

A scenic landscape of snow-capped mountains and a valley with a lake. The mountains are in the background, with snow on their peaks and slopes. The valley in the foreground is filled with green and brown vegetation, and a lake is visible in the distance. The sky is blue with some clouds.

Interagency Monitoring of Protected Visual Environments (IMPROVE)

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

Bret Schichtel NPS

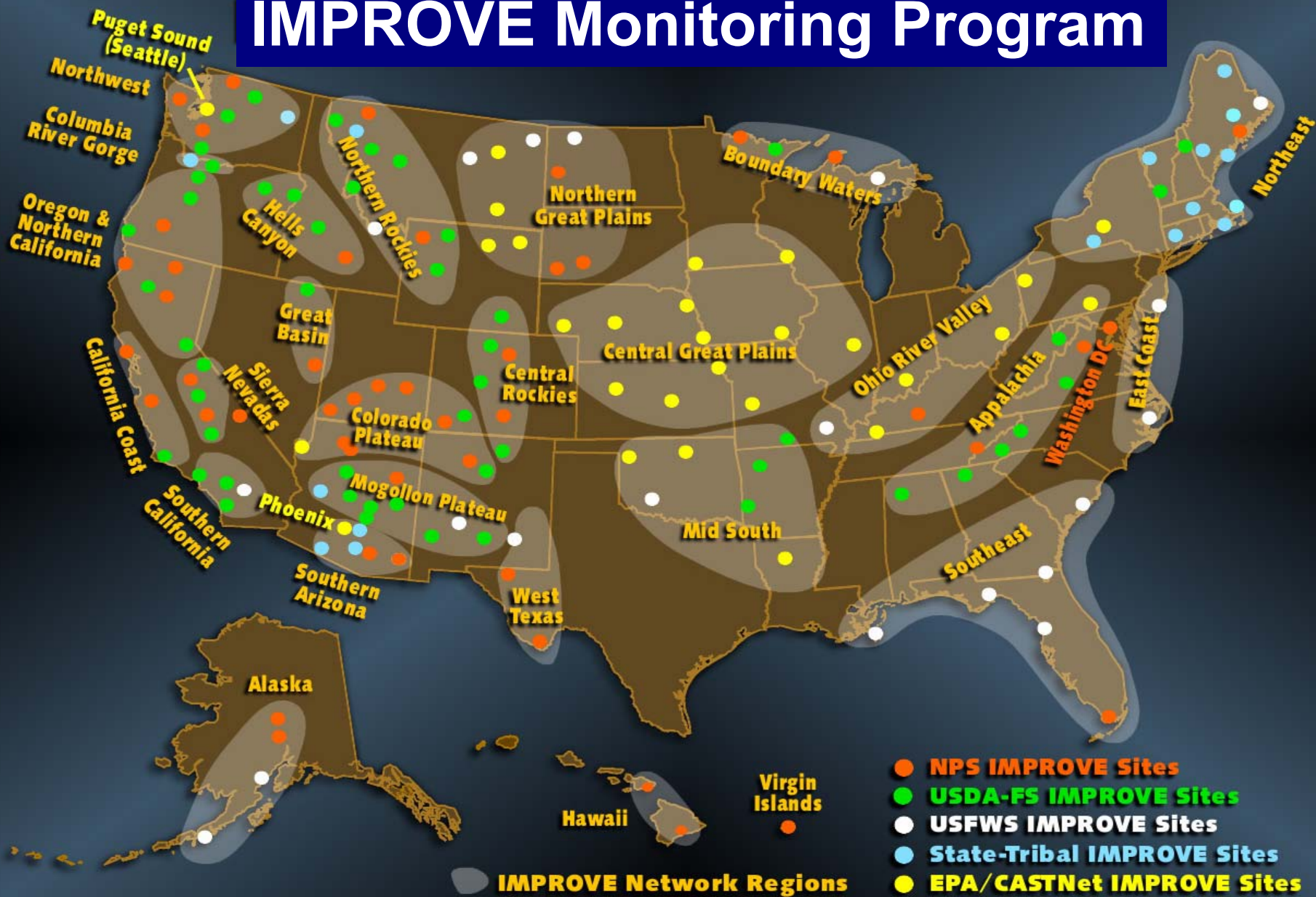
William Malm NPS

Marc Pitchford NOAA/EPA

Lowell Ashbaugh UCD

Chuck McDade UCD

IMPROVE Monitoring Program

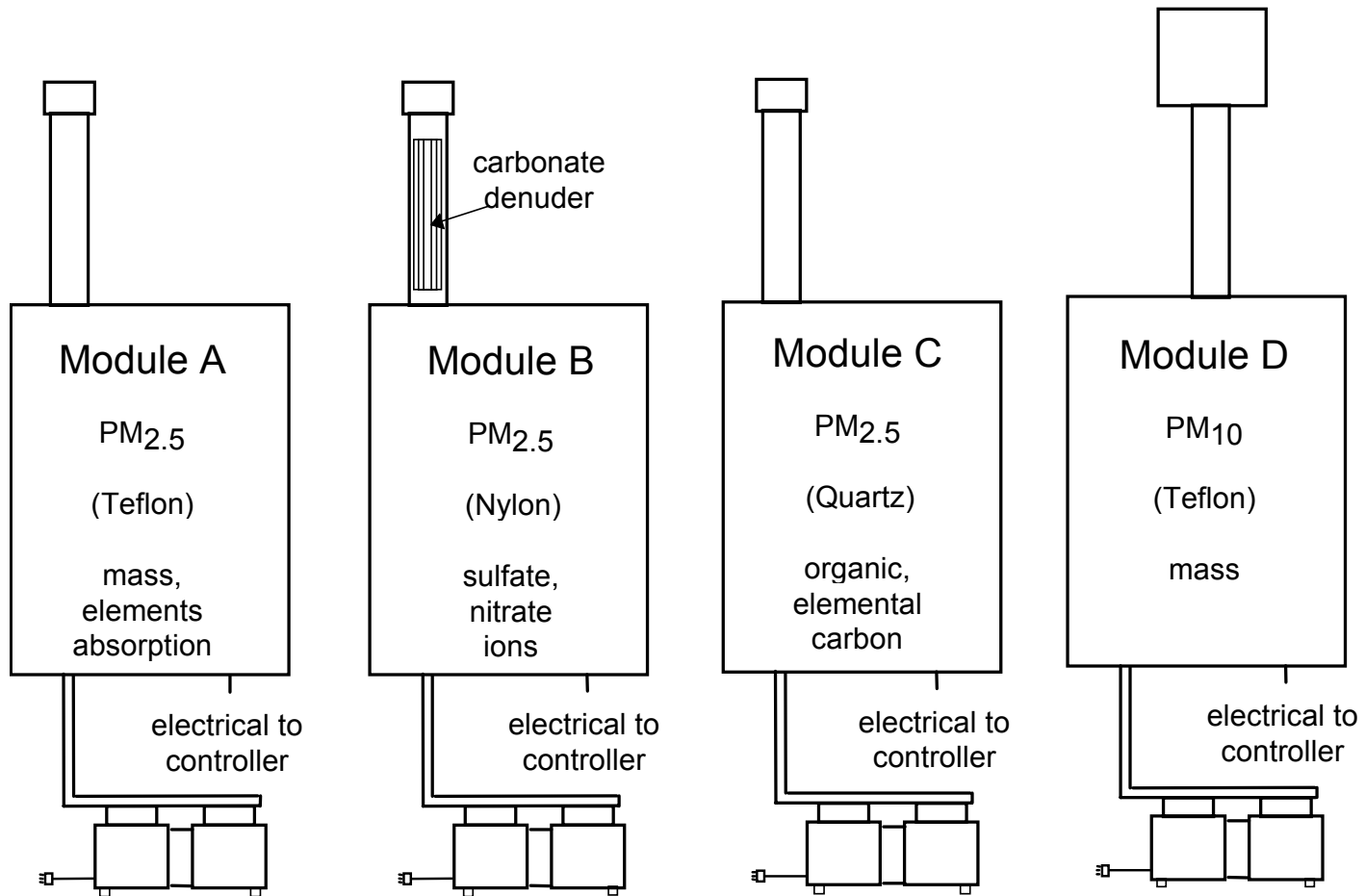


- Began operating in spring of 1988 with 20 monitoring sites
- Today has 165+ sites - 54 sites with eight or more years of data.

Chiricahua, NM



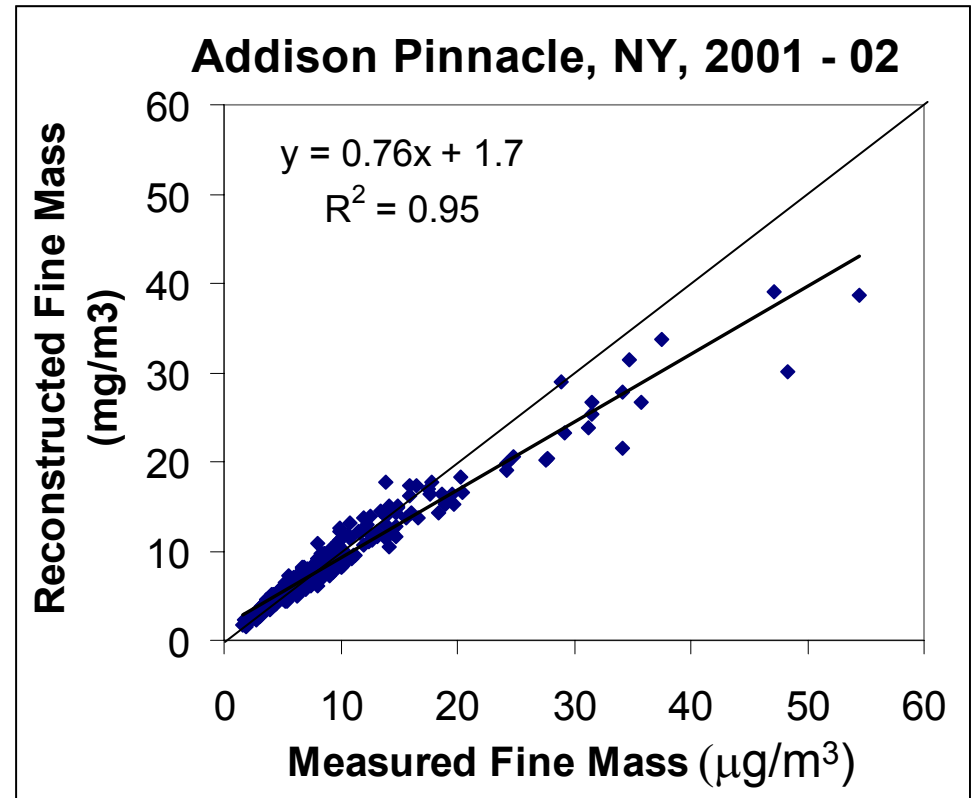
IMPROVE Aerosol Monitor



- 24 hour samples collected every 3 days

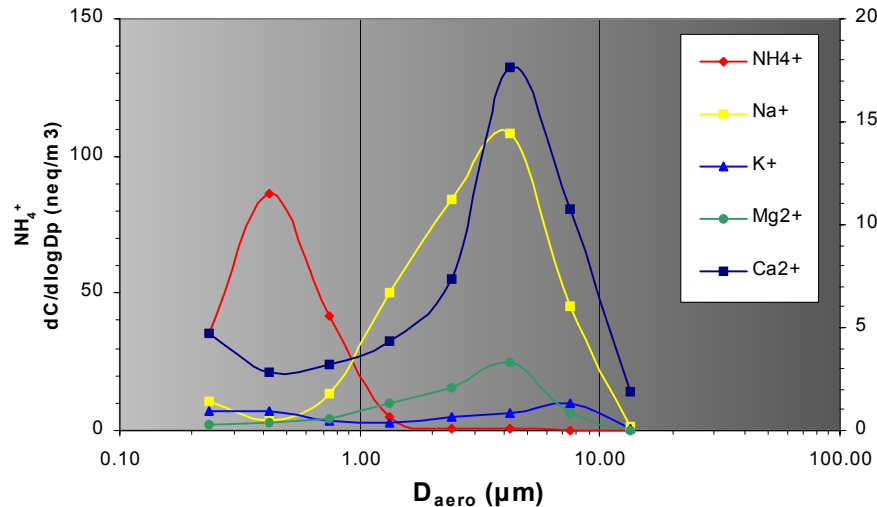
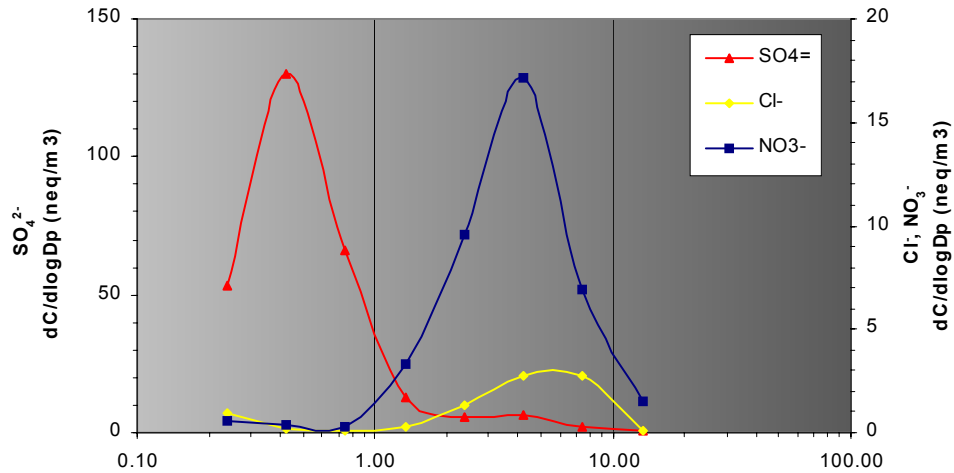
Fine Aerosol Composite Components

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

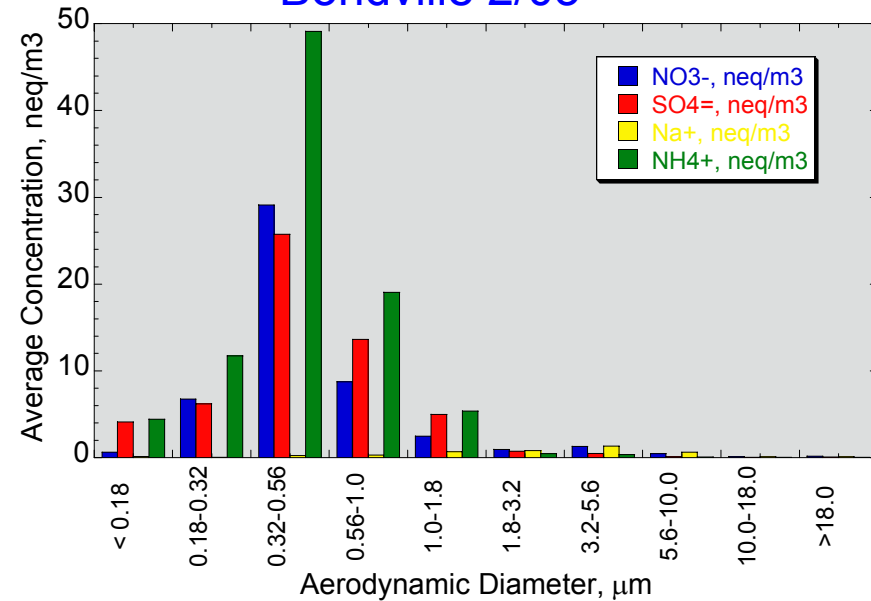


Size Distributions

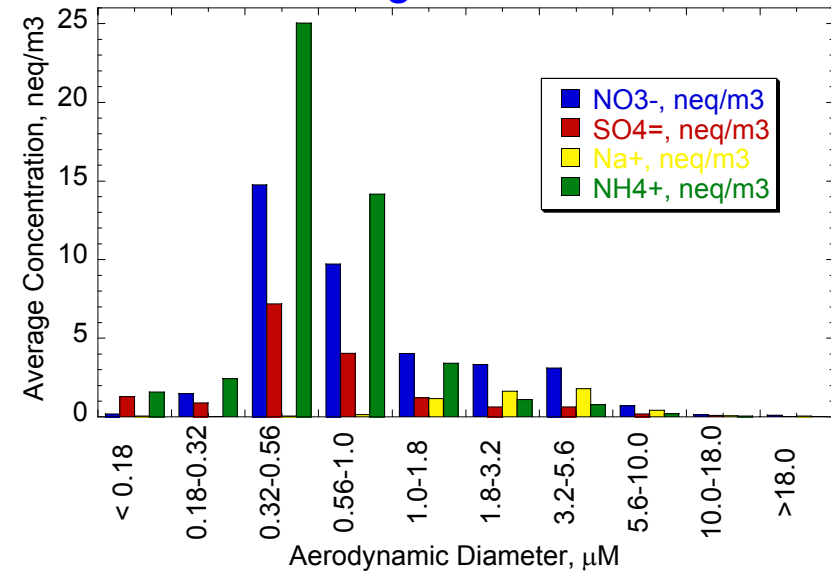
Big Bend Texas - August 1999



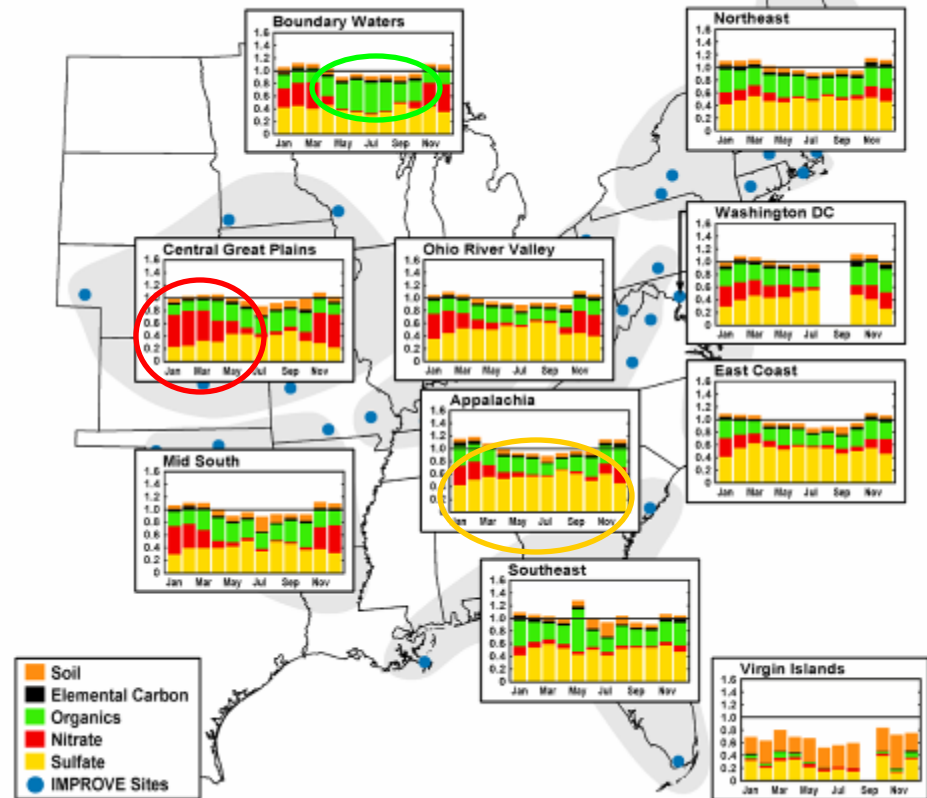
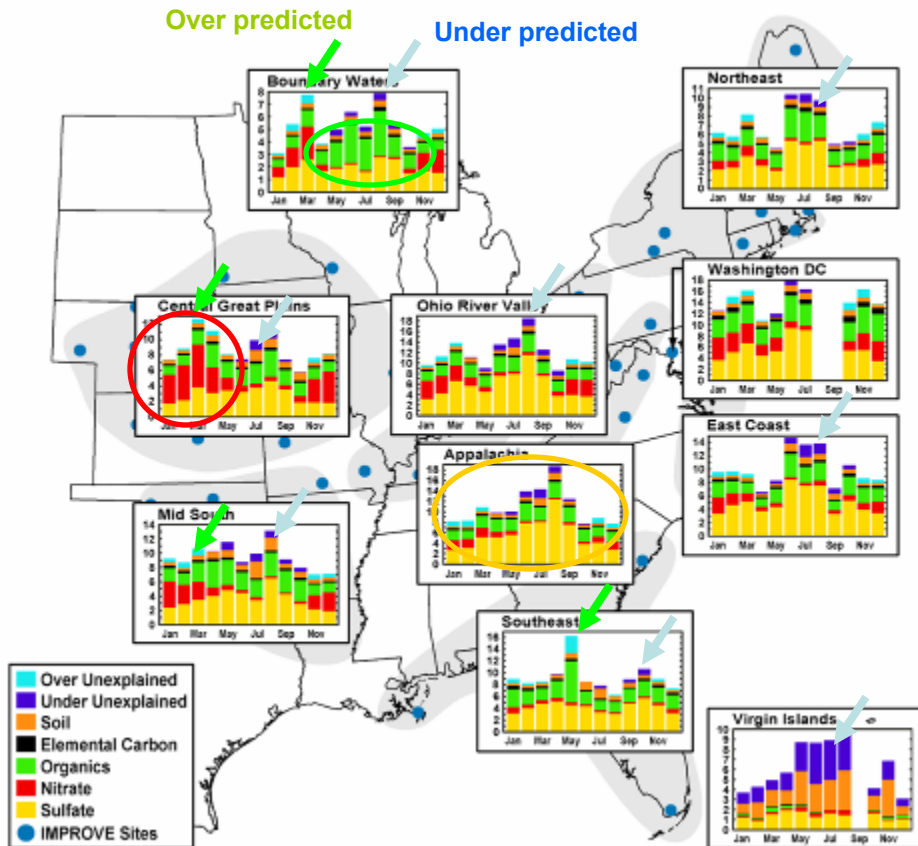
Bondville 2/03



