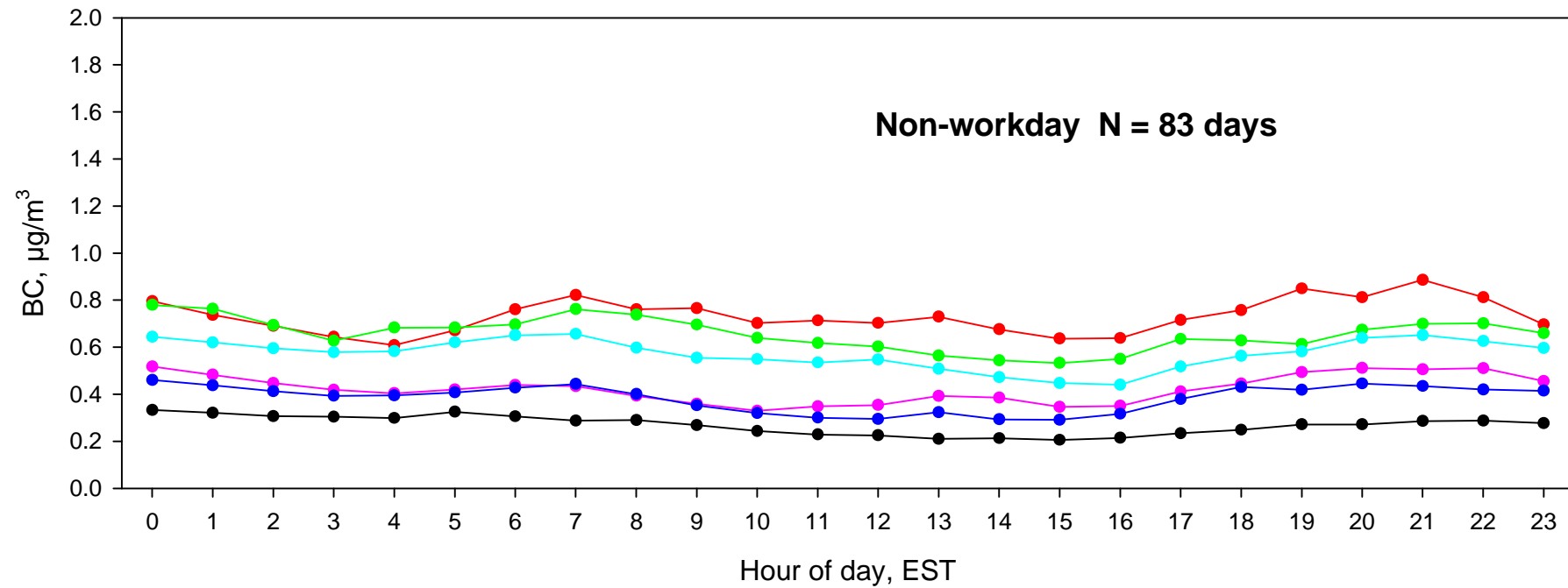
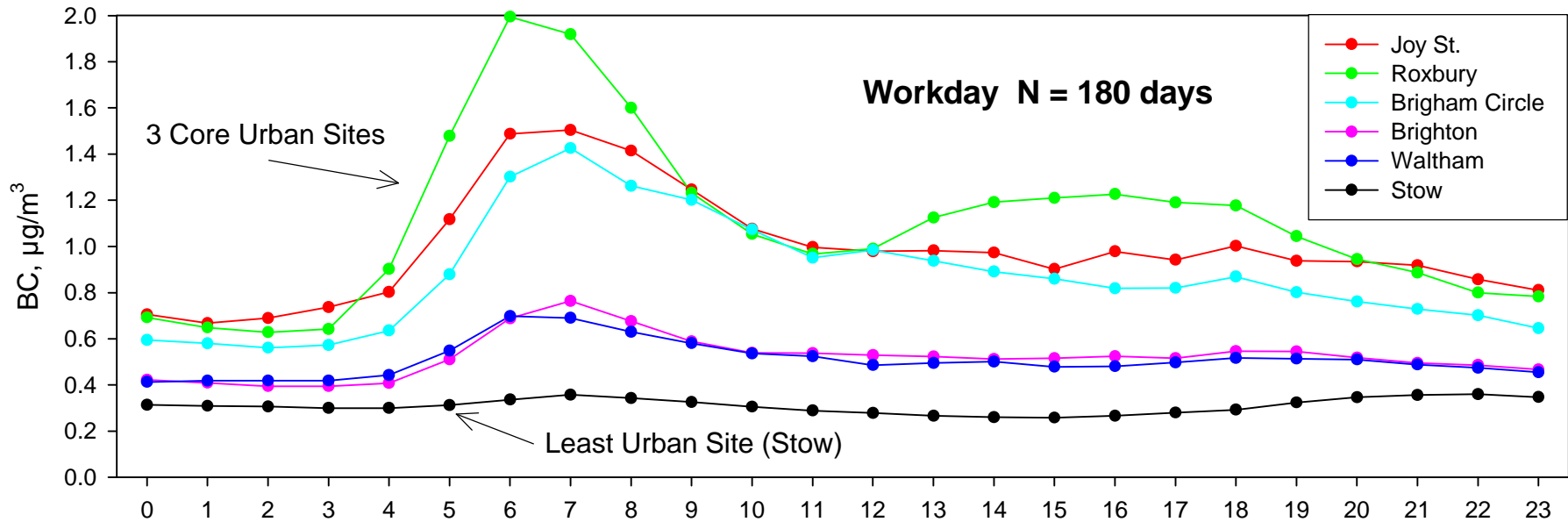
# Sunset Labs 1-Hour Organic Carbon and Ozone Philadelphia-Baxter (NEOPS)



