Interagency Monitoring of Protected Visual Environments (IMPROVE)

Fine Mass Spatial and Seasonal Patterns in the Rural U.S.

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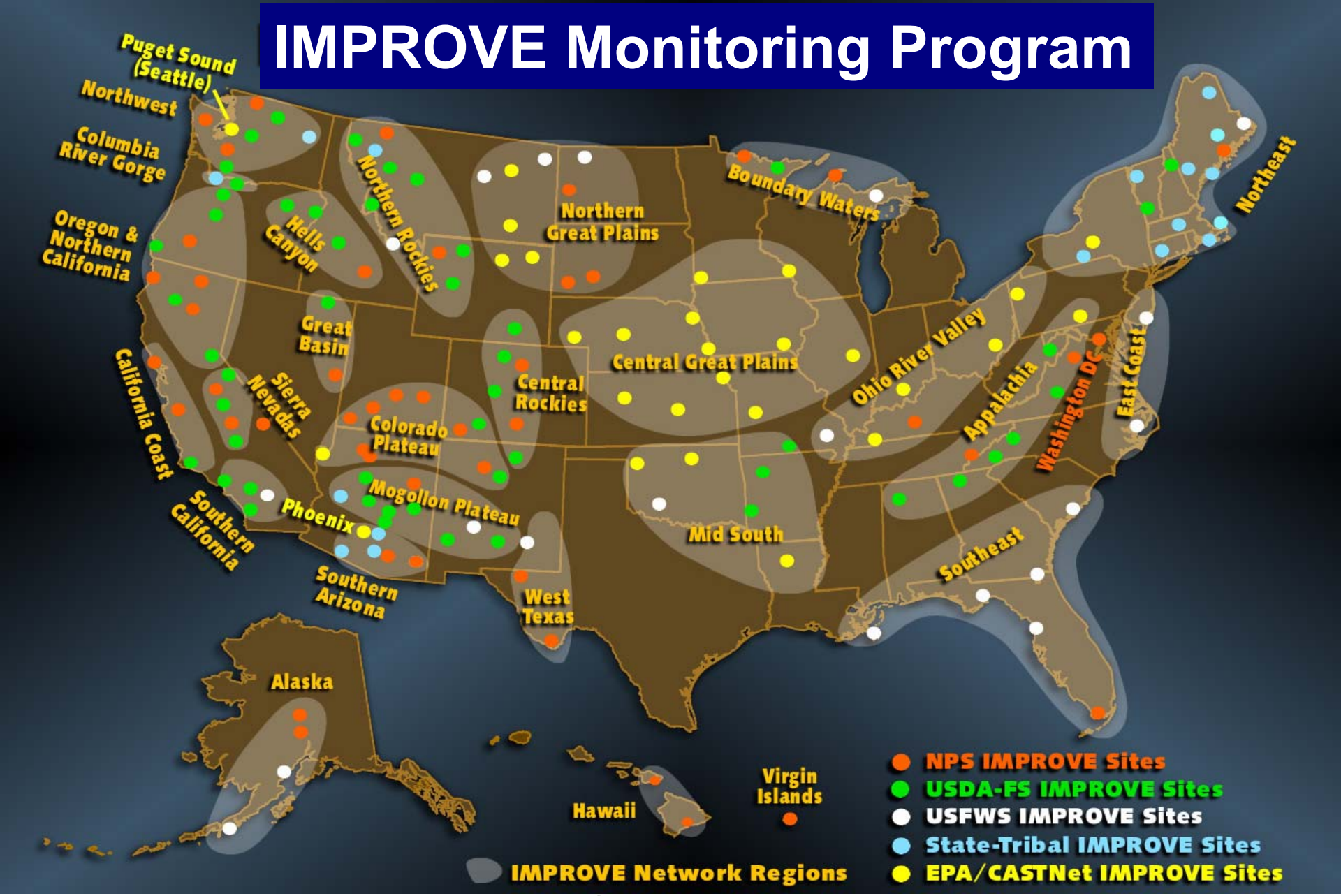
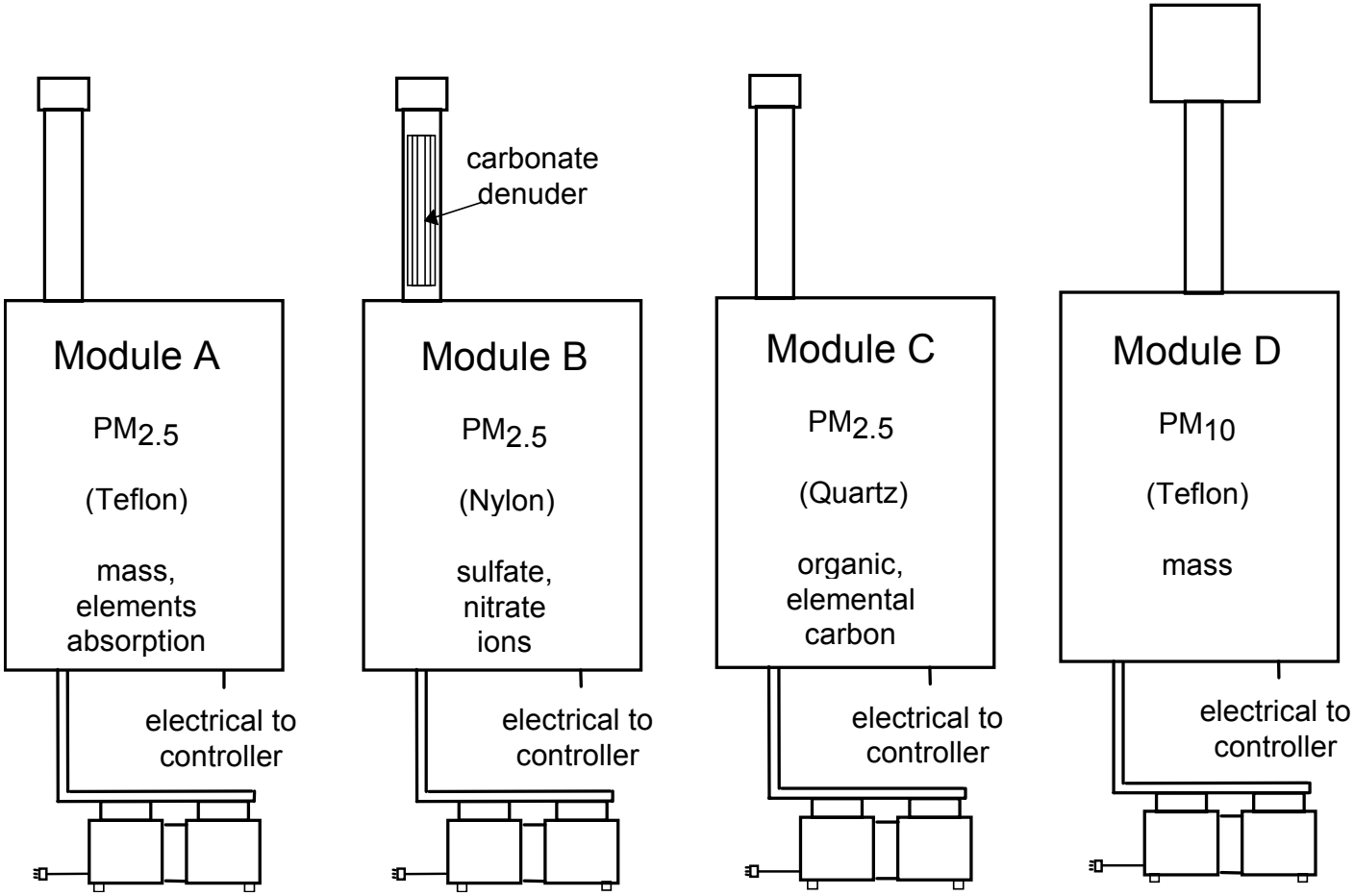
IMPROVE Monitoring Program



- Began operating in spring of 1988 with 20 monitoring sites
- Today has 165+ sites - 54 sites with eight or more years of data.

Chiricahua, NM

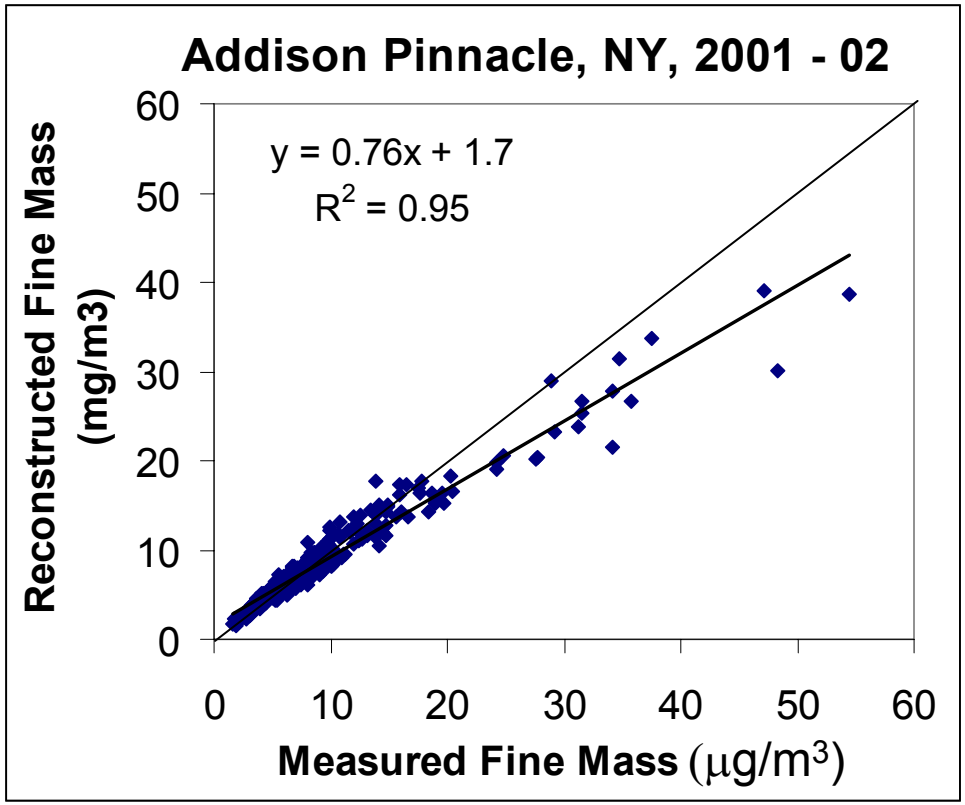
IMPROVE Aerosol Monitor



- 24 hour samples collected every 3 days

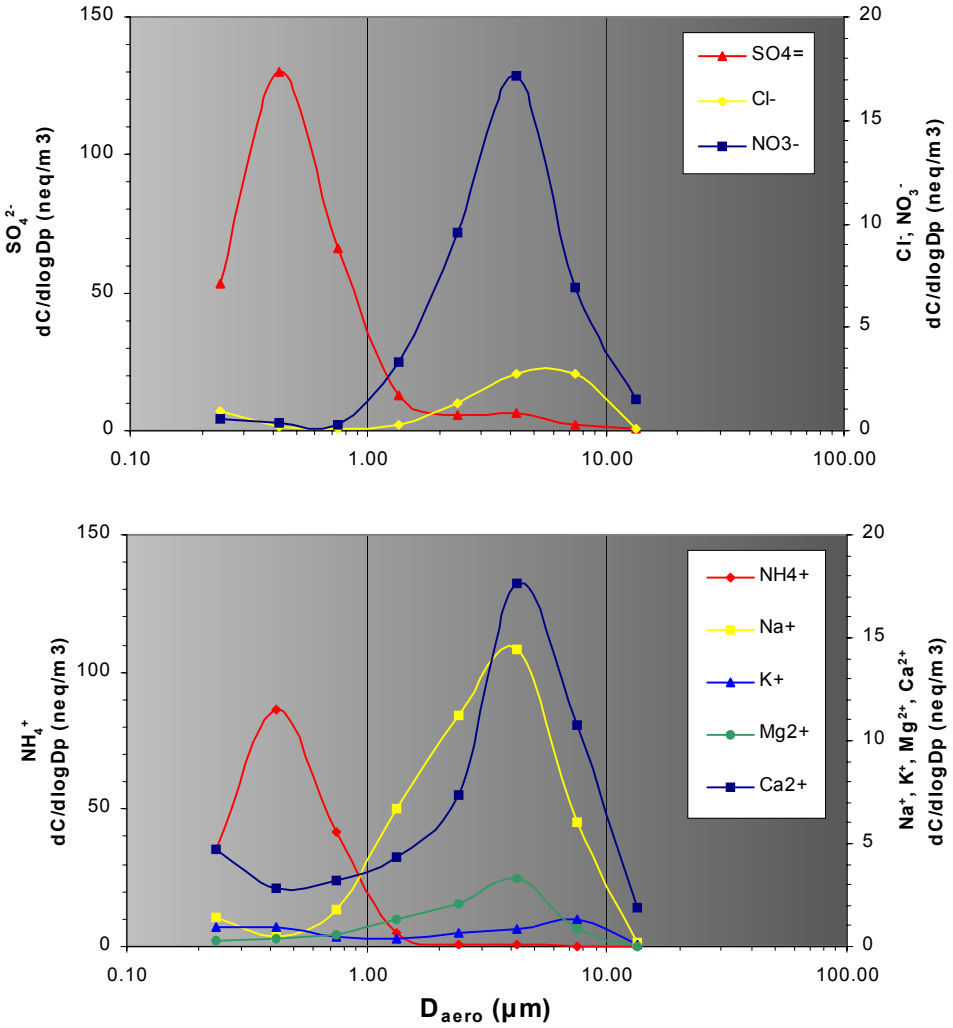
Fine Aerosol Composite Components

- Ammonium Sulfate
  - 4.125 * [S]
- Ammonium Nitrate
  - 1.29 * [NO_3]
- Organics
  - 1.4 [OC]
- Elemental Carbon
  - [EC]
- Soil
  - oxides of crustal elements

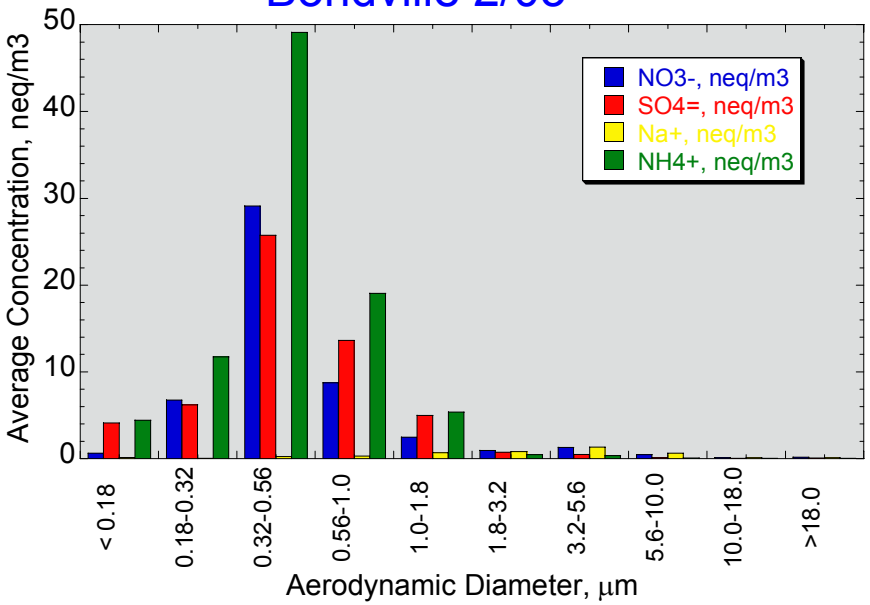


Size Distributions

Big Bend Texas - August 1999



Bondville 2/03



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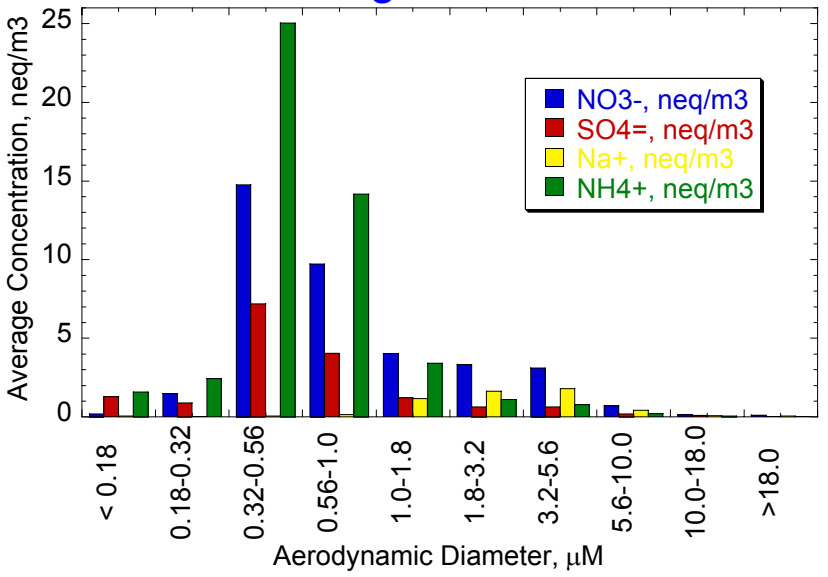
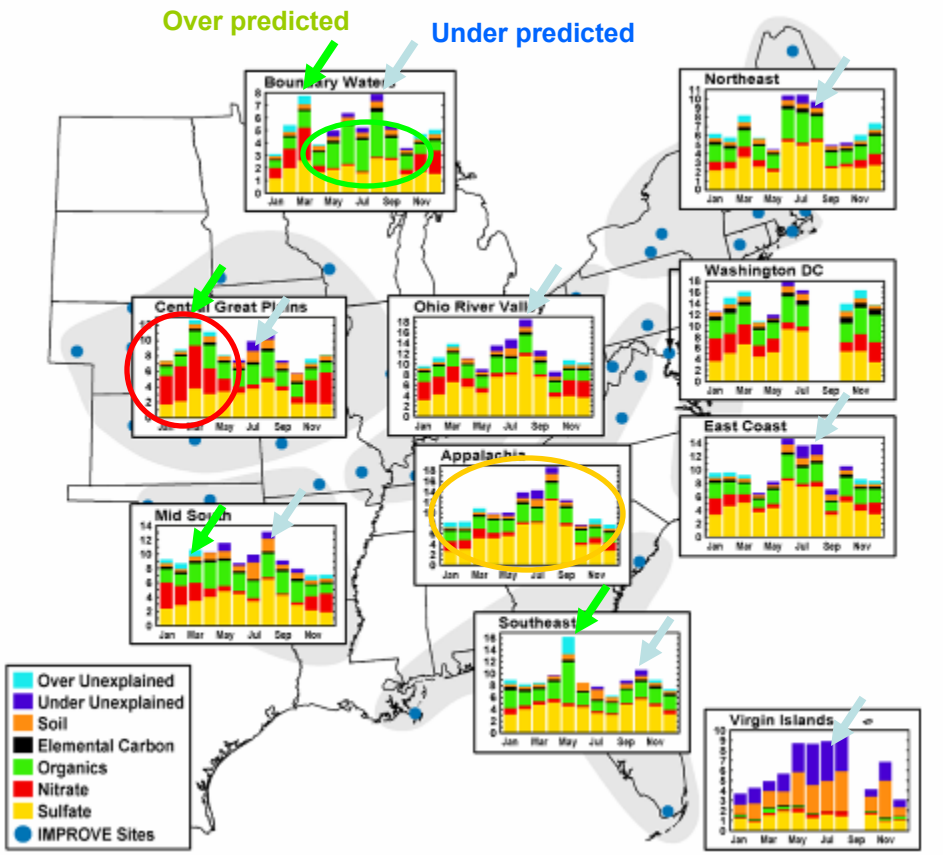
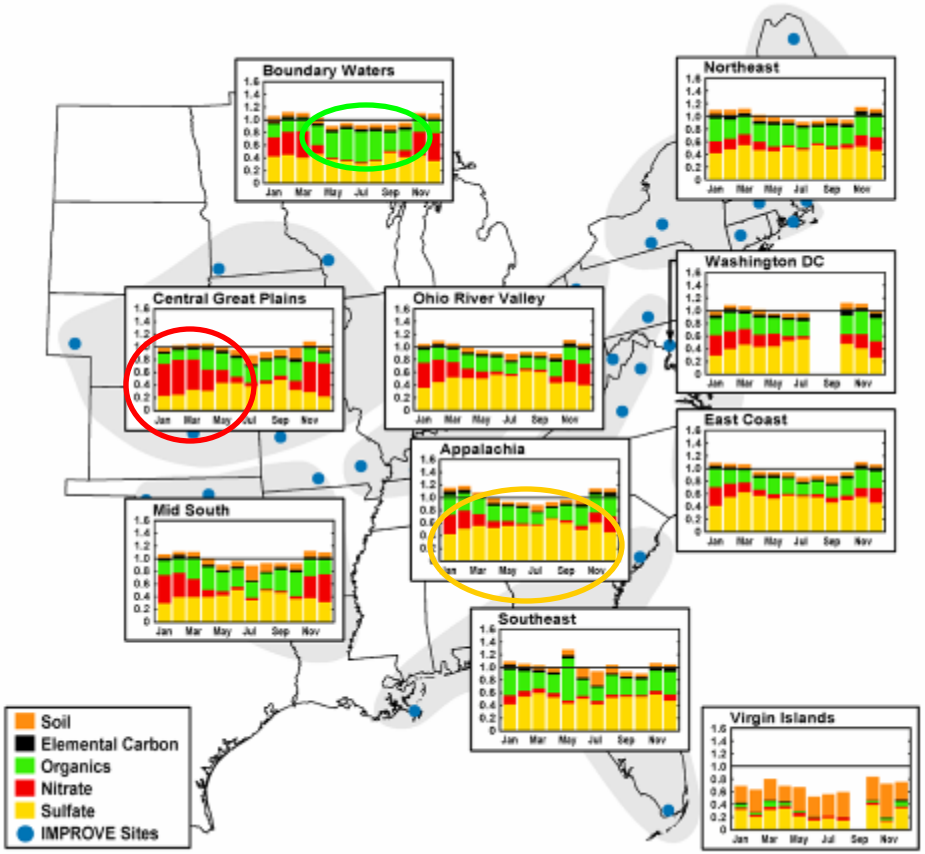


Monthly Fine Mass Budget - 2003





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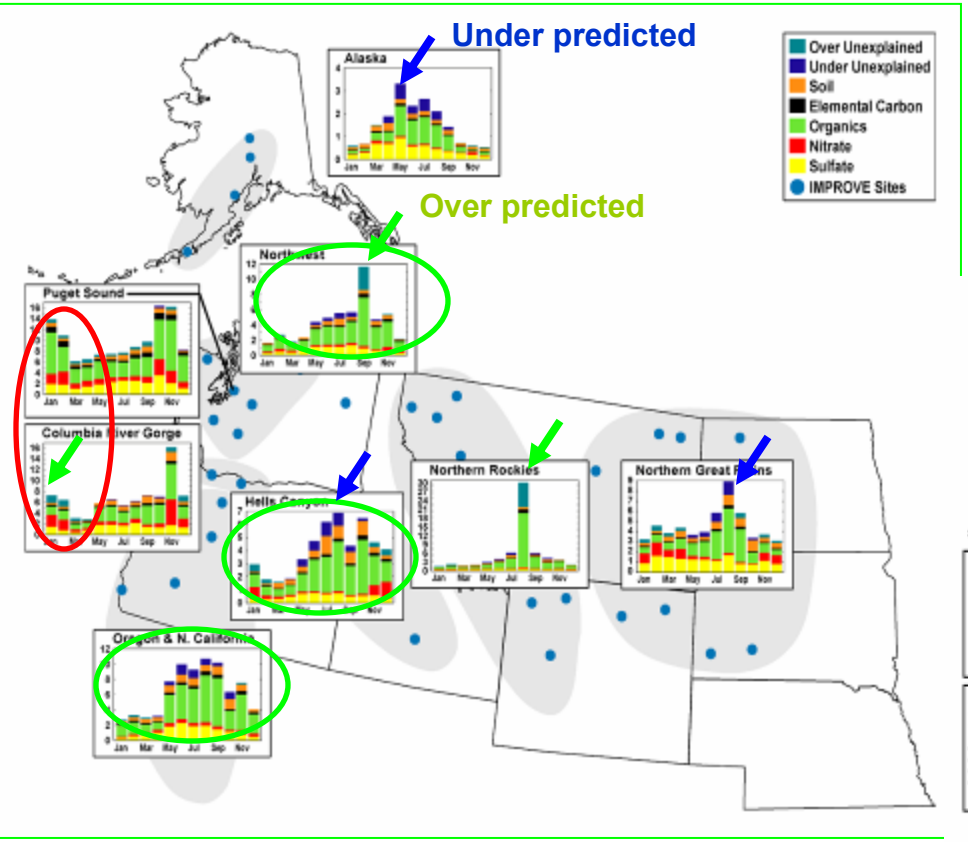

