



# VISTAS Special Monitoring Studies Carbon Analyses for PM<sub>2.5</sub> and Haze

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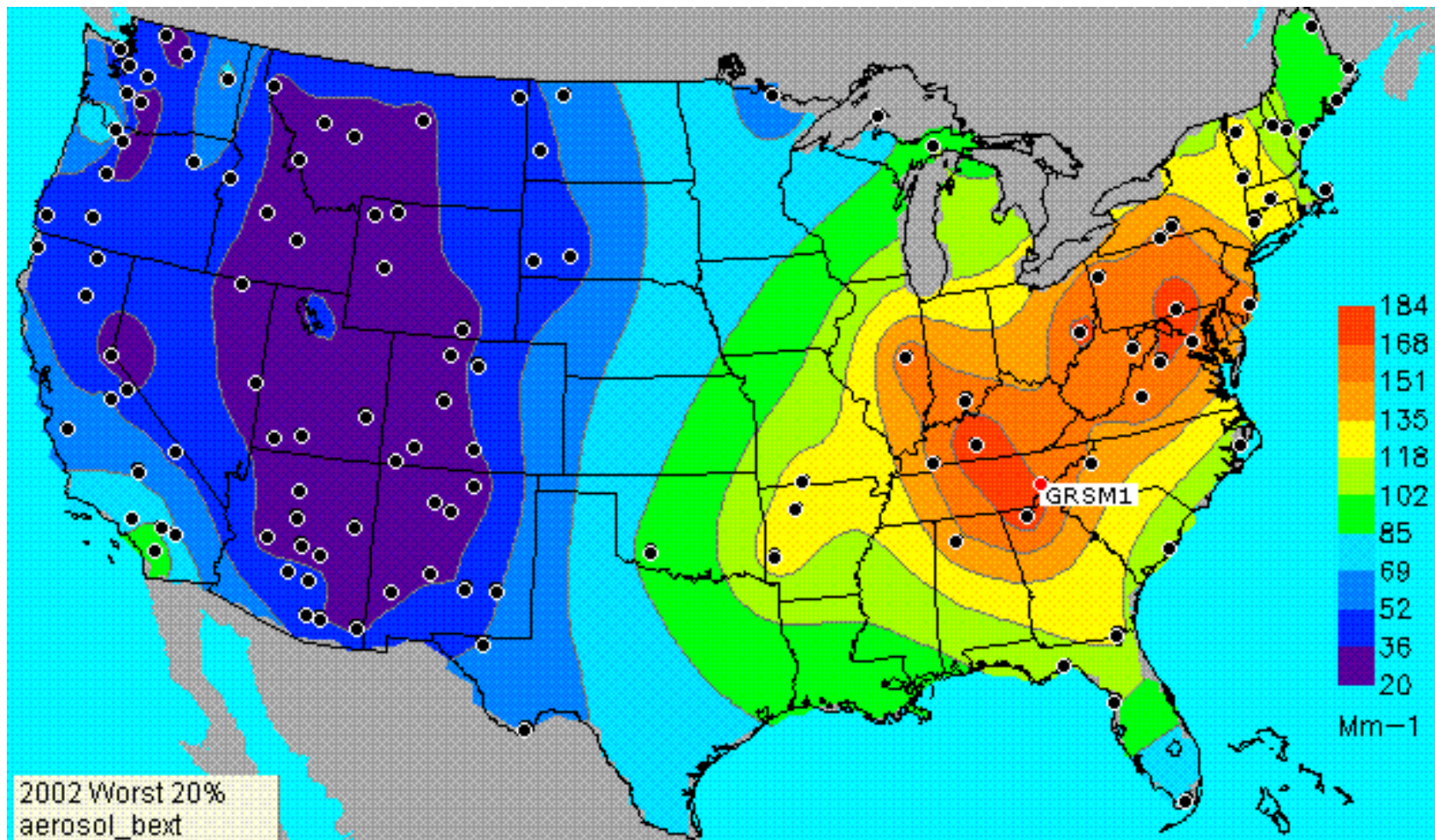
<sup>5</sup>Environmental Protection Agency

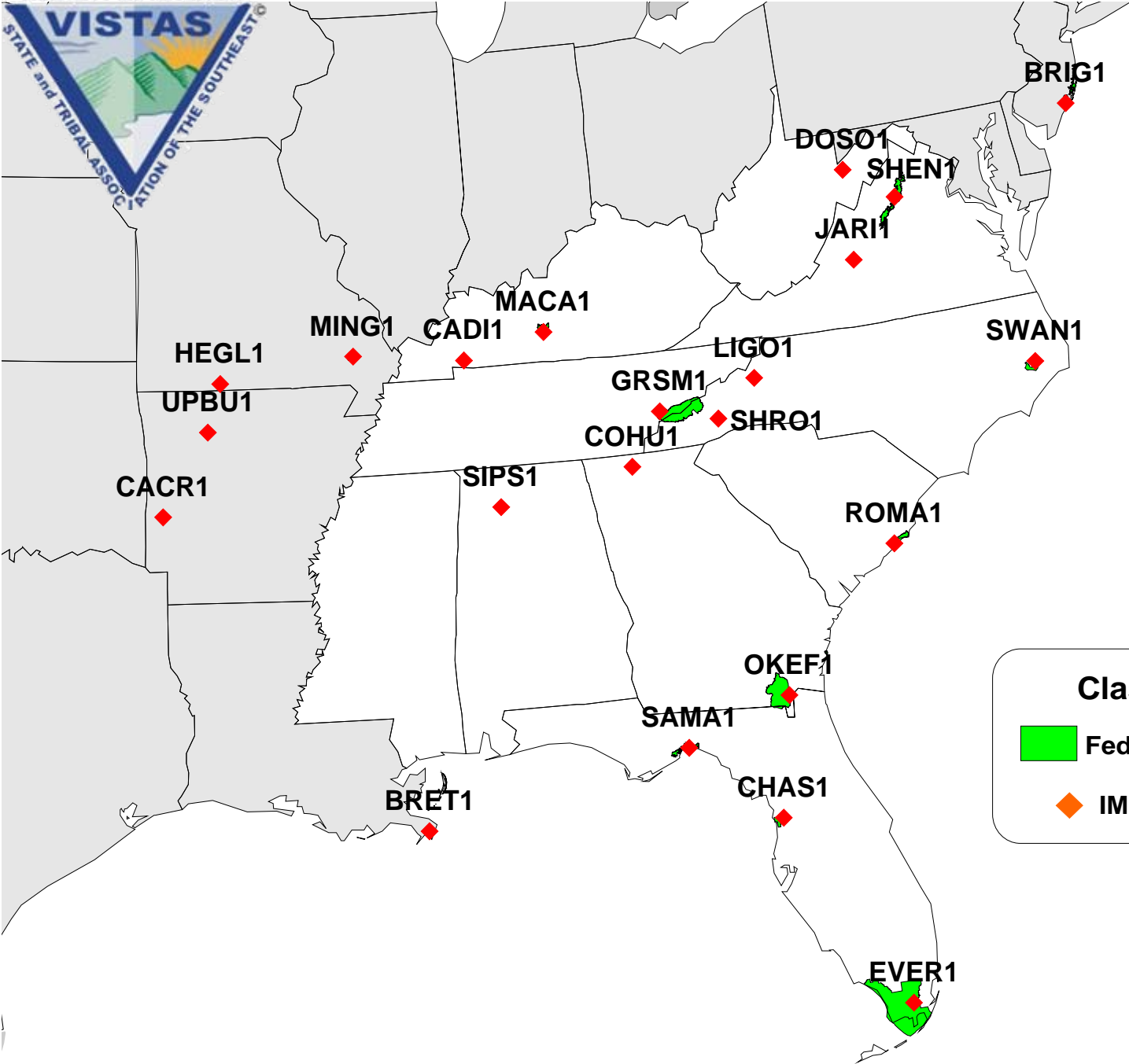


# Presentation Objectives




- VISTAS Data Analysis
- Special Monitoring Studies
  - Carbon Studies: C<sup>14</sup> isotope, Positive Matrix Factorization, and Chemical Mass Balance

