Real-Time PM2.5 and Speciation Measurements: Needs, Practical Approaches, and Methods Issues

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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 pm2.5 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 3rd or 6th 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

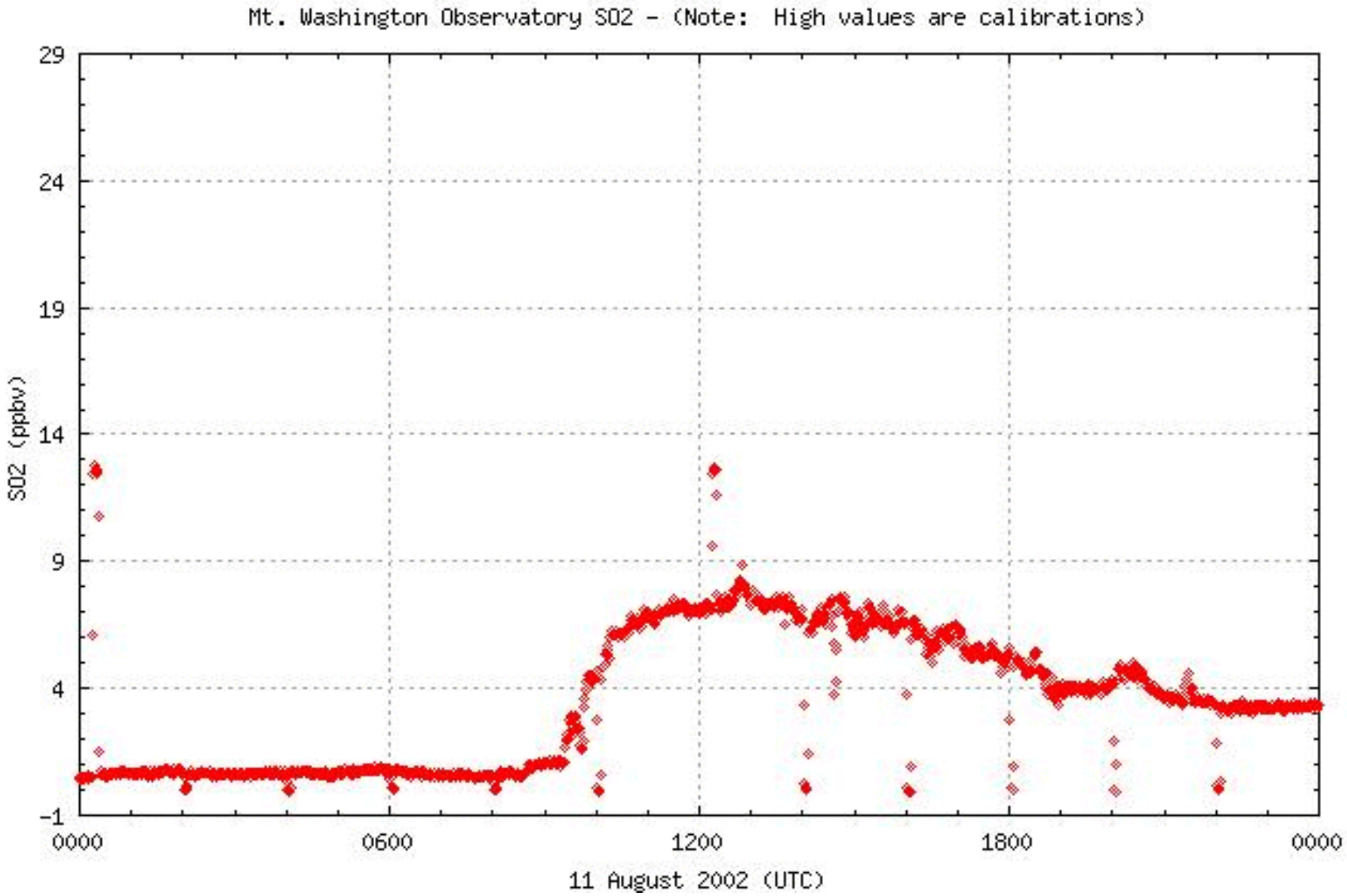
24-hour duration integrated samples often “smear” different regimes
    -- difficult to observe and understand sub-daily processes