Sunset Labs Hourly OC vs. EC  
Philadelphia PA, July 15-29 2001



# Diurnal BC, Six Greater Boston Sites Dec. 20, 2002 - Sep. 9, 2003



Available “Commercial” Methods for real-time aerosol measurements  
Commercial includes non-production methods [PILS, SEAS etc.]  
that can be purchased and have been widely used in research studies

PM2.5: BAMs, various TEOM flavors, Light Scattering  
Carbon: Sunset and R&P EC/OC thermal analysis  
BC: Magee Scientific Aethalometer, RR PSAP, Teco “Caruso”  
Sulfate: Hering/R&P flash volatilization, Allen/Teco CASM, PILS  
Nitrate: Hering/R&P flash volatilization, PILS (Weber)  
Ammonium: PILS, ARA (both work in progress)  
Metals: SEAS (Ondov)

Gases relevant to aerosol modeling: SO<sub>2</sub>, NO<sub>x</sub>, ozone, NH<sub>3</sub>, HNO<sub>3</sub>

Field validation of real-time aerosol methods: a critical accuracy need  
*Ongoing* collocation with integrated filter samples is essential  
Unlike gas analyzers, field calibration with aerosol is not practical

PM2.5: BAMs, various TEOM flavors, Light Scattering

BAM: Beta Attenuation on a filter that is changed often, can run close to ambient temperature; surrogate measurement of PM  
Several vendors

TEOM: Inertial mass measurement

Filter not changed often, requires fixed temp for operation  
Single vendor, 3 different configurations (50C, 30C, FDMS)

Light Scattering: Nephelometers

Surrogate of PM, sensitive to size and composition of aerosol.  
Multiple vendors

All have limitations... potential water interference, SVM loss

Most need corrections to be “FRM-like” across seasons and sites

# My Continuous PM Data Correction Mantra:

The best continuous data correction is no correction

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Why?

Any correction based on daily FRM data is inherently flawed as we go toward sub-daily PM data metrics... for health standards, AQI, or modeling use.

## No PM2.5 correction?

– we're not quite there yet... but getting closer!

Potential commercial methods for “no correction”:

Cold BAM?            Work in progress; evaluations this winter.

NYC, others?

FDMS TEOM<sup>®</sup>: The best TEOM yet!