# Areas with Poorest Visibility are similar to PM2.5 Non-attainment Areas



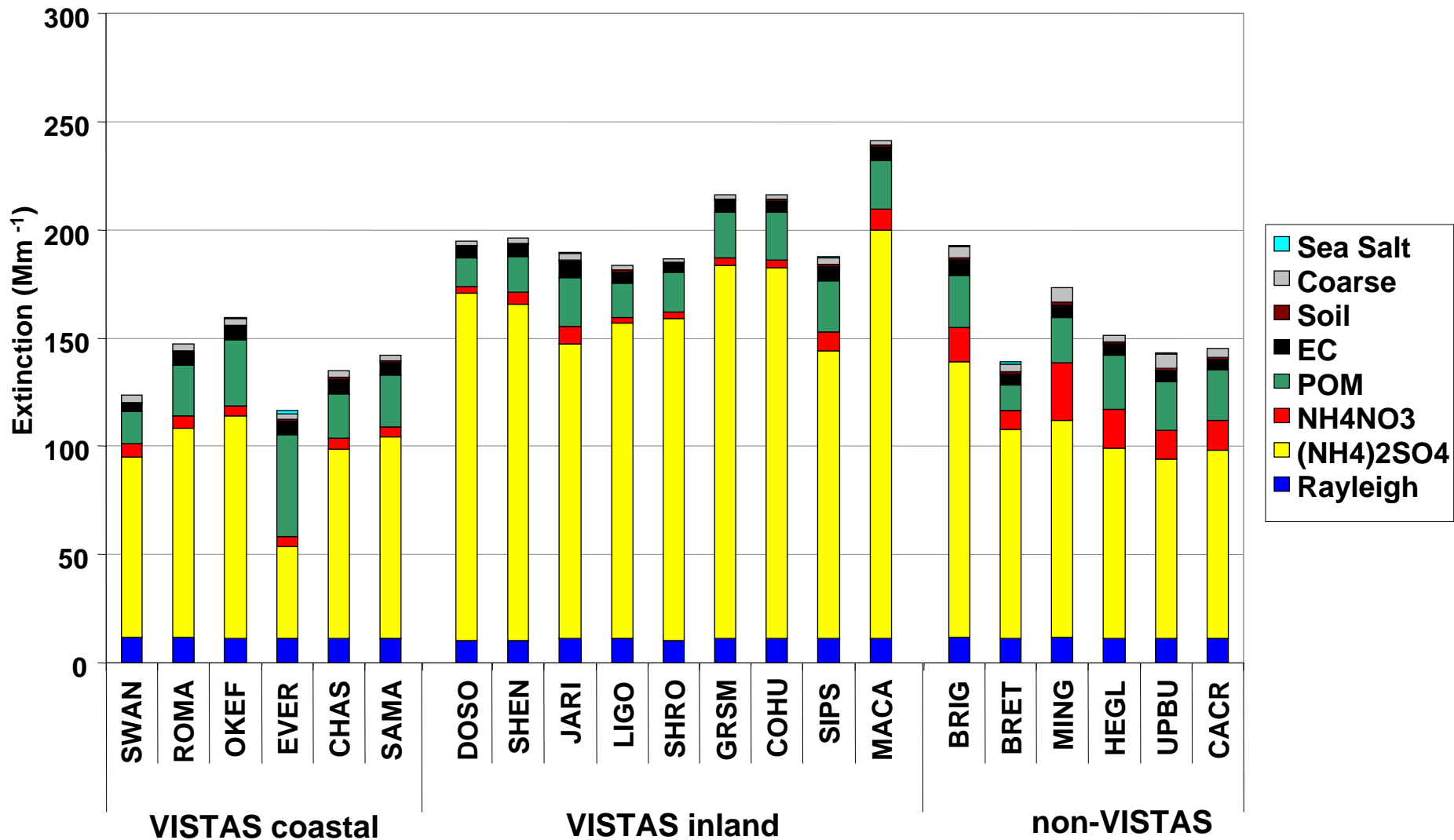


**Class I Areas**

	Federal		Tribal
	IMPROVE Site		

# Average Extinction for 20% Haziest Days 2000-2004

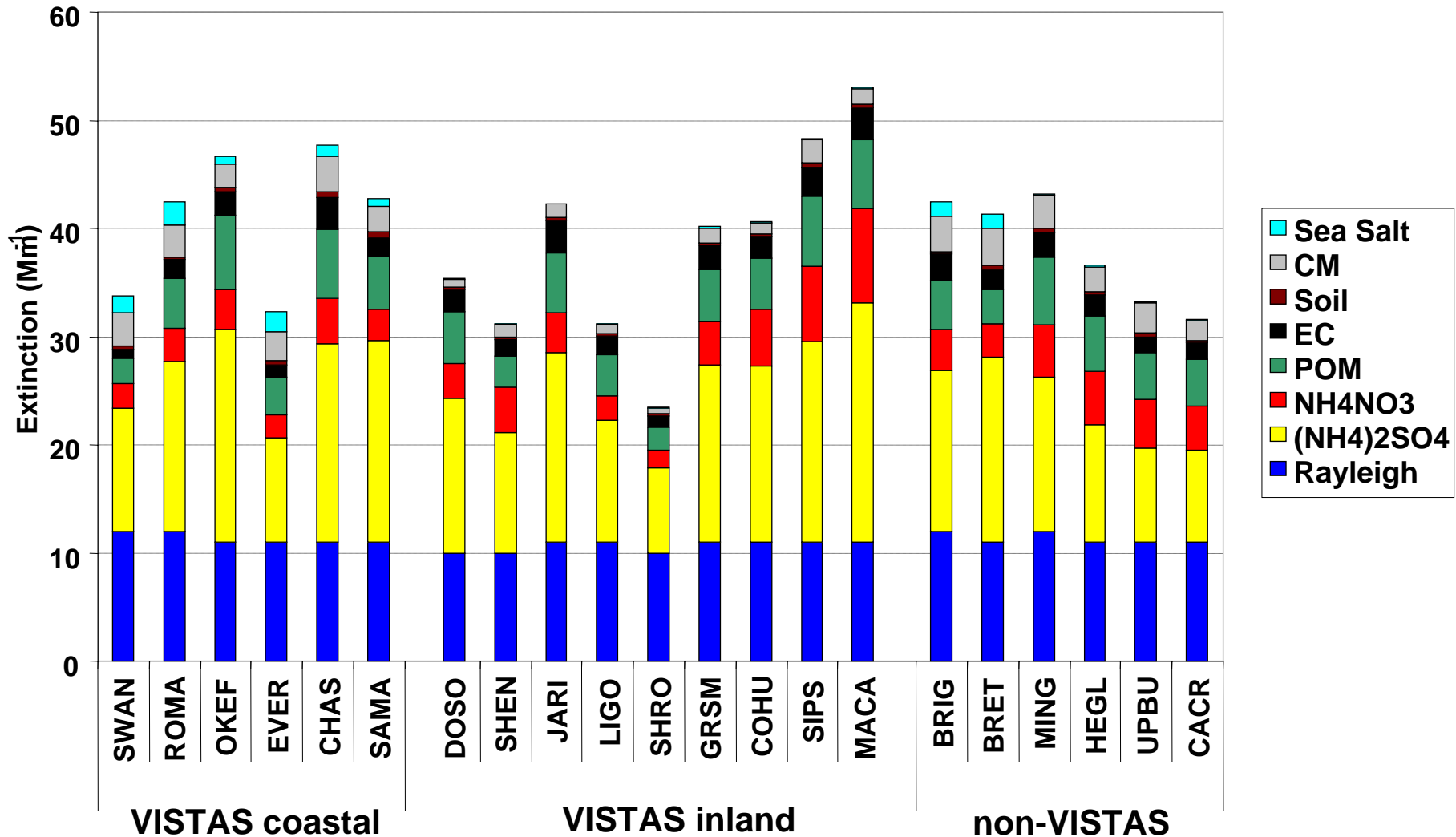
New IMPROVE Algorithm



Sulfate dominates the 20% Haziest Days at VISTAS Class I areas

# Average Extinction for 20% Best Days 2000-2004

New IMPROVE Algorithm

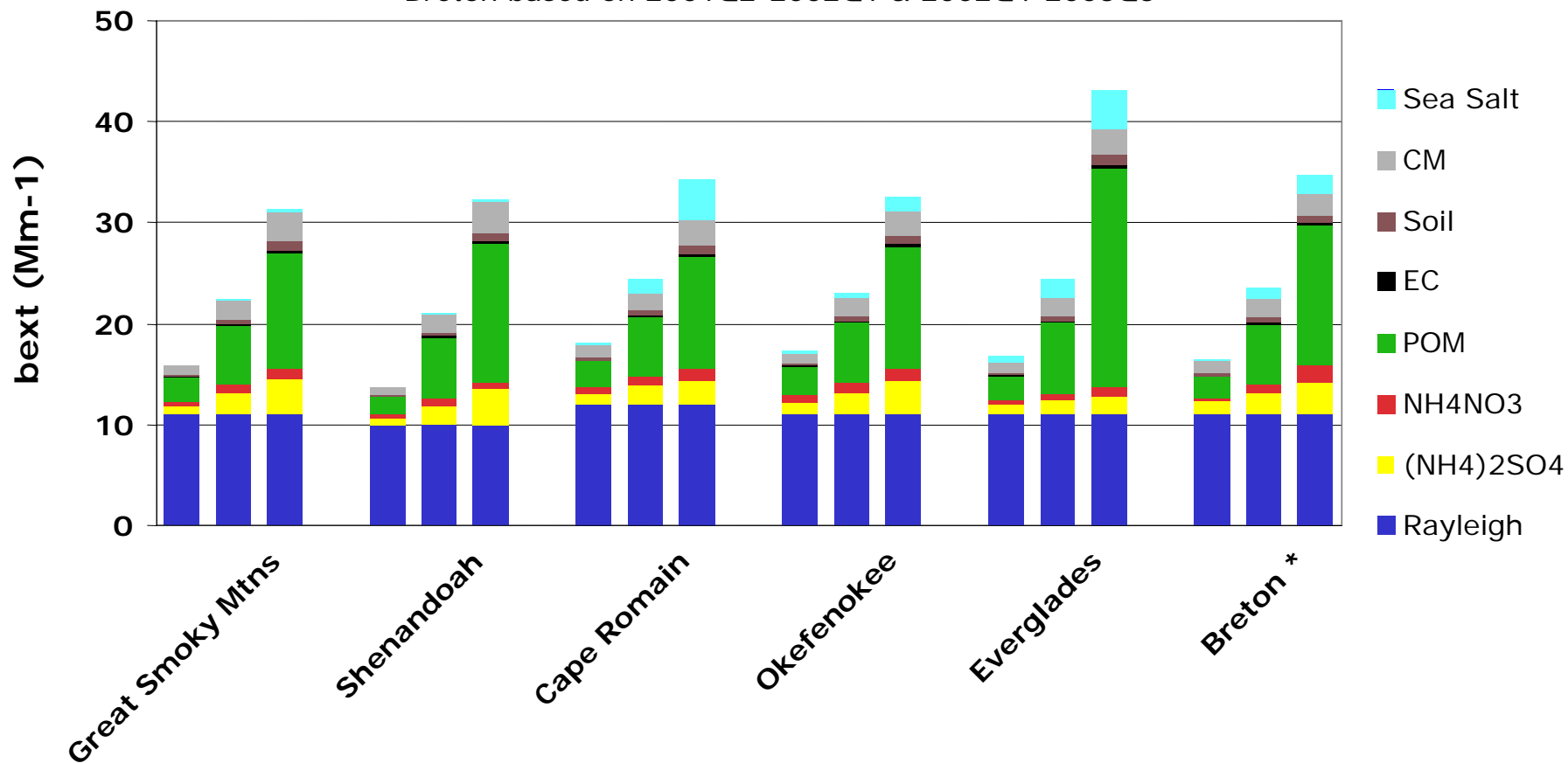


Sulfate also dominates the 20% Clearest Days at VISTAS Class I areas

# Natural Conditions -- New IMPROVE Algorithm -

Left = B20%; Center = Average; Right = W20%

\*Breton based on 2001Q2-2002Q1 & 2002Q4-2003Q3





# Monitoring Objectives

- Identify sources of organic carbon
  - Use high volume samplers with PM2.5 head and quartz filters at 5 sites
  - Samples collected April 2004 – May 2005
  - Analyses by Desert Research Institute
  - Select 250 samples for carbon analysis (5 sites, 50 samples per site including field and lab blanks)
  - Define carbon mass of each sample
  - Characterize organic composition (GC/MS)
  - Identify tracers of primary sources of carbon (Chemical Mass Balance and Positive Matrix Factorization)