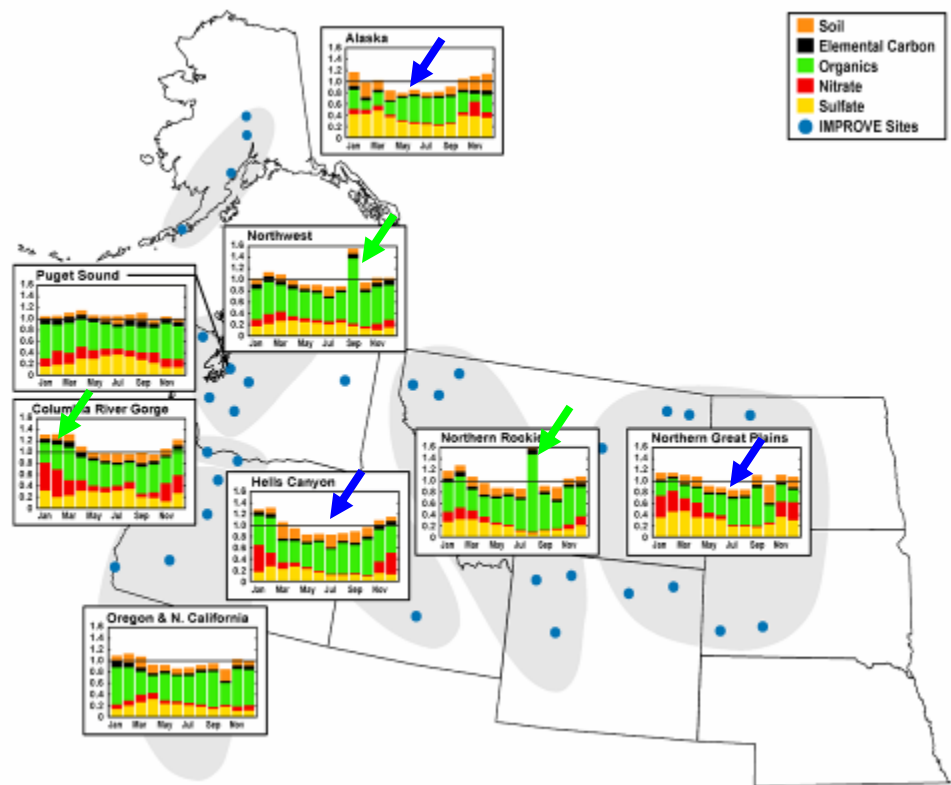
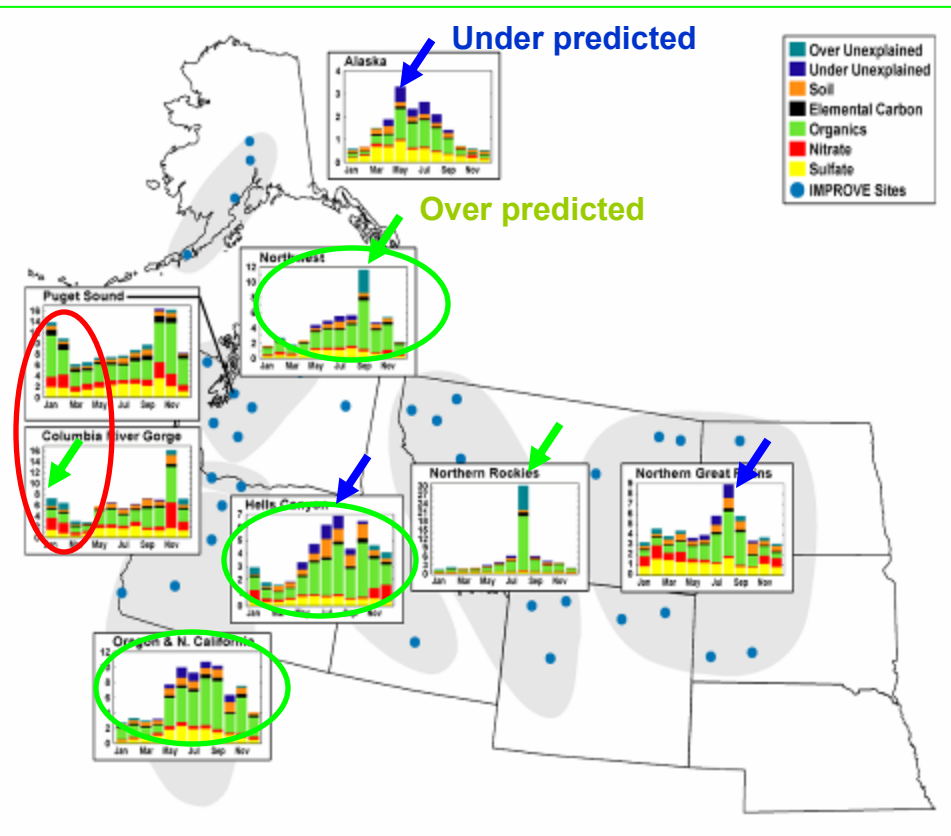
San Geronio, CA - 4/2003



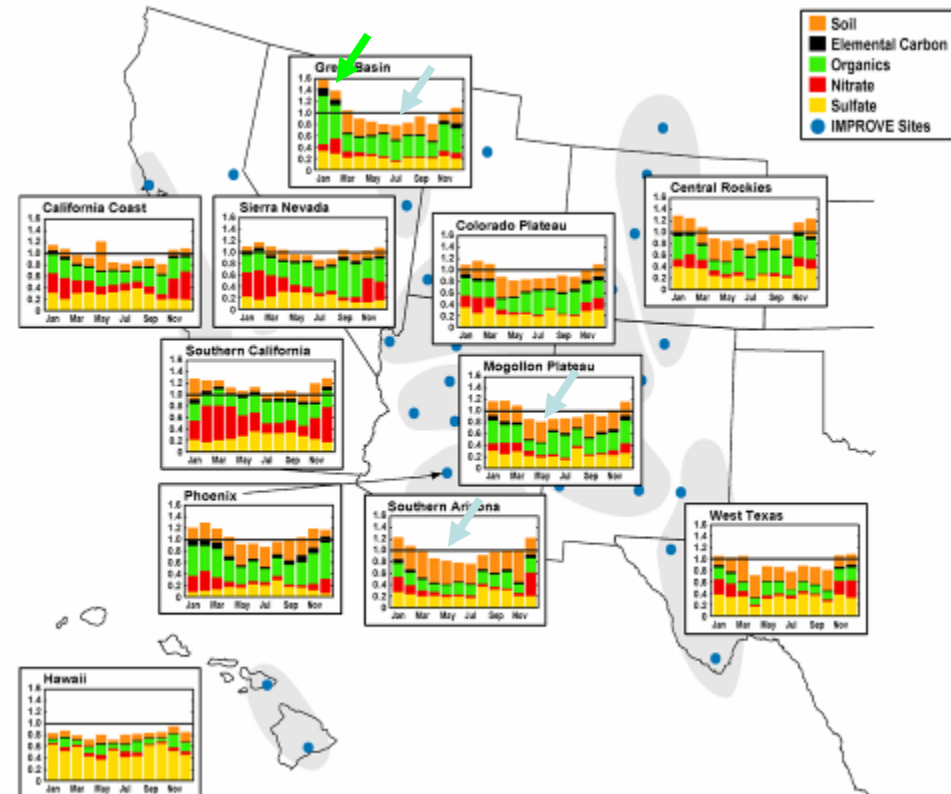
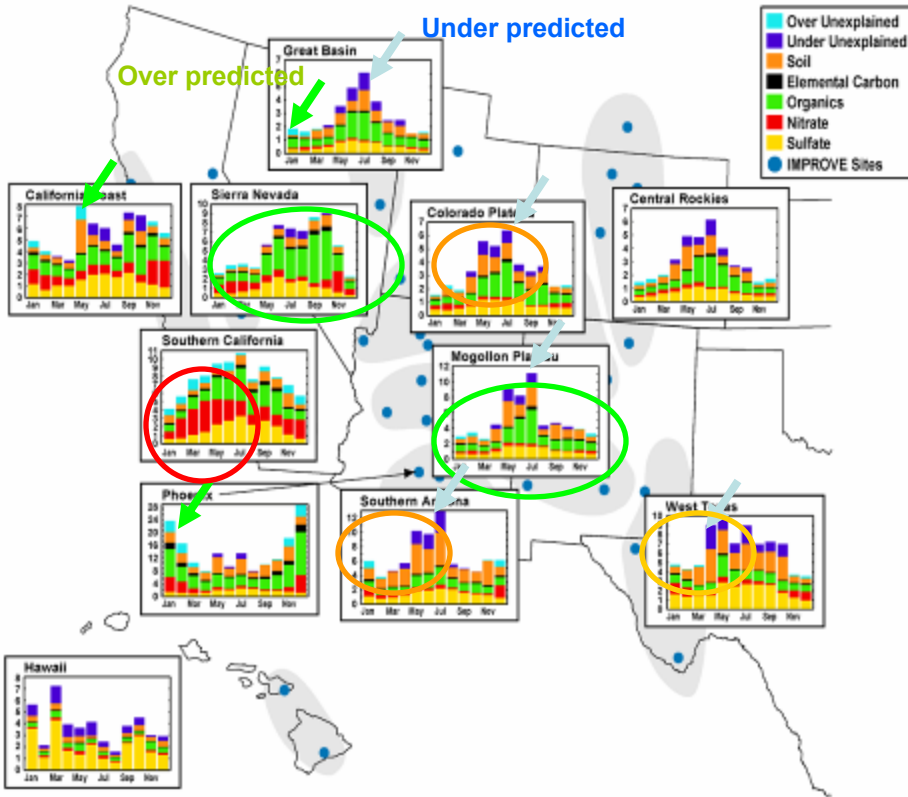
Monthly Fine Mass Budget - 2003



Monthly Fine Mass Budget - 2003

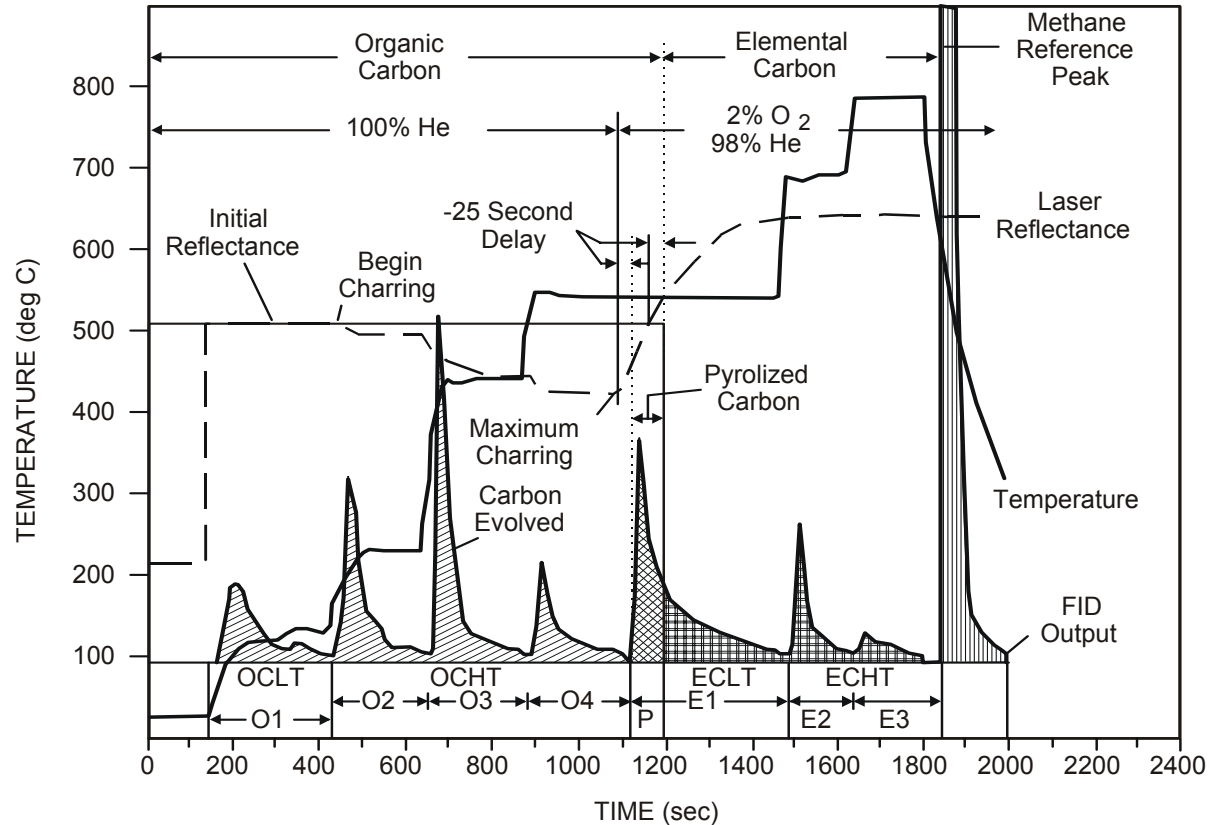


Monthly Fine Mass Budget - 2003



**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:

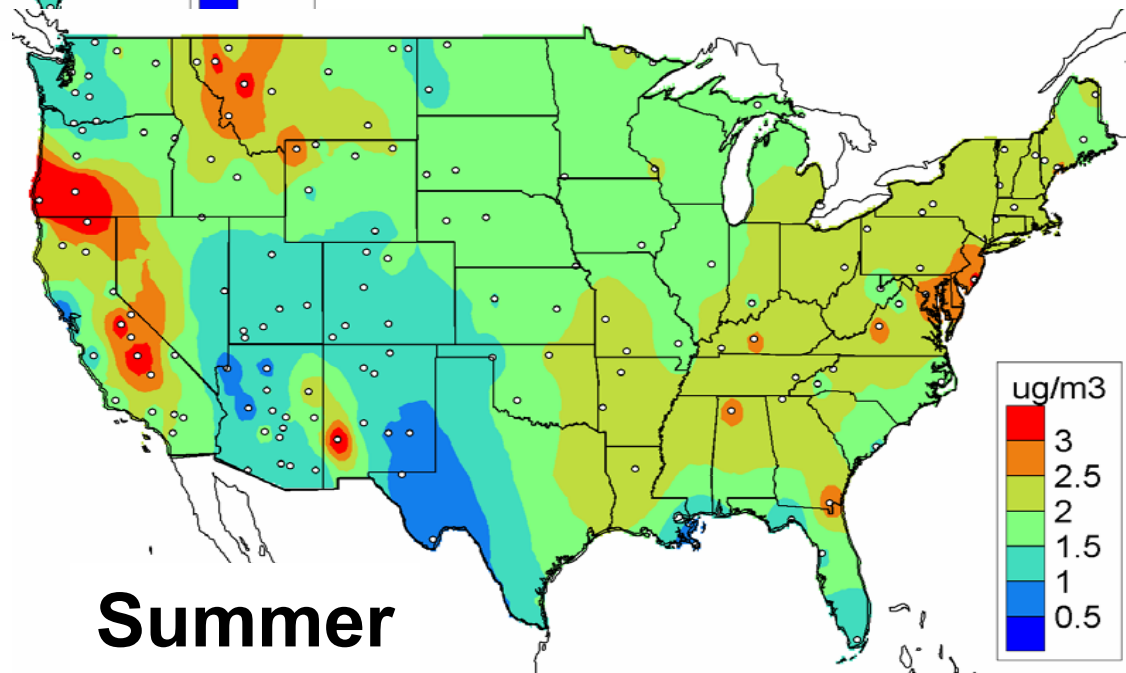
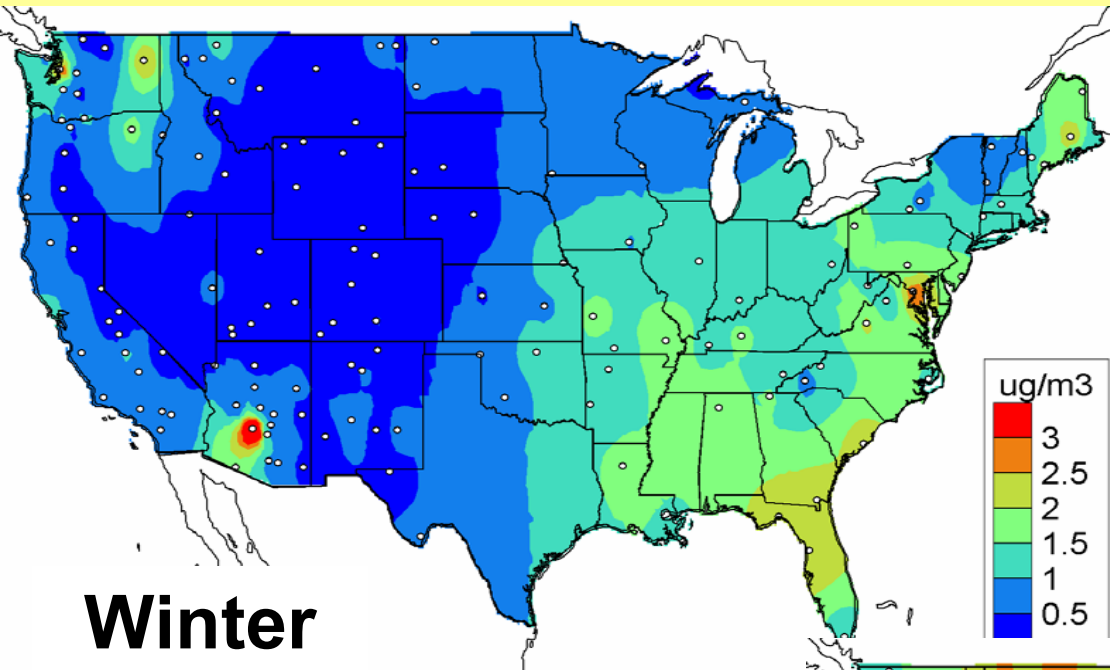
Range: 0.07 to 0.52

Mean: 0.27 ± 0.15

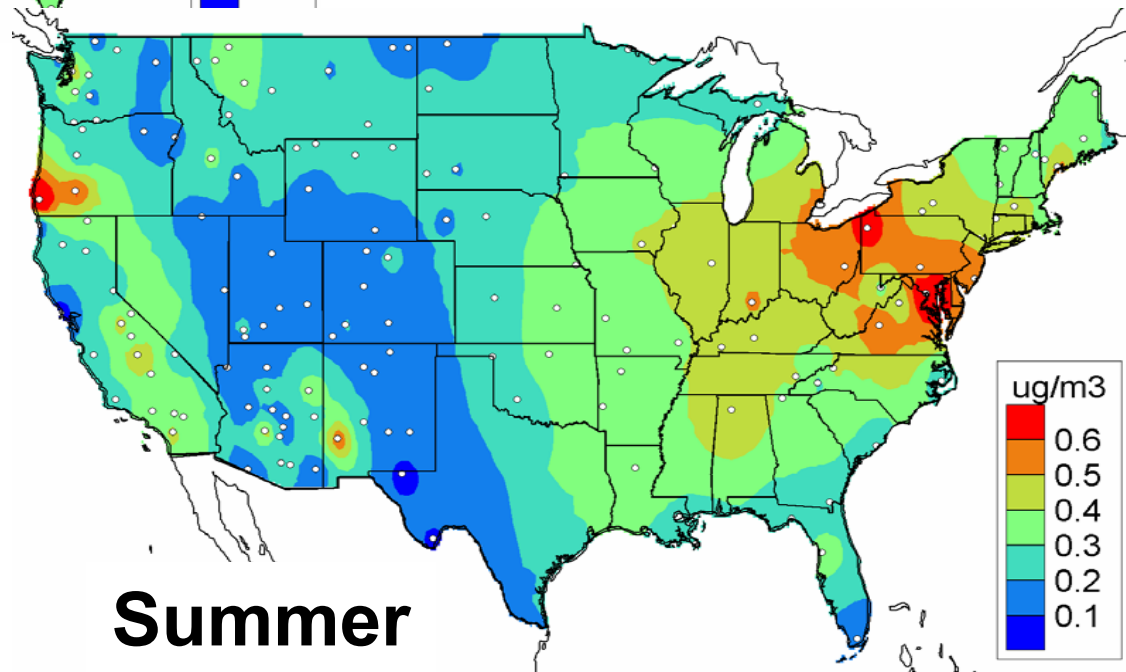
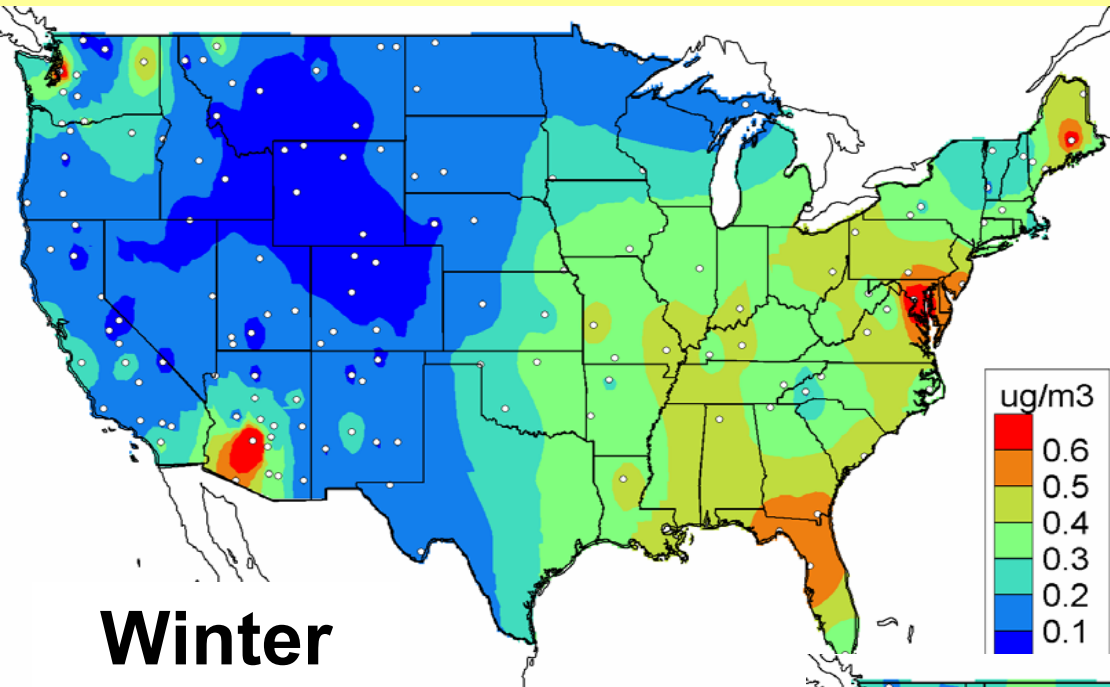
TOR: 0.432 ± 0.009