Solves the often large negative bias problem

But complex, and can have positive bias

Caution: Hourly PM2.5 data in AQS are not corrected for site/seasonal biases; data may not be “FRM-like” -- potential for short term biases ranging from -50% (hot urban TEOM) to +30% (wet summer BAM, some summer FDMS TEOM)

FDMS TEOM: A work in progress

Solves some problems of earlier versions, creates others

VT and NY early experiences good, some others not

Does a good job with SVOC aerosols [Mimics FRM loss??]

May have problems with water interference in summer

BAMs: Getting Better; stay tuned.

BAMs potential: can run closer to ambient temp; simpler.

Need 'next generation' technologies!!!

Still need 2x better LOD for stable 1-hour means

Generally simpler than FDMS TEOM

Multiple vendors in US market: MetOne, Teco, (BGI)

MetOne has substantial U.S. and Canada market penetration

Light Scattering: Seems to work in AZ and WA

Not for areas with complex aerosol mixtures...

NGN-3a, Teco/MIE, Radiance Research, others

## Carbon and BC

EC/OC thermal analysis: Sunset Labs and R&P

Different approaches, Different data (welcome to the carbon world...)

Sunset is denuded filtration with OP-corrected thermal ramp analysis

Default is NIOSH 5040 TOT - different than STN or DRI-TOR

TC is comparable with properly blank corrected filter networks

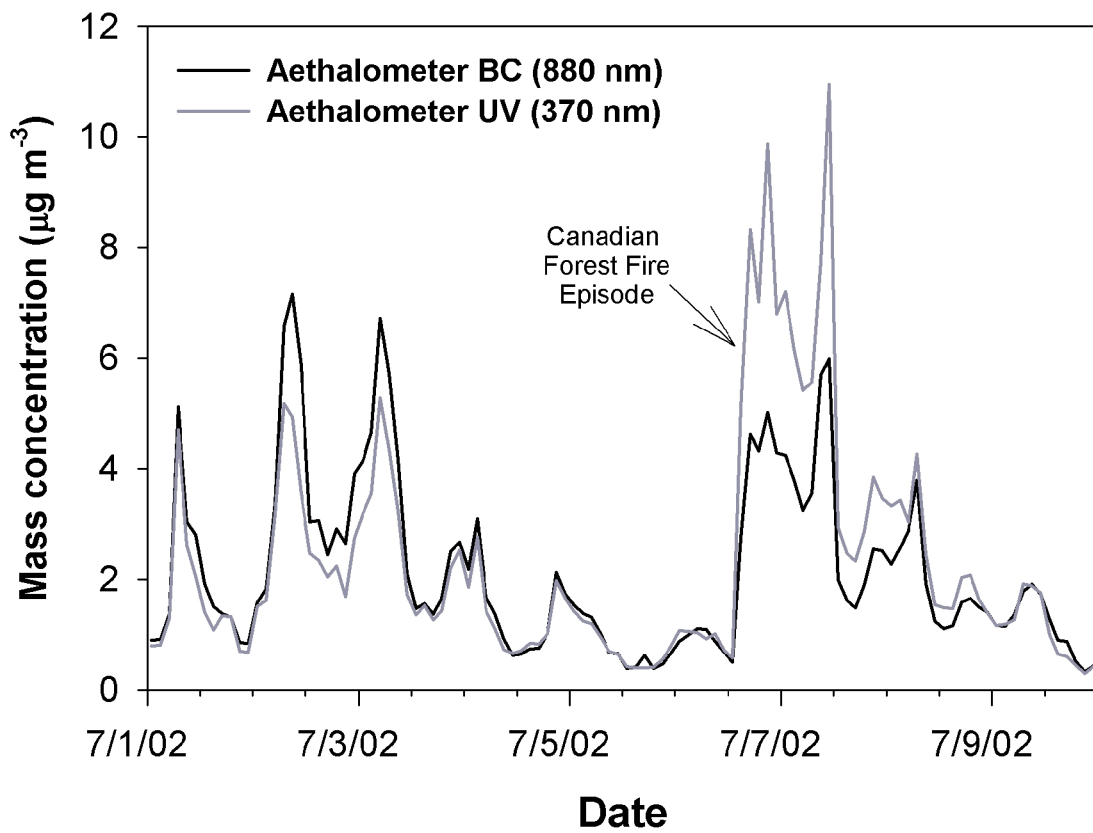
R&P 5400 is impaction without OP correction