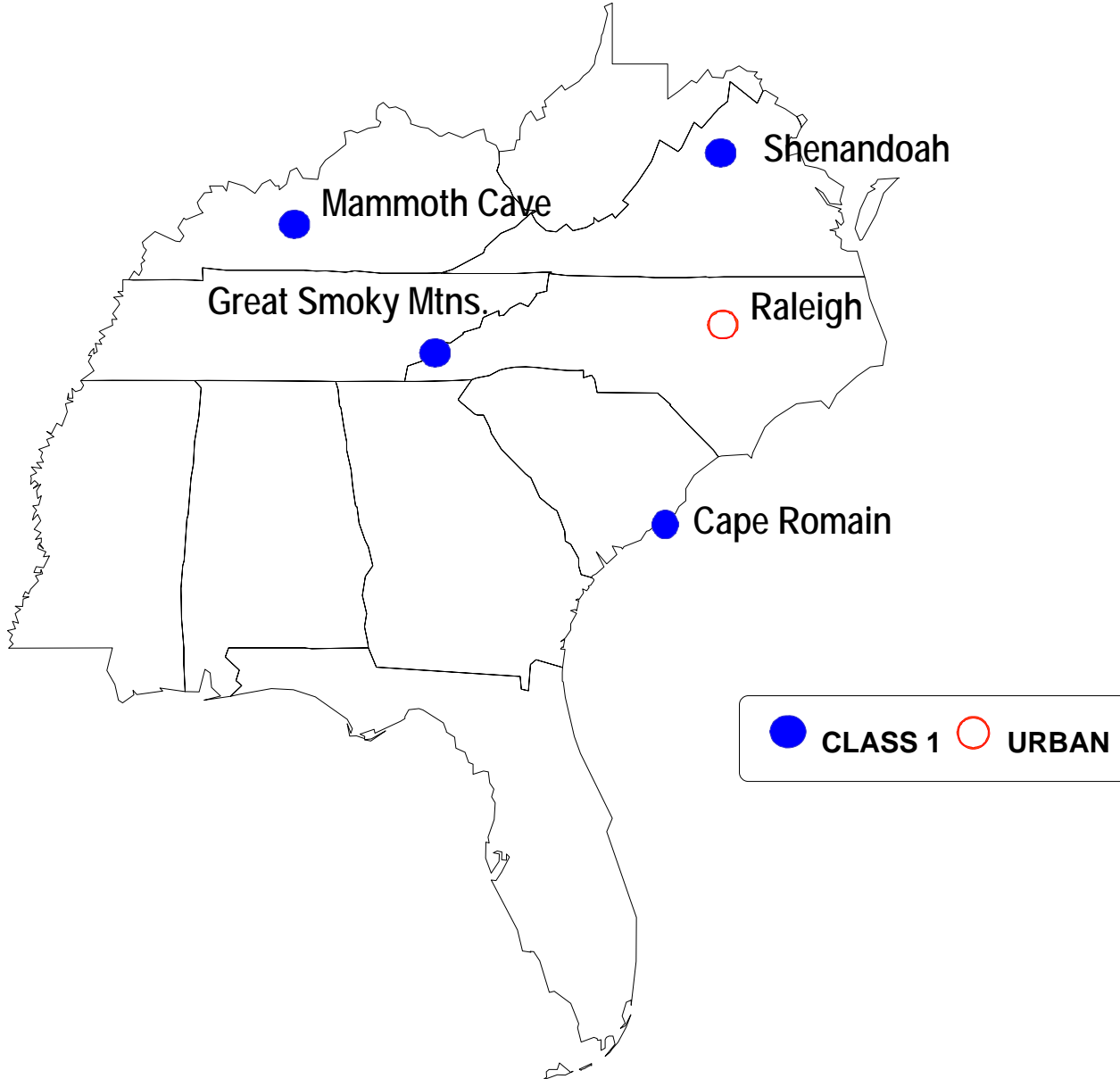


# Monitoring Objectives

- Identify sources of organic carbon
  - For same samples, characterize C<sup>14</sup> isotope and ratio of modern to fossil carbon
    - Analyses by Woods Hole Oceanographic Institute's National Oceanographic Sciences Accelerator Mass Spectrometry (NOSAMS)
  - Sources of modern carbon: vegetative emissions, wood burning, agricultural burning, cooking
  - Sources of fossil carbon: gasoline, diesel, oil



# VISTAS Carbon Study Sites



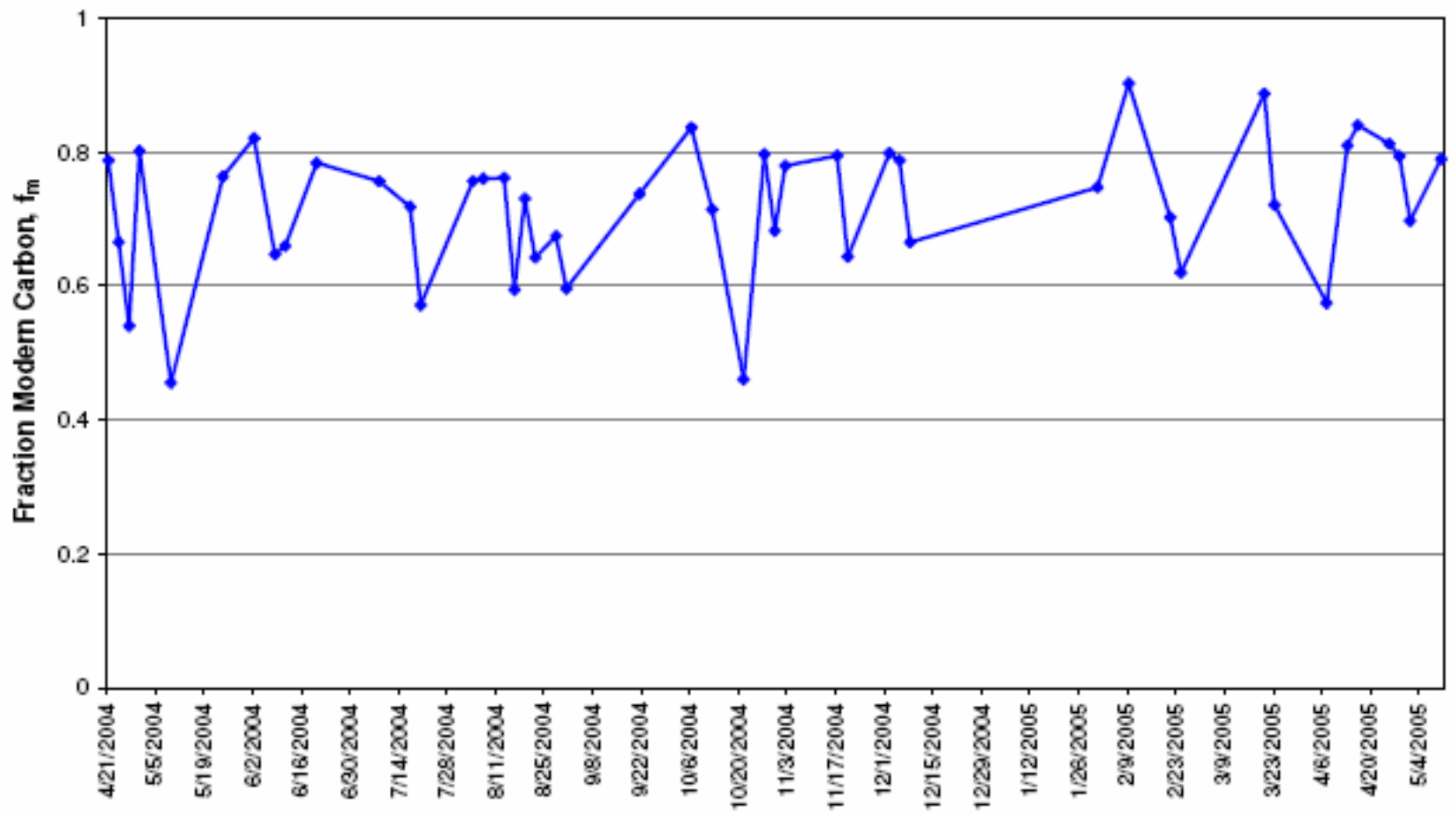


# Sources of Organic Carbon: Lessons Learned

- Modern carbon fraction seldom  $<0.60$ , usually  $>0.70$
- Higher modern carbon at forested sites (GRSM and MACA) than coastal (ROMA) or urban (MILL) sites
  - Higher total carbon and higher total  $PM_{2.5}$  at urban site correspond to lower modern carbon
- No clear seasonal trends in modern carbon
  - Hypothesize that greater wood burning in winter months and greater vegetative emissions in spring/summer