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

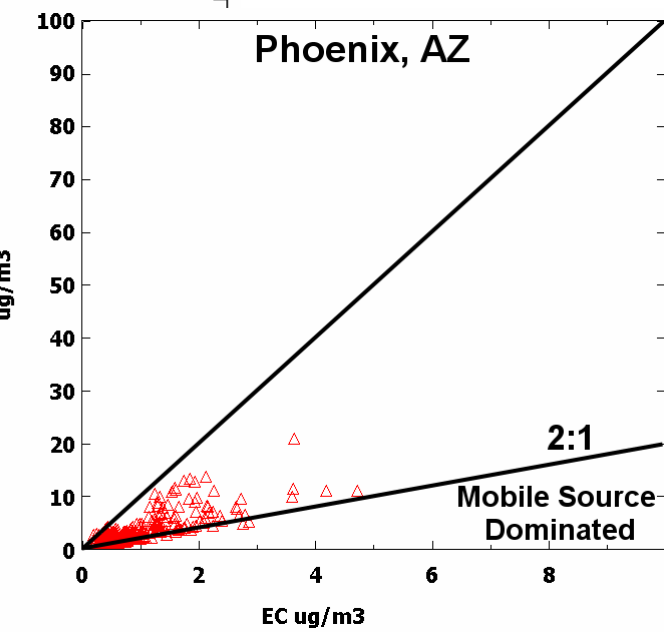
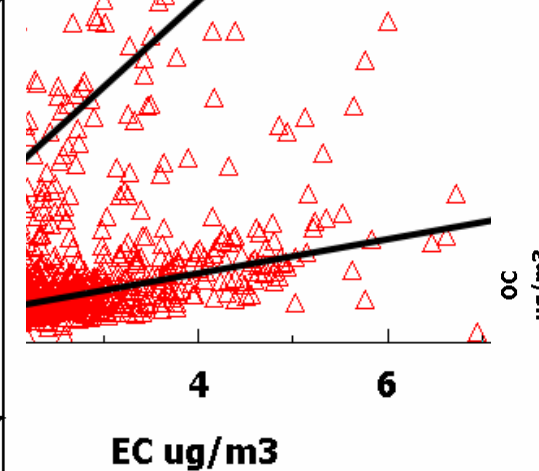
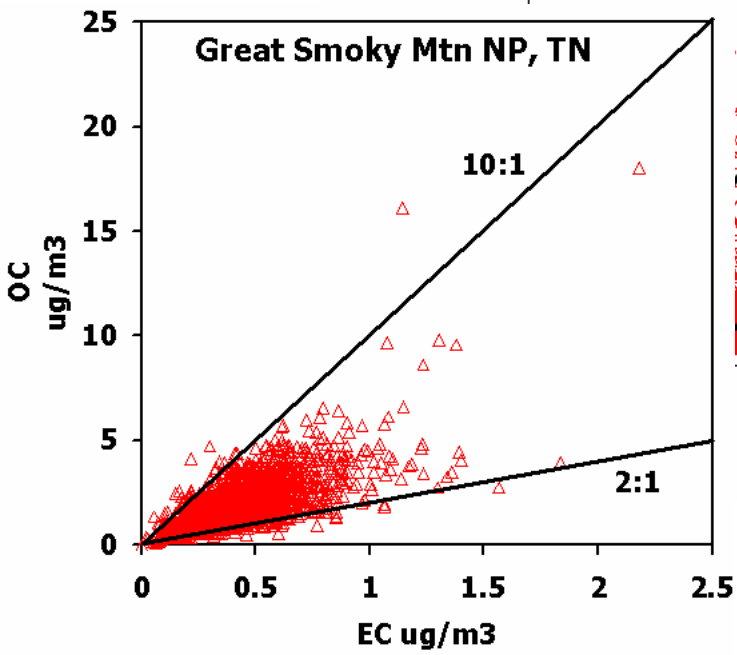
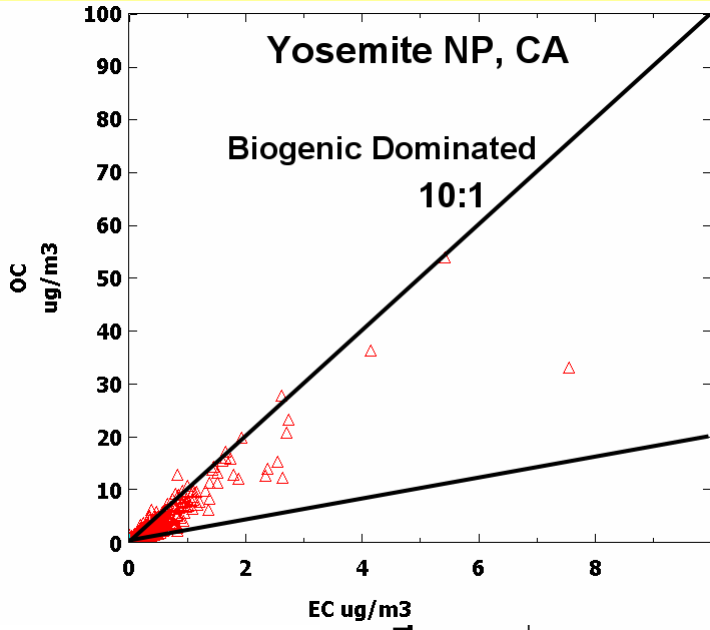
Organic Carbon – 2001-03



Elemental Carbon – 2001-03



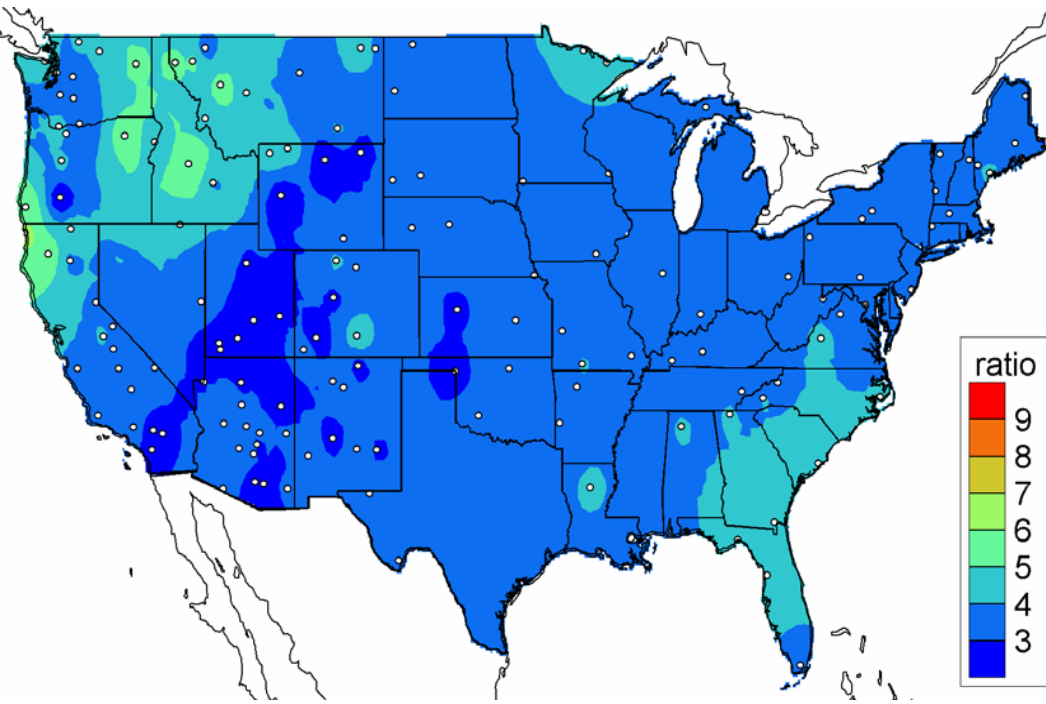
OC/EC Ratio – Indicative of Source Type



OC/EC – 2001-03

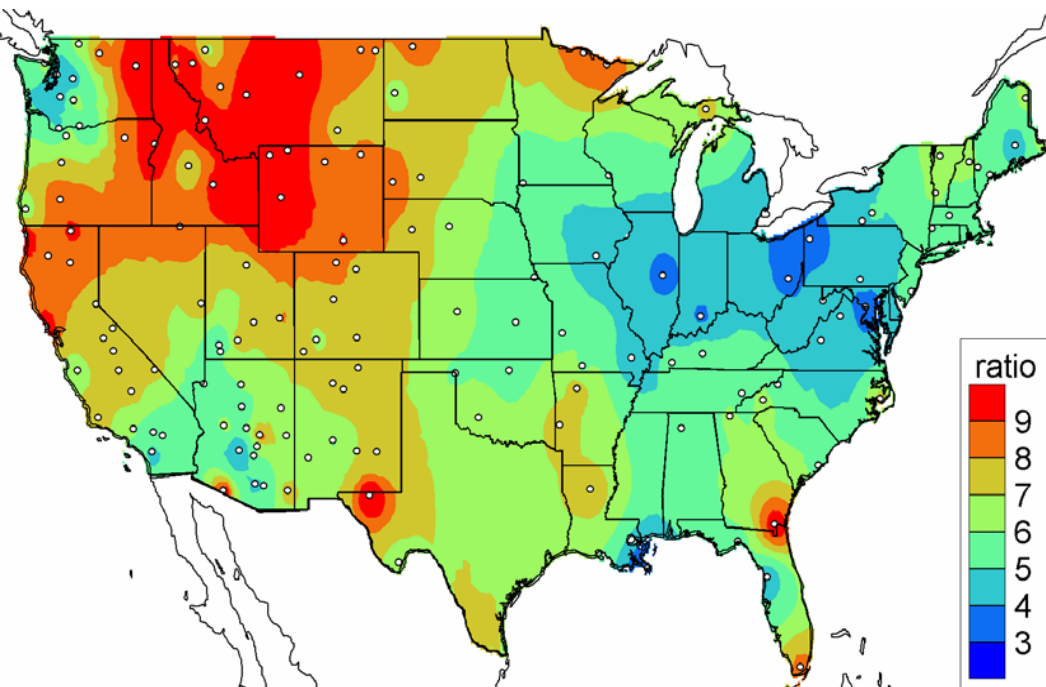
Winter

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

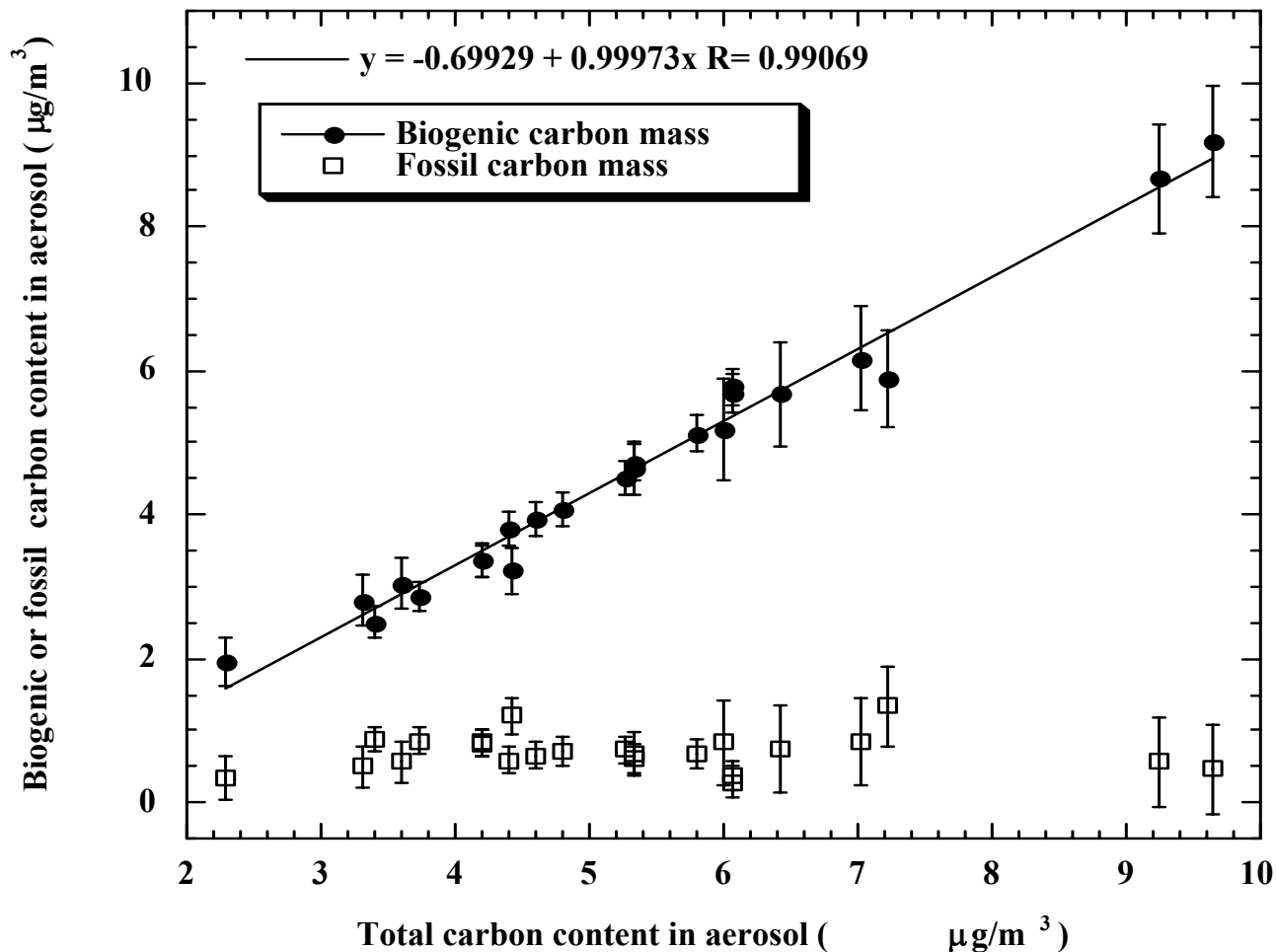


Summer

- 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

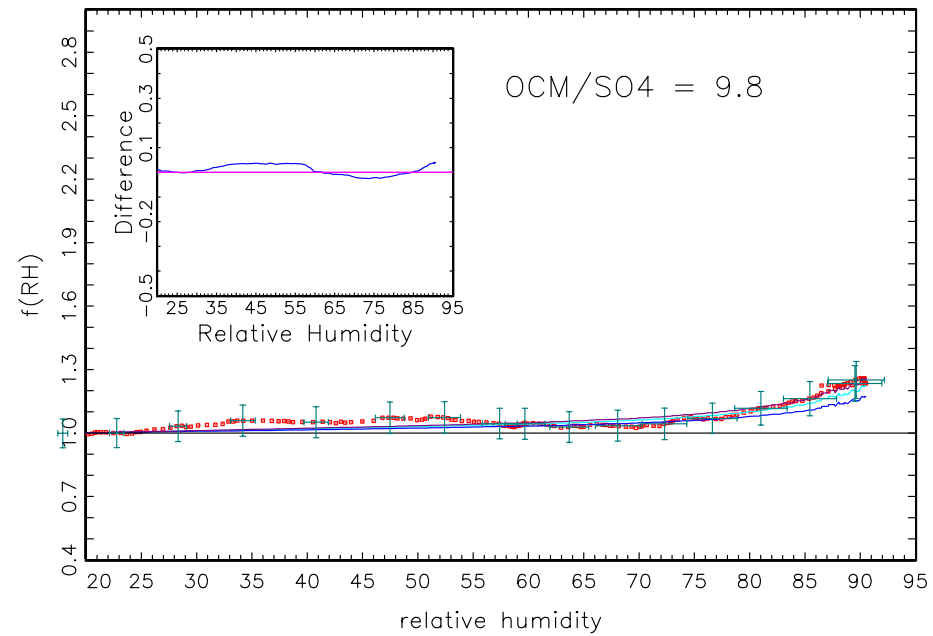
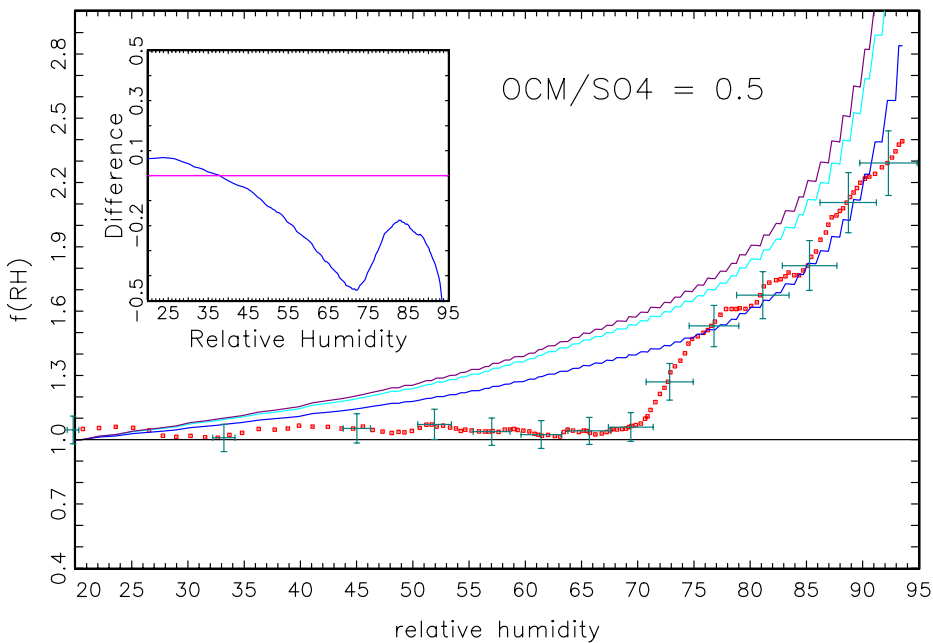
Location	Time Period	% Modern Carbon	% Old Carbon	
<u>Rural Sites</u>				
Yosemite NP, CA	Sum '02	95	5	Bench and Herckes, ES&T, 2004
Mt. Rainier NP, WA	6-8/04	81	20	Current C-12/14 Study – Bench et al.,
Proctor Maple, VT	6-8/04	94	6	Current C-12/14 Study – Bench et al.,
Brigantine NWR, NJ	6-8/04	75	25	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.,
<u>Urban Sites</u>				
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

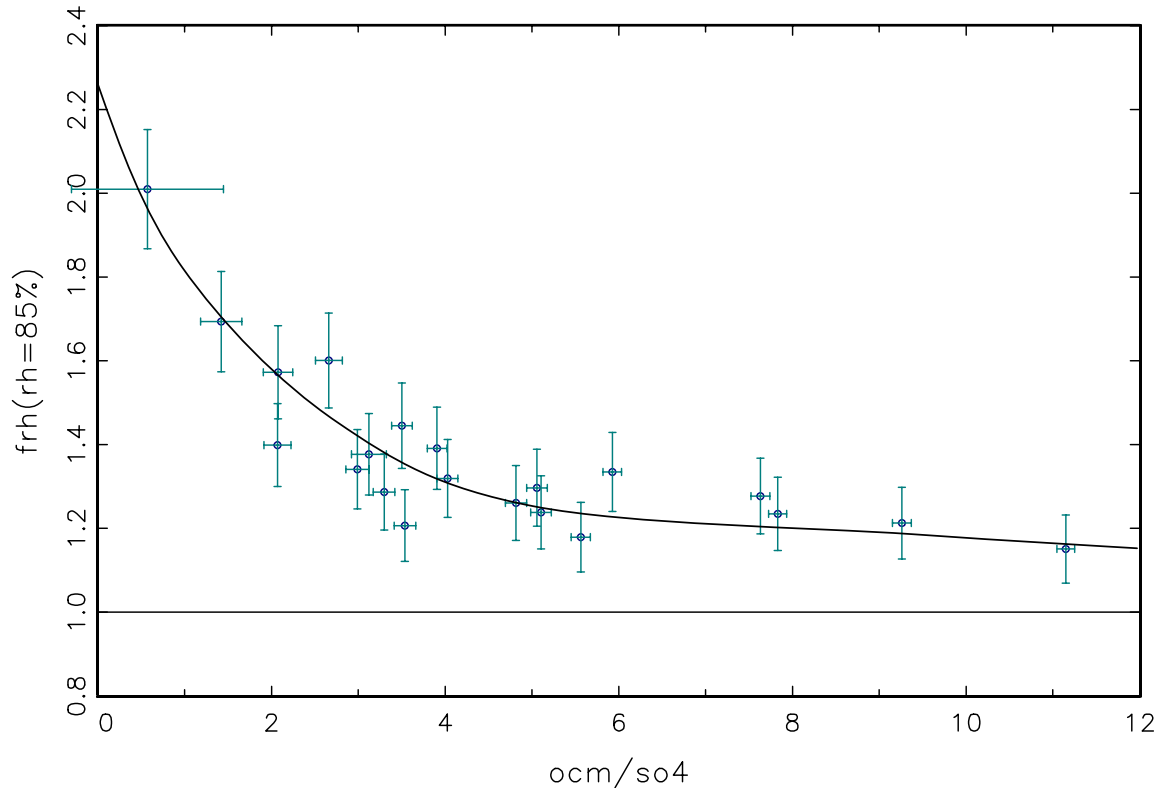
Julian day 246

Julian day 221



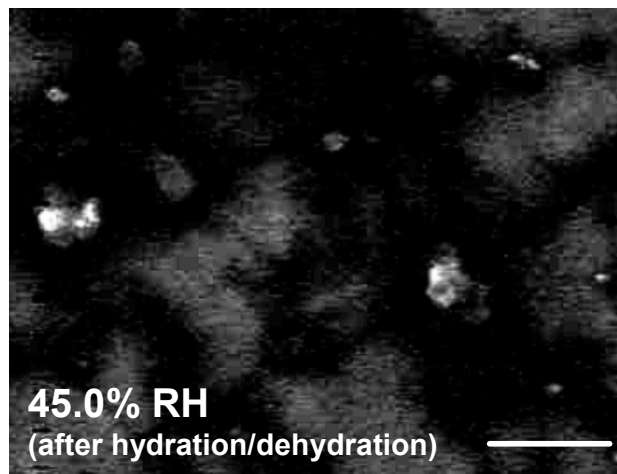
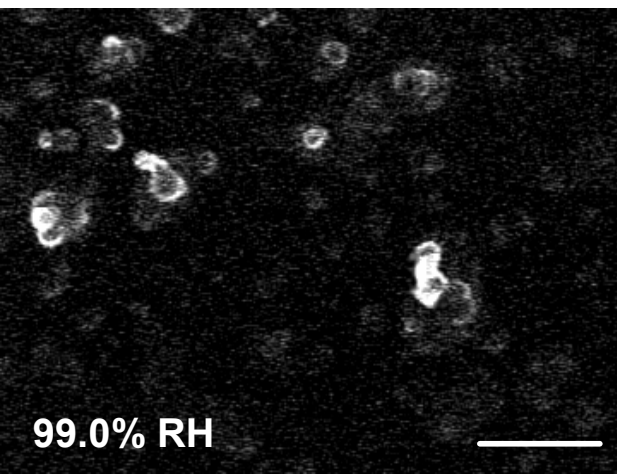
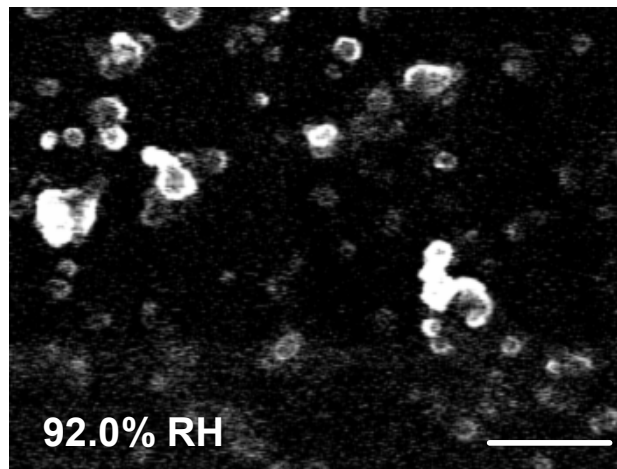
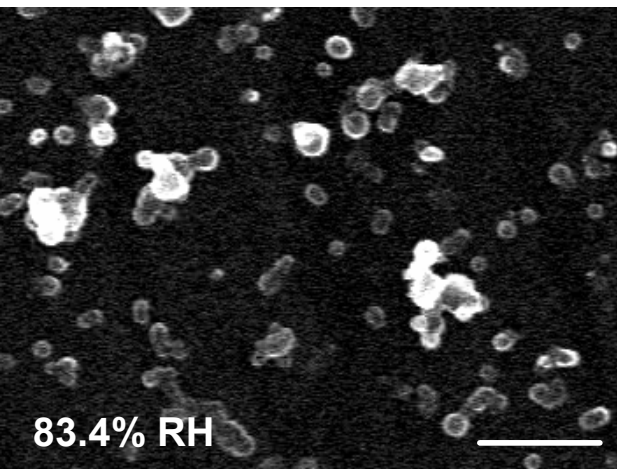
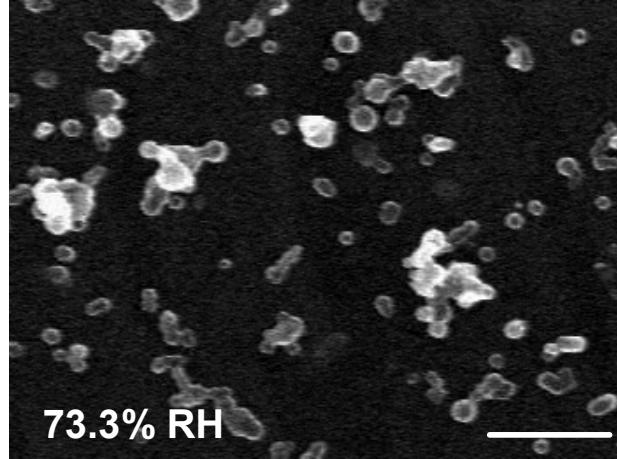
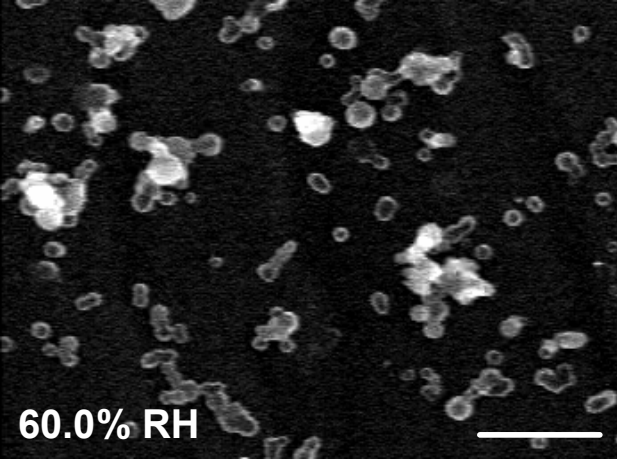
Hygroscopic Properties of Organics

$f(\text{RH}=85\%)$ plotted against the ratio of OMC to amm. sulfate.