No denuder, TC and EC/OC partitioning can vary widely compared to integrated filter samples (function of aerosol size & composition)

BC (OD): Magee Scientific Aethalometer, RR PSAP, Teco “Caruso”

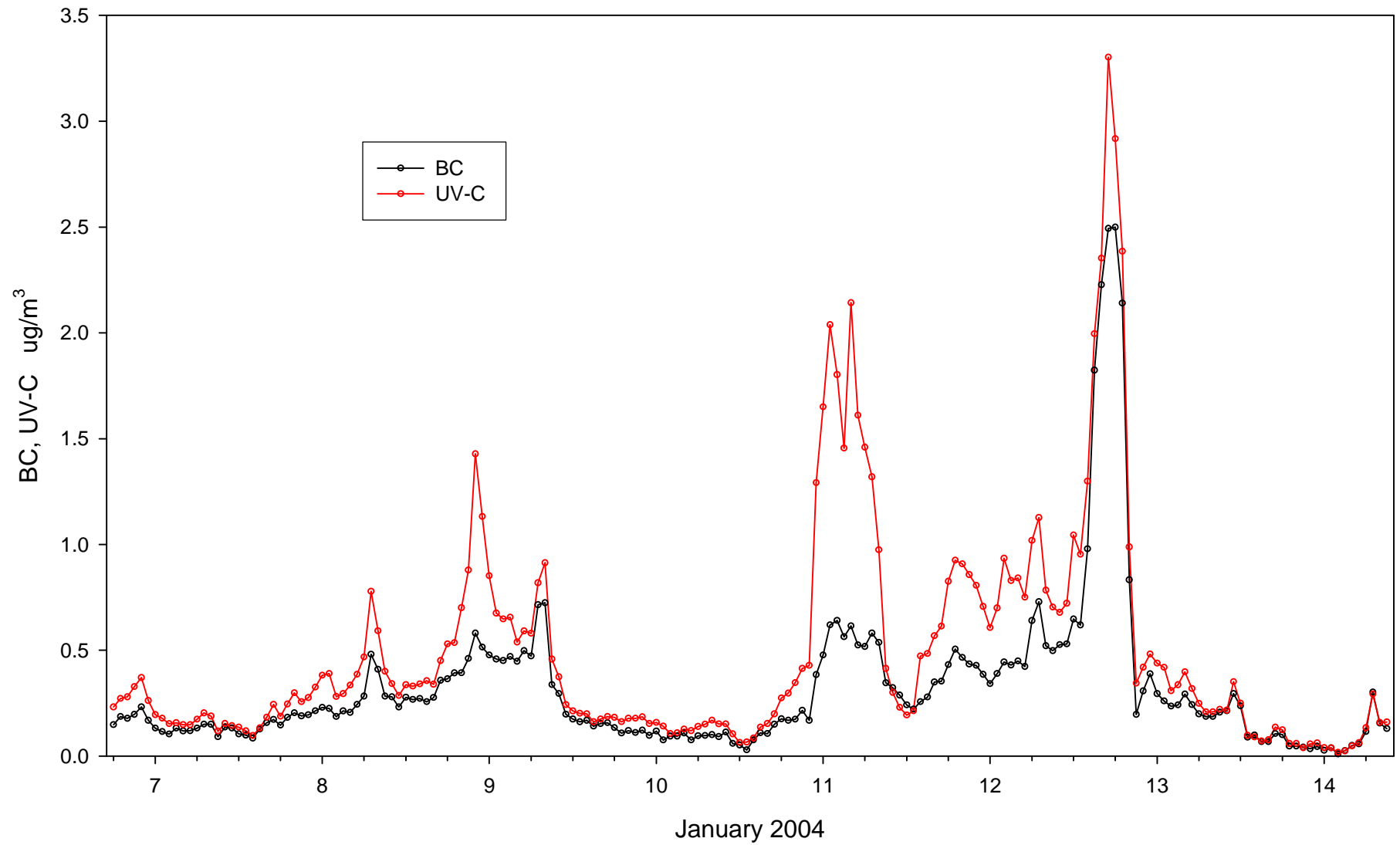
Good surrogate measurement of EC, easy to operate

