RESOLUTION OF CONTRIBUTIONS OF PRIMARY PARTICLE PLUMES FROM INDIVIDUAL POWER PLANTS WITH SEAS

Baltimore Supersite: Clifton Park

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Motivation: Aerosol Particles Kill/Impair health

Aerosol: Particles or Droplets subspended in the atmosphere

Particles smaller than 10 µm are respirable, contain accute toxins and carcinogens (largely from combustion sources)

EPA believes these responsible for

>30,000 premature deaths/year

>$100 M/yr in health care/lost productivity in Maryland alone

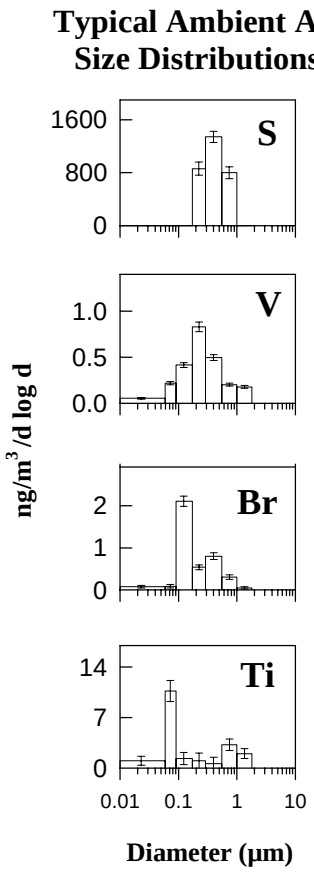
Accute Toxicity linked to

immuno inflamatory (cytokine) response

Affect cardio-pulmonary regulation

(coagulation in pulomonary capilaries; lung tissue permeability

Important Aerosol Components Reside in Particles as Small as 0.05 µm



Source

Secondary (Regional) Sulfate

Fuel Oil Combustion

Motor Vehicles and Incinerators

Paint Manufacture and Spraying

Rationale

Elemental composition measurements of PM needed to

- Apportion source contributions
- Understand Health Effects
- Ambient compliance monitoring
- Stack emissions monitoring

Current Methods

- 12 – 24 hour sampling on filters
- Temporal resolution insufficient for statistical (e.g., factor analysis),
  - long with respect to changes in wind direction, mixing height, source emission fluctuations

Design Characteristics:
UM High-Frequency Aerosol Slurry Sampler

- Develop low-pressure drop, practical device
- Quantitatively Collect ambient PM 0.05 to 1 µm
- 30-minute or less time resolution at AMBIENT concentrations
- Automated operation
- Provide samples in slurry form, 0.1 mL/min
  for analysis by multiplicity of widely available analytical instruments/methods,
  - GFAAZ, ICPMS, electrochem - metals
  - LC-MS for polar organic compounds
  - Biological tests (cytokine, mutagenicity assays, animal tests)
- Convenient collection in Fraction Collector - no difficult interfacing

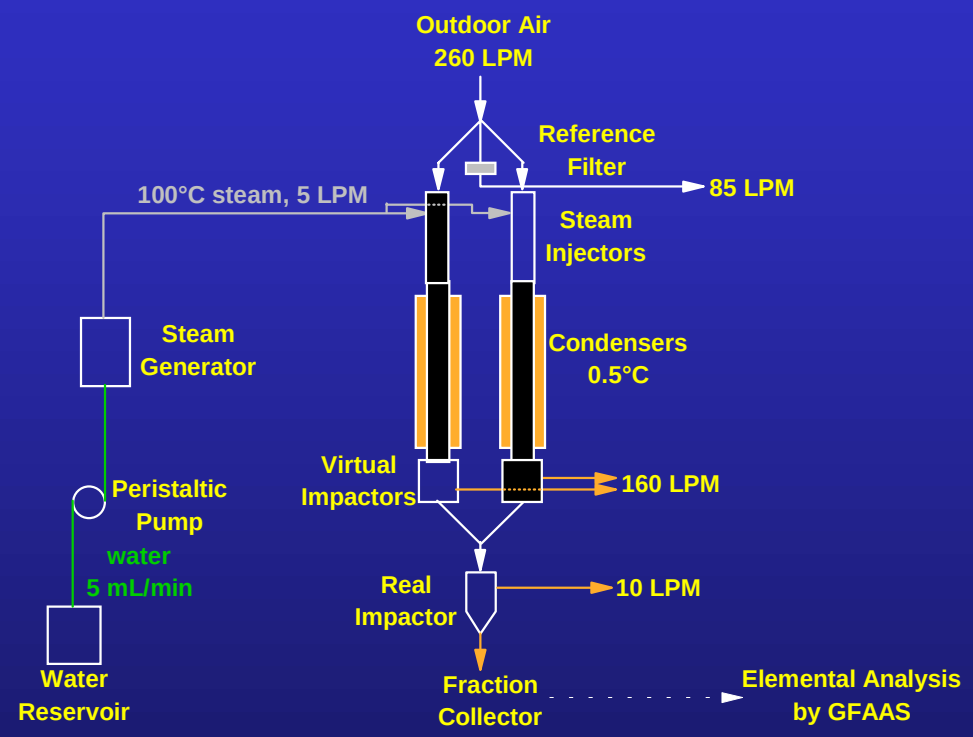
Approach: Condensational Growth followed by Dynamic Concentration and Separation by Inertial Impaction

Steam Injection
- saturates Air w/water

Condensors,
- create SR >1.25
- 0.03 µm particles grow to 3 µm in <30 ms

Dynamic Concentrator
- removes 85% of the air
- modest 12" Hg dP

Real Impactor
- collects droplets



Resulting slurry delivered to Fraction Collector

All-glass & plastic, low blank system

Kidwell and Ondov, AS&T-1, AS&T-2 accepted

Advantages of Growing Particles Before Separation

Eliminate large pressure drops

Collection of 0.05 µm particles by impaction at 170 LPM:

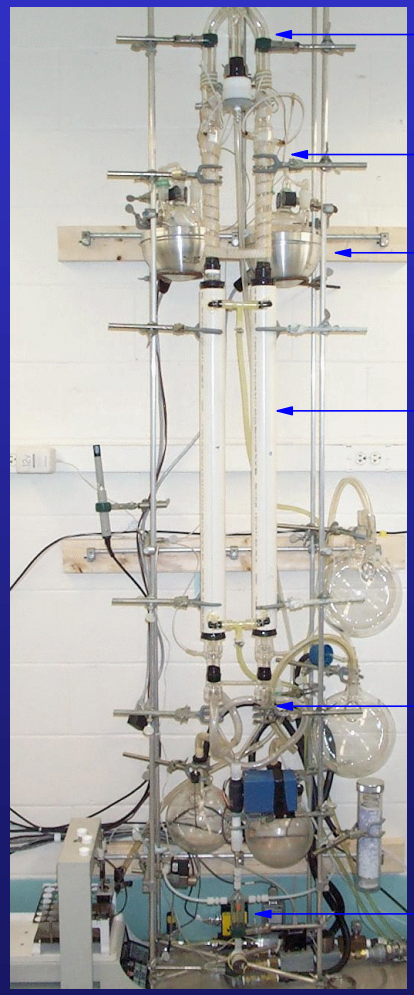
- 1600 jets
- 0.01 cm jet diameter
- 9" Hg pressure drop

Collection of 3 µm particles by impaction at 170 LPM:

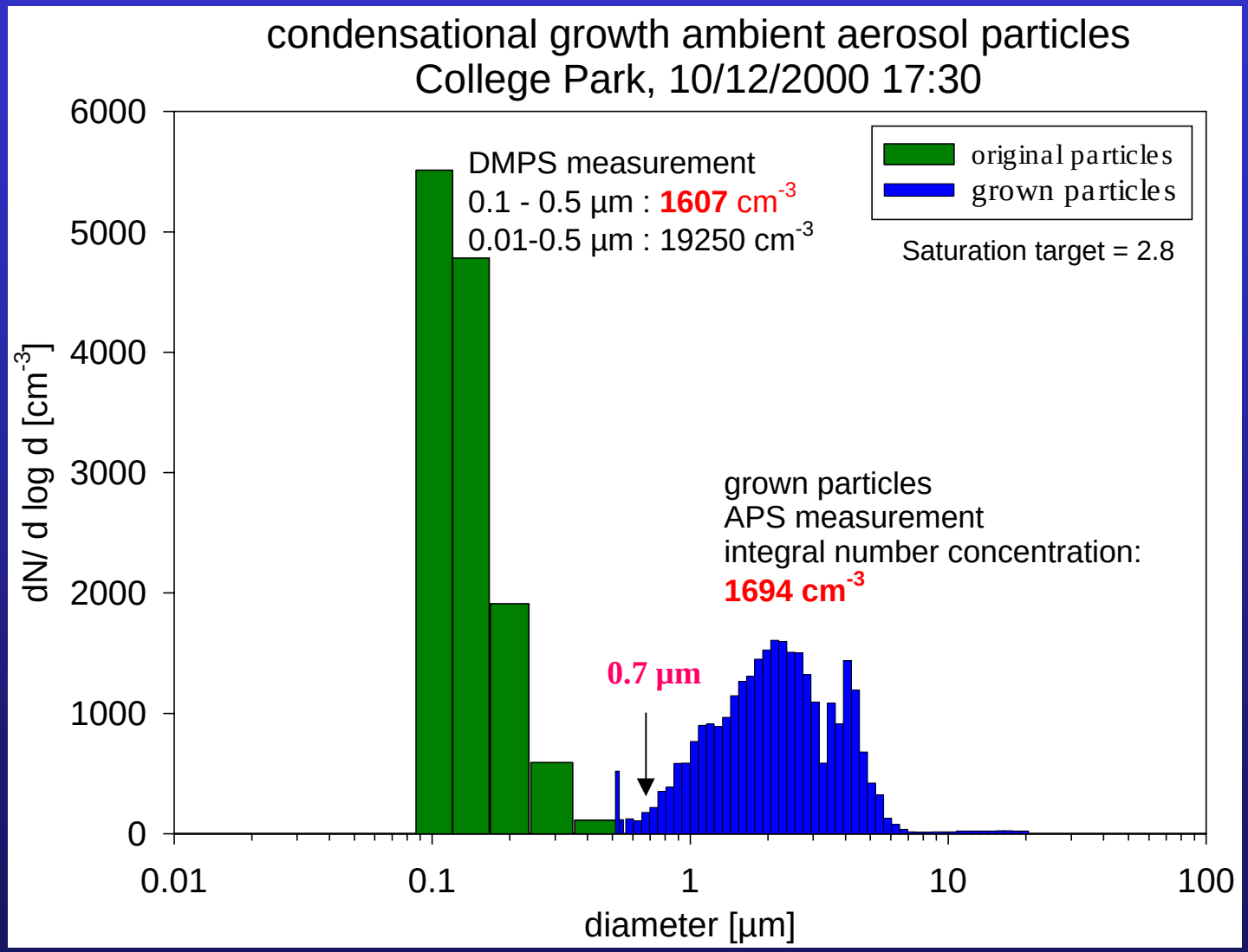
- 1 jet
- 1 cm jet diameter
- 0.3" Hg pressure drop

Losses are roughly independent of initial particle size because condensational growth favors a uniform droplet size

