

# Lessons Learned from **SEARCH**

**GA Air Policy  
Symposium  
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Atlanta, GA**

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# Outline

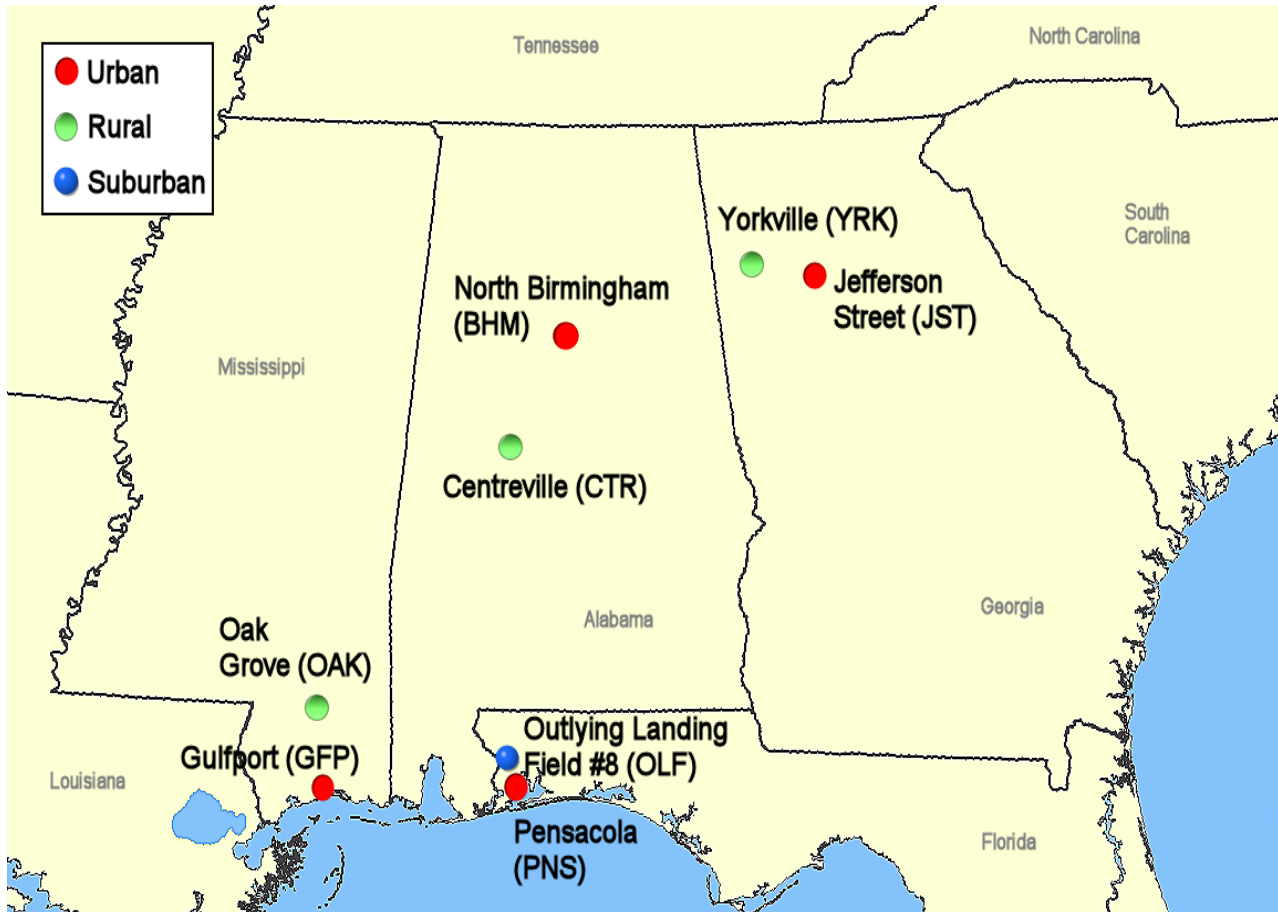
- **SEARCH Background**
- **PM<sub>2.5</sub> Mass and Composition 1999-2004**
- **Carbon Source Matrix**
- **First Look at Ammonia**
- **Atmospheric Mercury**

# SEARCH Objectives

- Develop a PM Climatology for 8 Sites **(7+ years & growing)**
- Understand Composition and its Variability
  - Year to Year, Season to Season
  - Rural vs. Urban
  - Coastal vs. Inland
- Estimate Source Contributions
- Provide Data Sets to Health Researchers and Atmospheric Modelers
- Test and Improve Methods
- Collaborate with States and Others (SuperSites)

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# SEARCH Network



**4 urban-rural pairs in GA, AL, FL and MS**

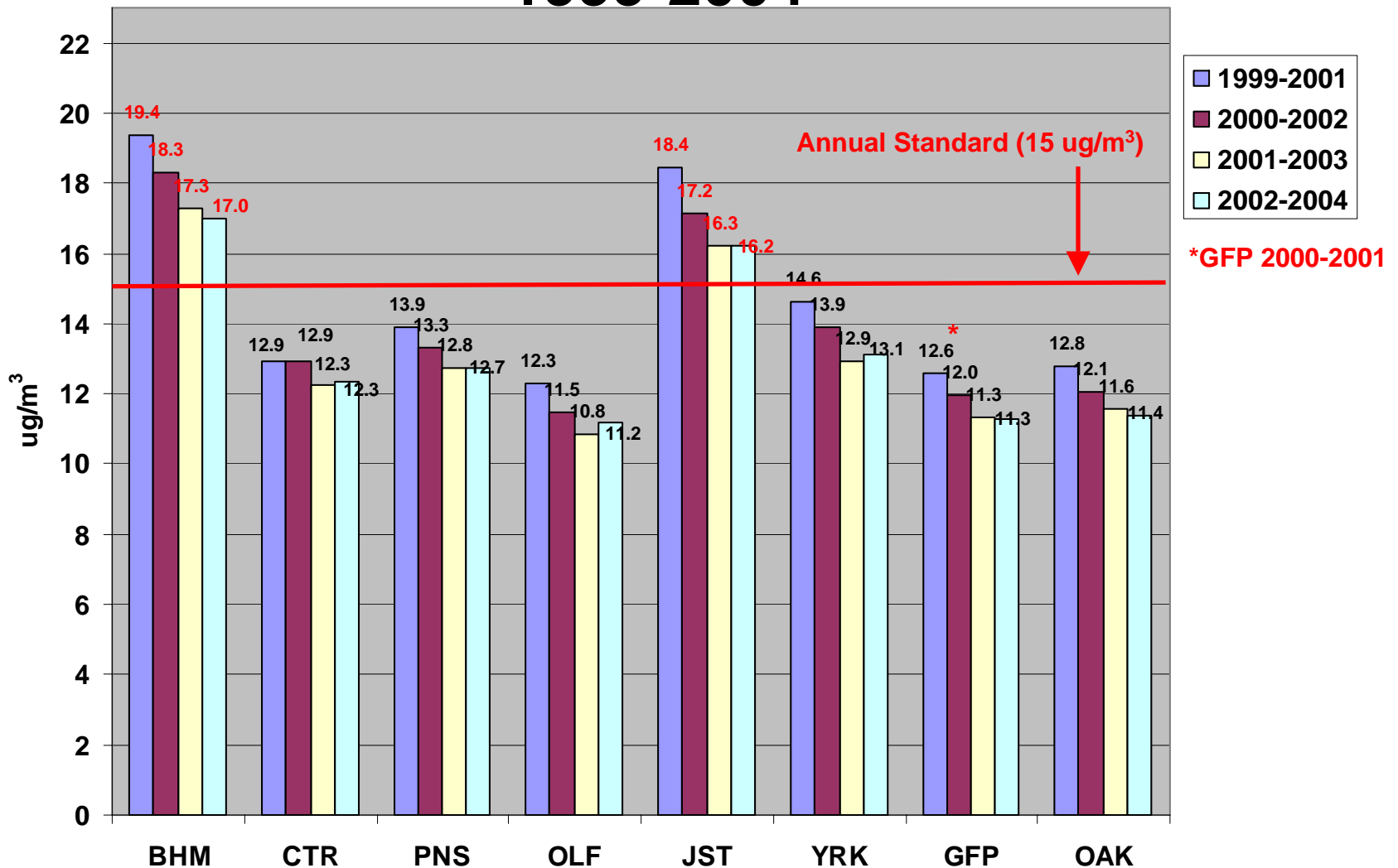
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# SEARCH Measurements

- Discrete Particles and Gases (24-hour)
  - PM<sub>2.5</sub>, PM<sub>10</sub> and Speciation
  - NH<sub>3</sub>, VOCs/OVOCs (>80 compounds, JST only)
- Continuous PM<sub>2.5</sub> (1-min to 1-hr)
  - Dry, 30C TEOM: mass
  - R&P 5400: TC
  - Aethelometer: BC
  - SEARCH/ARA: Ammonium/Nitrate
  - Modified HSPH: Sulfate
  - Nephelometer: light scattering
- Trace Gases (1-min)
  - O<sub>3</sub>, NO, NO<sub>2</sub>, NO<sub>y</sub>, HNO<sub>3</sub>, SO<sub>2</sub>, CO, CO<sub>2</sub>, NH<sub>3</sub> (3 sites)
- Meteorology (1-min)
  - WS, WD, T, RH, BP, SR, rainfall
- Mercury (1-hour): Hg(0), Hg<sub>p</sub>, RGM

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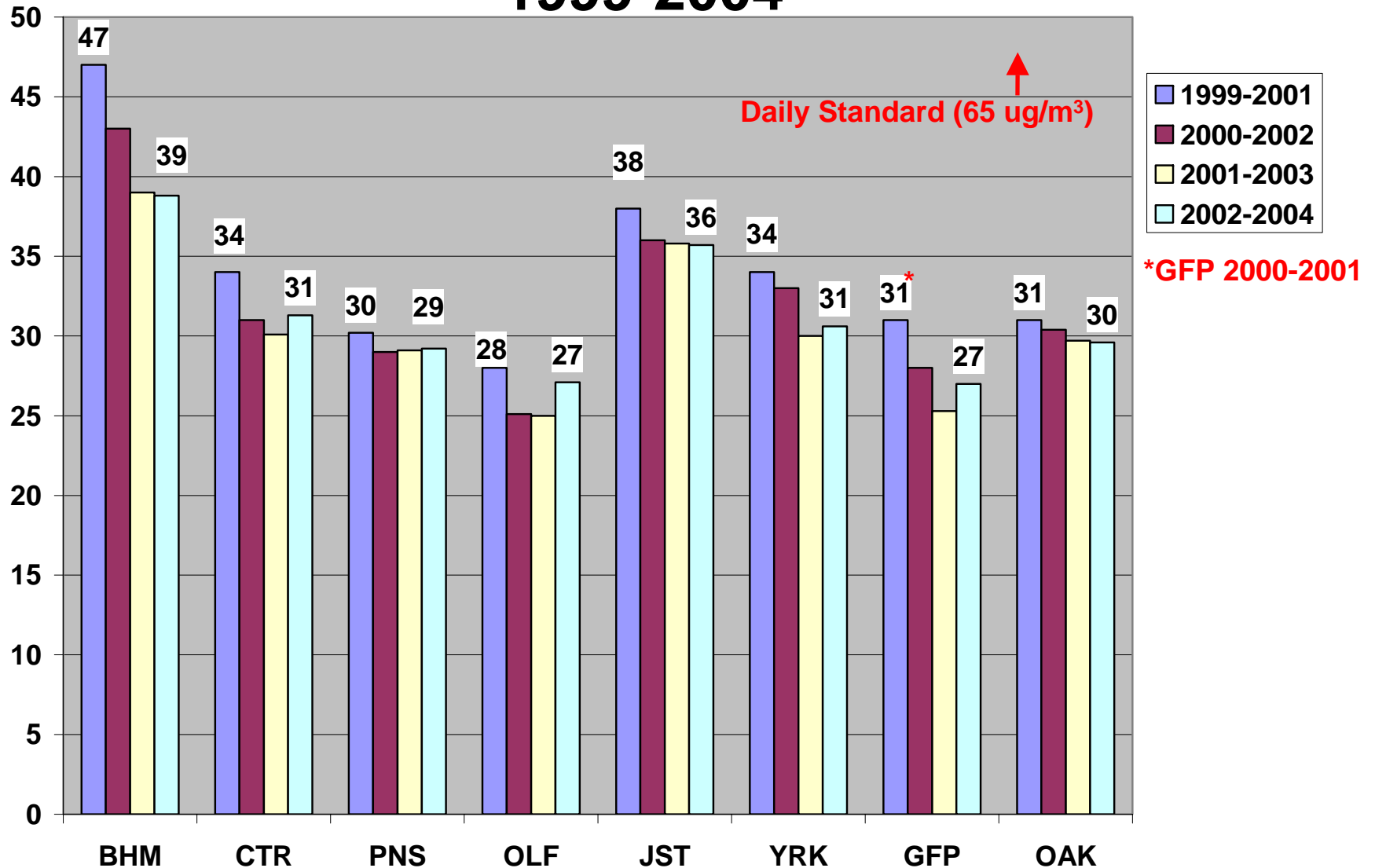
# PM<sub>2.5</sub> Annual Design Values for SEARCH 1999-2004



Annual DVs decline from 1999-2001 to 2001-2004. Only Atlanta (JST) and Birmingham (BHM) violate the Annual NAAQS.