Multi-wavelength OD: Aethalometer (woodsmoke indicator!)



**Figure 8.** Black carbon measured using 880 nm wavelength and UV absorbing organic matters using 370 nm wavelength for Philadelphia, PA, during the Canadian forest fire episode.

# Millersville Surface Aethalometer Data - 1-hour means



## Sulfate:

Hering/R&P: flash volatilization

collection by wet impaction on 10-min cycle

thermal SO<sub>2</sub> analysis

recovery issues for pure sulfate aerosol (needs other “stuff”)

Allen/Teco: CASM - SS converter (commercial product this summer)

true continuous method [no sample collection]

thermal SO<sub>2</sub> analysis

>95% recovery for pure sulfate aerosol

Weber/GIT: PILS (Particle into Liquid Sampler)

Steam impaction collection for 5-15 minutes

Analysis by IC

Robust data but requires skilled operator

Not [yet?] commercial product, widely used in research studies

## Nitrate

### Hering/R&P flash volatilization

collection by wet impaction on 10-min cycle  
thermal NO<sub>x</sub> analysis  
variable recovery for nitrate aerosol (40 to 100%)

### PILS (Weber/GIT)

Steam impaction collection for 5-15 minutes  
Analysis by IC  
Robust data but requires skilled operator  
Not [yet?] commercial product, widely used in research studies

## Ammonium

Nothing commercial yet  
Potential methods in R&D phase: PILS, ARA/Edgerton-Hartsell

Trace Metals: a powerful approach; can isolate specific point sources

SEAS (Slurray Elemental Aerosol Sampler):

Ondov/UMD-CP; used in 3 supersites

Steam collection into vials; 10 to 30 minute intervals

Off-site selective event analysis (limited # of elements/run):

Graphite Furnace Atomic Absorption Spectroscopy (GFAAS)

DRUM (Davis Rotating Drum Unit for Monitoring):