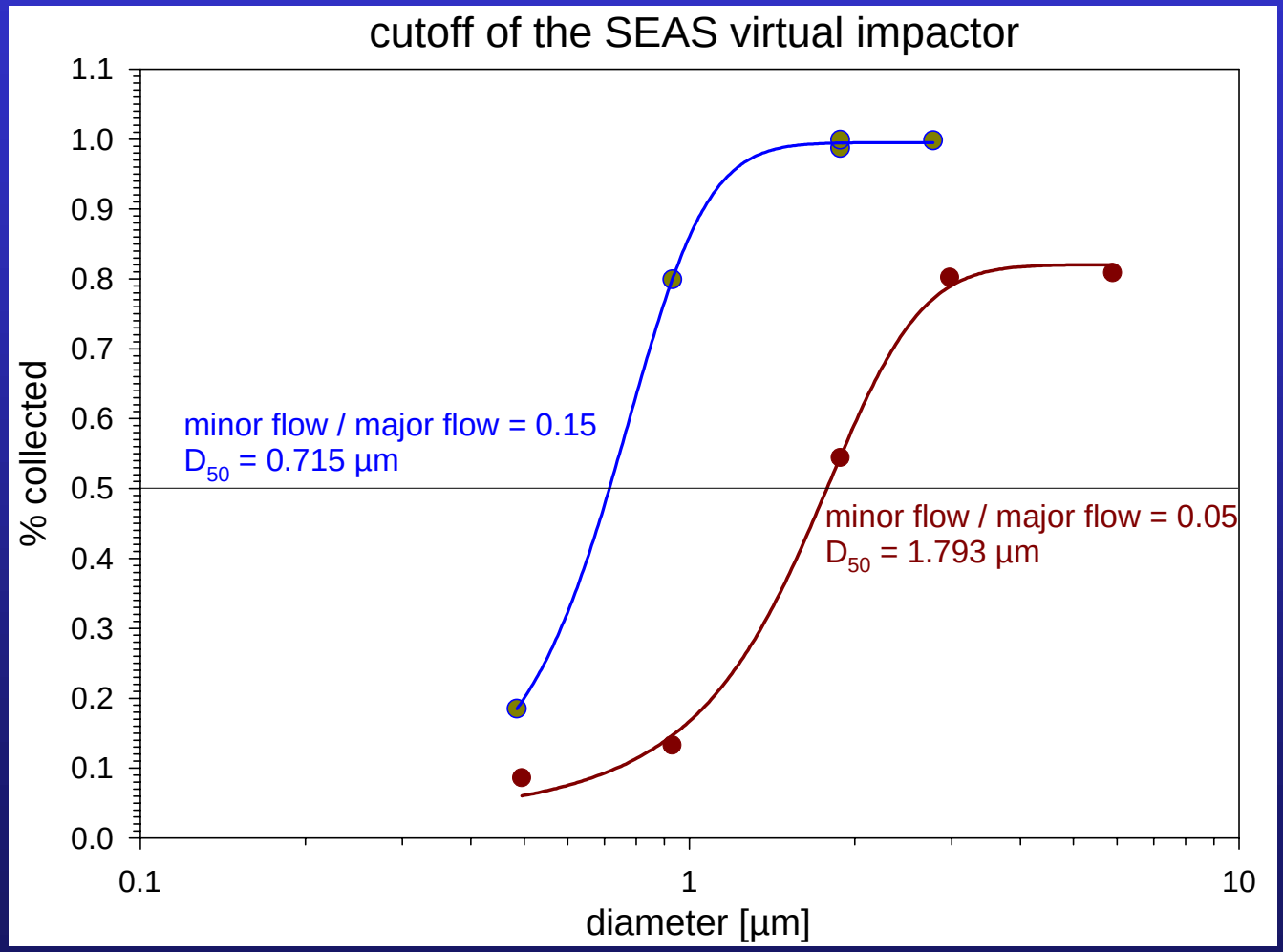
Our Original Prototype HFAS



Particles (>80 nm) In = # Droplets Out!



Virtual Impactor Captures >95% of the Droplets



Sample Collection, College Park, MD

- Inlet located 2 m above ground level on east side of Chemistry building near Lot T
- 30-minute samples collected 5 am - 7 pm into pre-cleaned glass vials
- Blanks collected each day before and after sampling
- Size distribution (0.5 - 8 µm) measured with forward scattering laser spectrometer
- Temperature and relative humidity measured at inlet
- Wind speed and direction measured on roof of Computer and Space Sciences building
- Vials weighed before and after sample collection to determine slurry volume
- Air volume measured with mass flow meters

Chemical Analysis: Graphite Furnace AA

Elements were grouped according to atomization temperatures
Matrix modifier: 5 µg Pd + 3 µg $Mg(NO_3)_2$

- High Temperature Elements:
  As, Cu, Cr, Mn, Ni

- 50 µL injection
- Dry: 30 s at 130°C
- Char: 20 s at 1100°C
- Atomize: 5 s at 2300°C
- Cleanout: 3 s at 2450°C

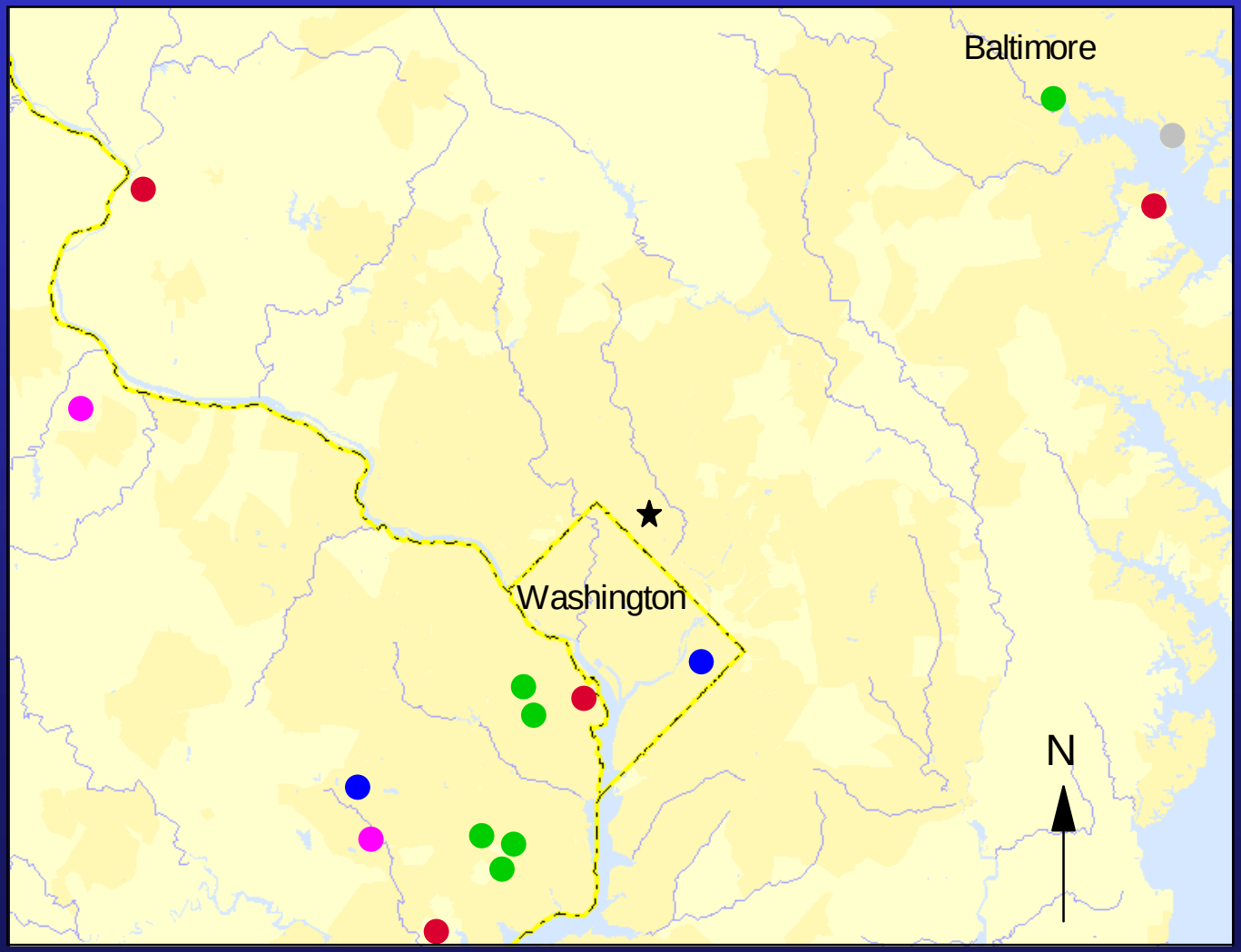
- Low Temperature Elements:
  Cd, Pb, Sb, Se

- 50 µL injection
- Dry: 30 s at 130°C
- Char: 20 s at 500°C
- Atomize: 5 s at 1900°C
- Cleanout: 3 s at 2450°C

- High Concentration Elements:
  Al, Fe, Zn

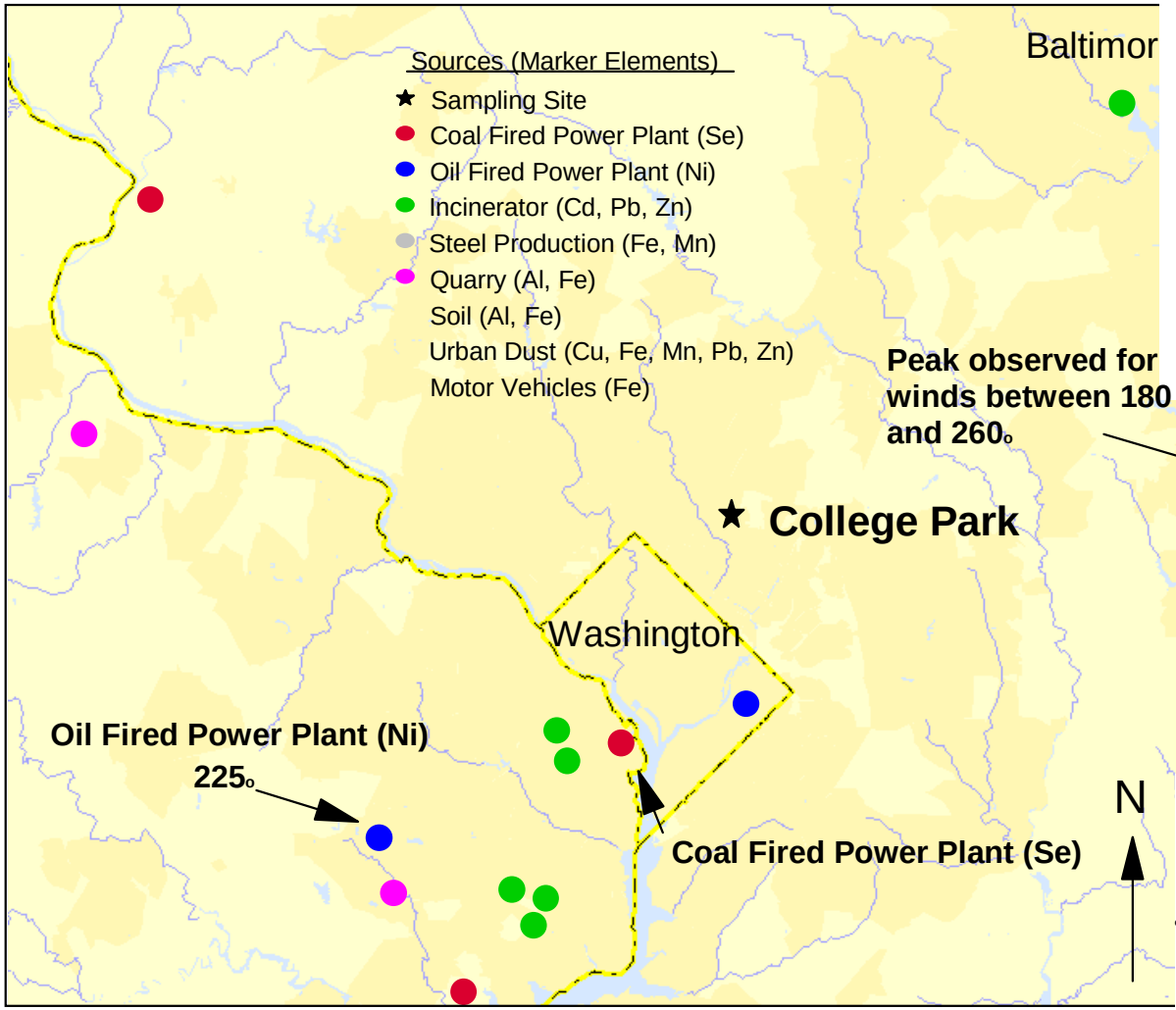
- 20 µL injection
- Dry: 30 s at 130°C
- Char: 20 s at 800°C
- Atomize: 7 s at 2300°C
- Cleanout: 3 s at 2450°C