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# PM<sub>2.5</sub> 24-Hour Design Values for SEARCH 1999-2004

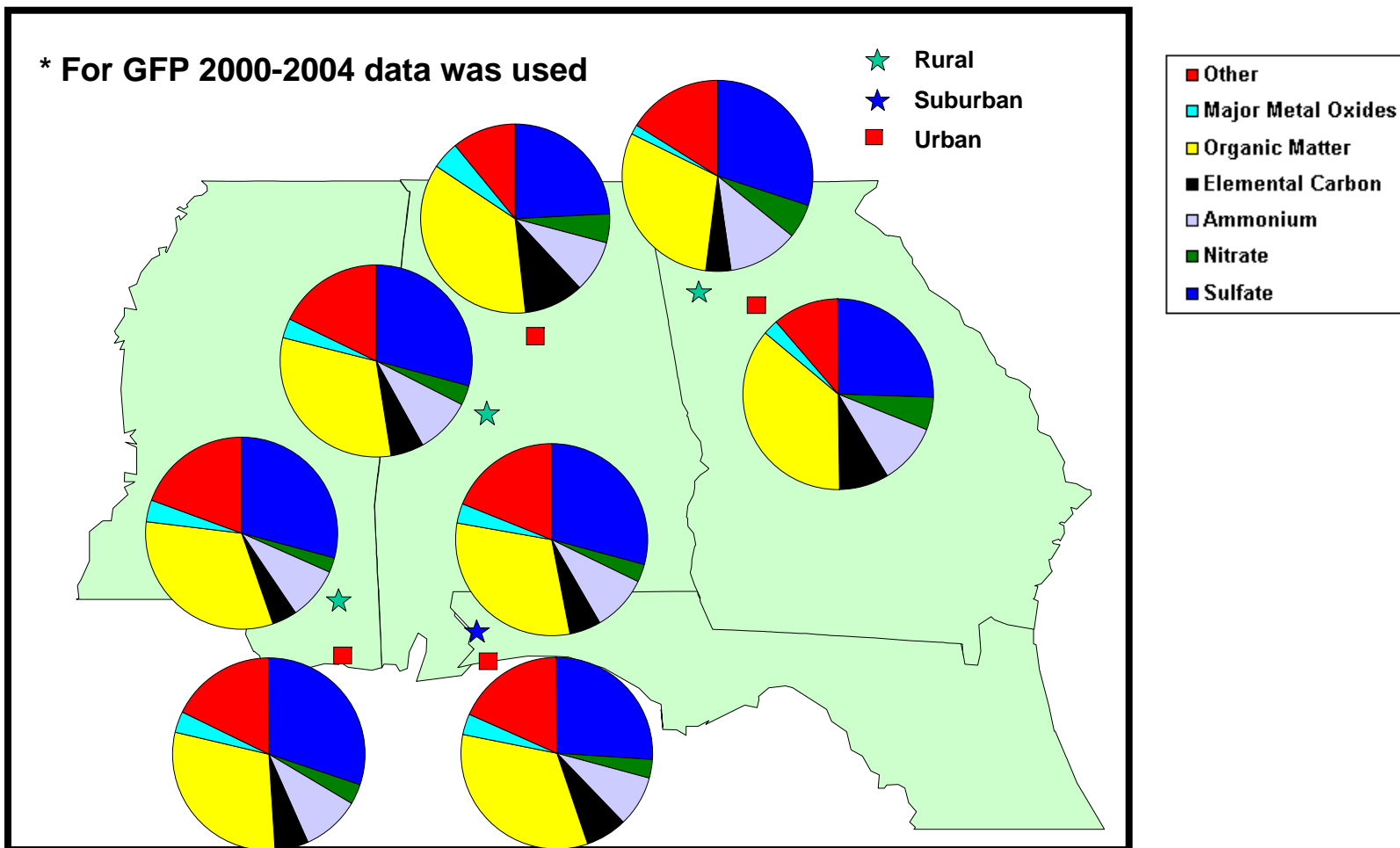


Daily DVs show a declining trend, with some rebound in 2002-2004.

No site violates the Daily NAAQS.

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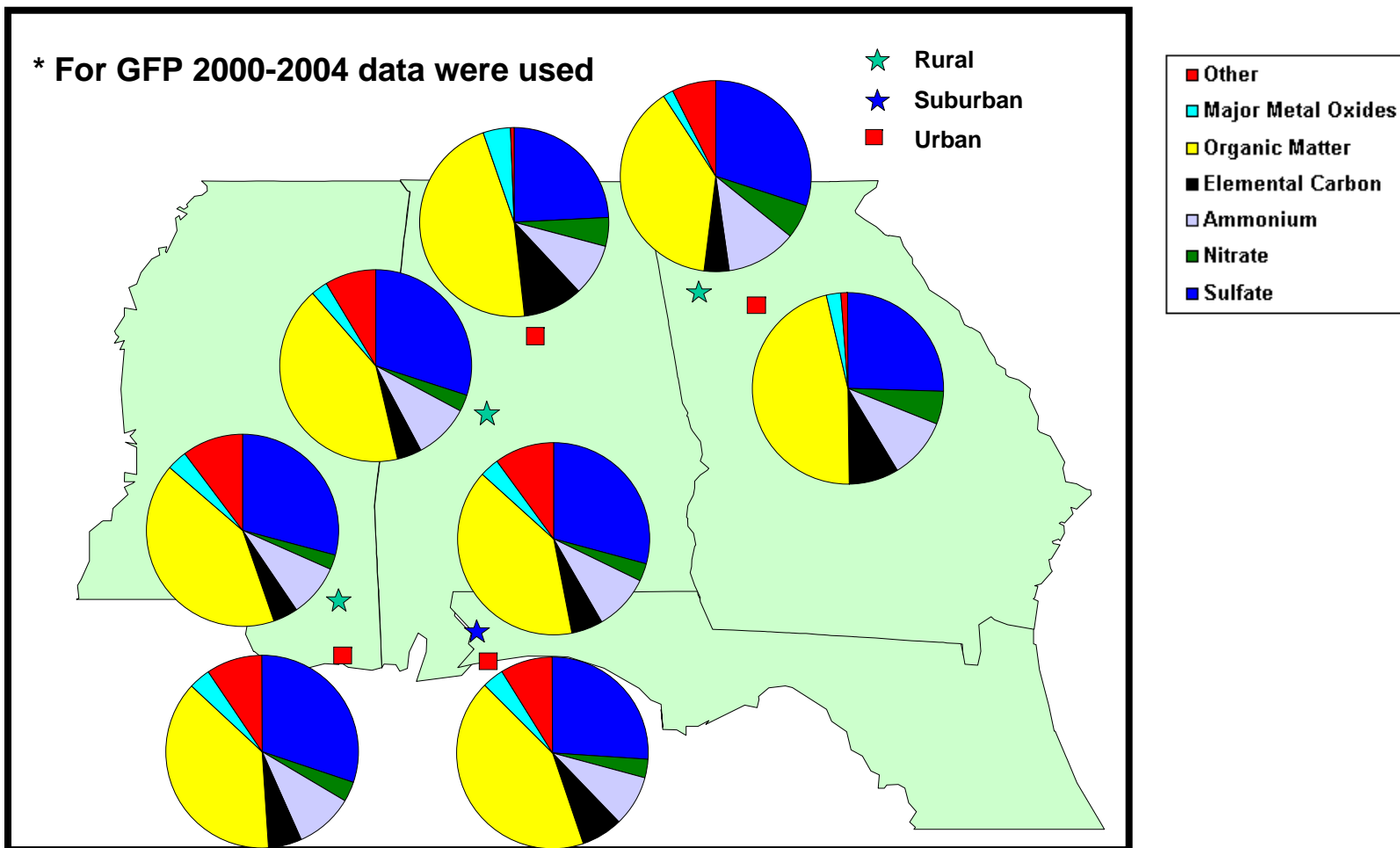
# Best Estimate PM<sub>2.5</sub> Composition at SEARCH Sites (ug/m<sup>3</sup>) 1999-2004\*



Organic matter (OC \* 1.4) and sulfate are the major components of PM<sub>2.5</sub>  
For Best Estimate: Organic matter is the largest component at all sites

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# Best Estimate PM<sub>2.5</sub> Composition at SEARCH Sites (µg/m<sup>3</sup>) using OM = OC\*1.8



Recent evidence suggests a Carbon scaling factor >1.4 may be appropriate. Using 1.8 simply enhances dominance of OM.

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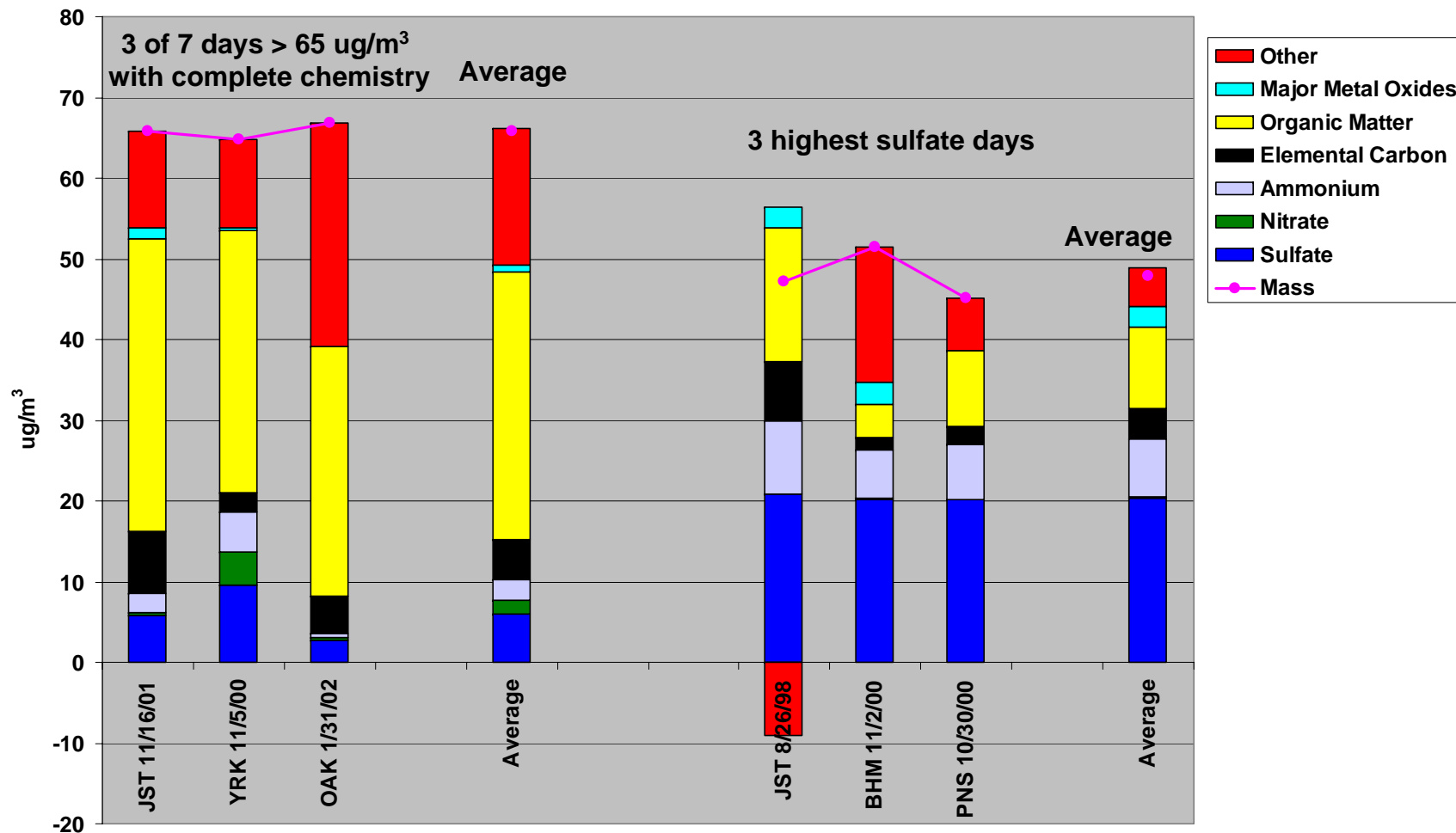
# FRM Equivalent Urban-Rural Differences 1999-2004 ( $\mu\text{g}/\text{m}^3$ )

Site Pair	Urban-Rural Differences							
	PM <sub>2.5</sub>	SO <sub>4</sub>	NH <sub>4</sub>	OM	EC	NO <sub>3</sub>	MMO	Total
BHM/CTR (AL)	5.1	0.6	0.4	2.3	1.4	0.1	0.6	5.4
PNS/OLF (FL)	1.8	0.2	0.1	0.8	0.3	0.0	0.1	1.5
JST/YRK (GA)	3.4	0.3	0.1	2.0	0.9	0.0	0.2	3.5
GFP*/OAK* (MS)	-0.1	0.0	0.1	-0.4	0.1	0.0	0.0	-0.2

Urban-rural increments are driven by OM and EC.