- As OMC/SO_4 increases, aerosol hygroscopicity decreases.
- Relationship suggests an OMC $f(\text{RH}=85\%)$ 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 $T = 5\text{ }^{\circ}\text{C}$: 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>

Interagency Monitoring of Protected Visual Environments (IMPROVE)

Our national Parks and Wilderness Areas possess many stunning vistas and scenery. Unfortunately, these scenes are diminished by uniform [haze](#) causing discoloration and loss of texture and visual range. [Layered hazes](#) and [plume blight](#) also detract from the scene. Recognizing the importance of visual air quality, congress included [legislation in the 1977 Clean Air Act](#) to prevent future and remedy existing visibility impairment in [Class I areas](#). To aid the implementation of this legislation, the [IMPROVE program](#) was initiated in 1985. This program implemented an extensive long term monitoring program to establish the current visibility conditions, track changes in visibility and determine impairment in the National Parks and Wilderness Areas.

The [purpose](#) of this website is to provide access to the IMPROVE educational material on the science of visibility and regulatory [Overview](#) section which summarizes the IMPROVE network a

Diminishing View
Diminishing View
Diminishing View
Diminishing View

West Elk Mountains, Colorado



Best
Dec
V.R.

IMPROVE and Visibility



IMPROVE Resources



Bulletins

VIEWS

Visibility Information Exchange Web System

Home What's New Tour Site Map Contact Us Your Account

Data

- All Data
- Metadata
- Query Wizard
- ASCII Data Files

Annual Summary

- Spatial Patterns
- Composition
- Trends
- Back Trajectories
- Summary Data
- Archived Graphics

Catalogs

- Air Quality Catalog
- Weather Catalog
- Emissions Catalog

Imagery

- Visibility Photos
- Class I Webcams
- Forest Service

Guest List

For best results, please use:

Internet Explorer 5 (or higher)
Netscape 6 (or higher)

Dedicated to reducing [Regional Haze](#) in [Class 1 Areas](#) through the exchange of [Data, Tools, and Ideas](#)



The Visibility Information Exchange Web System is an online exchange of visibility data, research, and ideas designed to support the Regional Haze Rule enacted by the U.S. Environmental Protection Agency (EPA) to reduce regional haze in national parks and wilderness areas. In addition to this primary goal, VIEWS supports global efforts to better understand the affects of air pollution on visibility and to improve air quality in general.



VIEWS Data

The VIEWS website provides access to a wide variety of visibility data resources, including metadata from several networks of air quality monitoring sites, an integrated aerosol database, graphical summaries of data analyses, extensive catalogs of air quality information, and many others. (Mouse-over the icons above for more info.)

QUICK VISITOR'S GUIDE

- Use the top navigation bar for general information about the website.
- Use the left navigation area to browse and search for **data**.
- Click on the photographs at the very top to find out more about selected Class I Areas.
- Learn about the Regional Planning Organizations by following the **"Partners"** links.
- Click on the VIEWS logo to to download the logo in various formats and sizes.

PARTNERS



OF INTEREST

- Visibility
- About Air Pollution
- Regional Haze Rule
- Class I Areas
- IMPROVE Program
- RPO Information
- Software Tools
- Our Staff
- Fire & Air Presentations

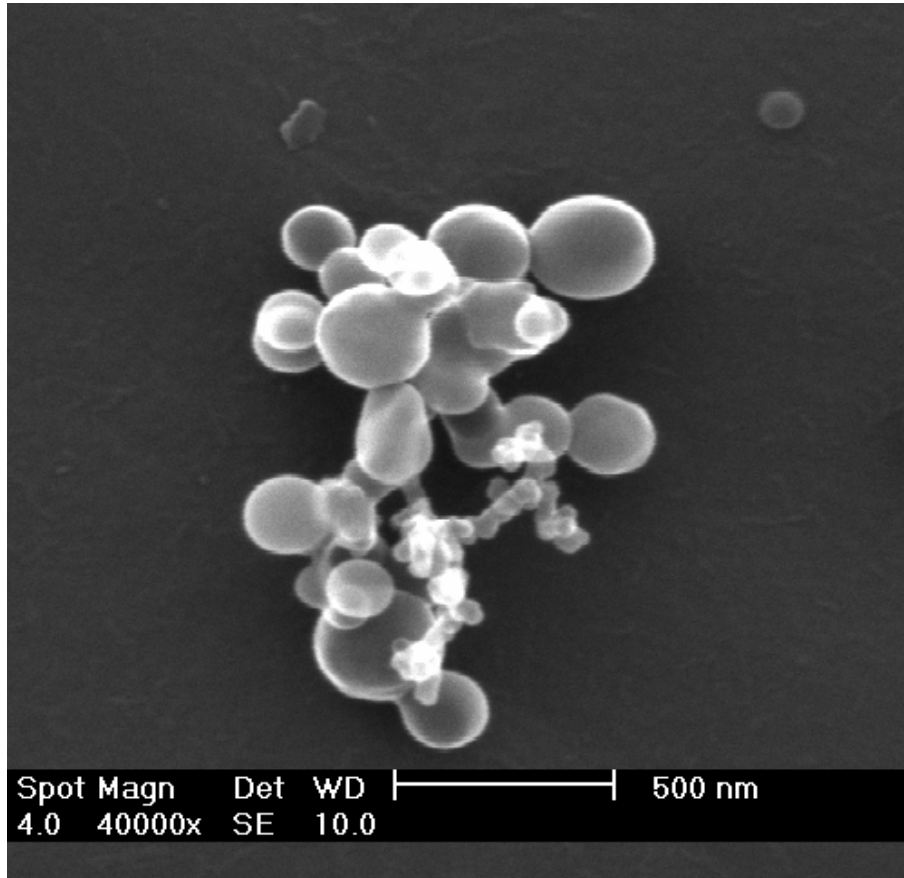
NEWSLETTER

Signup for the VIEWS

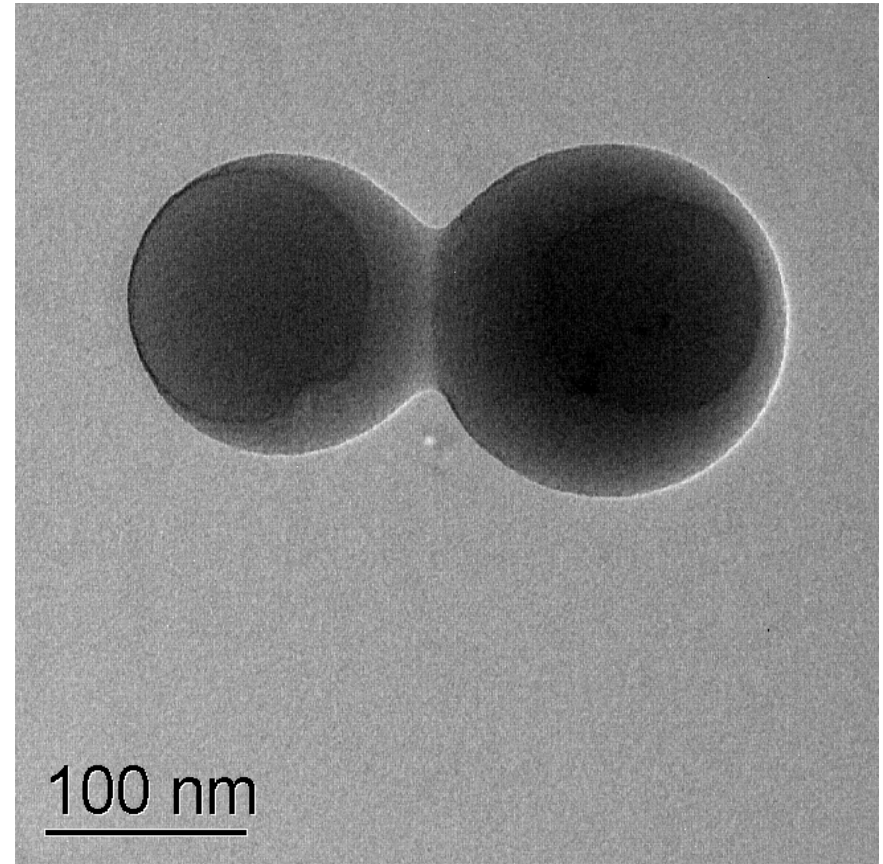
<http://vista.cira.colostate.edu/VIEWS>

END

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



Chain of soot particles stuck to an agglomerate of organic "tar balls"

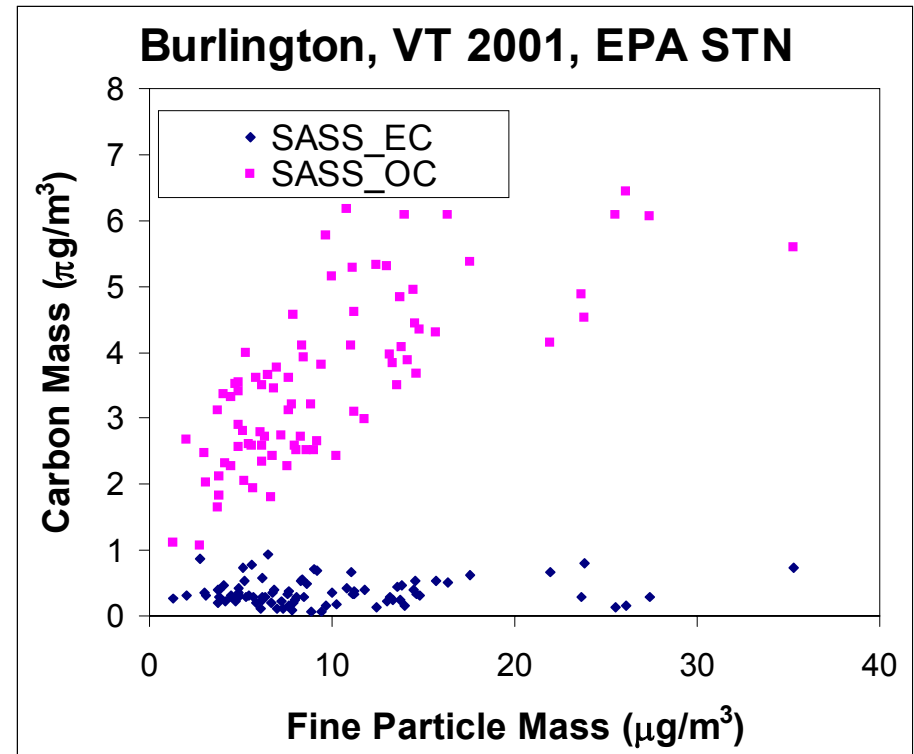
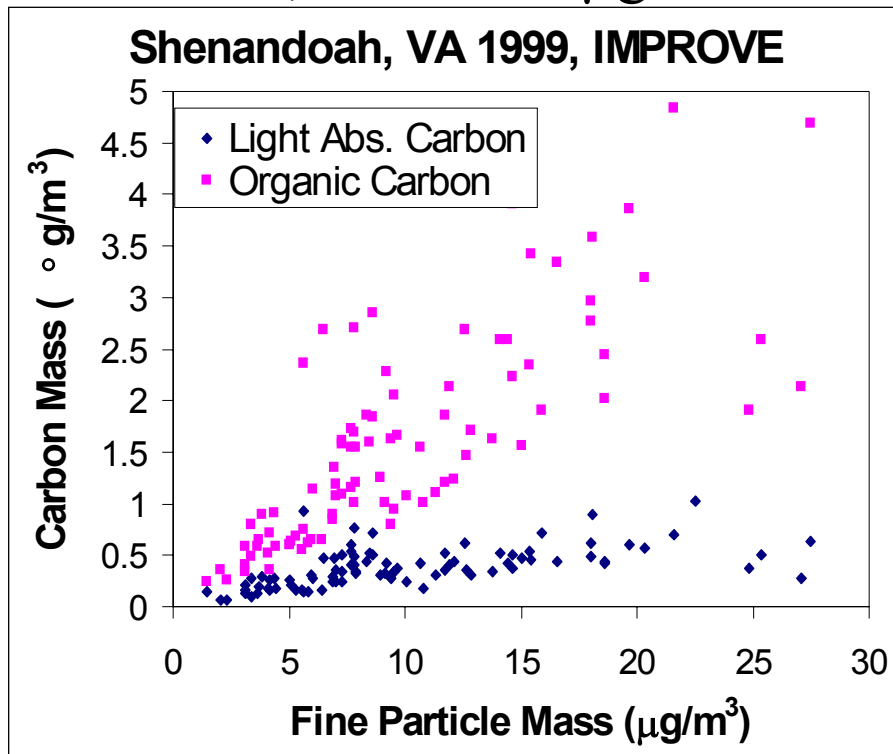


Organic particles with sulfate inclusions (Transmission Election Microscope)

IMPROVE Corrects OC and EC for a Positive Artifact

IMPROVE: Artifact Corrected
OC ~ 0.3 , EC ~ 0.02 $\mu\text{g}/\text{m}^3$

EPA STN monitoring site: No
carbon artifact correction

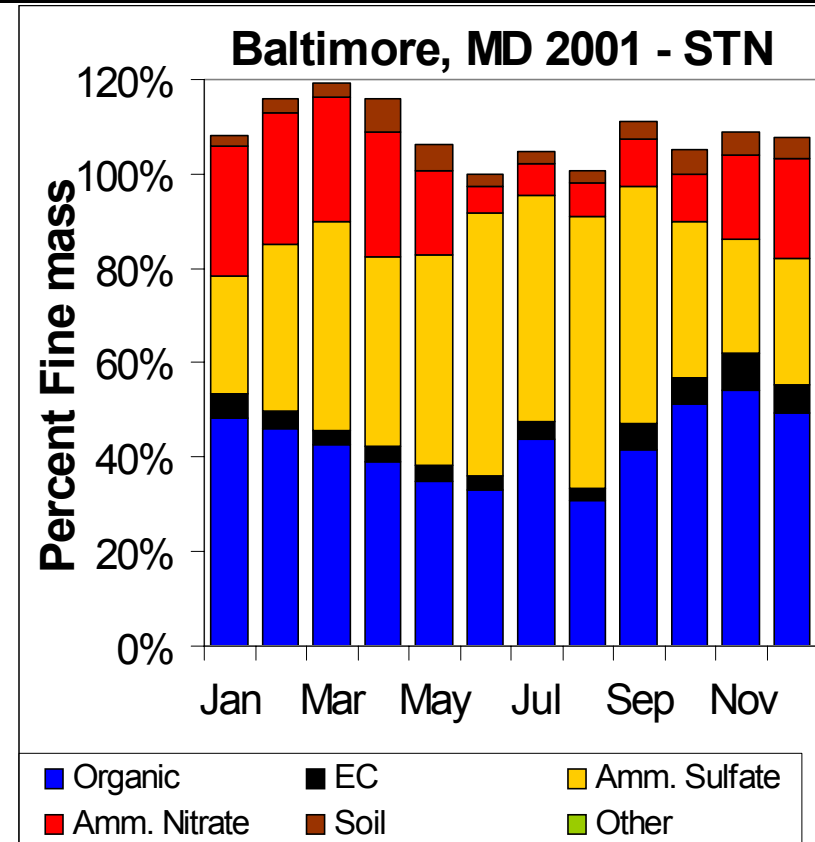
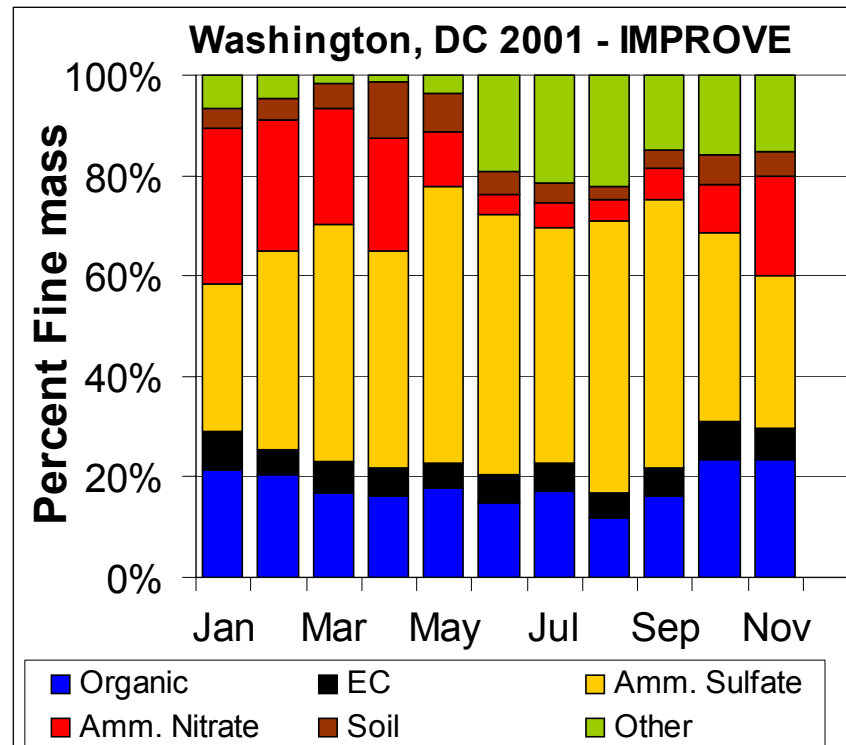


The positive artifact correction causes the organic and elemental carbon to approach zero as fine mass goes to zero

IMPROVE and STN Fine Mass Budgets

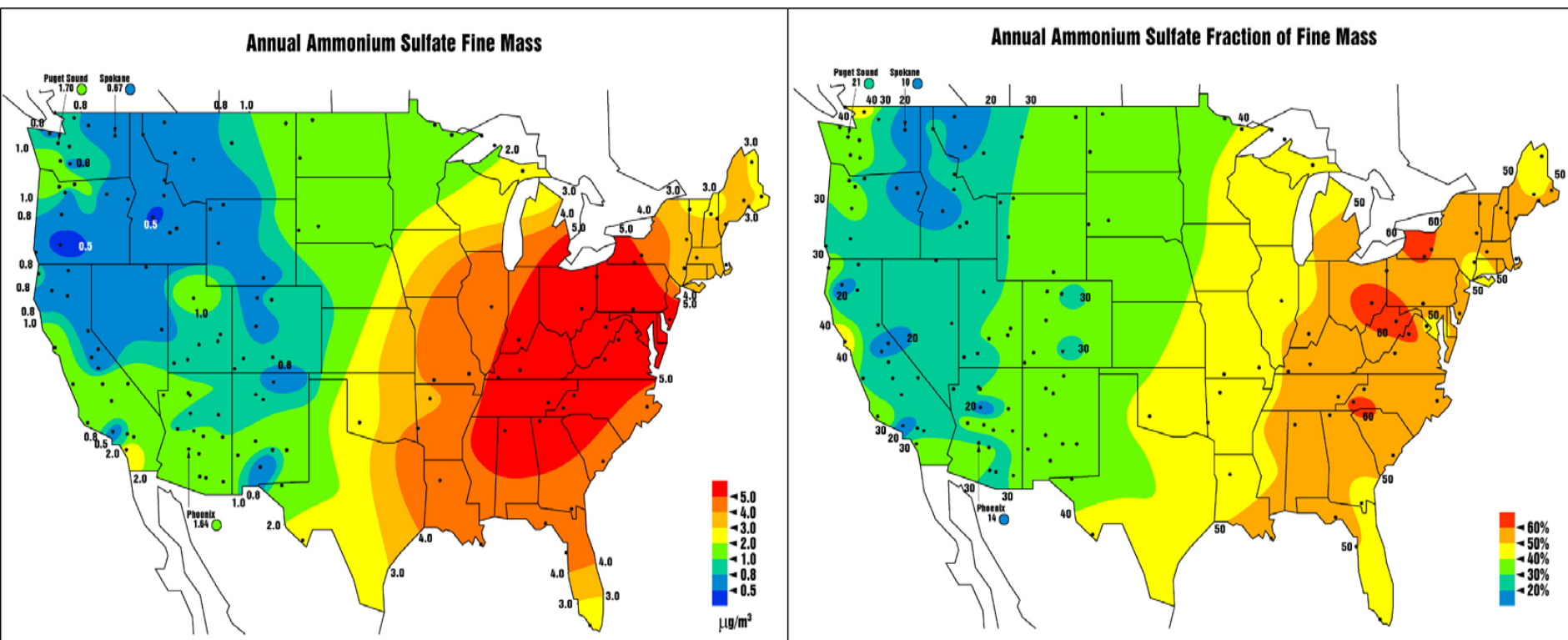
Reconstructed fine

mass.