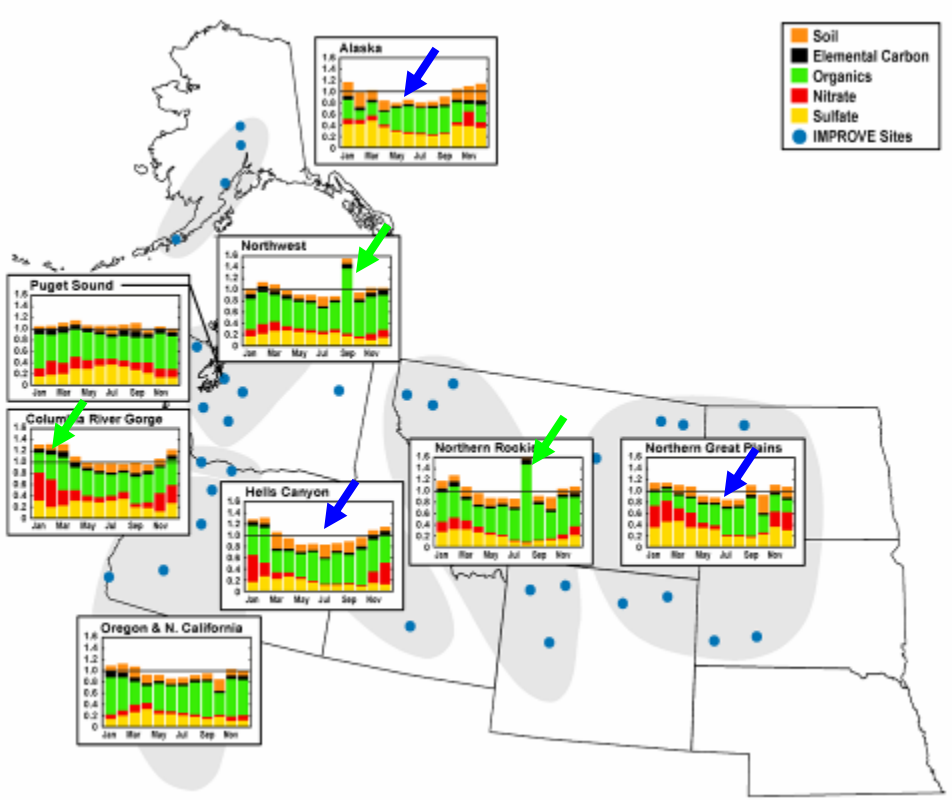

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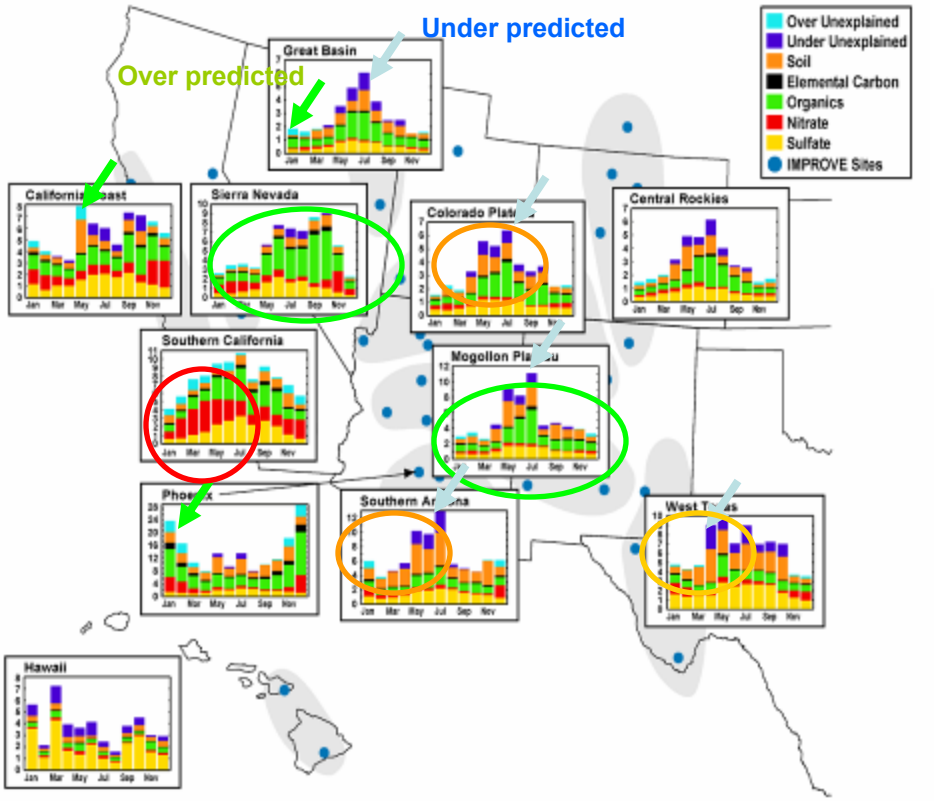
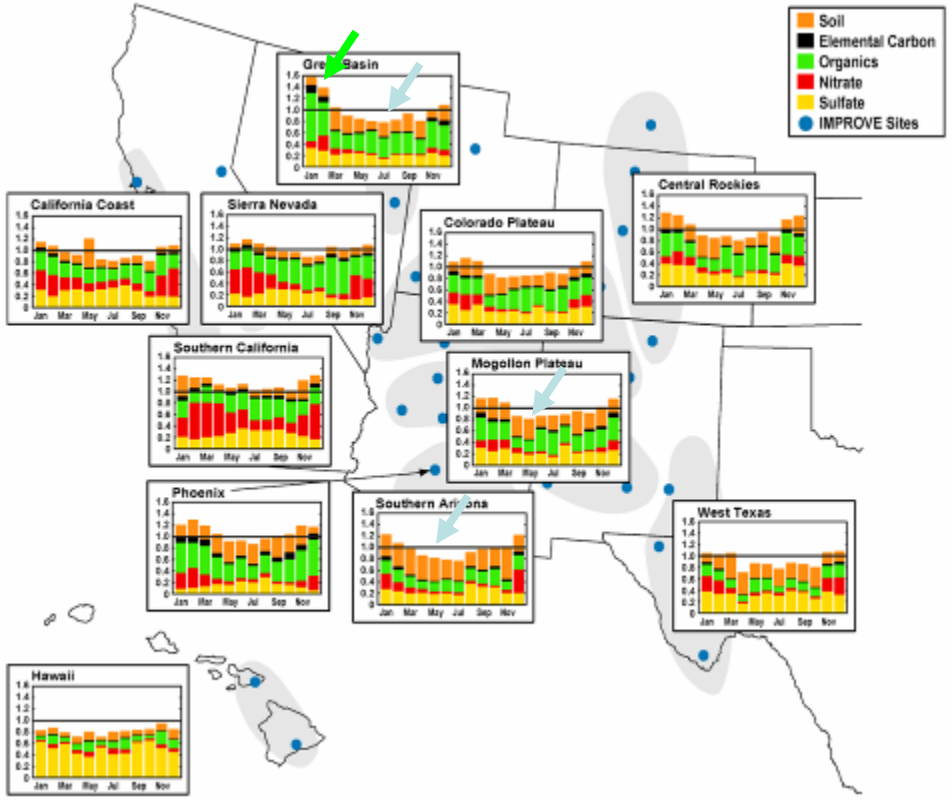
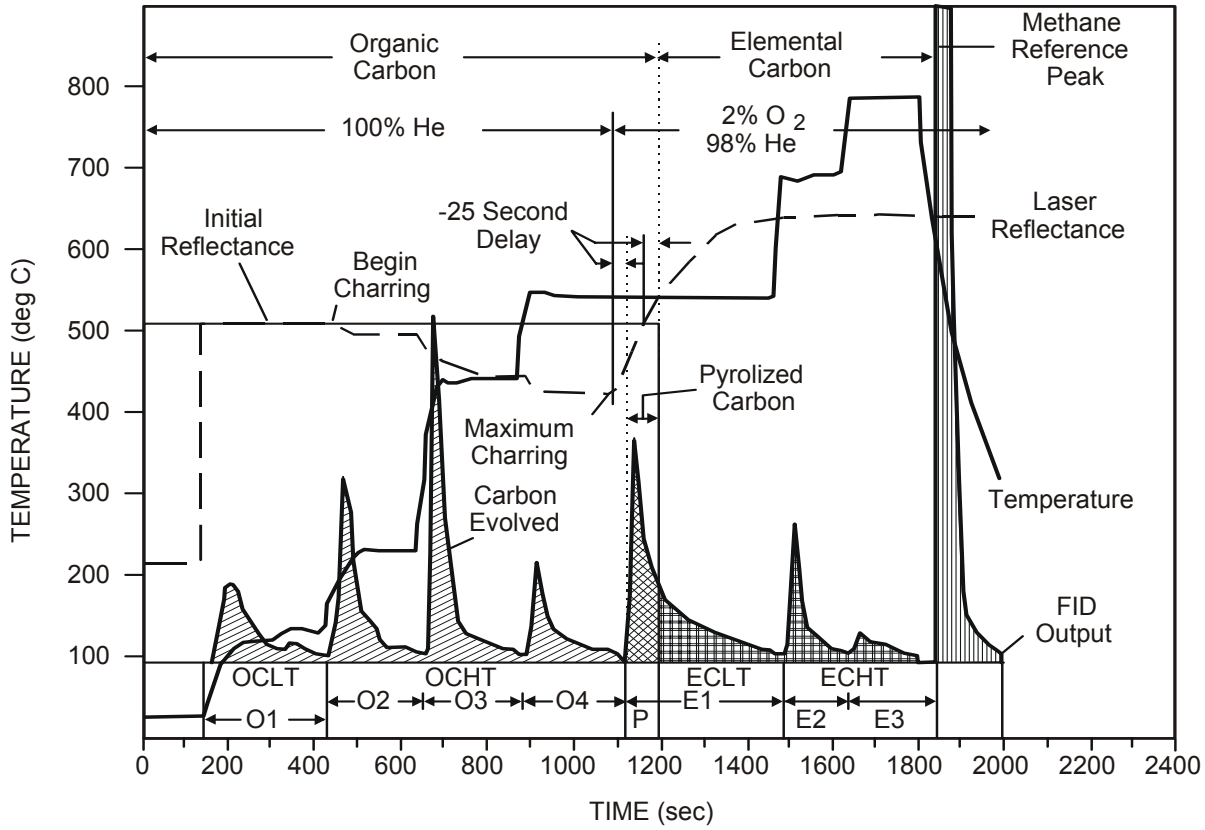




Carbonaceous Compounds Spatial and Seasonal Patterns and Hygroscopicity

Thermal Optical Reflectance (TOR)



- IMPROVE collects fine particulates on a quartz filter which is analyzed for organic and elemental carbon in 7 temp. bands.
- EC is **operationally** defined as carbon evolved after oxygen is added to the environment and reflectance returns to initial value (pyrolysis correction).
- Data are corrected for a positive artifact

TOR OC/EC vs Other Methods

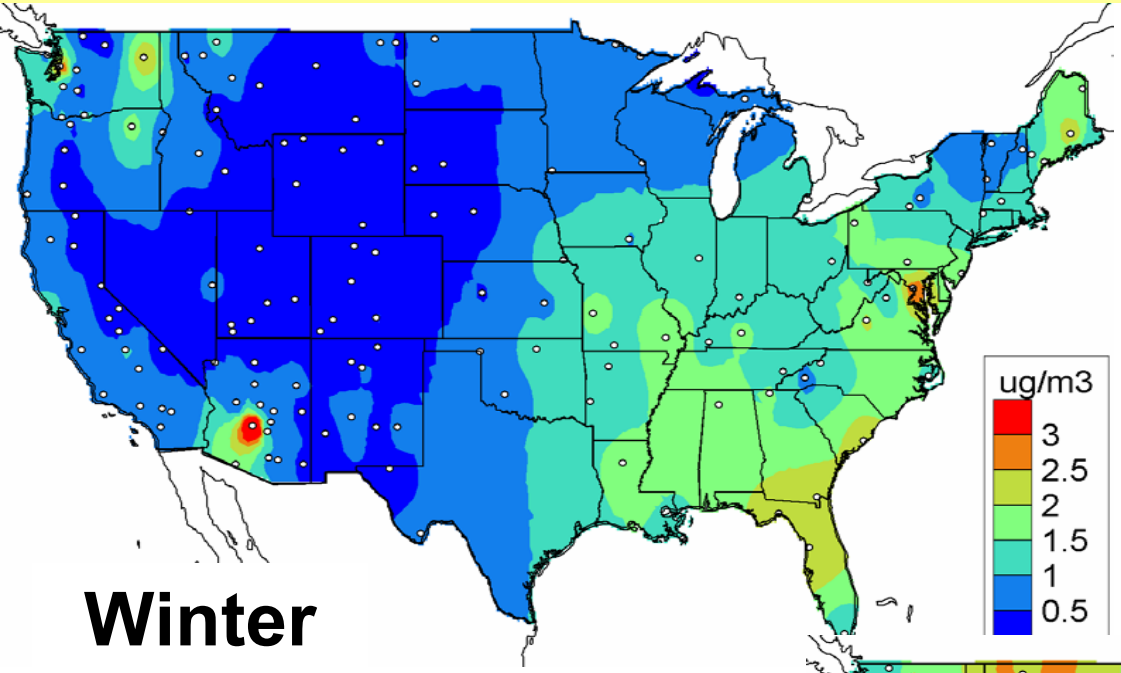
Numerous studies have been conducted comparing total, organic and elemental carbon estimates from thermal, chemical extraction and optical techniques.

- Total carbon is measured accurately and precisely. Measurements techniques are typically within 5%
- EC/TC ratios vary widely depending on technique
  - EC/TC ratios in NIST urban dust (SRM 1649a) varied over a factor of 7:

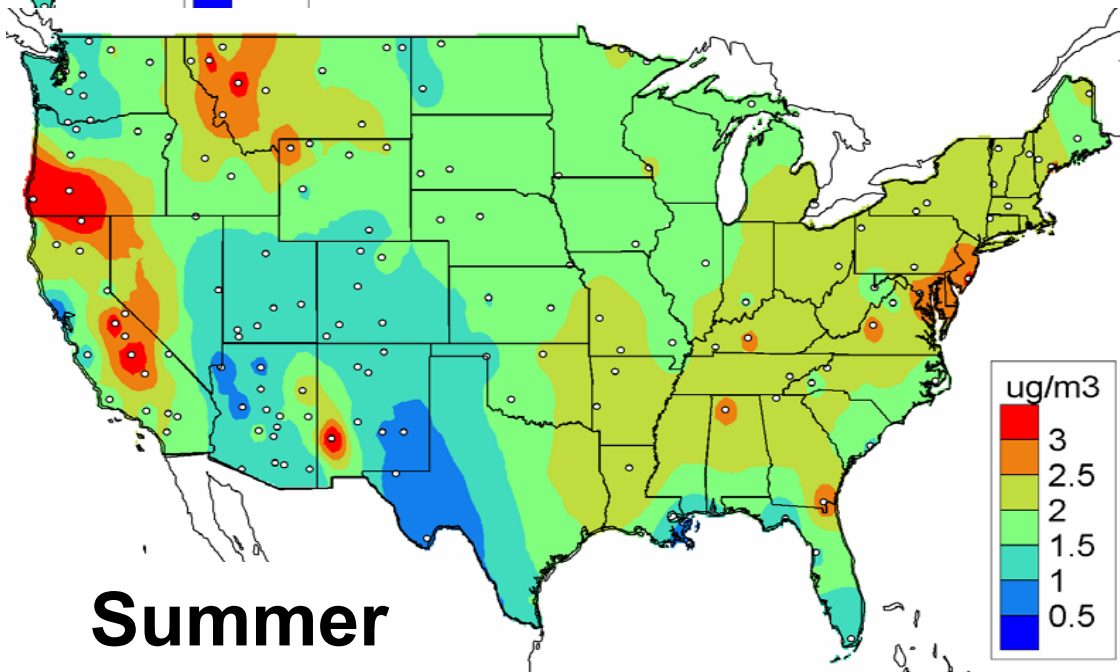
Range: 0.07 to 0.52
Mean: 0.27 ± 0.15
TOR: 0.432 ± 0.009

"No method or result can in principle be judged "correct" (or incorrect)" (Currie, *et al.*, 2002)