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# Comparison of **FRM Equivalent High Mass** and **High Sulfate Days** at **SEARCH** Sites

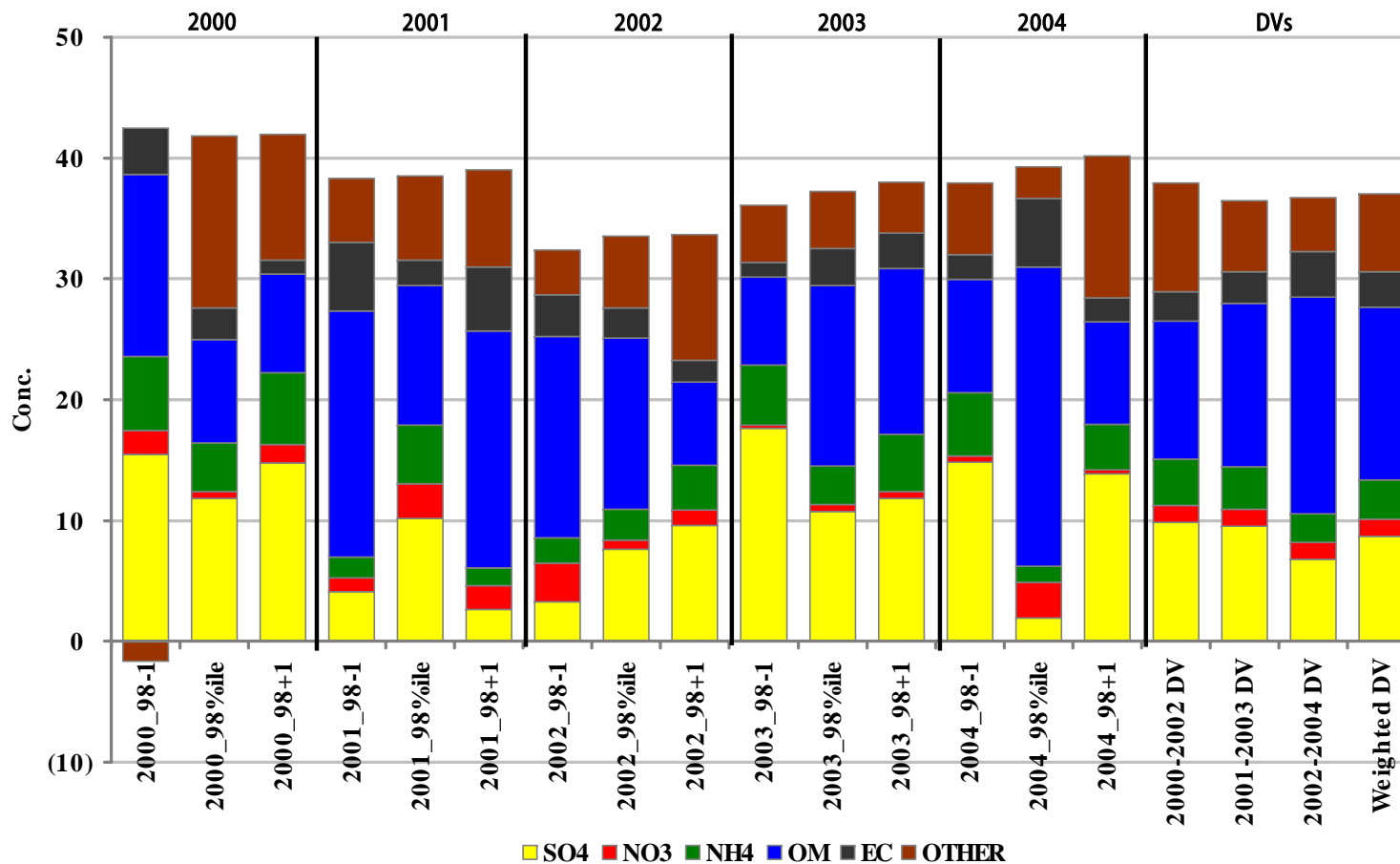


**OM+EC dominates composition on days >65  $\mu\text{g}/\text{m}^3$ . Sulfate never >50% mass on highest sulfate days.**

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# 98<sup>th</sup> %ile Composition at JST

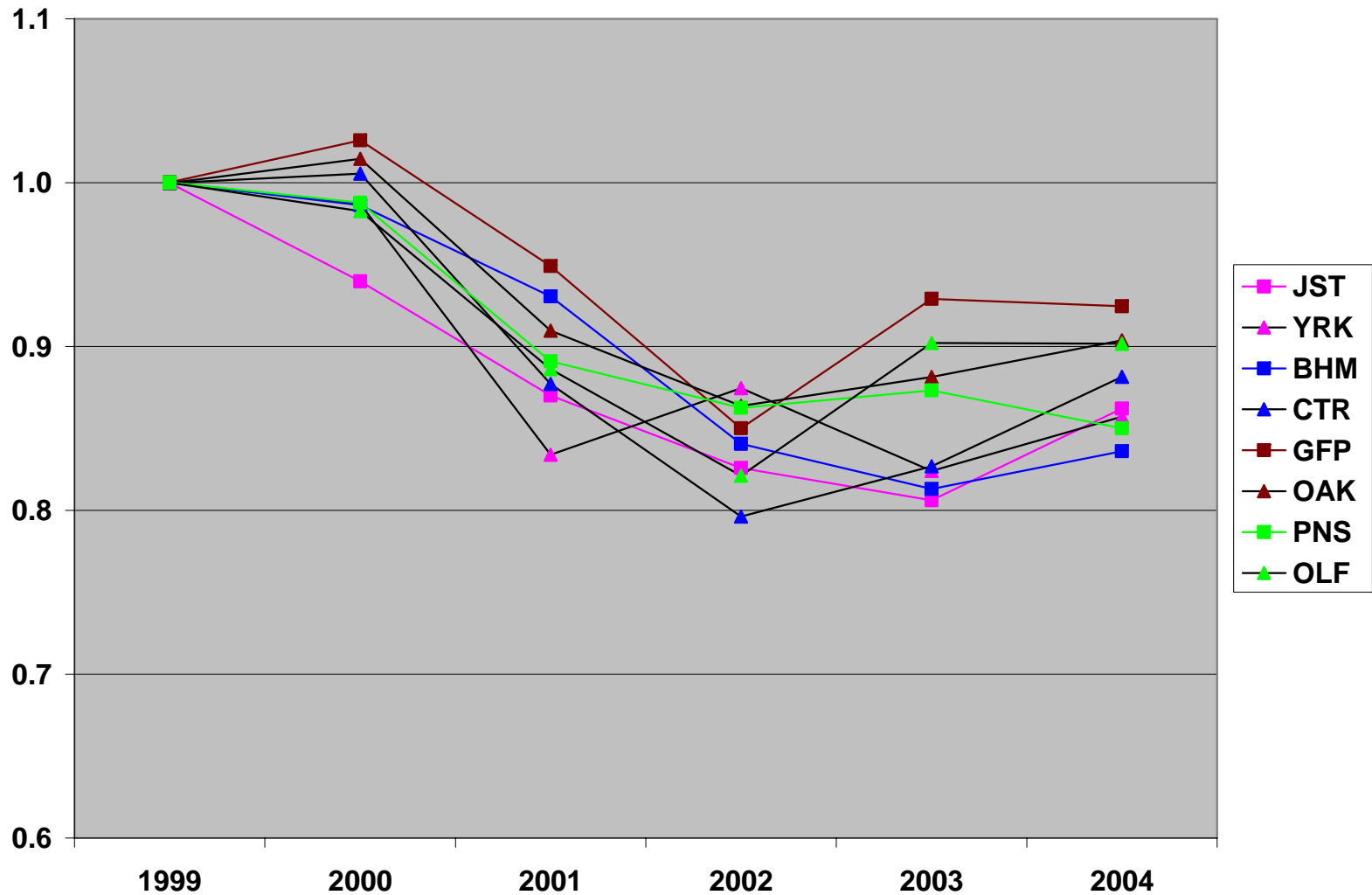
Composition of 98th Percentile Days at JST  
Including Adjacent Days, 3 Three-Year Design Values, and Weighted DV



PM<sub>2.5</sub> composition at the 98<sup>th</sup> %ile highly variable from year to year.

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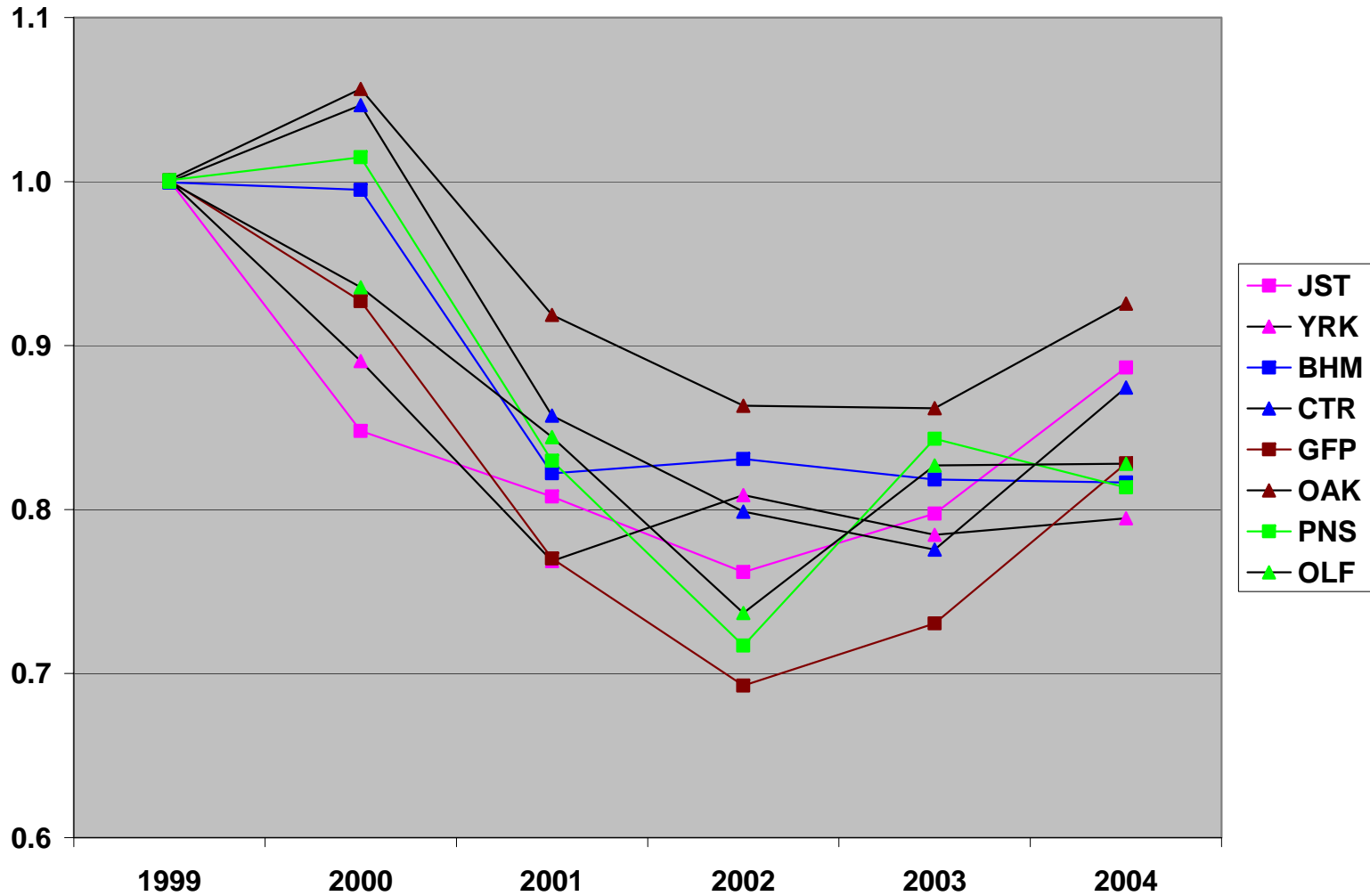
# Normalized PM<sub>2.5</sub> (relative to 1999)



**Year to year variability of PM<sub>2.5</sub> similar, but not identical,  
across SEARCH sites**

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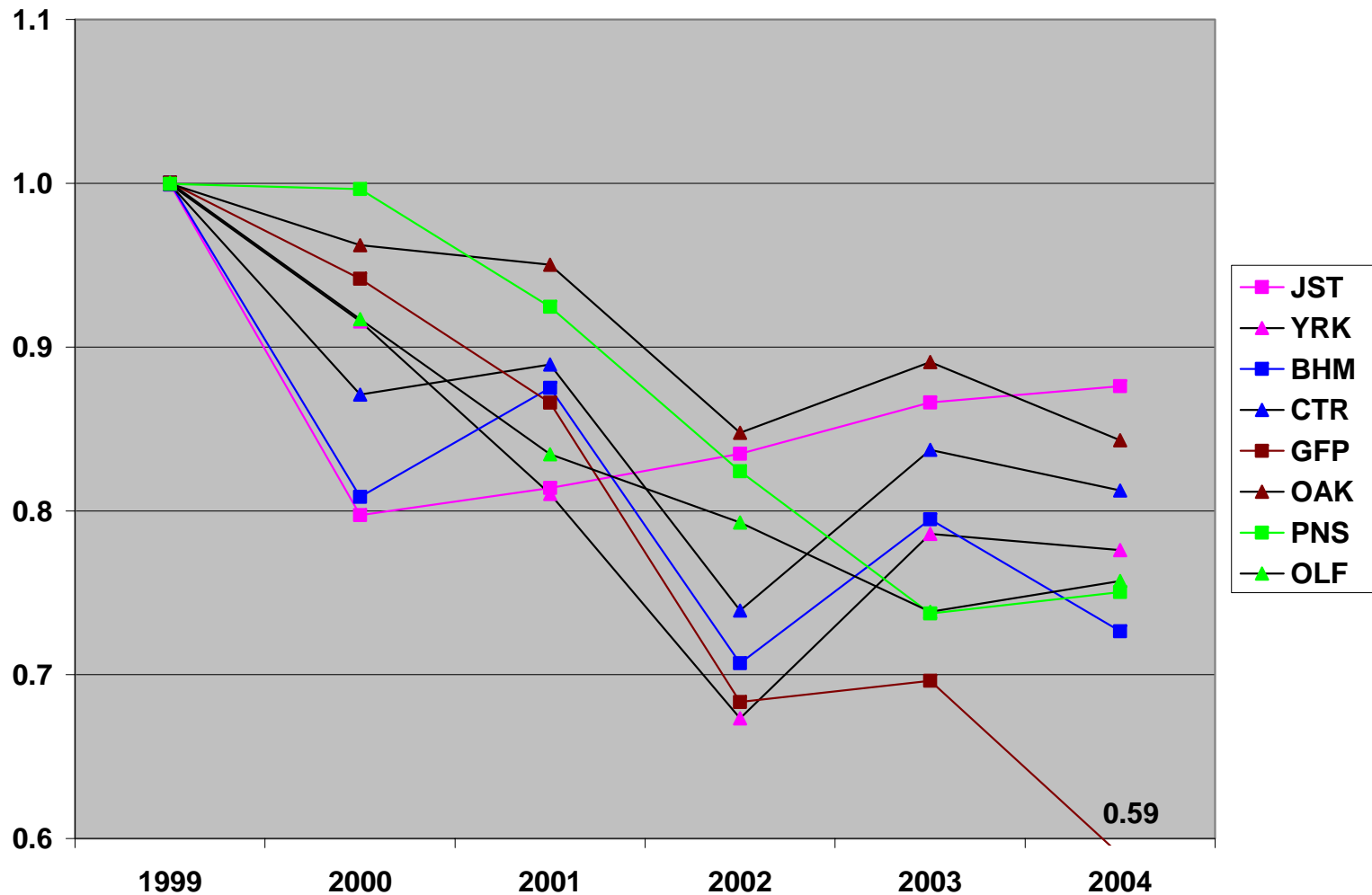
# Normalized $\text{SO}_4^{2-}$ (relative to 1999)