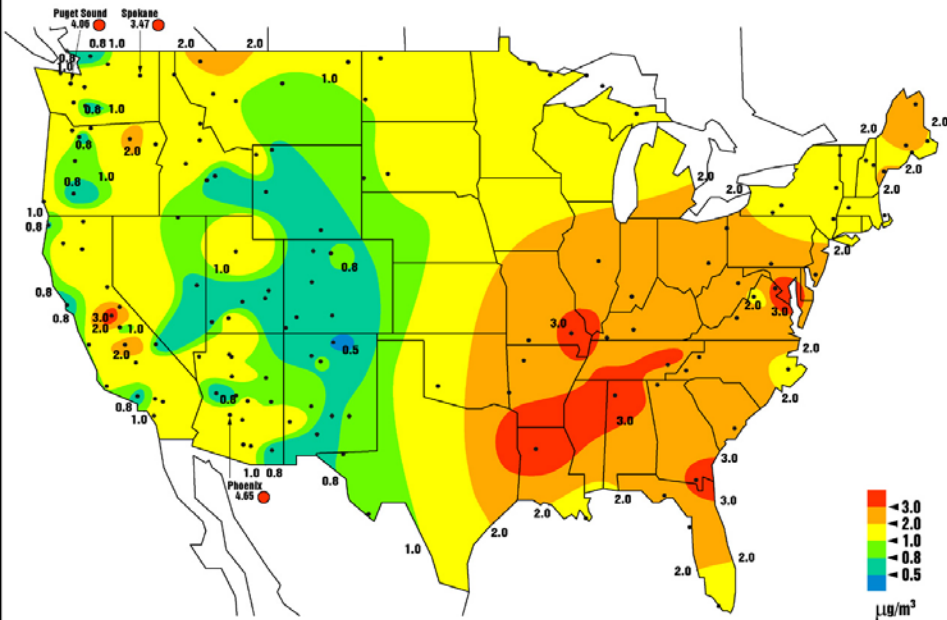
- OC is scaled by 1.4 to account for oxygen and hydrogen mass
- Organics accounts for ~20% of fine mass at Washington, ~43% at Baltimore
- EC accounts for ~6% of fine mass at Washington, ~4.4% at Baltimore

Annual Ammonium Sulfate - 2001

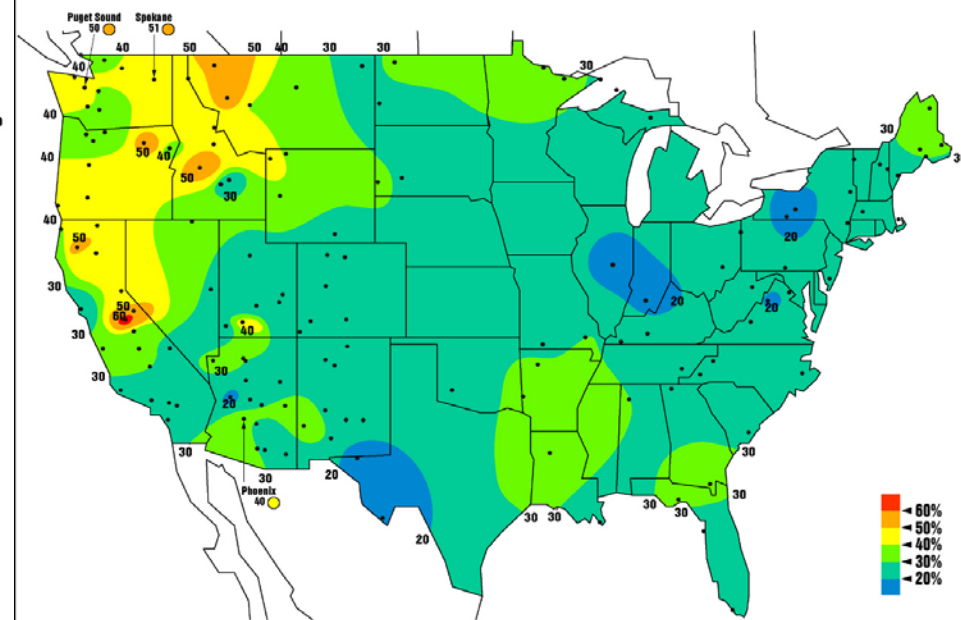


Annual Organic (1.4*OC) - 2001

Annual Organic Fine Mass

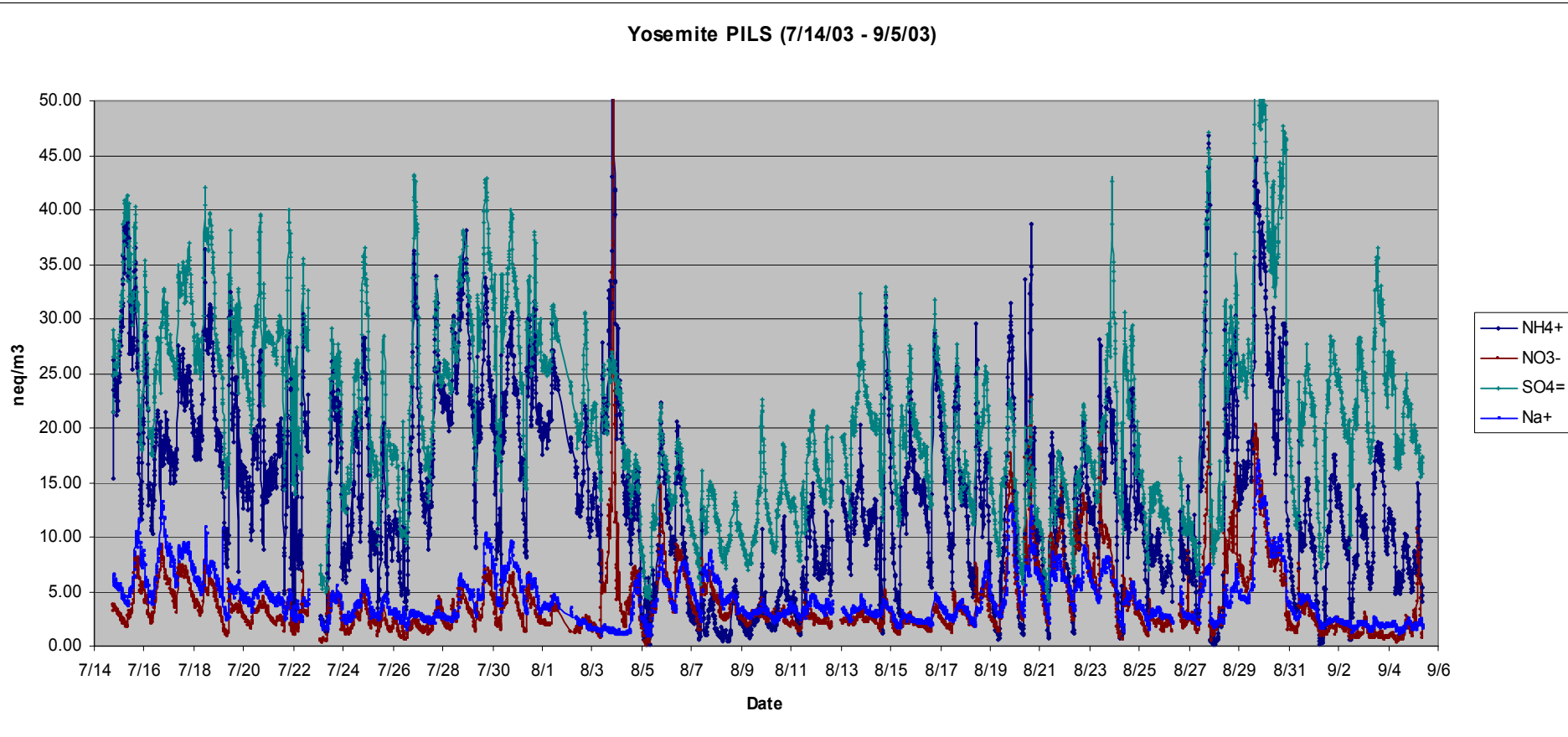


Annual Organic Fraction of Fine Mass



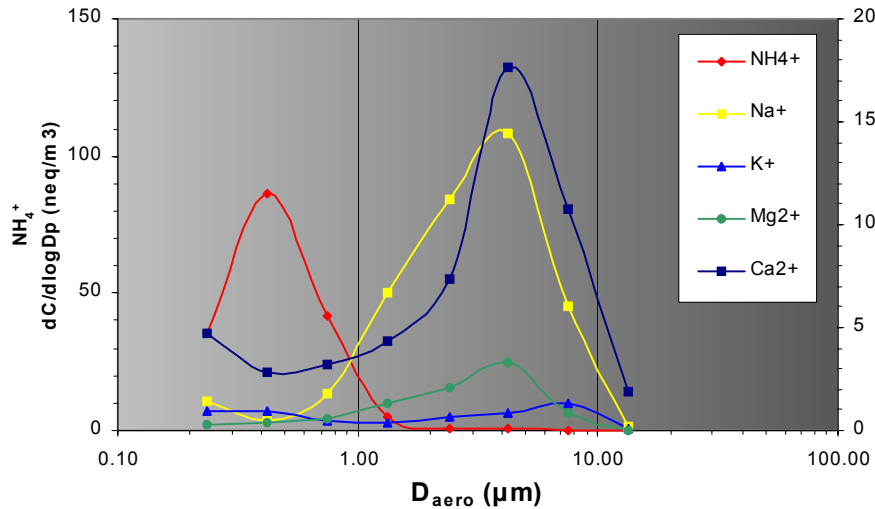
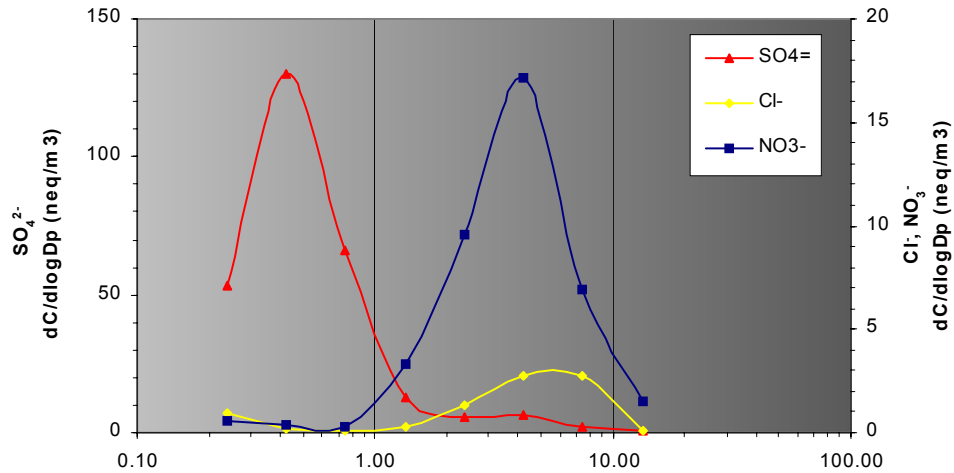
Yosemite NP Ionic Concentrations PILS

15 minute ion data from the PILS inlet

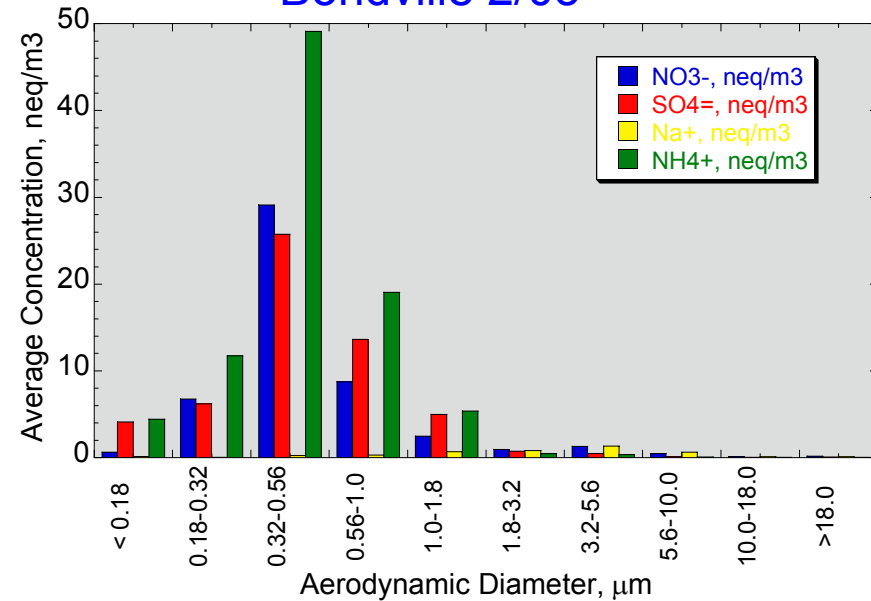


Size Distributions

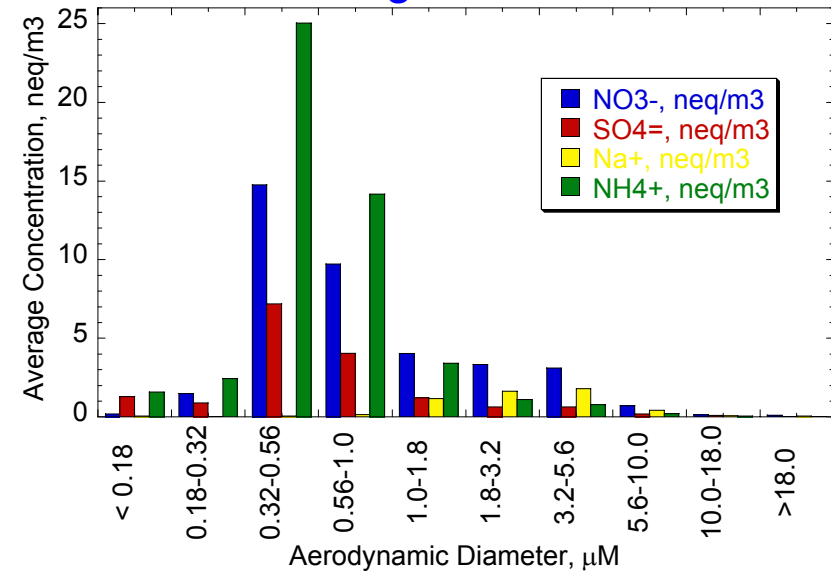
Big Bend Texas - August 1999



Bondville 2/03

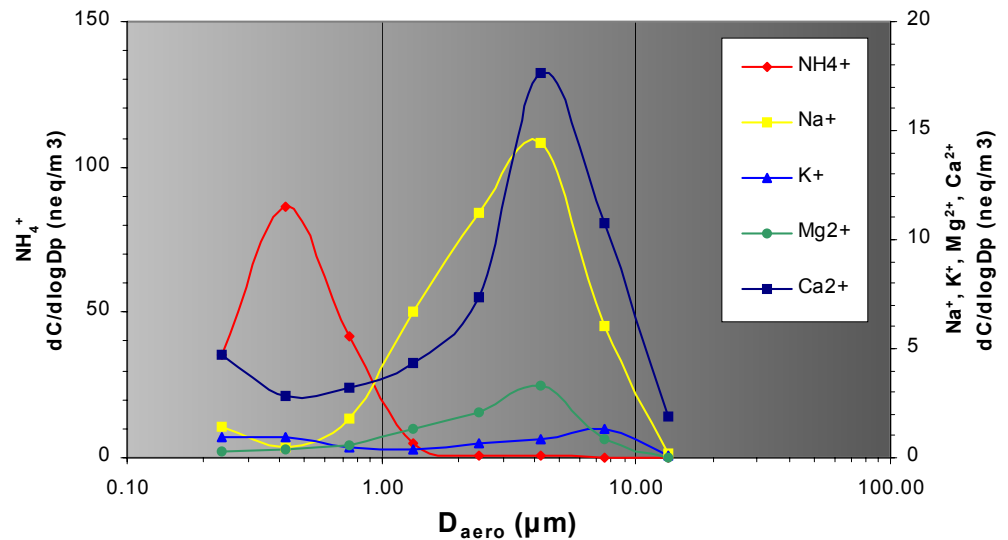
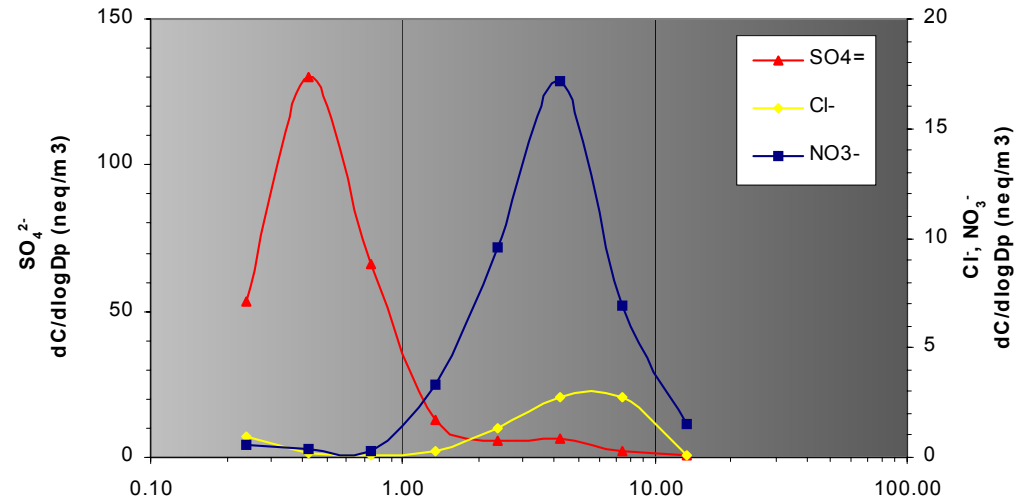


San Geronio, CA - 4/2003

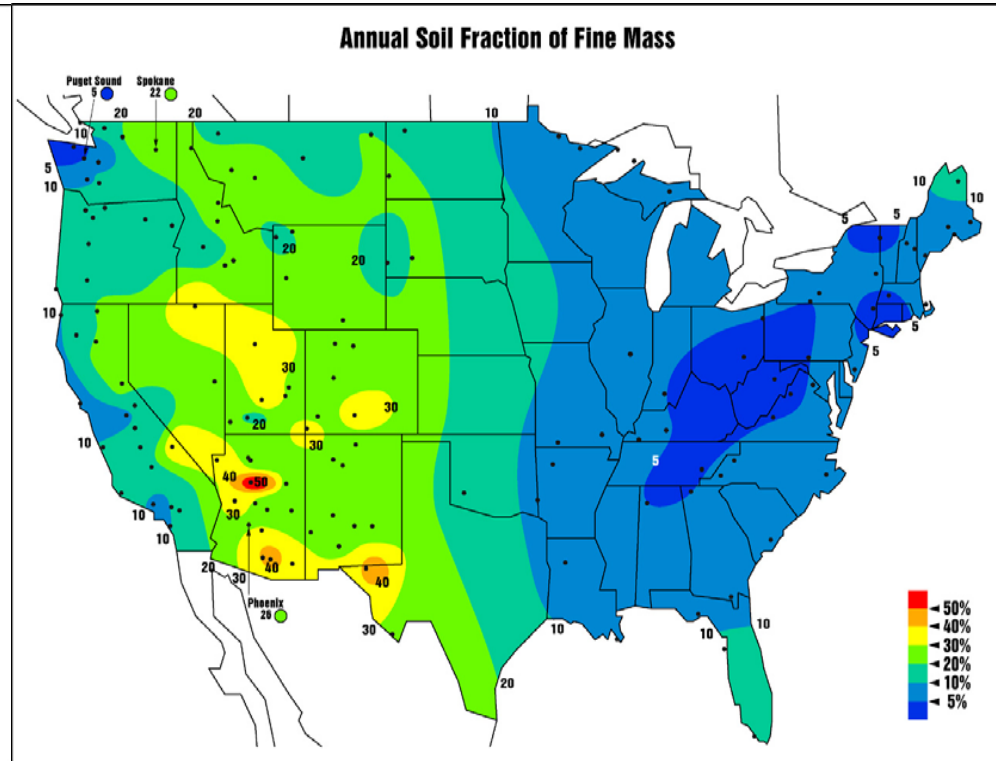
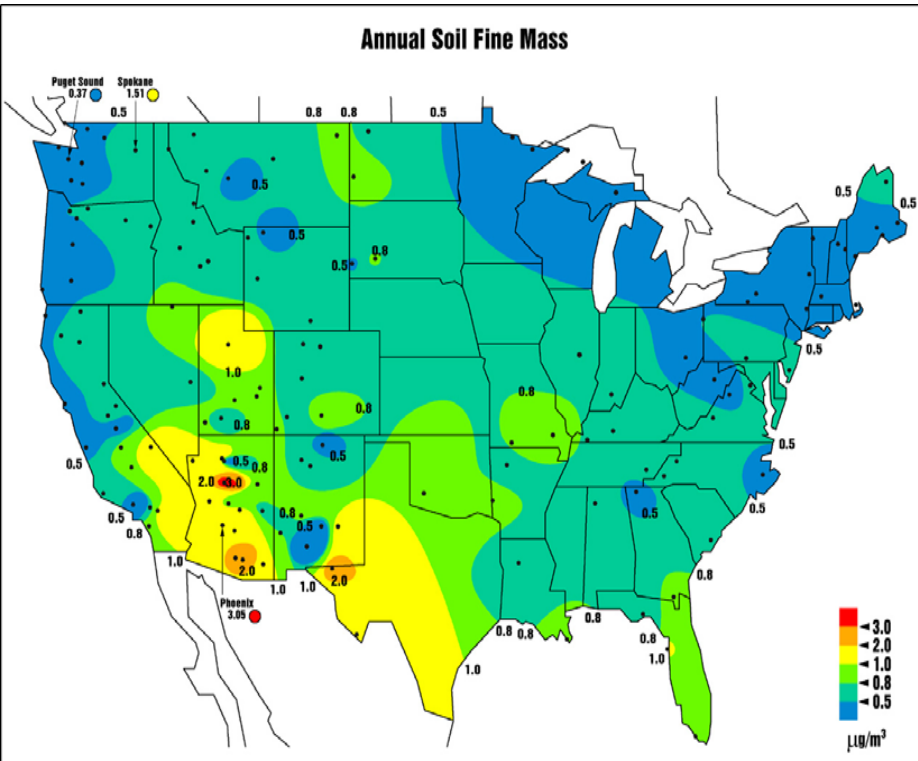


