

SEARCH: The PM_{2.5} NAAQS and Particulate Matter Composition

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Presented at the
PM_{2.5} and Electric Power Generation: Recent Findings and Implications
Conference

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Pittsburgh, PA

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SouthEastern Aerosol Research and CHaracterization Study



Yorkville Site (YRK)
Yorkville, GA

SEARCH

Sponsors

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- ◆ Municipal Electric Authority of Georgia
- ◆ NISOURCE
- ◆ Oglethorpe Power
- ◆ Southern Company
- ◆ TXU Electric

Principal Investigators

- ◆ Eric Edgerton - ARA
- ◆ Ben Hartsell - ARA
- ◆ Alan Hansen - EPRI

Contractors

- ◆ Atmospheric Research & Analysis, Inc.
- ◆ Chester Labnet
- ◆ Desert Research Institute
- ◆ Harding - ESE

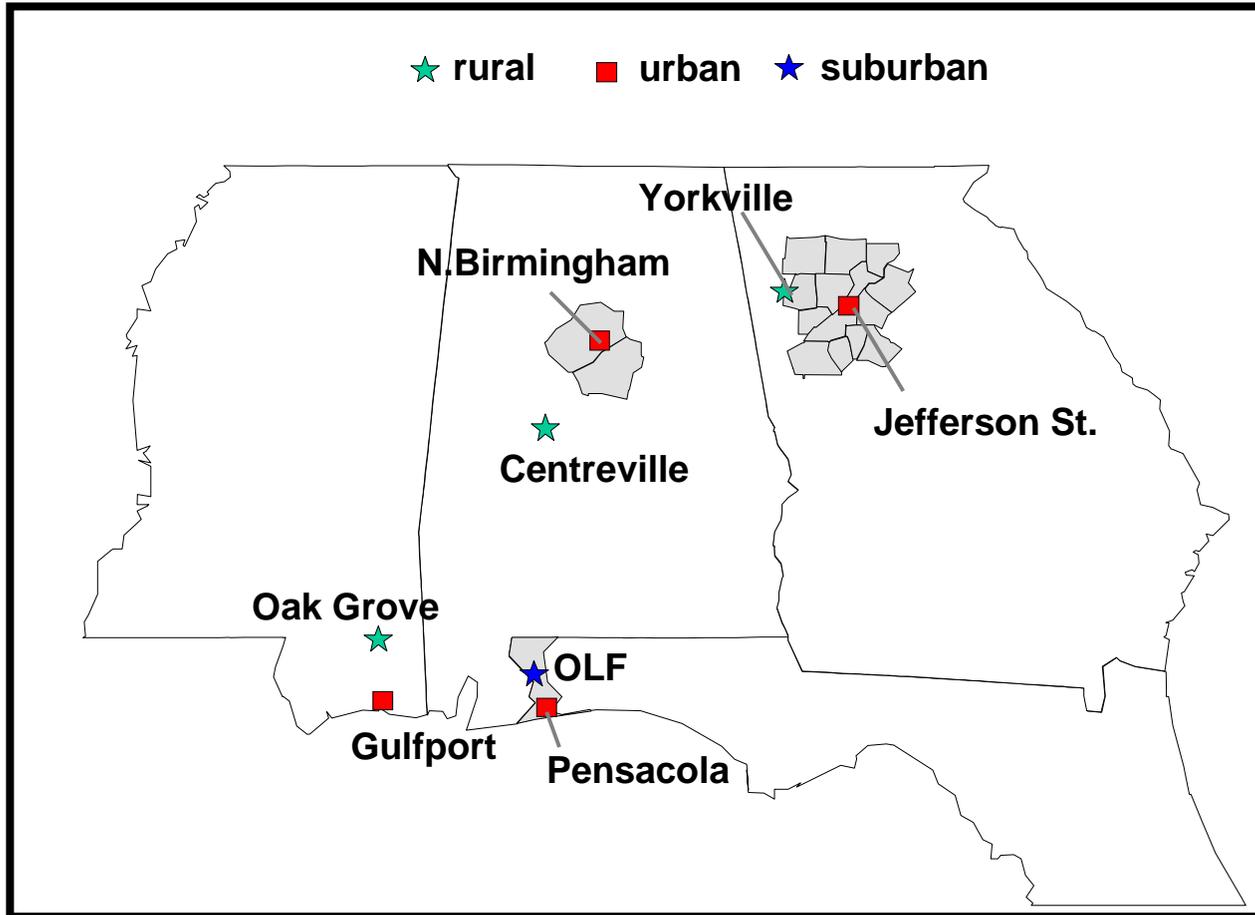
SEARCH Objectives

- ◆ Develop a PM_{2.5} Climatology for 8 Sites
- ◆ Understand Composition and its Variability
 - Year to Year, Season to Season (1999-2005)
 - Rural vs. Urban
 - Coastal vs. Inland
- ◆ Test, Improve, and Deploy Measurement Methods for Pollutant Gases and Continuous PM Components
- ◆ Estimate Source Contributions Understand Formation Processes
- ◆ Provide Comprehensive Data Set for Use in SIP Development
- ◆ Collaborate with States and Others

SEARCH Measurements

- ◆ Discrete Particles (24-hour)
 - FRM: PM2.5
 - PCM and Dichot: PM2.5, PM10 and Speciation
- ◆ Continuous Particles (1-min to 1-hr)
 - TEOM: mass
 - R&P 5400: OC/EC
 - Ammonium/Nitrate
 - Sulfate
 - Total Reduced Nitrogen -- Ammonia by Difference (under develop.)
- ◆ Trace Gases (1-min)
 - O3, NO, NO2, NOy, HNO3, SO2, CO, CO2
- ◆ Meteorology (1-min)
 - WS, WD, T, RH, BP, SR, rainfall
- ◆ Visibility
 - Dry Extinction
 - Adsorption

SEARCH Network



SEARCH PM2.5 FRM Summary

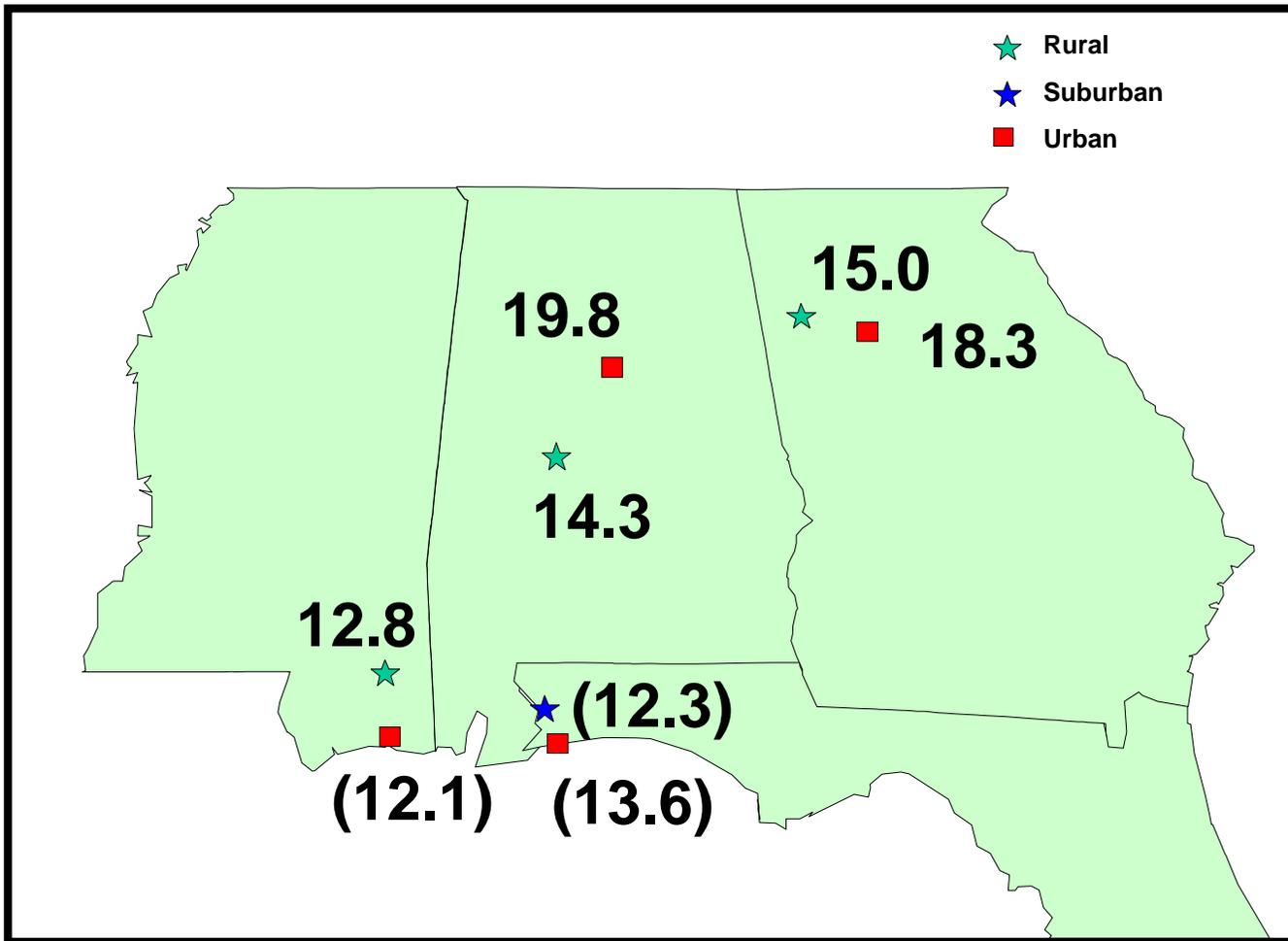
3-Year PM_{2.5} (FRM) at SEARCH Sites (ug/m³)

Notes:

1) Project Year Begins 10/1/98, except for PNS, OLF, and OAK (in Parentheses) Begins 10/1/99.

2) CTR includes 2 months of substituted TEOM data.

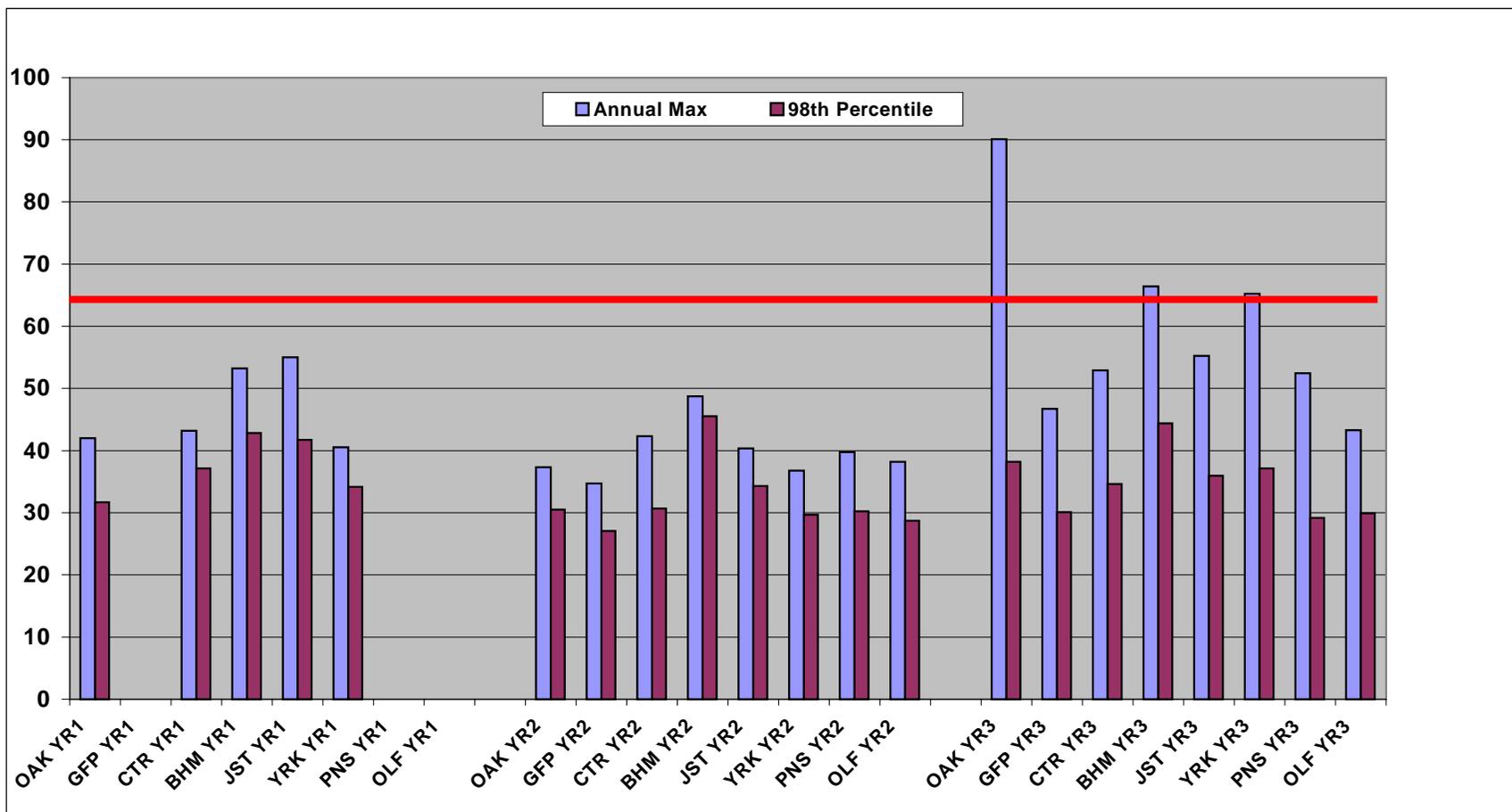
3) GFP includes six months of substituted PCM data.



Atlanta and Birmingham Above Standard. Others Below.