Organic Carbon – 2001-03

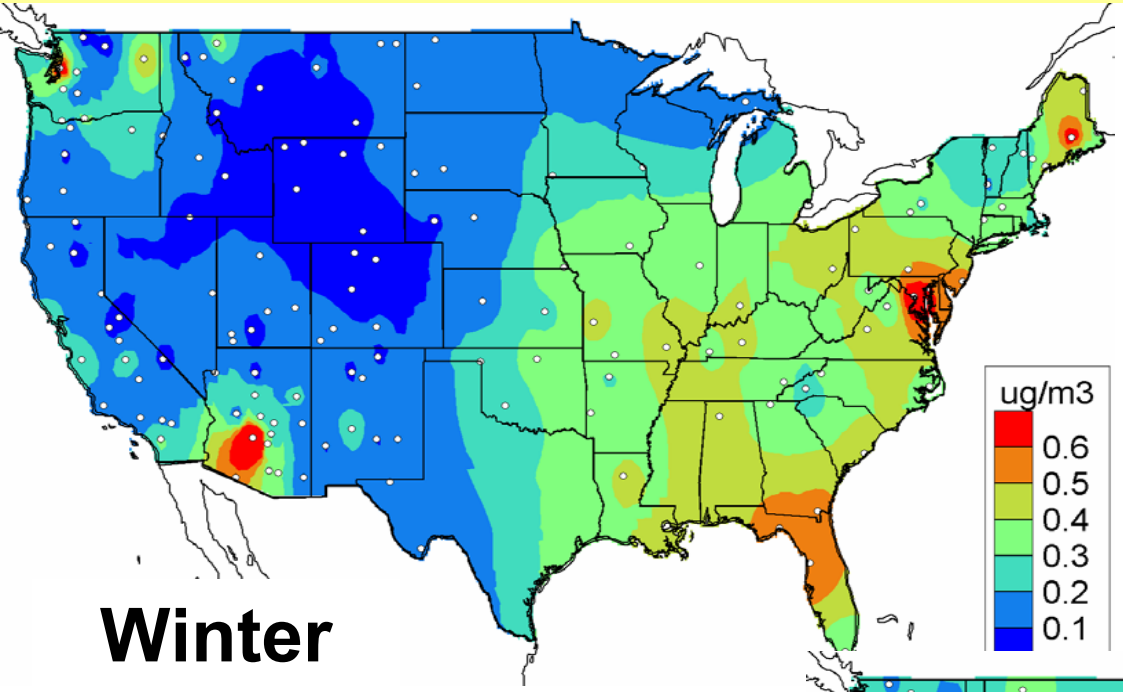


Winter

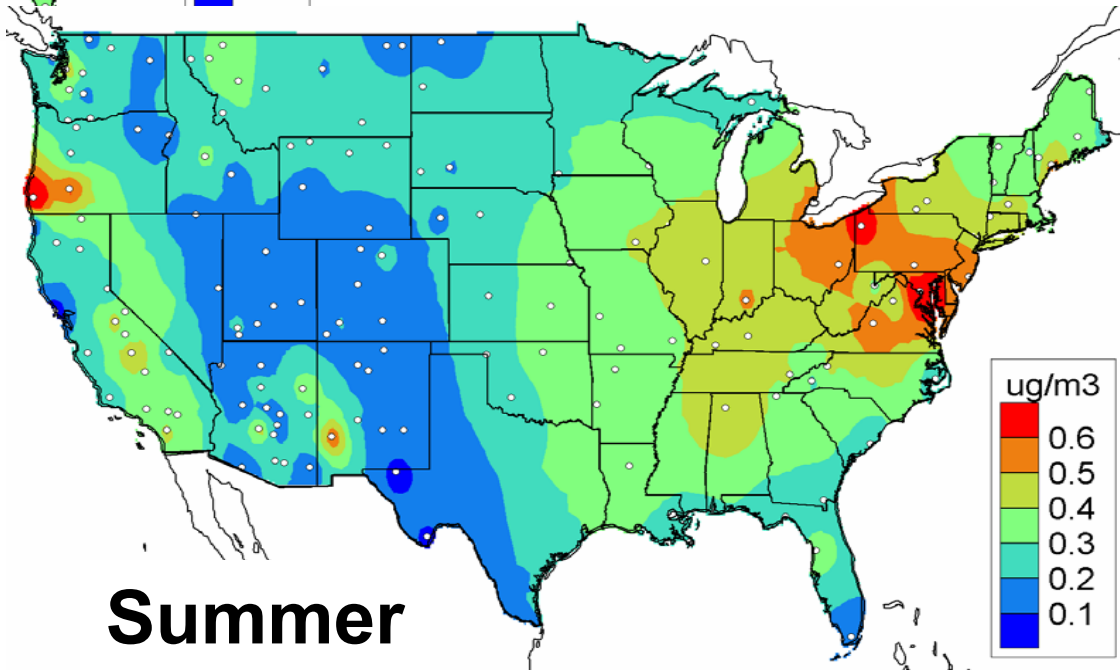


Summer

Elemental Carbon – 2001-03

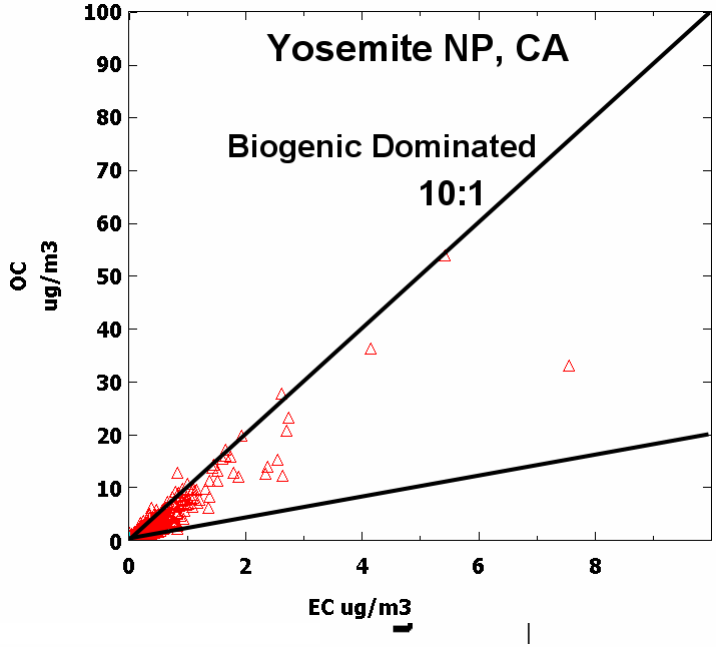


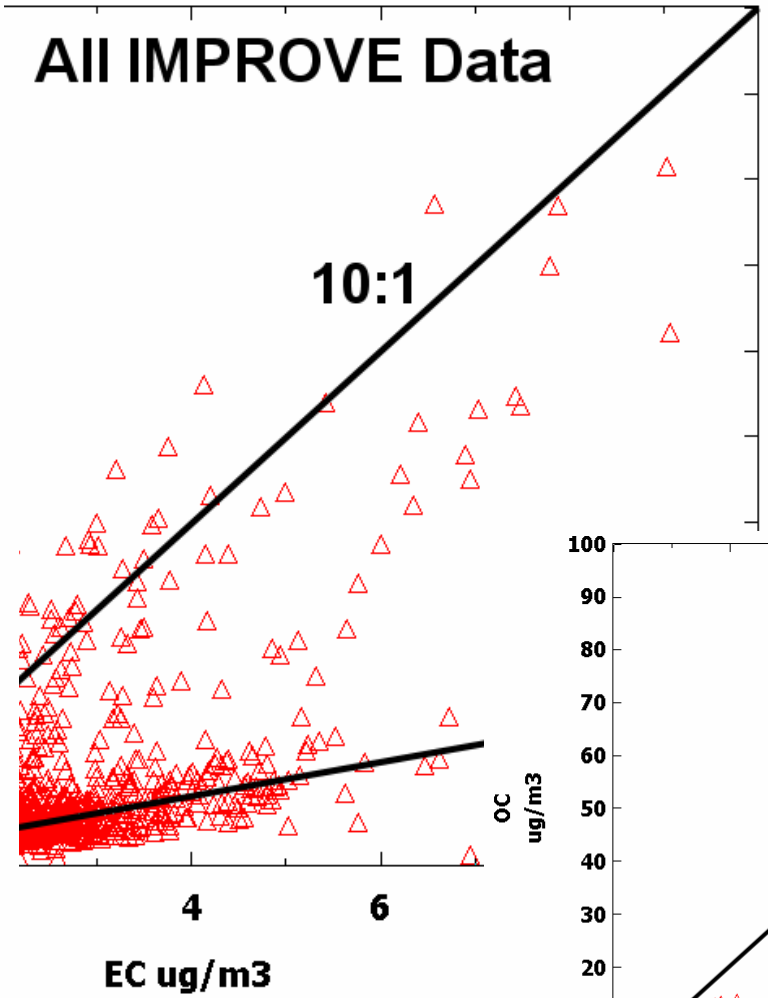
Winter

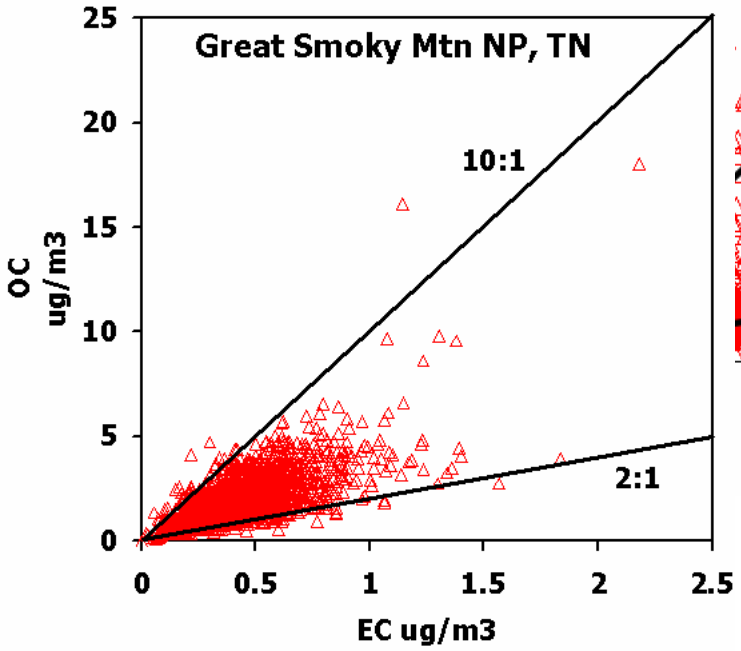


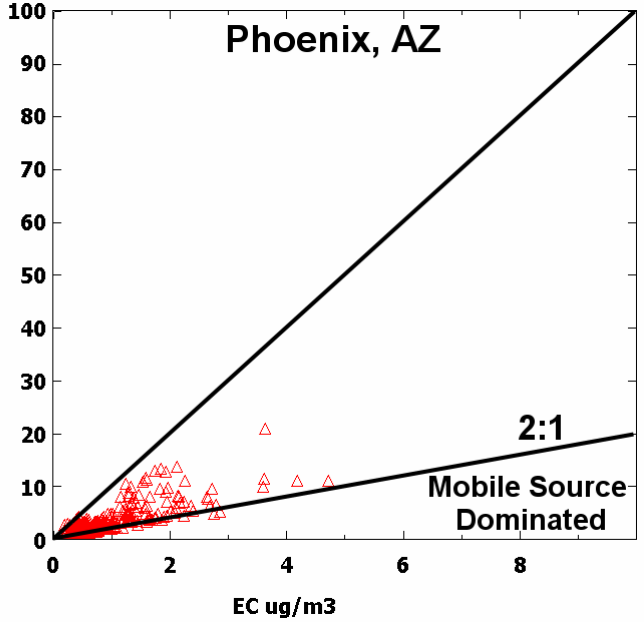
Summer

OC/EC Ratio – Indicative of Source Type

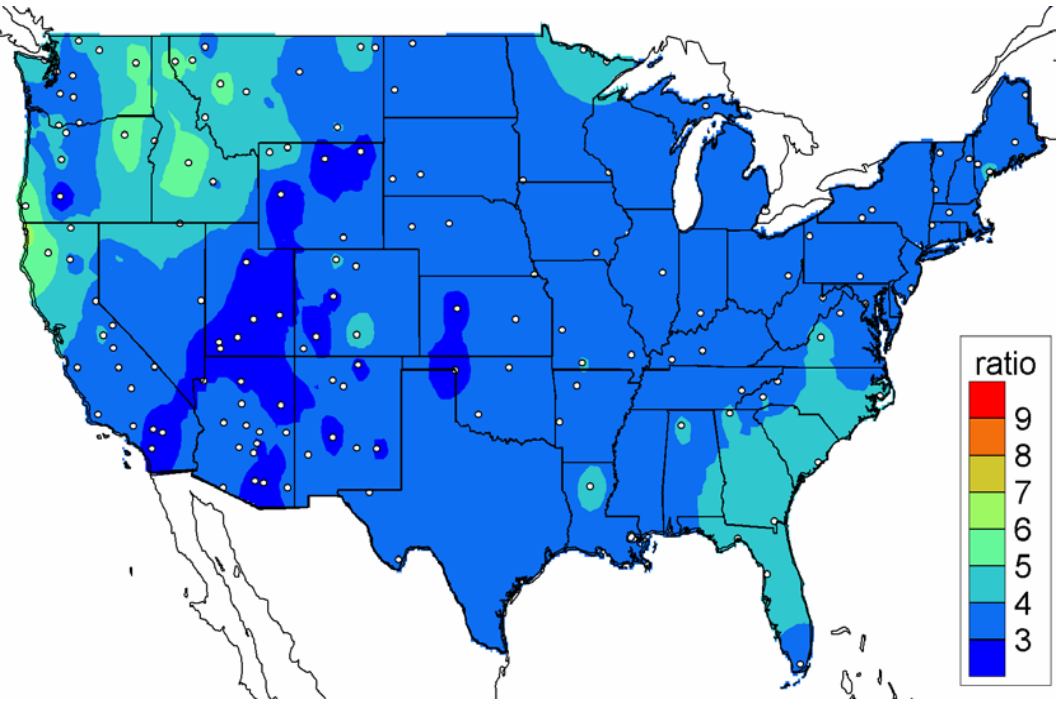






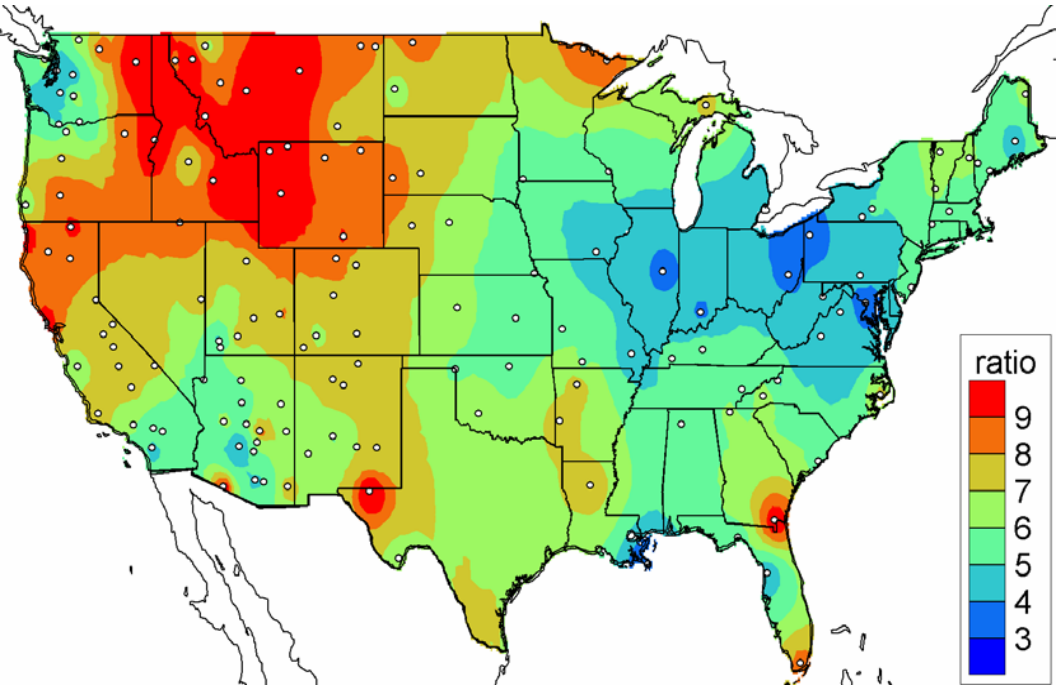


OC/EC – 2001-03



Winter

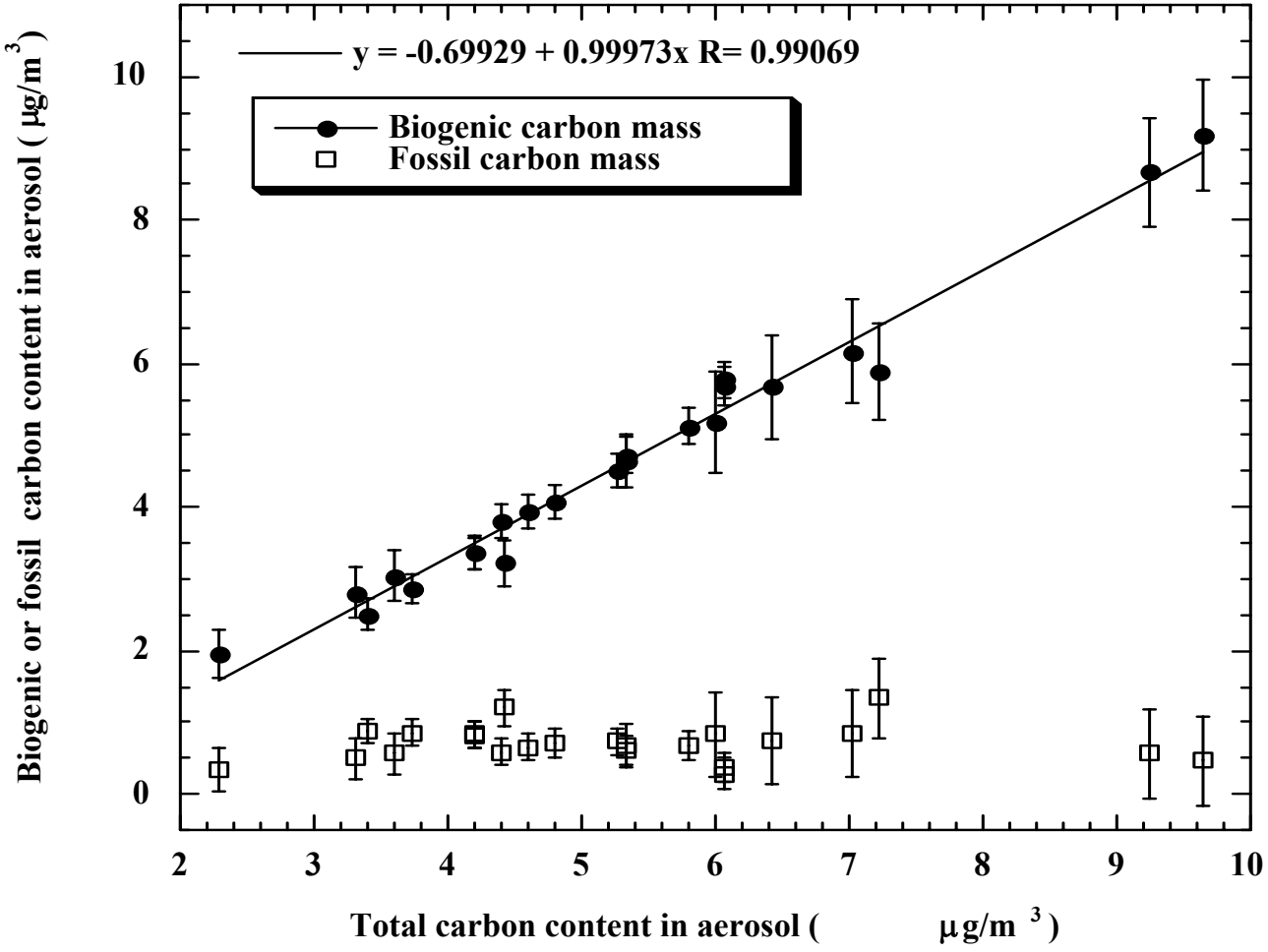
- OC/EC ~ 3-5 in urban and rural regions – indicative of primary urban emissions



Summer

- OC/EC ~ 3 - 4 in urban sites and in Industrial Midwest
- OC/EC > 7 in rural west from W. Texas to Montana
- OC/EC = 4 – 6 in Southern CA, western AZ, Southeast and New England

Biogenic vs Fossil Carbon – Summer of 2002 at Yosemite National Park



C12 - Old Carbon C14 - New Carbon

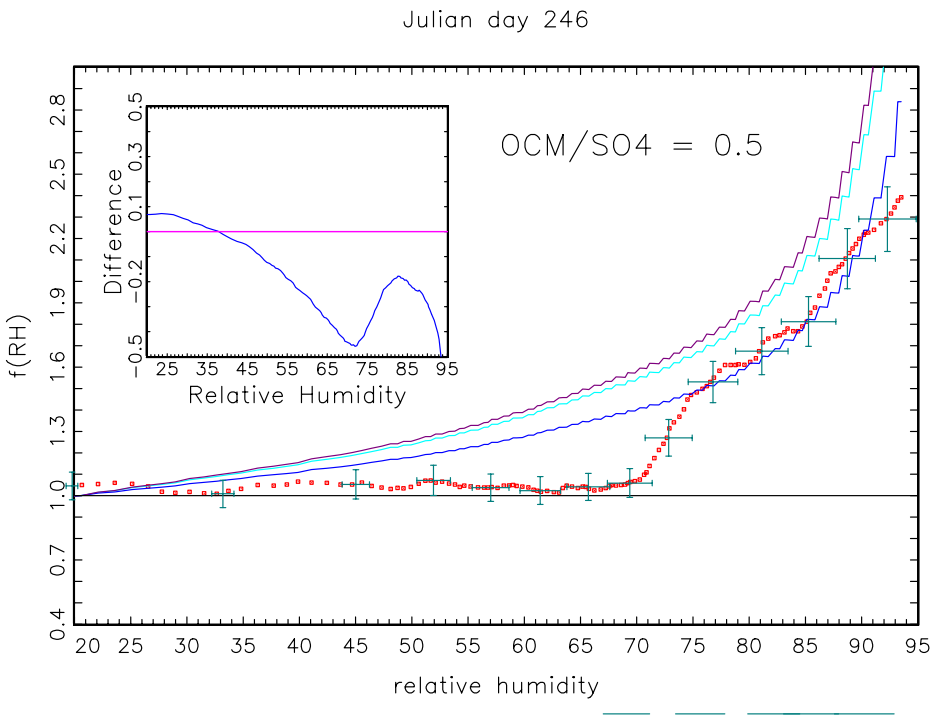
C14 half life ~ 5000 years

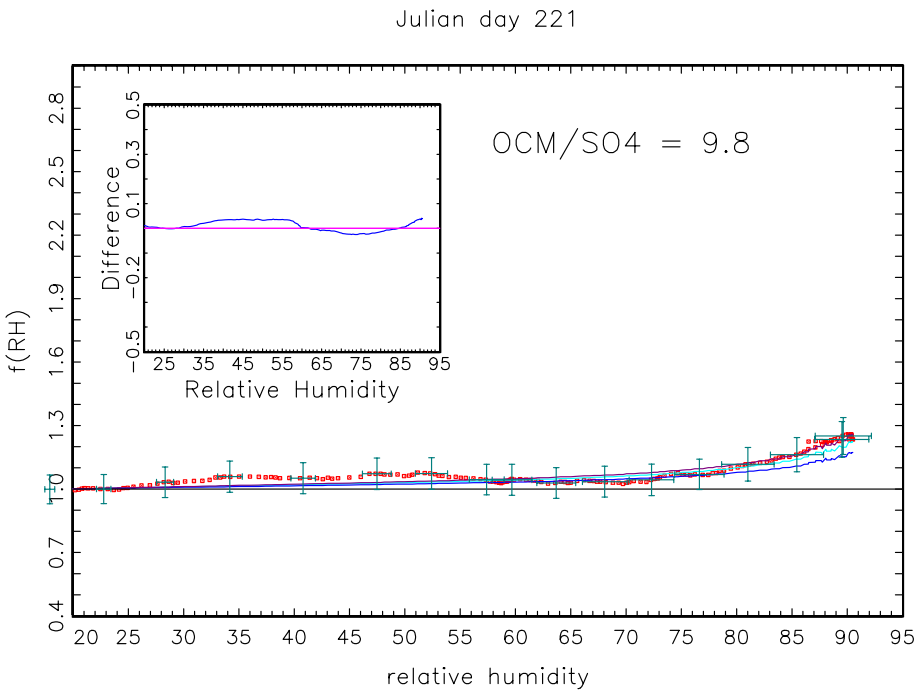
Modern (Biogenic) and Old (Fossil) Carbon Studies

Location	Time Period	% Modern Carbon	% Old Carbon	
Rural Sites				
Yosemite NP, CA	Sum '02	95	5	Bench and Herckes, ES&T, 2004
Mt. Rainier NP, WA	6-8/04	81	20	Current C-12/14 Study – Bench et al.,
Proctor Maple, VT	6-8/04	94	6	Current C-12/14 Study – Bench et al.,
Brigantine NWR, NJ	6-8/04	75	25	Current C-12/14 Study – Bench et al.,
Smoky Mtns NP, TN	6-8/04	90	10	Current C-12/14 Study - Bench et al.,
Bondville, IL	6-8/04	C-14 Contamination		Current C-12/14 Study – Bench et al.,
Urban Sites				
Puget Sound, WA	6-8/04	50	50	Current C-12/14 Study – Bench et al.,
Nashville, TN	6/21 - 7/13/99	69	31	Lewis et al., Atm Env 2004
Atlanta, GA	Jan 2000	61	39	Zheng et al., ES&T, 2002, Edgerton et al., 2003
Atlanta, GA	Jul 2000	60	41	Zheng et al., ES&T, 2002, Edgerton et al., 2003

- In the current study, we will sample during winter, Dec – Feb, at the same sites, but the Bondville monitoring is being moved to an Iowa site
- Next year will sample at 4 southwestern sites and 2 more northwestern site

Hygroscopicity of Ambient Aerosol – Yosemite NP, Summer 2002

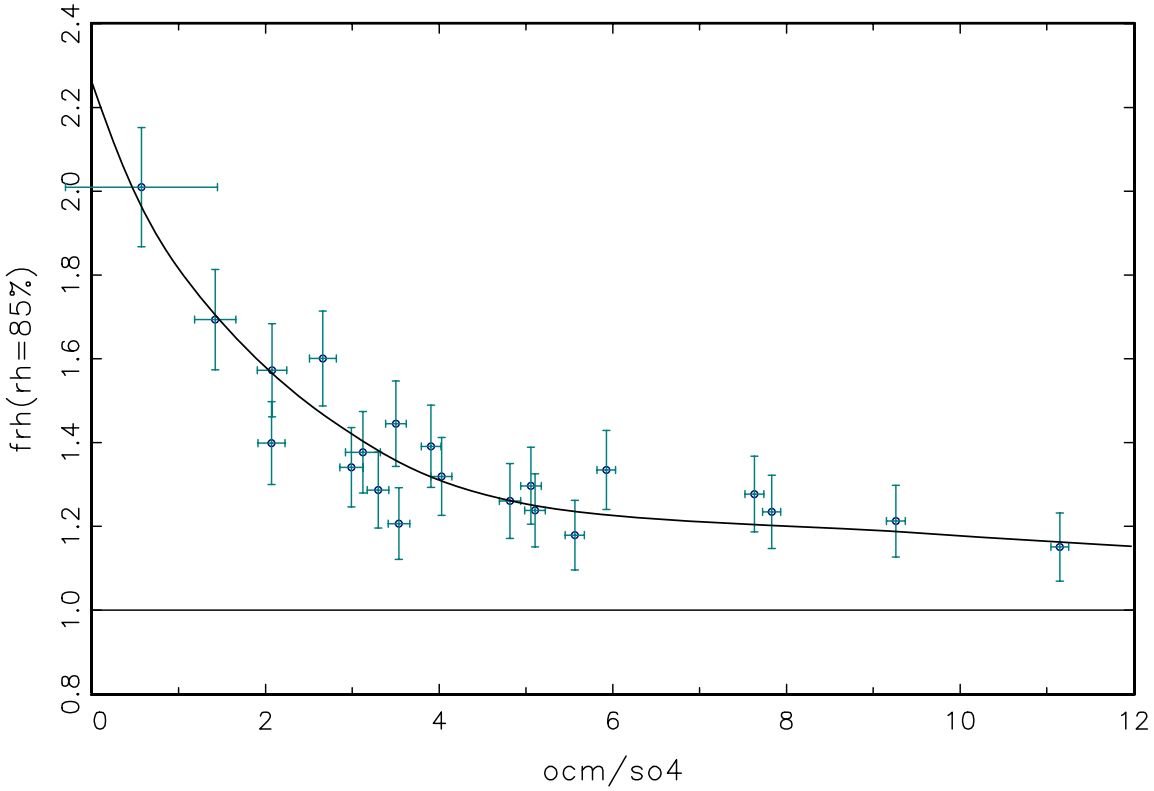




Malm et al., JGR 2005

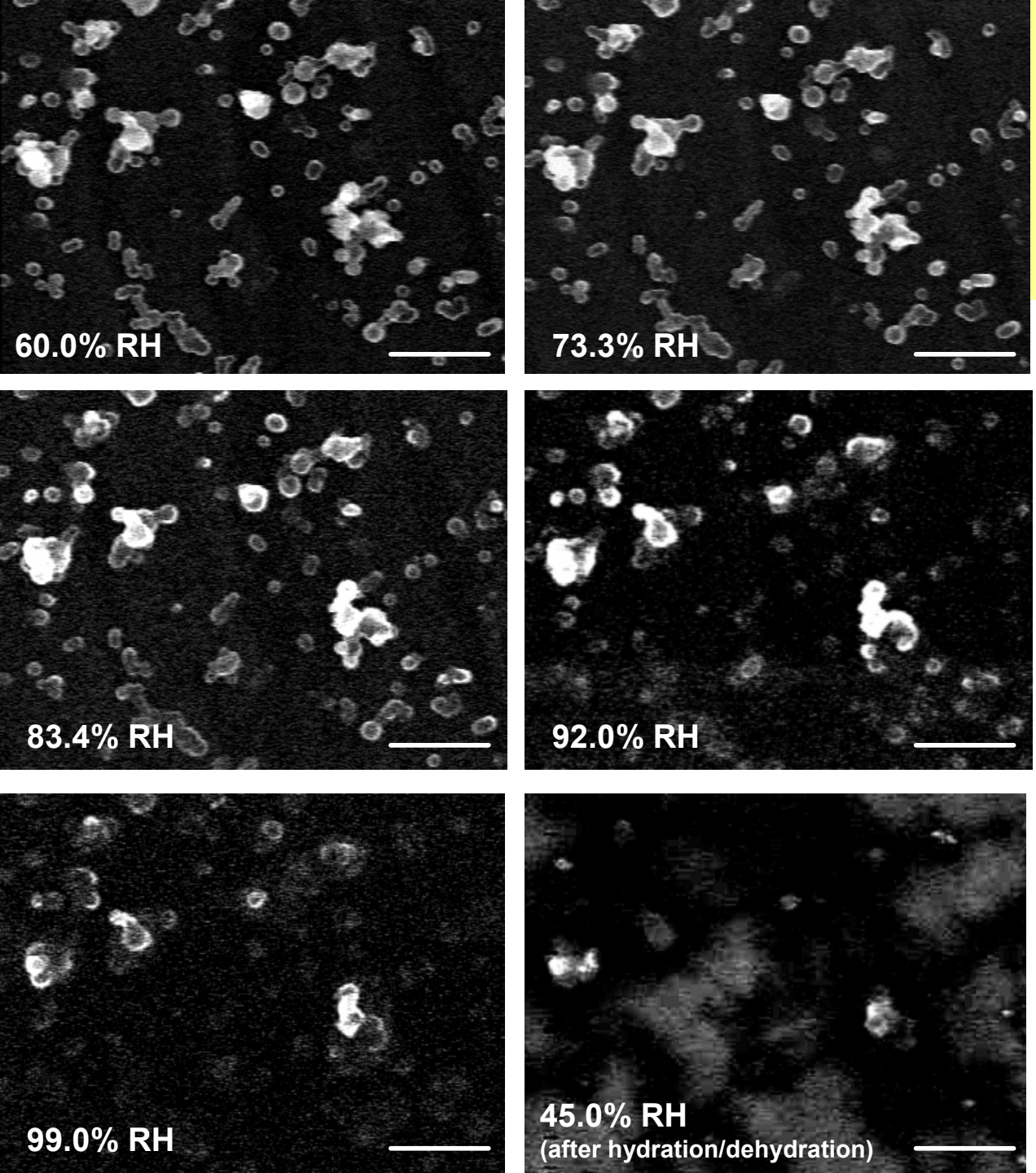
Hygroscopic Properties of Organics

F(RH=85%) plotted against the ratio of OMC to amm. sulfate.