Big Bend NP Size Distributions - August 1999

- Nitrate found in coarse mode particles
 - Mode size $\sim 4\text{-}5\ \mu\text{m}$
 - Size distribution similar to Na^+
- $\text{PM}_{2.5}$ includes tail of coarse mode



Annual Fine Soil - 2001



IMPROVE Seasonal EC and OC

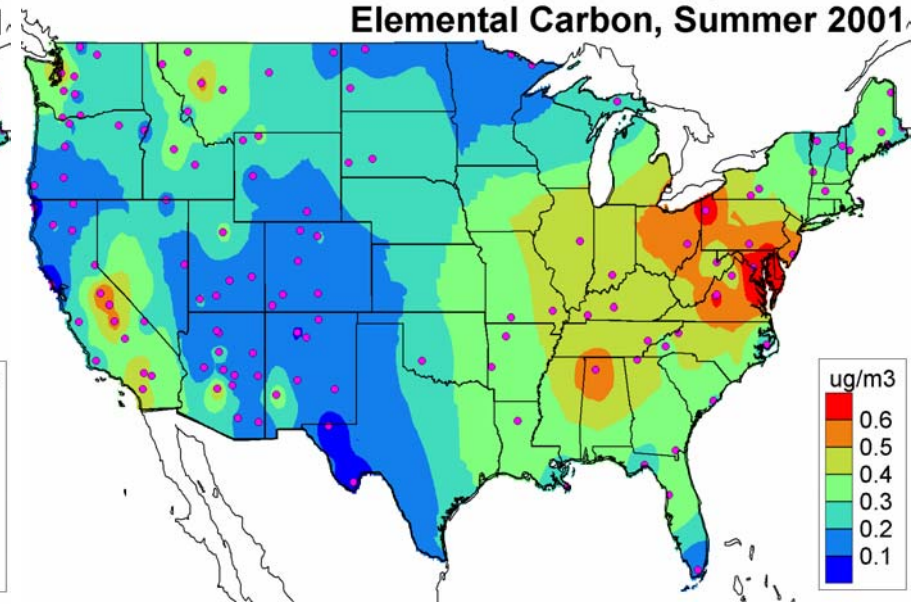
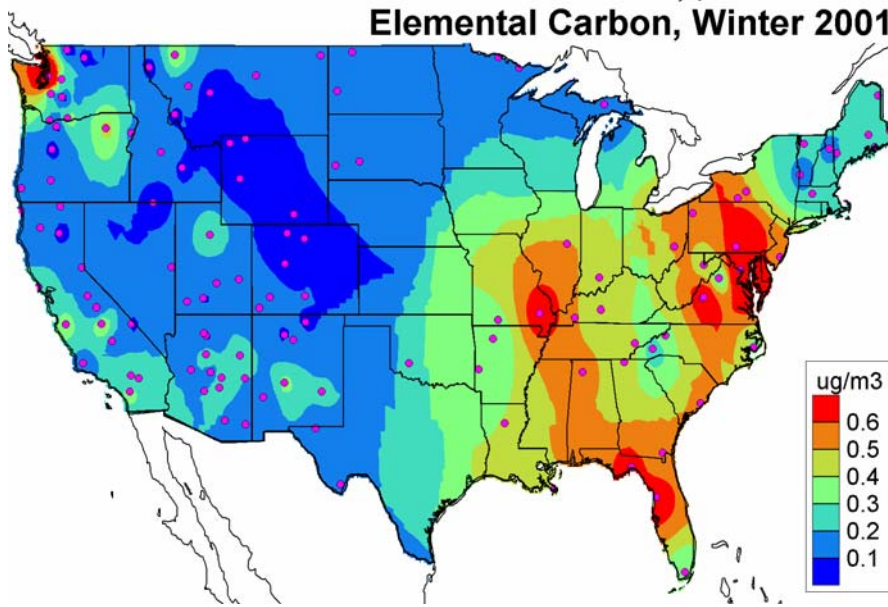
Winter 2001, Dec, Jan, Feb

Summer 2001, Jun, Jul, Aug

Elemental Carbon, Winter 2001

Elemental Carbon, Summer 2001

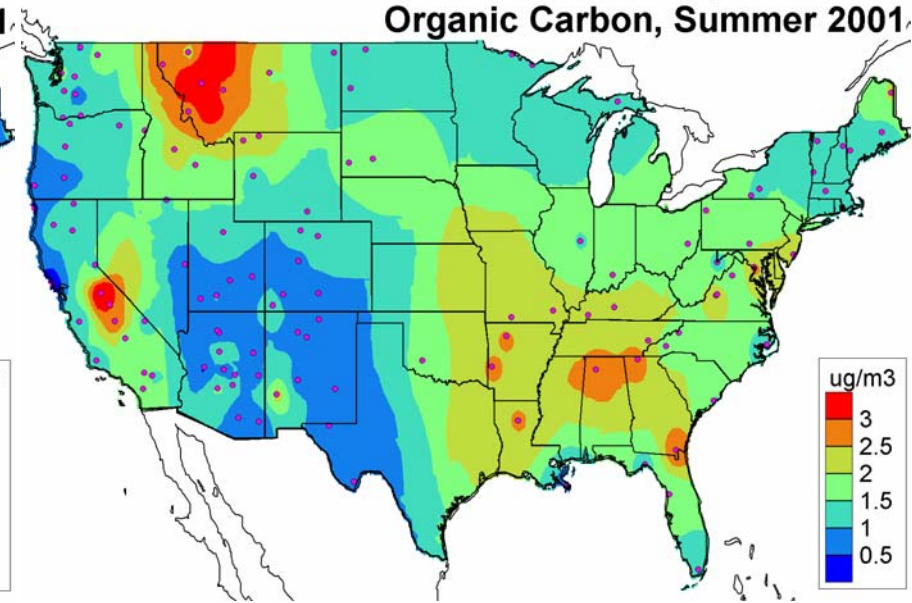
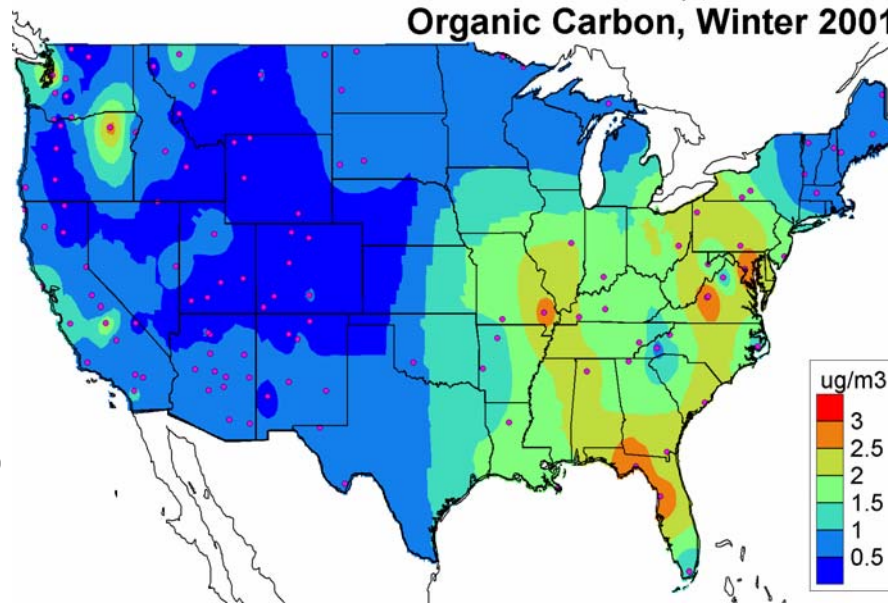
Elemental Carbon



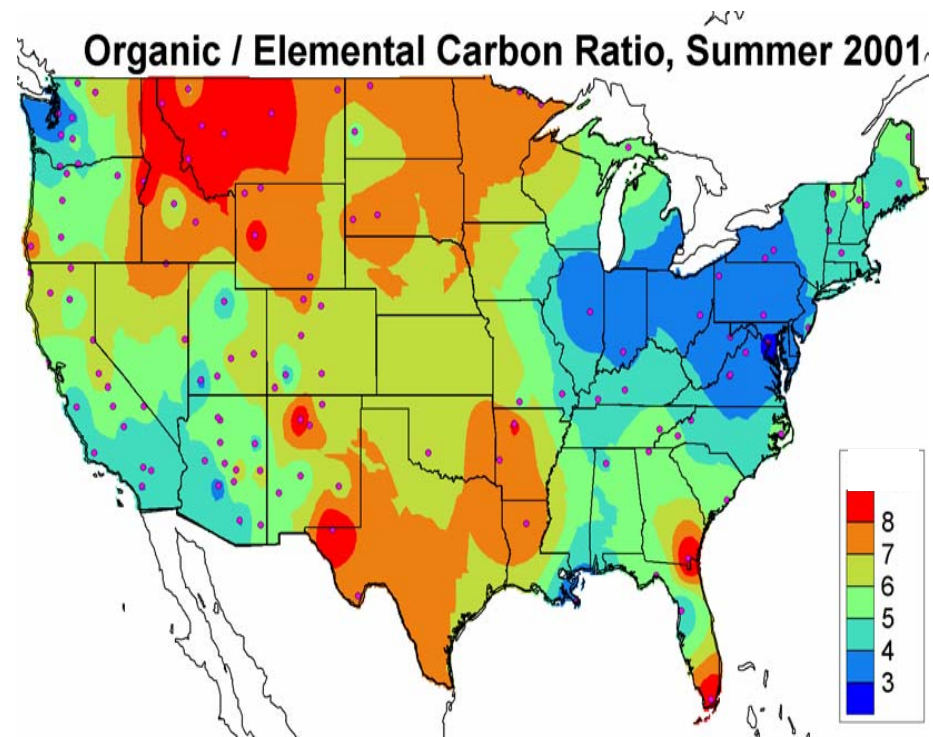
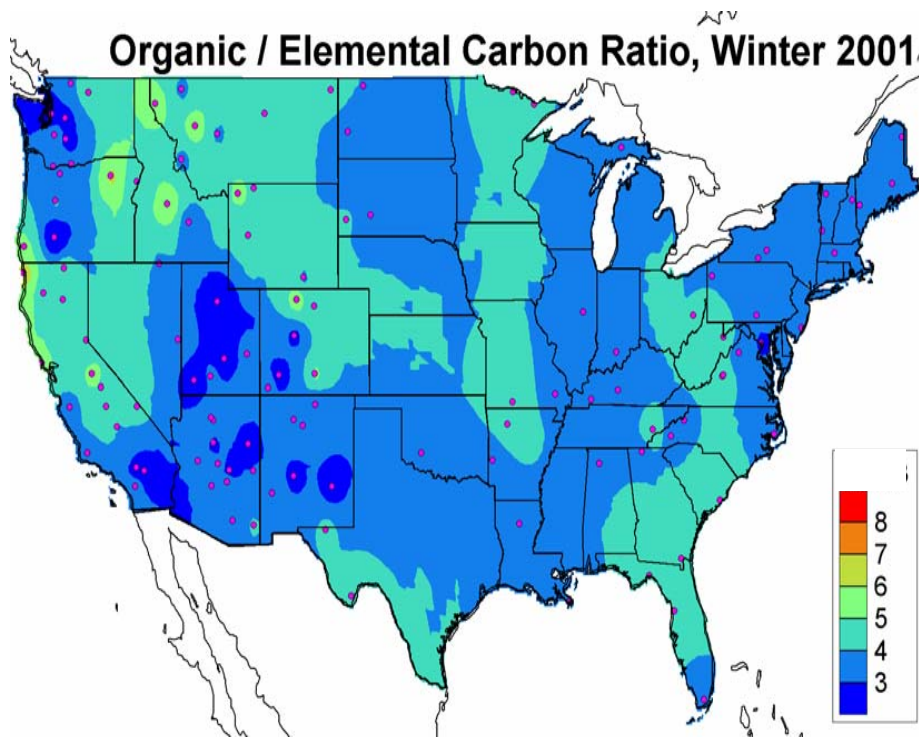
Organic Carbon, Winter 2001

Organic Carbon, Summer 2001

Organic Carbon



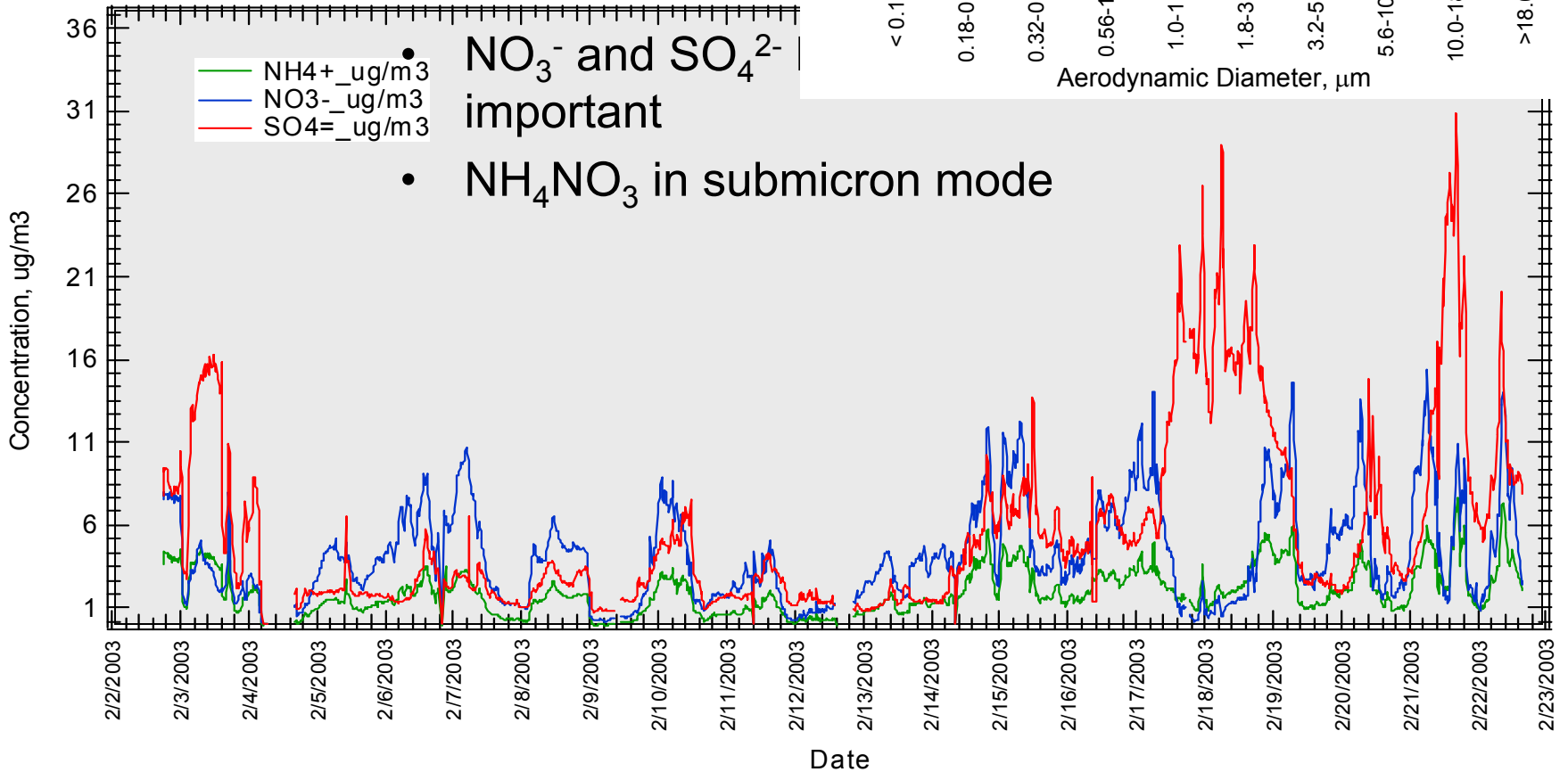
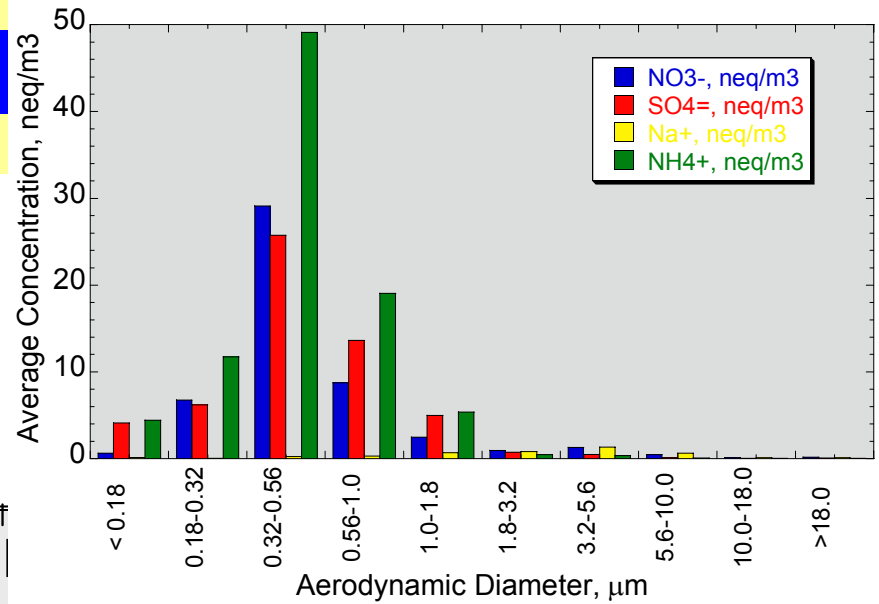
OC/EC Ratio



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

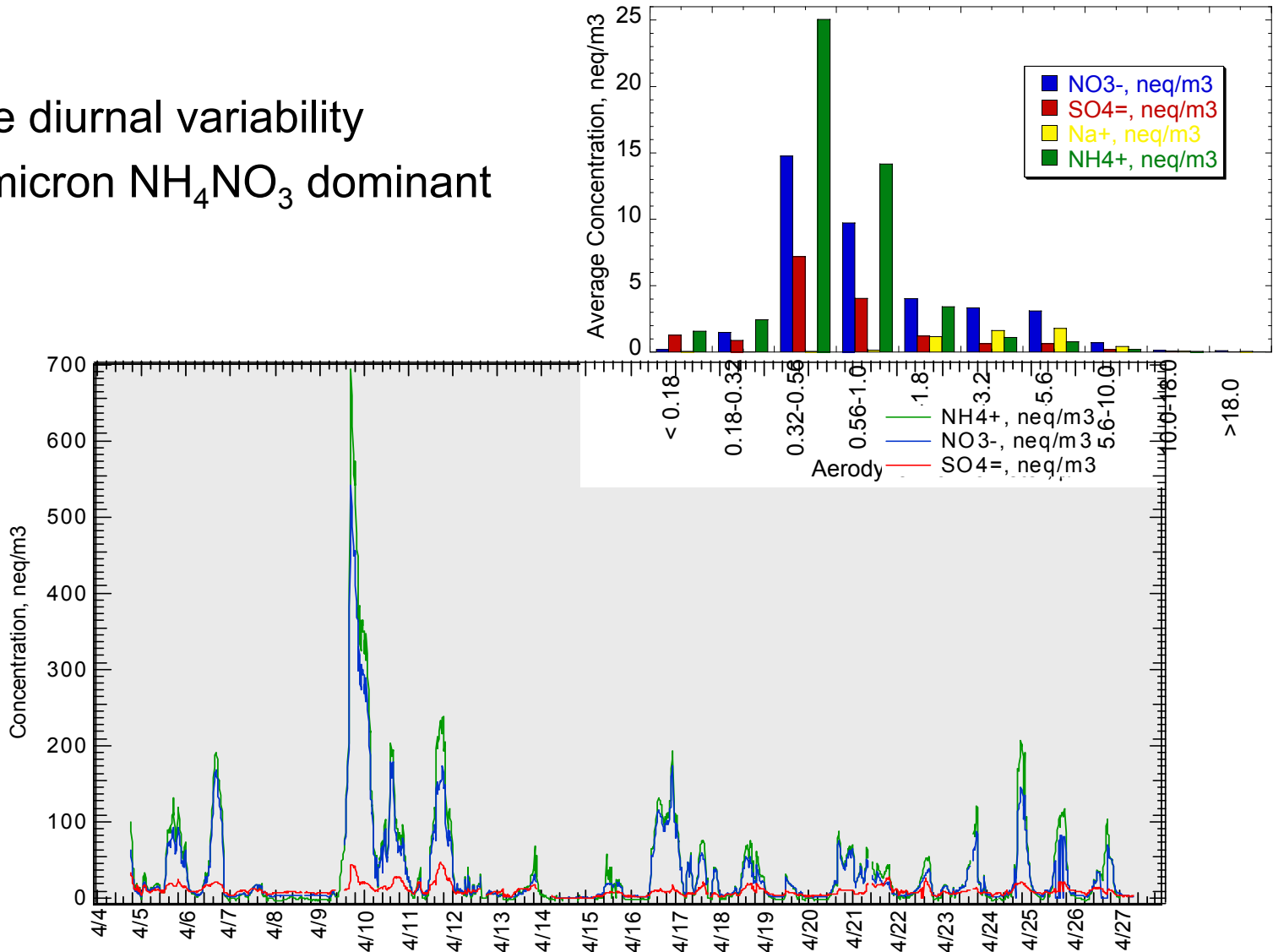
- OC/EC > 7 throughout upper West and Texas, Fires?
- OC/EC ~ 3 in Industrial Midwest, primary urban?
- OC/EC > 4-6 in southeast, increased secondary organics?