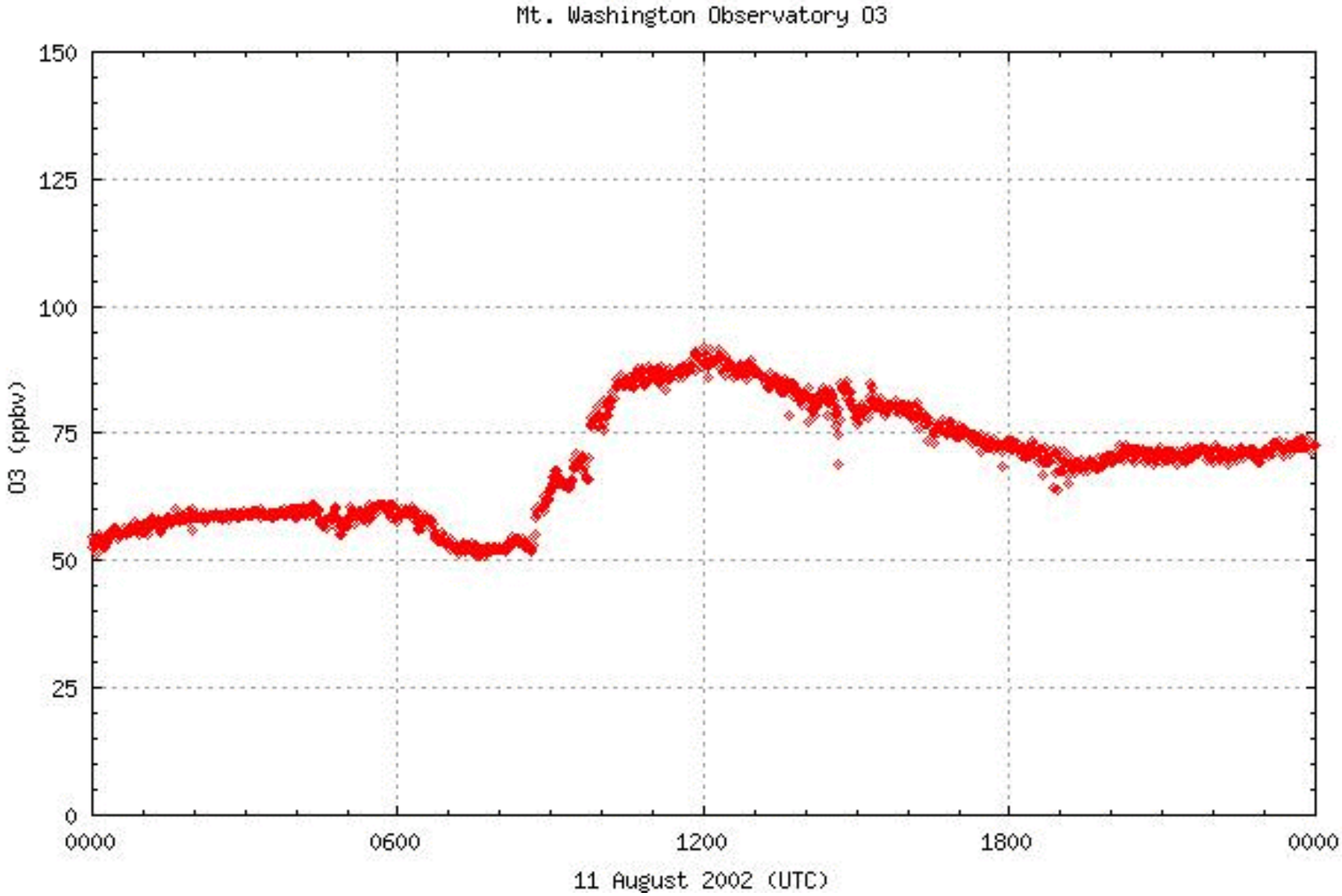
Sample durations of 3-hours or less provide **awesome** insight!
    Invaluable for aerosol model development and evaluation
    15-60 minute data can be used for “spatial scale” FDFT analysis

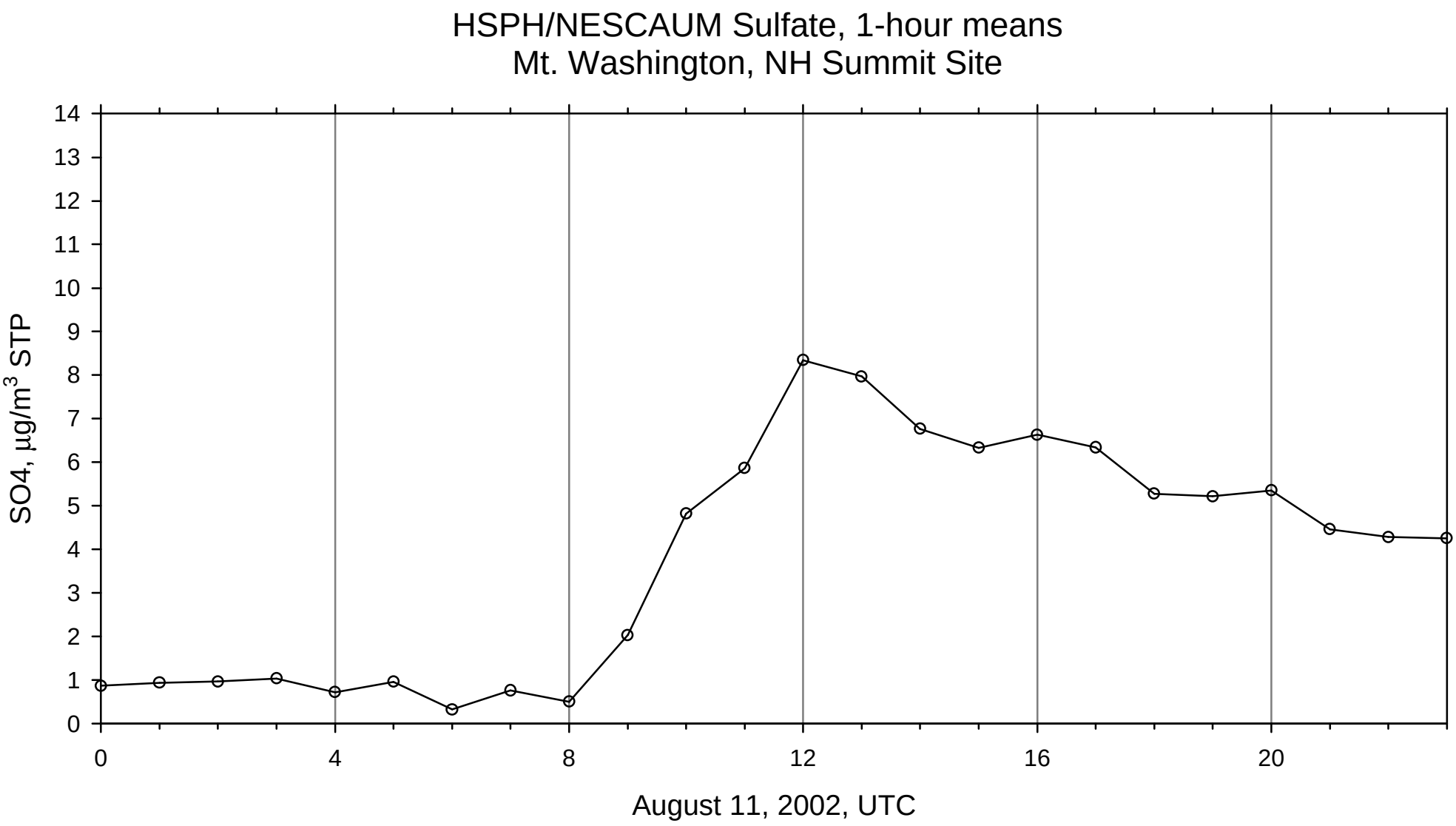
Forecast model use: real-time data are available as a “nowcast”
    Integrated samples: wait days to months