- As OMC/SO_4 increases, aerosol hygroscopicity decreases.
- Relationship suggests an OMC f(RH=85%) of about 1.1-1.2.
- Low hygroscopicity of ambient organic aerosols has also been observed at Grand Canyon, AZ; Big Bend, TX; Smoky Mtn, TN

Environmental SEM Imaging of Smoke



ESEM images of tar ball particles exposed to increasing water vapor pressure at T = 5 oC: 60.0% RH, 73.3% RH, 83.4% RH, 92.0% RH, 99.0% RH

and then 45% RH after completion of a hydration/dehydration cycle

Hand et al., JGR 2005

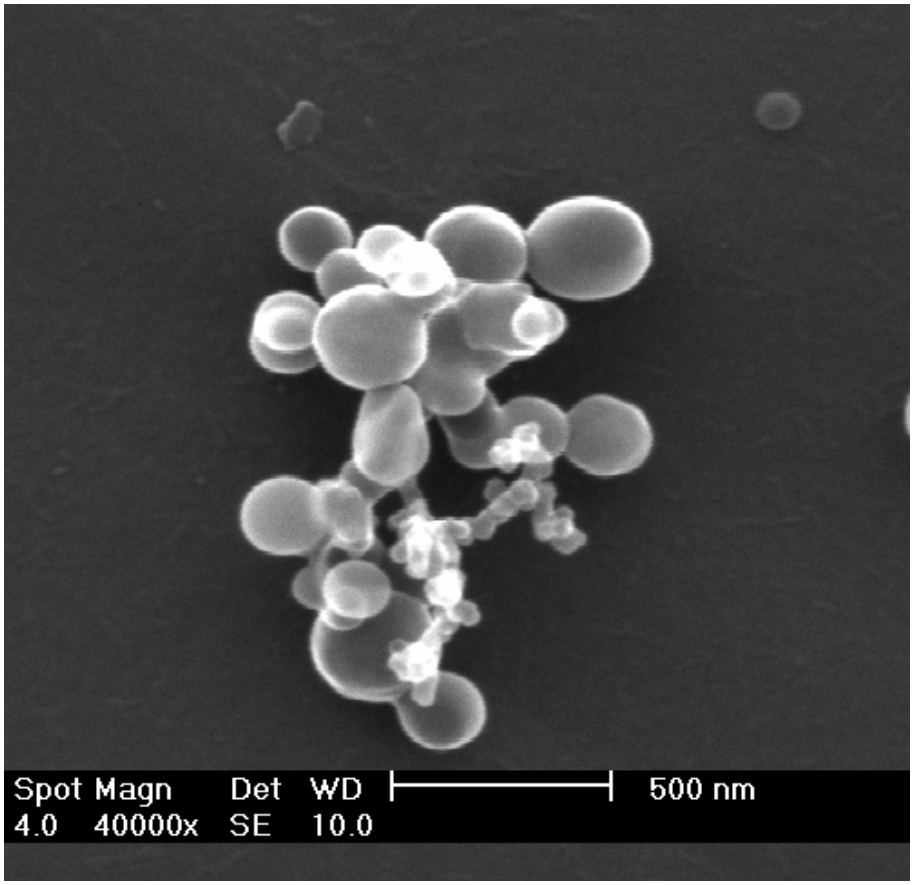
Data and Information Distribution Visualization and Analysis Websites

http://vista.cira.colostate.edu/IMPROVE

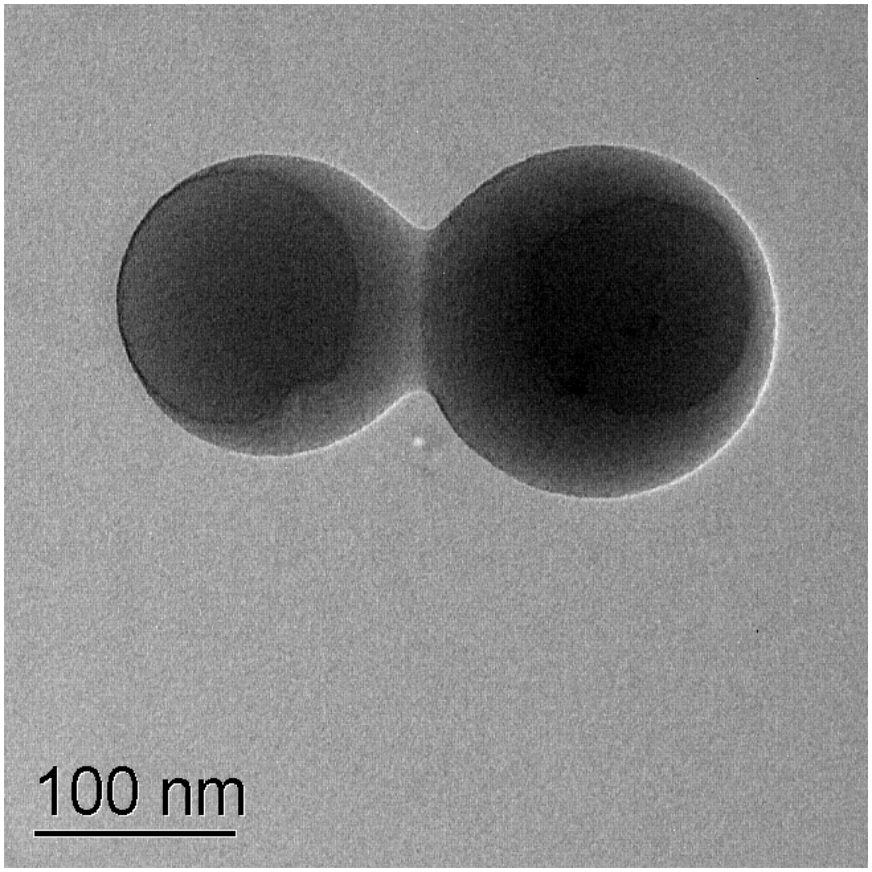
http://vista.cira.colostate.edu/VIEWS

END

Election Microscopic images of Carbon Particles Yosemite NP, August 17 2002



Chain of soot particles stuck to an agglomerate of organic “tar balls”

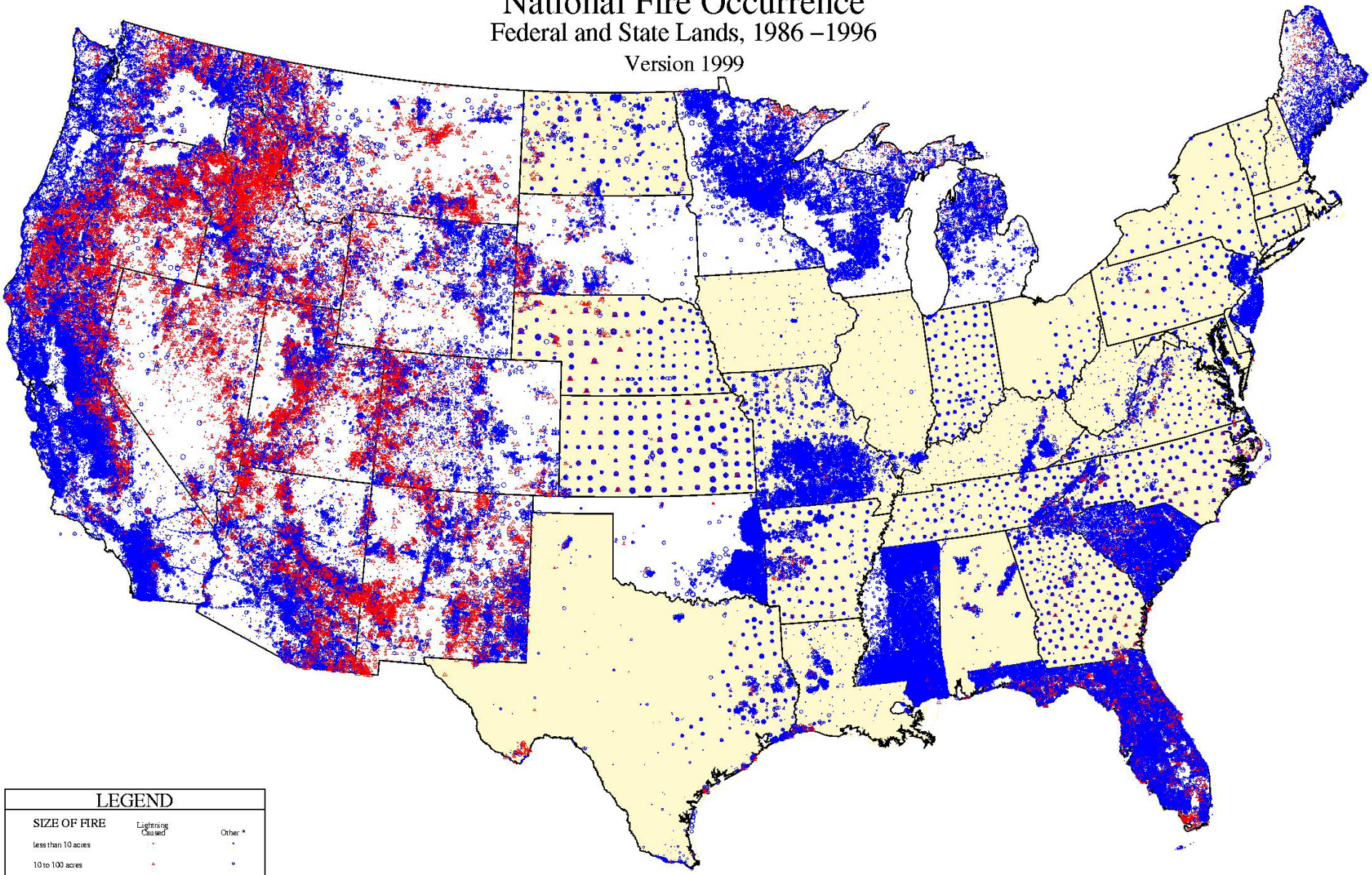


Organic particles with sulfate inclusions (Transmission Election Microscope

National Fire Occurrence

Federal and State Lands, 1986 –1996

Version 1999



LEGEND

SIZE OF FIRE	Lightning Caused	Other *
less than 10 acres	·	·
10 to 100 acres	△	○
100 to 1,000 acres	△	○
1,000 to 10,000 acres	△	○
10,000 acres or more	△	○

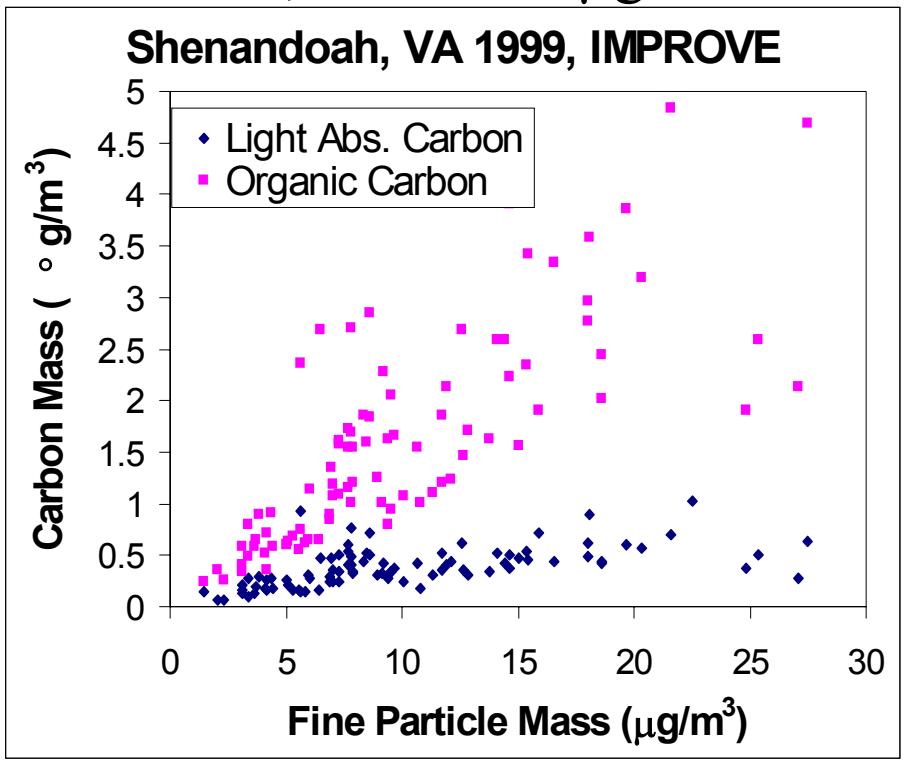
State Boundary

States with non –federal fire locations summarized to county

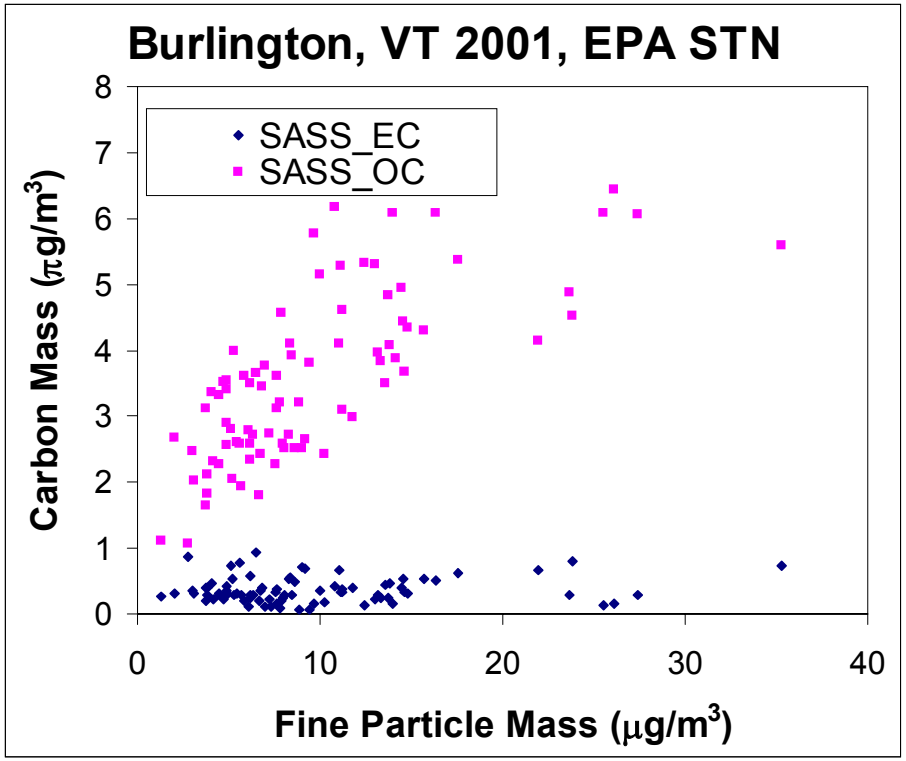
* Other types of fires included: Arson, Smoking, Recreational, Children, Debris Burning, Equipment Use, Railroad, and Miscellaneous.

IMPROVE Corrects OC and EC for a Positive Artifact

IMPROVE: Artifact Corrected OC ~ 0.3, EC ~0.02 μg/m^3



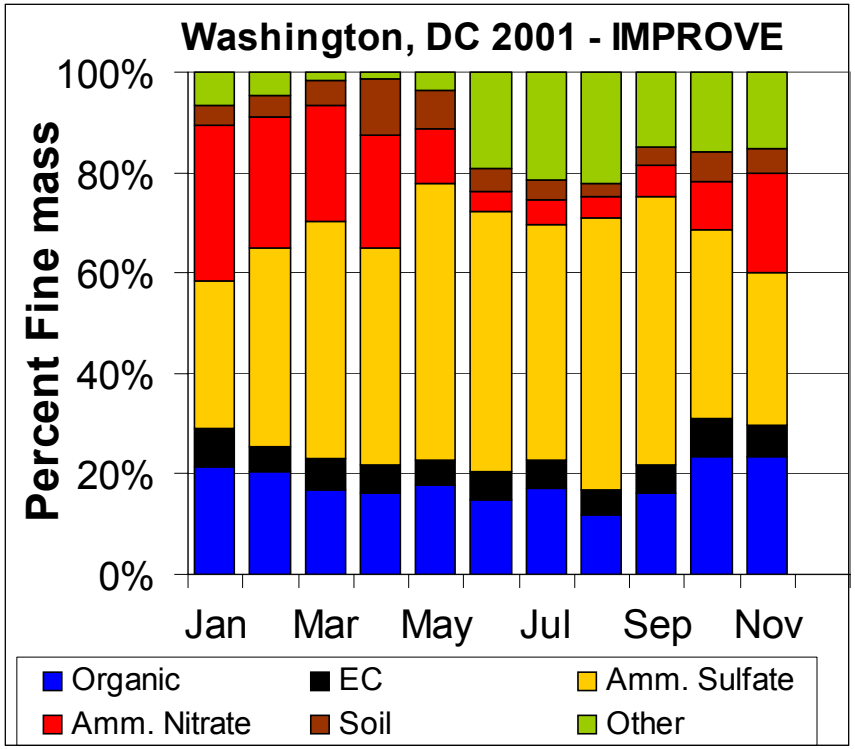
EPA STN monitoring site: No carbon artifact correction

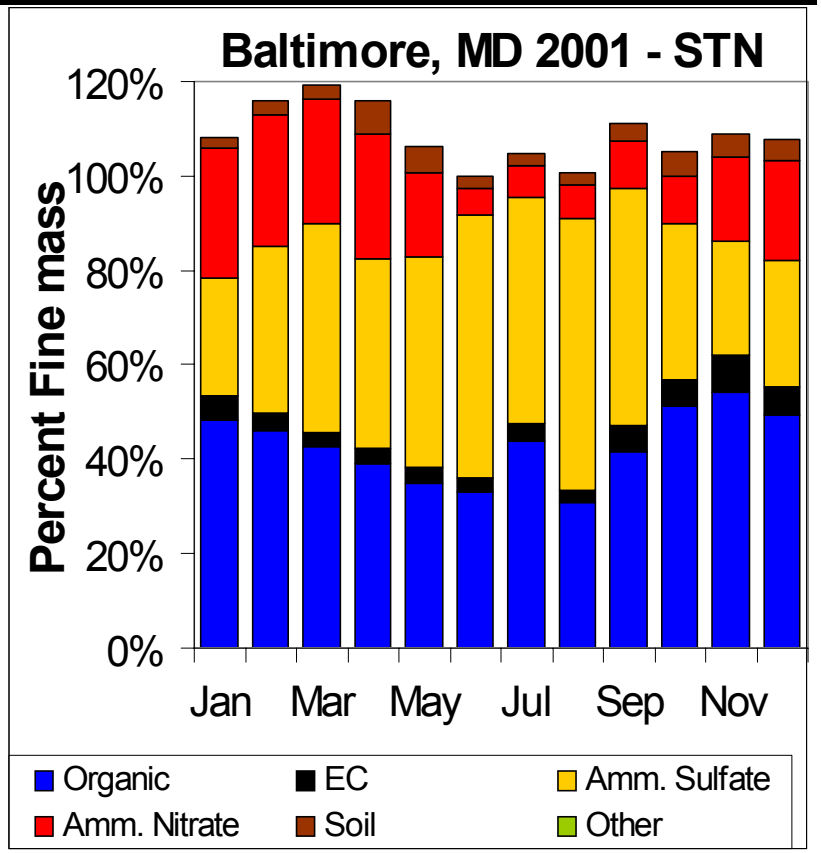


The positive artifact correction causes the organic and elemental carbon to approach zero as fine mass goes to zero

IMPROVE and STN Fine Mass Budgets

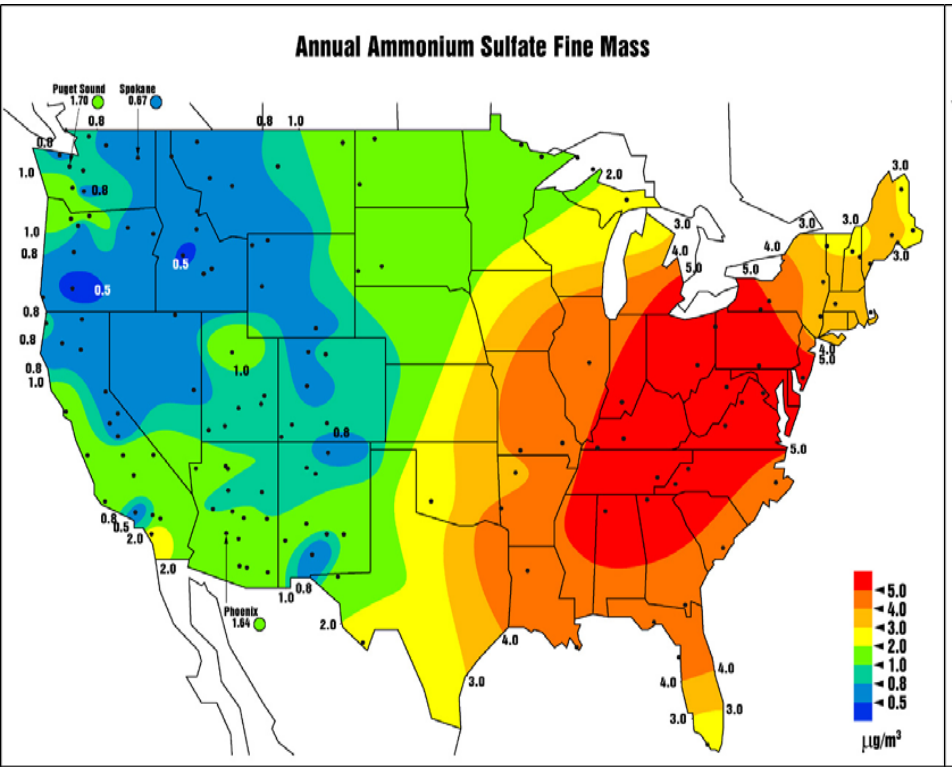
Reconstructed fine mass:

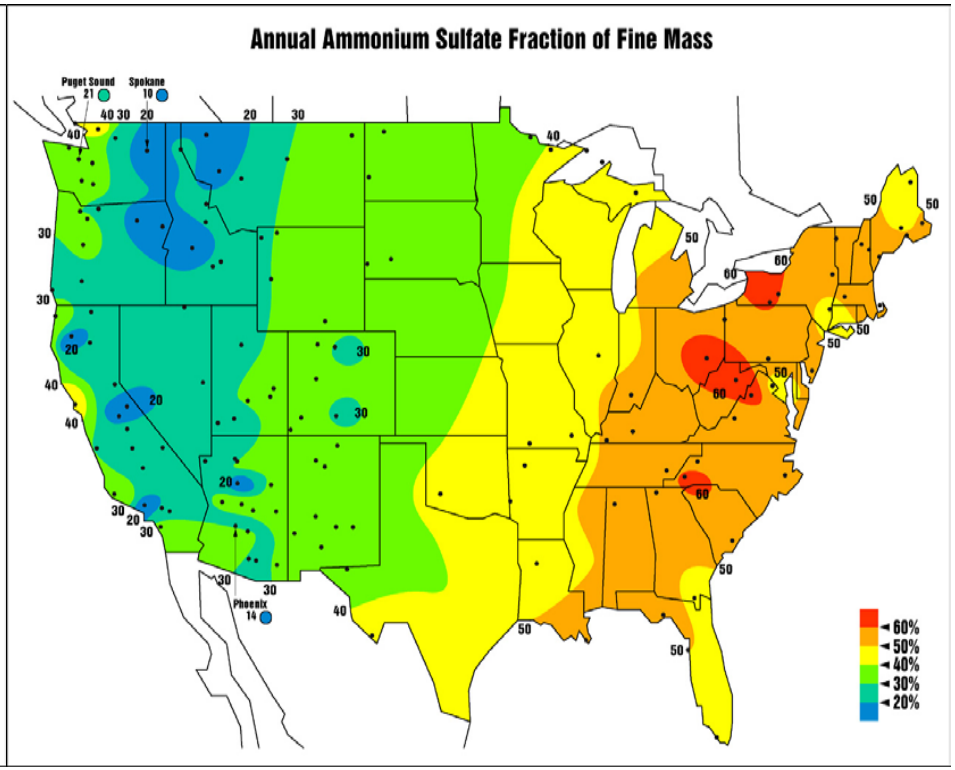




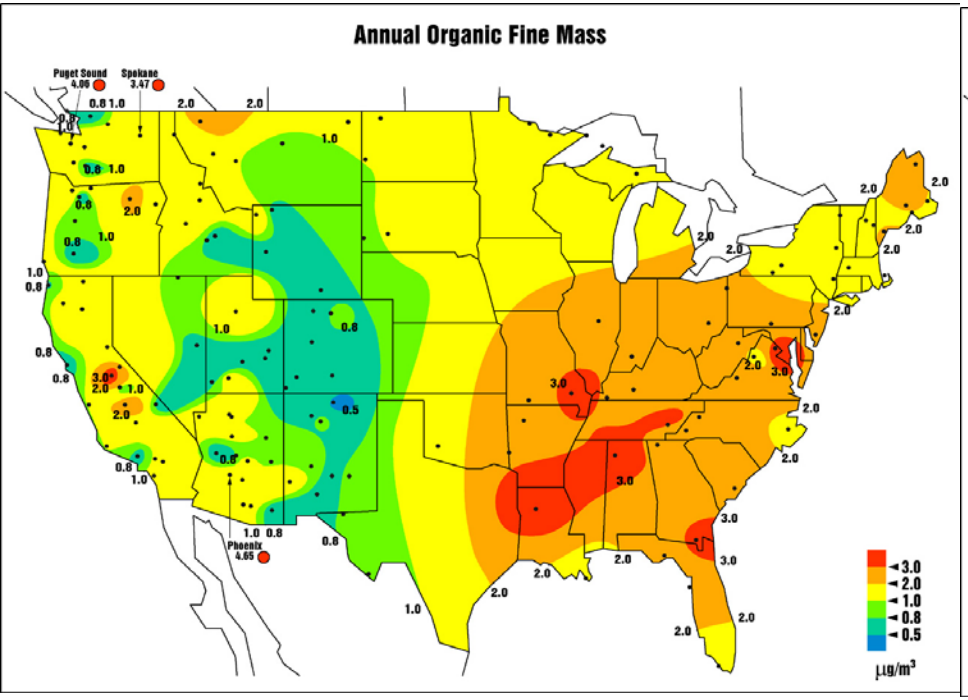
- OC is scaled by 1.4 to account for oxygen and hydrogen mass
- Organics accounts for ~20% of fine mass at Washington, ~43% at Baltimore
- EC accounts for ~6% of fine mass at Washington, ~4.4% at Baltimore