Bondvill



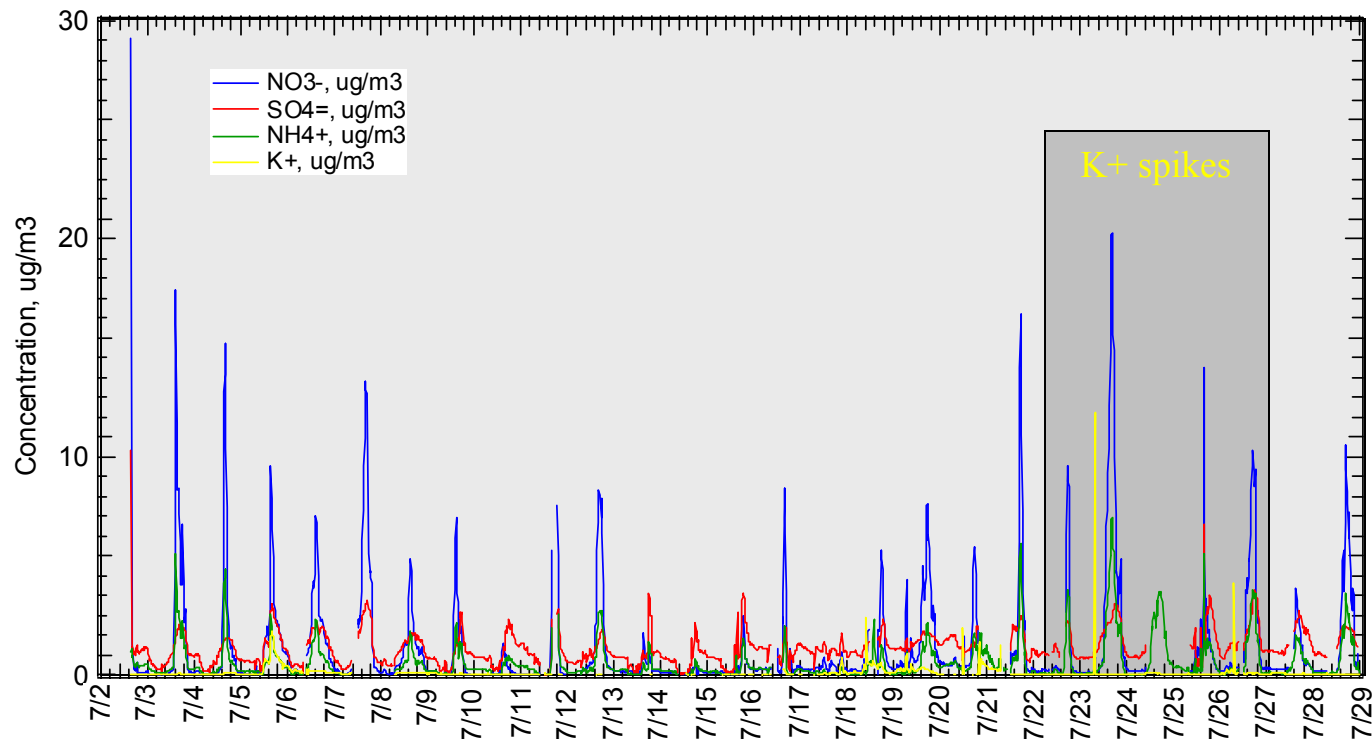
San Gorgonio 4/03

- Large diurnal variability
- Submicron NH_4NO_3 dominant



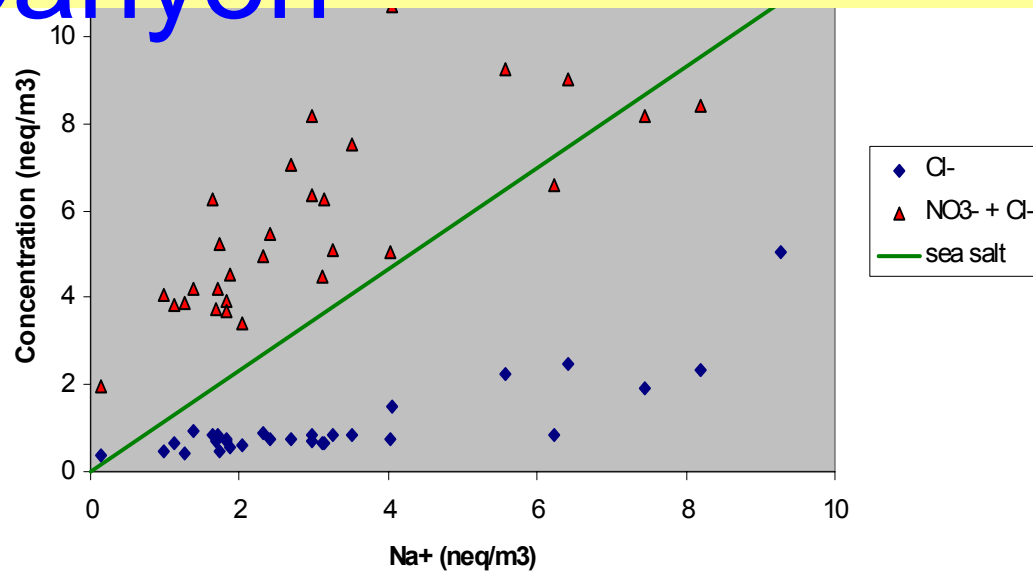
San Gorgonio 7/03

- More regular diurnal variability
- Some days sulfate-dominated

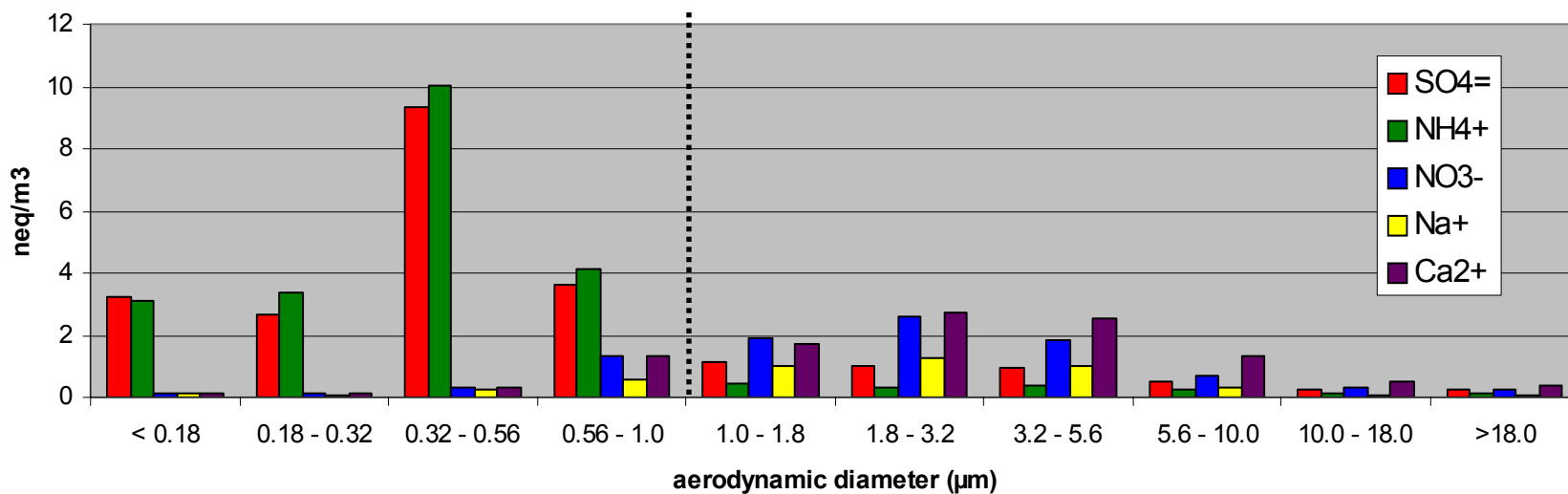


Grand Canyon

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



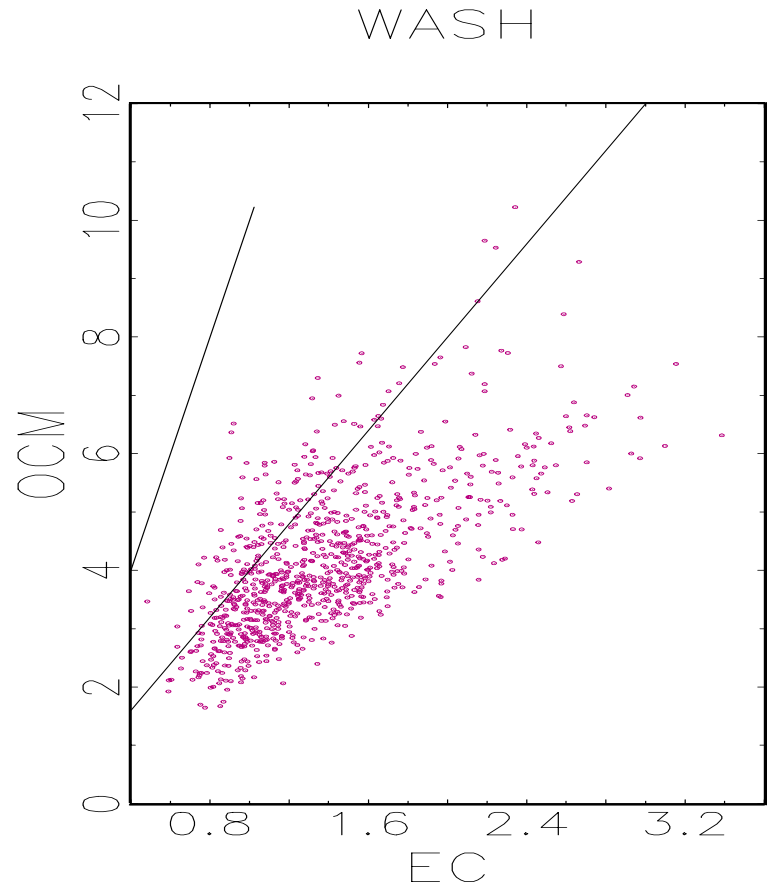
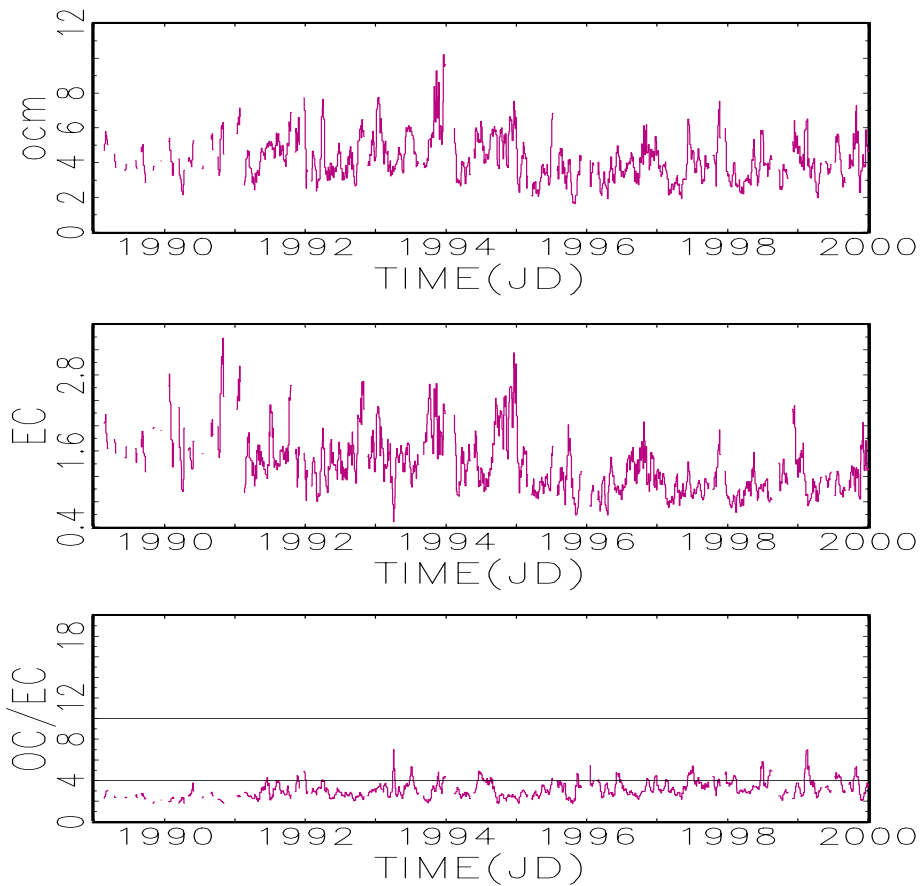
Grand Canyon MOUDI average



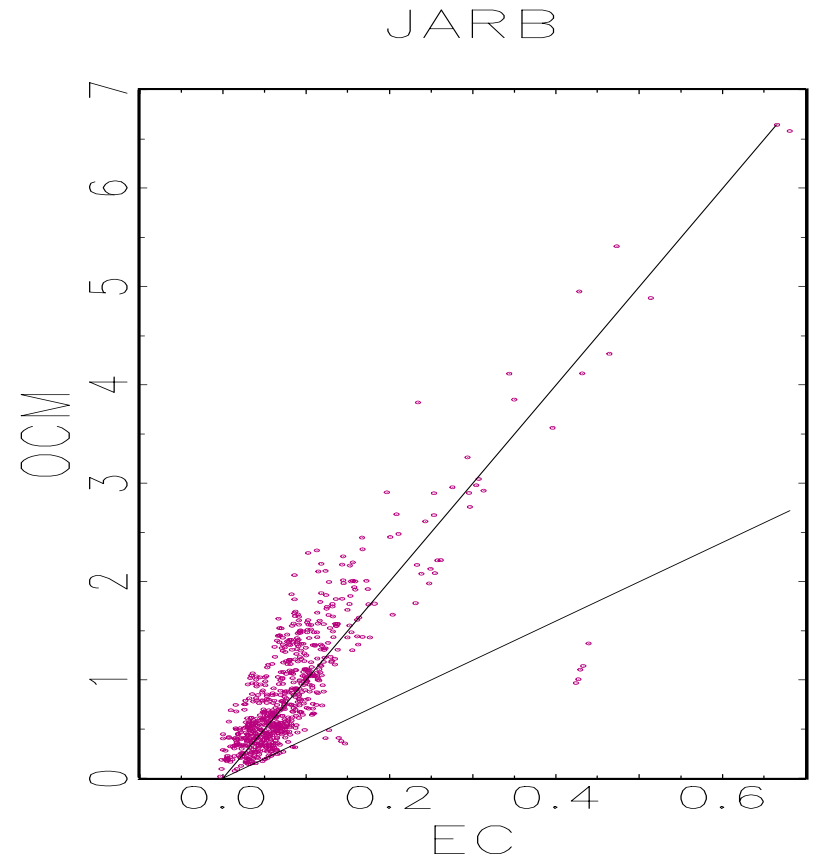
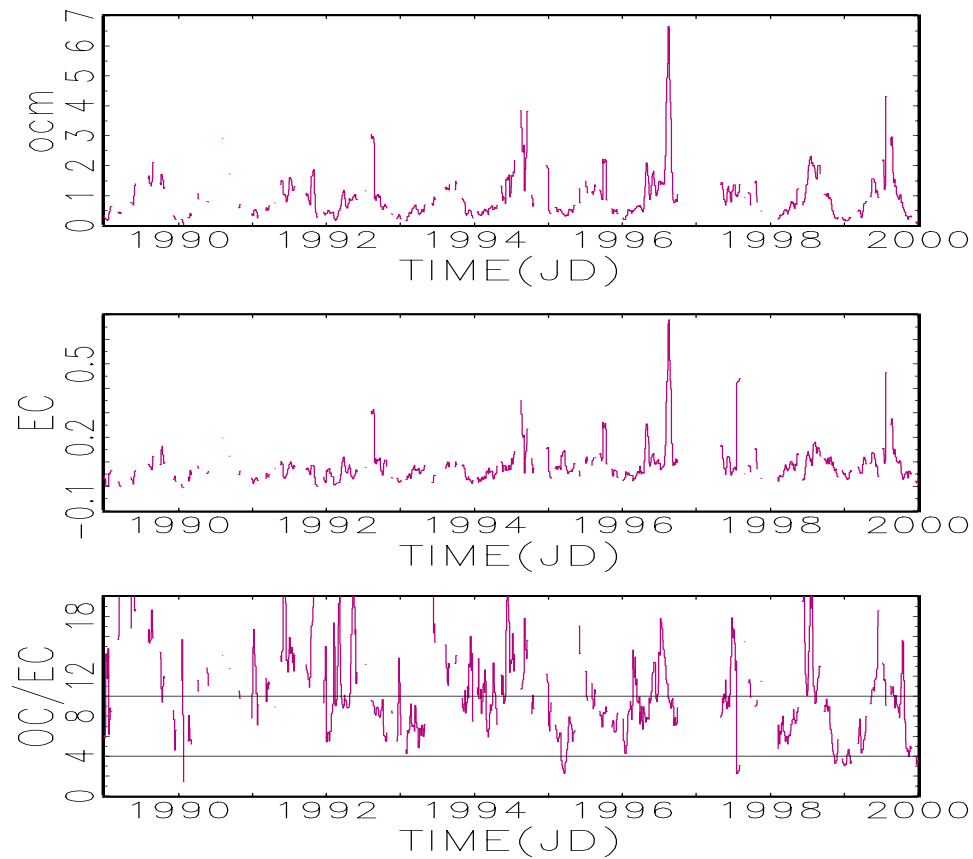
Source Profiles for OC/EC

- 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

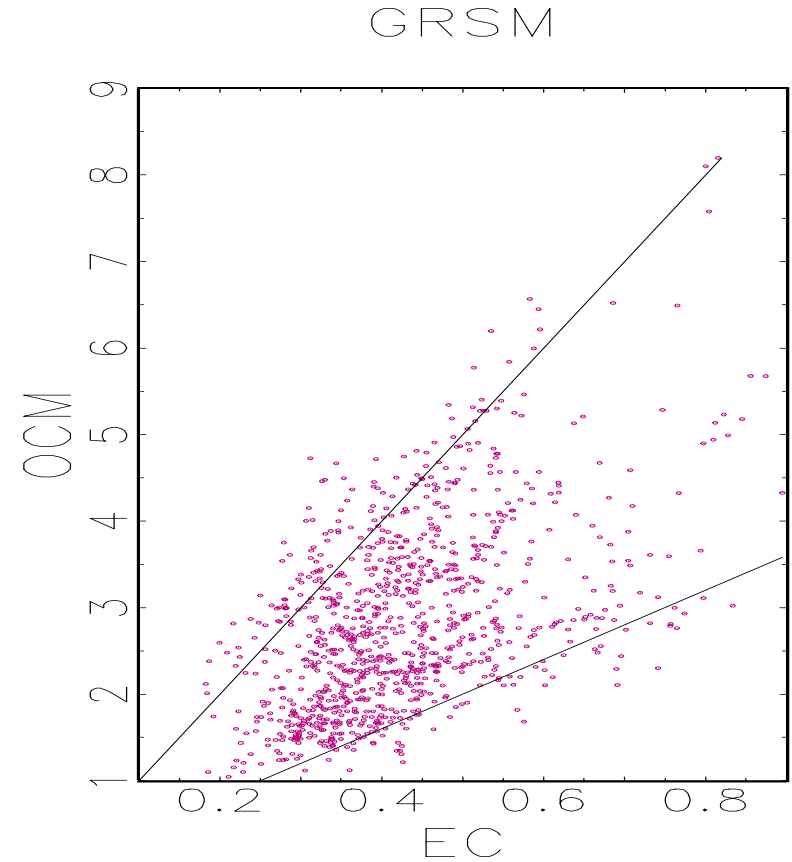
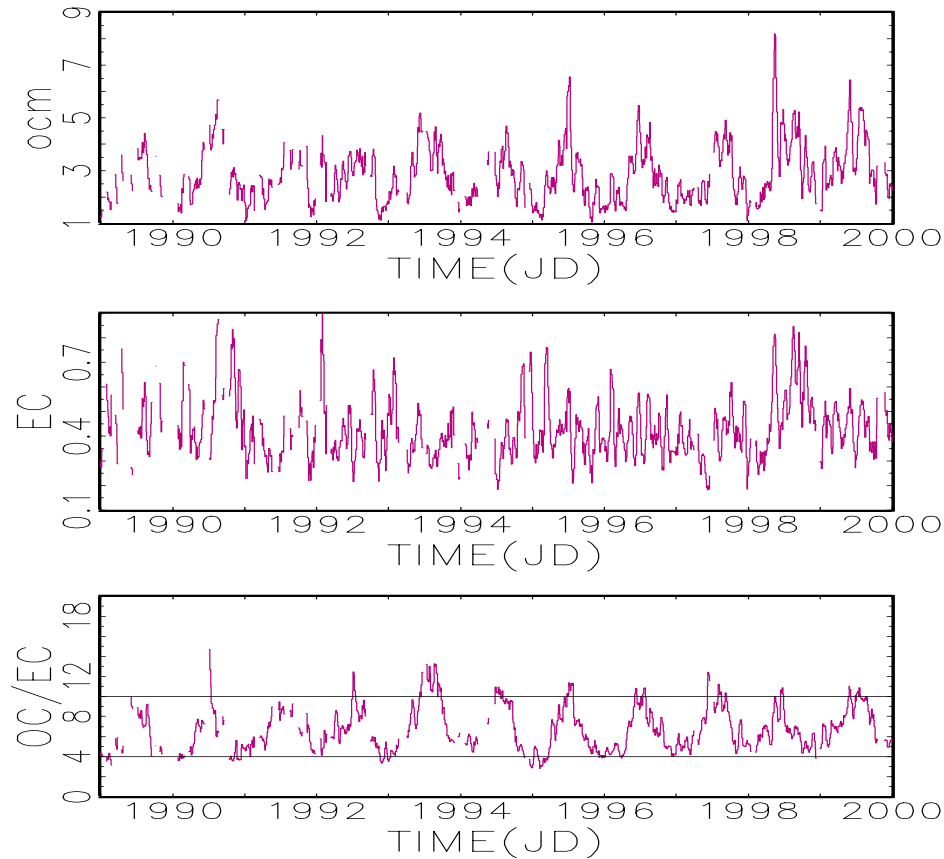
Washington DC Raw OC EC Data