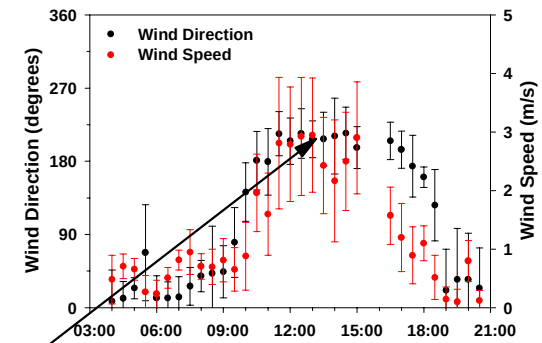
Major Sources in Washington Metropolitan Area

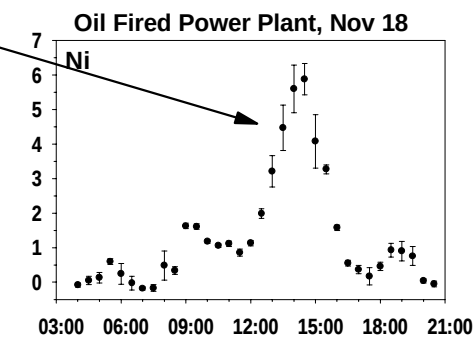


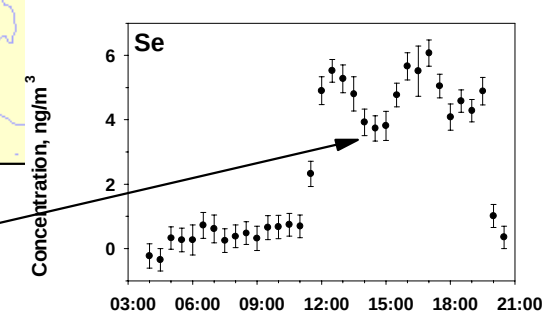
- Coal Fired Power Plant
- Oil Fired Power Plant
- Incinerator
- Steel Production
- Quarry
- Sampling Site

Resolution of Individual Sources with UMHFASS/GFAAZ







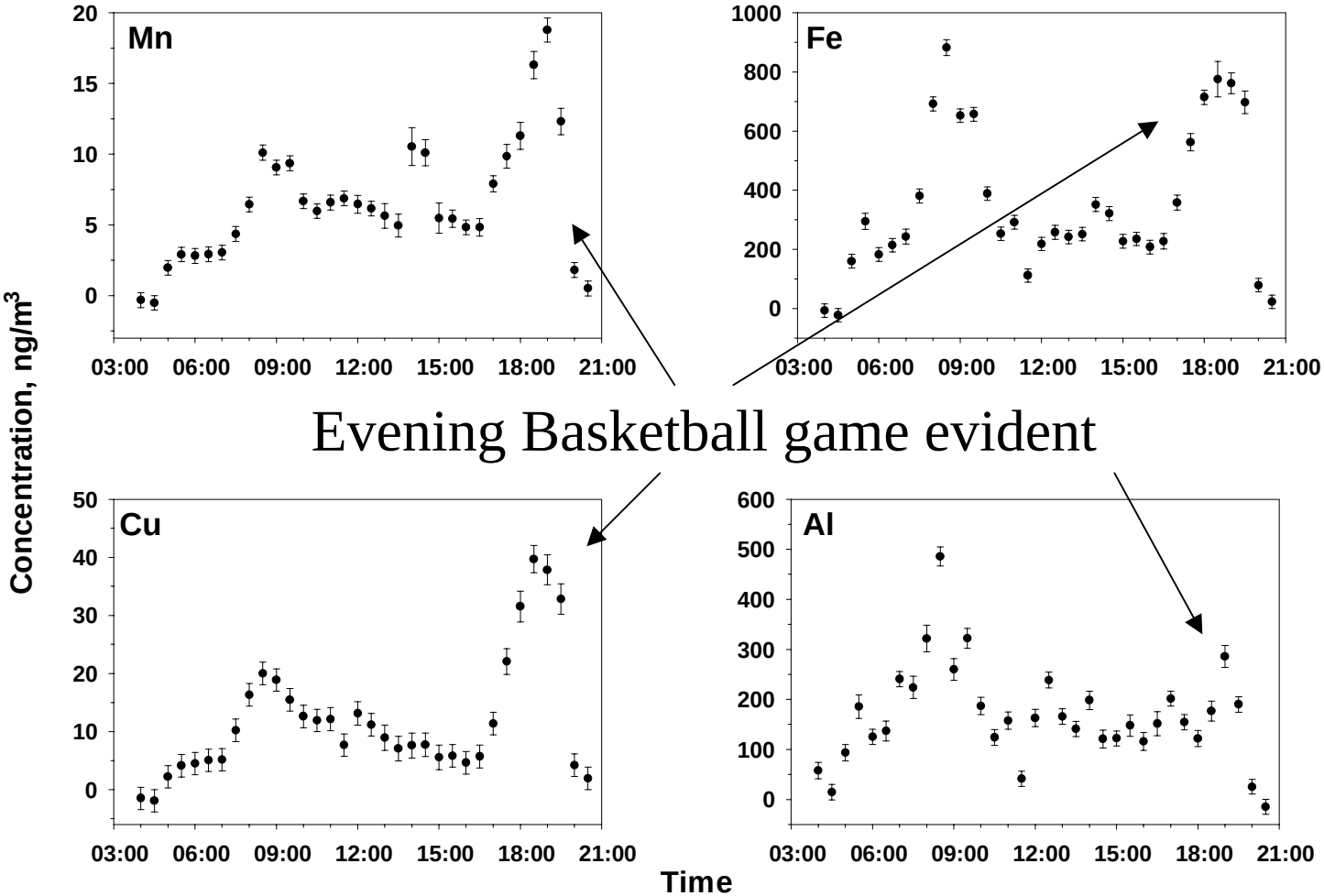


***Data suggest that Oil-fired unit came on when coal-fired boiler "tripped"**

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

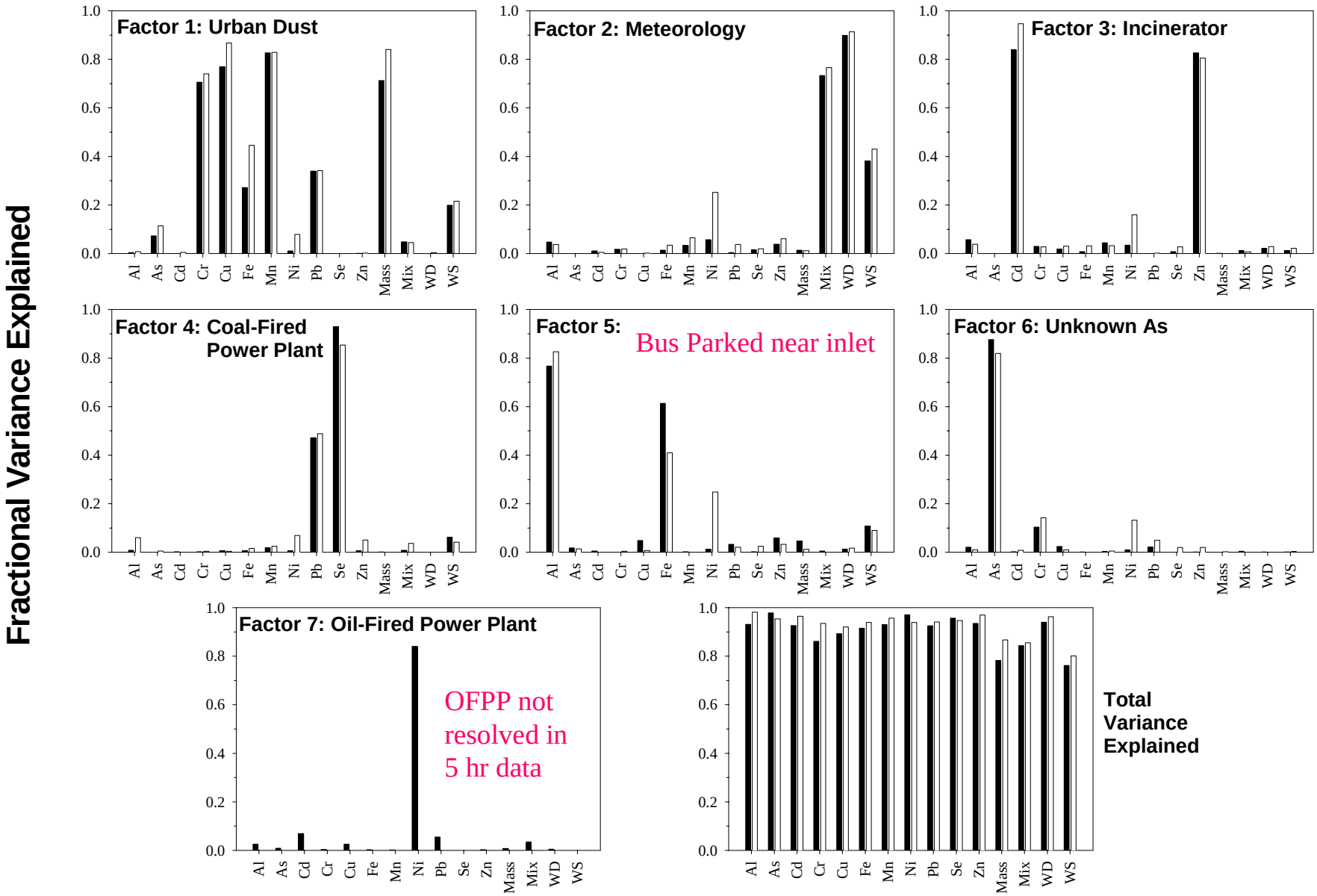
Kidwell and Ondov, University of Maryland, submittied to AS&T.

Influence of Motor Vehicle Traffic, Nov 18



Evening Basketball game evident

Standard Factor Analysis: Readily Resolves Sources



Sources are Correctly Resolved by Wind Direction Using Positive Matrix Factorization (advanced factor analysis method)