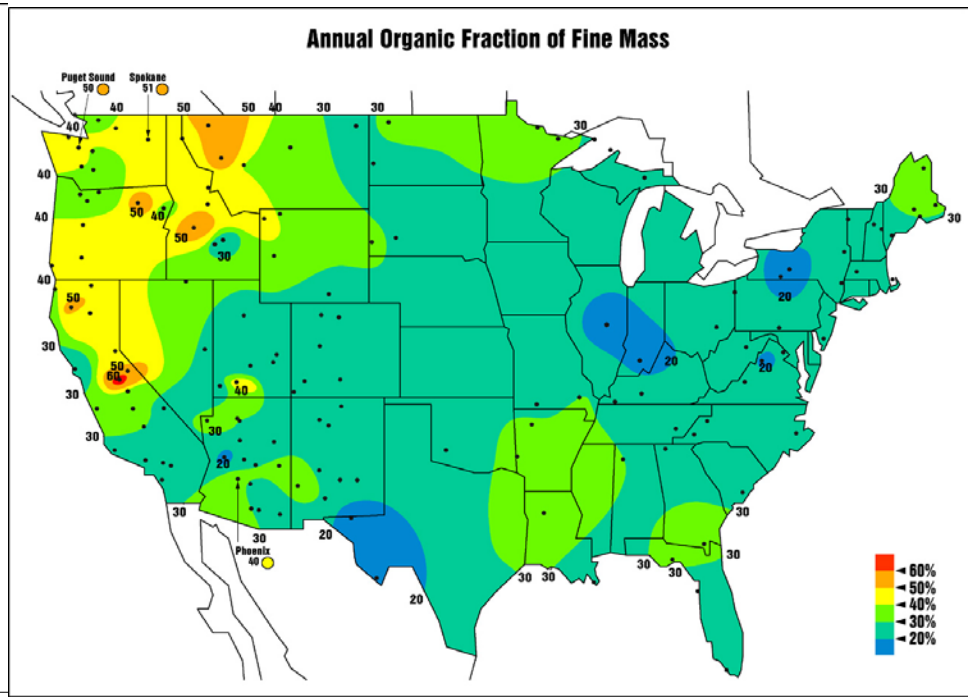
Annual Ammonium Sulfate - 2001



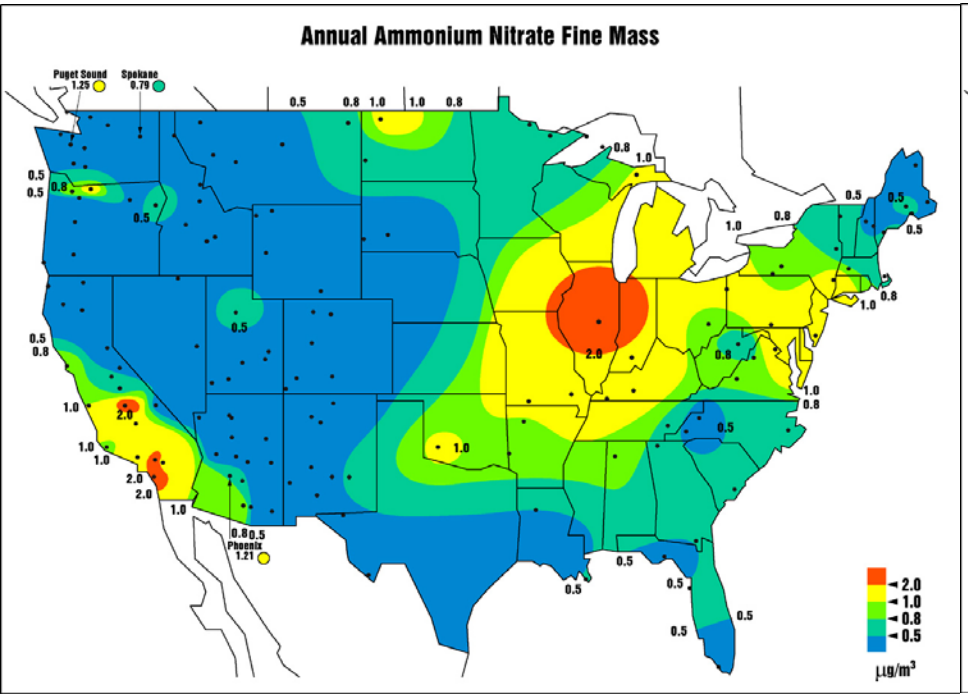


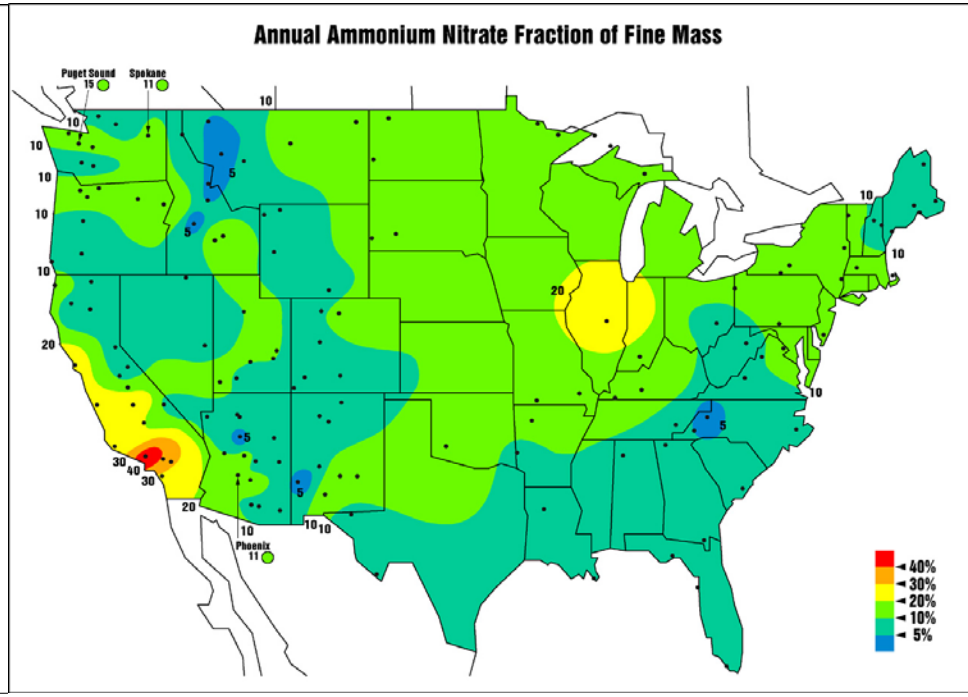
Annual Organic (1.4*OC) - 2001





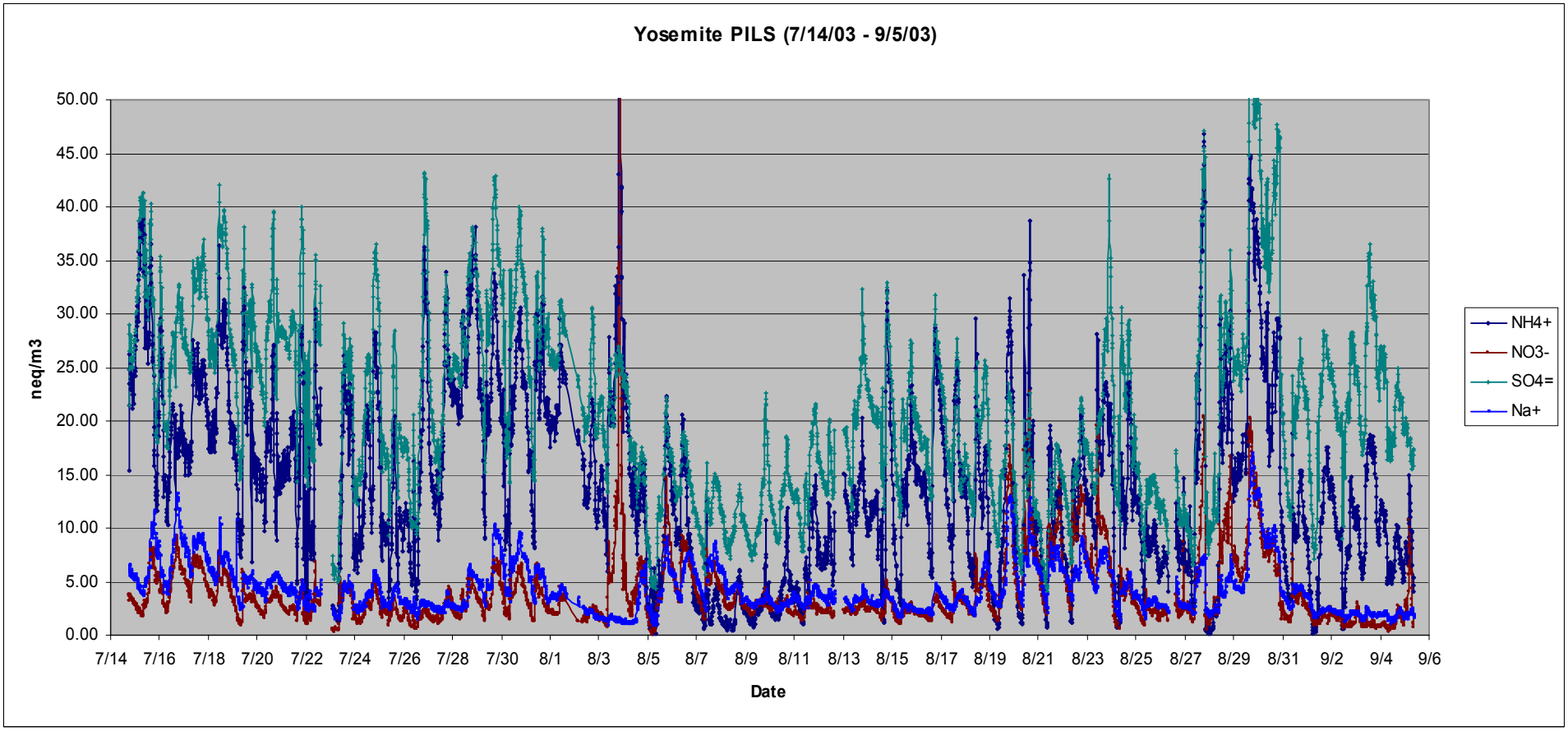
Annual Ammonium Nitrate - 2001





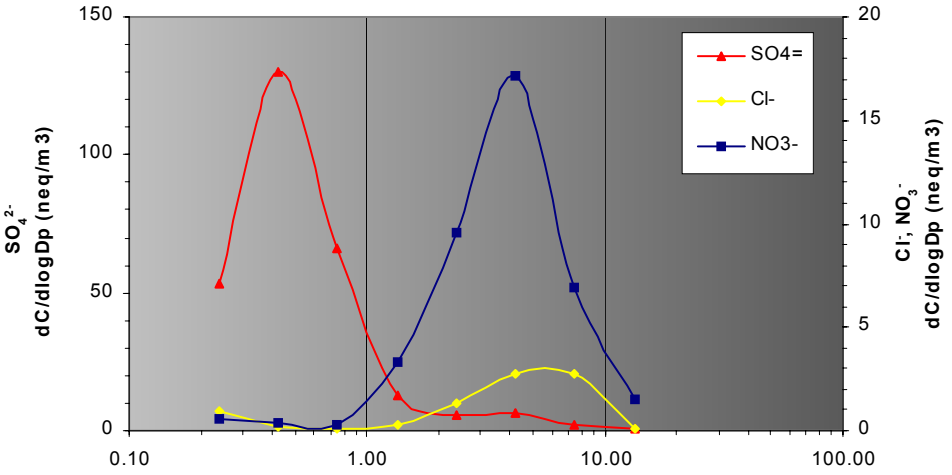
Yosemite NP Ionic Concentrations PILS

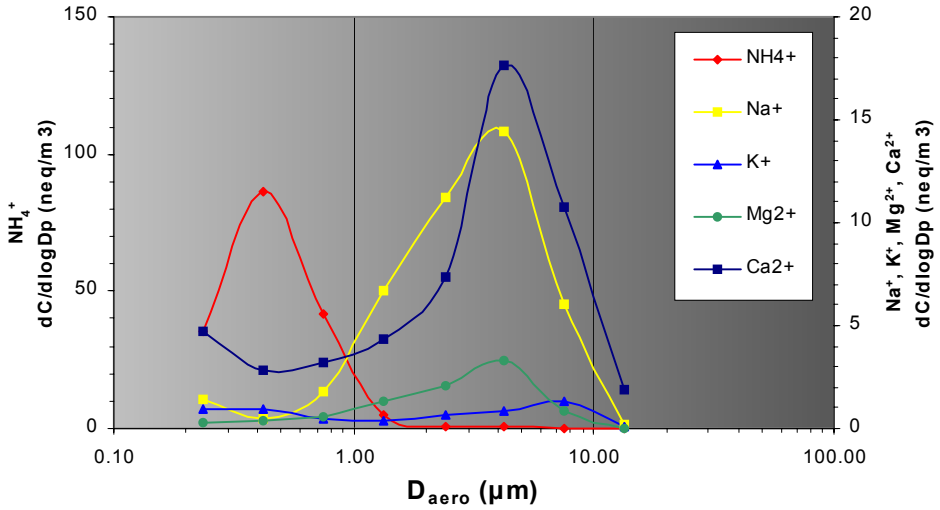
15 minute ion data from the PILS inlet



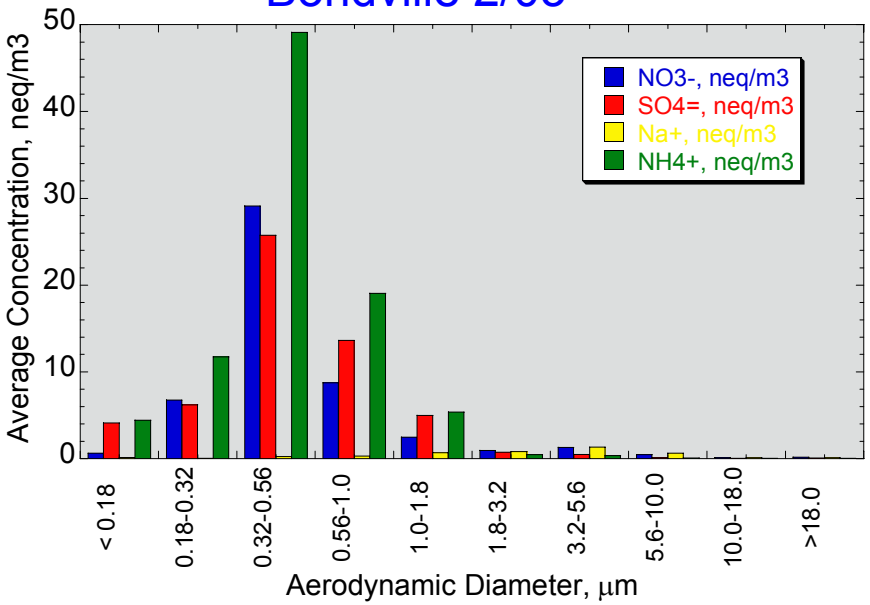
Size Distributions

Big Bend Texas - August 1999

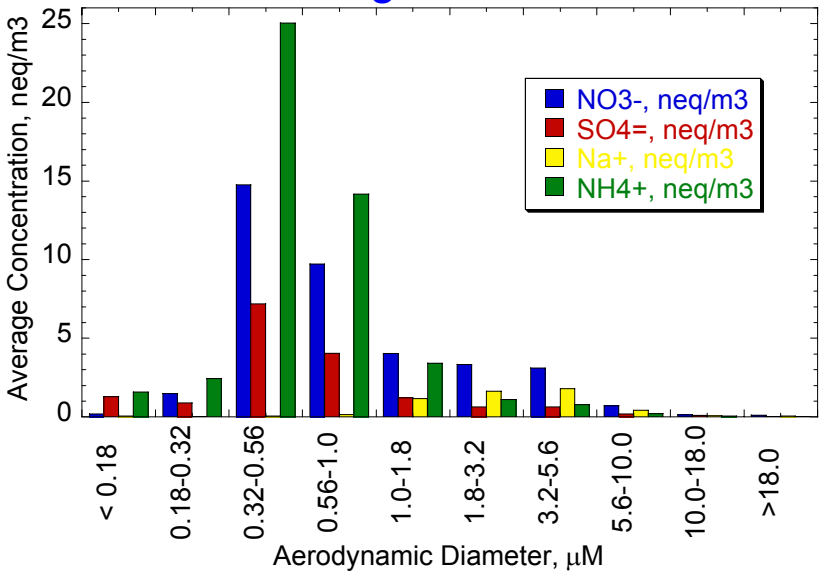




Bondville 2/03

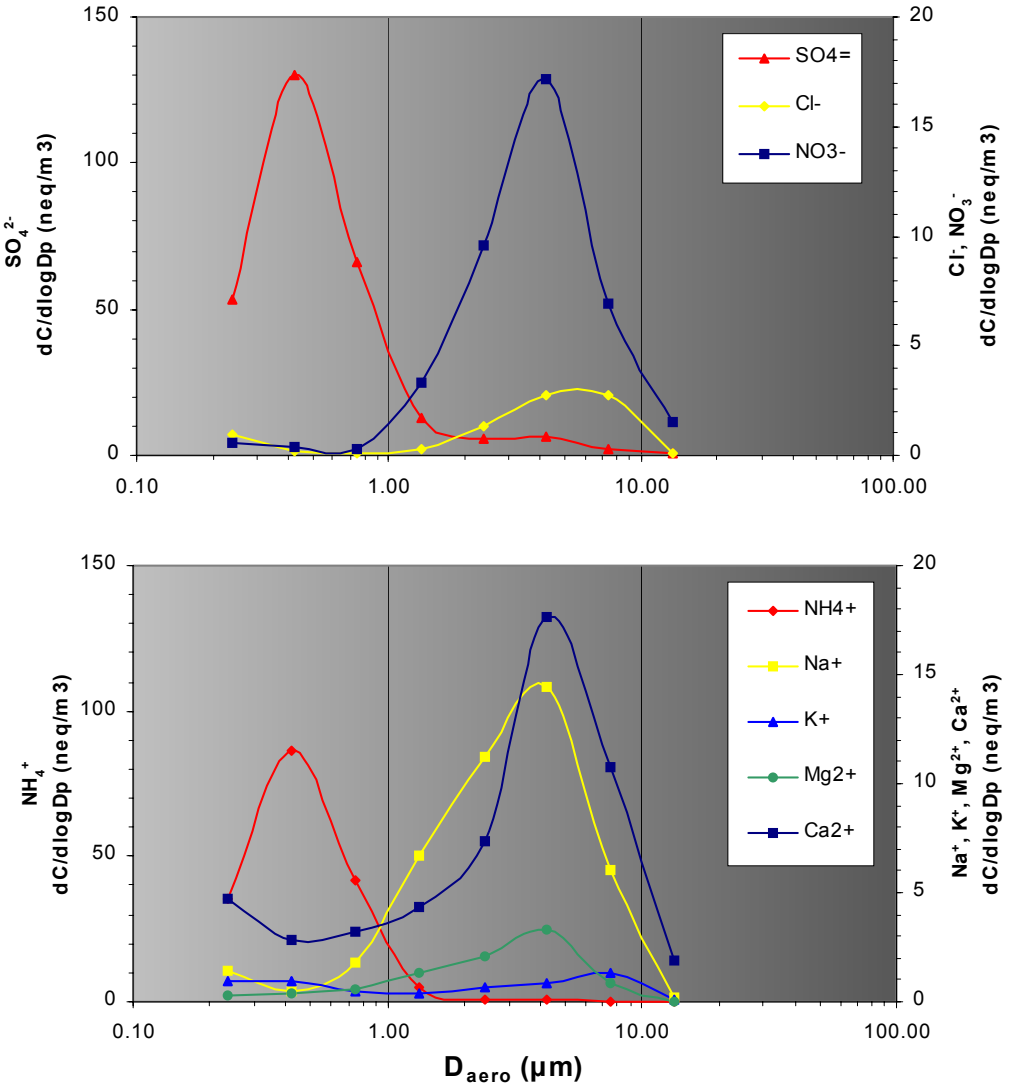


San Gorgonio, CA – 4/2003

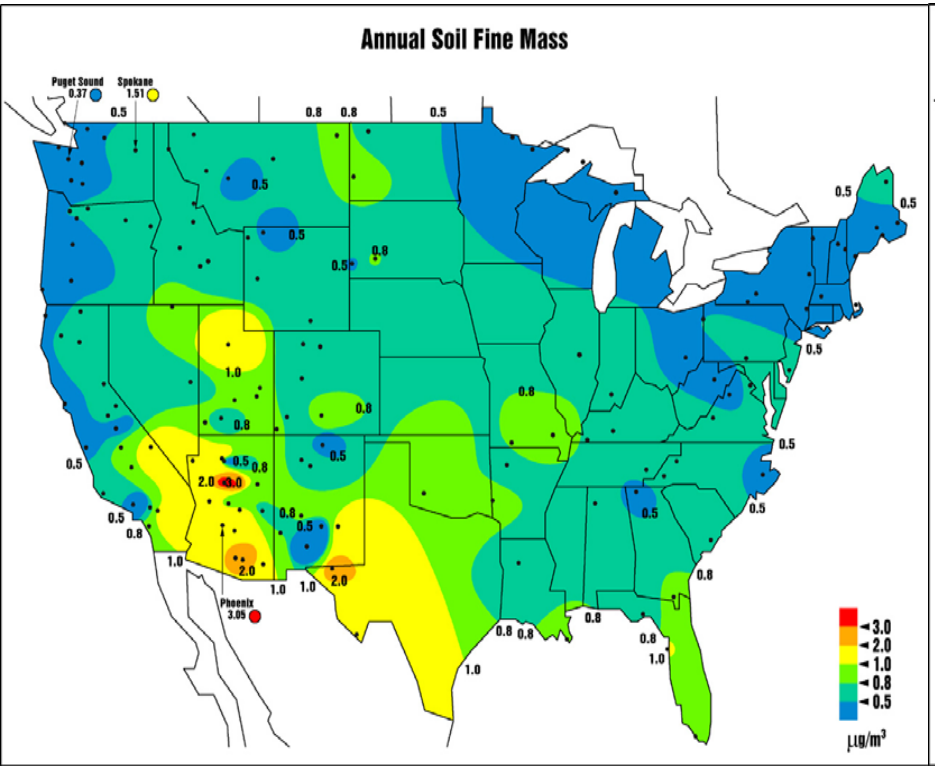


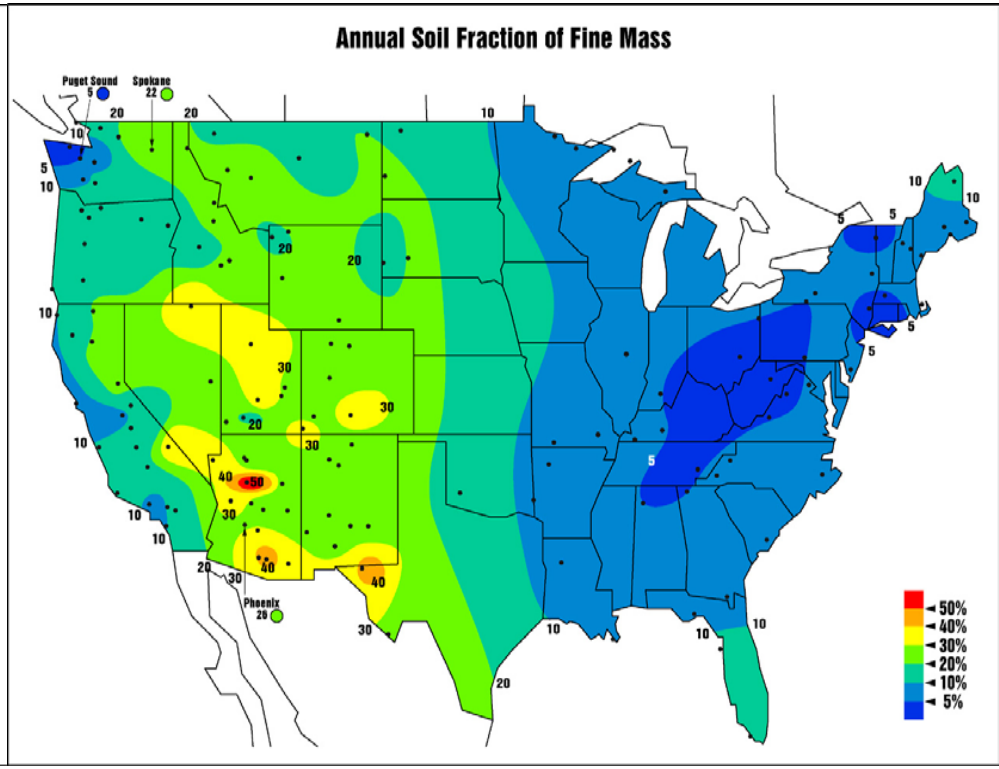
Big Bend NP Size Distributions - August 1999

- Nitrate found in coarse mode particles
  - Mode size ~4-5 μm
  - Size distribution similar to Na^+
- $PM_{2.5}$ includes tail of coarse mode