Annual FRM Max. and 98th Percentiles

(Note: Project Years Begin 10/1/98)



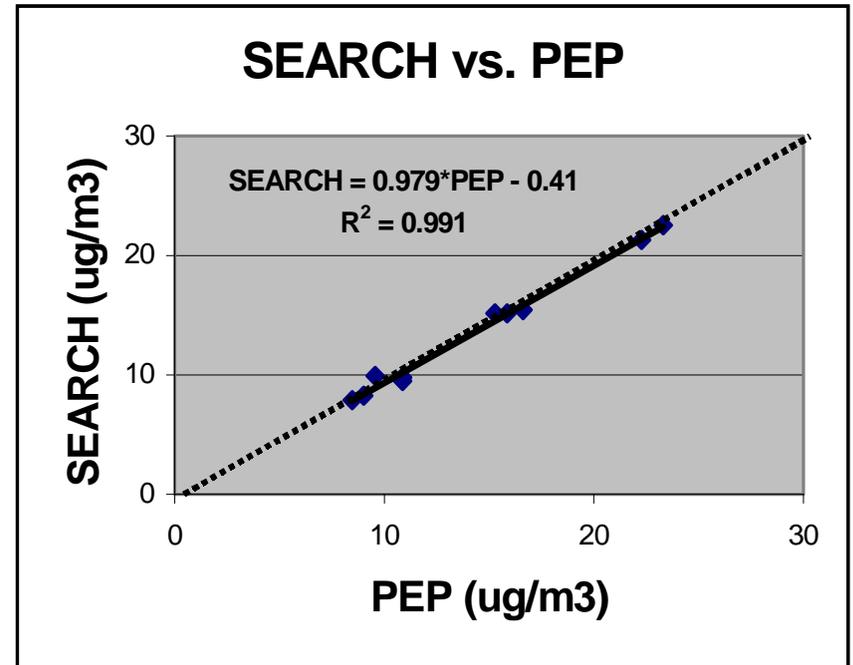
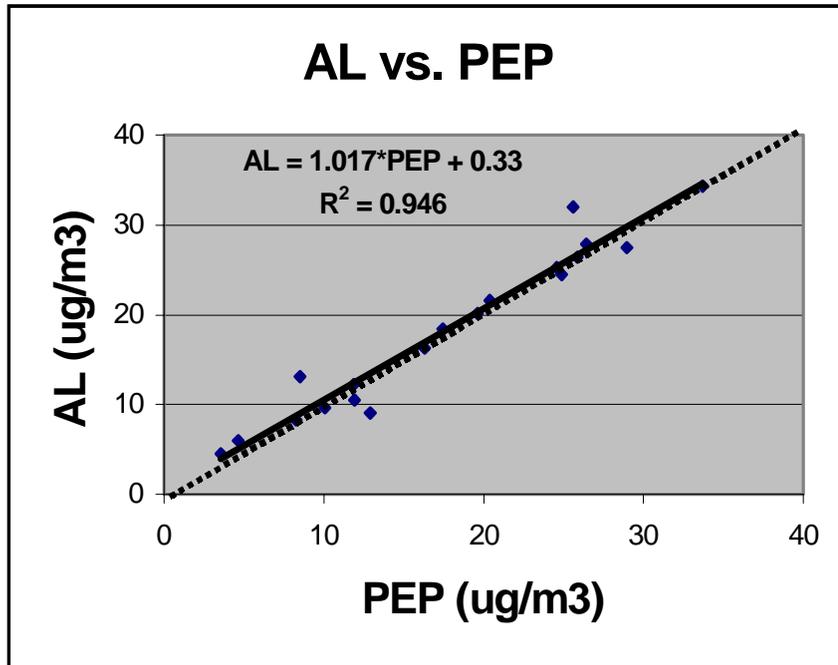
Several Observations >65 ug/m3 (2 out of 3 at Rural Sites), But No Site Close to Daily Standard.

QA Issues

- ◆ **Inter-Agency Bias (PEP audits)**
 - Are there differences from Agency to Agency?
 - What do differences mean in terms of
 - attainment and spatial patterns?
- ◆ **Blank Correction**
 - **FRM** does not recognize blank correction
 - (but requires collection/analysis of field blanks)
 - **SEARCH** advocates blank correction, as
 - good laboratory practice

PEP Audit Results

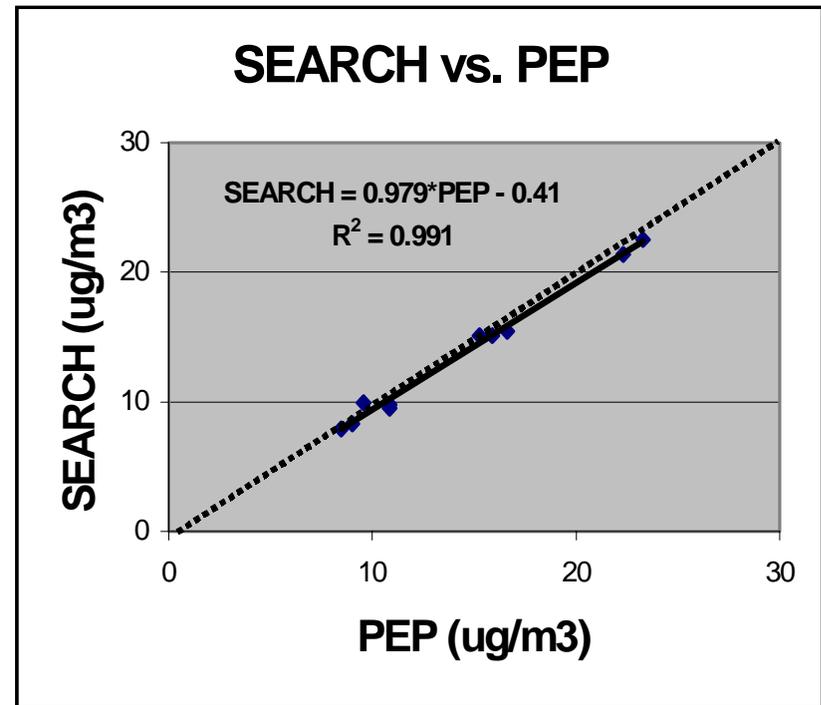
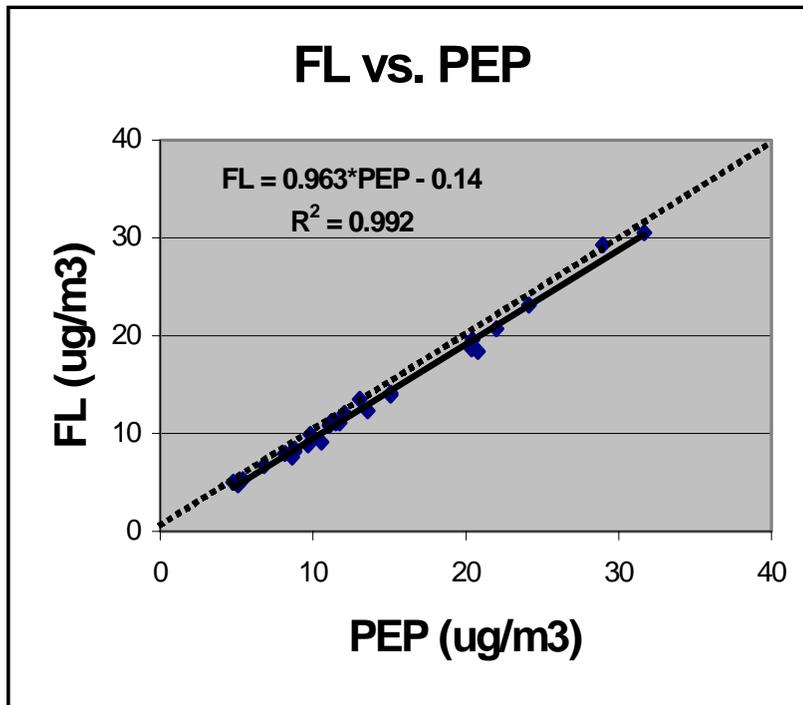
AL and SEARCH



**Inspection of PEP Results Shows Excellent Agreement,
But AL Generally > PEP and SEARCH Generally < PEP**

PEP Audit Results

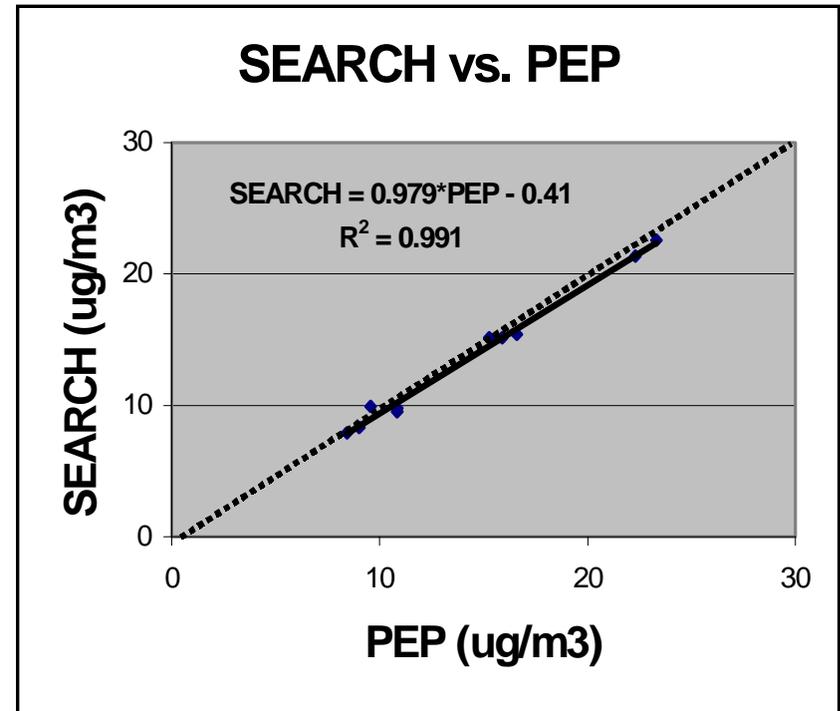
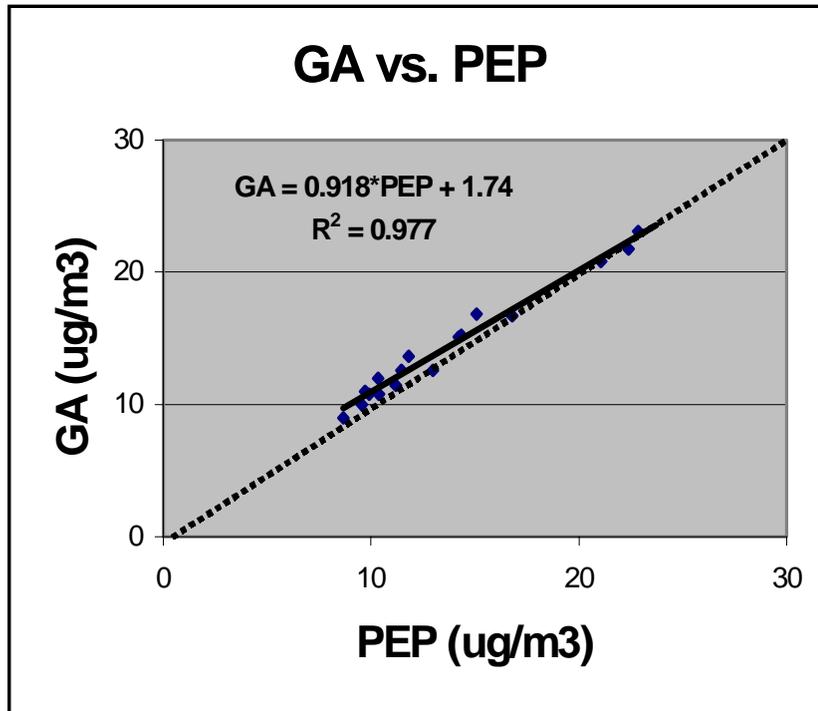
FL and SEARCH



**Inspection of PEP Results Show Excellent Agreement
But FL and SEARCH Generally < PEP**

PEP Audit Results

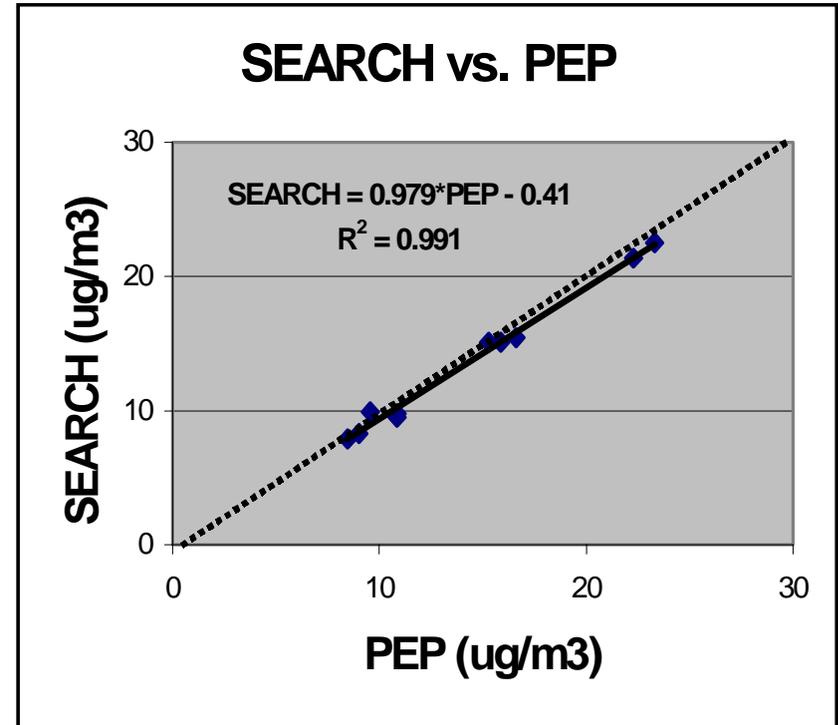
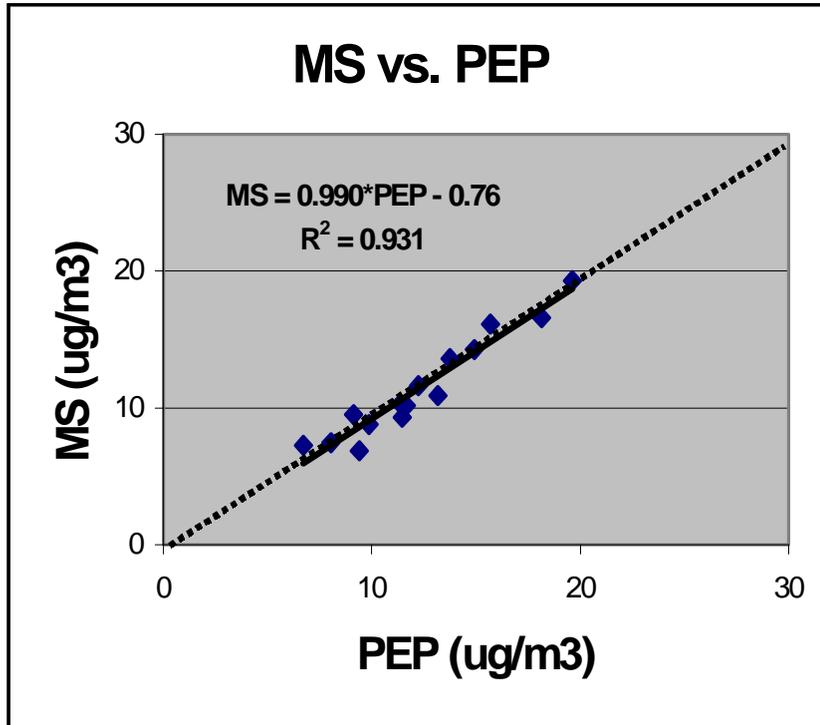
GA and SEARCH