# $^{14}\text{C}$ , Cape Romain National Wildlife Refuge, SC



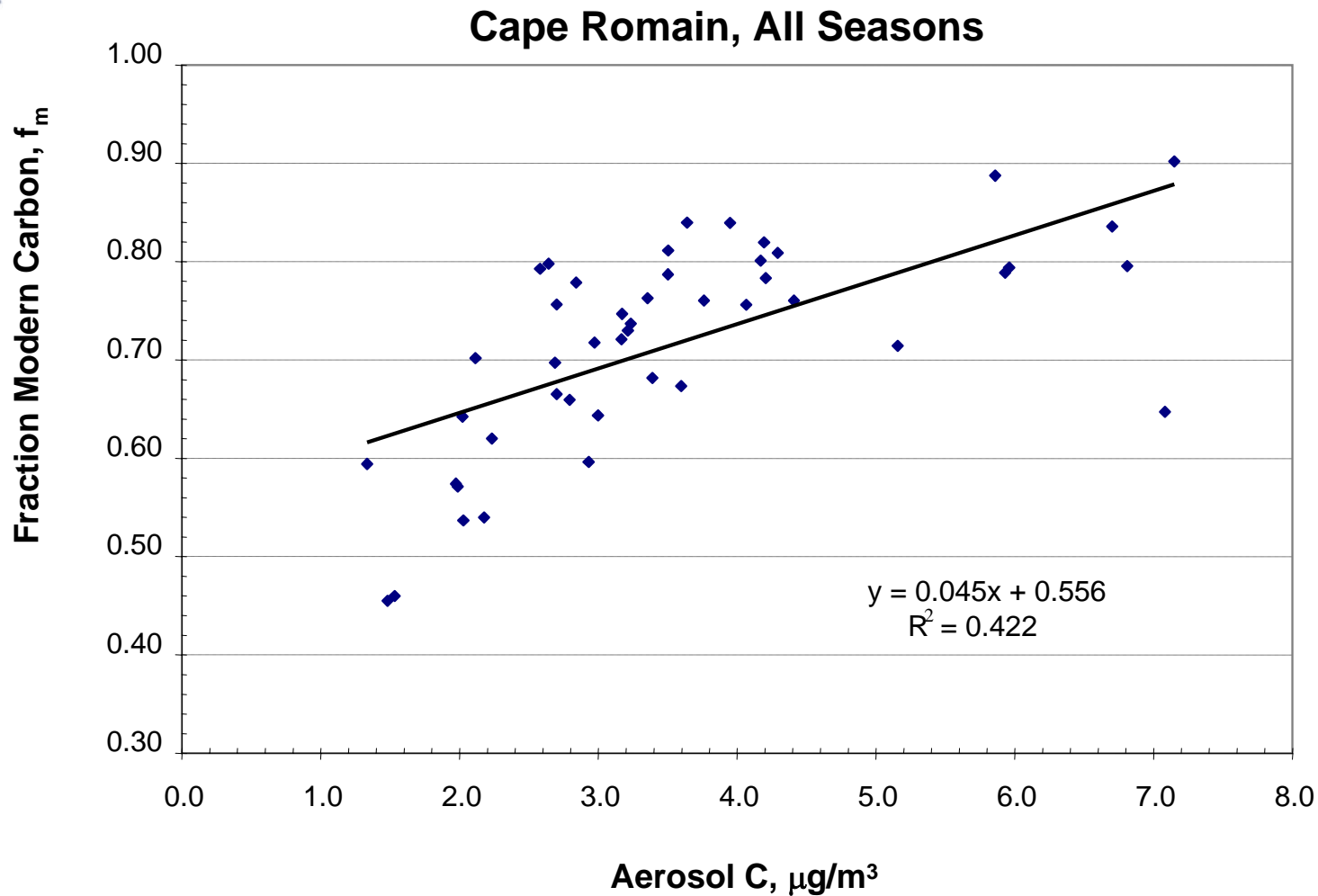
Apr 2004

Sampling Date

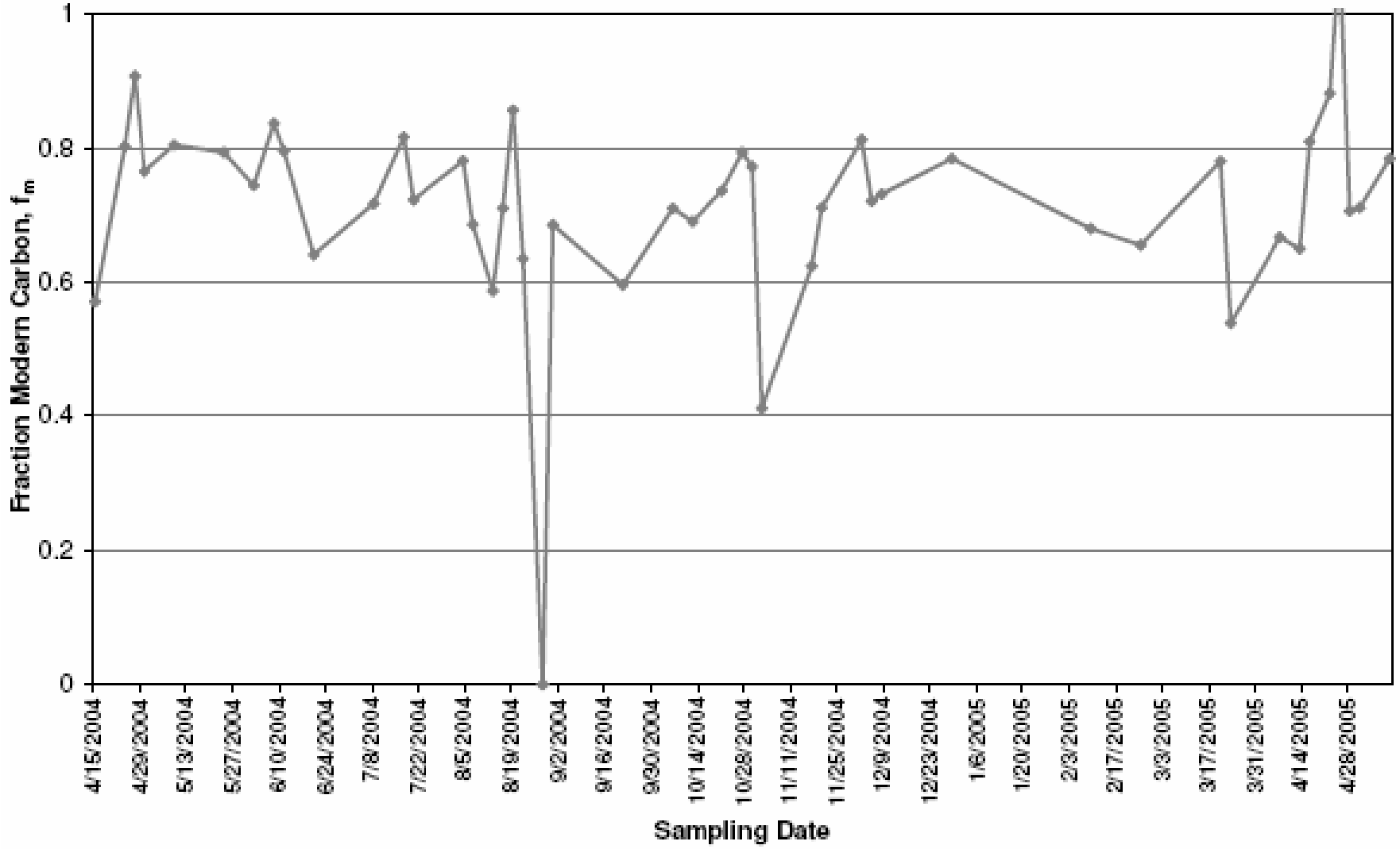
May 2005



# Fraction Modern Carbon vs. Aerosol Carbon



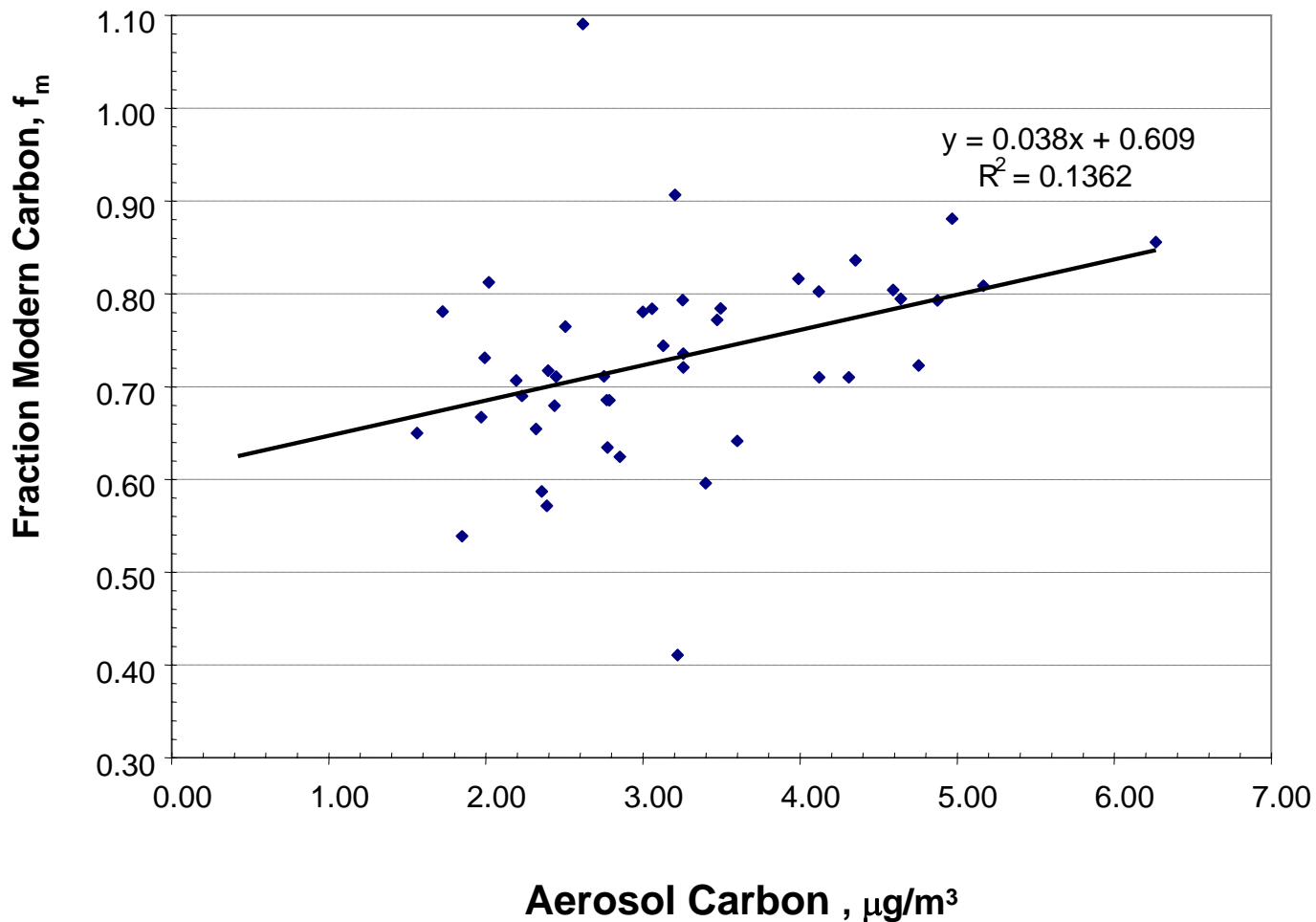
<sup>14</sup>C, Great Smoky Mountains National Park, TN (GRSM)