Annual Fine Soil - 2001



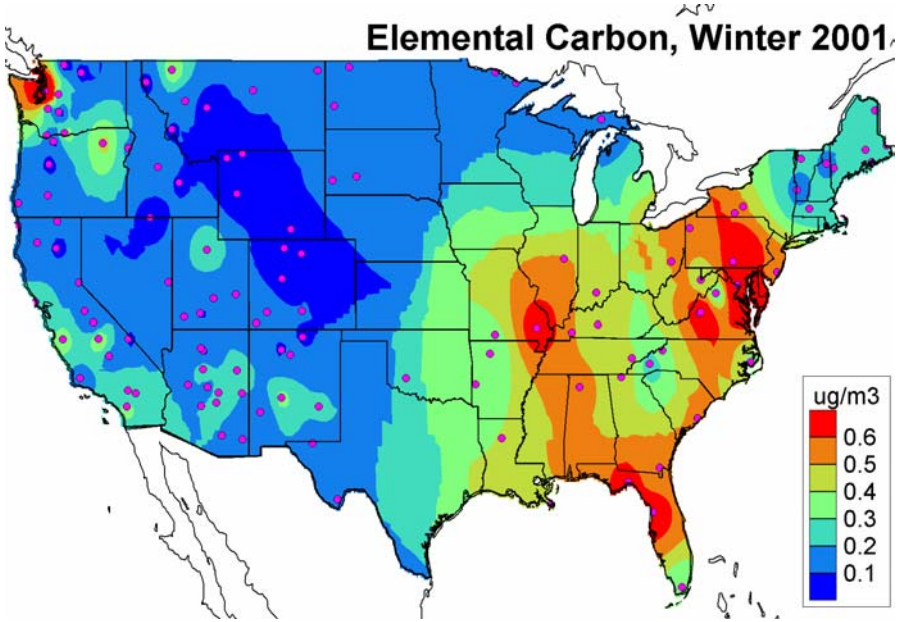


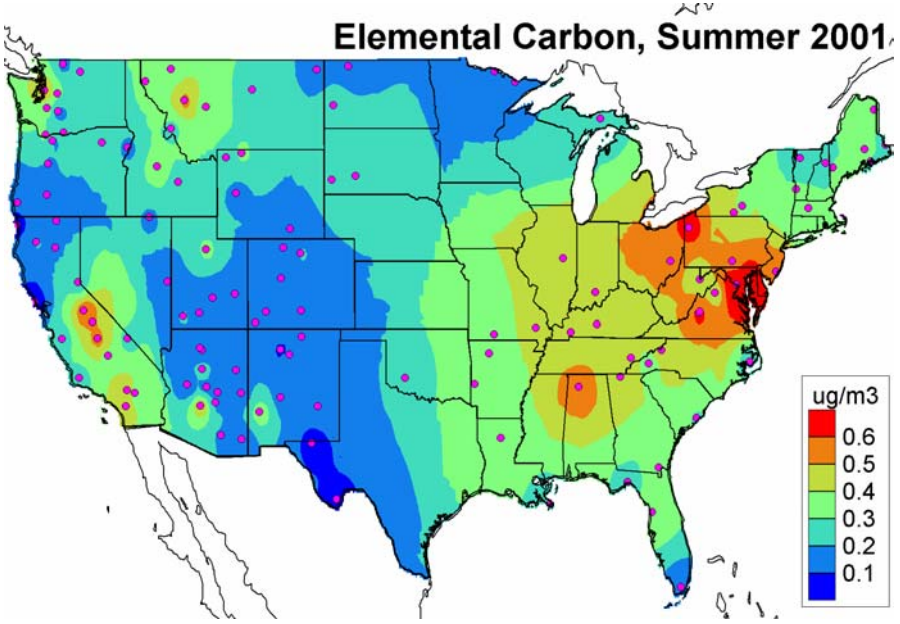
IMPROVE Seasonal EC and OC

Winter 2001, Dec, Jan, Feb

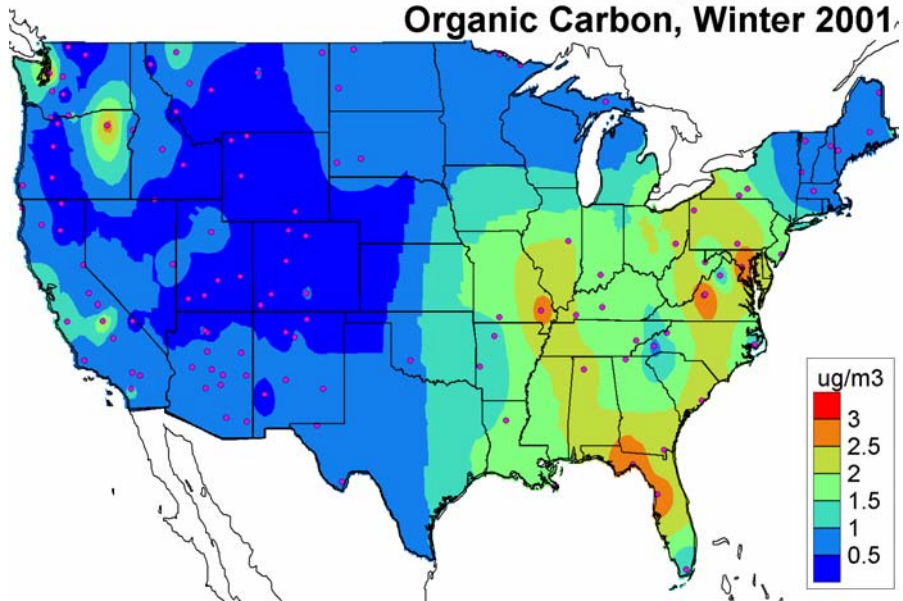
Summer 2001, Jun, Jul, Aug

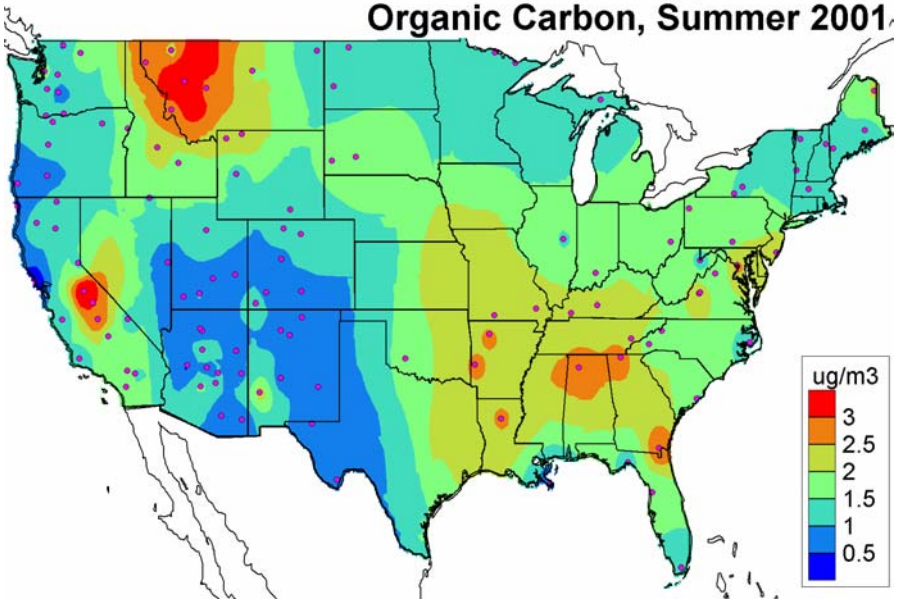
Elemental Carbon



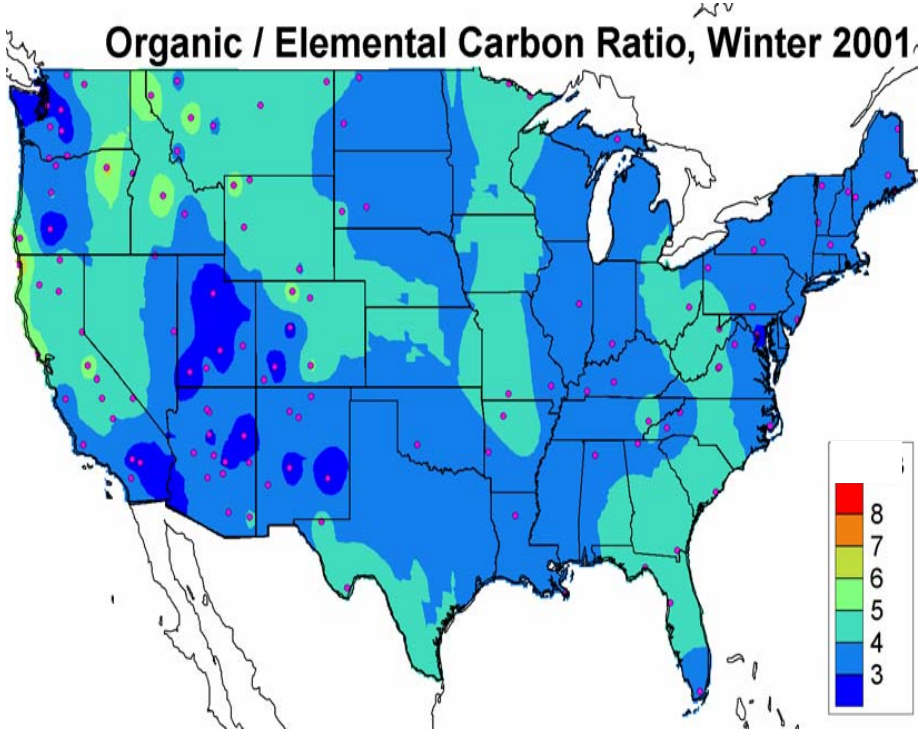


Organic Carbon

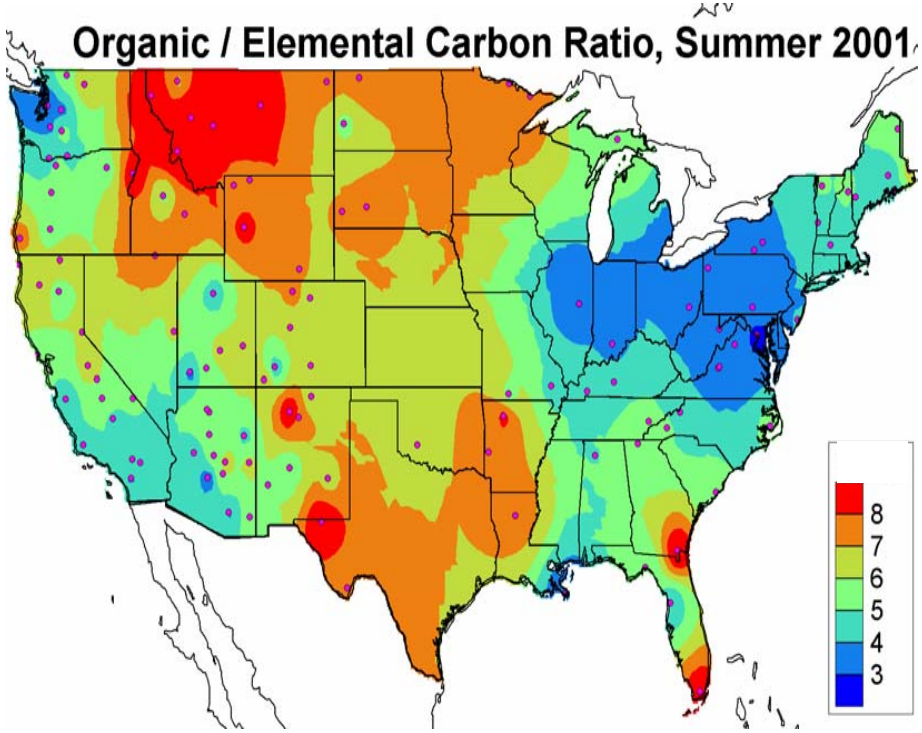




OC/EC Ratio

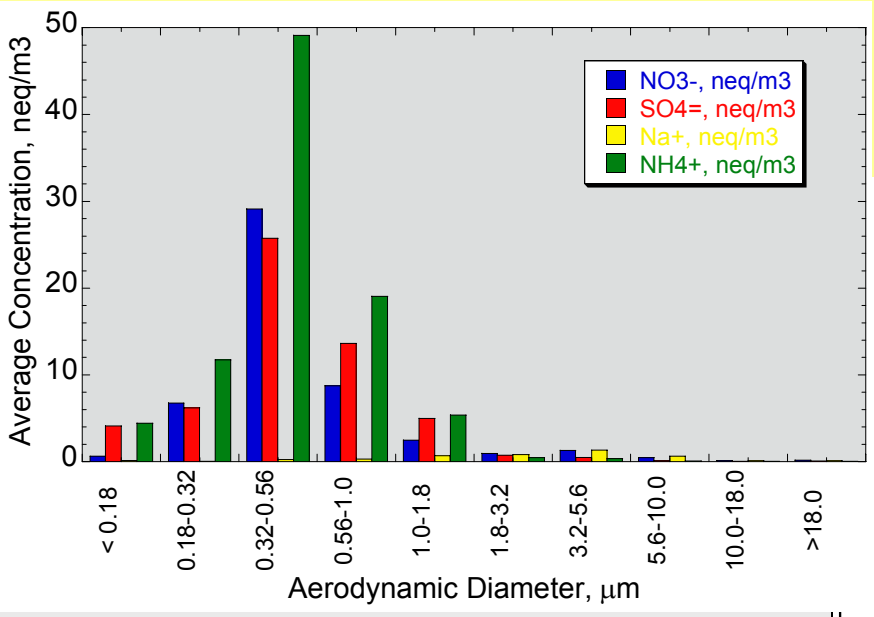


- OC/EC ratio varies between 3 - 5, indicative of more primary urban emissions

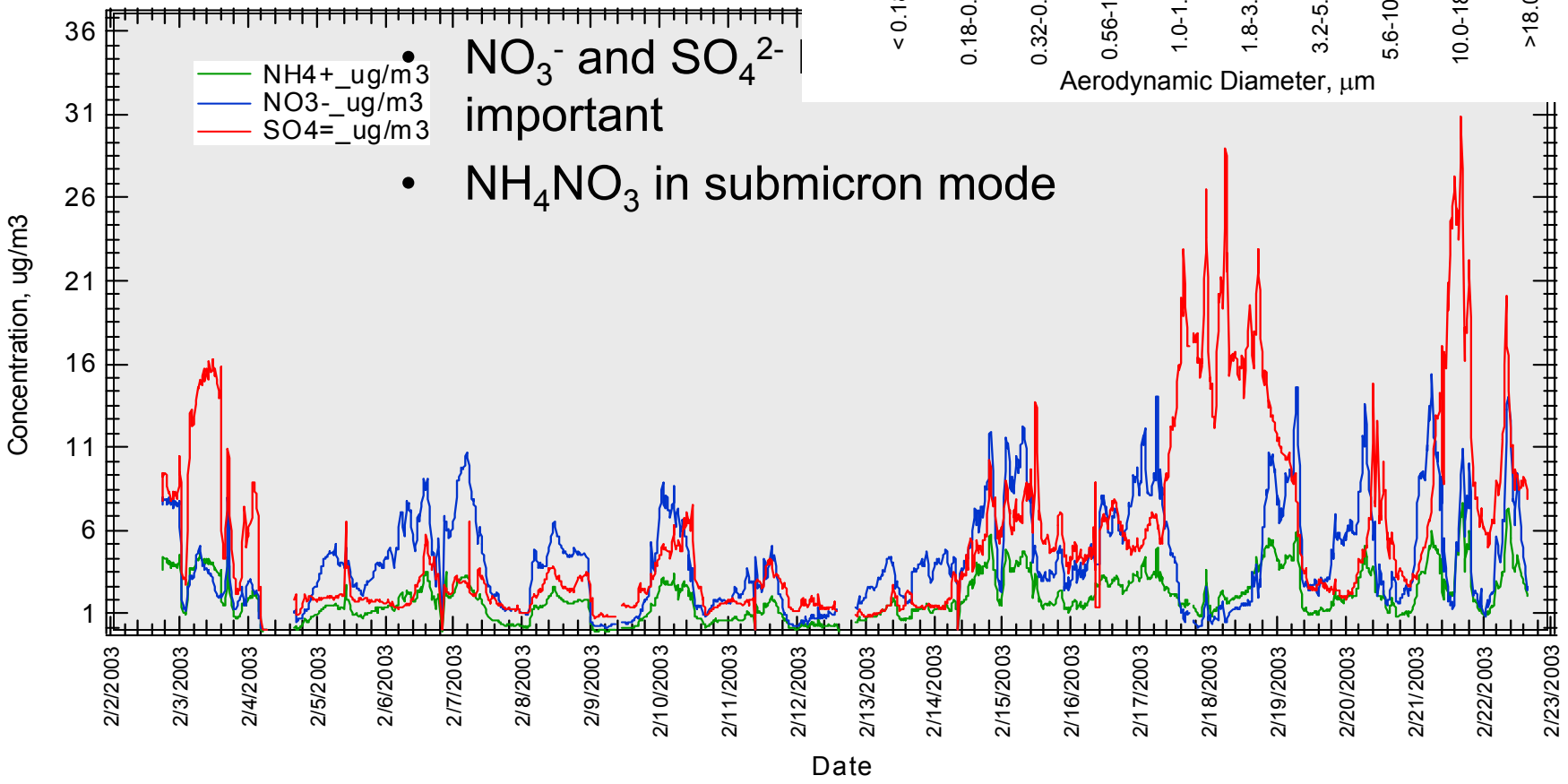


- OC/EC > 7 throughout upper West and Texas, Fires?
- OC/EC ~ 3 in Industrial Midwest, primary urban?
- OC/EC > 4-6 in southeast, increased secondary organics?

Bondvill

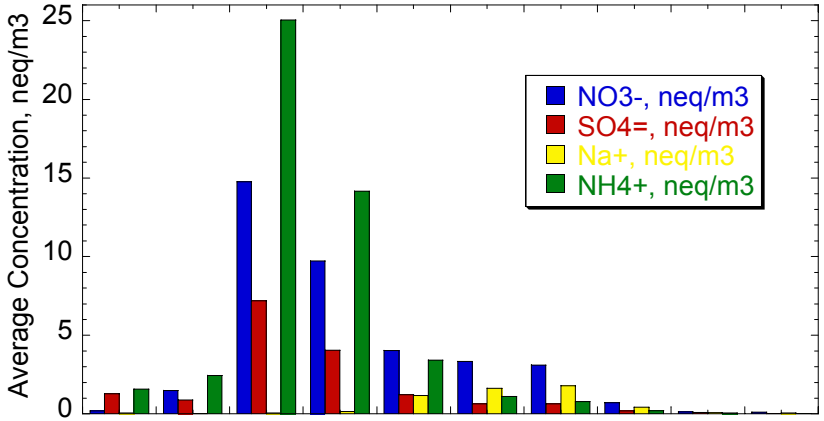


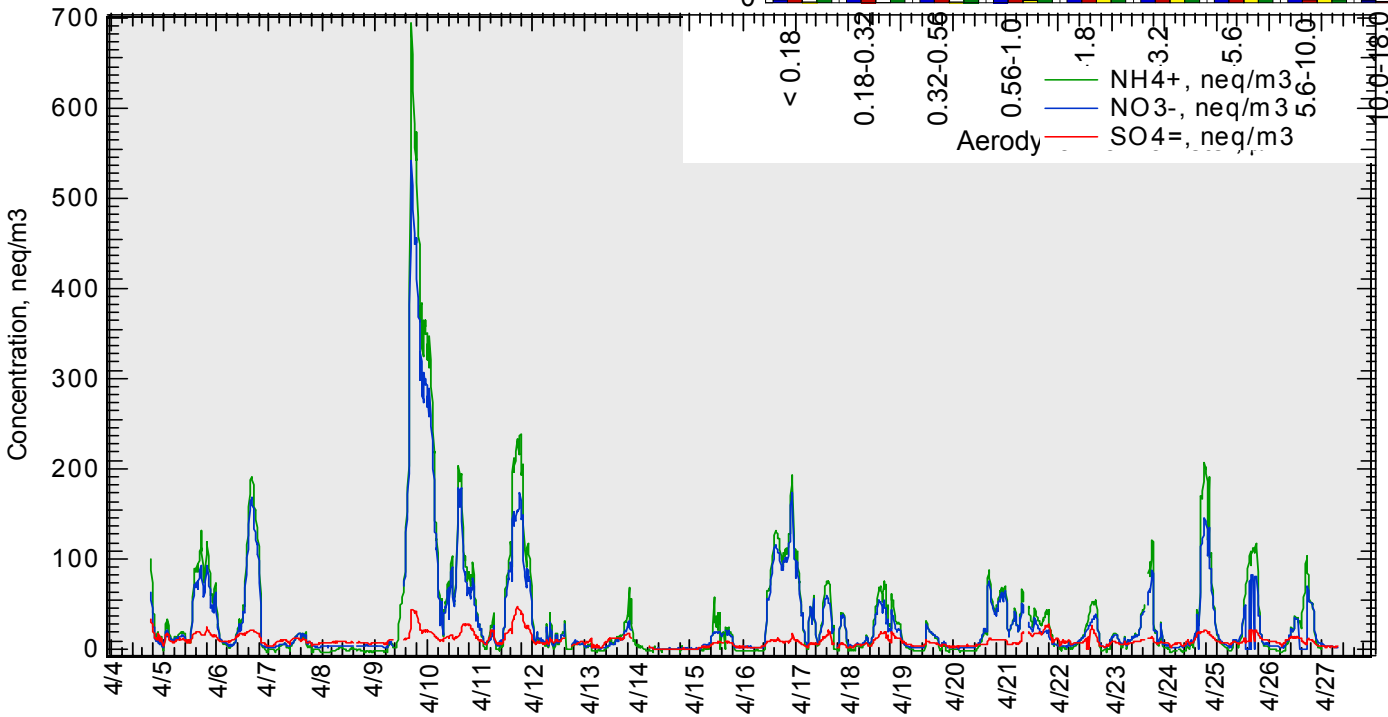
- NO_3^- and SO_4^{2-} important
- NH_4NO_3 in submicron mode



San Gorgonio 4/03

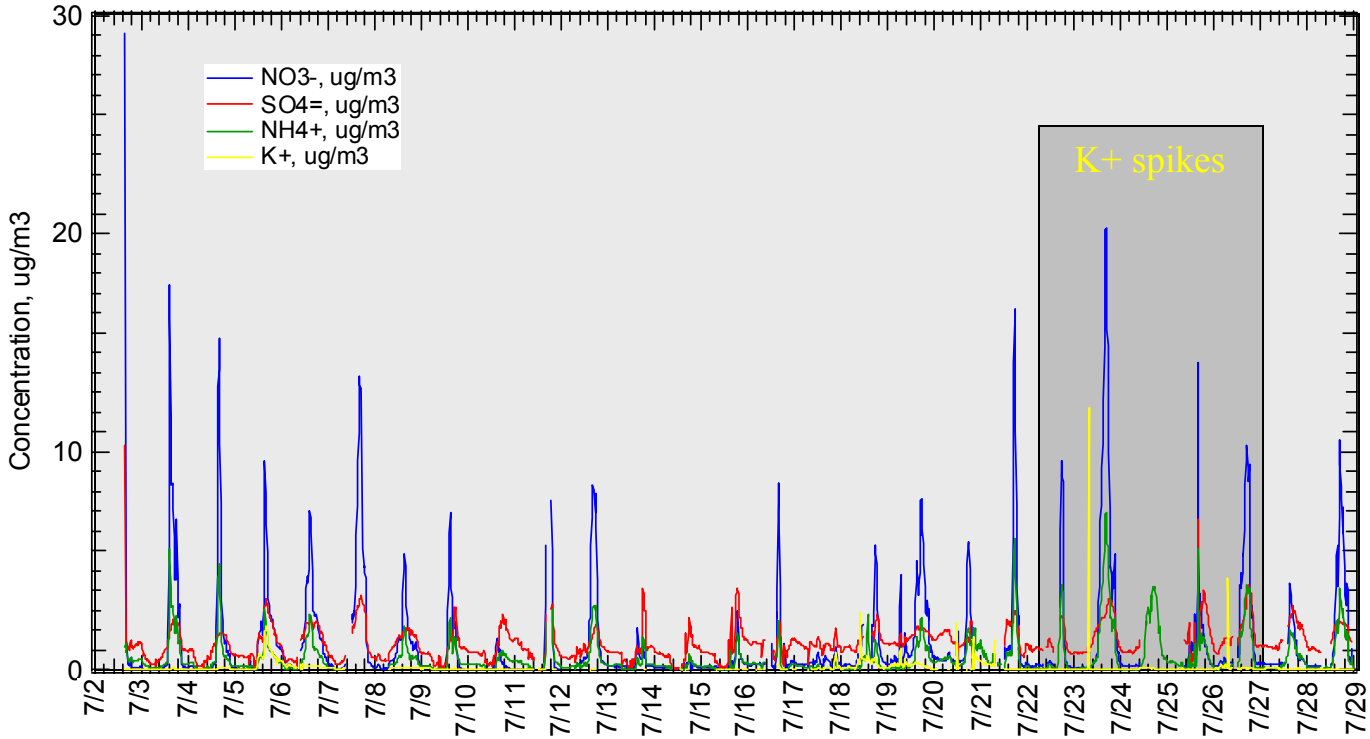
- Large diurnal variability
- Submicron NH_4NO_3 dominant