**Inspection of PEP Results Show Excellent Agreement
But GA Generally > PEP and SEARCH < PEP**

PEP Audit Results

MS and SEARCH



**Inspection of PEP Results Show Excellent Agreement
But MS and SEARCH Generally < PEP**

PEP Audit Results

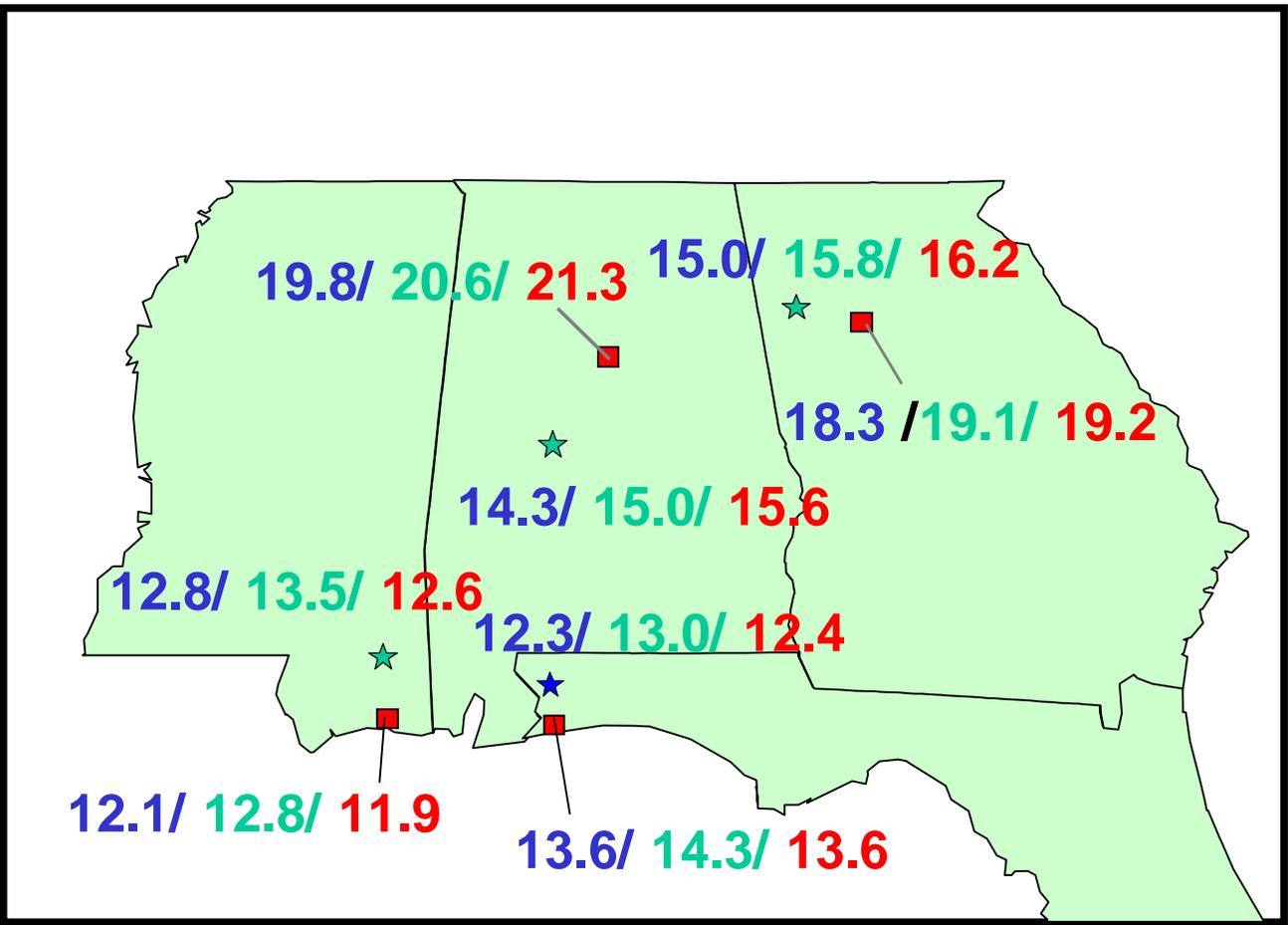
Percent Differences by Agency/Network

Network	FRM Vendor	n	Mean	95% CI		Sig.	Corr. Coeff.
				Lower	Upper		
MS	R&P	25	-6.3	-13.4	-5.3	99+	0.97
FL	R&P	40	-5.8	-7.4	-4.2	99+	0.99
SEARCH	R&P	11	-5.5	-10.0	-1.9	95+	0.99
SC	R&P	21	-4.9	-7.0	-2.7	99+	0.99
TN	R&P	28	-3.9	-7.7	-0.1	95+	0.98
NC	R&P	48	-2.9	-4.6	-1.1	99+	0.99
AL	Andersen/BGI	27	1.3	-5.5	8.0	ns	0.97
GA	Andersen	34	5.3	1.6	9.0	99+	0.97

All 6 Agencies/Networks with R&Ps Significantly Lower Than PEP, 1 Agency Higher than PEP

PEP Audit Implications (relative to **SEARCH FRM**)

SEARCH
(Actual)
PEP
(Adjusted)
S&L
(Adjusted)

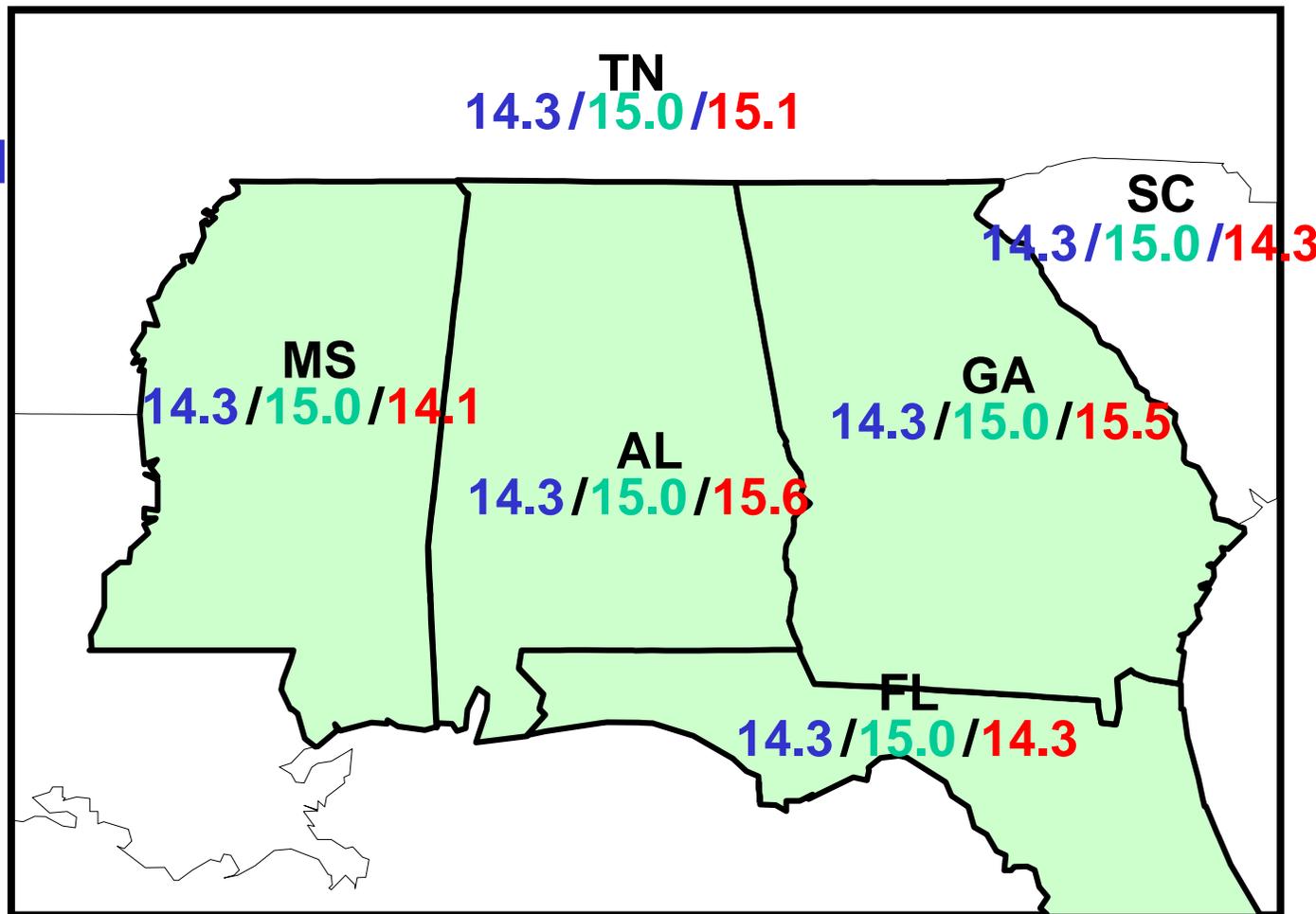


Notes:

- 1) Project Year Begins 10/1/98, except for PNS, OLF, and OAK (in Parentheses) Begins 10/1/99.
- 2) CTR includes 2 months of substituted TEOM data.
- 3) GFP includes six months of substituted PCM data.

**PM_{2.5} Concentrations Vary, Sometimes Significantly,
from Organization to Organization**

PEP Audit Implications (for 15.0 ug/m3 Target)



SEARCH
(Adjusted)
PEP
(Assumed)
S&L
(Adjusted)

PEP Results Suggest Significant Variability at Level of Annual Standard with Some States Well Above and Some Well Below

Blank Correction Implications (relative to **SEARCH FRM**)

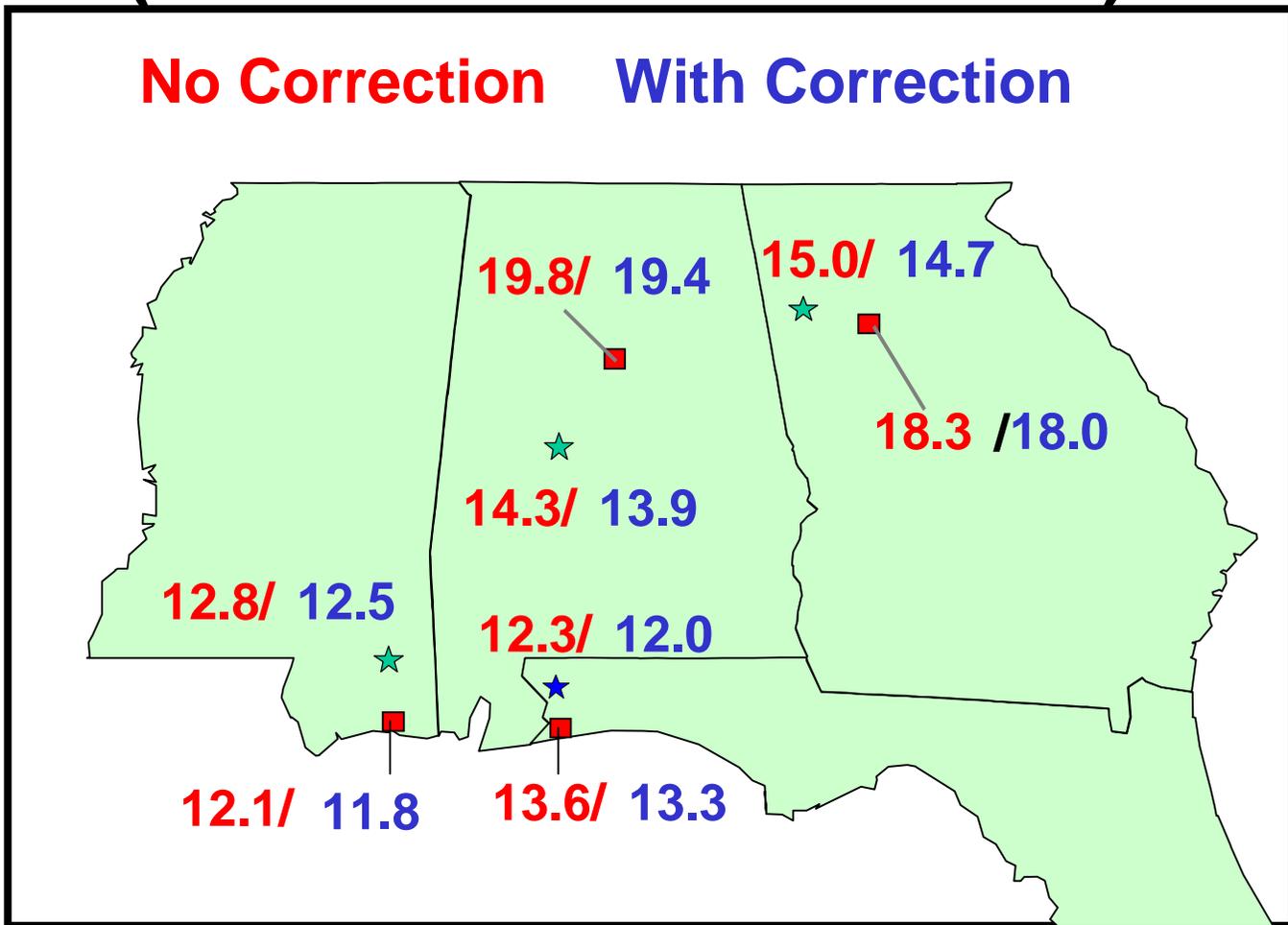
Notes:

1) Project Year Begins 10/1/98, except for PNS, OLF, and OAK (in Parentheses) Begins 10/1/99.

2) CTR includes 2 months of substituted TEOM data.

3) GFP includes six months of substituted PCM data.

No Correction **With Correction**



Blank Correction Potentially Significant for Sites Near Standard

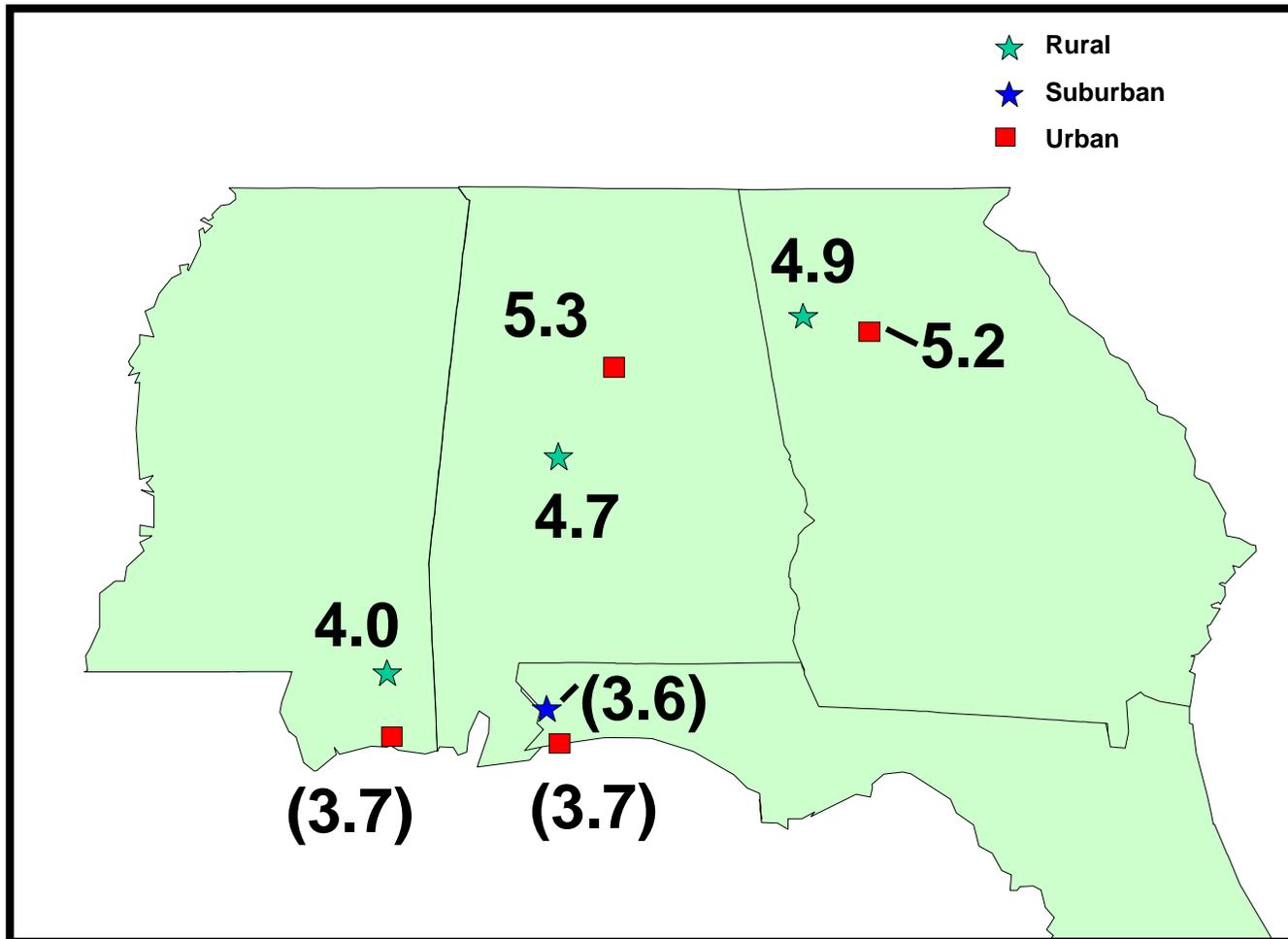
SEARCH PM2.5 Composition Summary

Two Approaches

FRM Equivalent: Attempts to describe what is on the **FRM** filter.