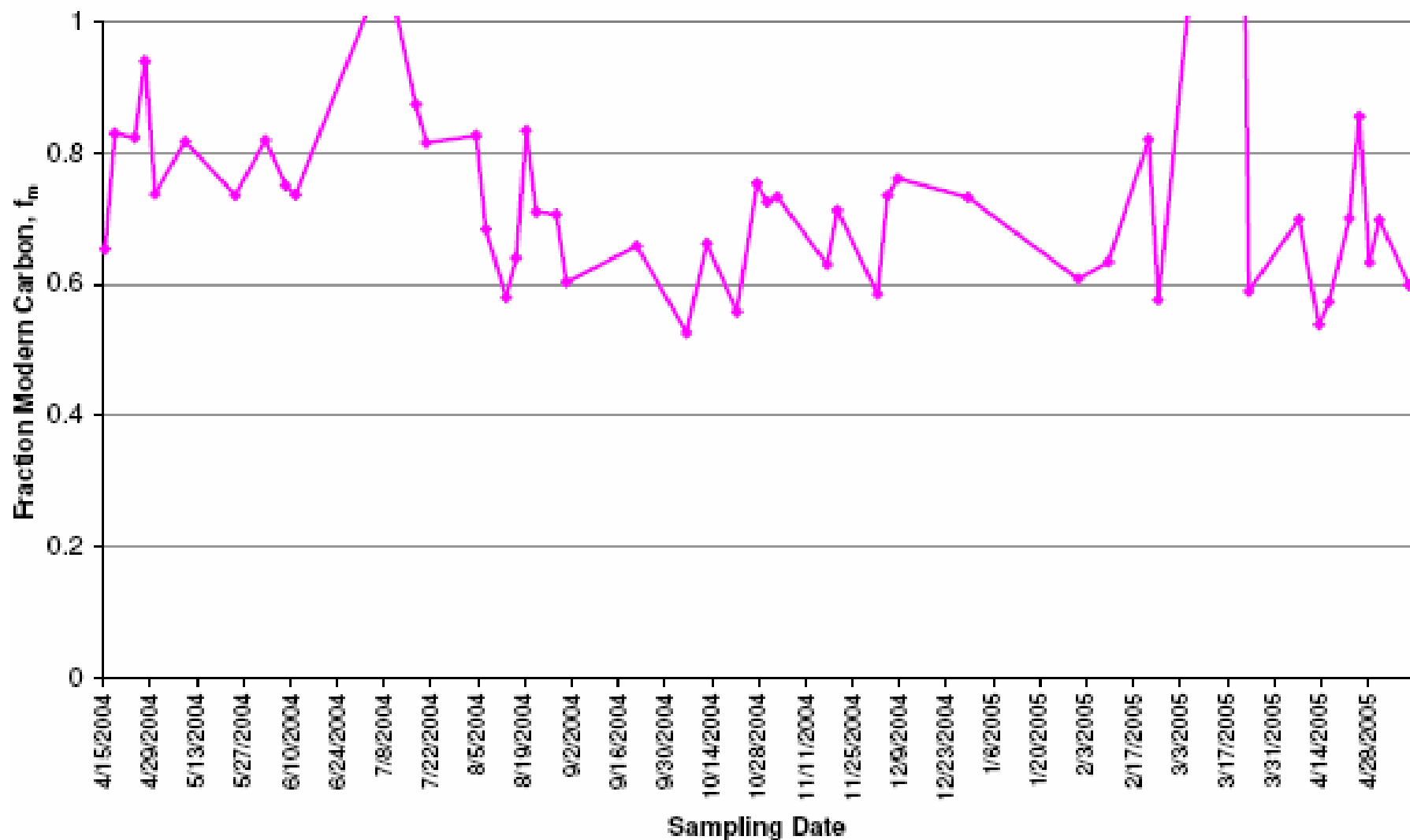


# Fraction Modern Carbon vs. Aerosol Carbon

## Great Smoky Mtns, All Seasons



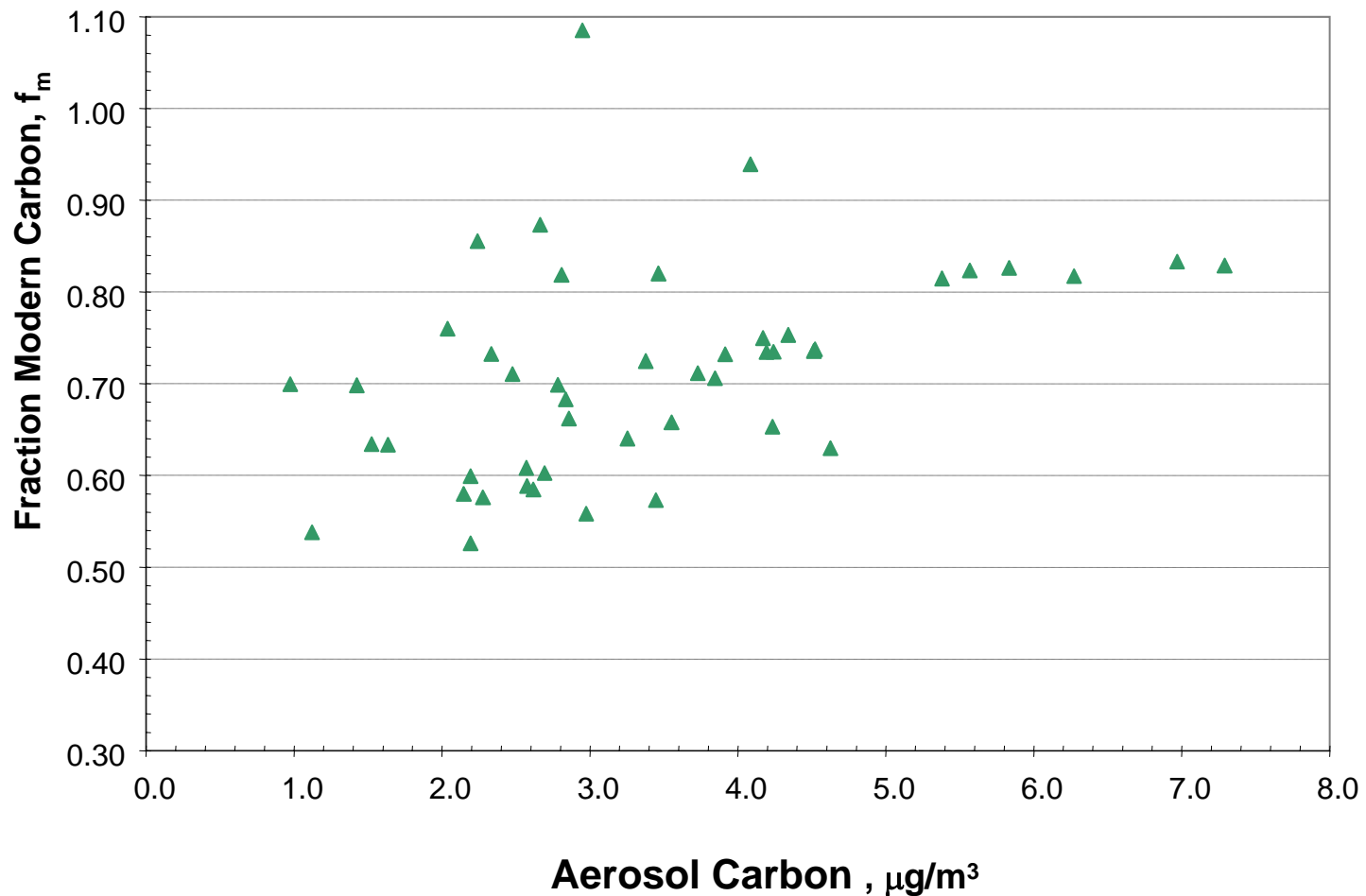
### $^{14}\text{C}$ , Mammoth Cave National Park, KY (MACA)