Cahill/UC-Davis DELTA group

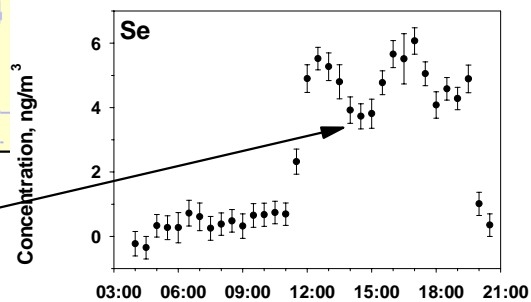
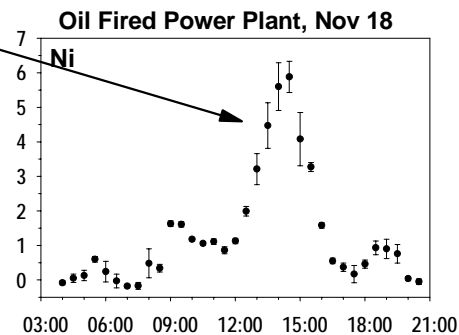
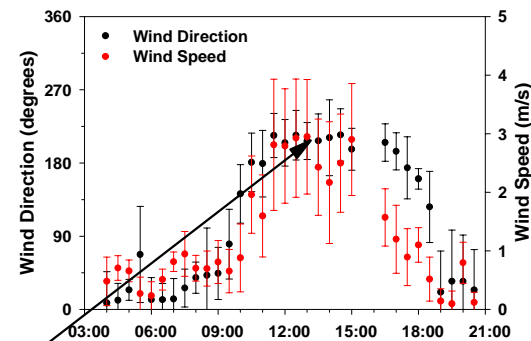
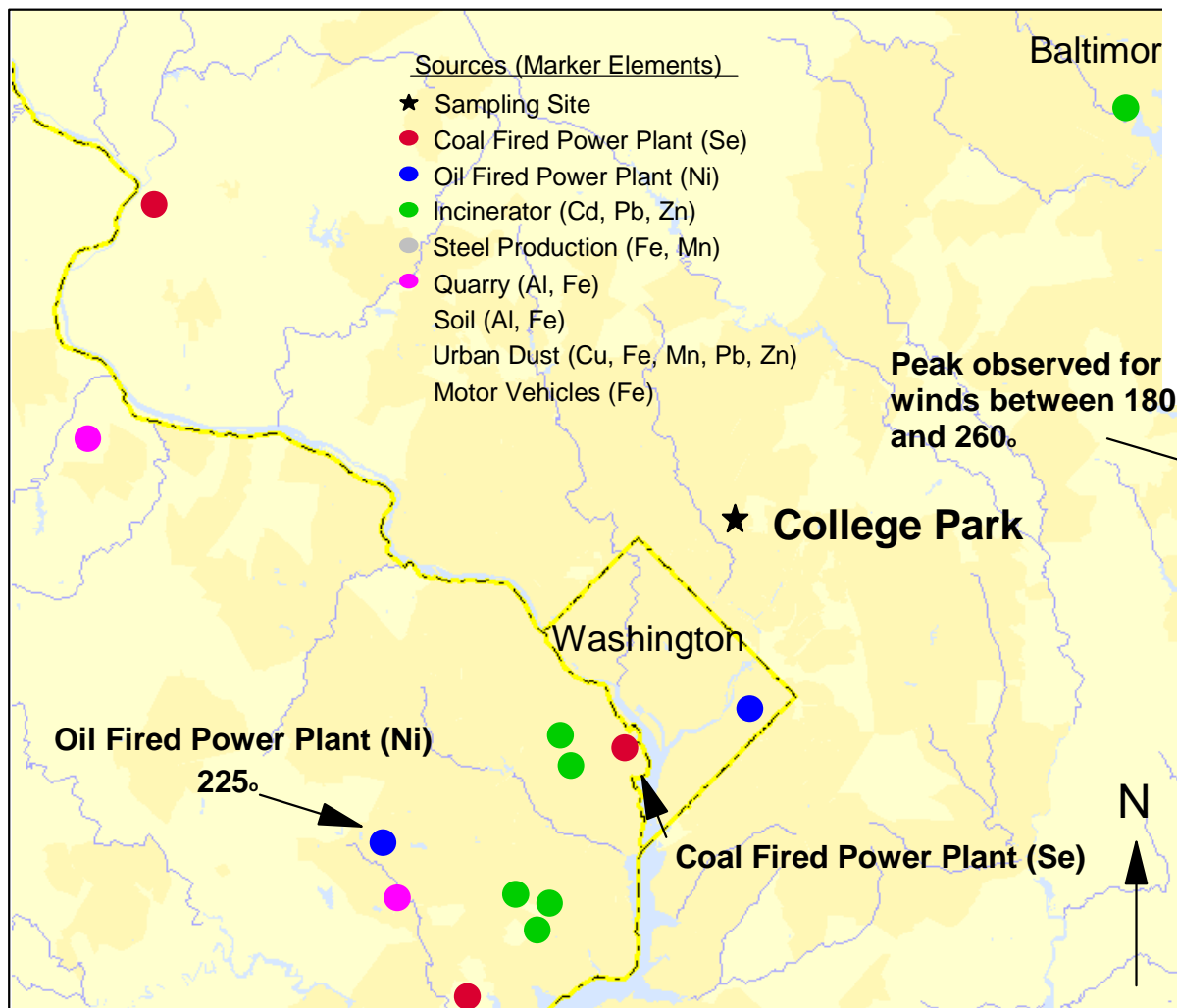
Multi-sized moving strip, inertial impaction collection (like streaker)

Down to 3-hour resolution

Off-site selective analysis by various lab methods - many elements

Neither method commercially available, but can be obtained from developers

# Resolution of Individual Sources with UMHFASS/GFAAZ



\*Data suggest that Oil-fired unit came on when coal-fired boiler "tripped"

\*Resolution of single sources, not just "generic" source types.