Best Estimate: Attempts to describe actual Atmospheric concentrations.

FRM Equivalent & Best Estimate PM_{2.5} Sulfate at SEARCH Sites (ug/m³) 10/98-9/01



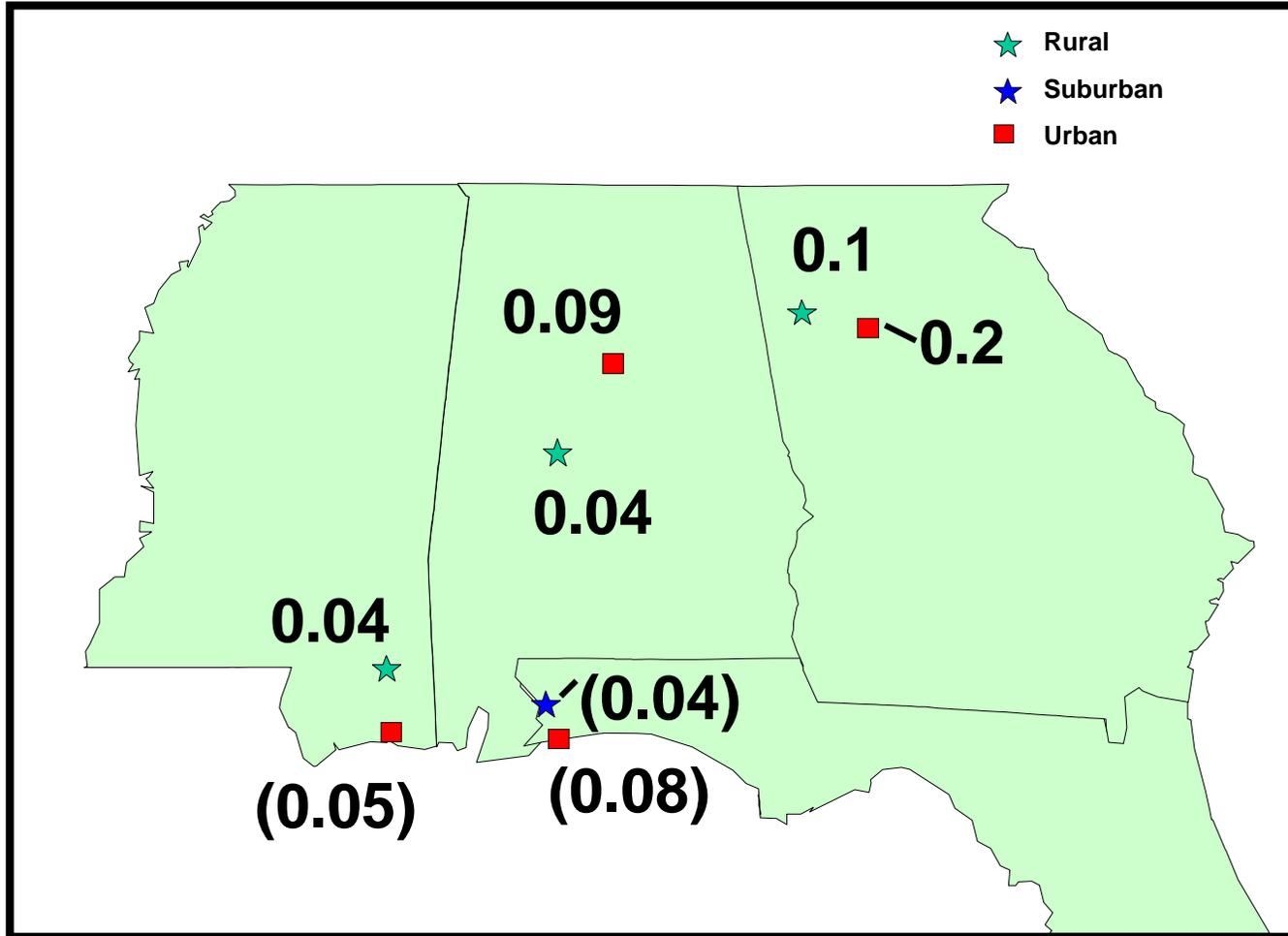
Note: Project Year Begins 10/1/98, except for PNS, OLF, and OAK (in Parentheses) Begins 10/1/99

Minimal Urban Rural Difference in Sulfate. Possible North/South Gradient (or Big/Small City, Or Inland/Coastal)

SEARCH

FRM Equivalent PM_{2.5} Nitrate at SEARCH Sites (ug/m³) 10/98-9/01

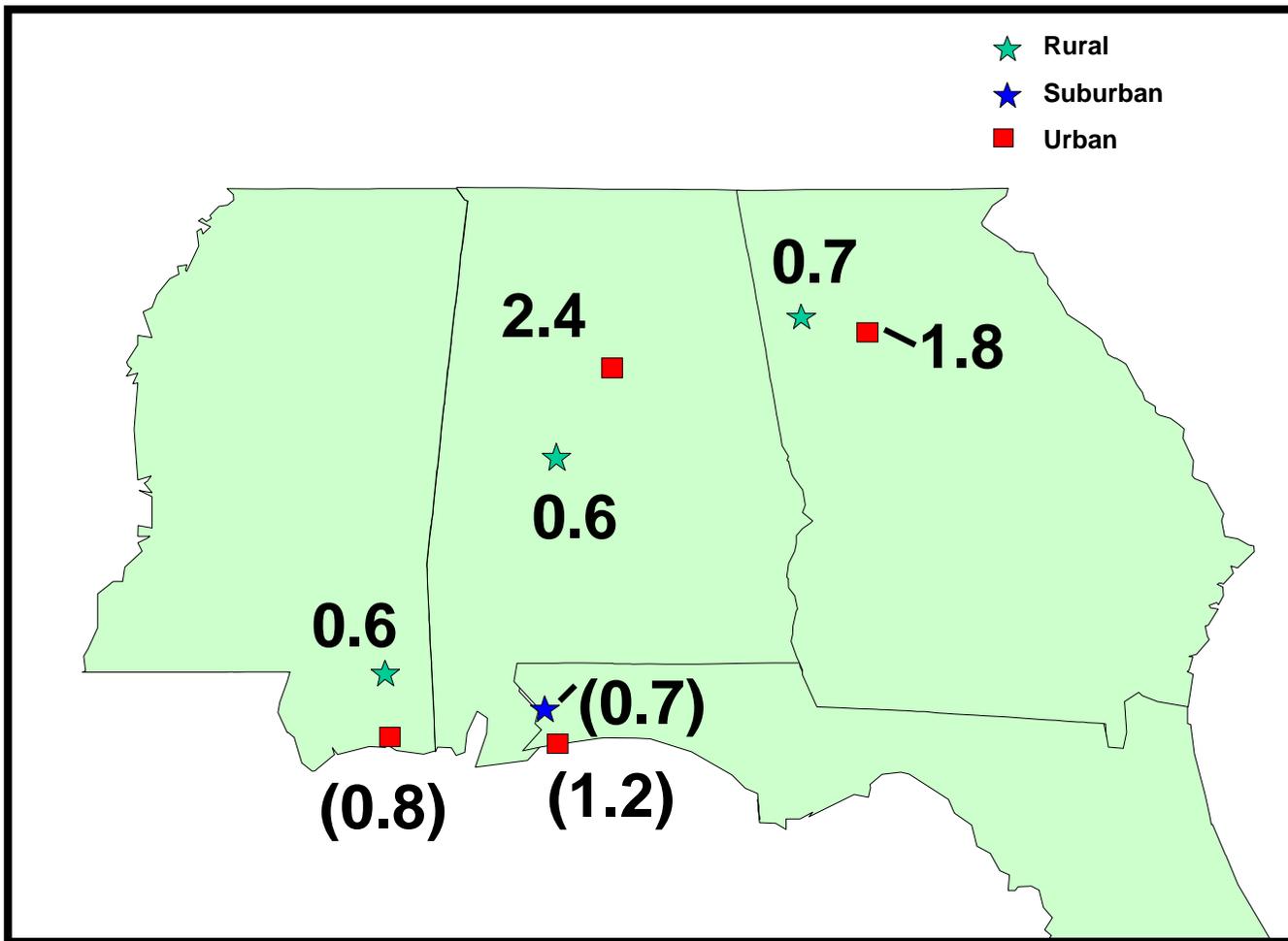
Note: Project Year Begins 10/1/98, except for PNS, OLF, and OAK (in Parentheses) Begins 10/1/99



Nitrate is a Very Small Component of FRM Mass.

FRM Equivalent & Best Estimate PM_{2.5} Elemental Carbon at SEARCH Sites (ug/m³) 10/98-9/01

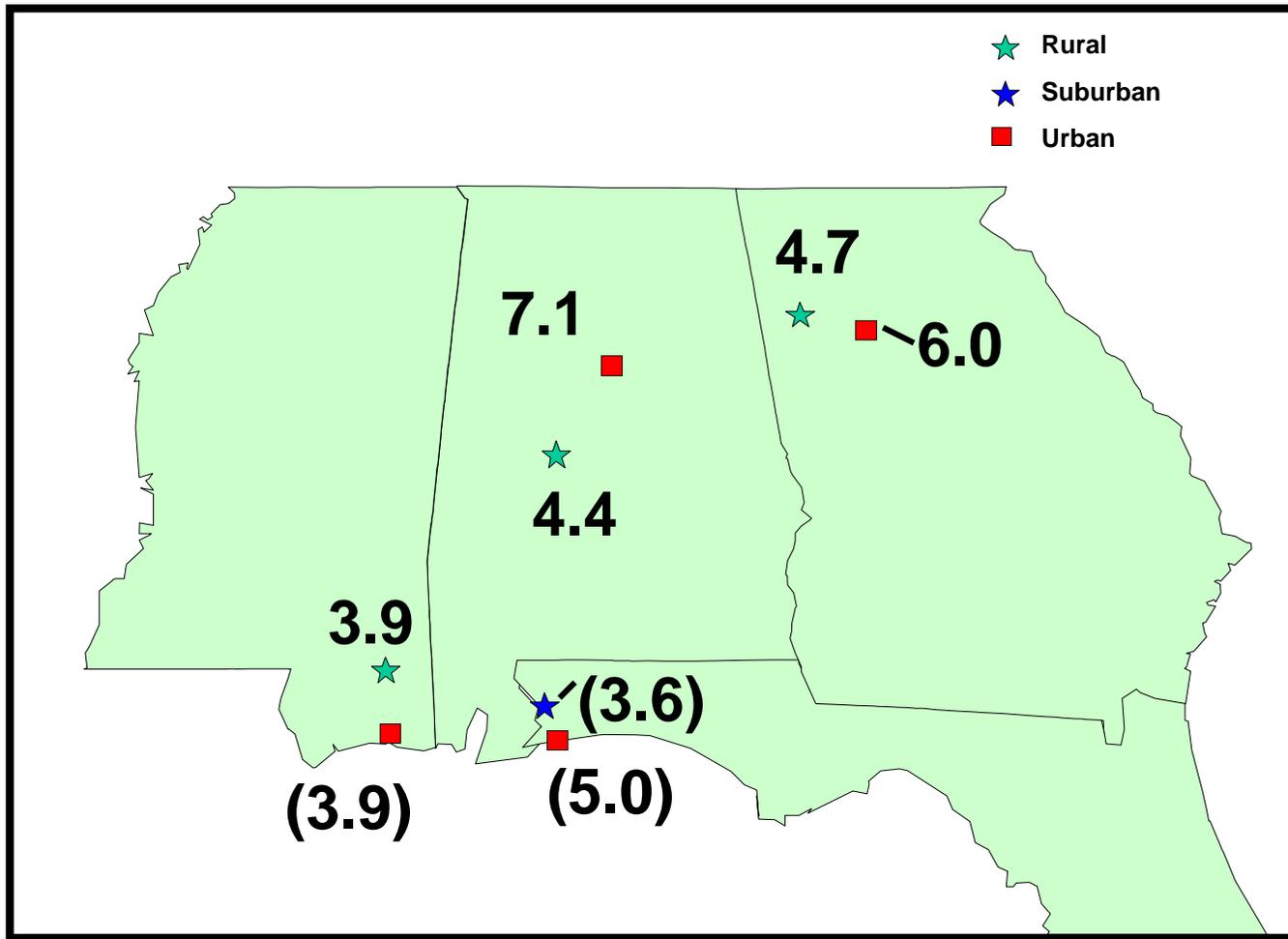
Note: Project Year Begins 10/1/98, except for PNS, OLF, and OAK (in Parentheses) Begins 10/1/99



Strong Urban/Rural Gradients in Elemental Carbon, Especially in Larger Cities.