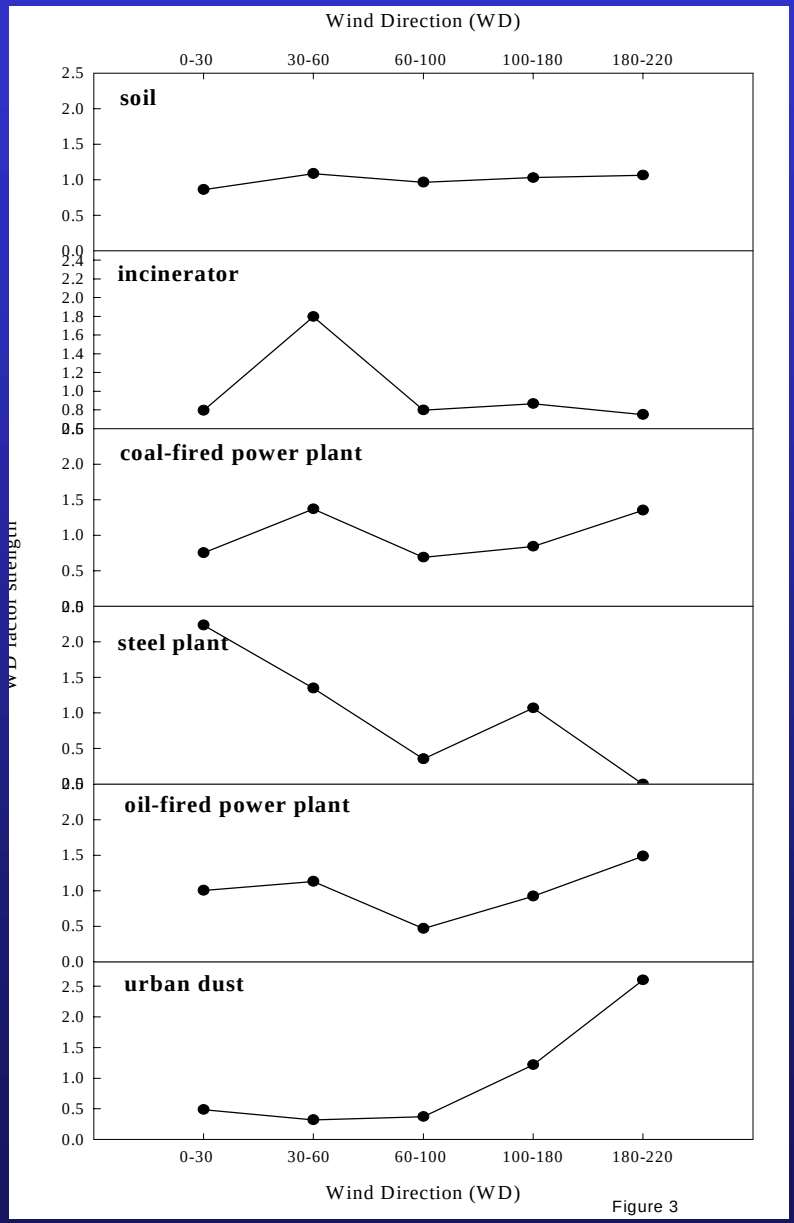
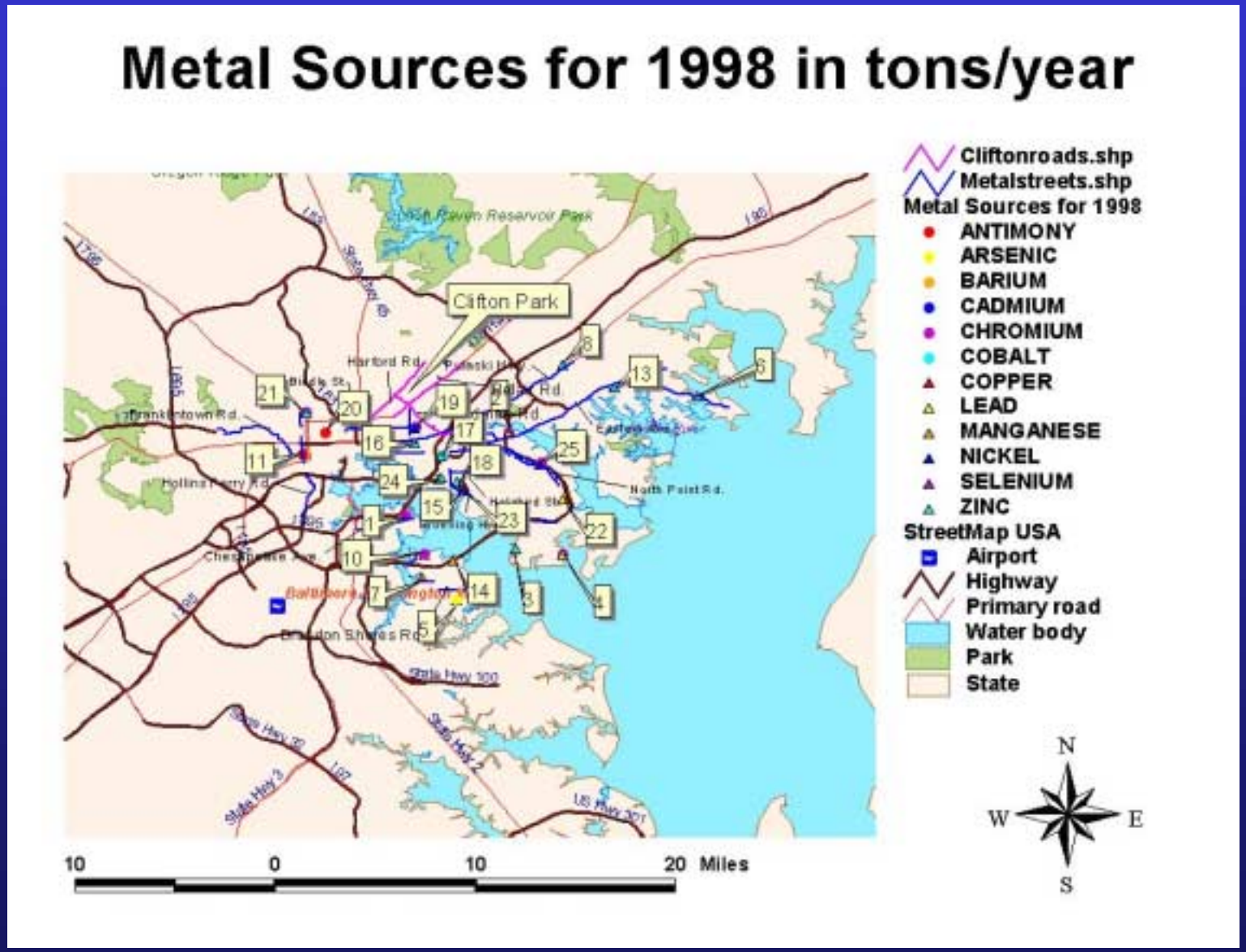


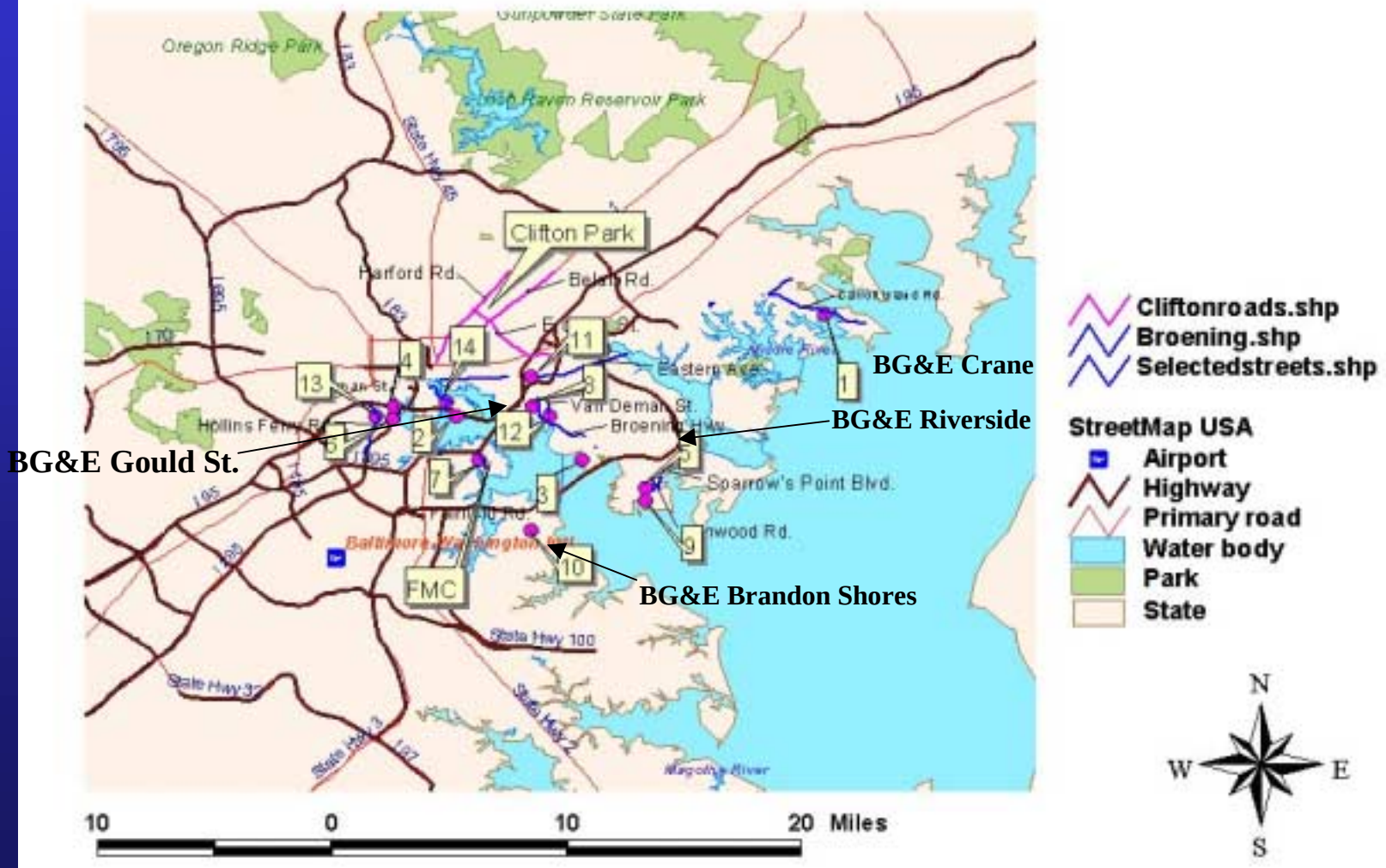
Figure 3

Phil Hopke's Group, Clarkson Unviersity

Major Sources in the Baltimore, MD Area



PM10, SO2, and VOC Emission Sources (tons/year)



Baltimore Supersite Data for Se Show Coal Boiler Plume

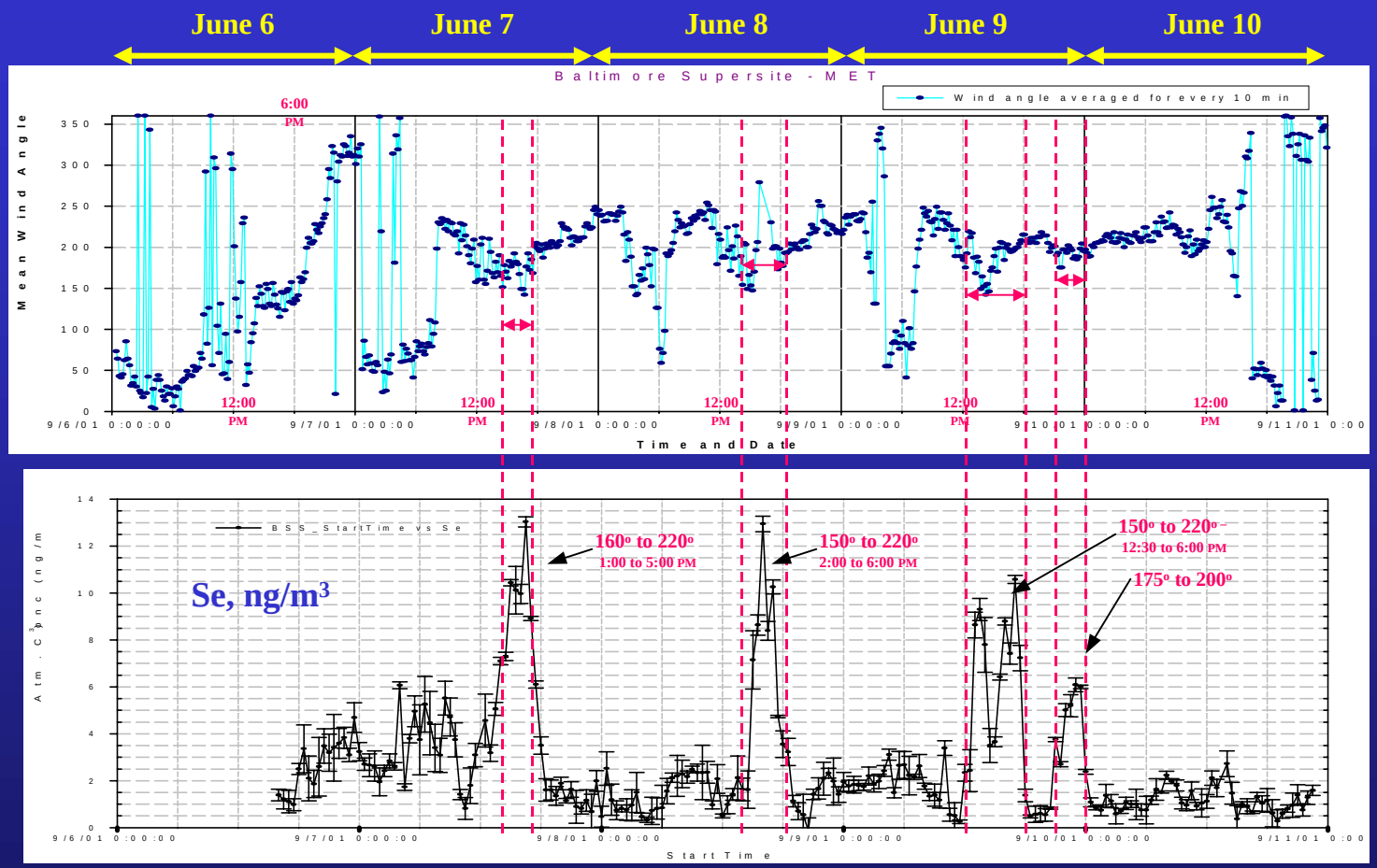
(each figure shows approx. 4 days of 30 min measurements)