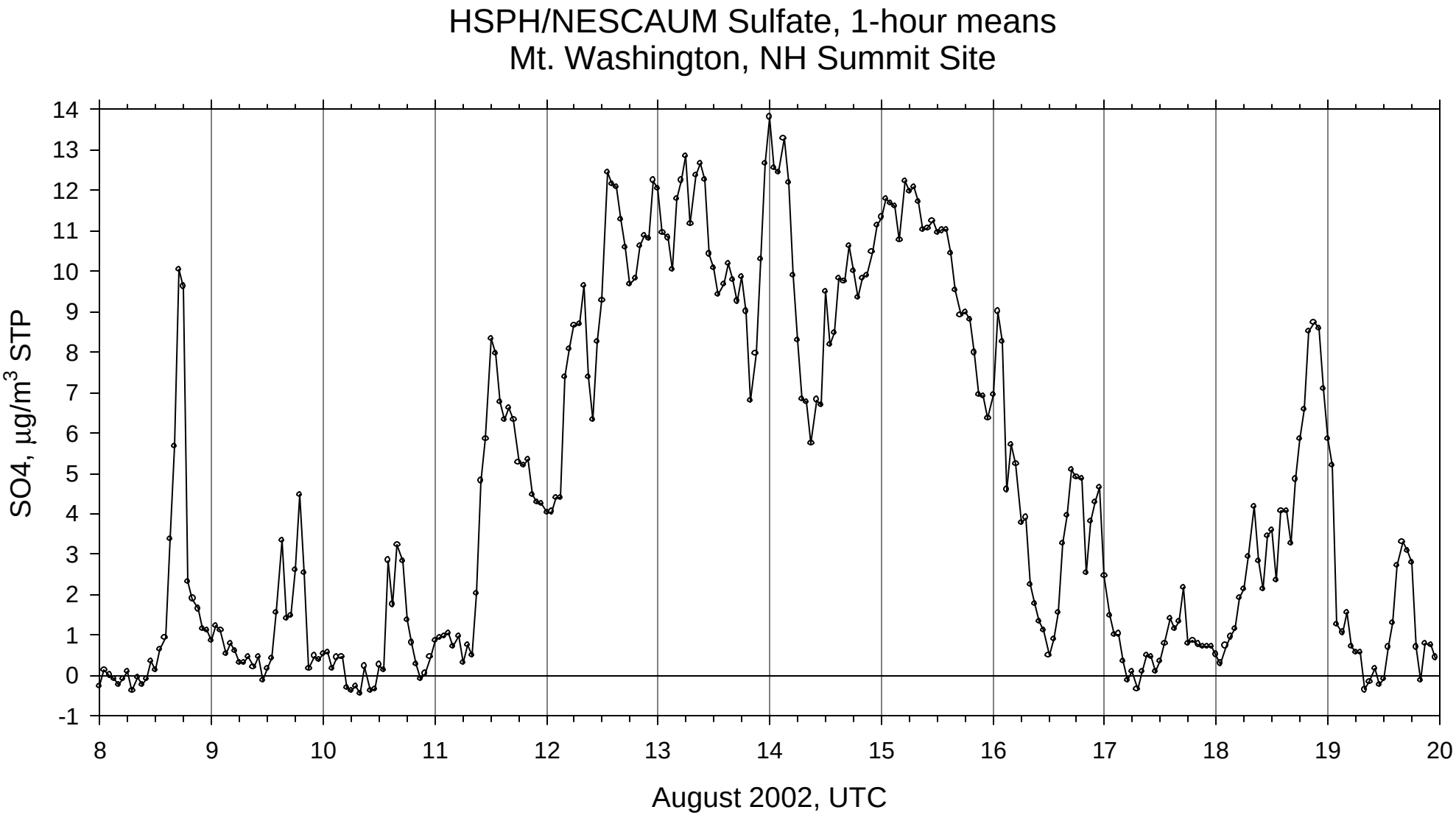
Examples of hourly S data demonstrate the additional information that can be obtained that is often lost with daily sampling: Example from Mt. Washington NH August 2002.

(SO2, O3 courtesy AIRMAP/UNH)


Mt. Washington Observatory SO2 - (Note: High values are calibrations)
SO2 (ppbv)
29
24
19
14
9
4
-1
0000
0600
1200
1800
0000
11 August 2002 (UTC)


Mt. Washington Observatory O3
150
125
100
75
50
25
0
O3 (ppbv)
0000
0600
1200
1800
0000
11 August 2002 (UTC)


HSPH/NESCAUM Sulfate, 1-hour means
Mt. Washington, NH Summit Site
SO4, µg/m3 STP
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
0
4
8
12
16
20
August 11, 2002, UTC