**Sulfate decrease similar to PM<sub>2.5</sub>, but steeper**

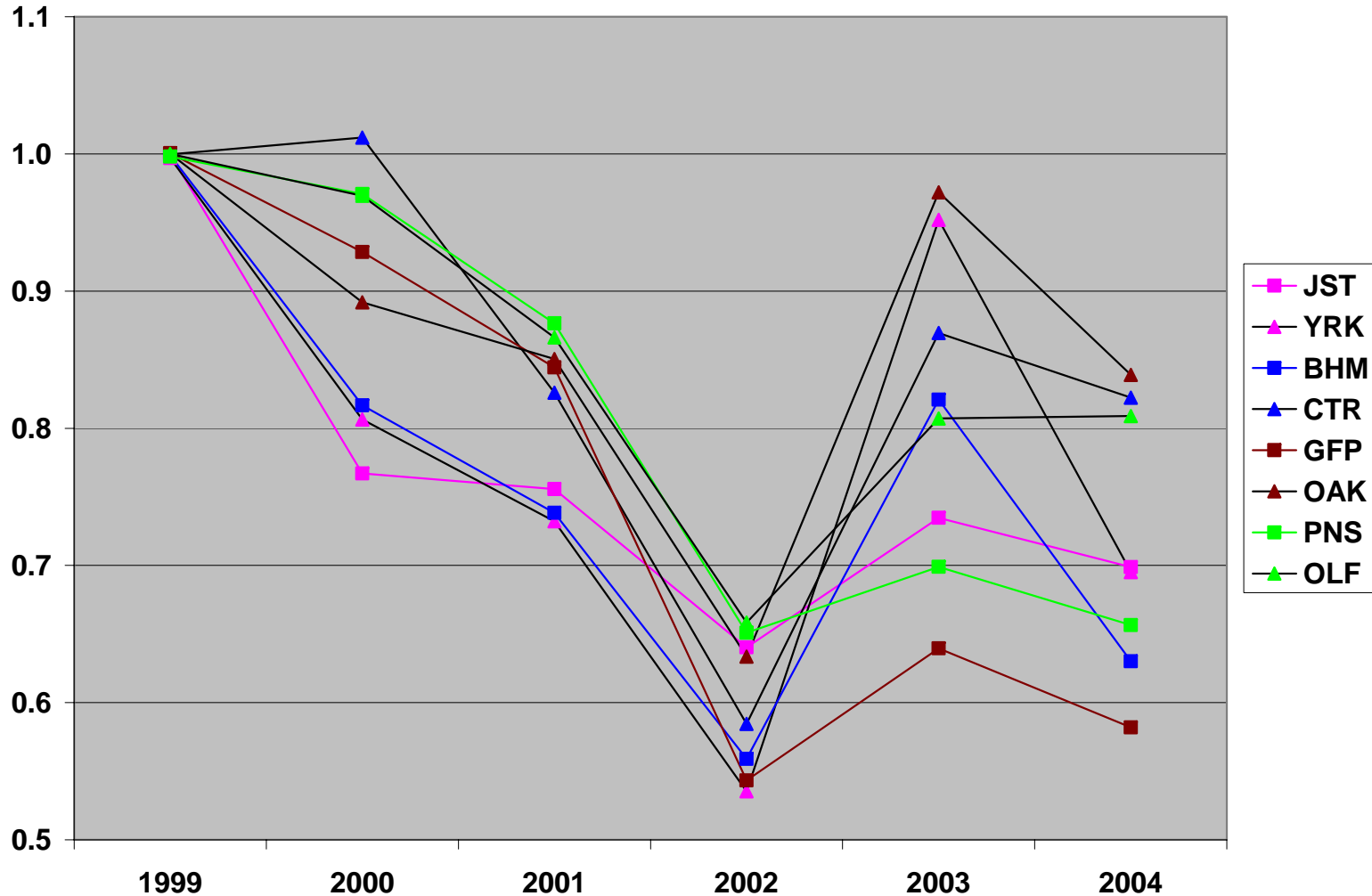
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# Normalized OM (OC\*1.4) (relative to 1999)



OM trend more variable than PM2.5 and sulfate

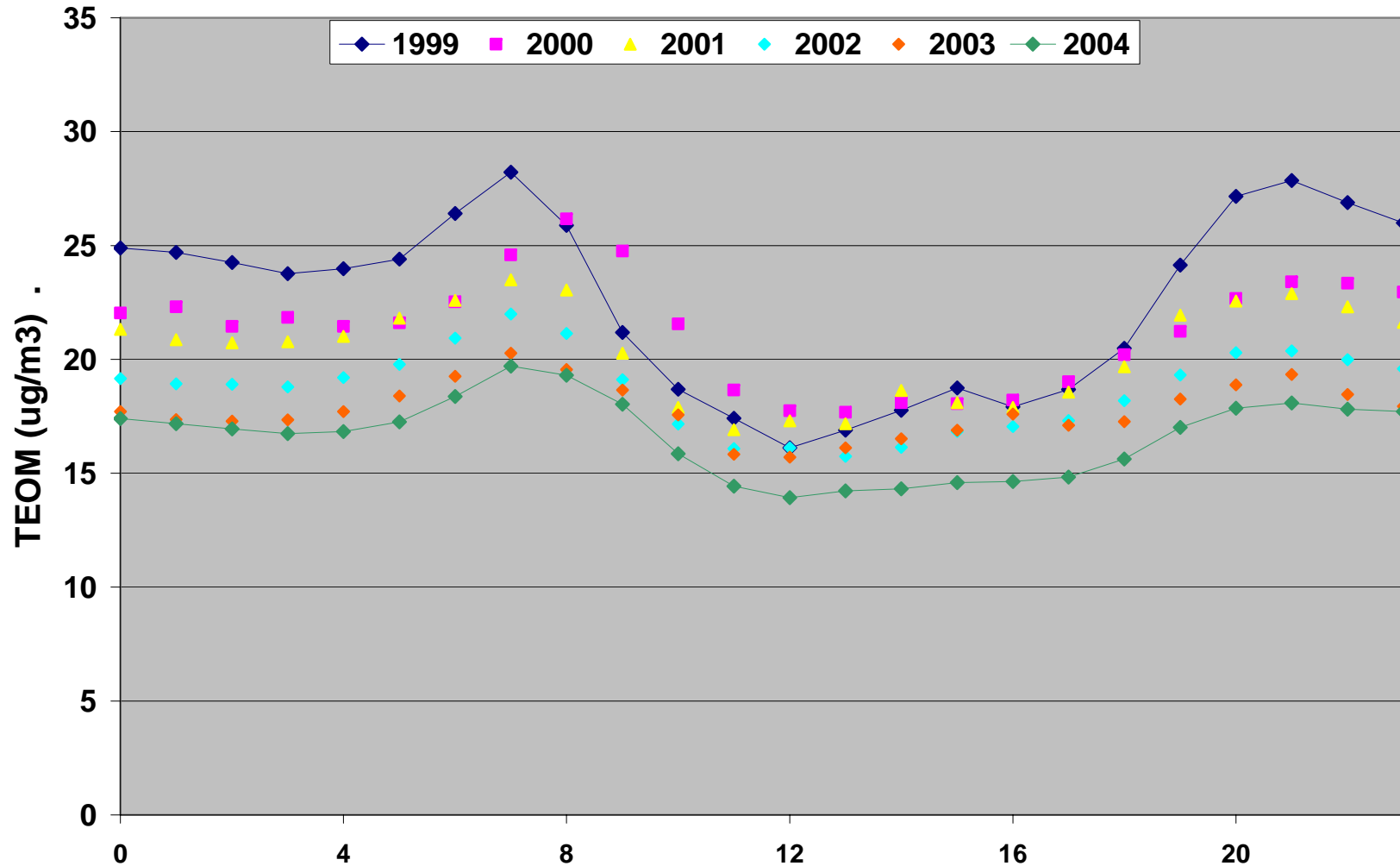
# Normalized EC (relative to 1999)



**EC trend very steep and coherent until 2003 and 2004**

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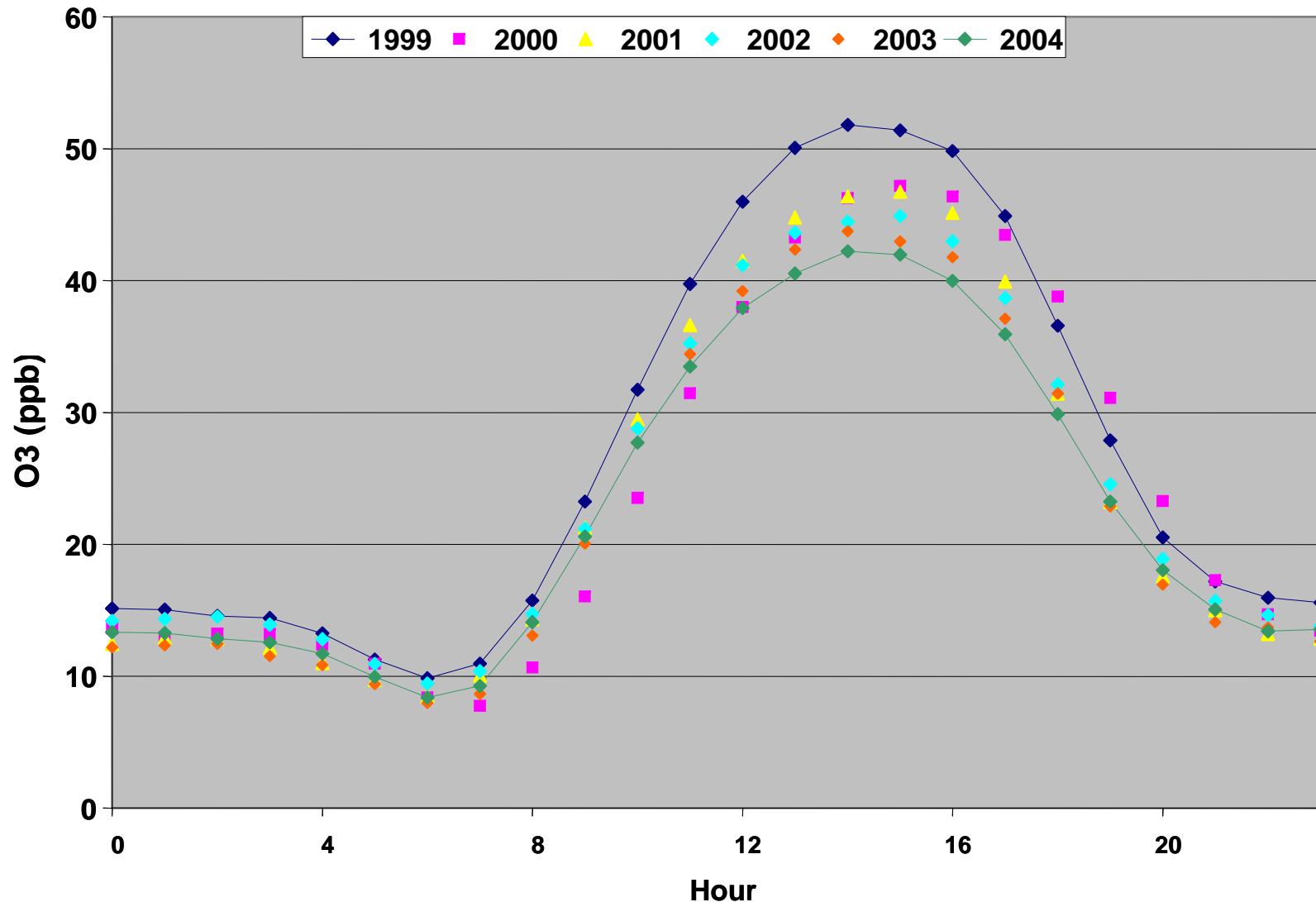
# Composite Diurnal Profile – PM<sub>2.5</sub> JST 1999-2004



Overnight PM<sub>2.5</sub> concentrations have decreased 6-10  $\mu\text{g}/\text{m}^3$  since 1999

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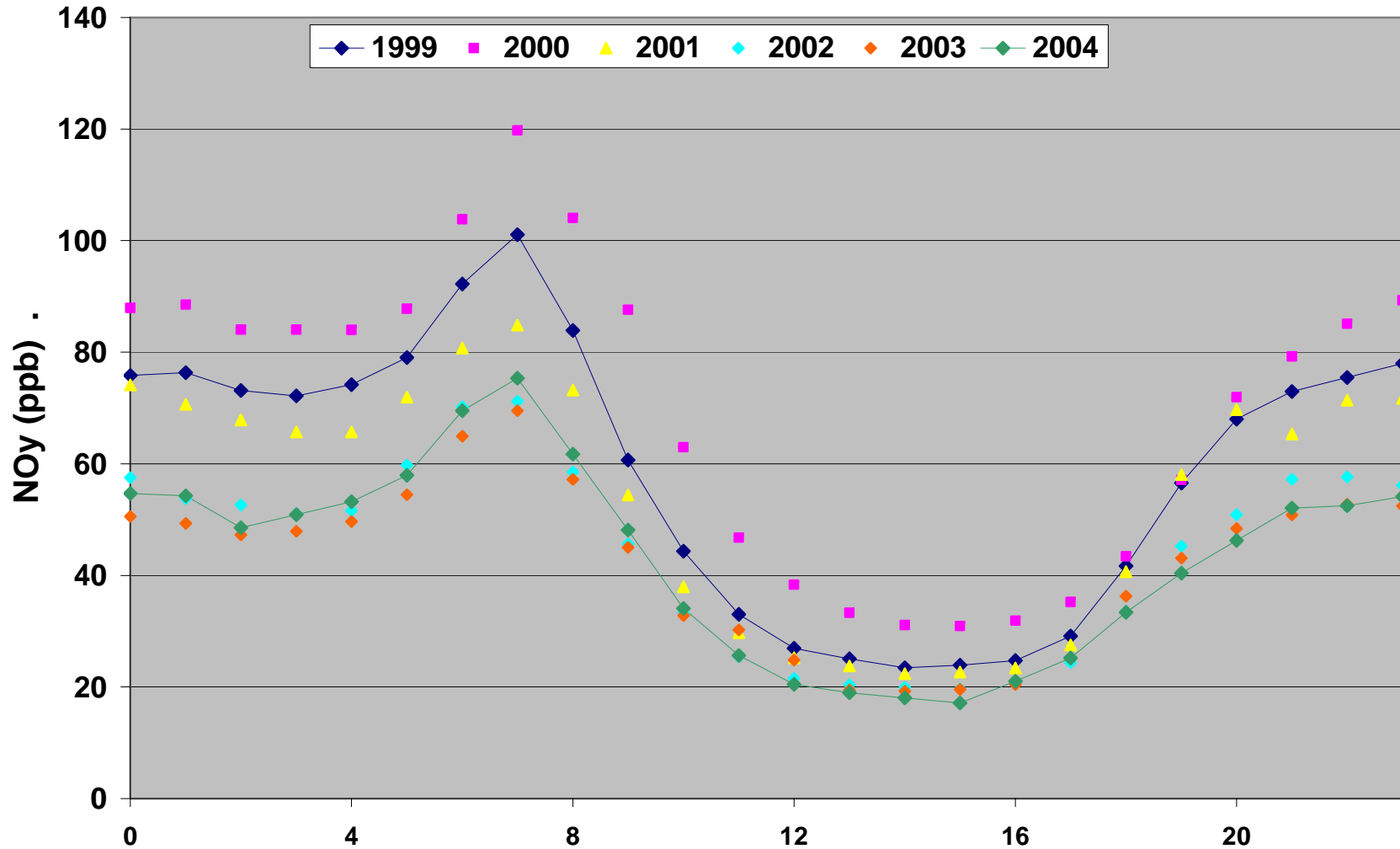
# Composite Diurnal Profile – Ozone JST 1999-2004