- Elevated concentrations are observed at WDs 150° to 220° and 175 to 200°, but not at other directions
- Peak Concs. 12x background; 6X 24-hr avg

Baltimore Supersite Data for Se Show Coal Boiler Plume

(each figure shows approx. 4 days of 30 min measurements)

Wind Direction



•**Plant location: 150° to 220°**

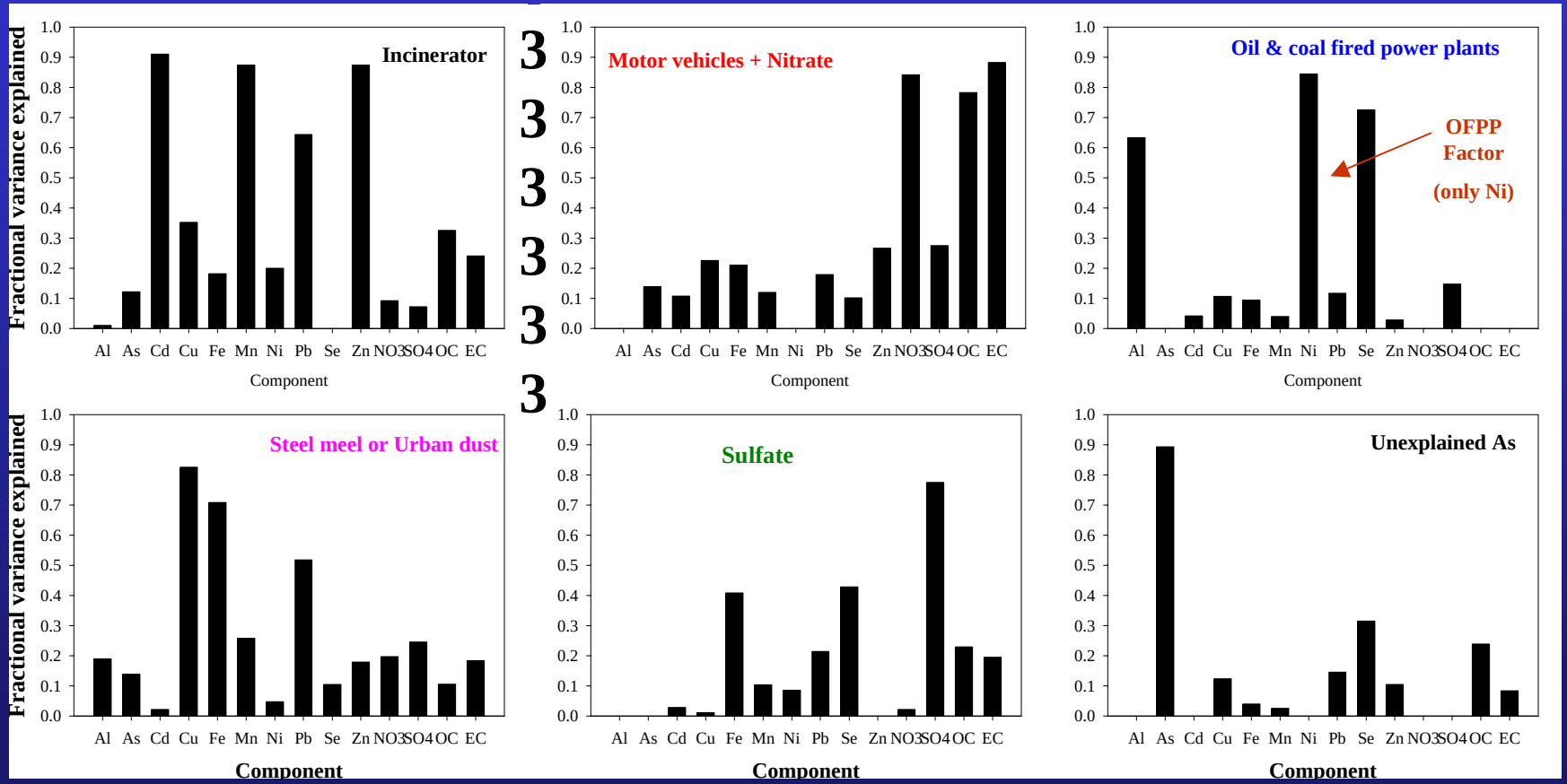
Principle Component Analysis

(Baltimore Clifton Park data)

- Large fractions of variance explained by 7 factors
- Coal- and Oil-fired power plants resolved
- Inspection of temporal profiles of markers & WD gives location
- Unknown As source consistent with impactor size distribution data and CMB results

Principal Component Analysis Results

Large fractions of the variance are explained for marker species



Baltimore Supersite Data for Se/Ni Show Coal/Oil Boiler Plumes

(each figure shows approx. 4 days of 30 min measurements)

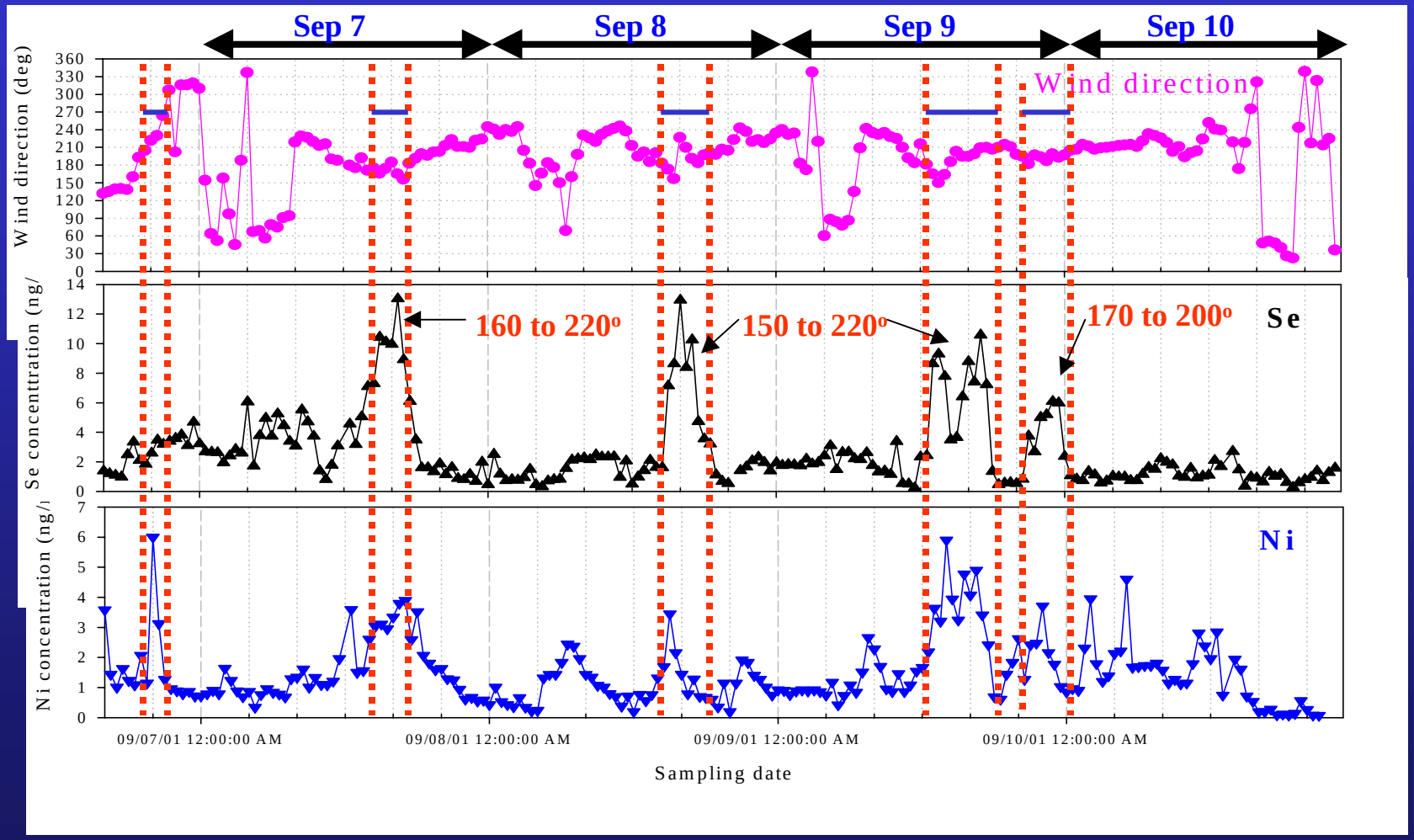
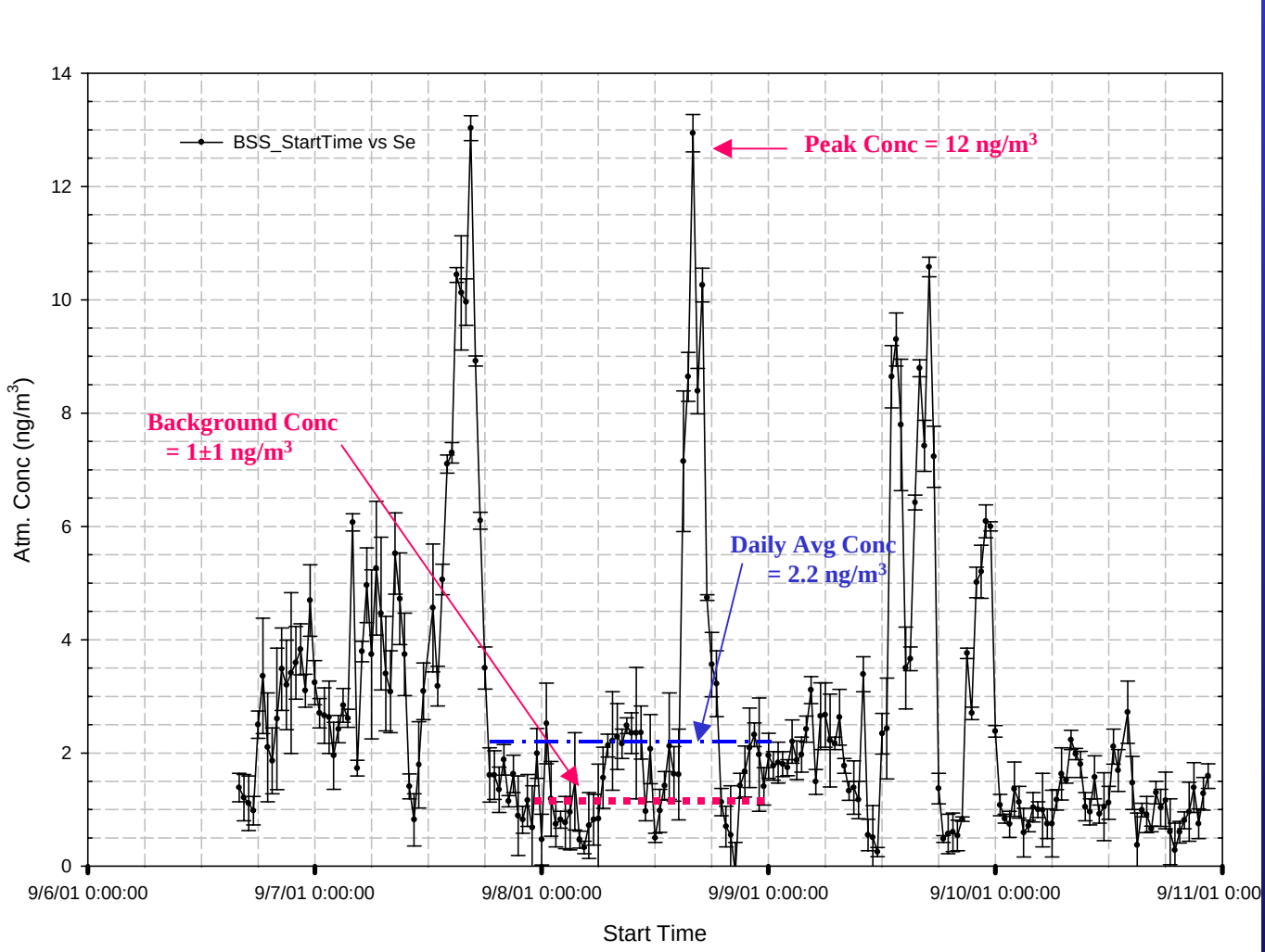
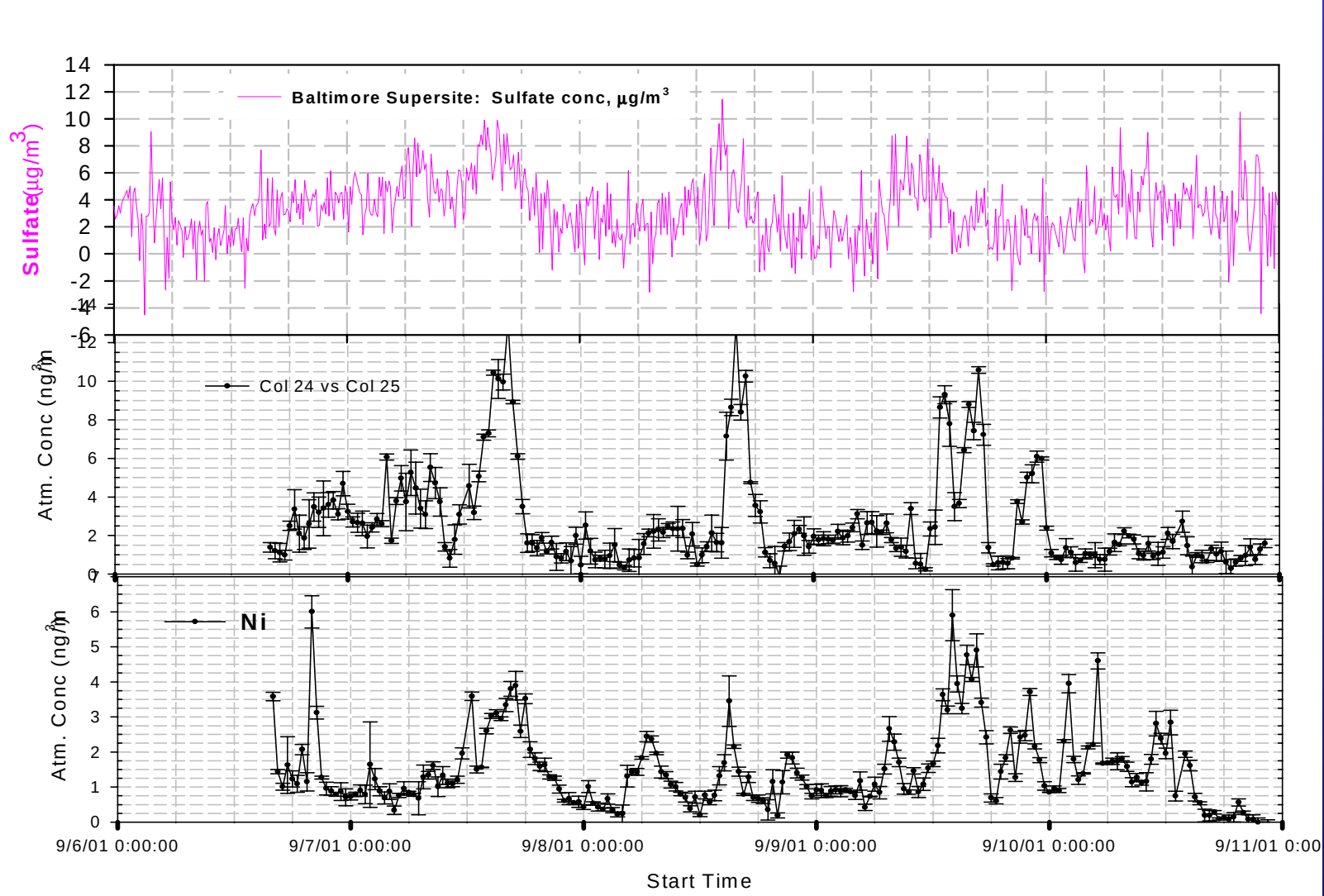