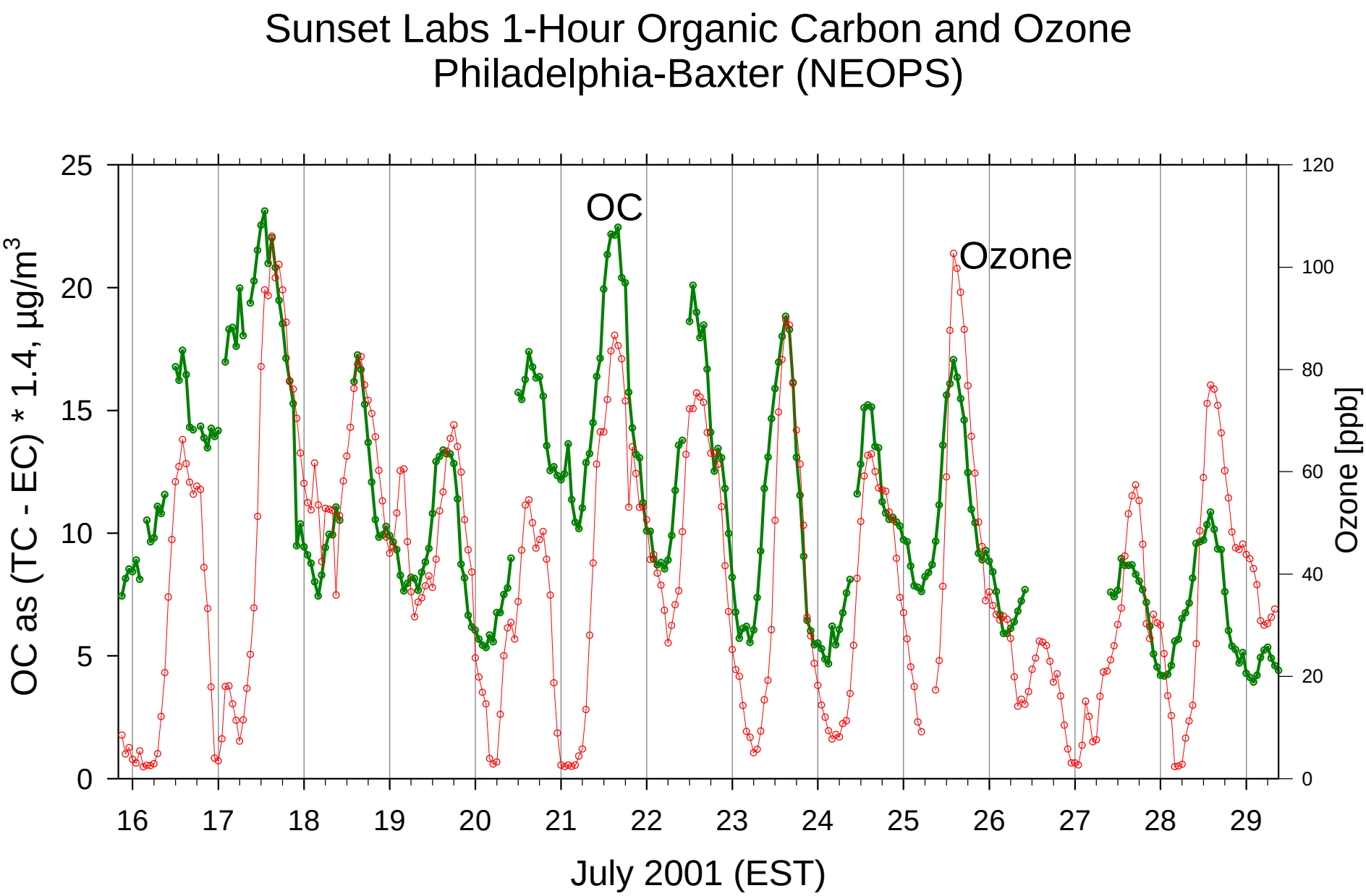

HSPH/NESCAUM Sulfate, 1-hour means
Mt. Washington, NH Summit Site
SO4, µg/m3 STP
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
8
9
10
11
12
13
14
15
16
17
18
19
20
August 2002, UTC

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

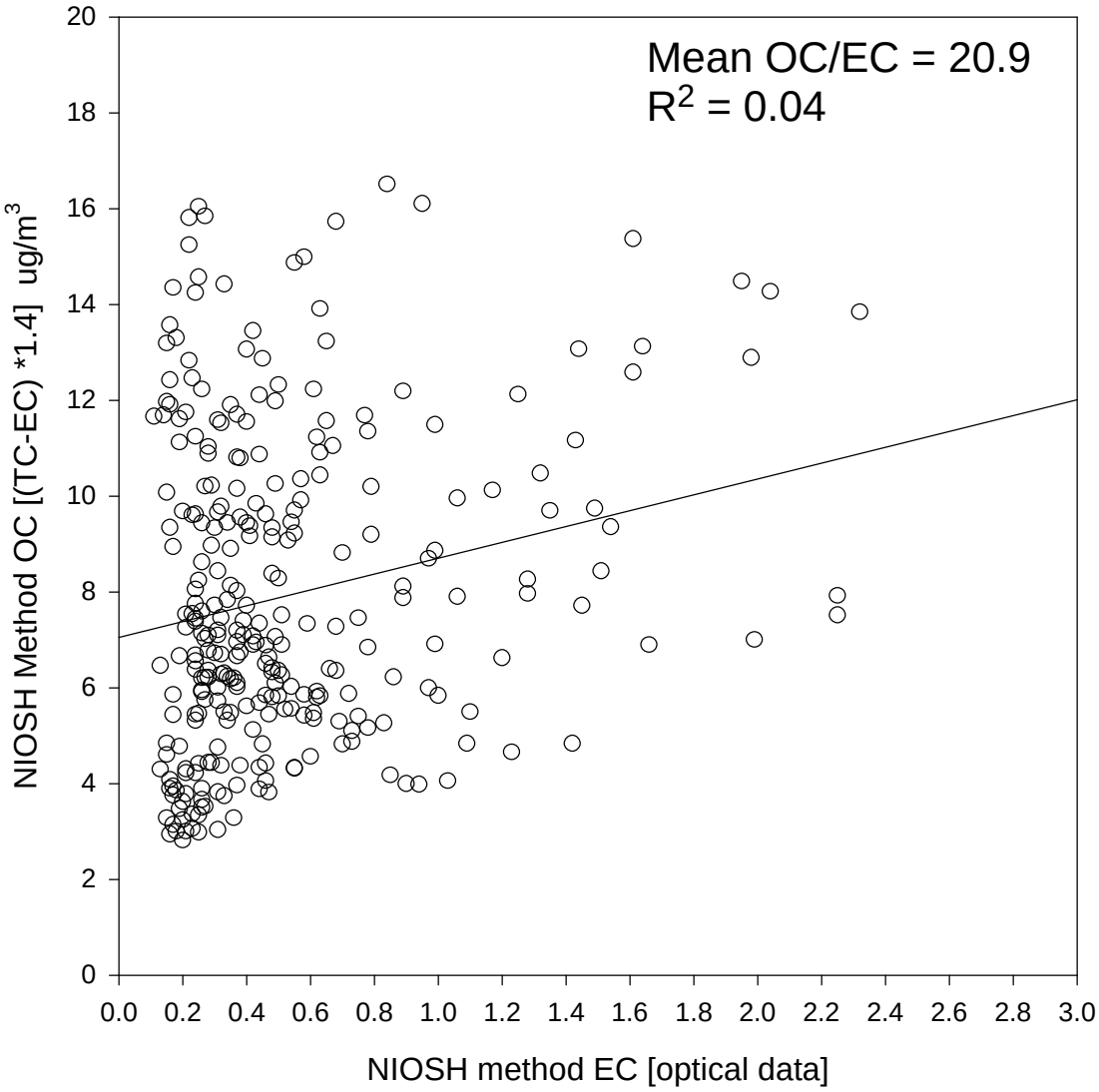
Philadelphia OC and Ozone peak at the same time of day every day during summer - indicative of a secondary regional OC component.