FRM Equivalent PM_{2.5} Organic Matter at SEARCH Sites (ug/m³) 10/98-9/01

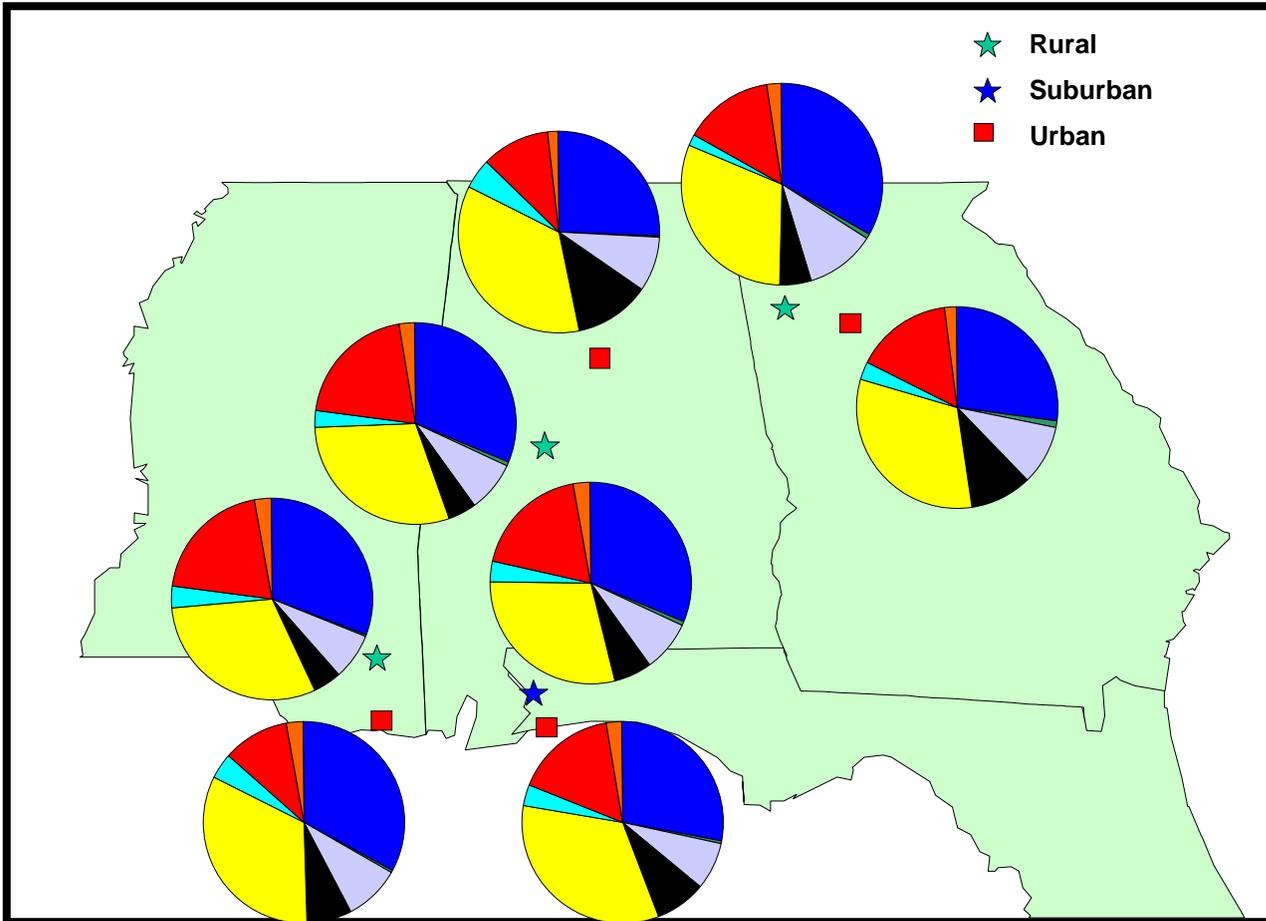
Note: Project Year Begins 10/1/98, except for PNS, OLF, and OAK (in Parentheses) Begins 10/1/99



Strong Urban/Rural Gradients in Organic Matter, Especially in Larger Cities.

FRM Equivalent PM_{2.5} Composition at SEARCH Sites (ug/m³) 10/98-9/01

Note:
Project
Year Begins
10/1/98,
except for
PNS, OLF,
and OAK
(Begins
10/1/99)



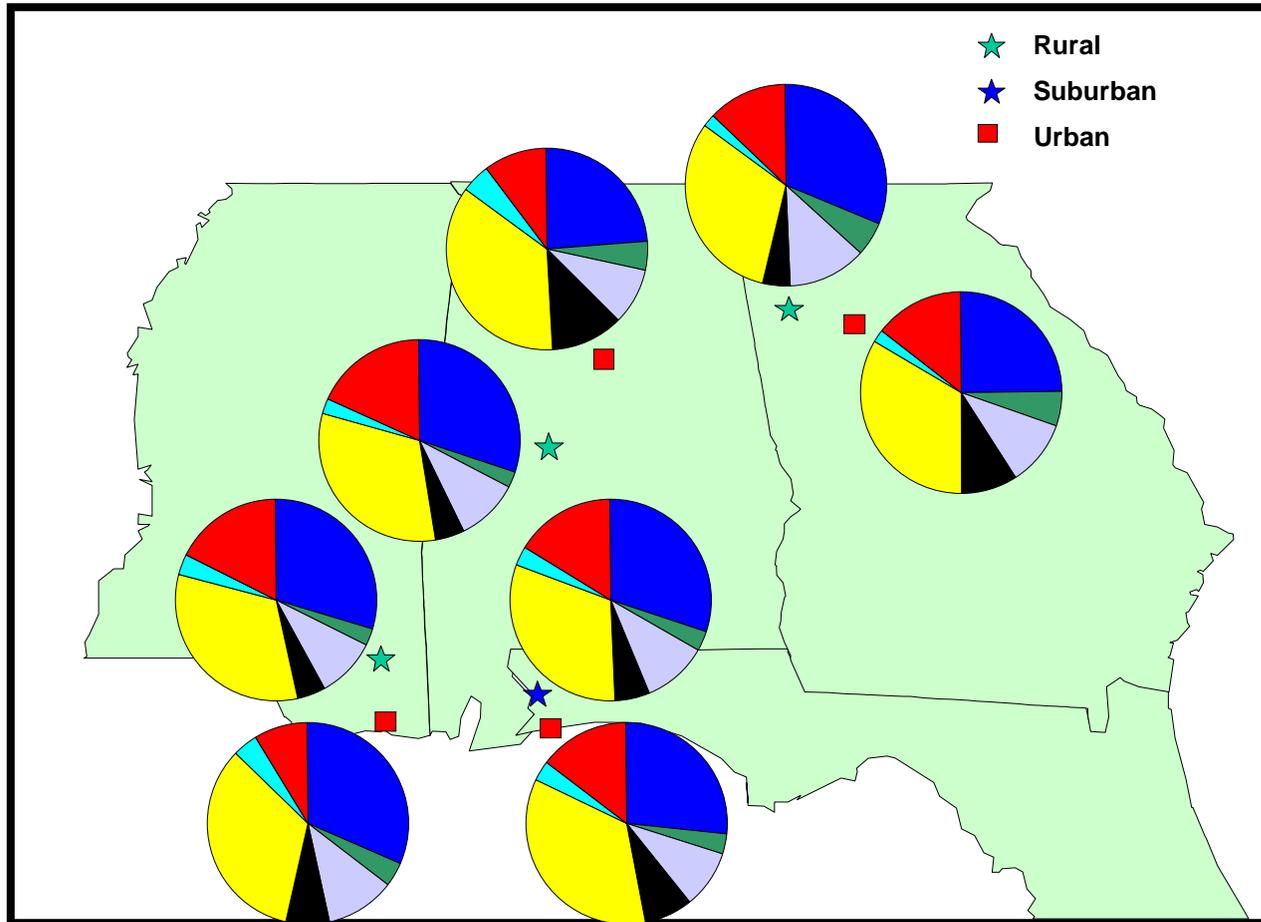
- Blank
- Other
- Major Metal Oxides
- Organic Matter
- Elemental Carbon
- Ammonium
- Nitrate
- Sulfate

"Other" is defined as the difference between measured components and measured mass. "Other" can be positive or negative and consists of particle bound water and other un-measured components, net measurement uncertainties and uncertainty in the OC scaling factor

Based on FRM Equivalent: Organic Matter Exceeds Sulfate at Urban Sites. Sulfate Exceeds or is Equivalent to Organic Matter at Rural Sites. Total Carbon Exceeds Sulfate at all Sites.

Best Estimate PM_{2.5} Composition at SEARCH Sites (ug/m³) 10/98-9/01

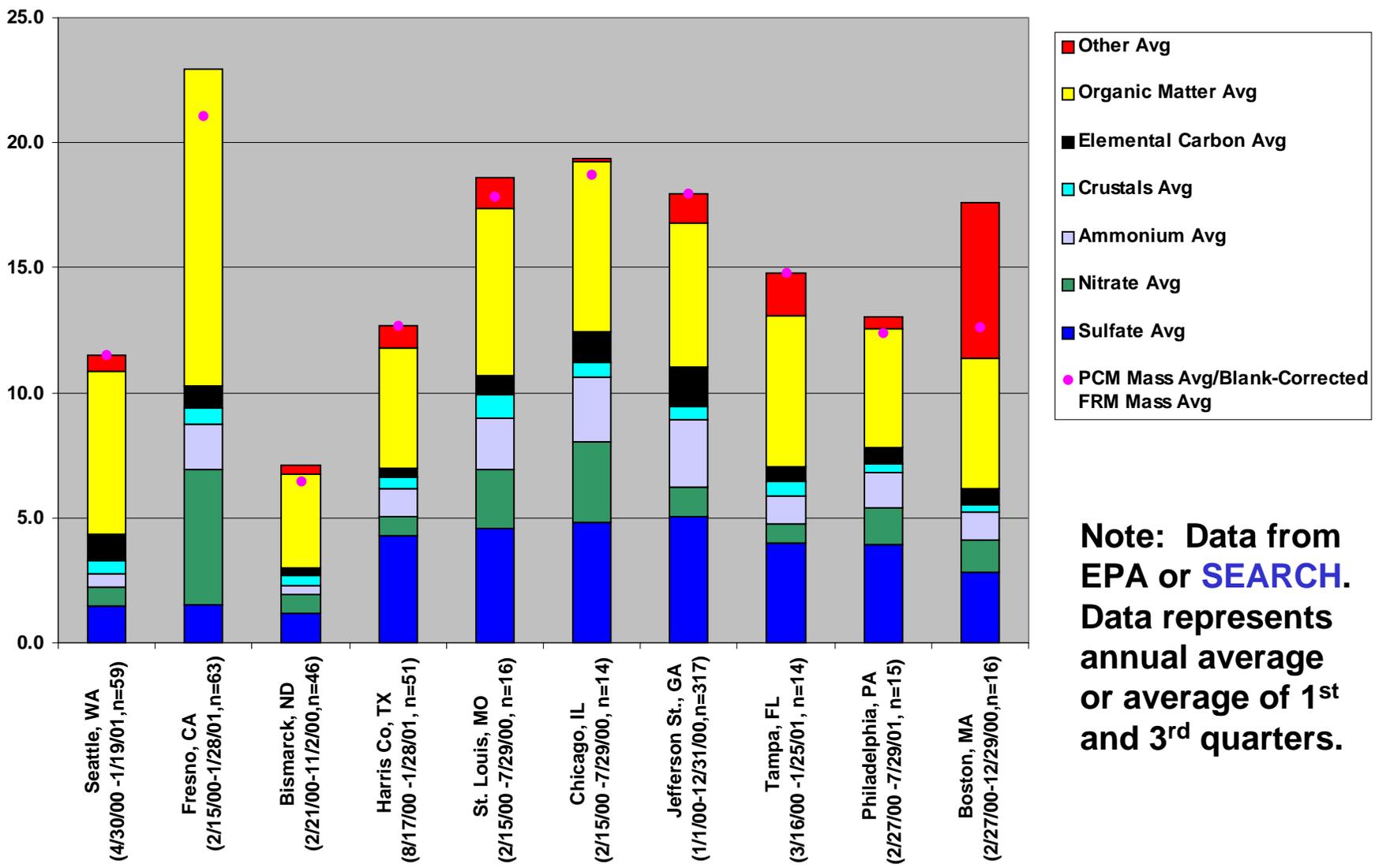
Note:
Project
Year Begins
10/1/98,
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(Begins
10/1/99)



"Other" is defined as the difference between measured components and measured mass. "Other" can be positive or negative and consists of particle bound water and other un-measured components, net measurement uncertainties and uncertainty in the OC scaling factor

**Based on Best Estimate:
Organic Matter Exceeds Sulfate at all Sites.
Total Carbon Exceeds Sulfate at all Sites.**

PM_{2.5} Composition in Urban Areas Across US



Note: Data from EPA or SEARCH. Data represents annual average or average of 1st and 3rd quarters.

Carbon is important at many urban sites across the U.S.

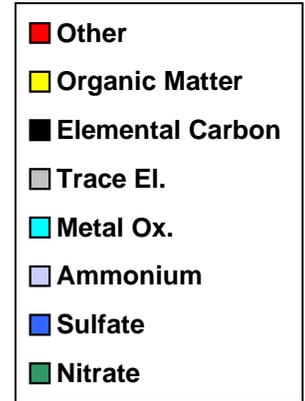
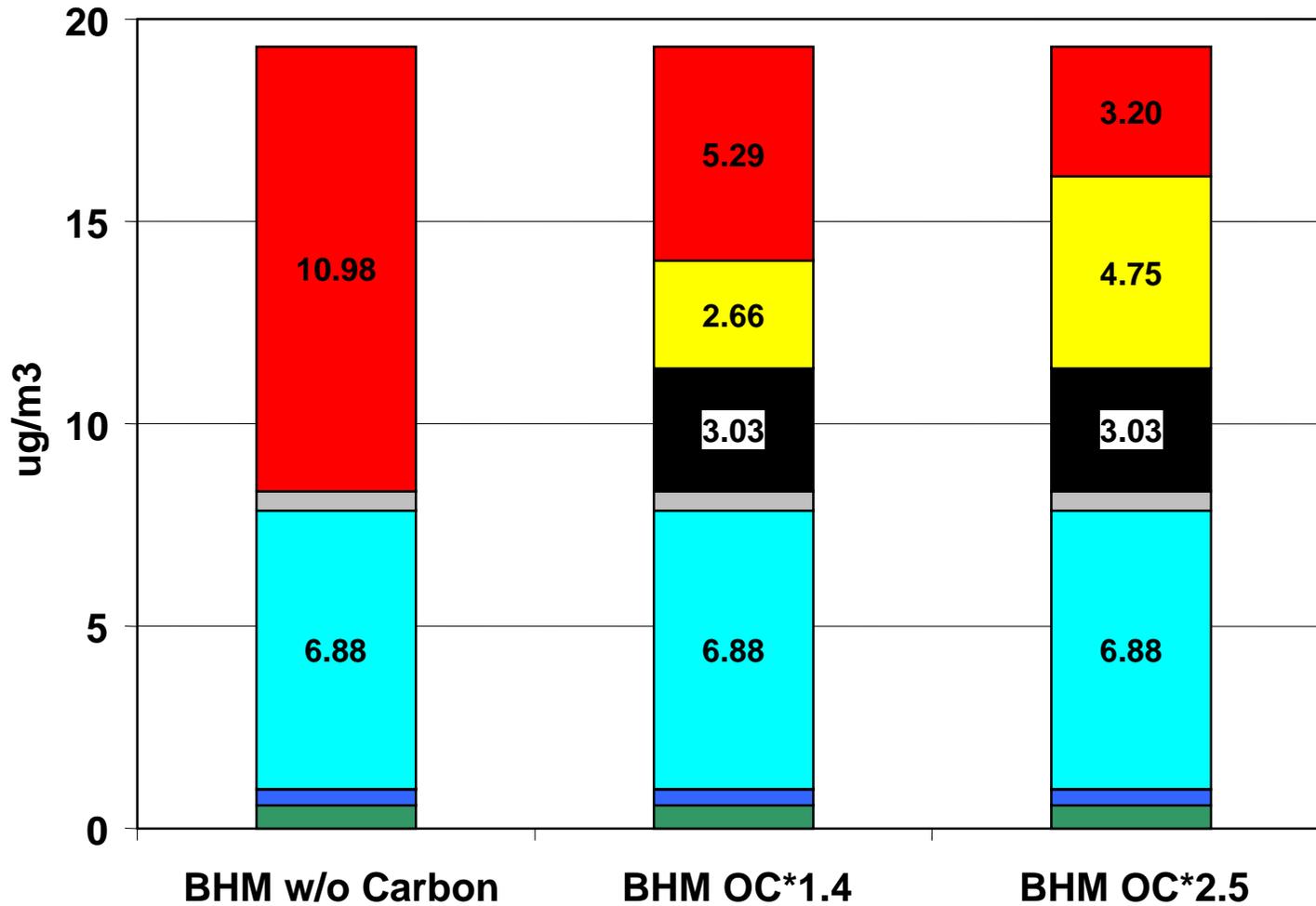
SEARCH

PM_{coarse} Update

PMcoarse Speciation at Birmingham, AL

August 2000-April 2001

PMcoarse Mass = 19.3 ug/m³



"Other" is defined as the difference between measured components and measured mass. "Other" can be positive or negative and consists of particle bound water and other un-measured components, net measurement uncertainties, and uncertainty in the OC scaling factor.