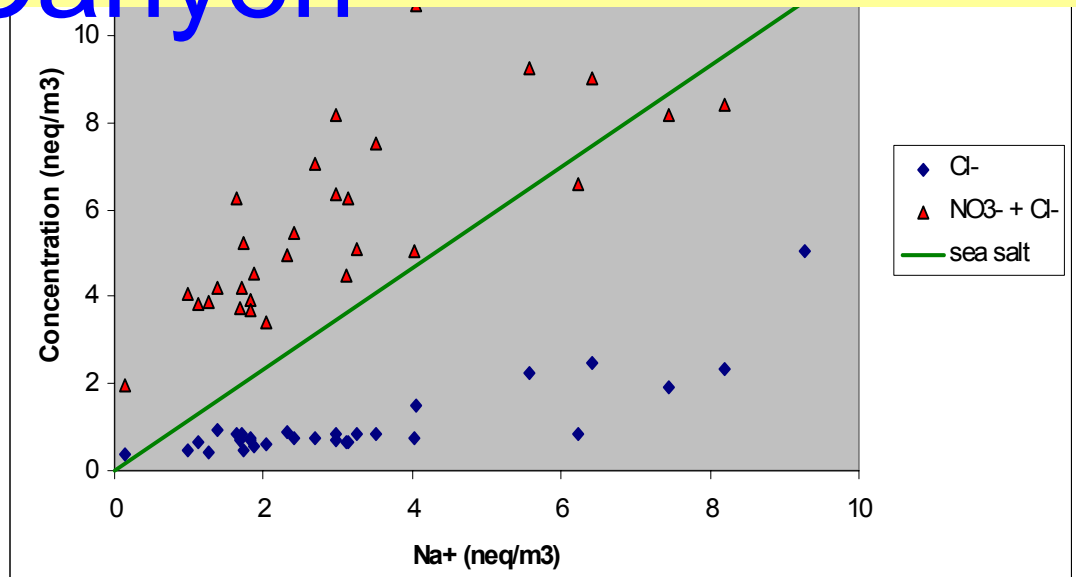
San Gorgonio 7/03

- More regular diurnal variability
- Some days sulfate-dominated

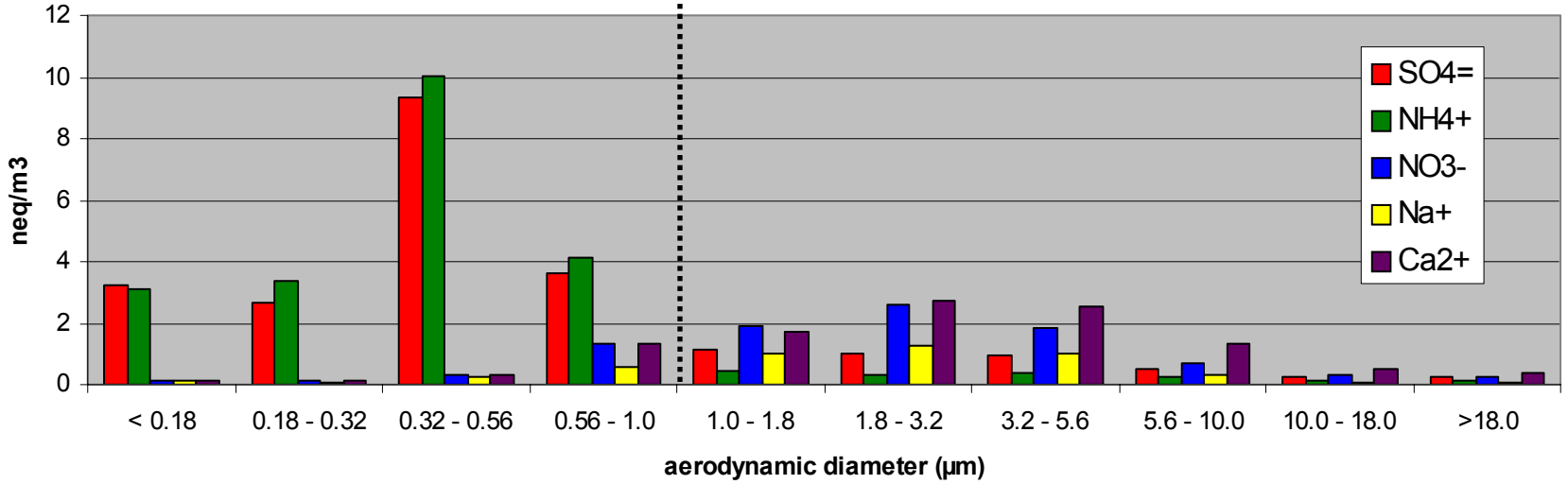


Grand Canyon

- Nitrate in coarse mode
- Appears to be associated with Na^{+} and Ca^{2+}



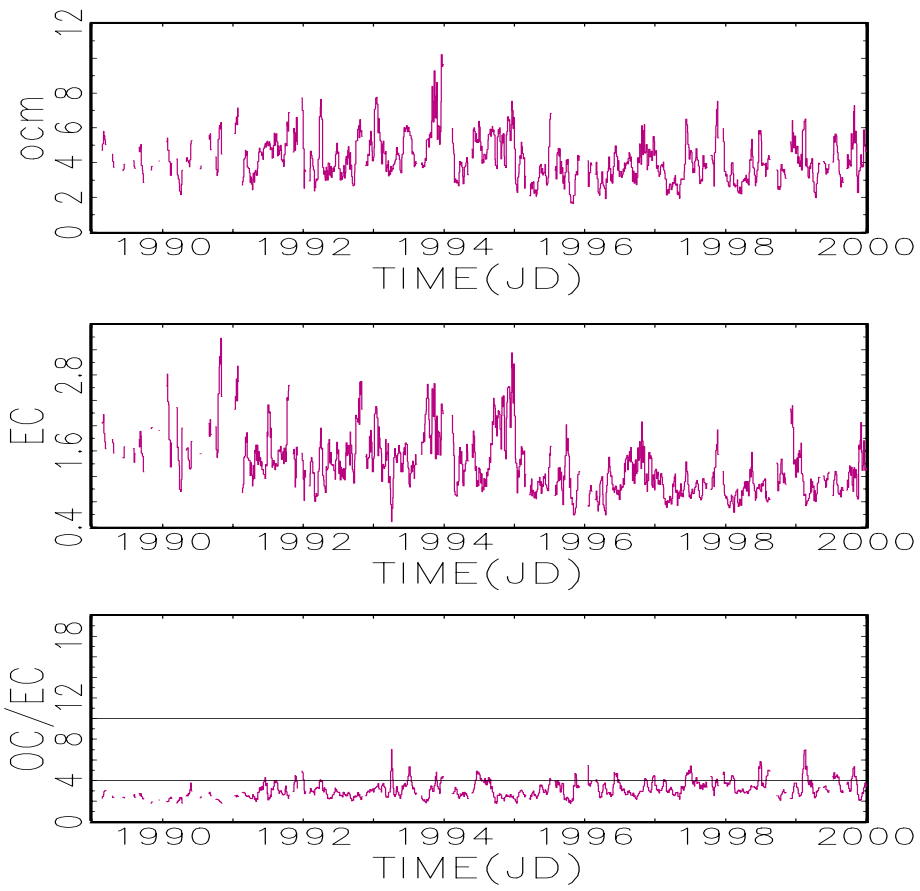
Grand Canyon MOUDI average

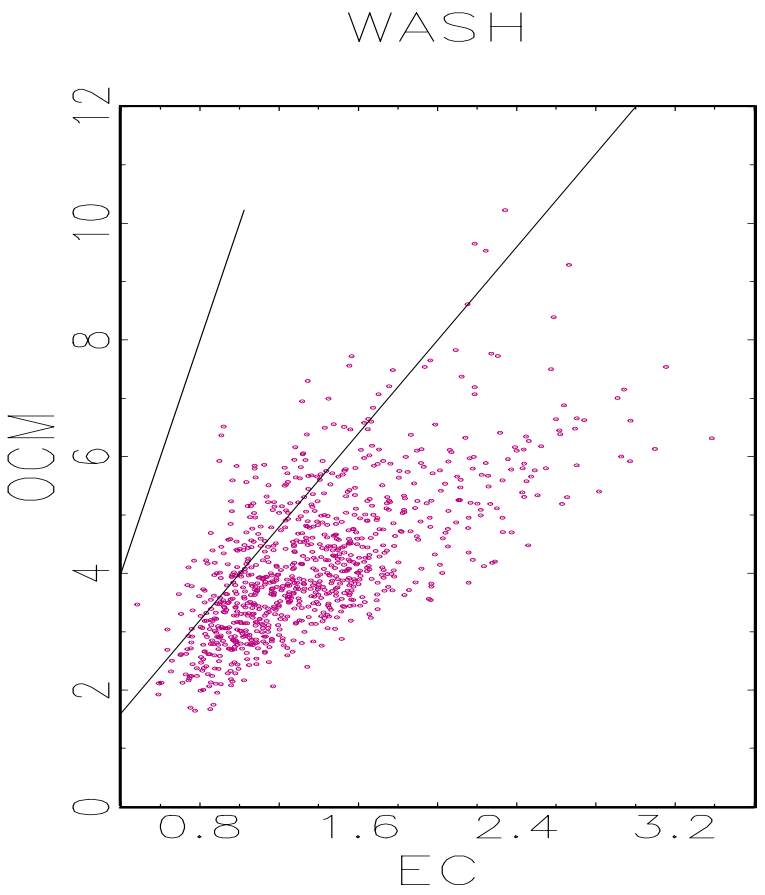


Source Profiles for OC/EC

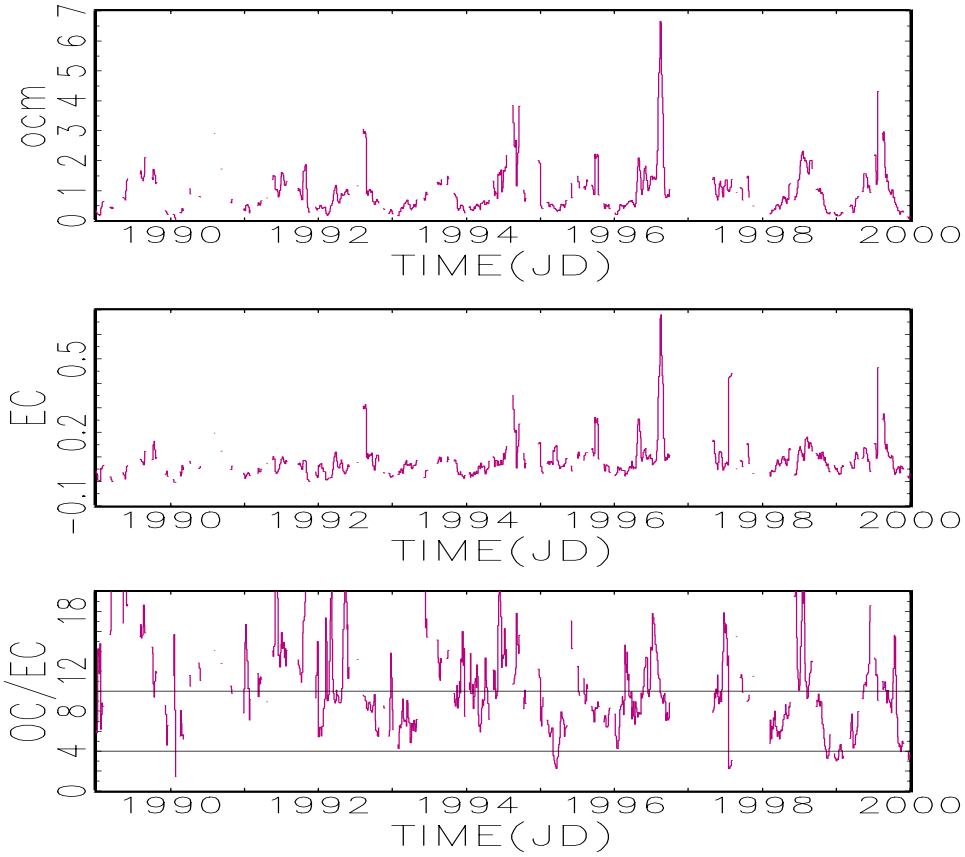
- Gillies, Gertler, Sagebiel, and Dippel (2001) EST 35, 1054: Tunnel measurements yield OC/EC = 2.66
- McDonald, Zielinska, Fujita, Sagebiel, Chow, and Watson (2000) EST 34 2080: Colorado hardwoods yield OC/EC =11

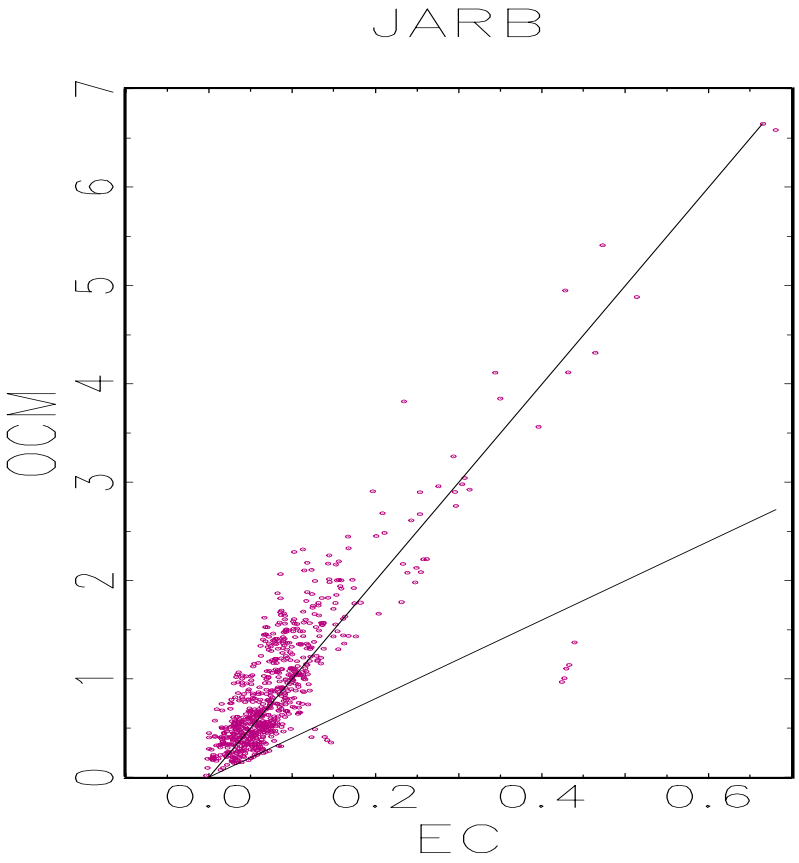
Washington DC Raw OC EC Data



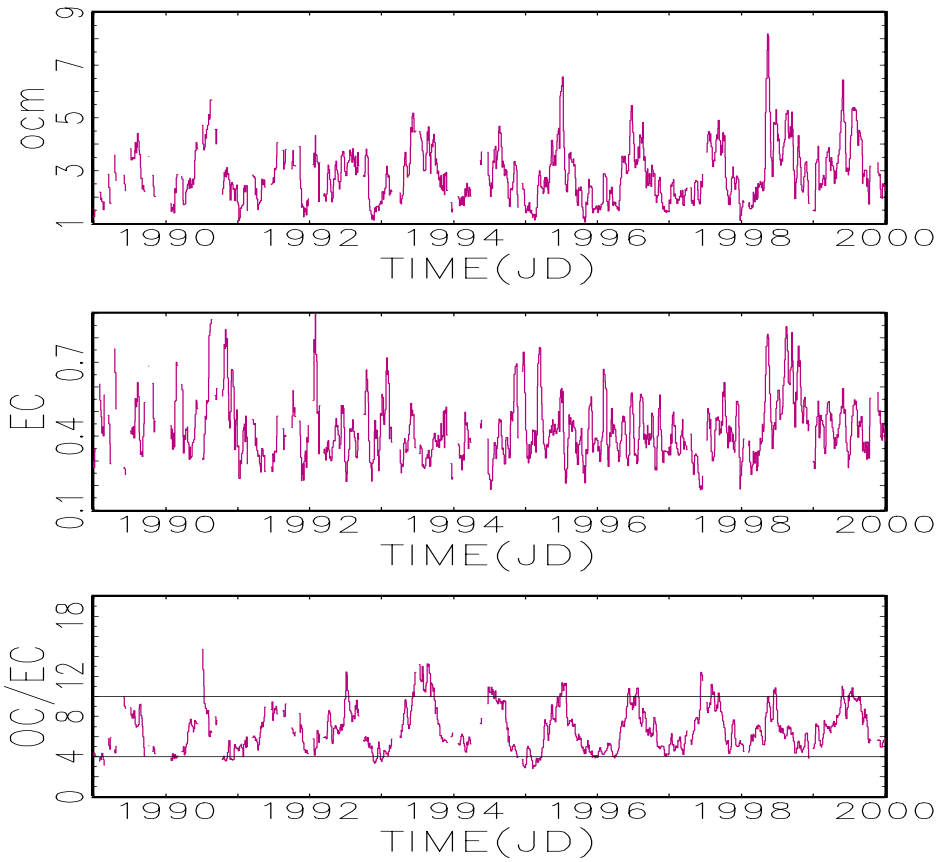


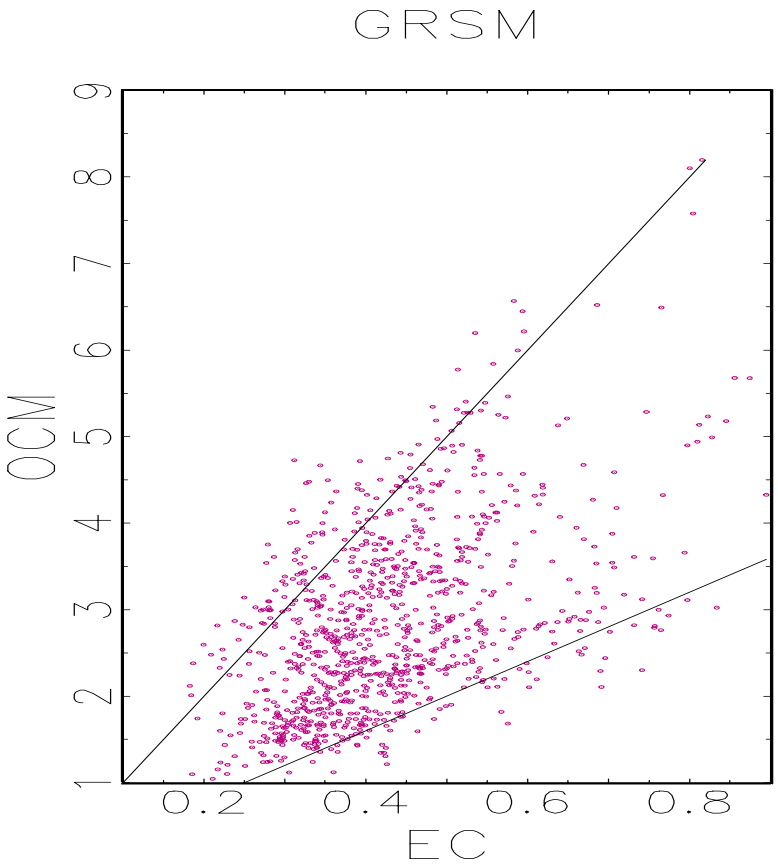
Jarbidge Raw OC EC Data



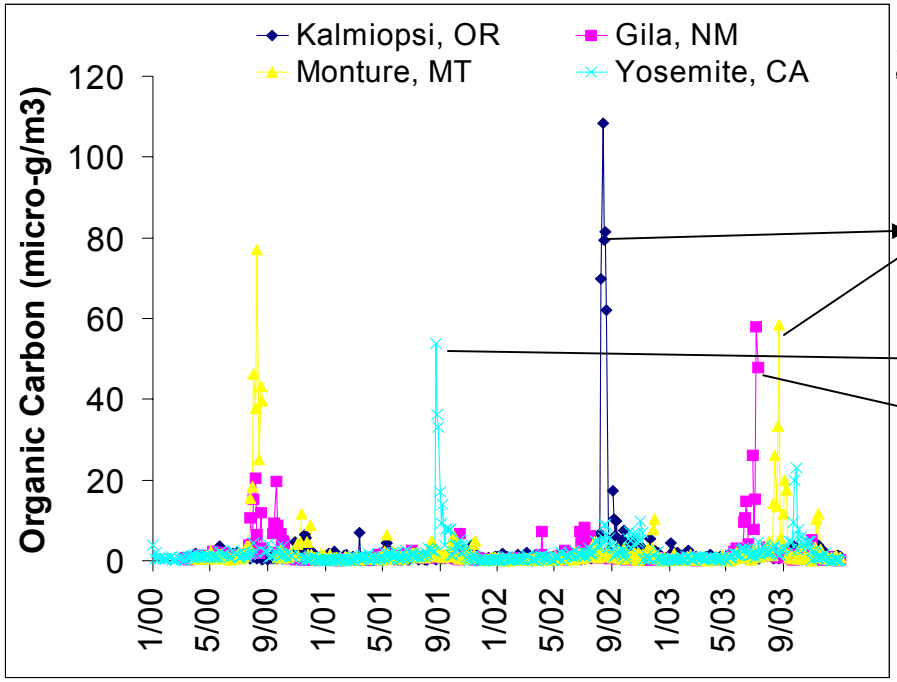


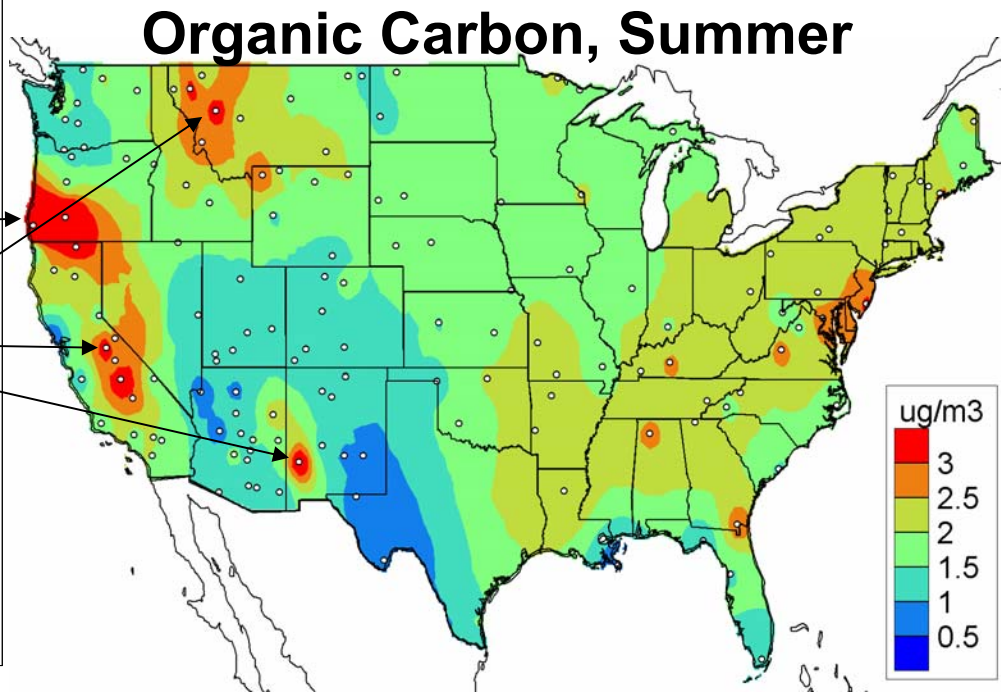
Great Smoky Raw OC EC Data





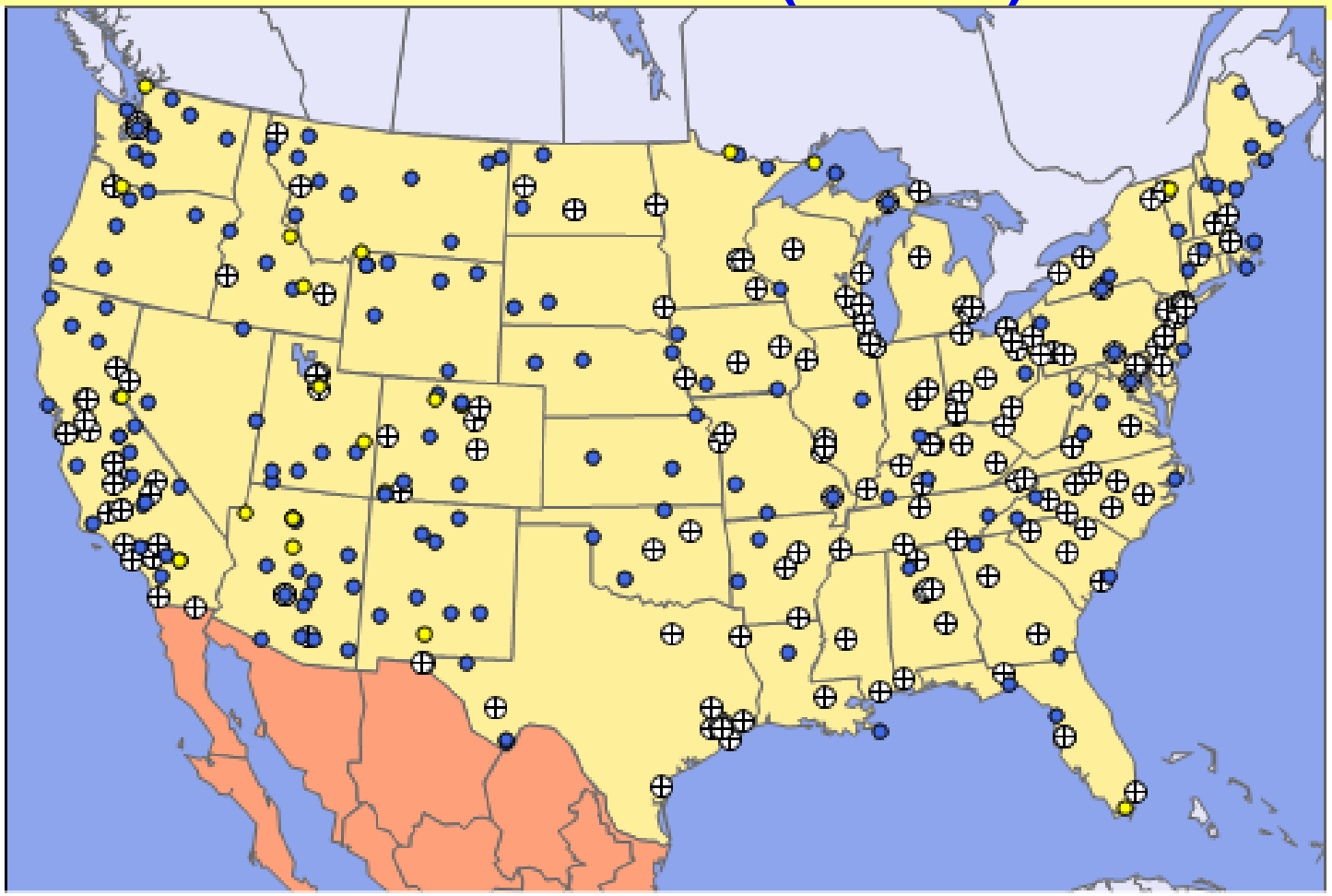
Smoke Contribution to Carbonaceous Material





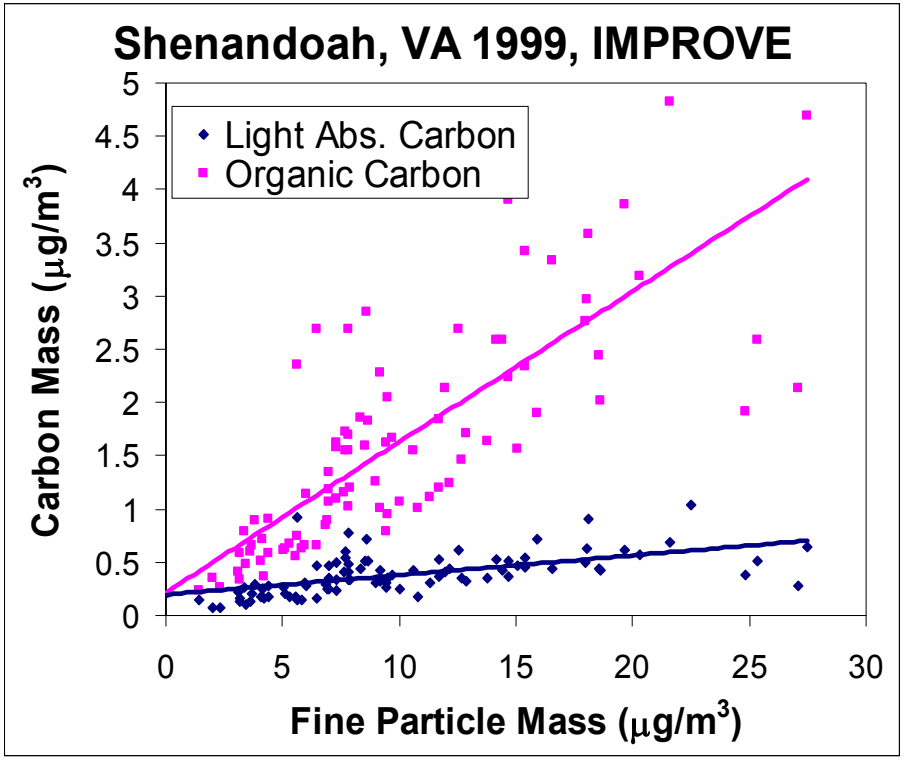
Wild fires occur every summer at some locations in the western U.S. leading to extreme carbon concentrations. These values can dominate multi-year seasonal averages.