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

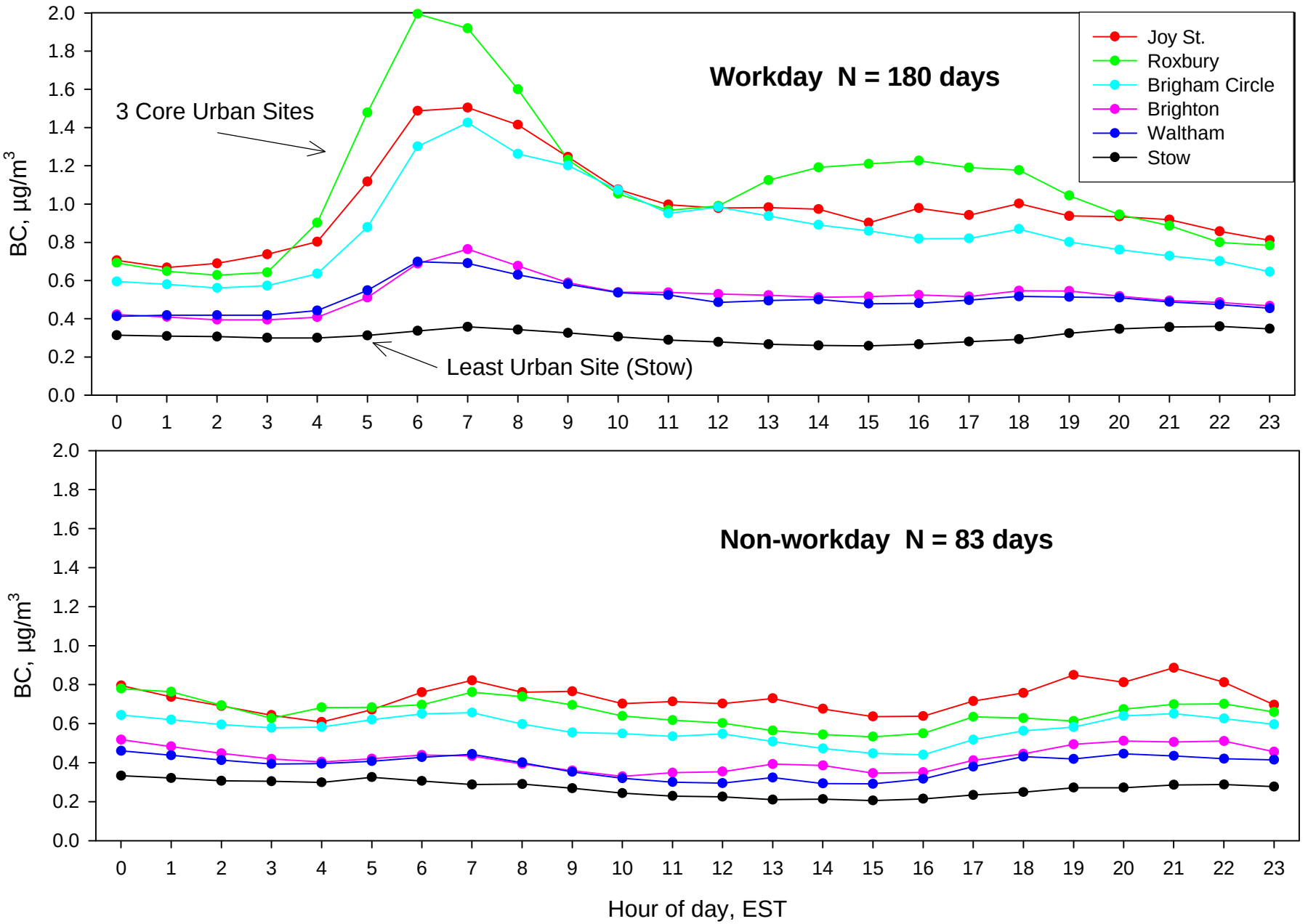
BC from multiple Boston area sites show traffic influence in urban areas but not outside of the urban area.


Sunset Labs 1-Hour Organic Carbon and Ozone
Philadelphia-Baxter (NEOPS)
OC
Ozone
OC as (TC - EC) * 1.4, µg/m3
Ozone [ppb]
July 2001 (EST)
0
5
10
15
20
25
0
20
40
60
80
100
120
16
17
18
19
20
21
22
23
24
25
26
27
28
29

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 volatization, Allen/Teco CASM, PILS
Nitrate: Hering/R&P flash volatization, PILS (Weber)
Ammonium: PILS, ARA (both work in progress)
Metals: SEAS (Ondov)

Gases relevant to aerosol modeling: SO2, NO-what, ozone, NH3, HNO3

Field validation of real-time aerosol methods: a critical accuracy need

Ongoing collocation with integrated filter samples <u>is essential</u>

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

The best continuous data correction is no correction

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The best continuous data correction is no correction

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®: 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!)