*Kidwell and Ondov, University of Maryland, submitted to AS&T.*

## Relevant Real-time Gas Measurements for Aerosol Modeling Use

SO<sub>2</sub>, NO<sub>x</sub>, ozone, NH<sub>3</sub>, HNO<sub>3</sub>, VOCs

Very limited or no NH<sub>3</sub>, HNO<sub>3</sub> at this time

VOCs limited to PAMS (usually summer only)

### Issues:

Some trace SO<sub>2</sub> methods have large NO interferences (Teco)

NO<sub>2</sub>/NO<sub>x</sub> is still fuzzy

OP-SIS DOAS open path for "true NO<sub>2</sub>", SO<sub>2</sub>, NH<sub>3</sub>, some VOCs

NH<sub>3</sub> at ambient levels: DOAS, Pranalytica PAS, [ARA?]

HNO<sub>3</sub>: research tool at this time - ARA/Edgerton-Hartsell

## Case Study: MANE-VU Rural Aerosol Intensive Network (RAIN)

Models need to know what's going on "up there"

Very limited aloft time and species-resolved aerosol data available

Intensive aircraft studies [DOE-G1: PNNL, BNL]

NESCAUM/MANE-VU contribution: RAIN

A new long-term network of sites in the MANE-VU haze RPO

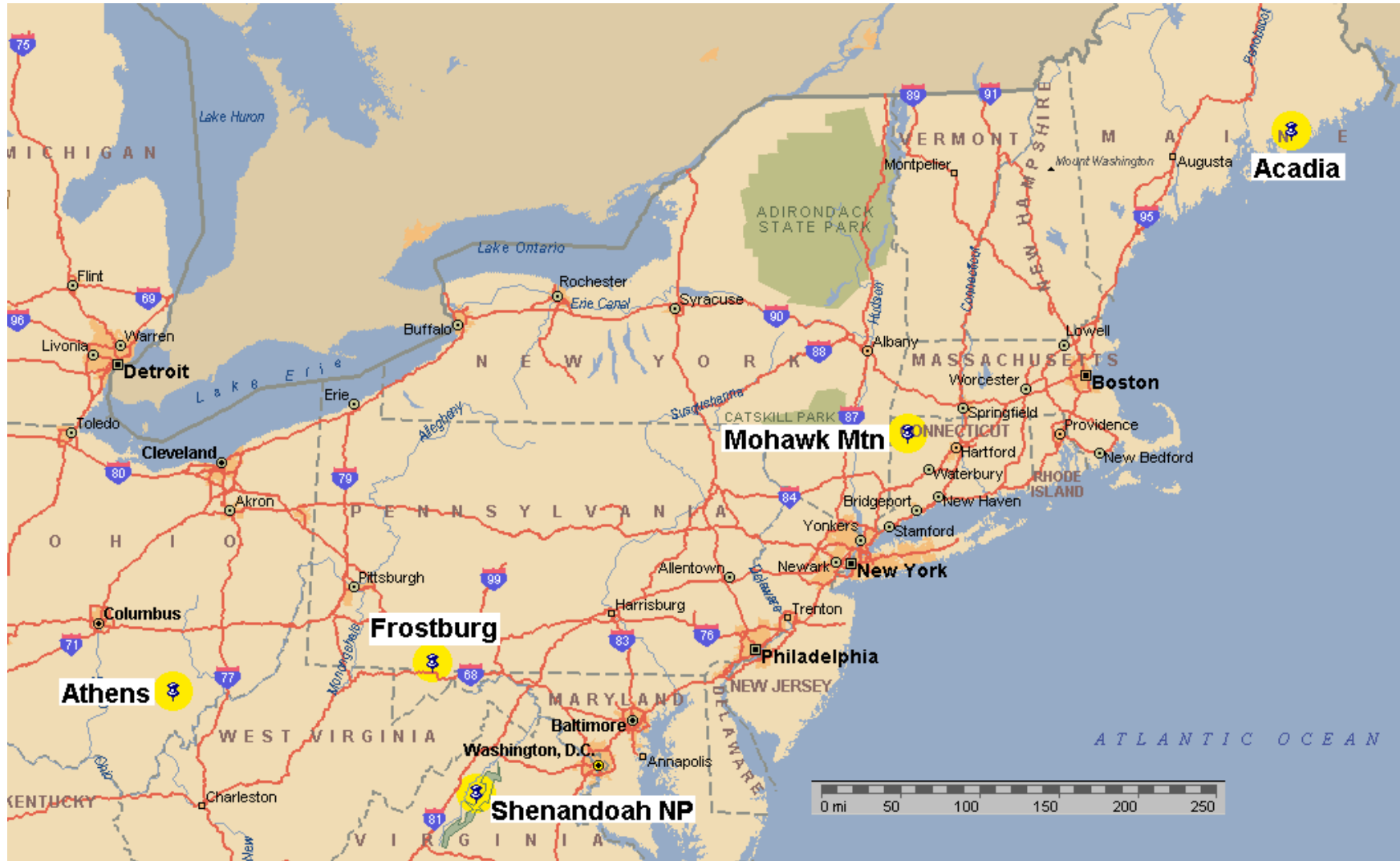
Domain: Western MD to Acadia NP (Maine)