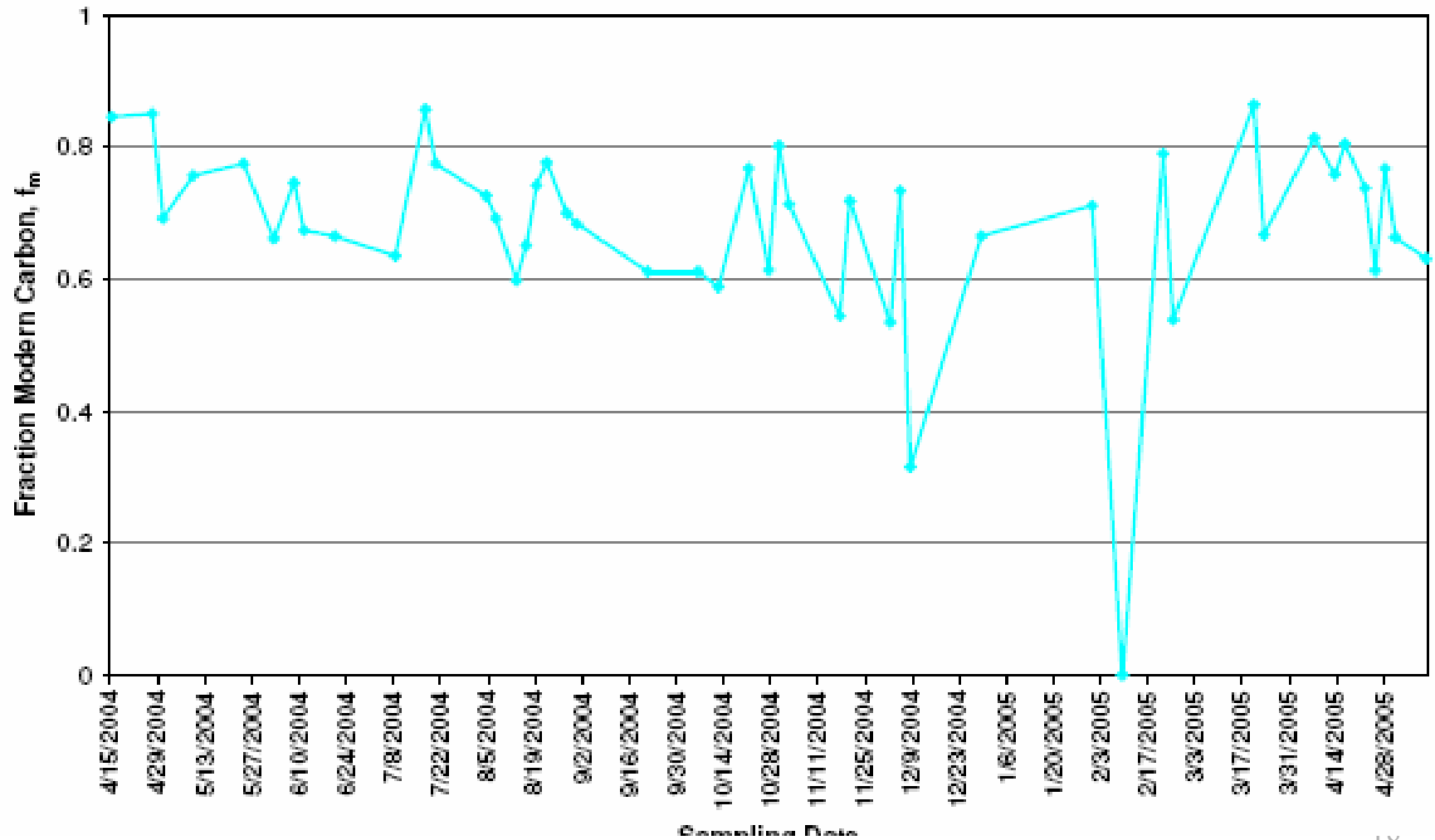


# Fraction Modern Carbon vs. Aerosol Carbon

## Mammoth Cave, All Seasons



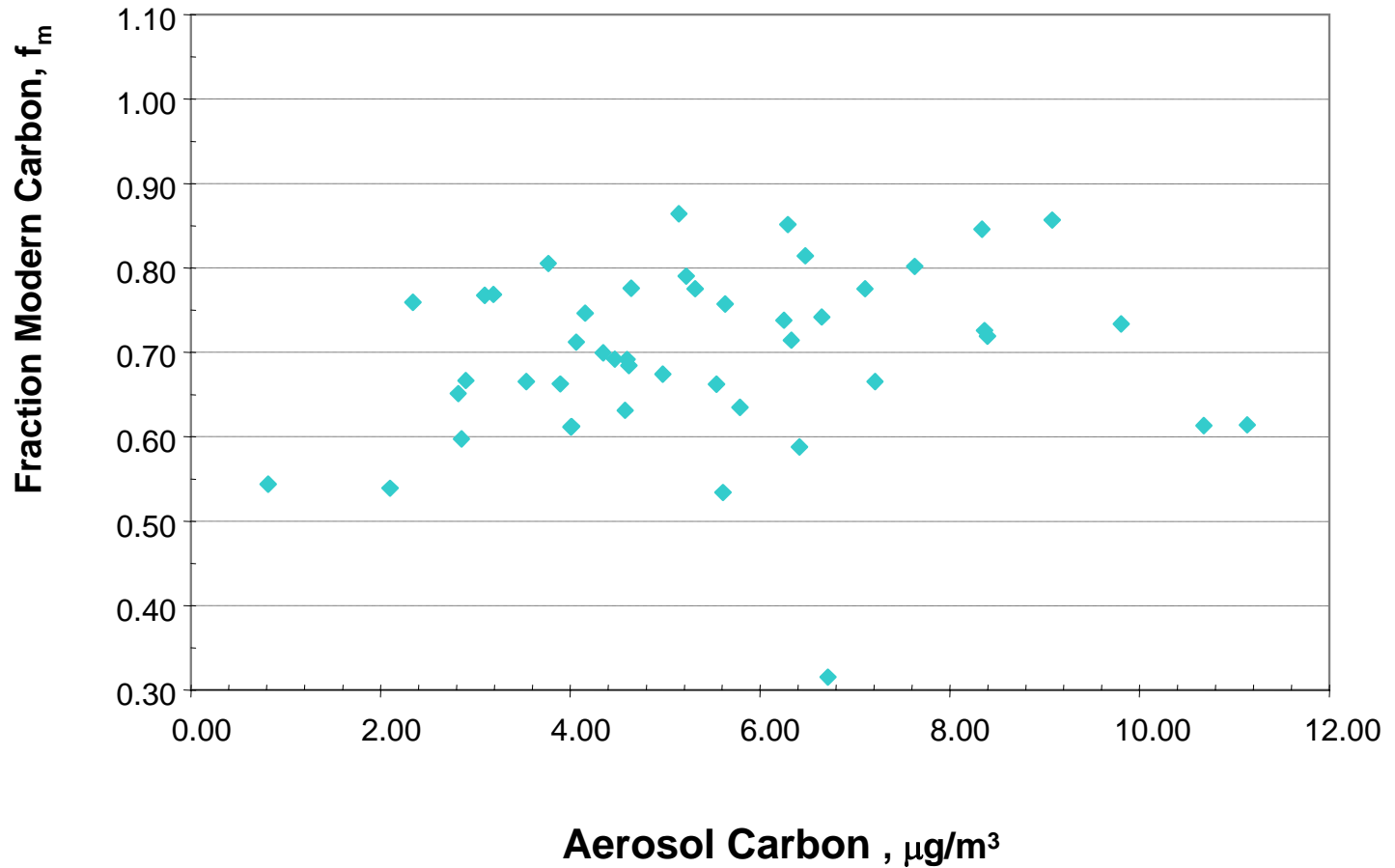
<sup>14</sup>C, Millbrook Station, Raleigh, NC (MILL)



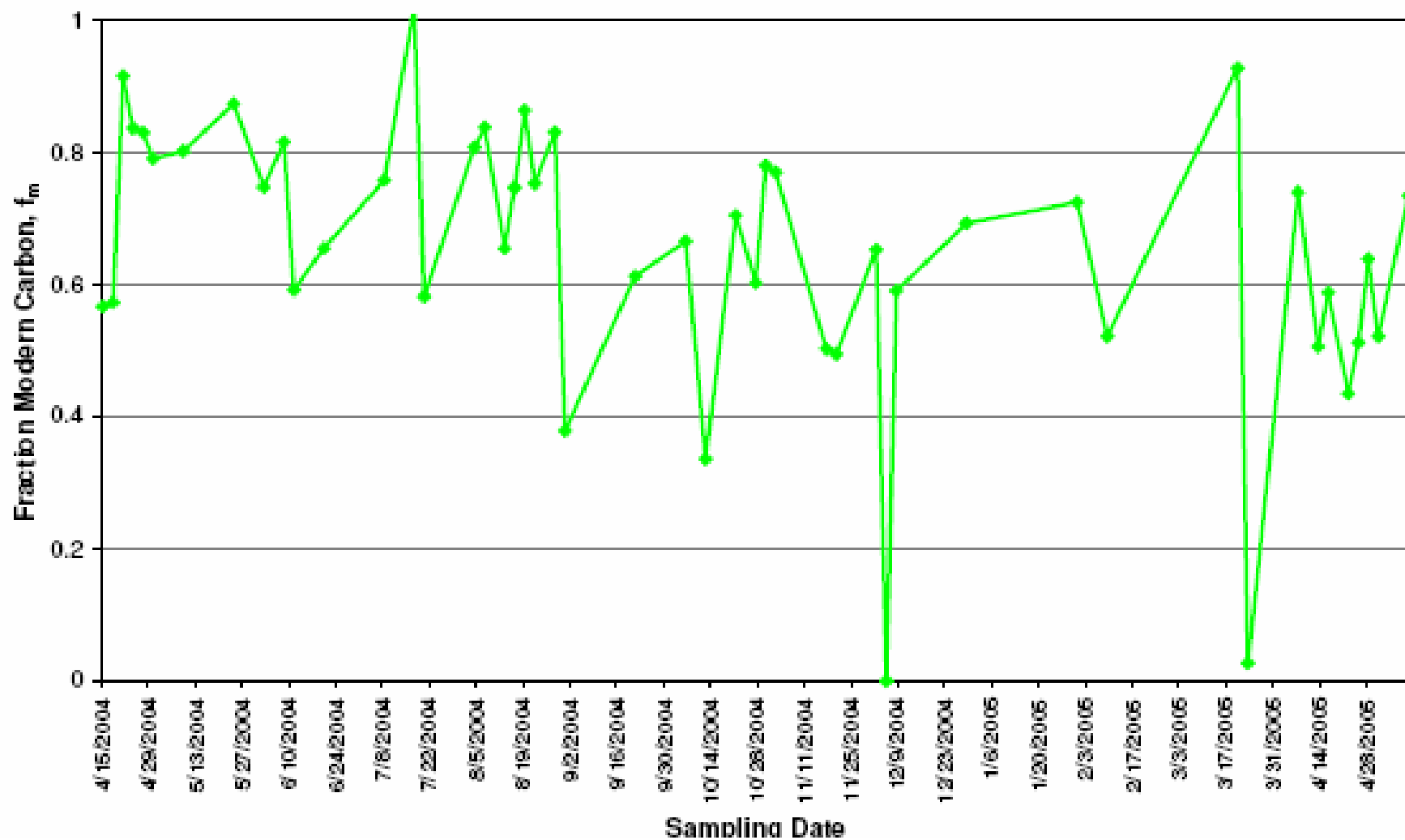


# Fraction Modern Carbon vs. Aerosol Carbon

## Millbrook, All Seasons



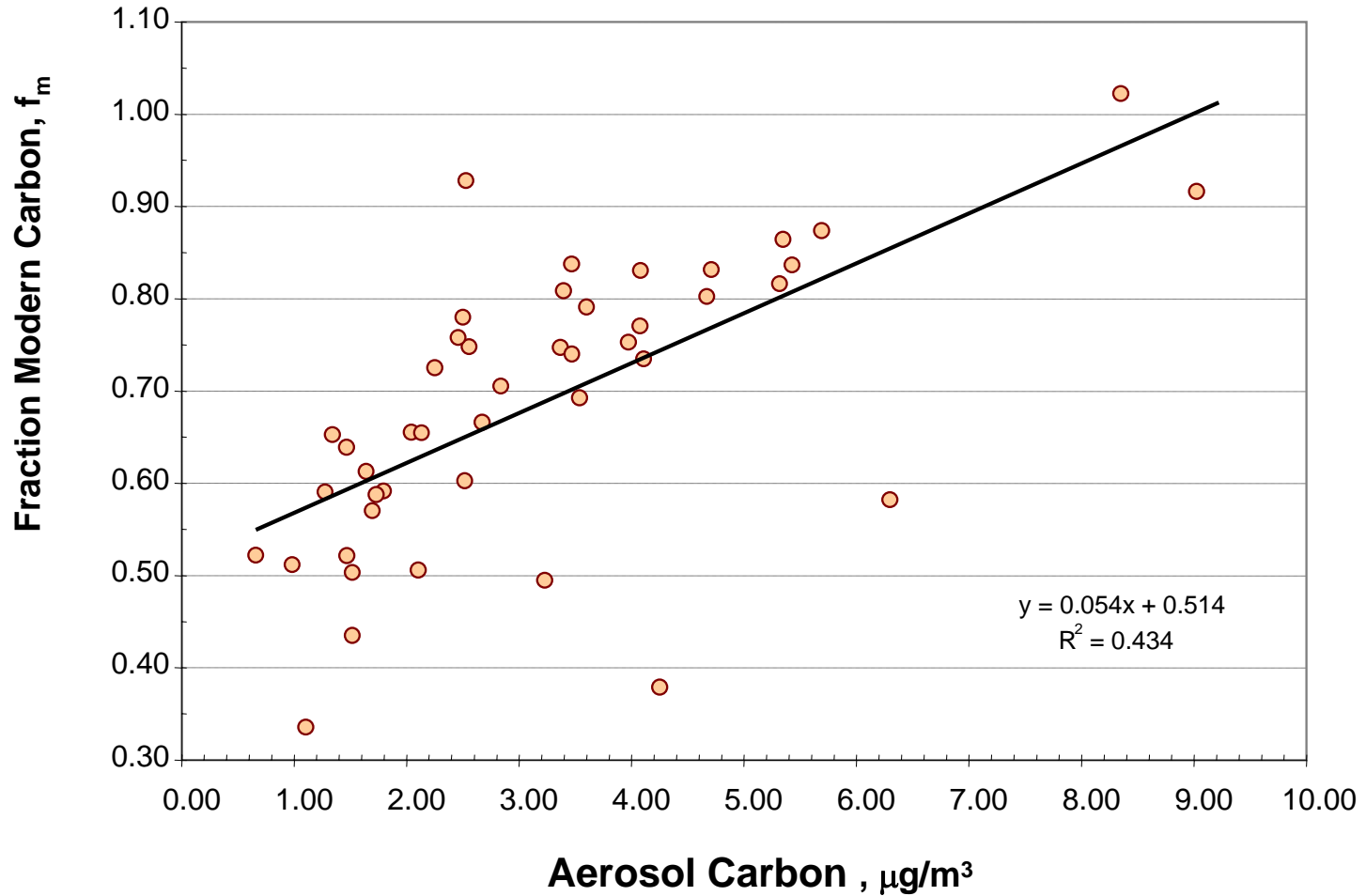
<sup>14</sup>C, Shenandoah National Park, VA (SHEN)