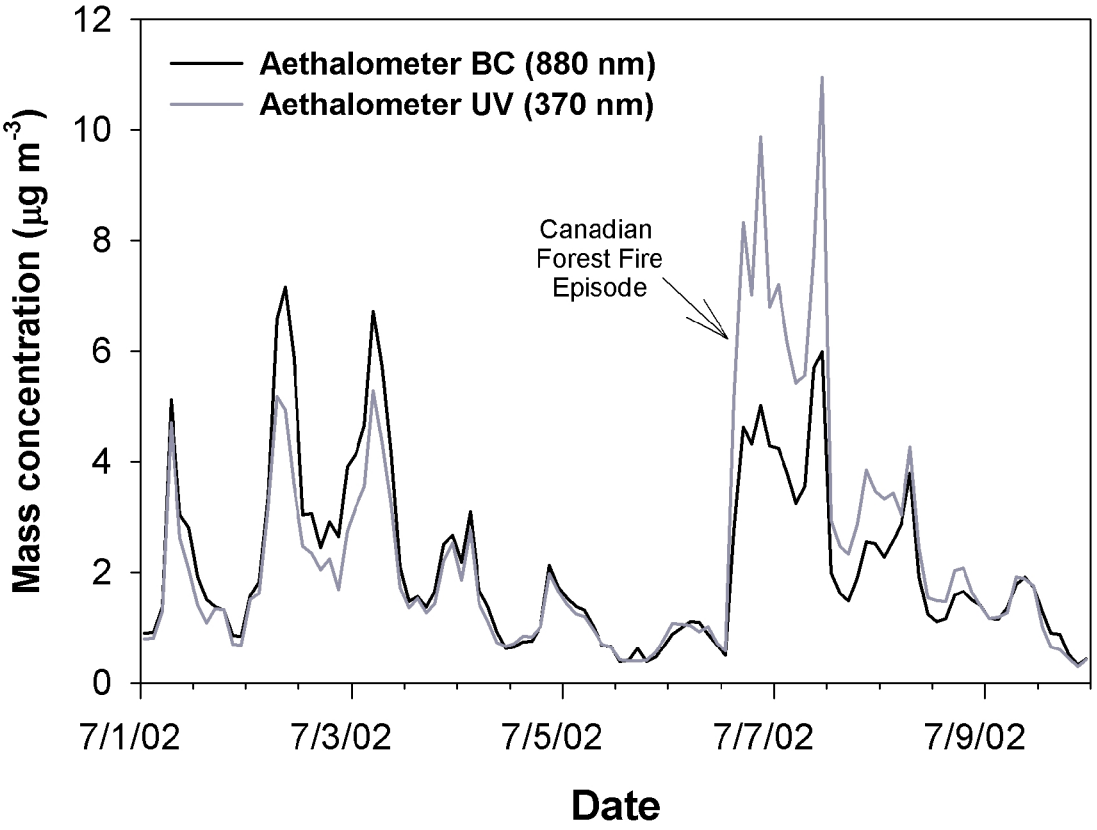
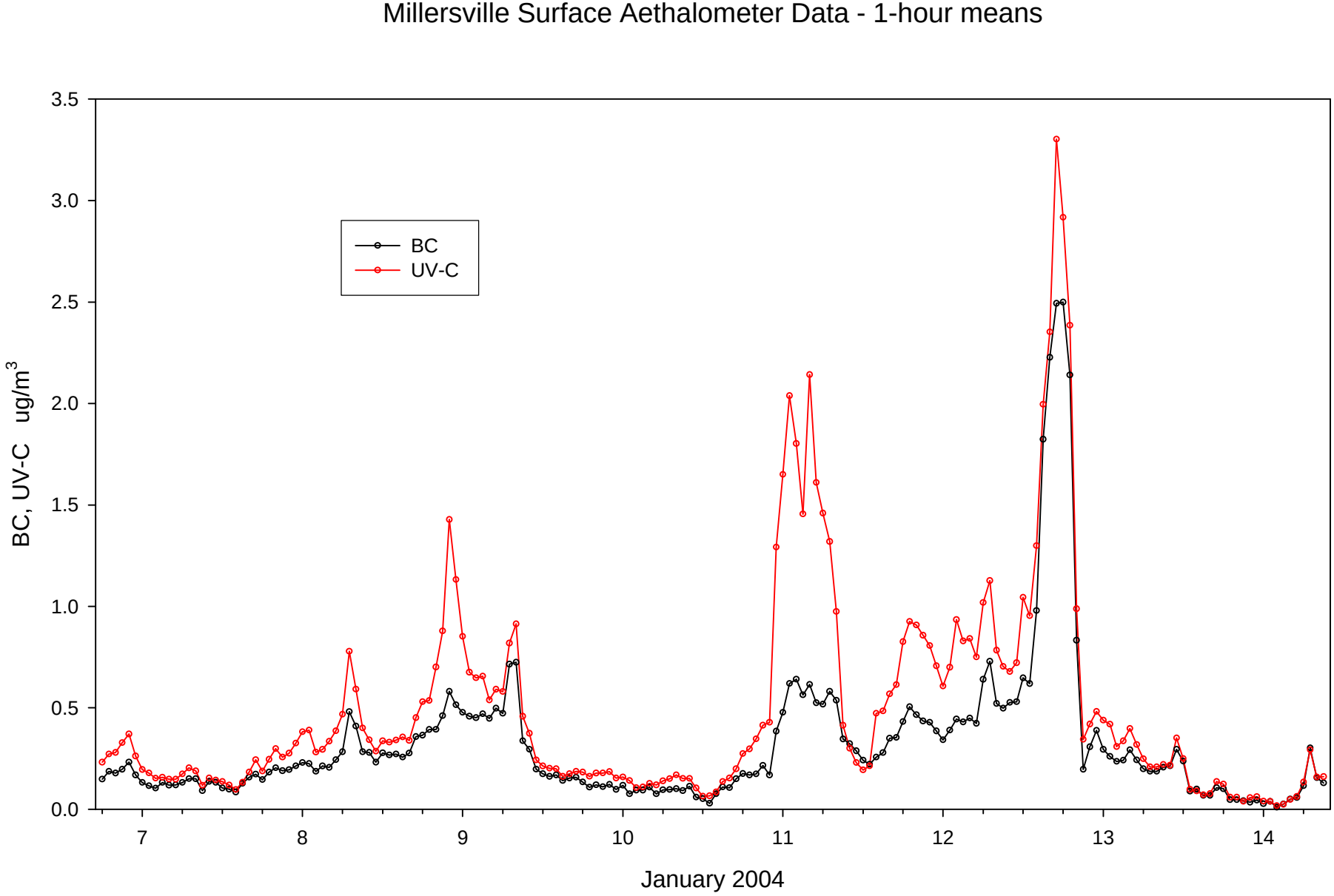


Figure 8. Black carbon measured using 880 nm wavelength and UV absorbing organic matters using 370 nm wavelength for Philadelphia, PA, during the Canadian forest fire episode.