Peak afternoon ozone has decreased by 10 ppb, on average

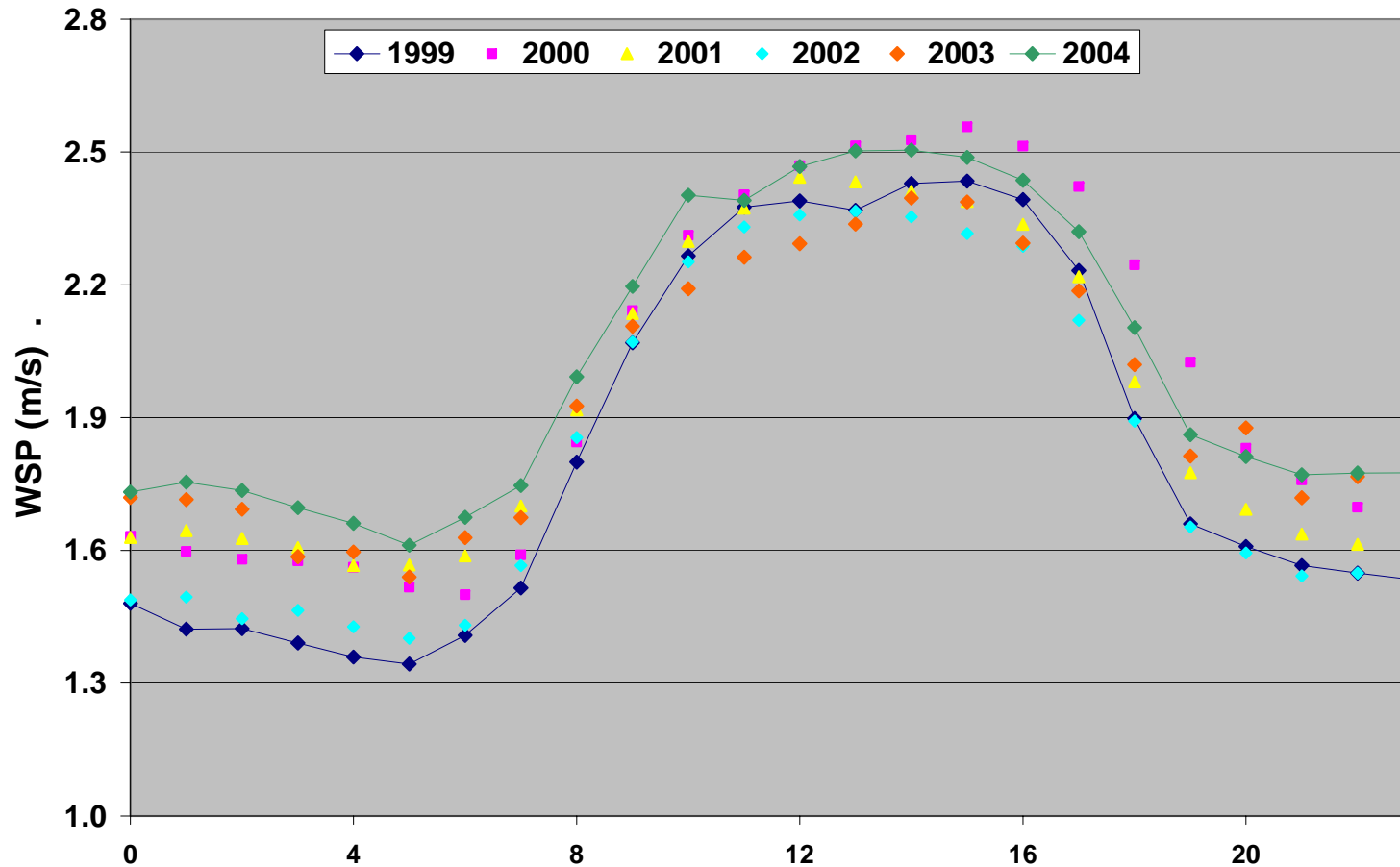
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# Composite Diurnal Profile – NO<sub>y</sub> JST 1999-2004



**NO<sub>y</sub> shows a general decrease, but different year to year pattern than O<sub>3</sub> and PM<sub>2.5</sub>**

# Composite Diurnal Profile – Wind Speed JST 1999-2004



**Wind speed may play a role in reductions. Overnight increases suggest increased dilution of 25-40%**

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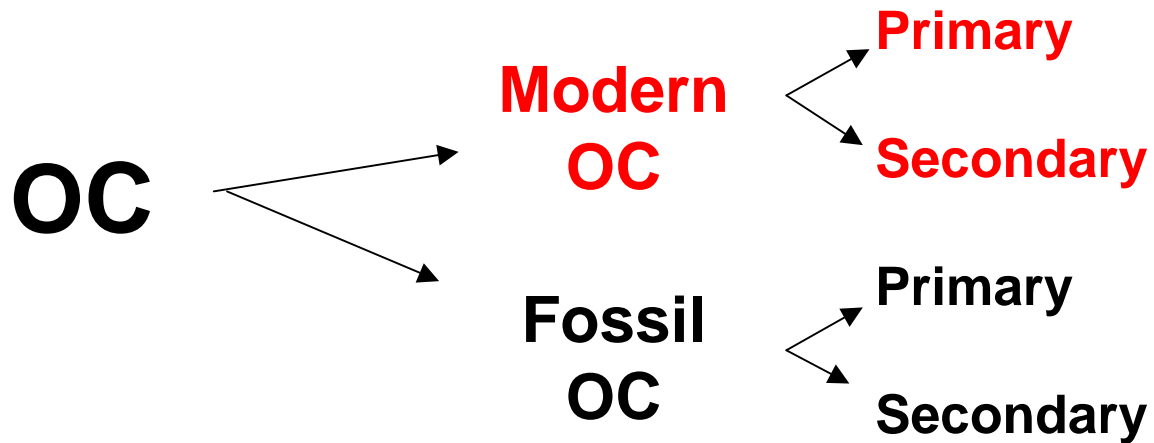
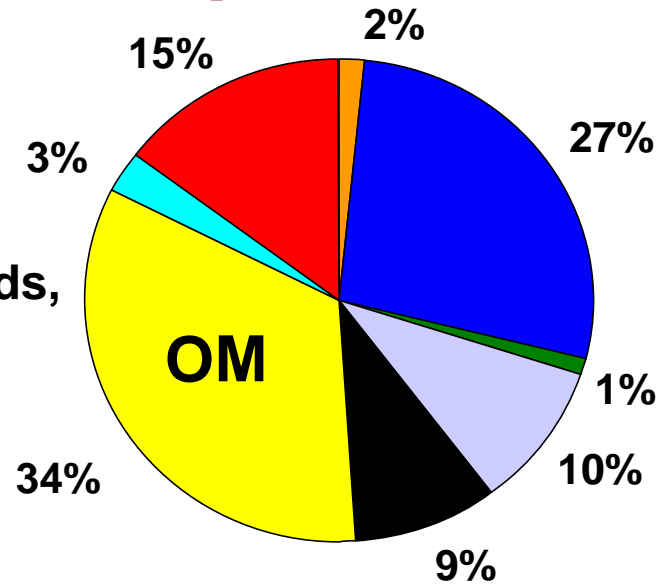
# Carbon Sources

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# Jefferson Street

Average **FRM Equivalent** mass =  $17.7 \mu\text{g}/\text{m}^3$

OM consists of hundreds, if not thousands, of individual compounds.



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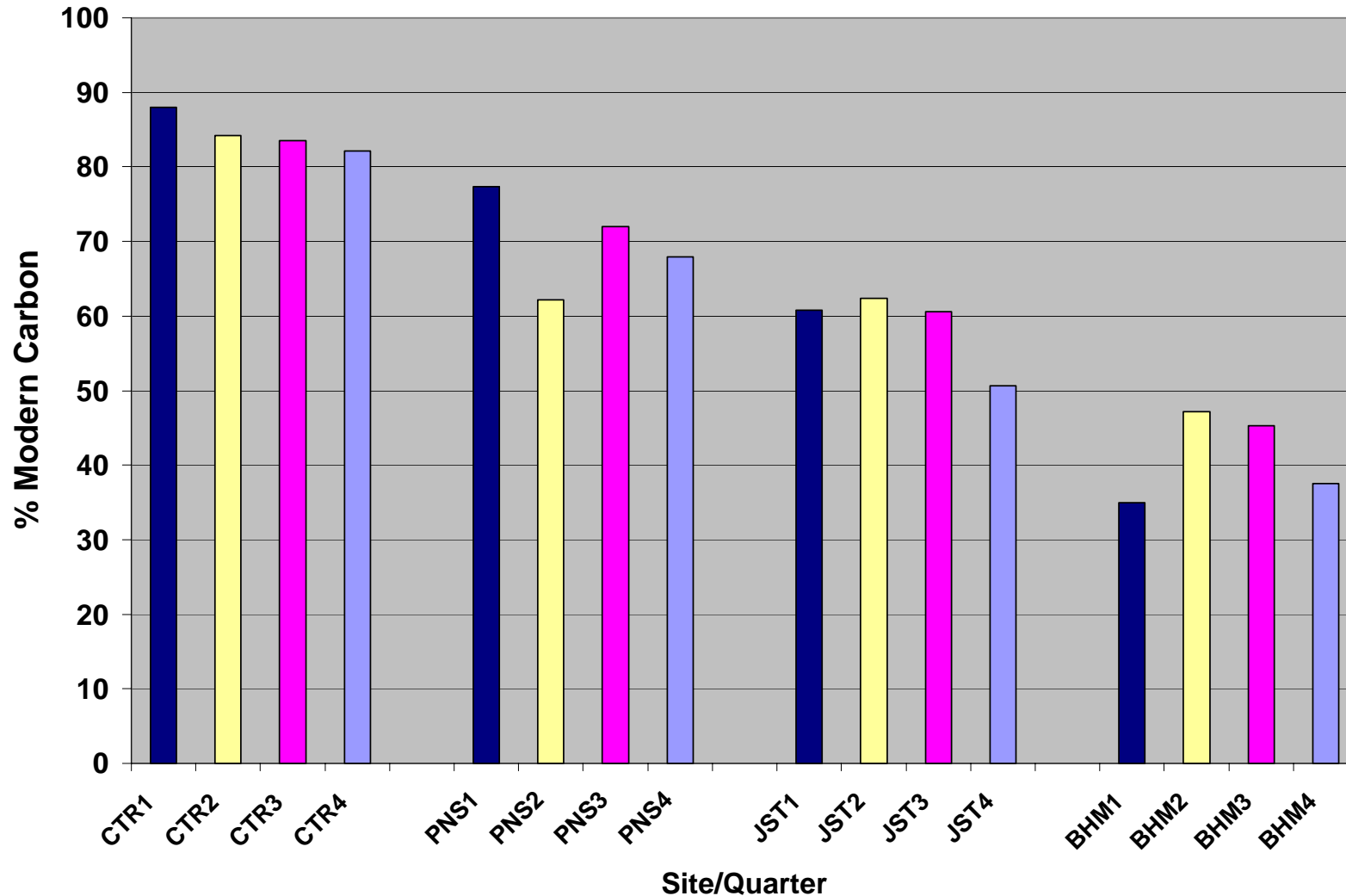
# Carbon Source Matrix Approach

Source Mech.	Primary	Secondary	Total
Modern	Speciation/CMB	(Difference)	$^{14}\text{C}$
Fossil	Speciation/CMB	(Difference)	$^{14}\text{C}$

Modern carbon refers to recently living material (e.g., plants, woodsmoke) and contains  $^{14}\text{C}$ . Fossil carbon refers to long-dead material (e.g., oil, coal) and is devoid of  $^{14}\text{C}$ .