# Fraction Modern Carbon vs. Aerosol Carbon

Shenandoah, All Seasons





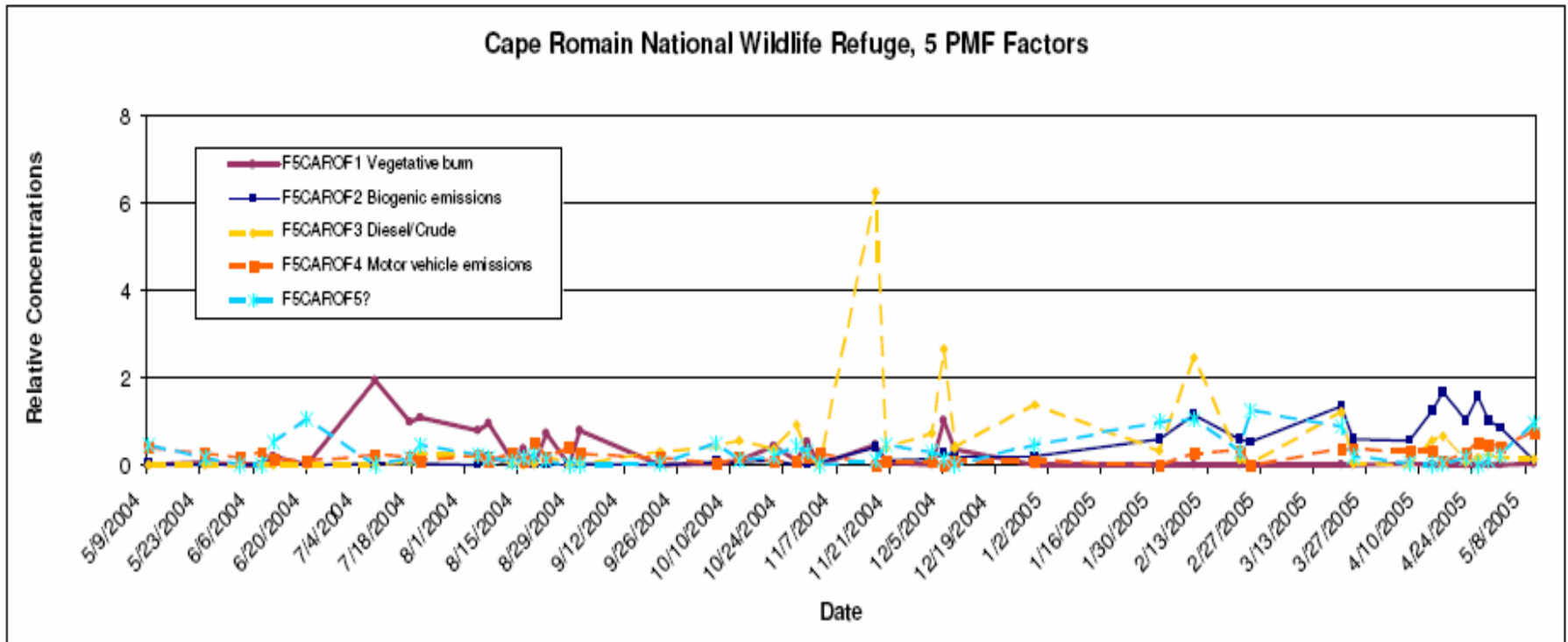
# Monitoring Objectives

- Positive Matrix Factorization applied to cluster organic compounds.
- Tracers identified for
  - Biogenic Emissions
  - Vegetative Burn
  - Gasoline emissions
  - Diesel emissions
  - Crude Oil (Commercial Marine, seen at ROMA)
- Analyses incomplete: tracers still need to be related back to total carbon to understand relative importance