Millersville Surface Aethalometer Data - 1-hour means
BC
UV-C
BC, UV-C ug/m3
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
7
8
9
10
11
12
13
14
January 2004

Sulfate:

Hering/R&P: flash volatization

collection by wet impaction on 10-min cycle

thermal SO2 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 SO2 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 volatization

- collection by wet impaction on 10-min cycle
- thermal NOx 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

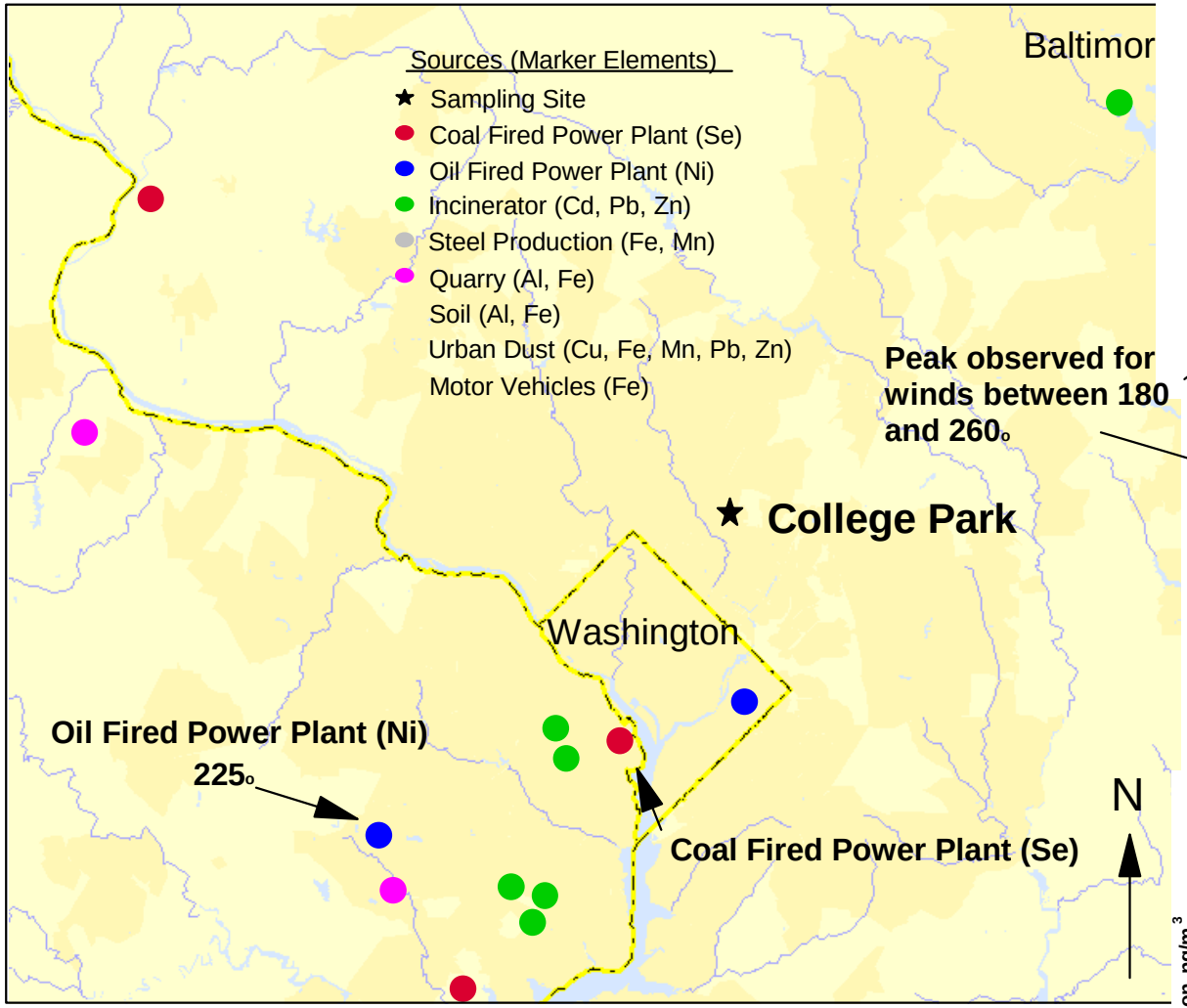
Trace Metals: a powerful approach; can isolate specific point sources

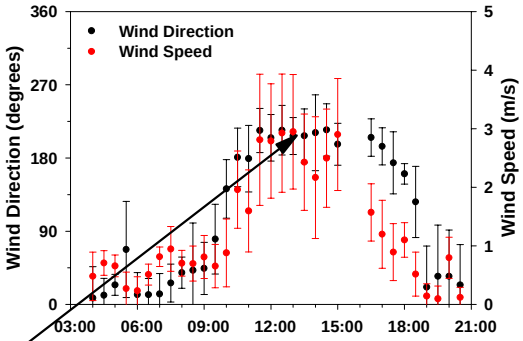
SEAS (Slurray Elemental Aerosol Sampler):
Ondov/UMD-CP; used in 3 supersites
Steam collection into vials; 10 to 30 minute intervals
Off-site selective event analysis (limited # of elements/run):
Graphite Furnace Atomic Absorption Spectroscopy (GFAAS)