Carbon is an Important Component of PMcoarse

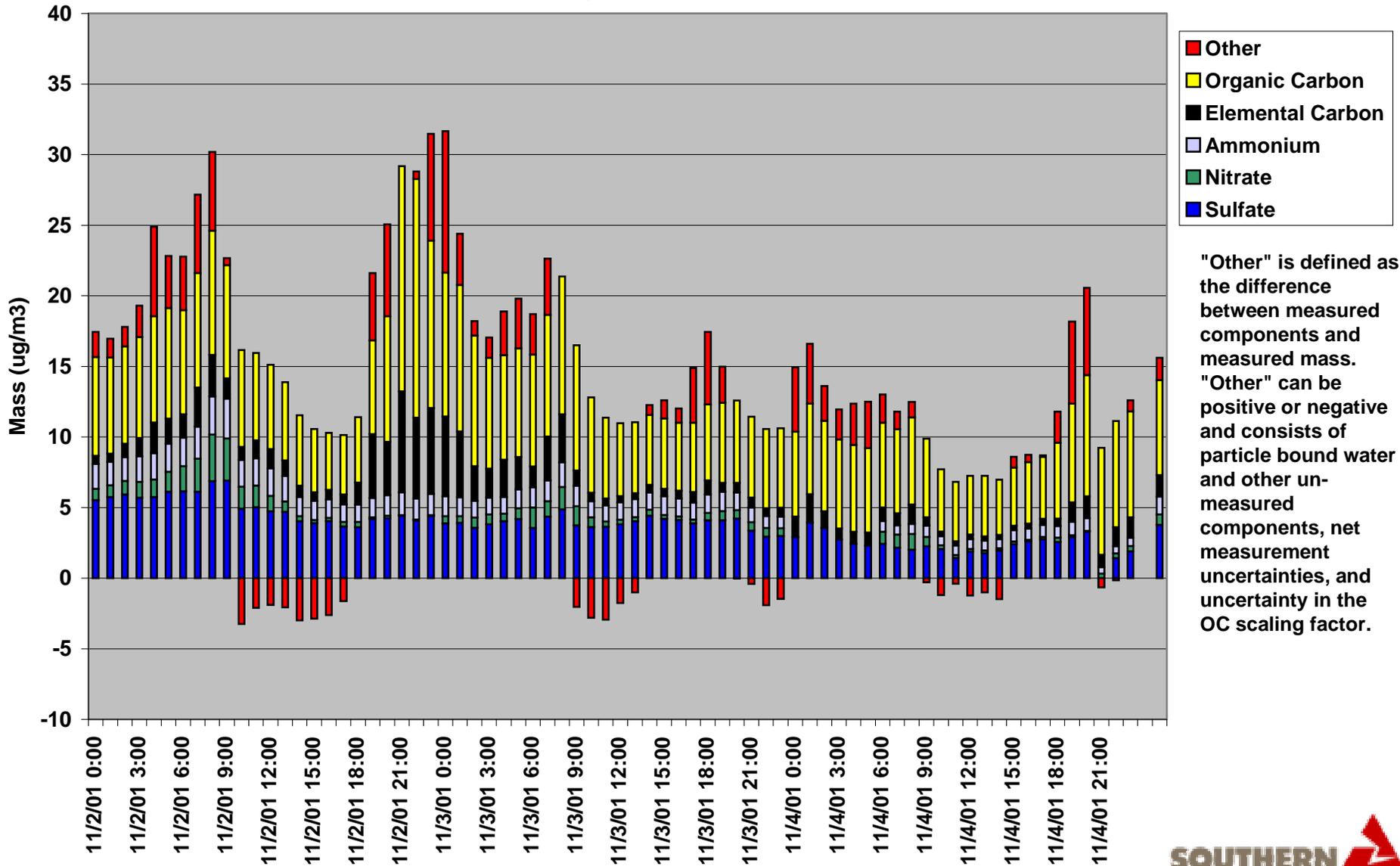
SEARCH Continuous Methods Update

SEARCH Continuous Trace Gas and Particle Measurements

<u>Species</u>	<u>Method</u>	<u>Time Resolution</u>	<u>Status</u>
O3, NO, NO _y , SO ₂ , NO ₂ , CO	various	1-minute	commercialized
HNO ₃	denuder diff.	1-minute, 60-minute	routine
NH ₃ /TRN	cat. oxid. To NO	< 60-minute	drawing board
PM _{2.5} Mass	TEOM, dry, 30C	5-minute	commercialized
PM _{coarse} Mass	TEOM, dry, 30C	5-minute	developmental
Part. Black Carbon	optical absorption	5-minute	commercialized (aethalometer))
Part. Carbon	combustion to CO ₂	60-minute	commercialized
Part. SO ₄	reduction to SO ₂	5-minute	modified Harvard approach
Part. NO ₃ /NH ₄	cat. red./ox. to NO	5-minute	ARA

Reconstructed Mass

Reconstructed Mass at Jefferson Street, Atlanta, GA 11/2-4/01



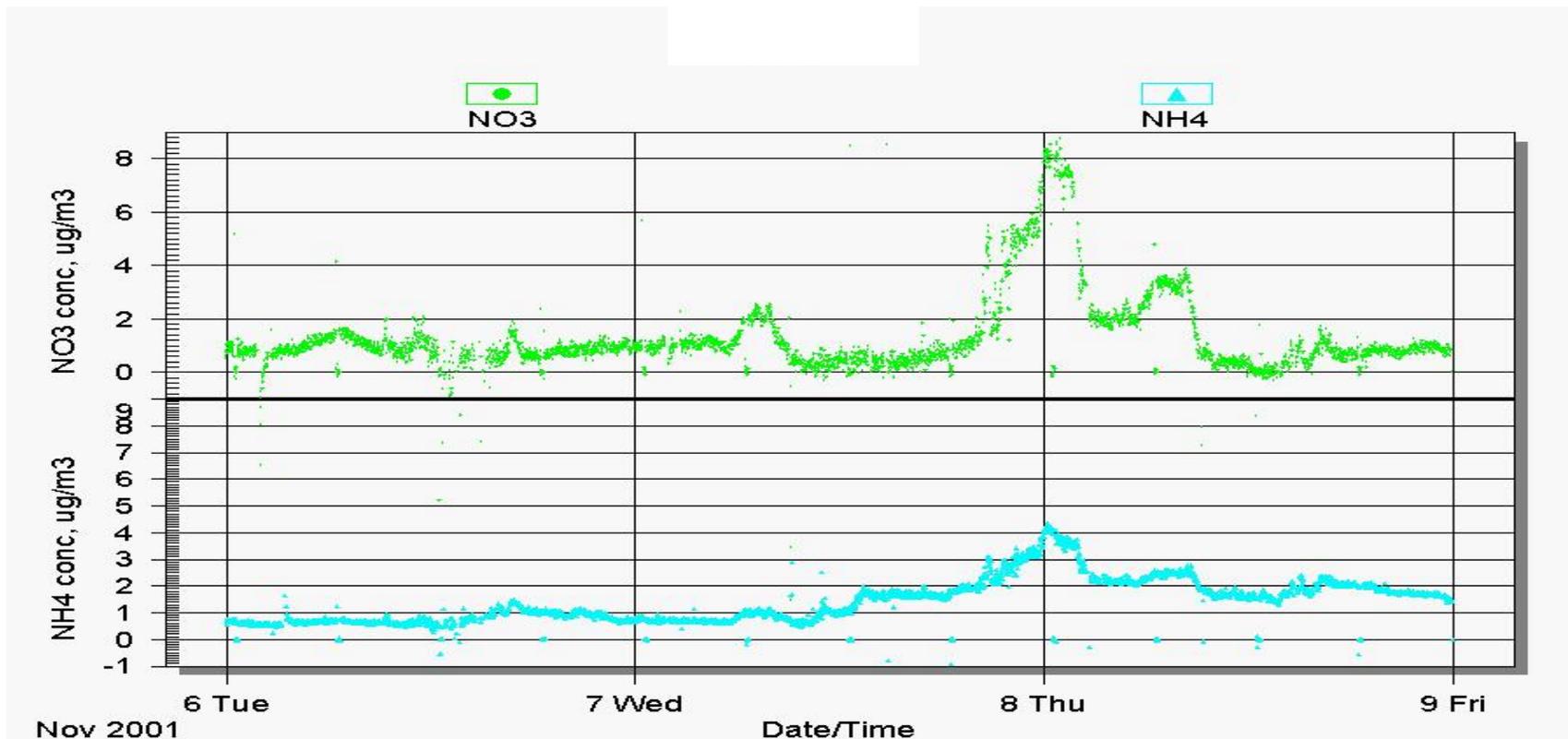
"Other" is defined as the difference between measured components and measured mass. "Other" can be positive or negative and consists of particle bound water and other un-measured components, net measurement uncertainties, and uncertainty in the OC scaling factor.

Formation Processes (Secondary Aerosol)

Gas-Particle Equilibrium

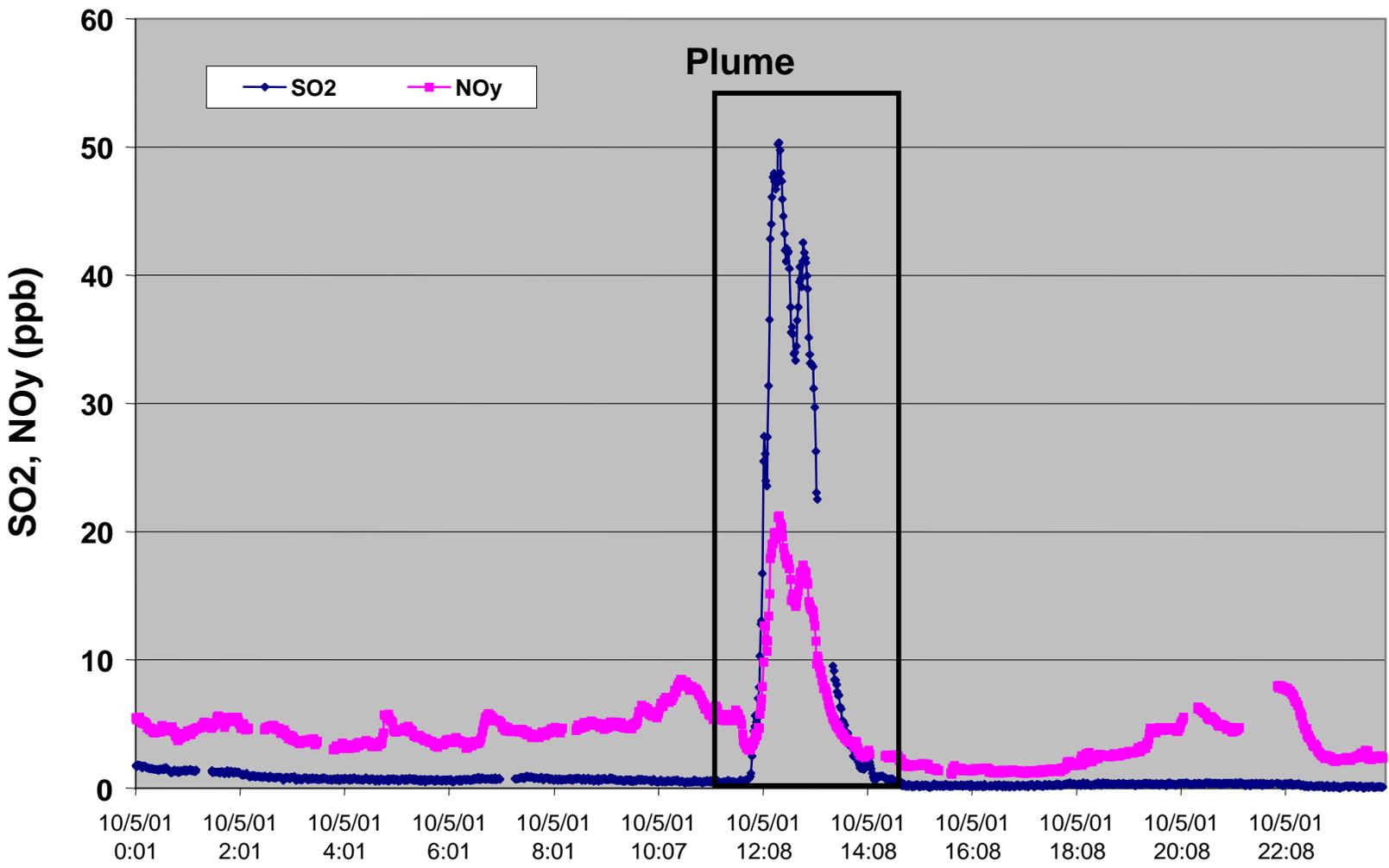
Photochemical Oxidation

Particulate NO_3 and NH_4 Yorkville, GA 11/6-8/01



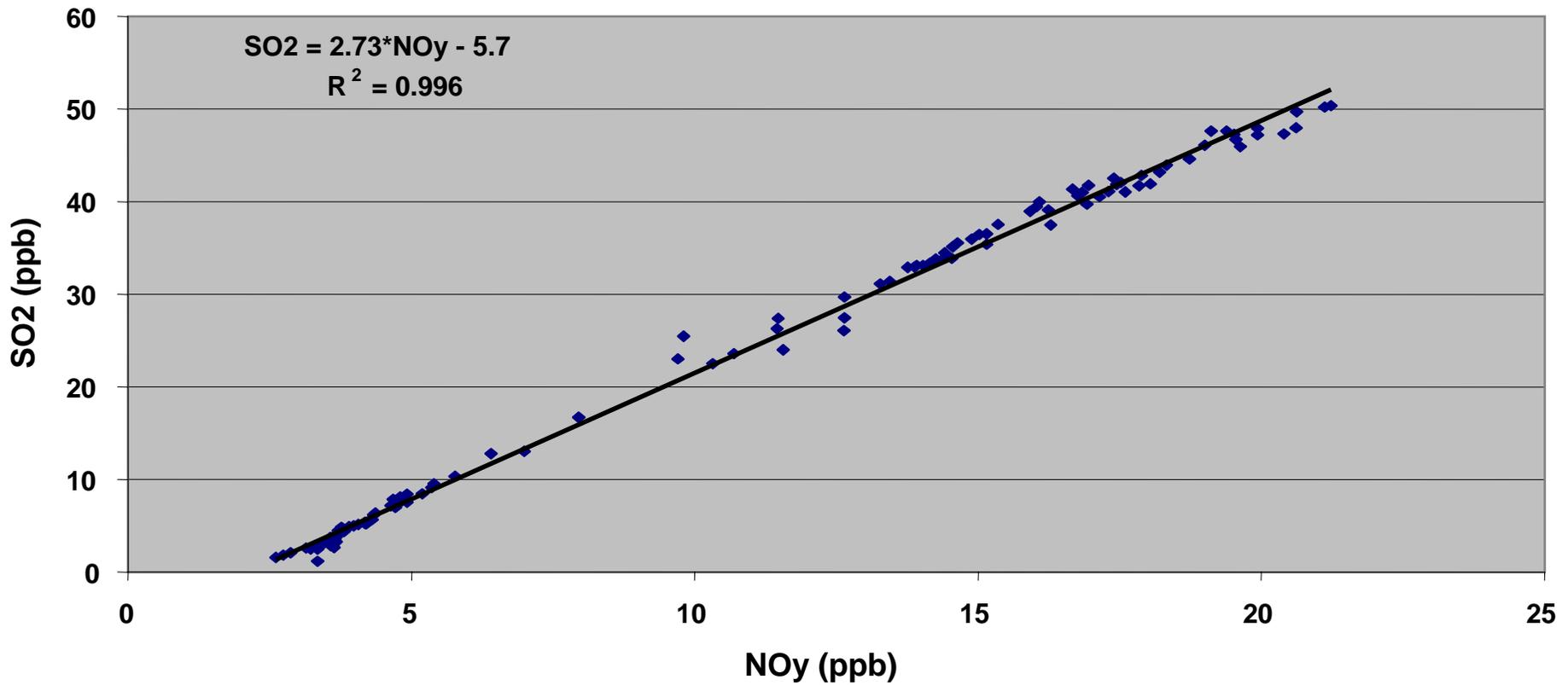
Mixing of Rural (NH_3) and Urban Pollutants (HNO_3) can Produce High Concentrations of Particulate Nitrate and Ammonium