## PM/Haze Rural “Transport Supersites” in MANE-VU domain

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- Multiple sites (3 or more) with detailed PM and visibility-related measurements
  - high-elevation (1000 - 3000 ft), rural, transport characterization
    - ==> contrast “Fresh” vs. Aged secondary aerosols
  - highly time-resolved (1-h) aerosol composition measurements
- Hourly aerosol composition data provide enhanced insight into:
  - regional aerosol generation and source characterization
  - factors that drive short-term visibility
  - aerosol model performance and evaluation

# Planned MANE-VU and potential other non-Mane-VU site locations:



[Athens and Shenandoah are only concepts at this time]

## What's in a PM/Visibility Transport "Supersite"?

- ! Core year-round components that need to be in place:
  - Continuous [hourly] PM<sub>2.5</sub>
  - Surface Met [wind, temp, RH, rain, ?]
  - IMPROVE measurements for carbon, ions and PM<sub>2.5</sub>
  - HazeCam in the general area
  
- ! MANE-VU and/or other funding sources add:
  - Continuous sulfate (Allen/Teco method)
  - Hourly EC/OC (Sunset Lab NDIR method, fast OC protocol)
  - NGN-2 (wet) nephelometer and trace SO<sub>2</sub>, ozone
  - Wish-List items (NH<sub>3</sub>, HNO<sub>3</sub>, H<sup>+</sup>, woodsmoke UVC)

==> No continuous NO<sub>3</sub>... methods not robust, NO<sub>3</sub> not major issue

## Conclusions

Growing network of highly time-resolved aerosol data is very relevant to PM modeling community's needs

Balance of urban & (hi-elevation) rural sites important; most sites urban

Many new methods now available, more coming soon  
(but never soon enough...)

Methods used for wide deployment in non-research routine networks must be robust and relatively simple to operate (not always the case)

Data Quality: Trust, but always Verify (on a continuing basis) w/ collos  
+/- 20% “accuracy” is not all that easy to do/get, even for PM<sub>2.5</sub>

==> Future Needs:

Modify AIRNow infrastructure to accommodate real-time reporting and access to non-criteria pollutant data (at least on a private basis such as airnowtech)

EPA must do or sponsor more critical method evaluation studies on the scale of the recent continuous coarse-mass method study

ETV may not be a viable model for this purpose

Supersites did some of this, but it is an ongoing need

Not an inexpensive task... Is an ongoing task