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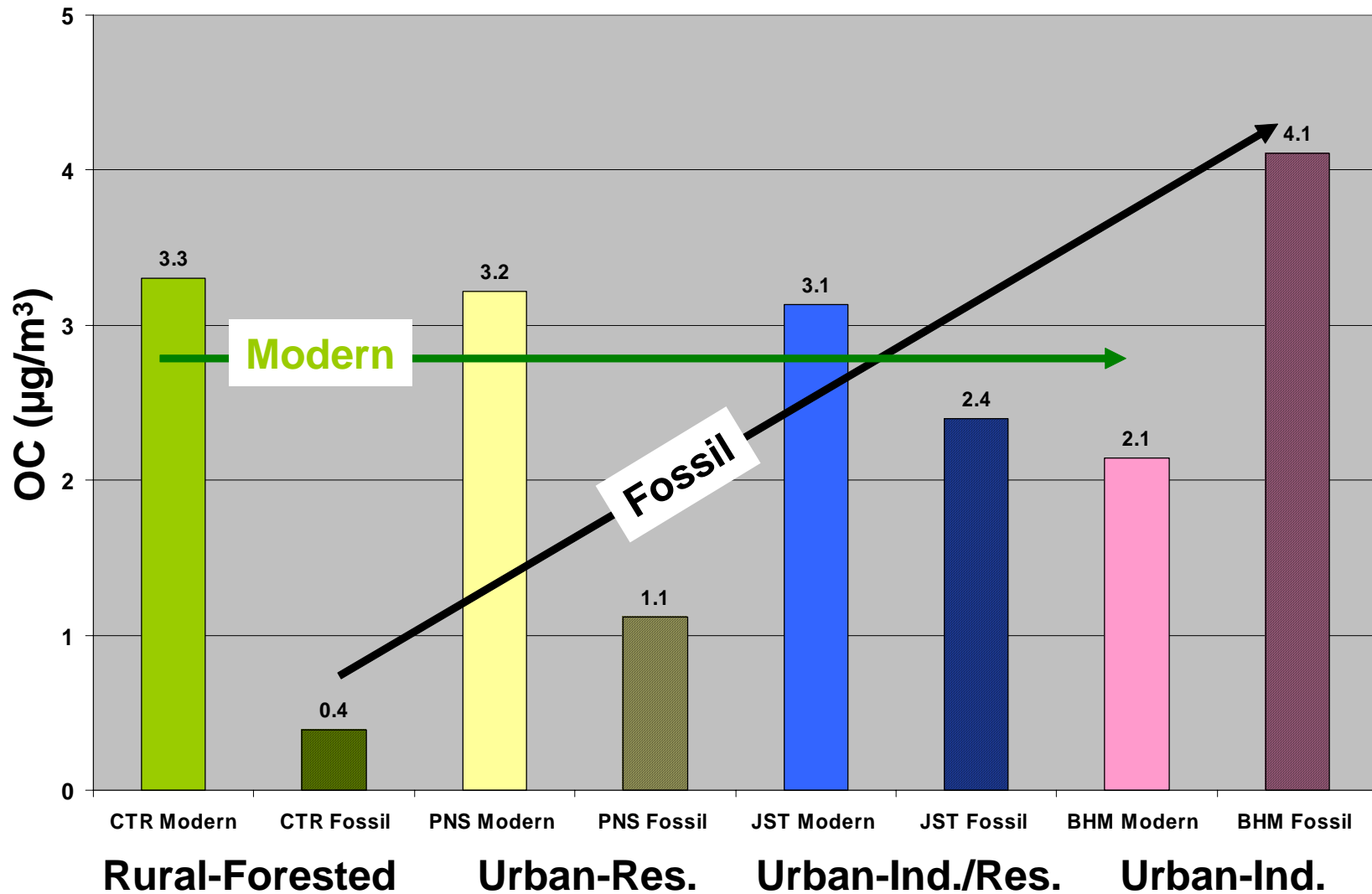
# Quarter to Quarter Variability of Modern Carbon



**Each site has a characteristic Modern/Fossil signature, with only modest quarterly variability.**

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# Modern and Fossil Carbon - Q4 2004



There appears to be a regional component for Modern carbon, plus a local component for Fossil carbon.

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# Carbon Source Matrix

## JST – July 2001

(unit is % of C)

	Primary*	Secondary	Total
<b>Modern</b>	<b>5 +/- 10</b>	<b>&gt;50</b>	<b>59 +/-6</b>
<b>Fossil</b>	<b>40 +/- 18</b>	<b>&lt;5</b>	<b>41 +/-6</b>

\* Zheng et al. Source Apportionment of Fine Particles at Atlanta, GA, AAAR 2002

**JST carbon dominated by fossil-primary and modern-secondary in summer**

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# Rural Source Matrix - Summer

(unit is % of C)

	Primary	Secondary	Total
Modern	16 +/- 6	67 +/-11	83 +/-5
Fossil	16 +/-8	<5 +/- 13	17 +/-5

Rural carbon dominated by modern-secondary in summer

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# Rural Source Matrix - Winter

(unit is % of C)

	Primary	Secondary	Total
Modern	86 +/- 11	<10	88 +/- 5
Fossil	14 +/- 6	<5	12 +/- 5

Rural carbon dominated by modern-primary in winter

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**NH<sub>3</sub> Measurements**

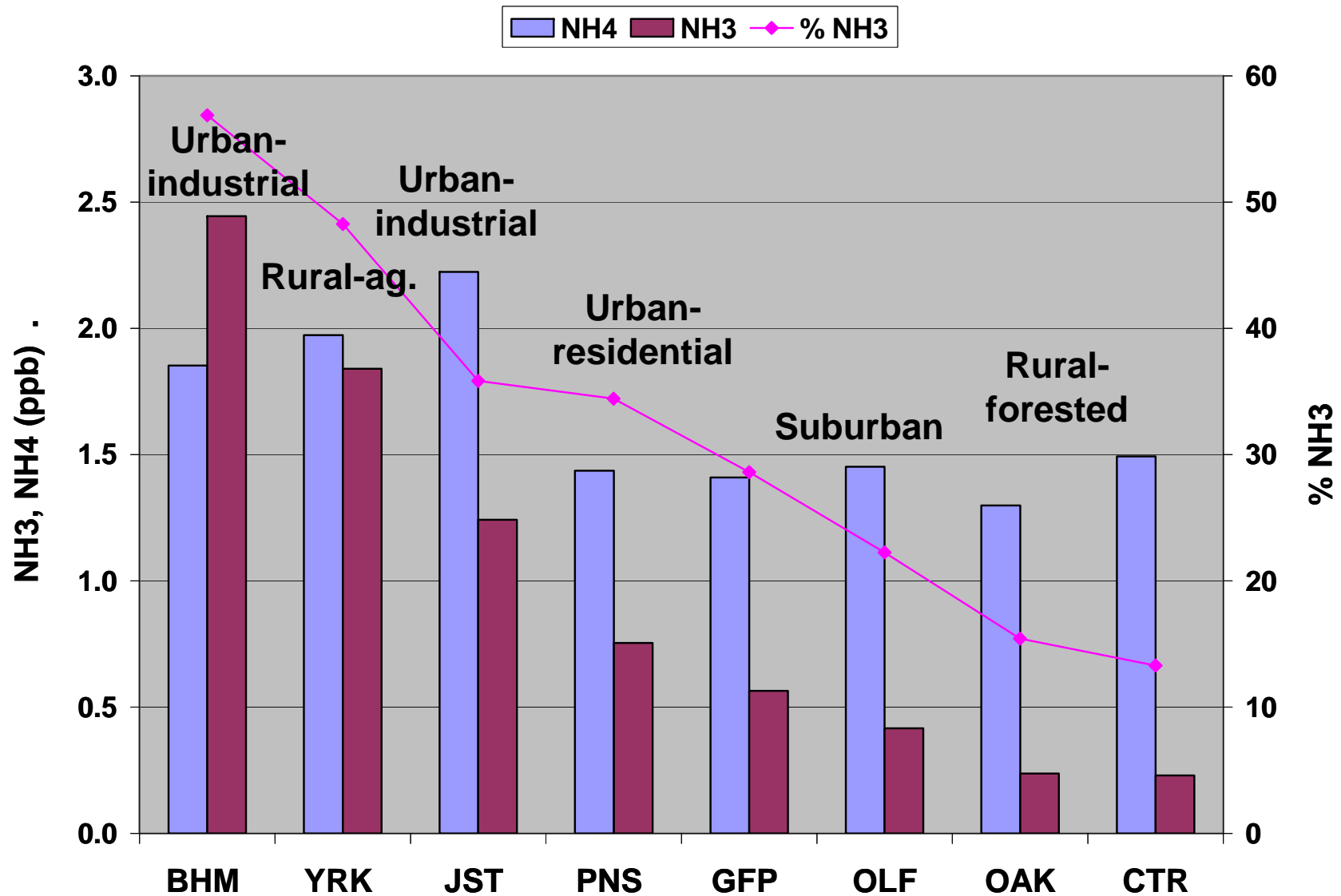
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# Why Measure NH<sub>3</sub>?

- Most important basic gas in the atmosphere
- Nutrient species (wet/dry deposition)
- Major anthropogenic sources (increasing with population?)
- Reacts reversibly with HNO<sub>3</sub> to produce NH<sub>4</sub>NO<sub>3</sub>
- Reacts with H<sub>2</sub>SO<sub>4</sub> to produce a range of ammoniated sulfates (impacts hygroscopicity and light scattering)

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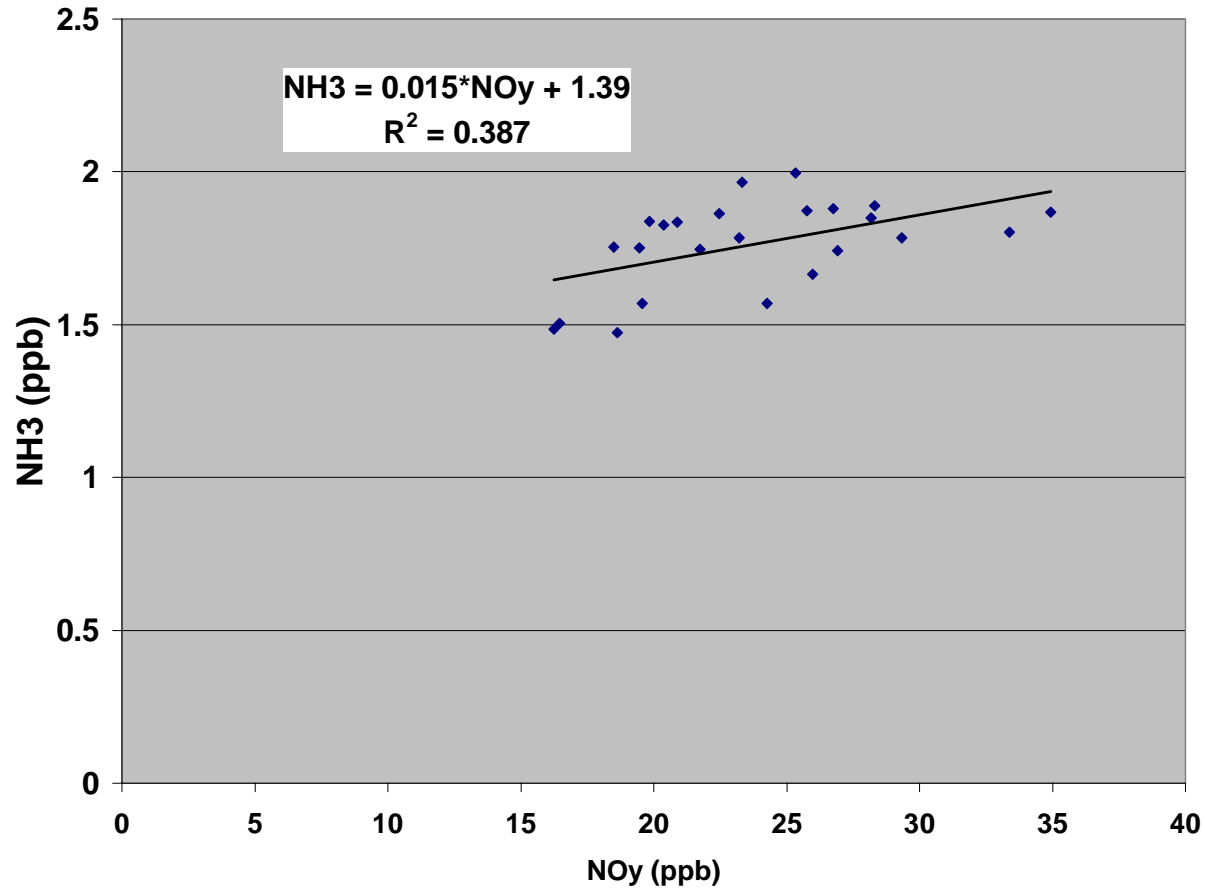
# SEARCH NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> Data - 2004



Large NH<sub>3</sub> gradients and shift in gas-particle partitioning across the network