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

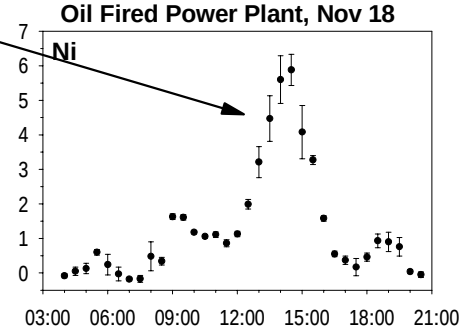
Neither method commercially available, but can be obtained from developers

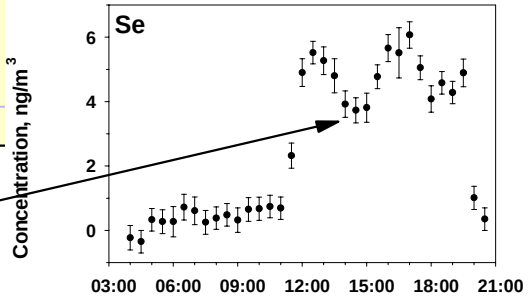
Resolution of Individual Sources with UMHFASS/GFAAZ





Peak observed for winds between 180 and 260o





***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, submittied to AS&T.

Relevant Real-time Gas Measurements for Aerosol Modeling Use

SO2, NO-what, ozone, NH3, HNO3, VOCs

Very limited or no NH3, HNO3 at this time
VOCs limited to PAMS (usually summer only)

Issues:

- Some trace SO2 methods have large NO interferences (Teco)
- NO2/NOxyz is still fuzzy
- OPSIS DOAS open path for “true NO2", SO2, NH3, some VOCs
- NH3 at ambient levels: DOAS, Pranalytica PAS, [ARA?]
- HNO3: 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

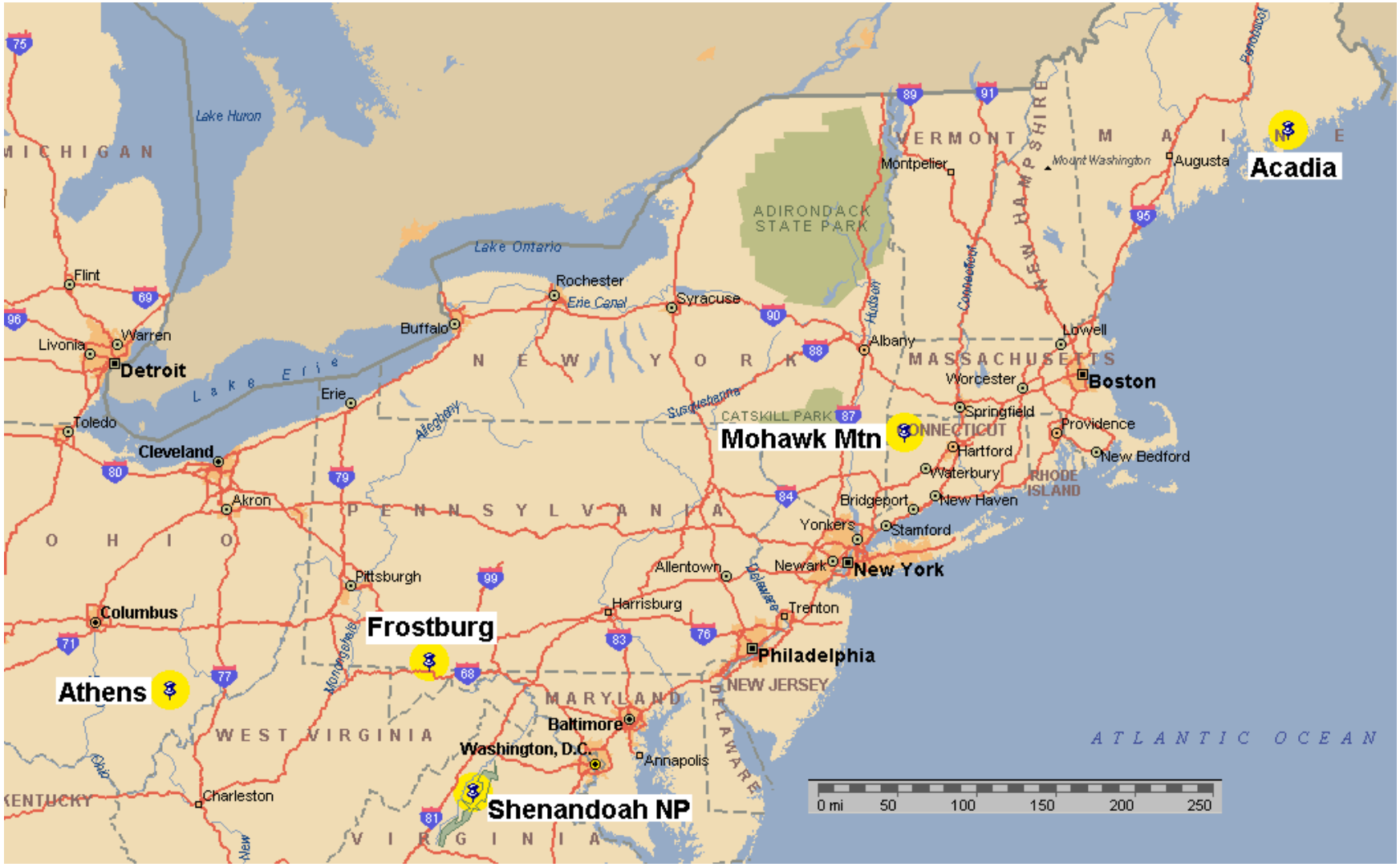
- A new long-term network of sites in the MANE-VU haze RPO
- Domain: Western MD to Acadia NP (Maine)

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

- 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] PM2.5
  - → Surface Met [wind, temp, RH, rain, ?]
  - → IMPROVE measurements for carbon, ions and PM2.5
  - → 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 SO2, ozone
  - → Wish-List items (NH3, HNO3, H+, woodsmoke UVC)

==> No continuous NO3... methods not robust, NO3 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 PM2.5

==> 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