Figure 1. Temporal trends of Se and Ni with wind direction

Peak Concentrations are Typically 6x Greater than 24-hr Avg. Conc.; and 12x the "Background.

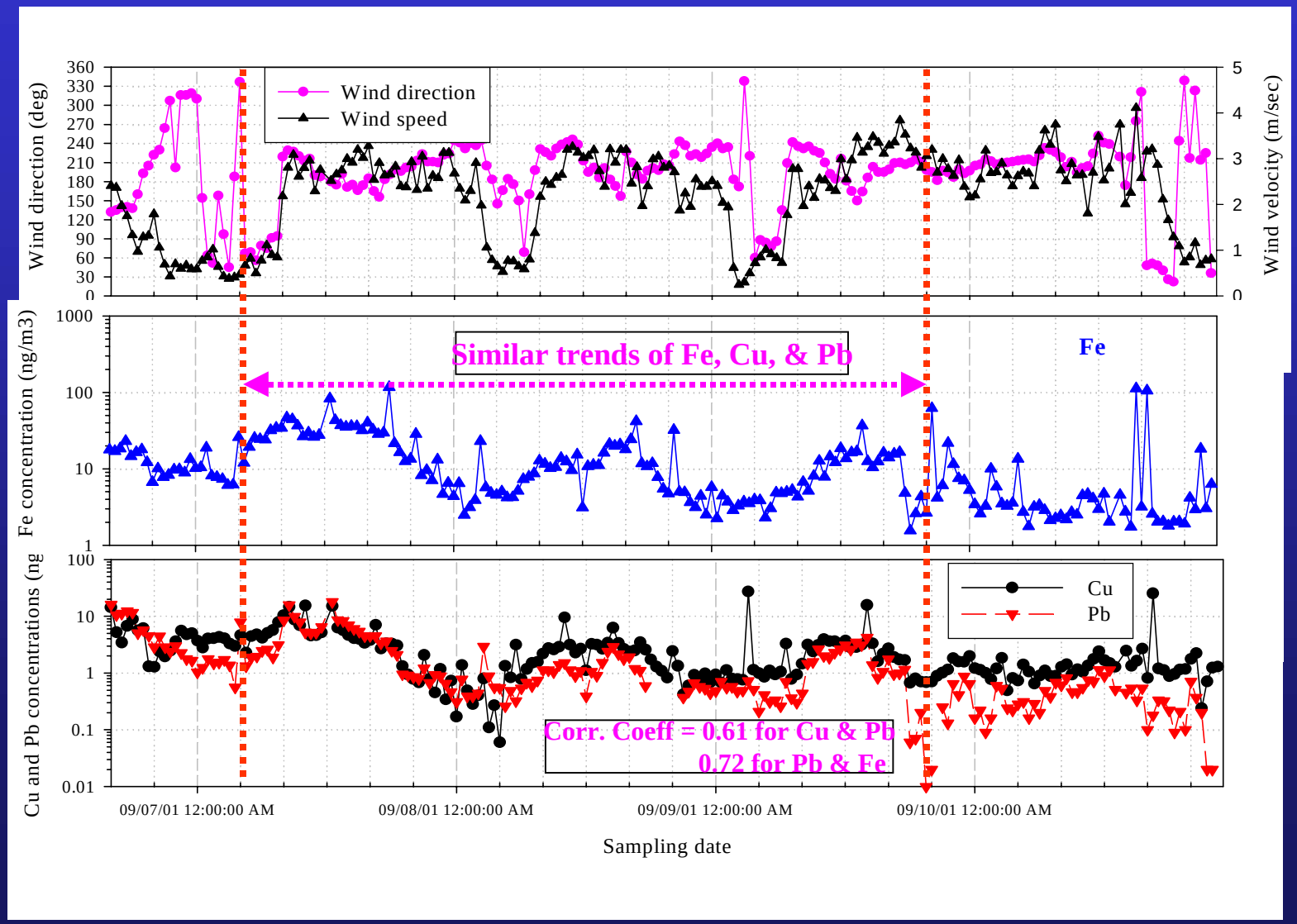


Se, Ni Concs more dynamic than Sulfate Sulfate.



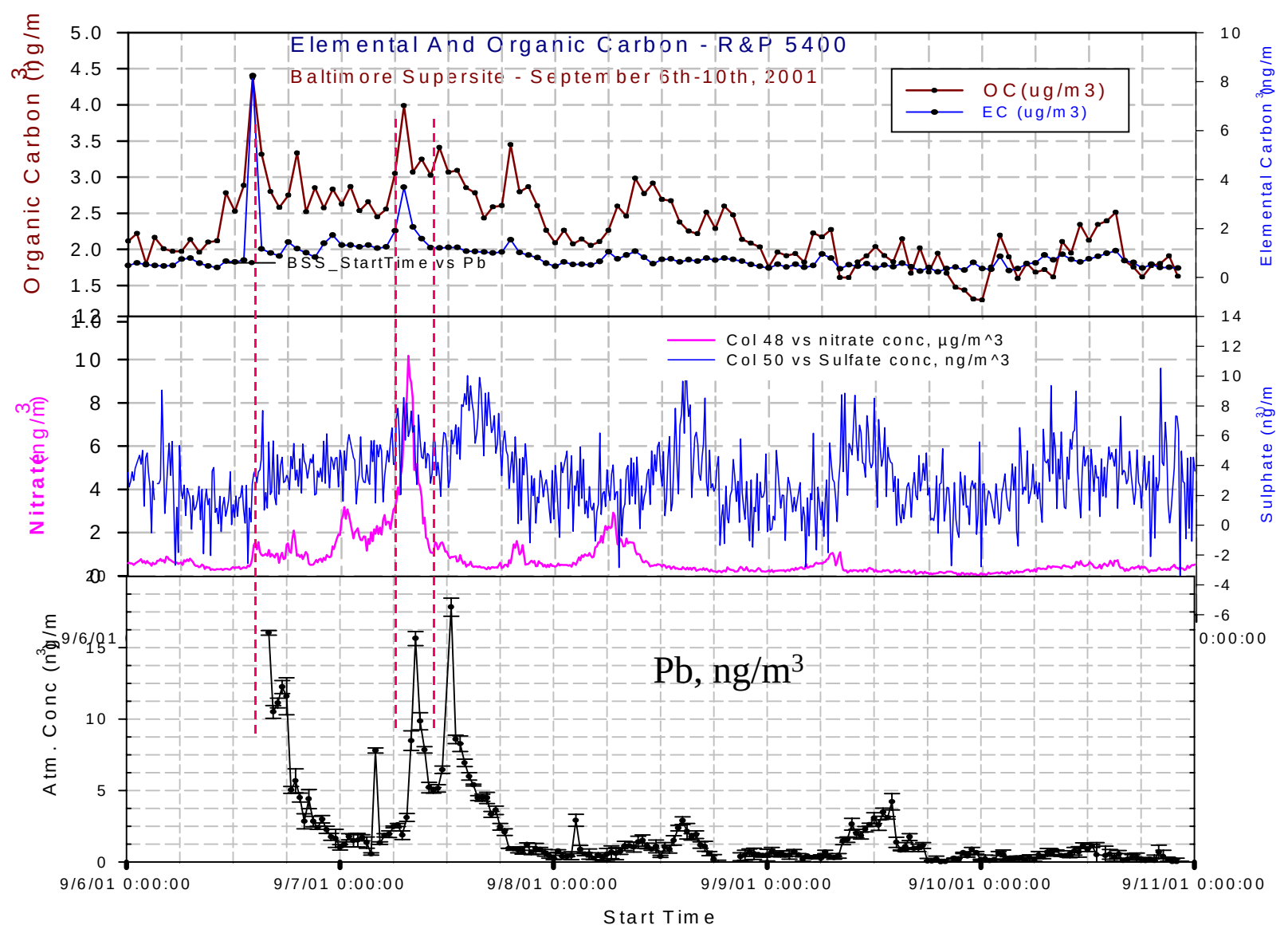
Steel/Dust Source: Fe, Cu, and Pb concentrations