# Mobile Sources at JST

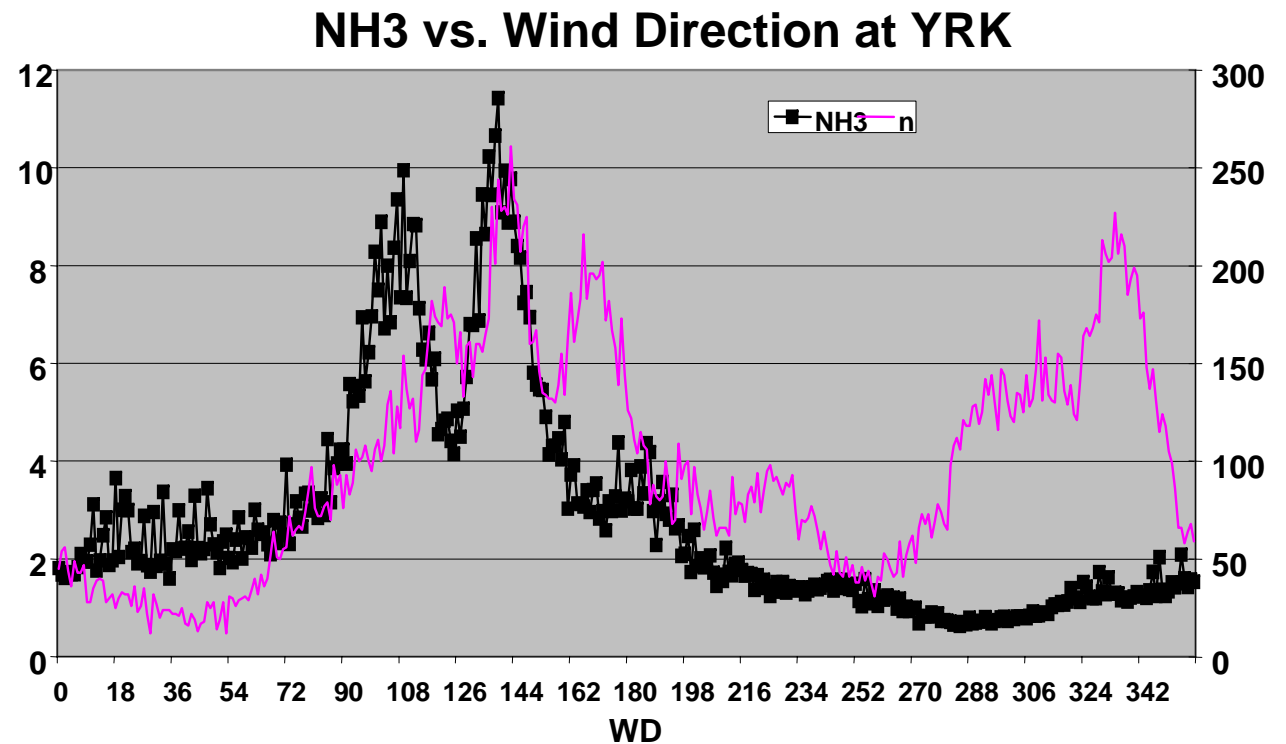
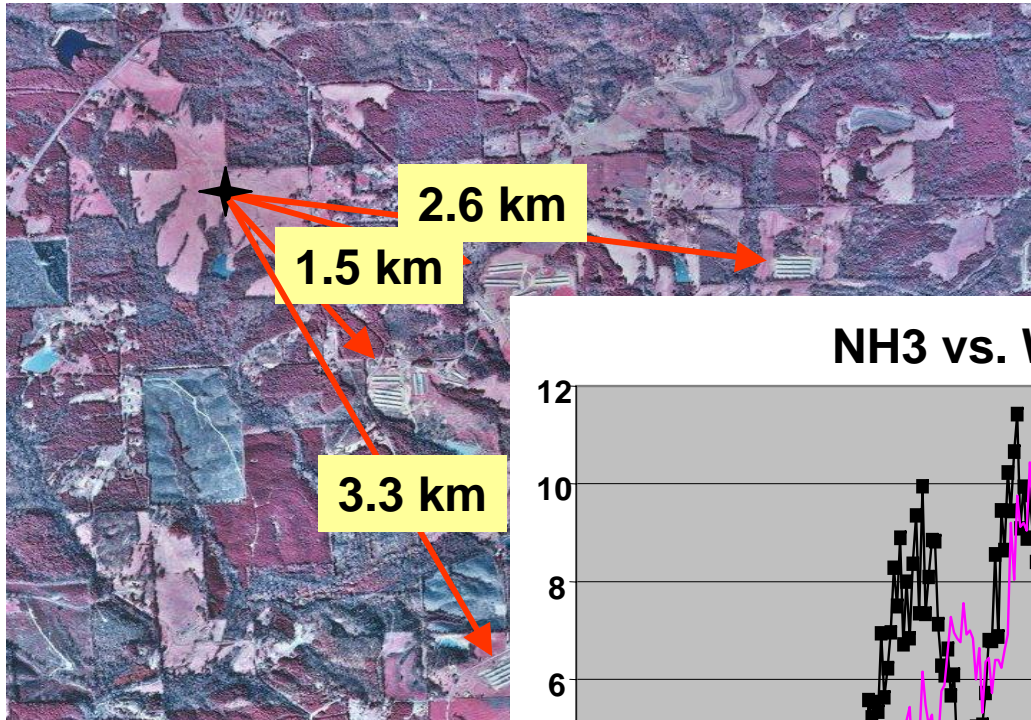
## NH<sub>3</sub> vs. NO<sub>y</sub> binned by Hour of Day



**Correlation analysis suggests mobile source (~1.5% of NO<sub>y</sub>).**  
**Literature suggests higher emissions (2-5% of NO<sub>y</sub>).**

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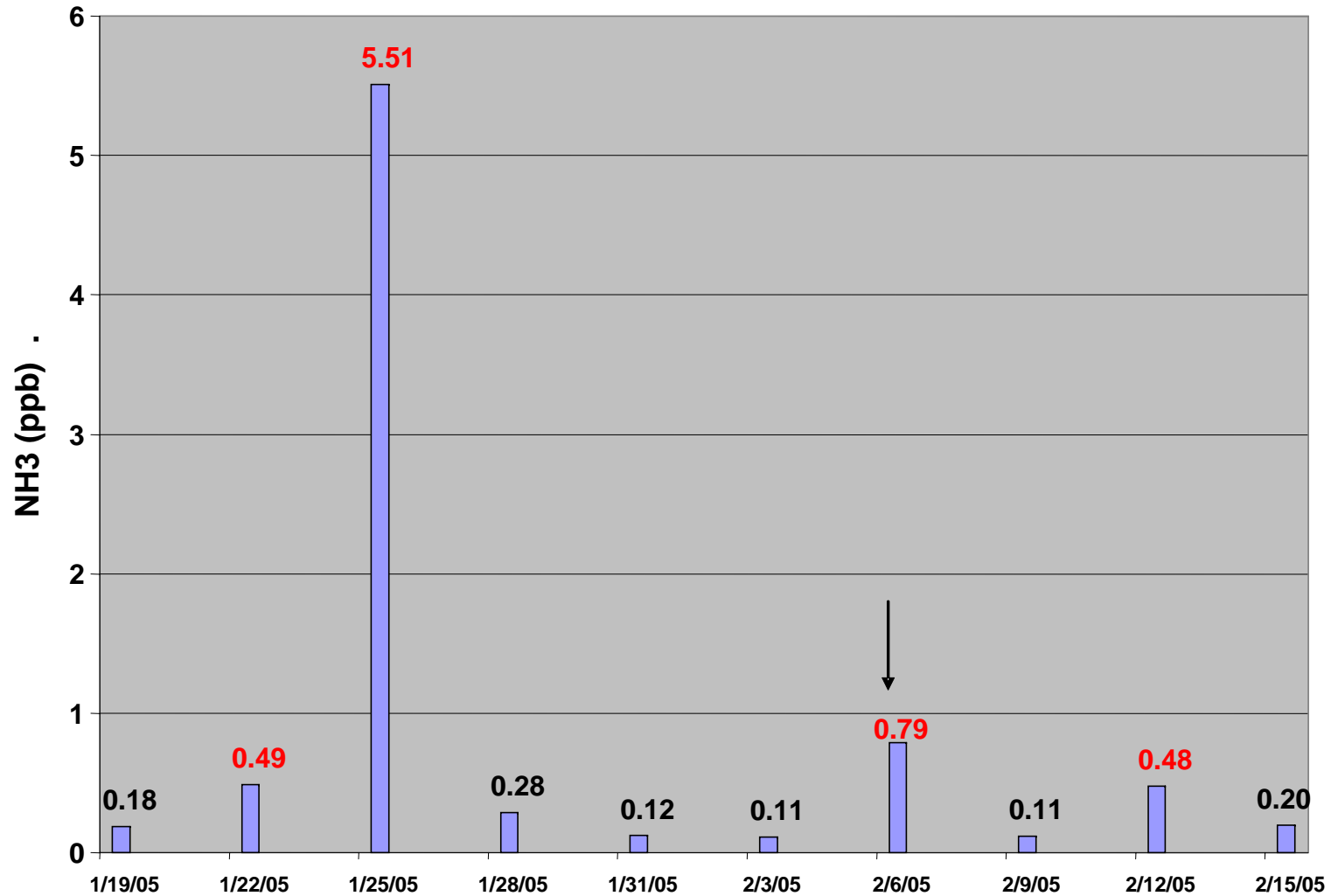
## Aerial view of YRK, showing poultry operations



**Wind direction analysis shows strong source(s) in direction of poultry operations.**

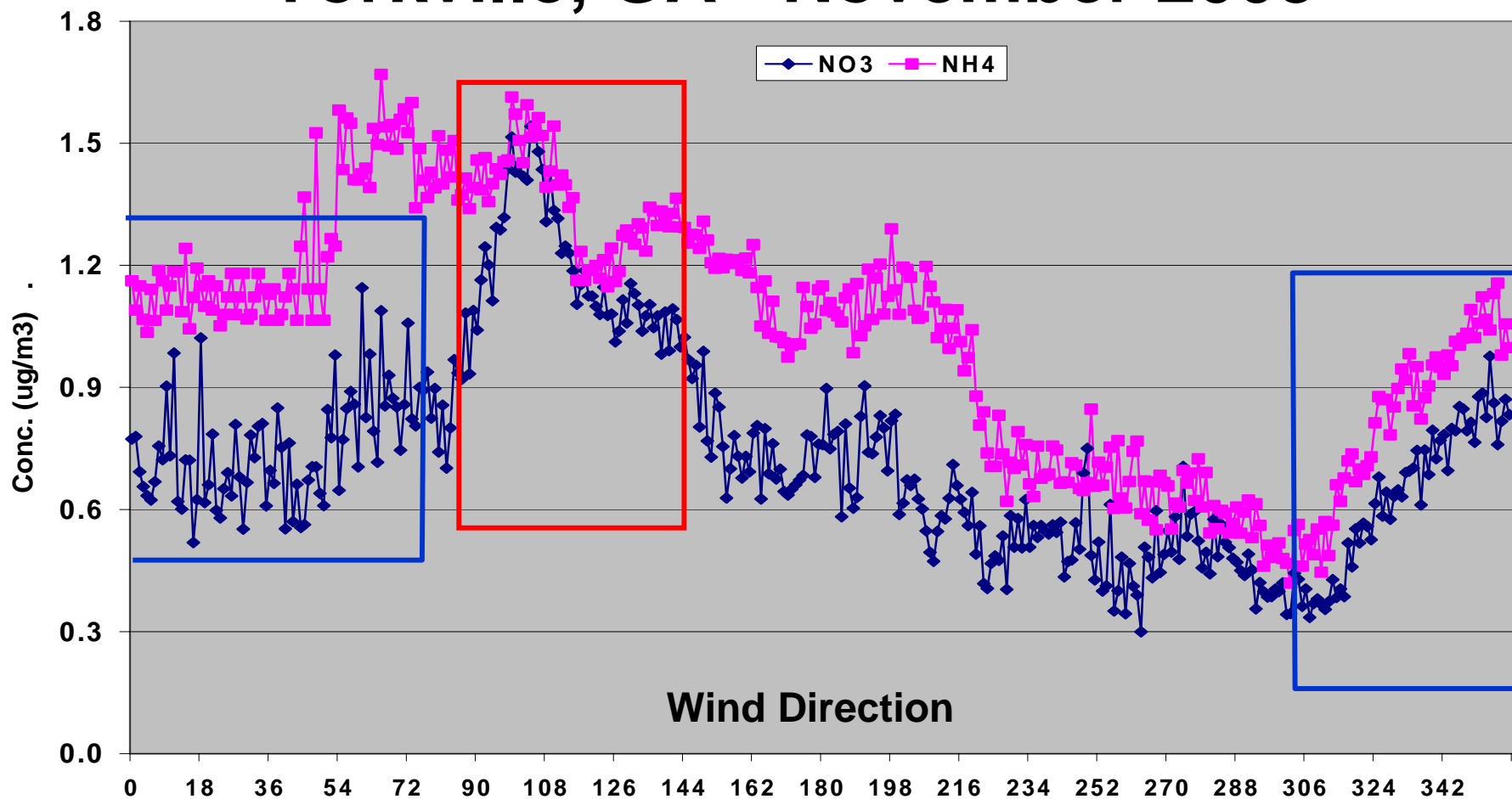
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# Oak Grove NH<sub>3</sub> – Early 2005



**Fire is also a source of NH<sub>3</sub>. Days with clear evidence of smoke (red) show elevated 24-hour NH<sub>3</sub>.**

# Continuous $\text{NH}_4^+$ and $\text{NO}_3^-$ vs. WD Yorkville, GA - November 2003



**Local sources of  $\text{NH}_3$  may also contribute to particulate formation.**

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# Atmospheric Hg

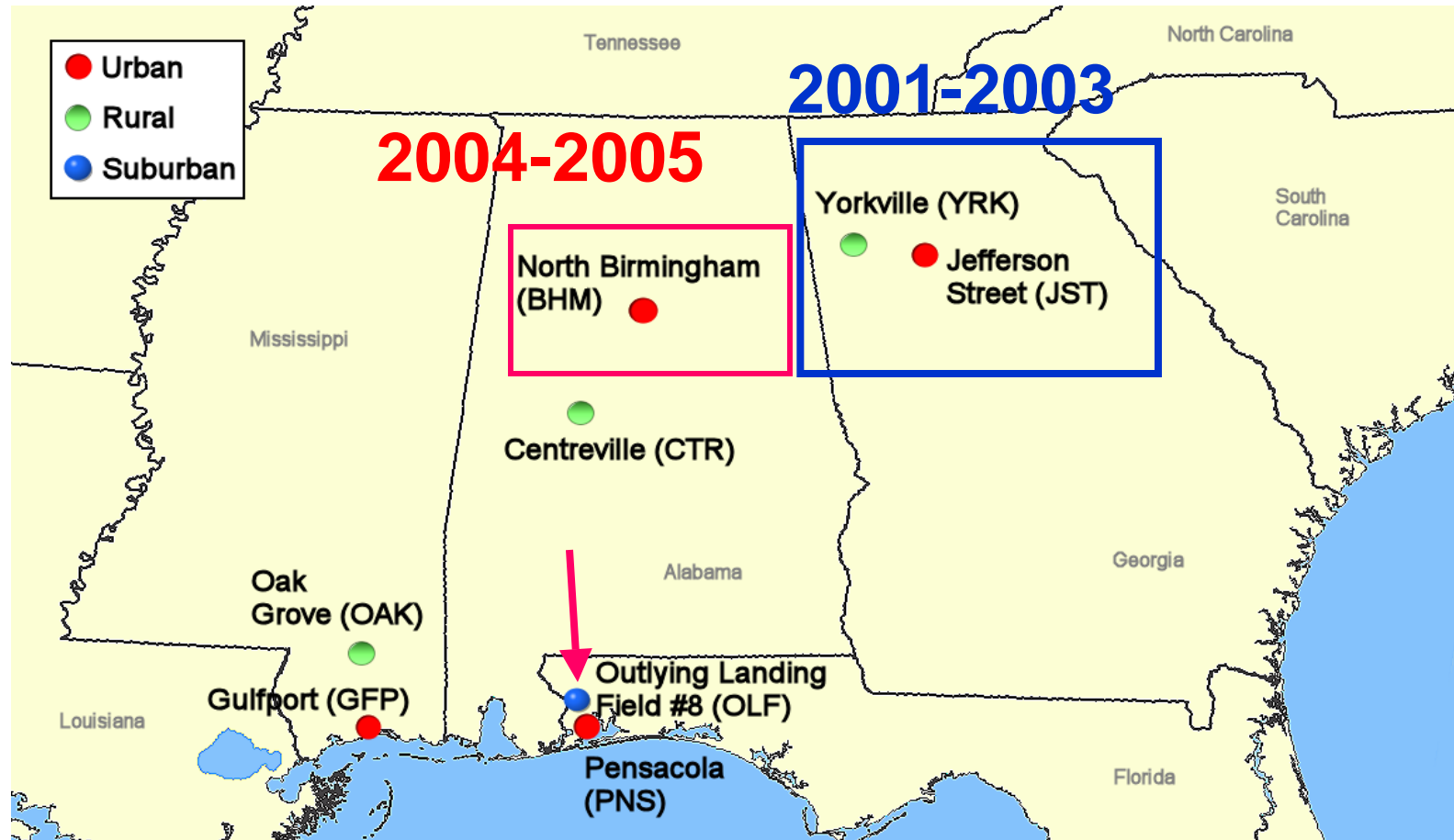
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# 3 Forms of Atmospheric Hg