Sulfate Production in a Point Source Plume Yorkville,GA 10/5/01



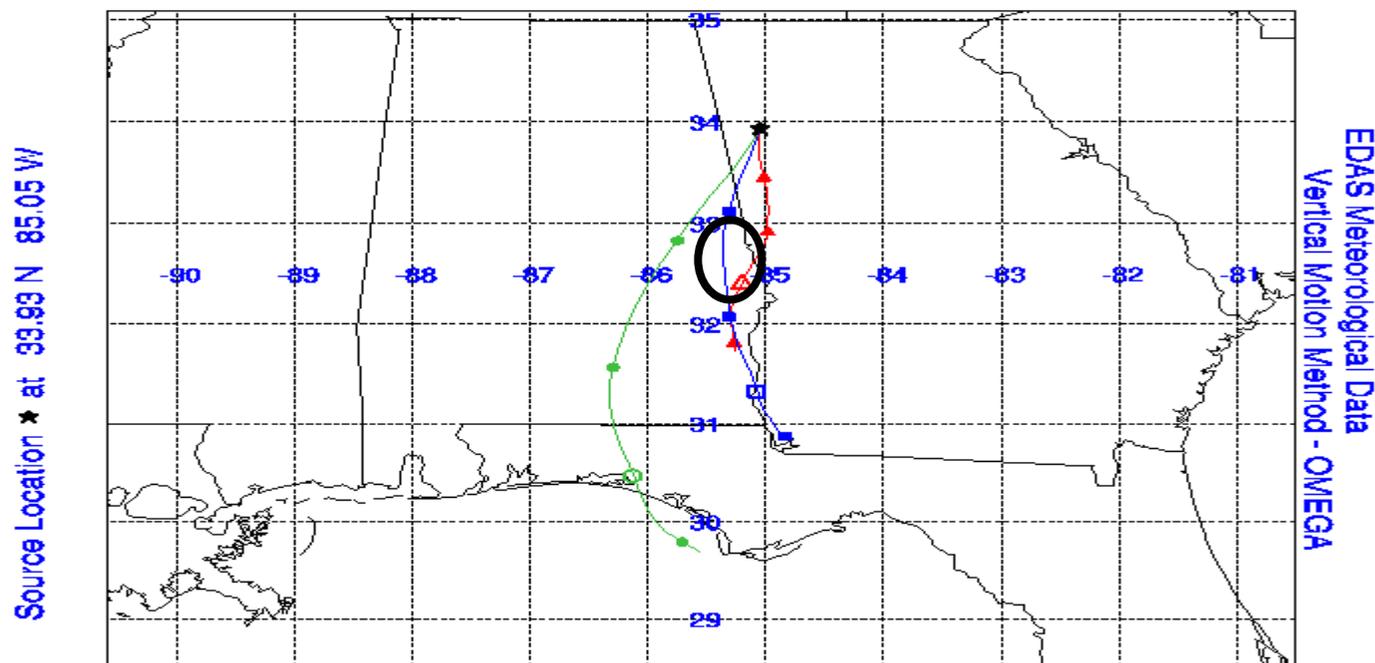
SO2 vs. NOy

10/5/01 Event, Yorkville, GA



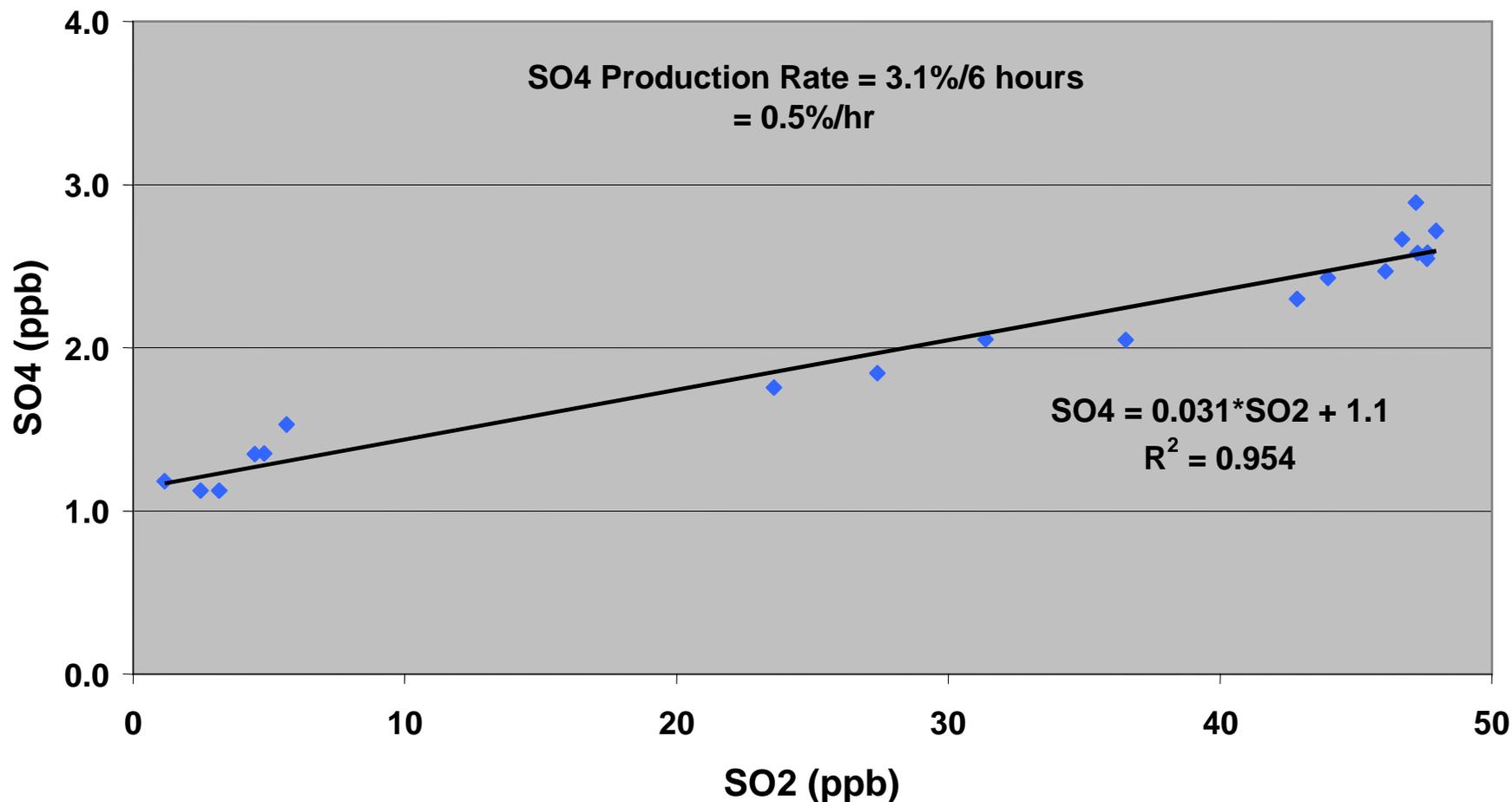
SO2/NOy Relationship Bears Signature of Known Point Sources SW of Yorkville

NOAA Trajectory Calculation



Back Trajectory Shows Air Mass Passed Near 1 or More Points Sources About 6 Hours Prior to Arrival at YRK

Sulfate Production Based on Relationship With SO₂ and Transit Time



Sulfate was Produced at a Rate of 0.5% per Hour in This Late Fall Event.

Emissions Estimates

Emission Factor Calculations

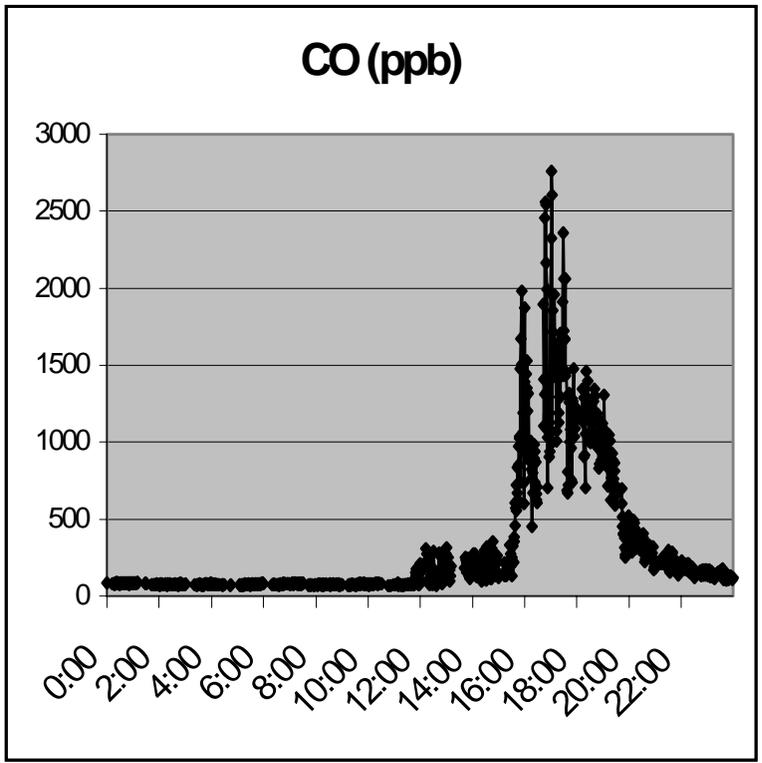
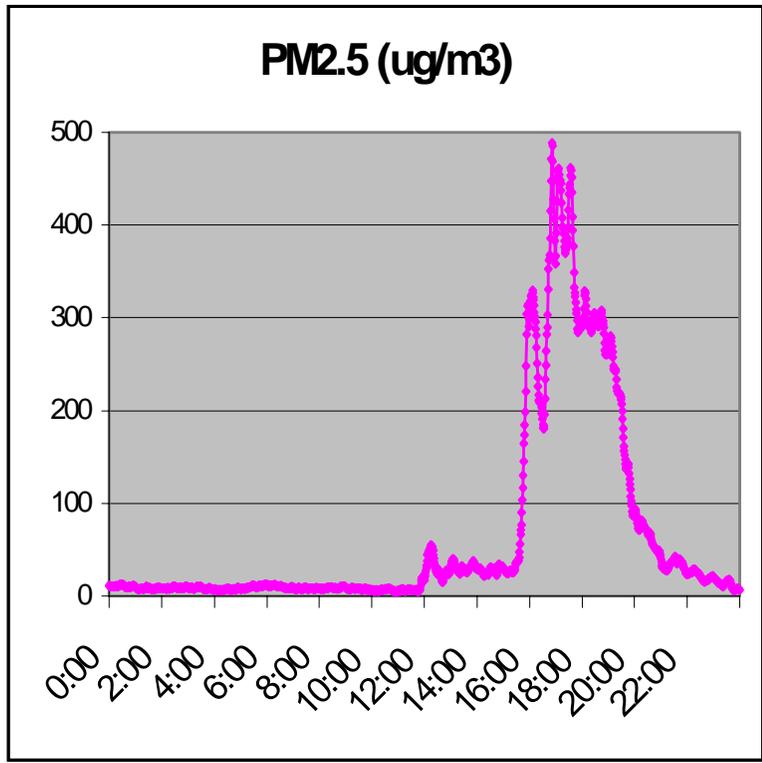
$$EF = \frac{[x]_{\text{event}} - [x]_{\text{background}}}{[\text{tracer}]_{\text{event}} - [\text{tracer}]_{\text{background}}}$$

where tracer is abundant and stable (e.g., CO).
EF expressed in units of ppb/ppm for gases and
ug-m⁻³/ppm for particulate species

Extreme Events

- ◆ Oak Grove – January 31, 2002
- ◆ FRM Mass – 67.1 ug/m³
- ◆ 24-Hour TEOM Mass – 66.2 ug/m³
- ◆ Site Operator Reports Wood Smoke

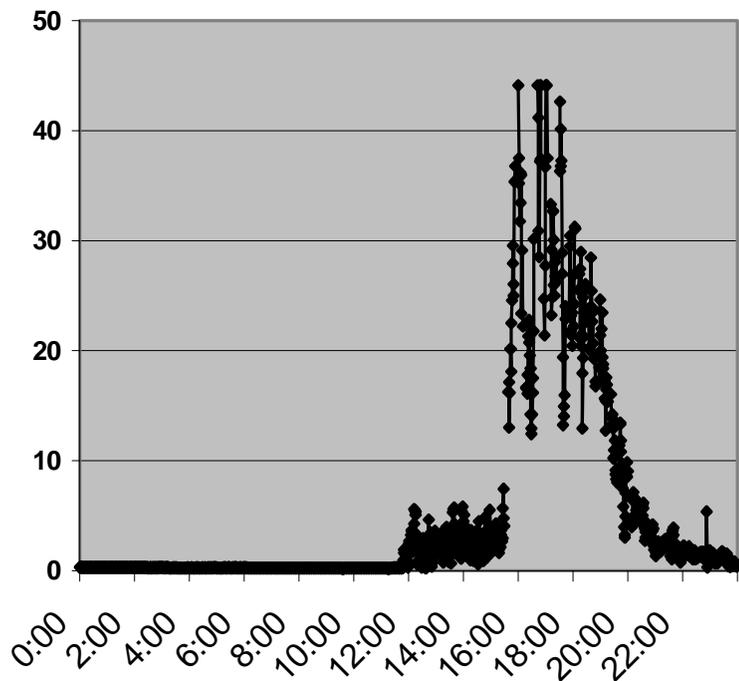
Time Series of PM2.5 and CO Oak Grove 1/31/02



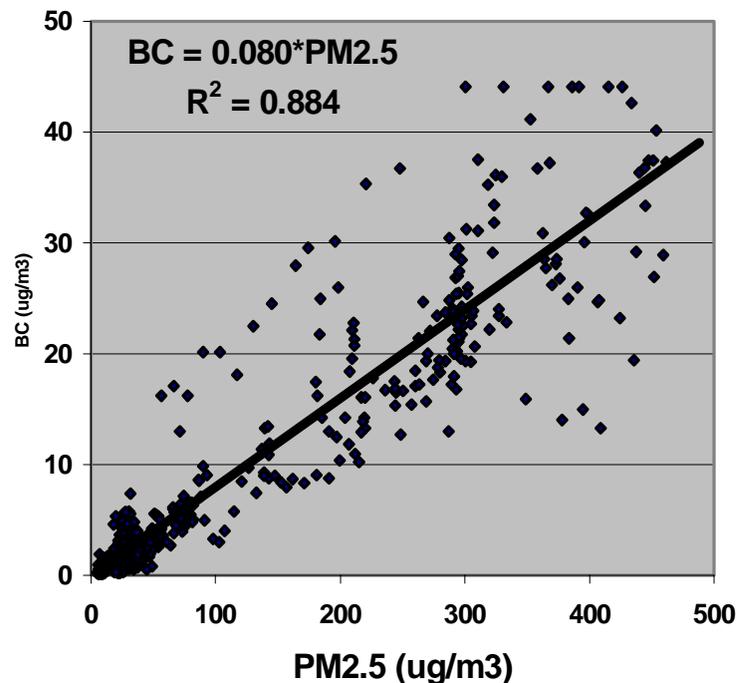
PM2.5 Increases Dramatically at 1600. CO Tracks PM2.5, Suggesting a Combustion Source.