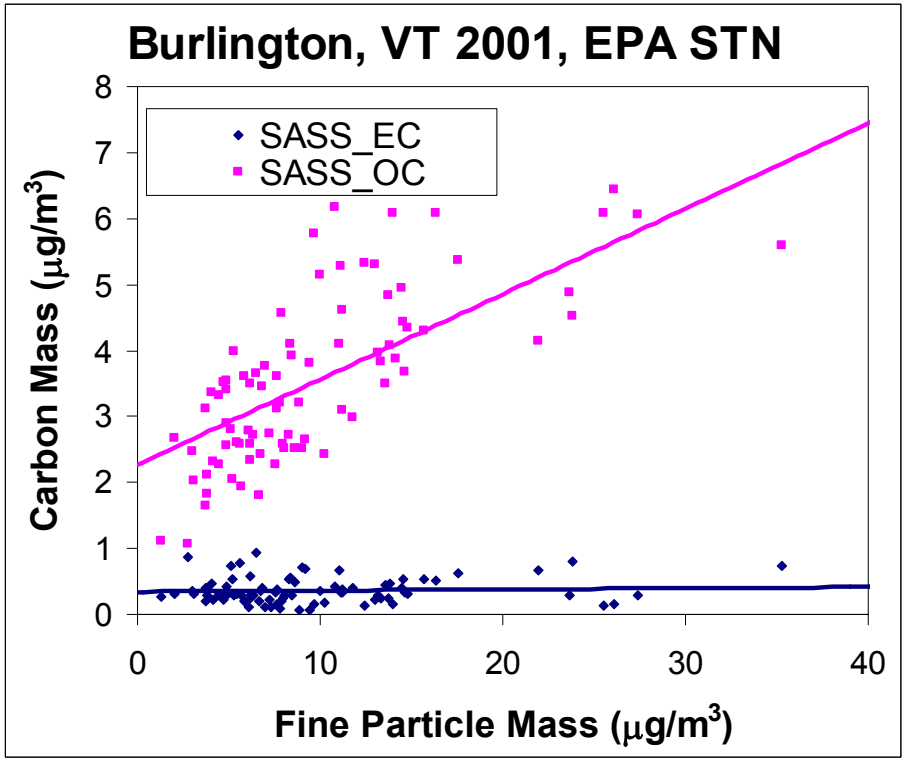
IMPROVE and EPA Speciated Trend Network (STN)



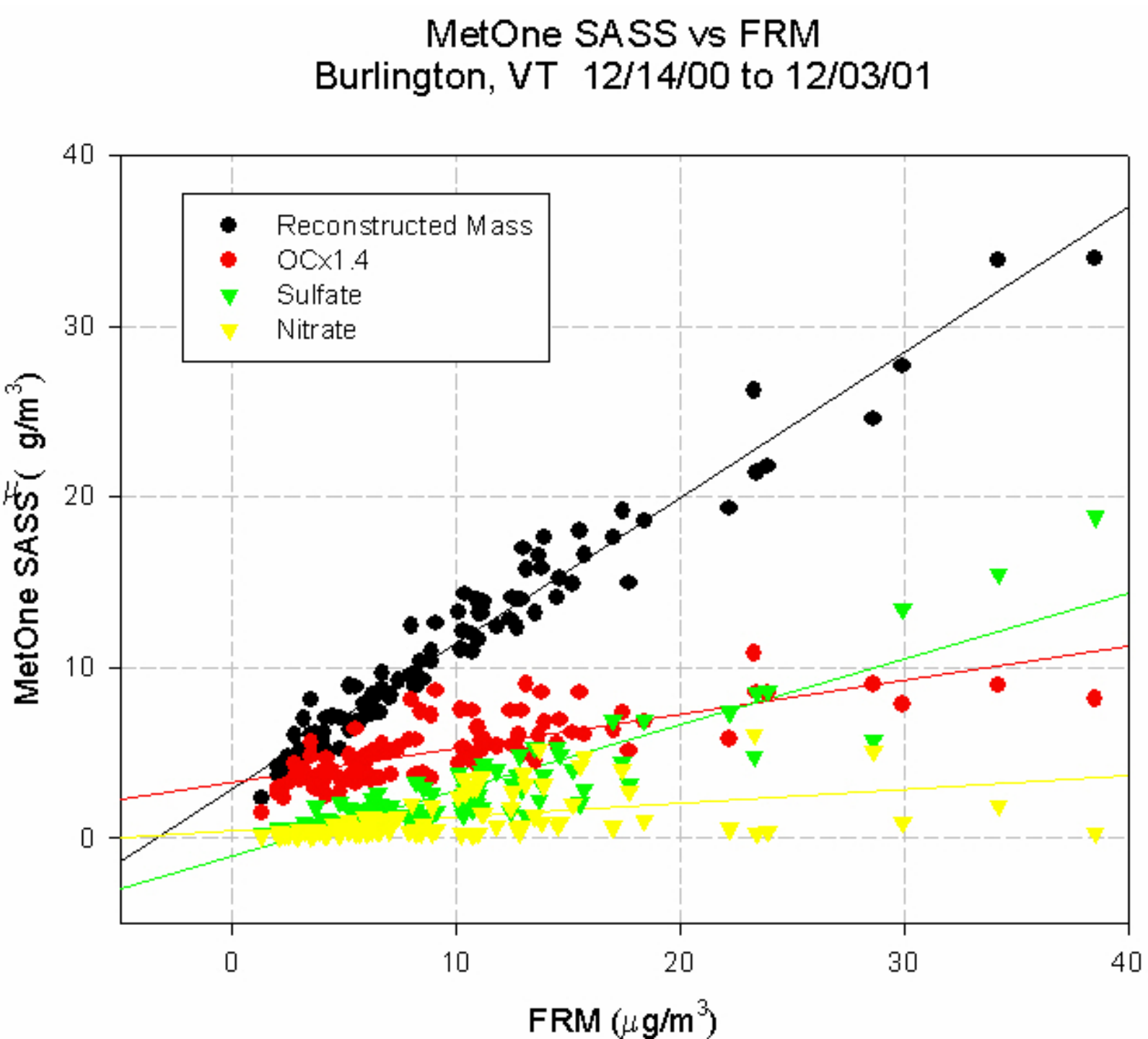
- IMPROVE – 165 monitoring sites in mostly rural areas
- STN - 250 m- 300 monitoring sites in mostly urban/suburban areas

IMPROVE Corrects OC and EC for a Positive Artifact





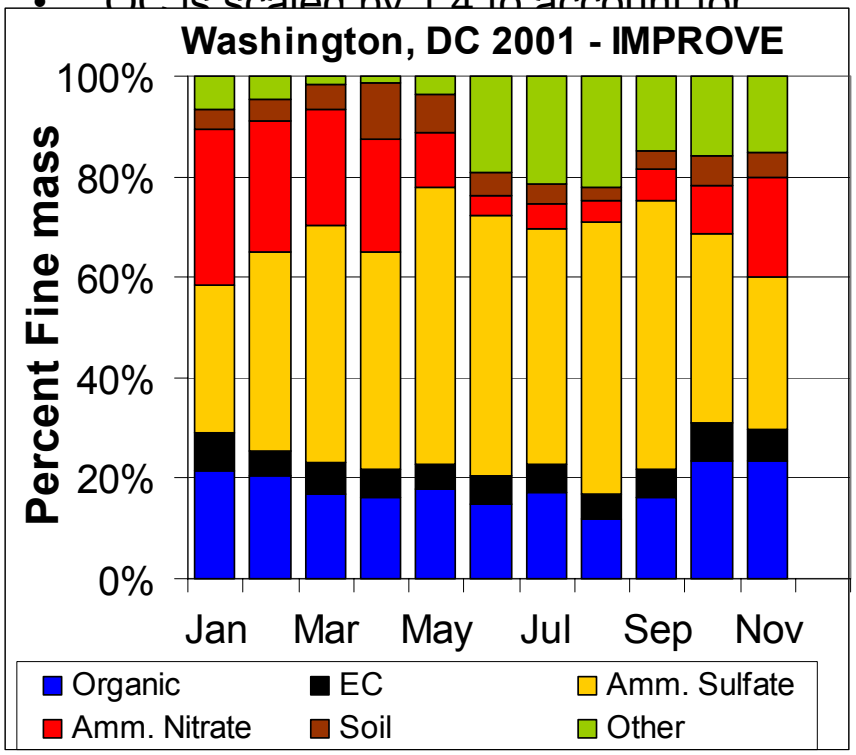
The positive artifact correction causes the organic and elemental carbon to approach zero as fine mass goes to zero

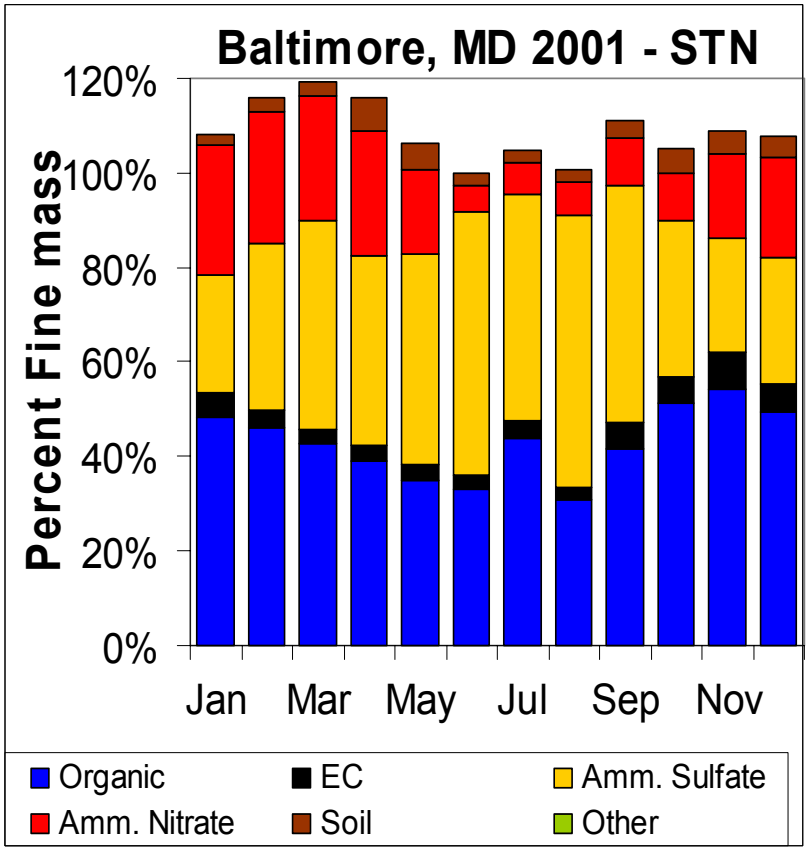

MetOne SASS vs FRM
Burlington, VT 12/14/00 to 12/03/01
Reconstructed Mass
OCx1.4
Sulfate
Nitrate
MetOne SASS (g/m3)
FRM (µg/m3)
0
10
20
30
40

IMPROVE and STN Fine Mass Budgets

Reconstructed fine mass: $= [Amm.Sulfate] + [Amm.Nitrate] + [Soil] + 1.4[Organic\ Carbon] + [Light\ Abs\ \ Carbon]$

- OC is scaled by 1.4 to account for

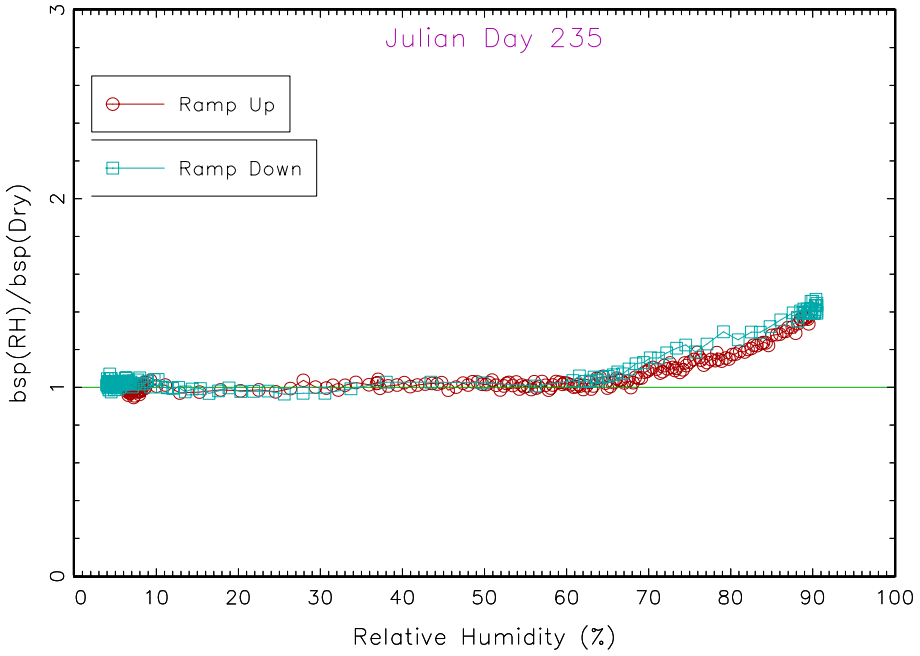


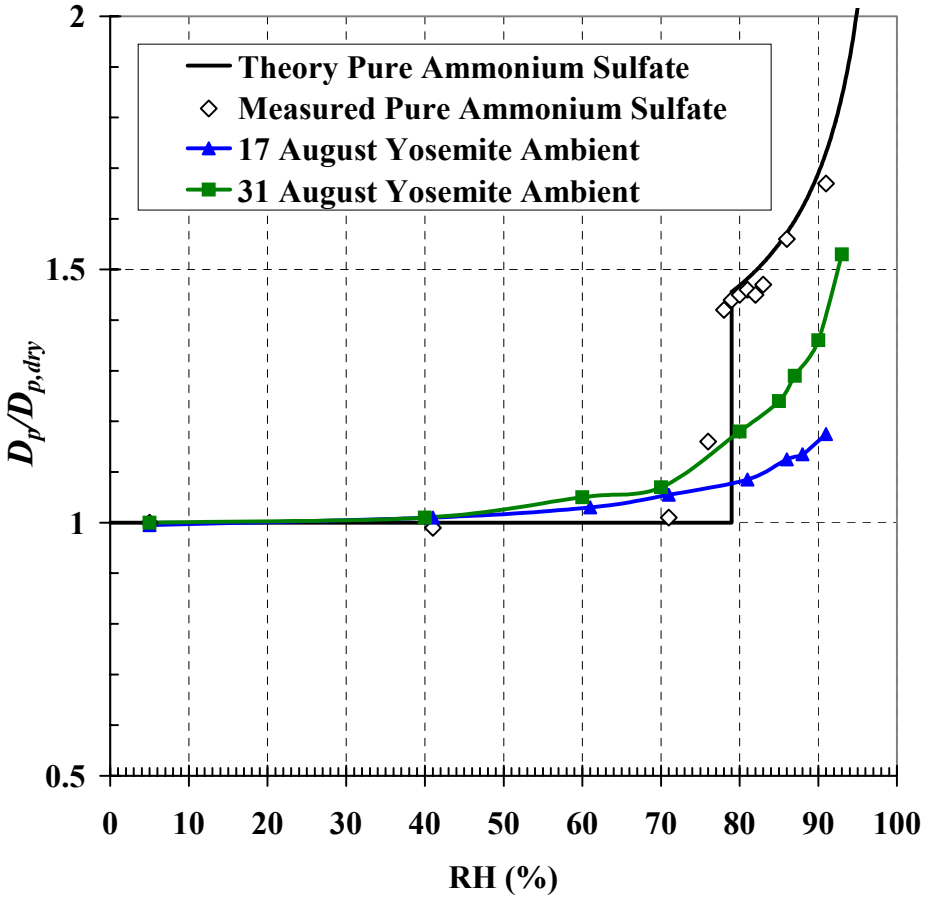


Conclusions – Spatial Patterns

- The largest carbon concentrations are in the southeastern US, but the largest carbon fine mass fractions are in the northwestern US
- The urban carbon “excess” appears to have a limited spatial extent
- OC/EC ratios imply:
  - Winter carbon aerosol is not biogenic (fire or secondary organics)
  - Summer carbon aerosol
    - High OC/EC ratio in the Northwest - smoke
    - Low OC/EC ratio in Ohio River Valley - urban/industrial
    - Middling OC/EC ration in Southeastern US - mix of urban, fire, biogenic.

Particle Hygroscopicity





Measurements with (a) nephelometery and a (b) hygroscopic tandem DMA (right) both showed very limited particle hygroscopicity. Diameter growth curves for ambient aerosol are shown on the right for roughly the most and least hygroscopic cases. All ambient measurements showed much lower hygroscopicity than ammoniated sulfates, the dominant ionic species (see Figure 9).

IMPROVE Monitoring Program

The Interagency Monitoring of Protected Visual Environments

- A cooperative measurement effort of particulate matter and haze in Class I Areas
- Governed by representatives from Federal and regional-state organizations
- Objectives:
  - Establish current visibility and aerosol conditions in federal class I areas
  - Identify chemical species and emission sources responsible for existing man-made visibility impairment in FCIA
  - Document long-term trends for assessing progress towards the national visibility goal to FCIA
  - With the enactment of the Regional Haze Rule, to provided regional haze monitoring representing all visibility-protected FCIA
- Conduct visibility/aerosol research: Intensive monitoring studies

IMPROVE Monitoring

- Monitoring Began in March 1988
- **Optical** – extinction by ***transmissometer*** &/or scattering by ***nephelometer*** (hourly) plus absorption on particle filters (24-hour)
- **Aerosol** – particle sampling/analysis for six major species & trace constituents to aid in source attribution (24 hour samples twice weekly; every 3rd day starting in 2000)
- **Scene** – color *photography* to document scenic appearance (typically 3 photos/day)
  - photographic spectrums of a range of visibility conditions are generated from 5 years of photos

IMPROVE Aerosol Samplers

- Four independent sampling modules
- Prior to 2000, two 24 hour samples were collected twice a week, after 2000, samples collected every three days.

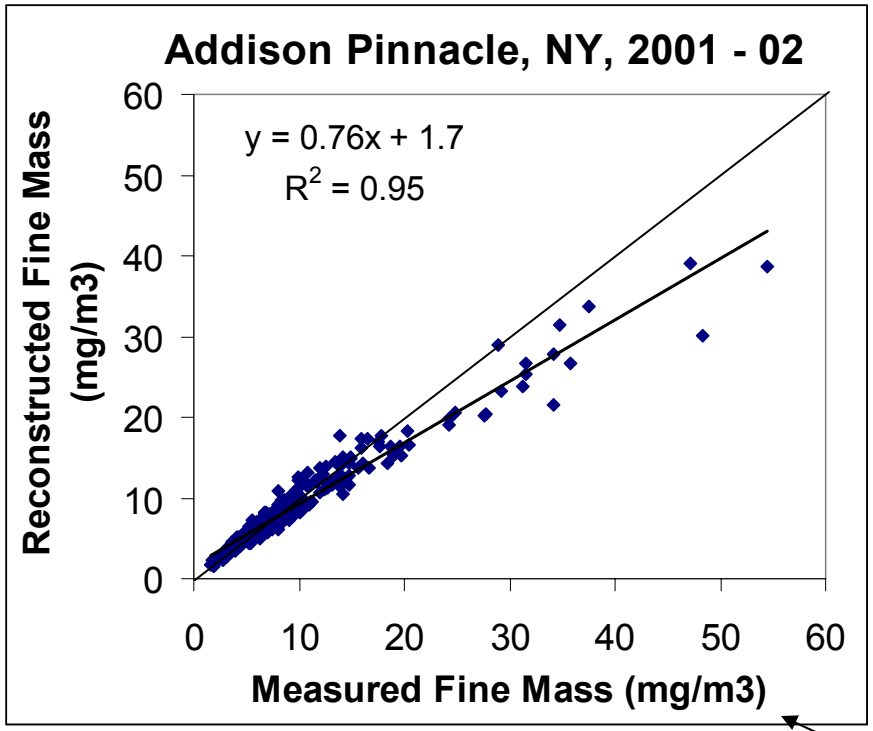
Module	Filter	Size	Variable	Analysis
A	Teflon	PM2.5	mass	gravimetric
			Na-Mn	Proton Induced X-Ray Emission
			Fe-Pb	X-ray Fluorescence
			total H	Proton Elastic Scattering
			optical absorption	Hybrid Integrating Plate/Sphere
B	Nylon	PM2.5	sulfate, nitrate	Ion Chromatography
C	Quartz	PM2.5	OC, EC in 8 fractions	Thermal Optical Reflectance
D	Teflon	PM10	mass	gravimetric

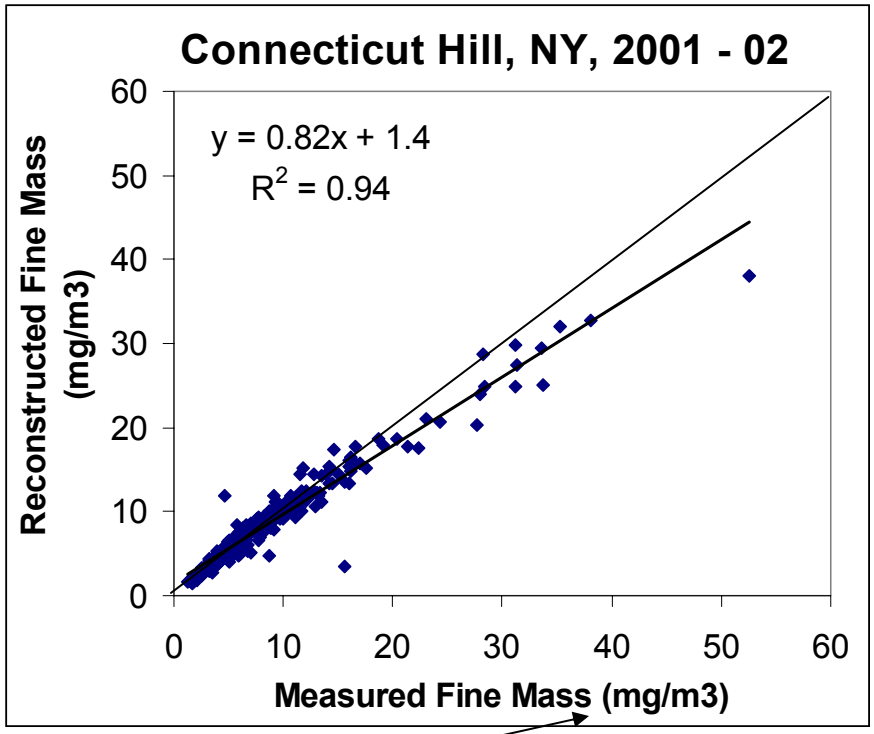
Aerosol Composite Components

- Ammonium Sulfate – 4.125 * [S]
- Ammonium Nitrate – 1.29 * [NO_3]
- Organics – 1.4 [OC]
- Elemental Carbon – [EC]
- Soil – as oxides of crustal elements

Reconstructed Fine Mass

- RCFM = Sulfate + Nitrate + Organics + EC + Soil





$\mu g/m^3$

The Regional Haze Rule

- Federal class I areas (including national parks, other wilderness areas) to return to "natural visibility" conditions by 2064
- Implementation
  - 20% worst haze days are to be brought back to natural conditions
  - 20% best haze days are to remain unchanged
  - Baseline haze calculated from 2000-2004 period
  - State Implementation Plans to be submitted by 2007 for linear improvement in visibility over the 2004-2018 period