- **Elemental – Hg(0)**
  - Dominant component (>99%), background 1500 pg/m<sup>3</sup>
  - Easily measured
  - Relatively inert and long lifetime
- **Reactive Gaseous – RGM**
  - Minor component (<1%), background 1-5 pg/m<sup>3</sup> (?)
  - Operationally defined measurement
  - Easily deposited (wet or dry), short lifetime
- **Particulate – Hg<sub>p</sub>**
  - Minor component (<1%), background ???
  - Difficult to measure (until recently)
  - Behavior same as fine particles, intermediate lifetime

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# Hg Measurement Locations



**Urban-rural pair in 2001-2003;  
coastal-inland/industrial pair in 2004-2005**

# Research Approach for Plume Analyses

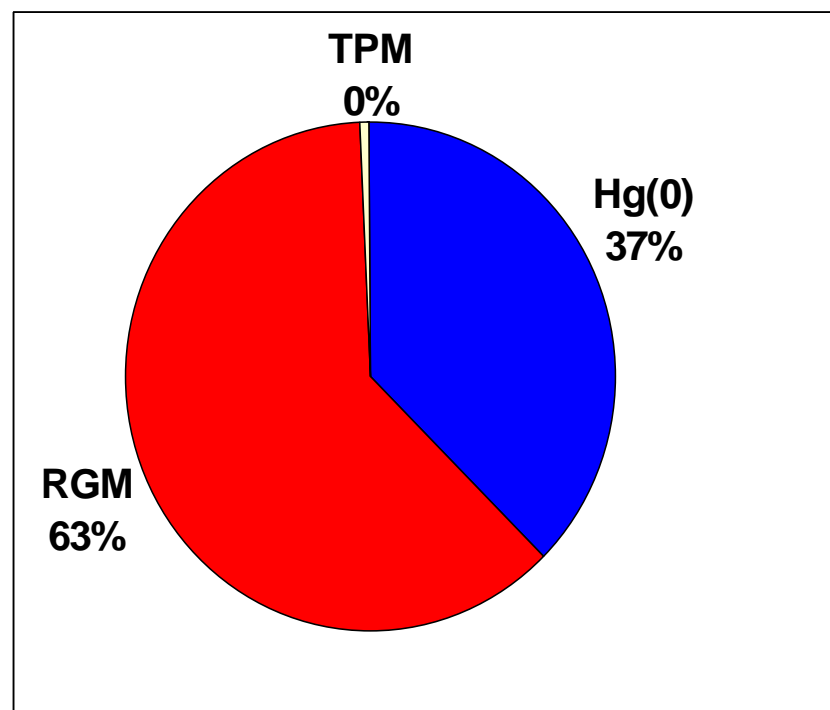
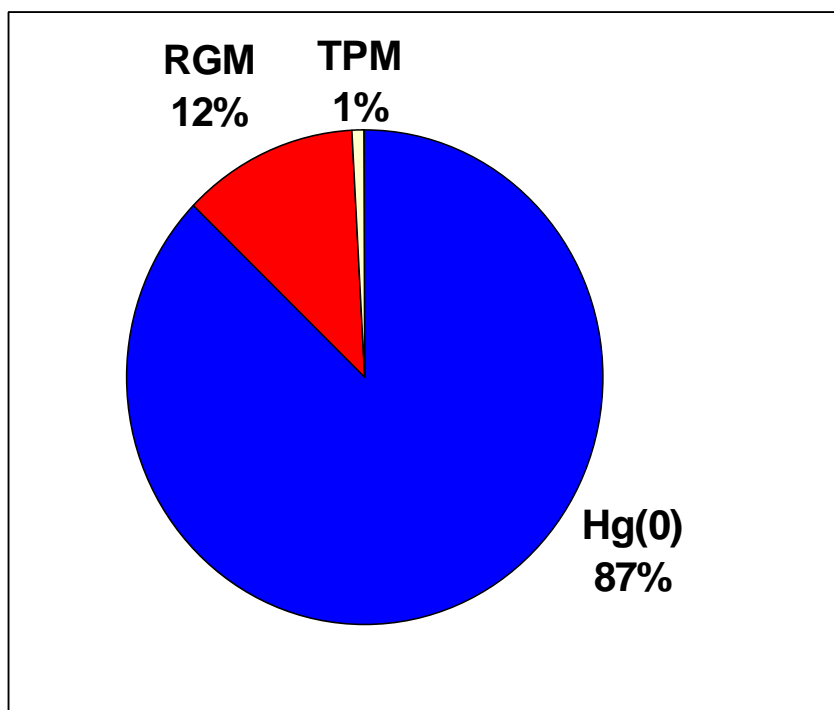
- Make precise, hourly measurements of speciated mercury
- Use **SEARCH** measurements, trajectory analyses, and other evidence to identify power plant (and other) plumes impacting site
- Measure the amount of speciated mercury, above ambient, attributable to the plume and calculate ratio
- Compare with expected emissions ratios
  - Based on event-specific coal analysis and EPRI empirical emissions model derived from ICR

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# Observed and Expected Hg Speciation Bowen Event at YRK - June 27, 2001

Observed Total-Hg = 11 pg/m<sup>3</sup>/ppb SO<sub>2</sub>

Expected Total-Hg = 10 pg/m<sup>3</sup>/ppb SO<sub>2</sub>



**Data show substantial differences in Hg speciation,  
well outside measurement uncertainties**

# Observed and Expected RGM and Hg(0) for Yorkville Plume Events\*

Units for ratios are: picograms/m<sup>3</sup>/ppb \* Events with mass closure only

Date	Probable Source	Observed RGM:SO <sub>2</sub>	Observed Hg(0):SO <sub>2</sub>	Obs. % RGM	Exp. % RGM	Obs. % Hg(0)	Exp. % Hg(0)
06/27/01	Bowen	1.2	9.7	11	54	89	46
07/20/01	Bowen	0.8	12.0	6	61	94	39
10/20/01	Wansley	0.9	6.3	13	52	88	48
10/22/01	Bowen	4.7	6.8	41	56	59	44
12/07/01	Gaston	0.9	12.4	7	39	93	61
12/13/01	Wansley	0.9	12.3	7	62	93	38
12/19/01	Hammond	0.8	11.3	7	58	93	42
12/26/01	Hammond	1.6	9.2	15	60	85	40
12/28/01	Gaston	1.3	13.9	9	42	91	58
12/29/01	Hammond	1.0	6.4	14	37	86	63
12/31/01	Hammond	0.6	10.4	5	40	95	60
01/03/02	Hammond	2.9	9.9	23	42	77	58
02/09/02	Bowen	1.0	8.7	10	67	90	33
06/17/02	Bowen	1.9	4.7	29	55	71	44
07/05/02	Bowen	0.9	4.0	18	61	82	39
10/12/03	Bowen	1.3	7.3	15	56	85	44
<b>Mean</b>		<b>1.4</b>	<b>9.1</b>	<b>14</b>	<b>53</b>	<b>86</b>	<b>47</b>
<b>s.d.</b>		<b>1.0</b>	<b>2.9</b>	<b>10</b>	<b>10</b>	<b>10</b>	<b>10</b>

**At YRK, observed Hg(0) was 86% of total, while expected Hg(0) 47%, and mean RGM:SO<sub>2</sub> was 1.4**

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# Observed and Expected RGM:SO<sub>2</sub> Jefferson Street Plume Events

units for RGM:SO<sub>2</sub> ratios are picograms/m<sup>3</sup>/ppb

Date	Probable Source	Observed RGM:SO <sub>2</sub>	Expected# RGM:SO <sub>2</sub>	Obs./Exp.(%)
1/6/2003	McDonough	1.5	3.7	41
1/6/2003	McDonough	0.9	3.7	24
1/13/2003	McDonough	0.8	3.4	24
1/17/2003	McDonough	1.2	3.1	39
1/17/2003	McDonough	2.0	3.1	65
2/24/2003	McDonough	1.7	3.3	52
2/25/2003	McDonough	1.0	3.3	30
3/10/2003	McDonough	1.2	4.0	30
3/26/2003	McDonough	0.6	3.4	18
4/12/2003	McDonough	1.4	3.4	41
4/22/2003	McDonough	1.9	3.0	63
<b>Mean</b>		<b>1.3</b>	<b>3.4</b>	<b>39</b>
<b>s.d.</b>		<b>0.4</b>	<b>0.3</b>	<b>15</b>

# based on coal analysis and CEM data

**At JST, RGM:SO<sub>2</sub> was 1.3, or about one-third expected**

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# CFPP Plume Events for OLF January-June 2004

(Plant Crist located 14 km from OLF)

Date	Probable Source	RGM:SO <sub>2</sub>	Hg(0):SO <sub>2</sub>	TPM:SO <sub>2</sub>	%RGM	% Hg(0)
1/11/2004	Crist	2.9	n.d.	0.2	n.d.	n.d.
1/16/2004	Crist	1.1	n.d.	0.1	n.d.	n.d.
2/1/2004	Crist	0.9	5.9	0.2	13	85
2/4/2004	Crist	1.4	4.6	0.1	23	76
2/8/2004	Crist	2.0	n.d.	0.1	n.d.	n.d.
2/9/2004	Crist	0.7	n.d.	0.1	n.d.	n.d.
3/15/2004	Crist	1.1	5.7	0.1	16	82
6/8/2004	Crist	2.4	7.4	0.03	22	78
<b>Mean</b>		<b>1.5</b>	<b>5.5</b>	<b>0.13</b>	<b>18</b>	<b>80</b>
<b>s.d.</b>		<b>0.8</b>	<b>0.7</b>	<b>0.03</b>	<b>5</b>	<b>5</b>

At OLF, RGM:SO<sub>2</sub> was 1.5, and Hg(0) >>RGM>>Hg<sub>p</sub>

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# Possible explanations for difference between observed and expected Hg speciation

- Dry Deposition
  - Not consistent with mass balance or models
- Wet Deposition
  - No precipitation between source and site
- **Emission Estimates Wrong (Inventories also Wrong)**
- **Chemical Reduction of RGM to Hg(0)**

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# Conclusions

- Declining, but variable, trend in PM<sub>2.5</sub> and components
- Trends complicated, but Wind Speed (meteorology) may play a role at JST
- Total Carbonaceous Material (TCM) and sulfate are dominant components with TCM > sulfate (even with C scaling factor = 1.4)
- Urban-rural increments in PM<sub>2.5</sub> and observations > 65 µg/m<sup>3</sup> are driven by TCM
- Composition of 98<sup>th</sup> %ile sample(s) is highly variable
- **SEARCH** studies beginning to bound carbon sources
- <sup>14</sup>C data show large range across sites (BHM = 40% modern; JST = 60%; PNS = 70%; CTR = 85%)
- Modern Carbon more regional than Fossil Carbon.
- Secondary organic aerosol very important in summer, less important in winter

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# Conclusions (cont'd.)

- First look at  $\text{NH}_3$  shows high spatial and temporal variability.
- Local sources of  $\text{NH}_3$  (e.g. poultry and fires) are important and may play a role in particulate formation and/or acid neutralization
- Emission ratio calculations show substantial differences between expected and observed Hg speciation in CFPP plumes (more  $\text{Hg}(0)$ , less RGM)
- Differences suggest important gap(s) in knowledge of plume chemistry, CFPP emissions, or both
- Differences also imply longer than expected atmospheric lifetime, hence broader spatial scale, for CFPP Hg emissions

# The Future of **SEARCH** ?

- Continue PM and related measurements through (2010)
- Continue Hg measurements
  - Tekran operations: OLF, BHM and YRK (mid-2006)
  - Wet deposition: OAK, CTR, OLF, BHM, YRK
- Enhance and improve measurements
  - Daily SVOCs at JST and BHM (TD/GC-MS)
  - Sunset Carbon Analyzer (continuous EC, TC)
- Continue to post 24-hr and 1-hr data ([www.atmospheric-research.com](http://www.atmospheric-research.com))
- Begin posting 5-minute data (mid-2006)
- Continue analysis of extensive and unique **SEARCH** data sets.

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# Acknowledgements

The SEARCH Network is funded by EPRI and Southern Company. Additional information and data sets are available at:

[www.atmospheric-research.com](http://www.atmospheric-research.com)

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