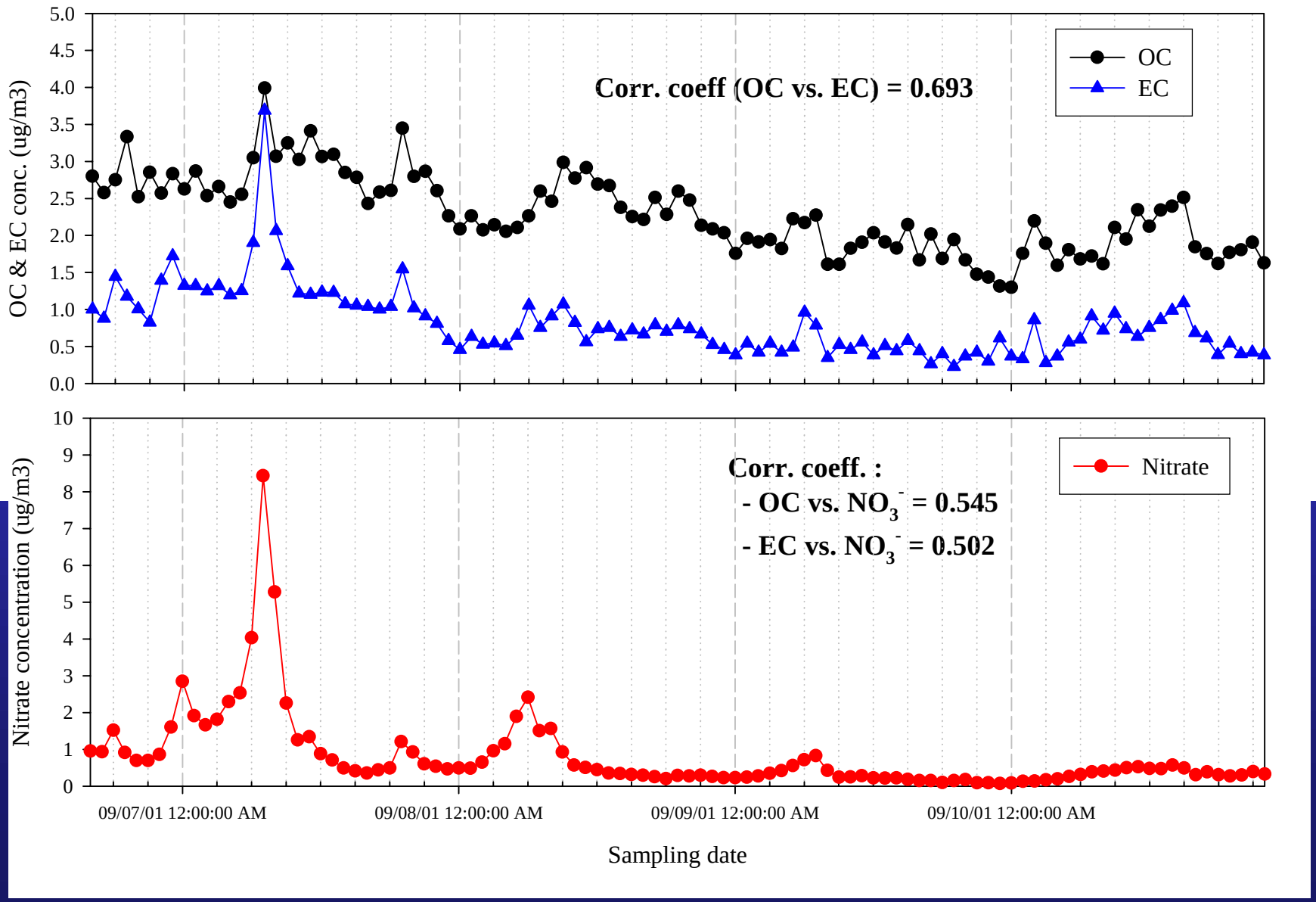
- occur near noon; decline at night (mixing height low); Winds 180 to 240°



In Baltimore: Pb peaks correlate with, but lag OC, but not always

Nitrate, Pb, EC, &OC occur together at 7:30 AM on Sept. 7th




OC & EC conc. (ug/m3)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Corr. coeff (OC vs. EC) = 0.693
OC
EC
Nitrate concentration (ug/m3)
10
9
8
7
6
5
4
3
2
1
0
Corr. coeff. :
- OC vs. NO_3^- = 0.545
- EC vs. NO_3^- = 0.502
Nitrate
09/07/01 12:00:00 AM
09/08/01 12:00:00 AM
09/09/01 12:00:00 AM
09/10/01 12:00:00 AM
Sampling date

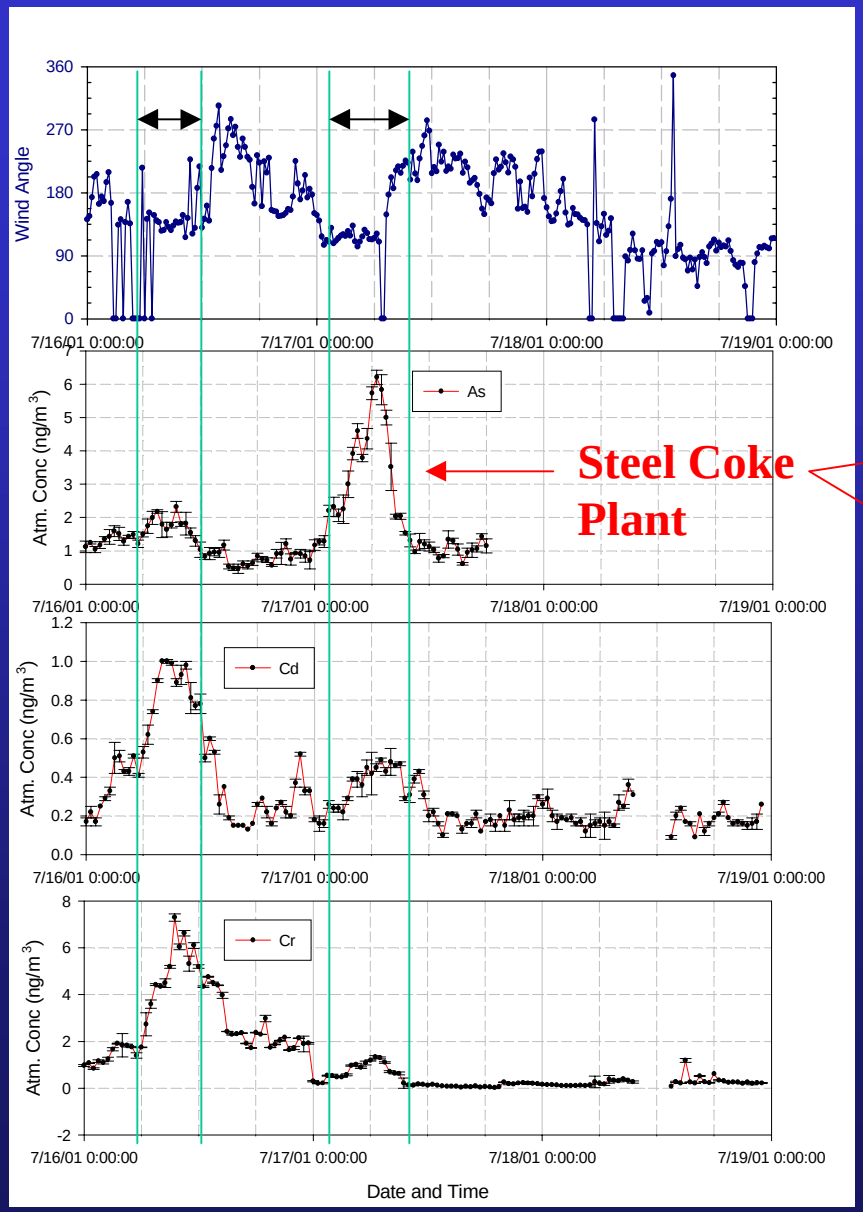
Pittsburgh Supersite

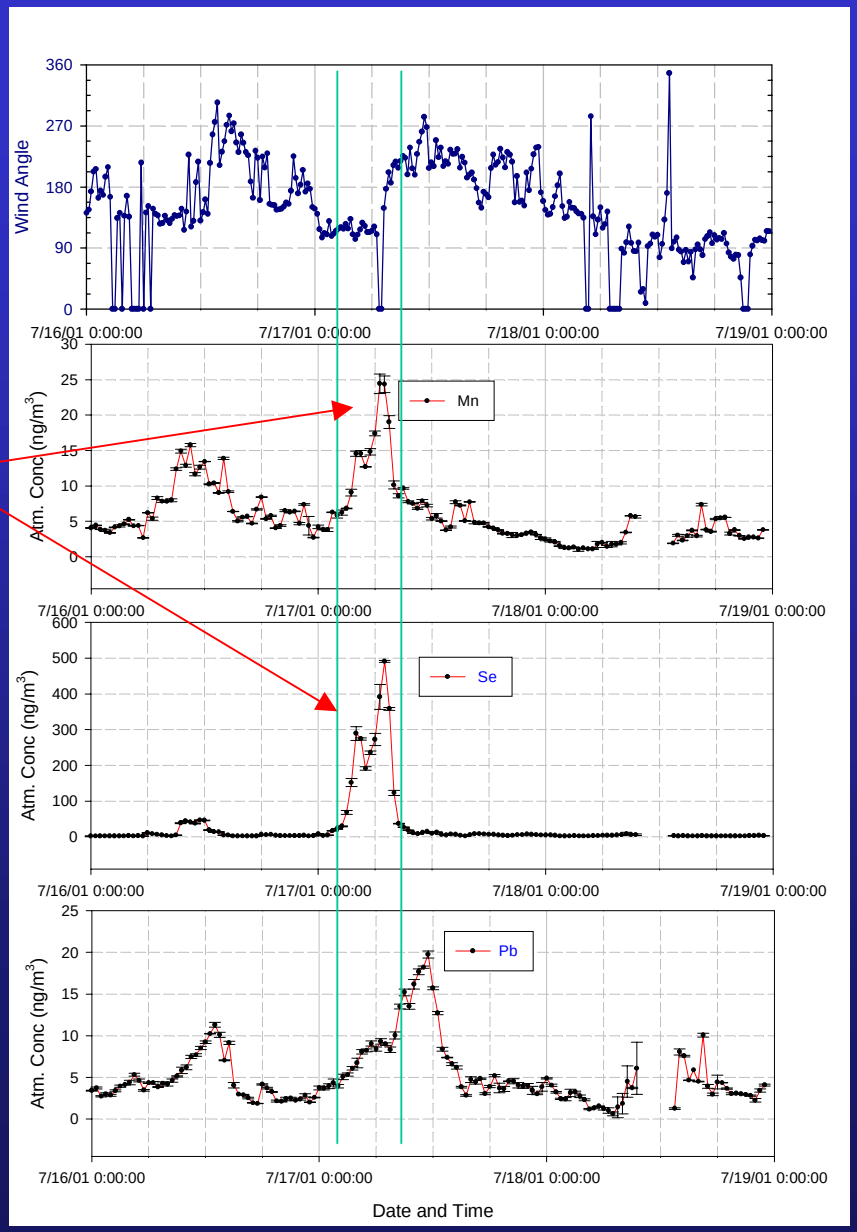
Data for Metals and Sulfate

(each figure shows approx. 2 days of 30 min measurements)