Continuous Black Carbon Oak Grove 1/31/02

Black Carbon (ug/m3)



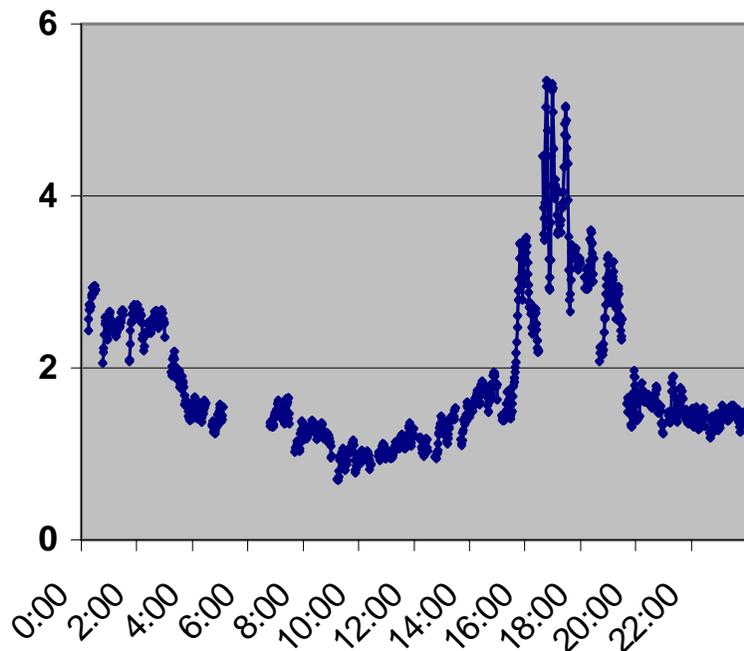
BC vs. PM2.5



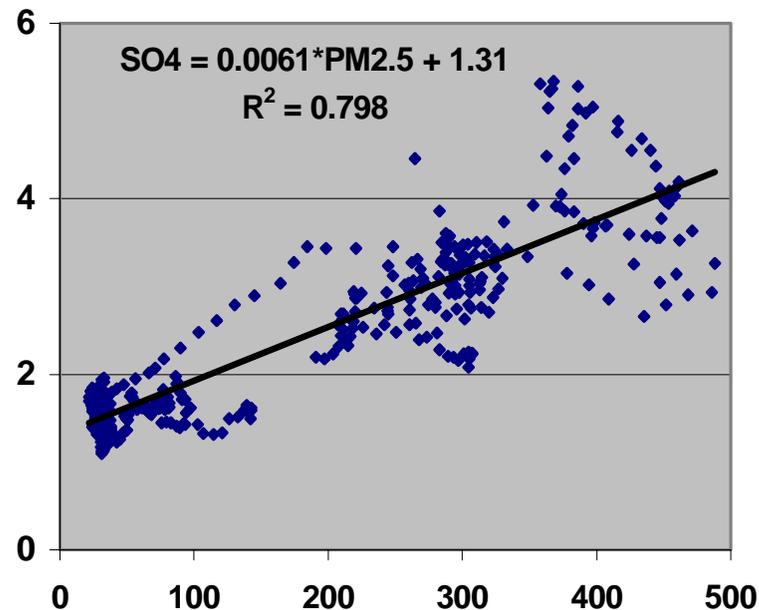
Black Carbon Tracks with PM2.5 and Represents About 8% of Incremental Mass, also Indicative of a Combustion Source.

Continuous SO4 Oak Grove 1/31/02

Continuous SO4 (ug/m3)



SO4 vs. PM2.5



SO4 also Tracks with PM2.5, but Represents Less than 1% of Incremental Mass.

Oak Grove Event

- ◆ Gas and Particle data together are diagnostic of biomass burning
- ◆ Continuous Speciation Data Suggest
 - 8% Black Carbon
 - <1% SO₄
 - <1 % NO₃
 - 2% NH₄
 - >85% Organic Matter, Water and Trace Elements

SEARCH Continuous Measurements Summary

- ◆ Methods Deployed for Mass and Major Components
- ◆ Significant (Real) Variability on all Time Scales
- ◆ Need Continuous Data to Understand Sources and Formation of PM_{2.5}
- ◆ Models Need to Replicate Observed Variability to be Reliable

SEARCH PM2.5 Primary Organic Carbon Source Identification

Zheng, Cass, Schauer, and Edgerton

**“Source Apportionment of PM2.5 in the
Southeastern United States Using Solvent-
Extractable Organic Compounds as Tracers”**

**Accepted for publication in Environmental, Science,
& Technology**

SEARCH PM2.5 Primary Organic Carbon Source Identification

◆ Investigators

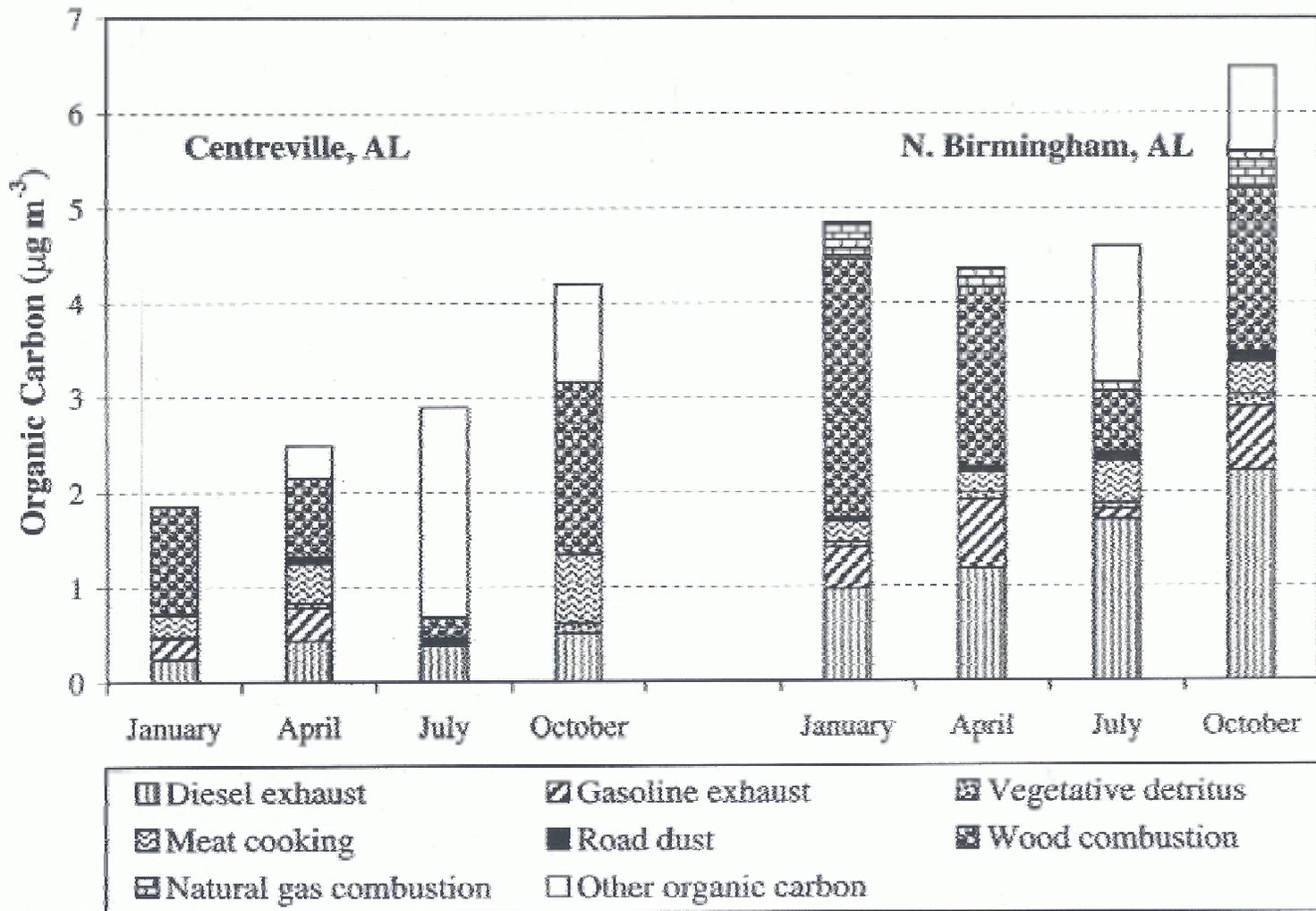
- Dr. Glen Cass
- Ms. Mei Zheng

◆ Description

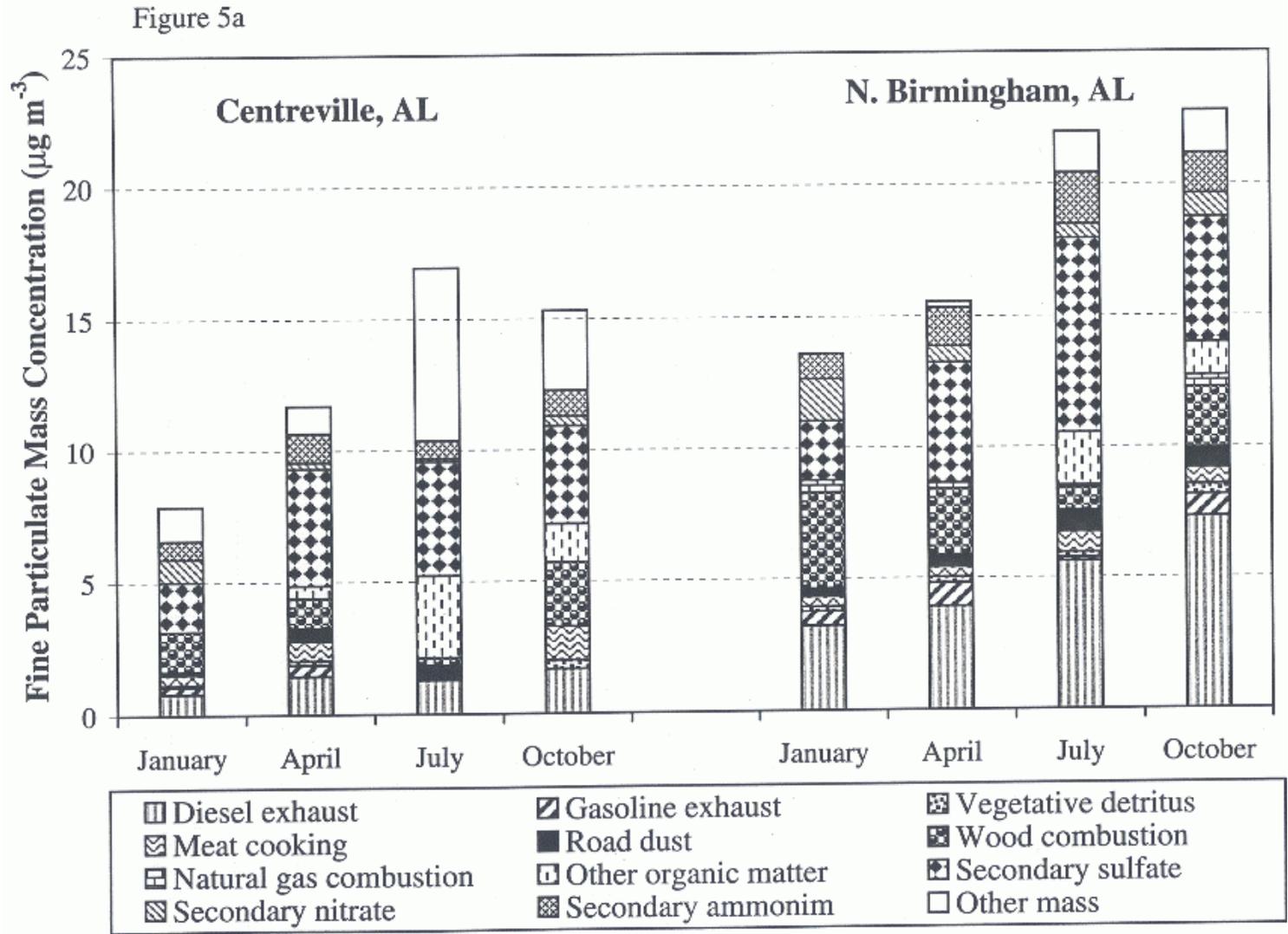
- Analyze one-month composite for each season at 8 **SEARCH** sites for primary organic carbon source tracers
- Estimate fractional contribution using receptor modeling technique

Source Contributions to Organic Carbon in Fine Particles

Figure 3a



Source Contributions to Fine Particle Mass Concentration



SEARCH PM_{2.5} Primary Organic Carbon Source Identification Future Work

- ◆ Extend Spatially (ASACA, FAQs, EUS)
- ◆ Extend Temporally (Daily, July 2001)
- ◆ Extend to PM_{coarse}, if possible
- ◆ EUS Work to be Done in Cooperation with EPA (July 2001, January 2002)

SEARCH Conclusions

SEARCH Conclusions

- ◆ Based on three years of data:
 - BHM, JST & YRK exceed annual standard
 - YRK would not exceed if blank correction were applied
 - No site exceeds daily standard (but occasional readings > 65 ug/m³)
- ◆ Initial EPA PEP results in SE suggest differences between FRM manufacturer
- ◆ Under **FRM Equivalent** Assumptions (representing what's on **FRM** filter):
 - ◆ Organic matter exceeds sulfate in urban areas
 - ◆ Sulfate exceeds or is equivalent to organic matter in rural areas
 - ◆ Total carbon exceeds sulfate at all sites
- ◆ Under **Best Estimate** Assumptions (representing what is in atmosphere):
 - ◆ Organic matter exceeds sulfate at all sites

SEARCH Conclusions

- ◆ Carbon is important at many urban sites across the U.S.
- ◆ Most of the urban-rural difference in PM_{2.5} is explained by differences in carbon
- ◆ Carbon is an important component of Pmcoarse
- ◆ Continuous mass and speciation monitors are important:
 - ◆ for describing the substantial diurnal and day-to-day variability of PM_{2.5} composition,
 - ◆ for understanding sources,
 - ◆ for understanding processes leading to PM_{2.5} formation, and
 - ◆ to provide rigorous constraints for models.
- ◆ Primary OC appears to dominate over secondary OC in SE
 - Diesel, gasoline, meat cooking, and wood smoke dominate Organic Carbon in the Southeast

Jefferson Street (JST) Atlanta, GA



ARIES
SEARCH
ASACA
MERCURY

SEARCH - Jun. 1998 to Dec. 2005

ARIES - Aug. 1998 to Aug. 2003

ASACA - April 1999 to Dec. 2005

MERCURY - 1-yr 2002

Atlanta Supersite - August 1999

ESP01, ESP02 - July 2001, Jan. 2002

U Minn - August 2002