## Positive Matrix Factorization (PMF) factor plots

Cape Romain National Wildlife Refuge, 5 PMF Factors



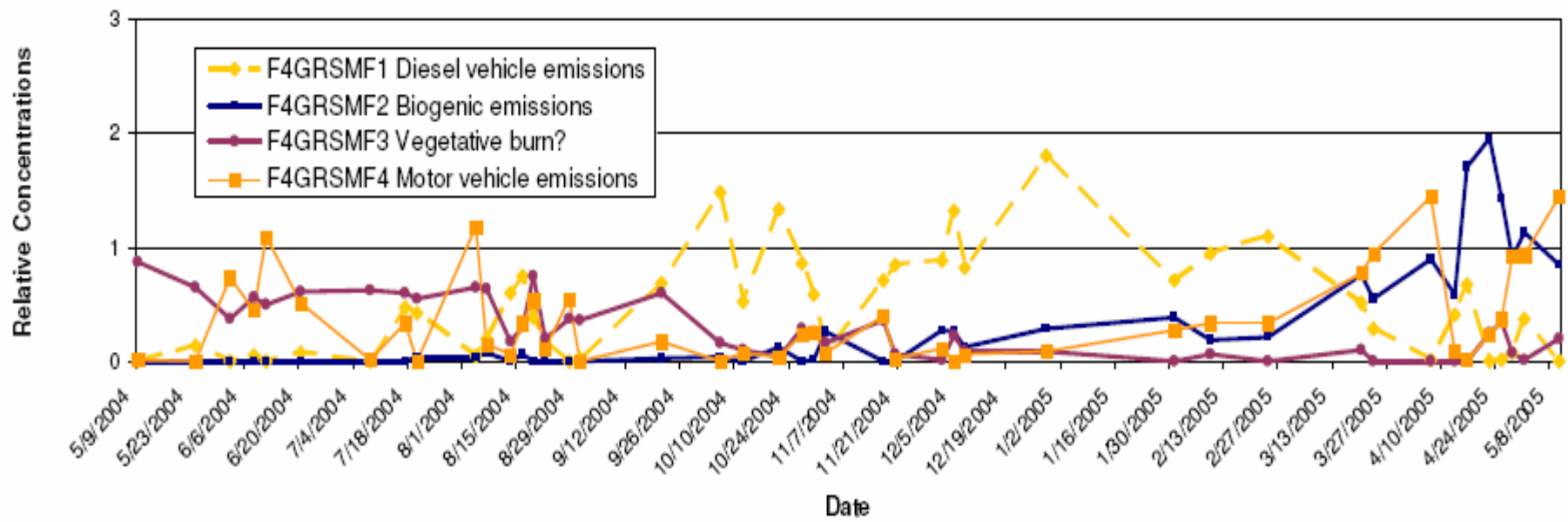
Vegetative burn

Biogenic Emissions

Diesel Crude

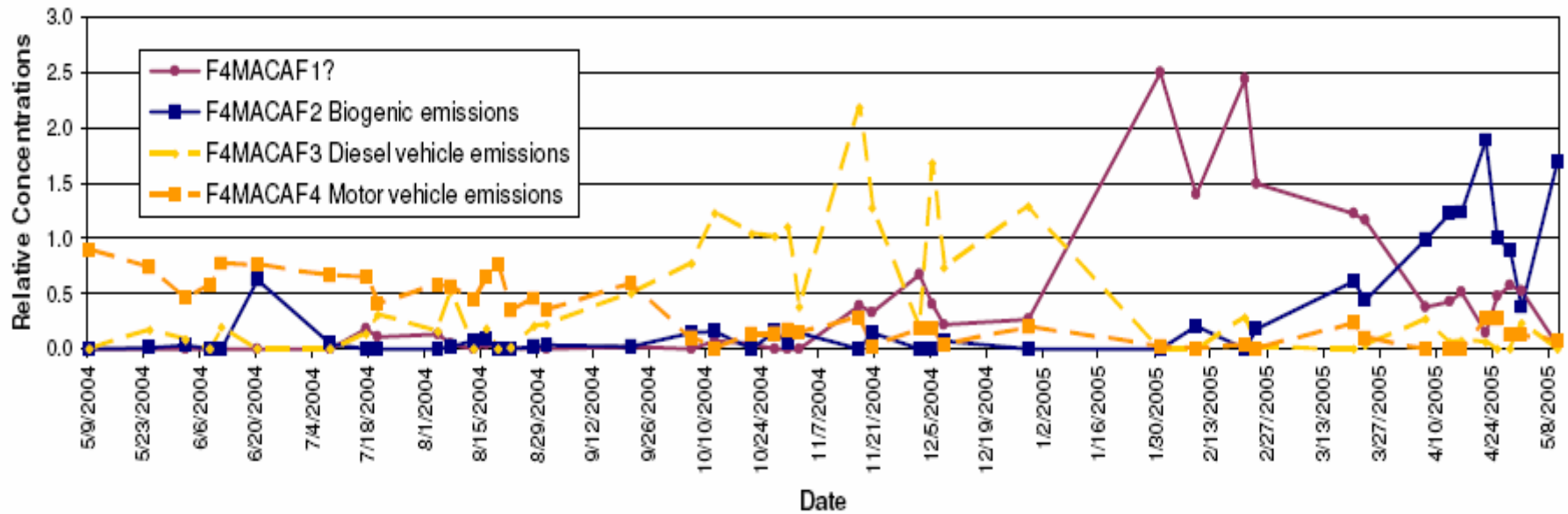
Motor vehicles

### Great Smoky Mountains National Park, 4 PMF Factors



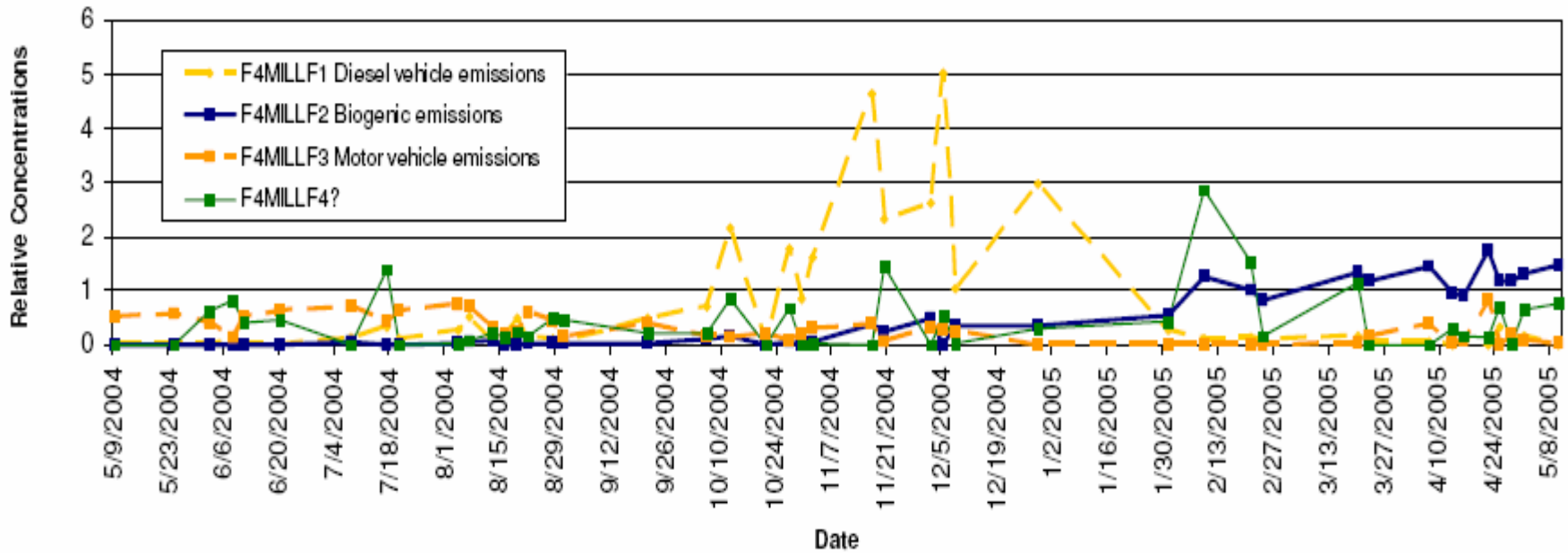


Mammoth Cave National Park, 4 PMF Factors



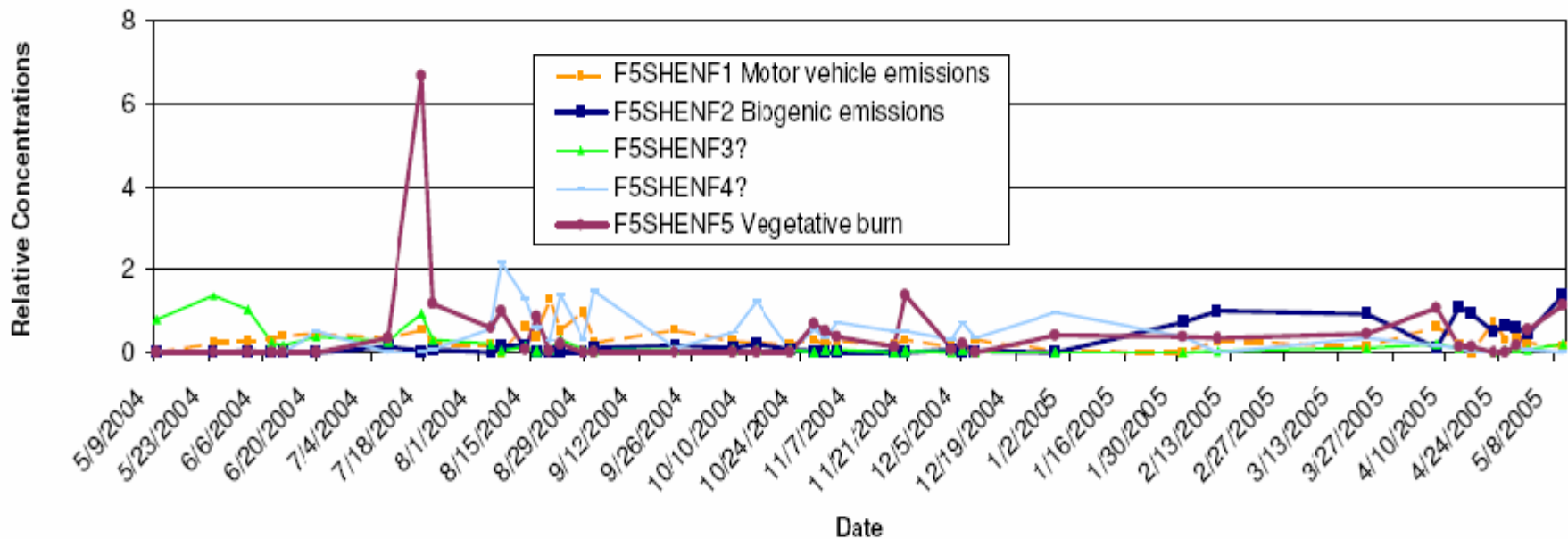


Millbrook Station, Raleigh NC, 4 PMF Factors





### Shenandoah National Park, 5 PMF Factors



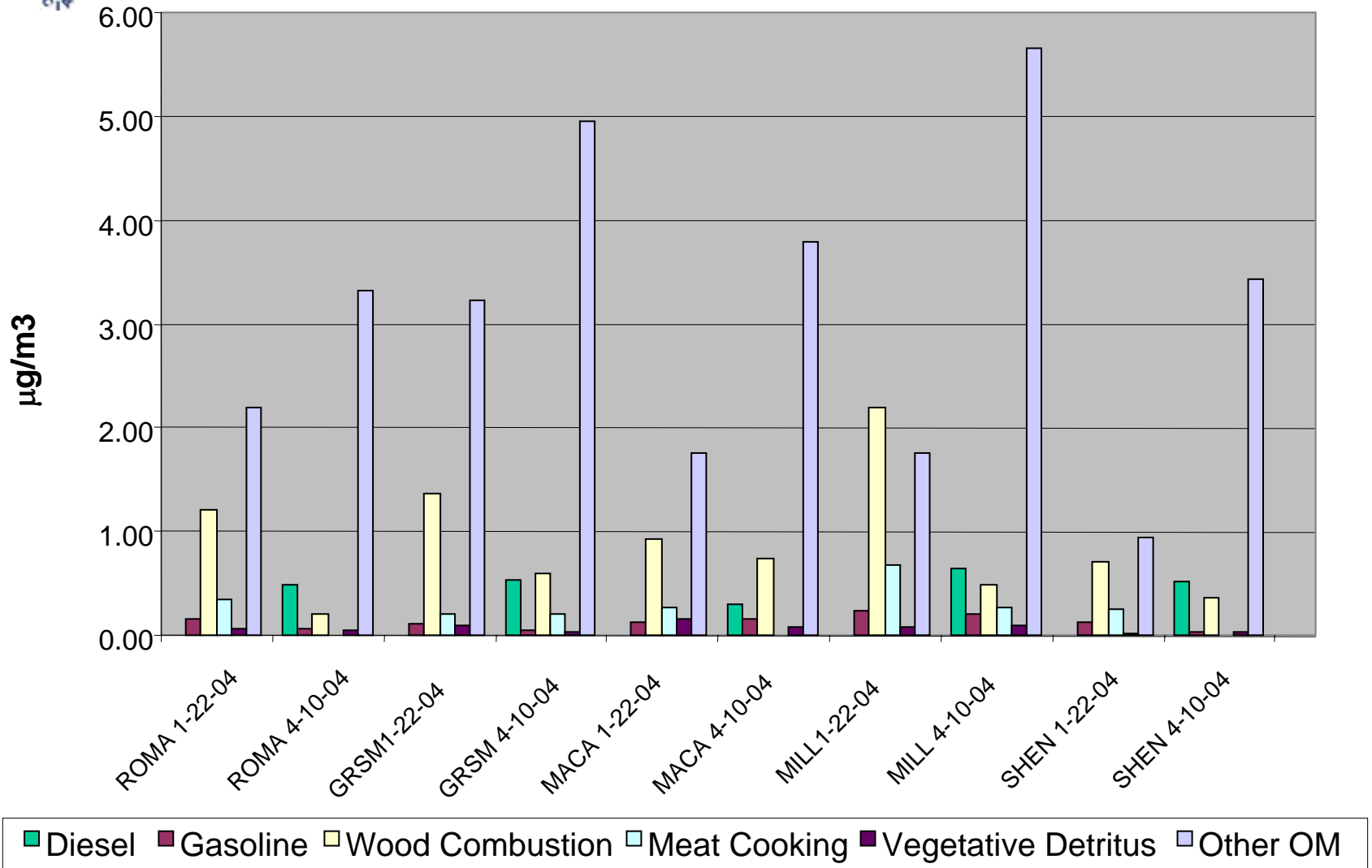


# Monitoring Objectives

- Chemical Mass Balance analyses
  - results to date from few samples analyzed by Mei Zheng, Ga Tech
- Chemical markers (profiles) for primary carbon sources:
  - Wood Combustion
  - Gasoline emissions
  - Diesel emissions
  - Meat Cooking
  - Vegetative detritus
  - Other Organic Matter (unidentified primary sources plus secondary organics)



## GT-CMB Results





# Carbon Source Attribution: Lessons Learned

- CMB Results from samples analyzed by Mei Zheng, Ga Tech
  - In April samples from all sites, unidentified component is largest fraction (>70%)
    - Likely secondary, likely biogenic
  - Wood combustion is largest identified component in Jan samples, all sites
  - Gasoline higher in Jan than Apr samples?
  - Diesel at all sites in Apr, not Jan samples?



# Carbon Source Attribution: Lessons Learned

- CMB analyses together with  $C^{14}$  results indicate that modern carbon is more important than fossil carbon at Class I areas and urban area sampled.
  - Little seasonal variability in modern carbon
    - wood burning vs biogenic
  - Still need integration to understand source contributions



# Next Steps

- Relate organic tracers used as PMF factors to larger population of organic compounds
- Complete CMB organic analyses all samples
- Relate organic profiles to measured carbon
- Integrate results with C14 analyses
- Interpret source attribution for organic carbon
- Integrate results with SOA production in CMAQ/CAMx air quality models
- Finalize project reports
- Submit manuscript for publication