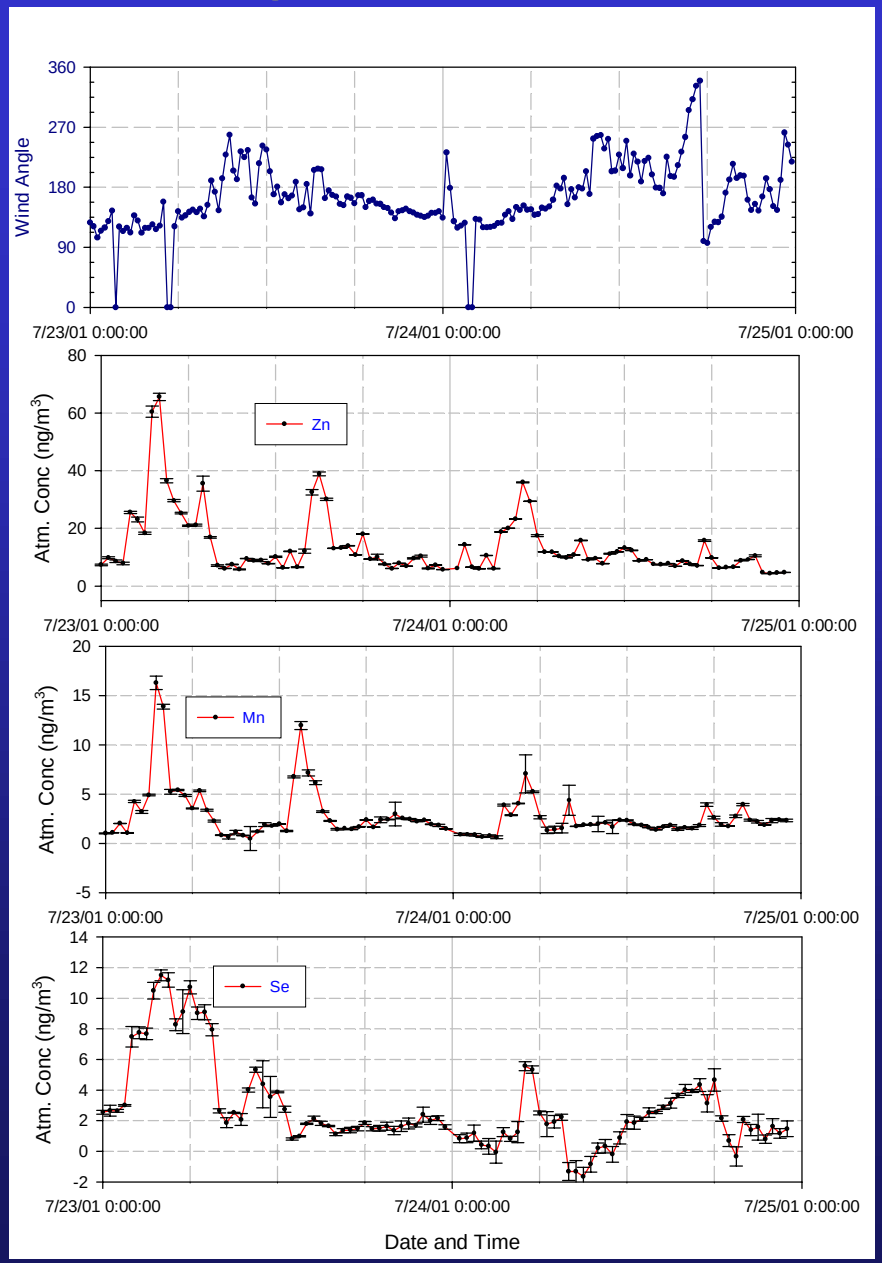
- Elevated concentrations are observed at WDs 0° to 120°
- Peak Concs. Up to 50x background
- Highest metals correspond to Lowest Sulfate concs.

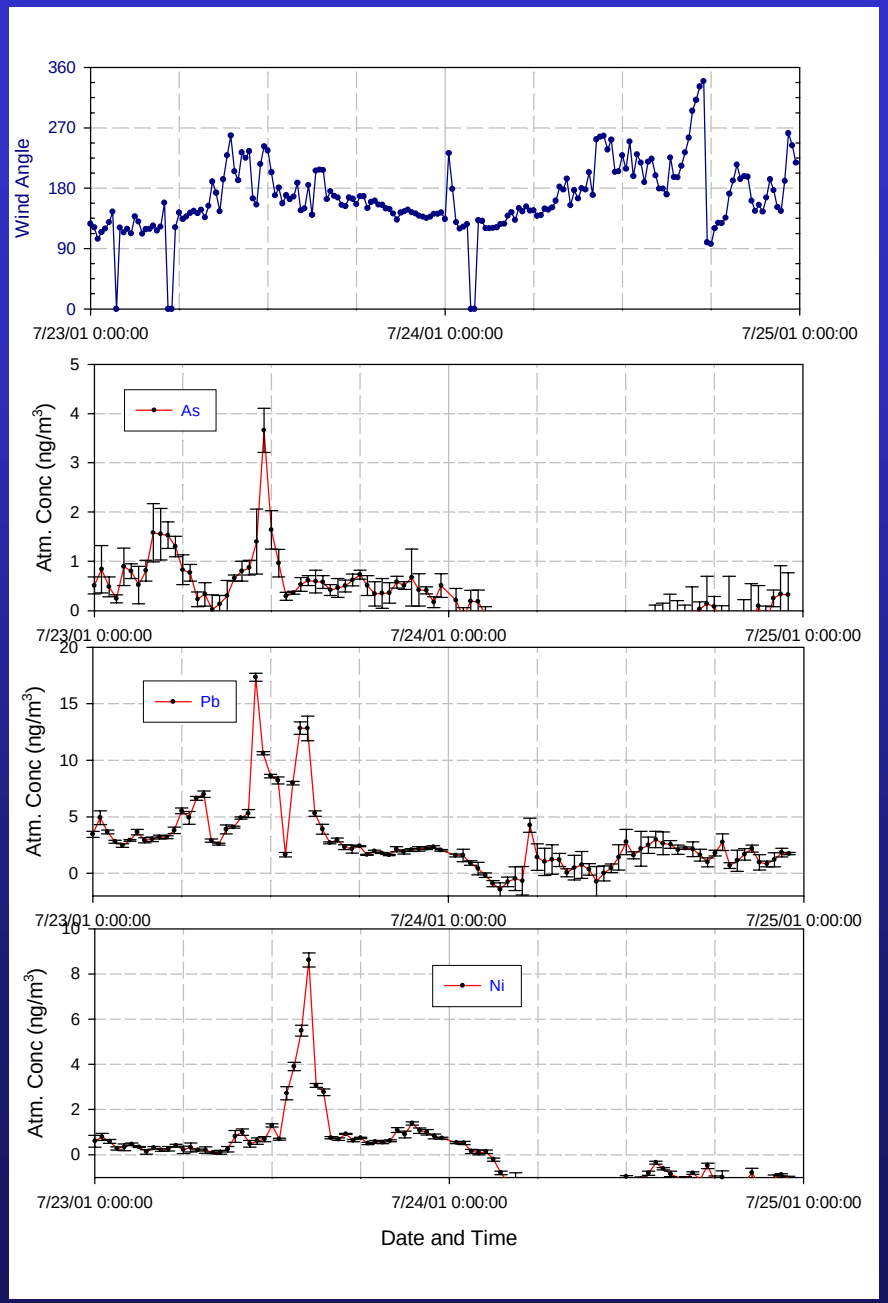
Pittsburgh Supersite: July 16, 17, 18 – Data show 3 major influences



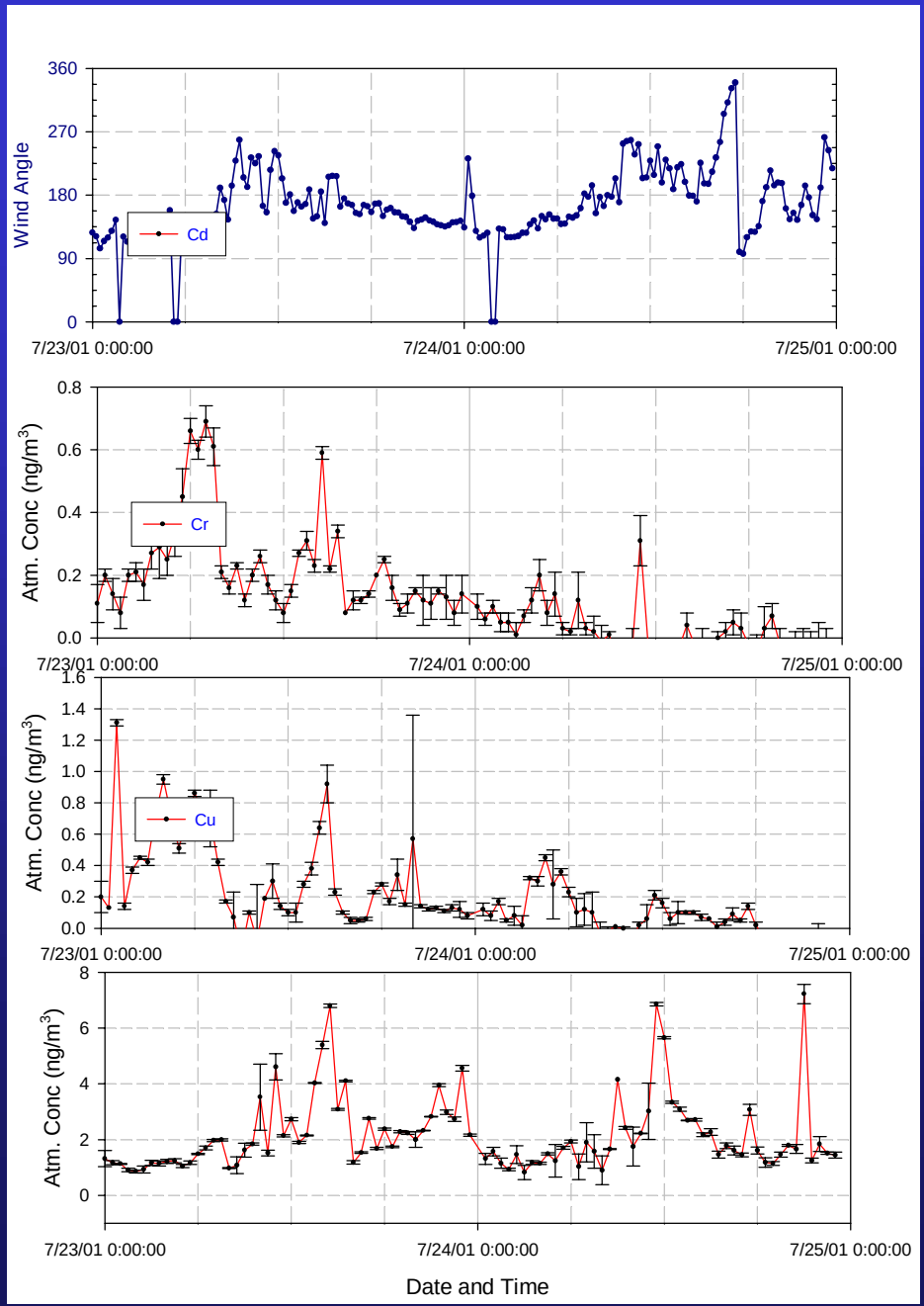


Pittsburgh Supersite: July 23, 24





Pittsburgh Supersite: July 23, 24; continue



Summary/Conclusions

- High temporal resolution reveals temporal emission characteristics of sources, and
- Concentration peaks readily related to wind directions
- Large data sets obtained in just a few days;

  ideally suited for Advanced factor analysis techniques
- Resolution of specific individual sources demonstrated

  Unprecedented degree of source resolution achieved

Chemical Analysis

Graphite Furnace Atomic Absorption Spectroscopy (GFAAS)
Perkin-Elmer SIMAA 6000

Advantages:

- very low detection limits
- Zeeman background correction
- handles slurry samples
- no nebulizer losses
- lower startup costs

Disadvantages:

- limited dynamic range
- maximum of 6 elements simultaneously
- compromise of furnace conditions