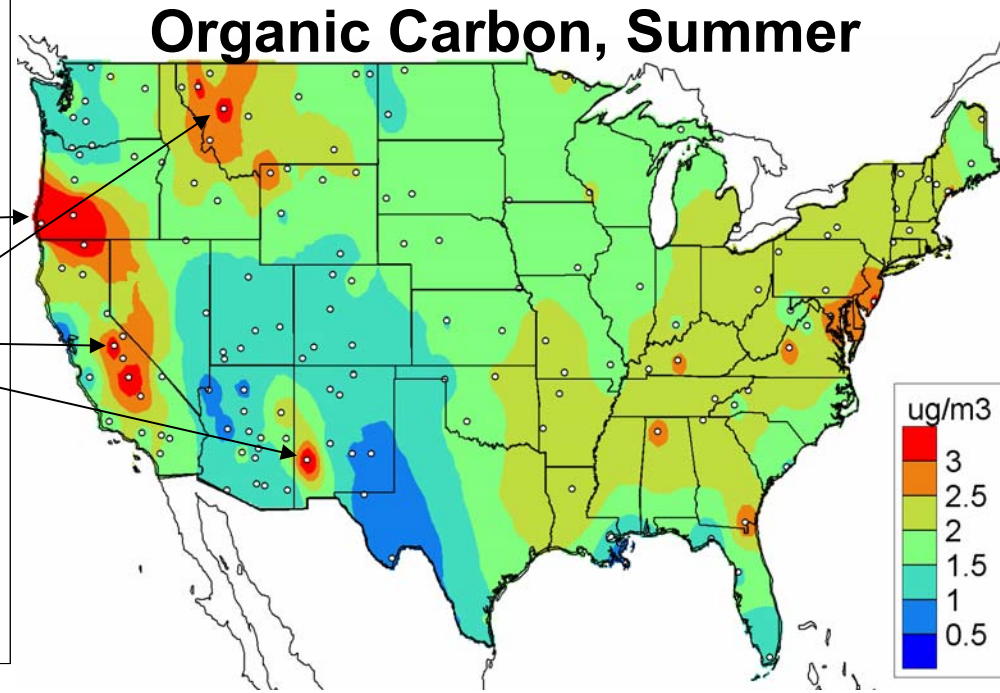
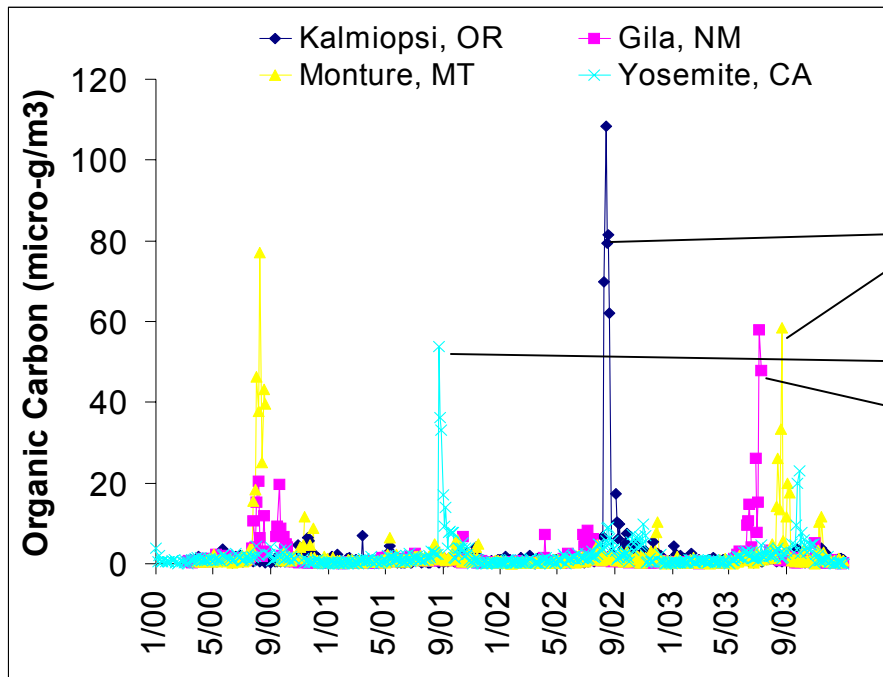
Jarbridge Raw OC EC Data



Great Smoky Raw OC EC Data

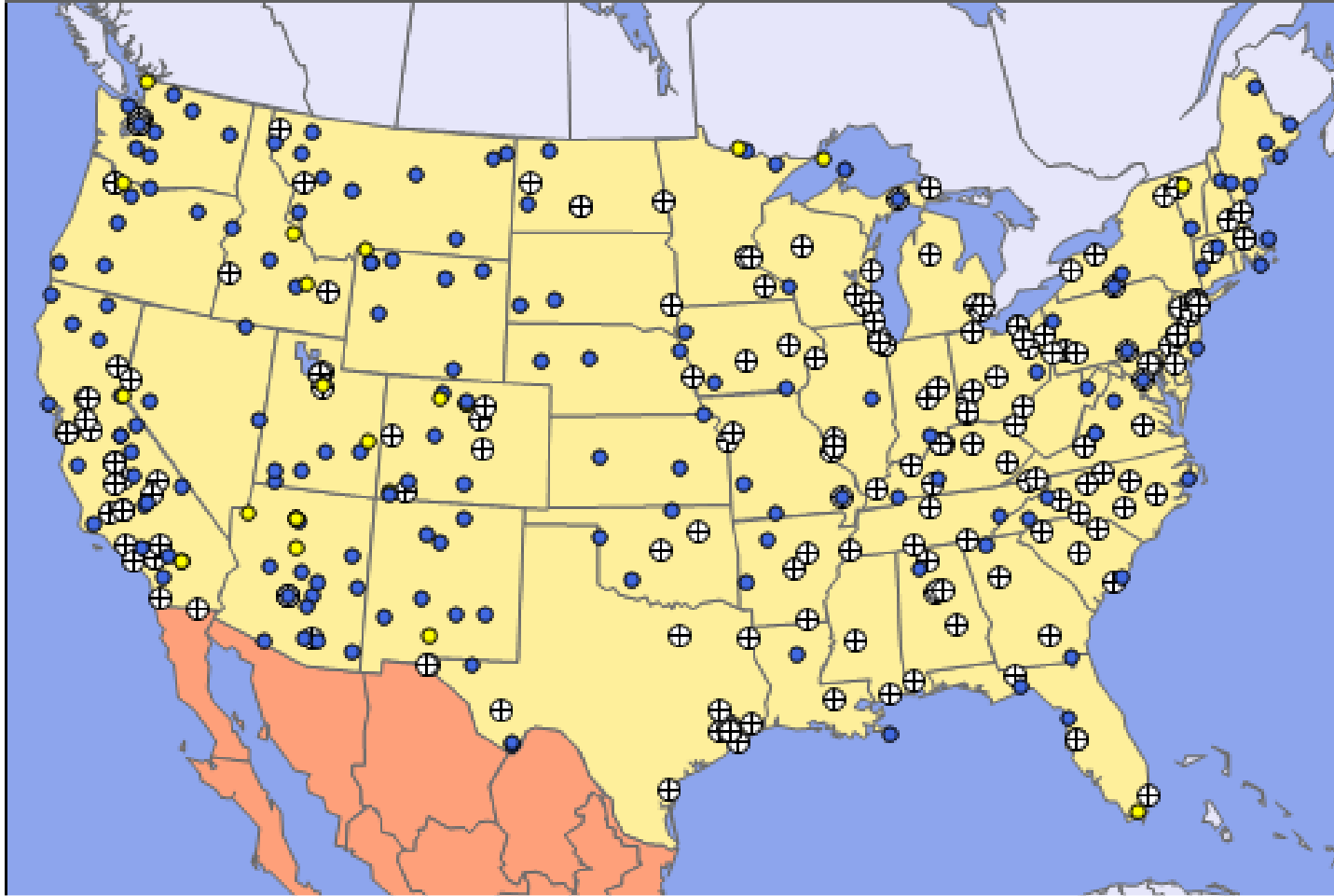


Smoke Contribution to Carbonaceous Material



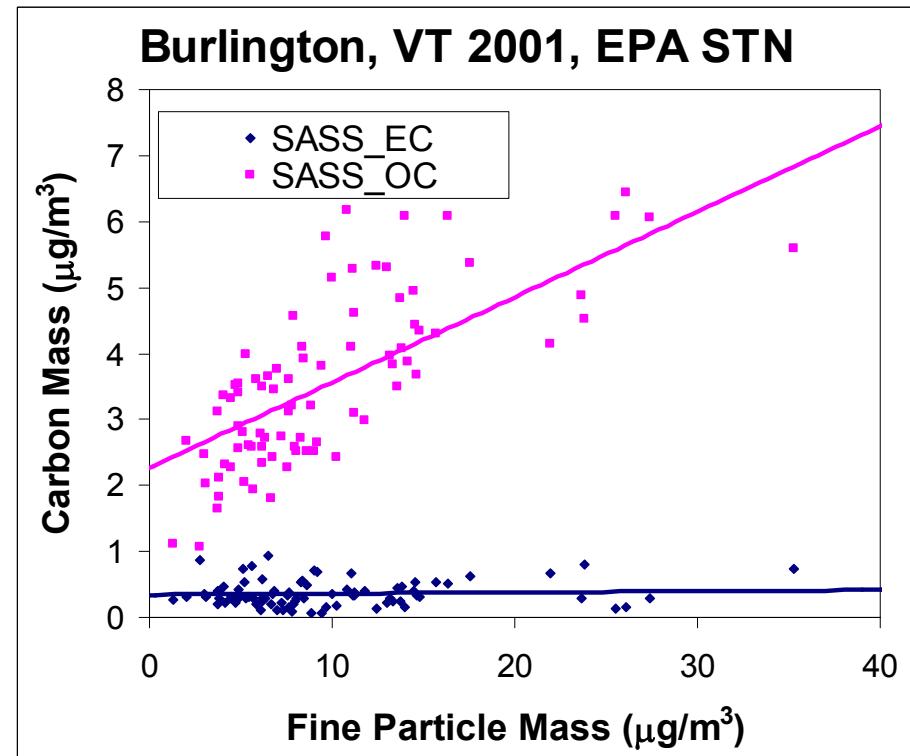
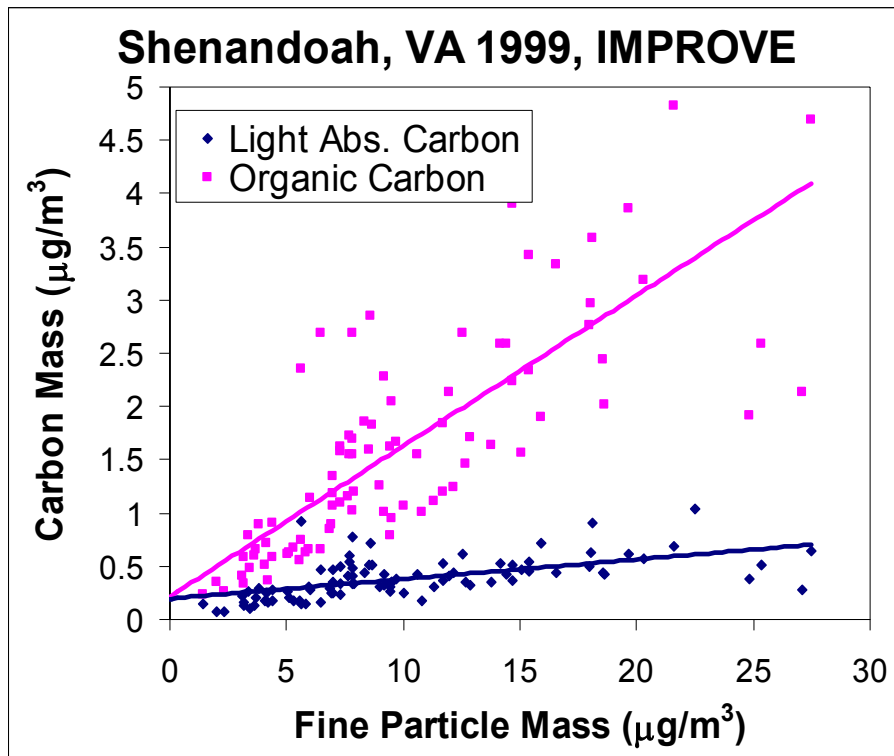
Wild fires occur every summer at some locations in the western U.S. leading to extreme carbon concentrations. These values can dominate multi-year seasonal averages.

IMPROVE and EPA Speciated Trend Network (STN)



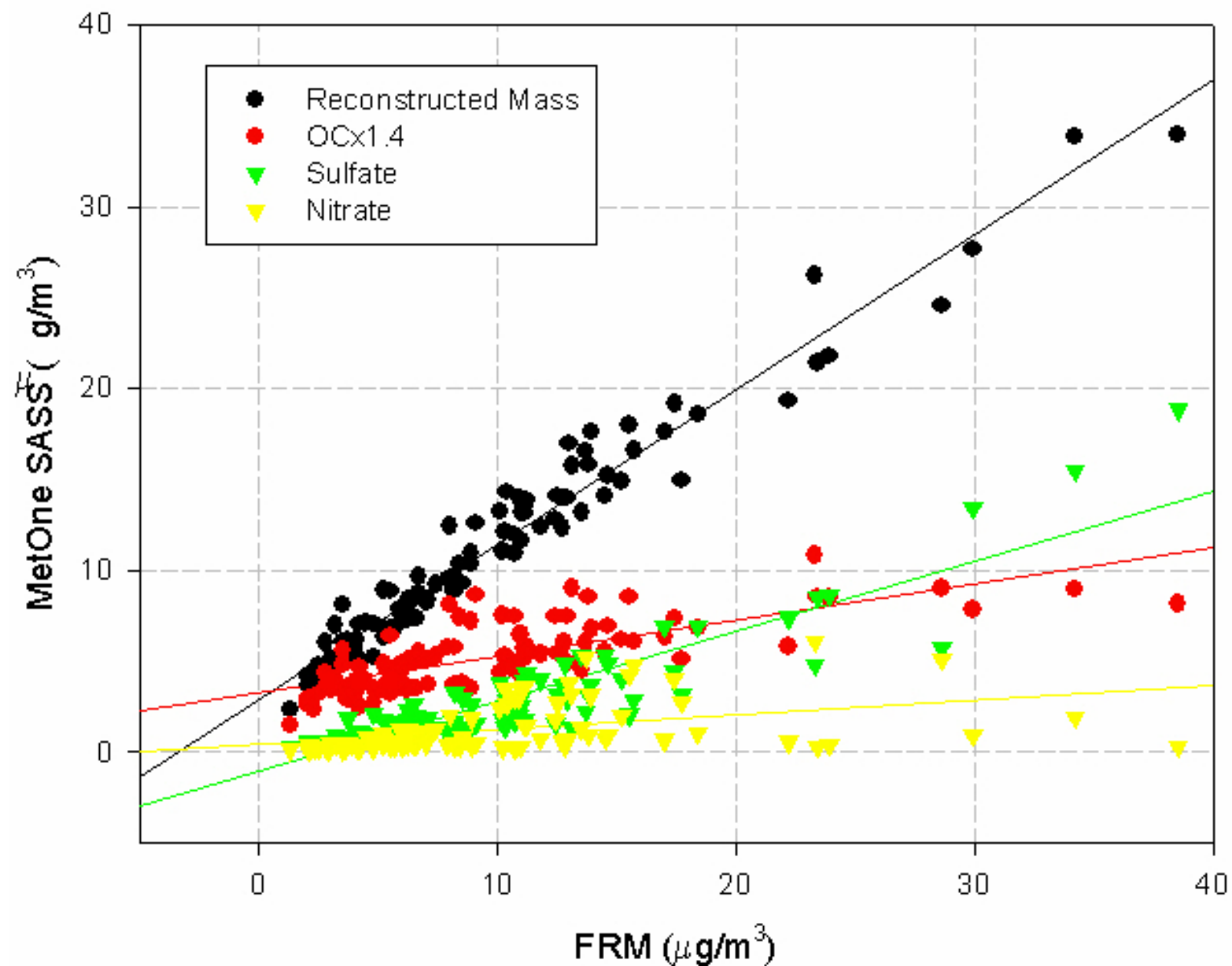
- IMPROVE – 165 monitoring sites in mostly rural areas
- ⊕ STN - 250 m- 300 monitoring sites in mostly urban/suburban areas

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

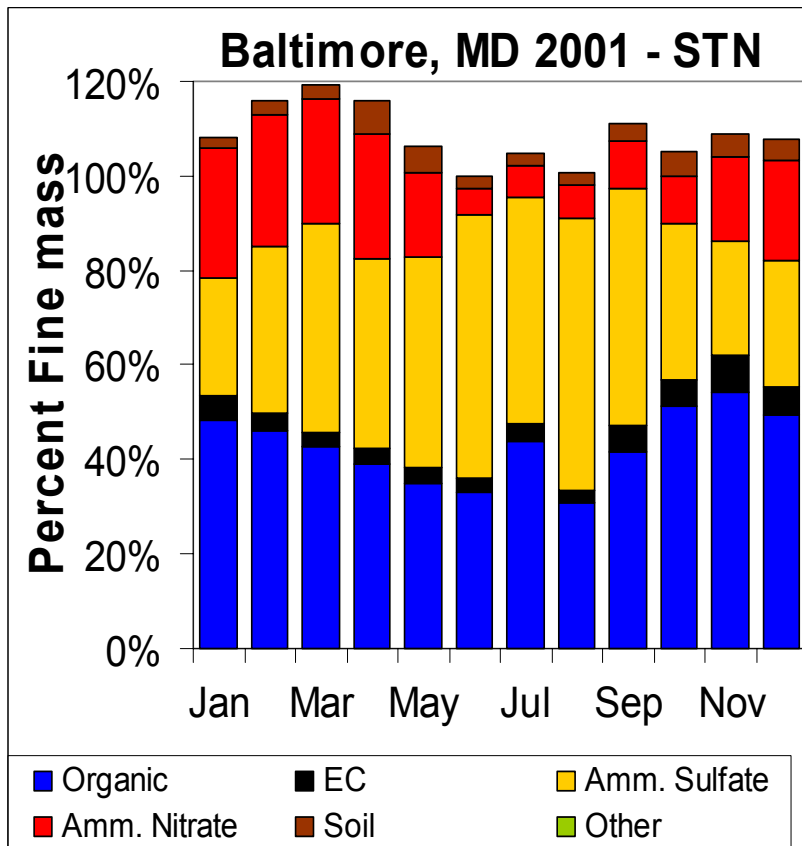
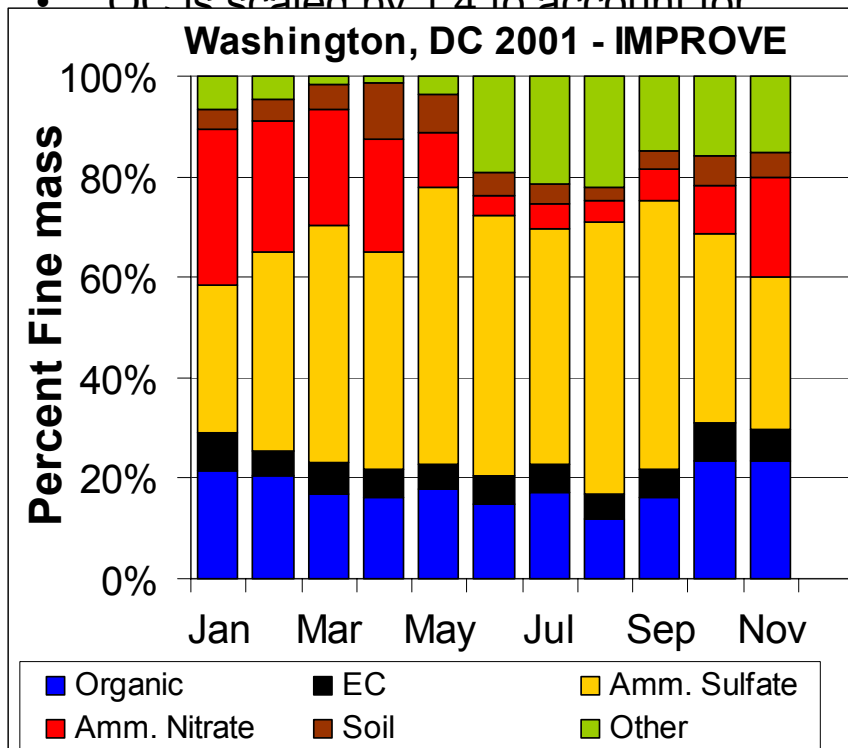


IMPROVE and STN Fine Mass Budgets

Reconstructed fine

$$\text{mass:} = [\text{Amm. Sulfate}] + [\text{Amm. Nitrate}] + [\text{Soil}] + 1.4[\text{Organic Carbon}] + [\text{Light Abs Carbon}]$$

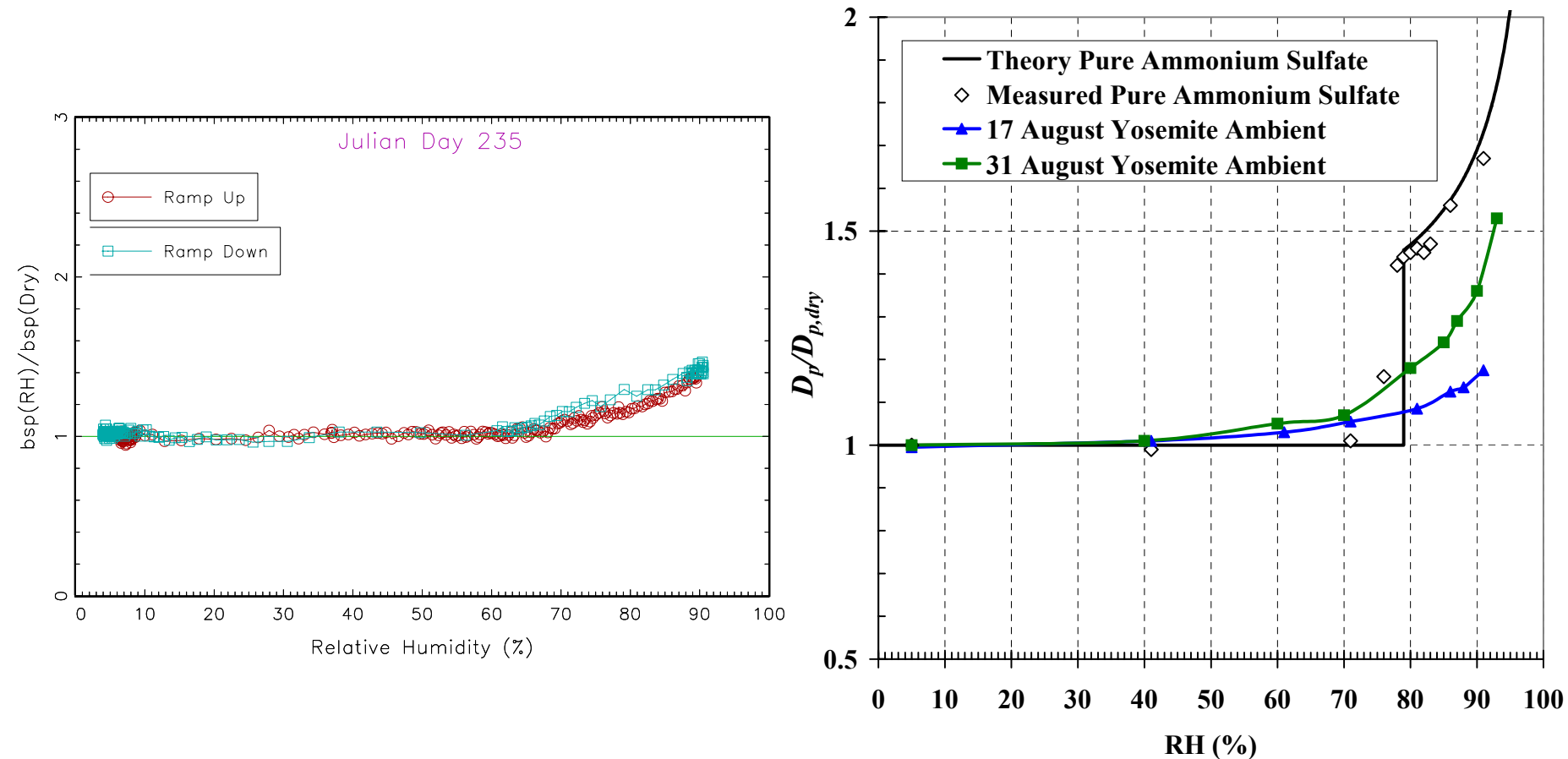
- OC is scaled by 1.4 to account for



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) nephelometry 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 provide 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.

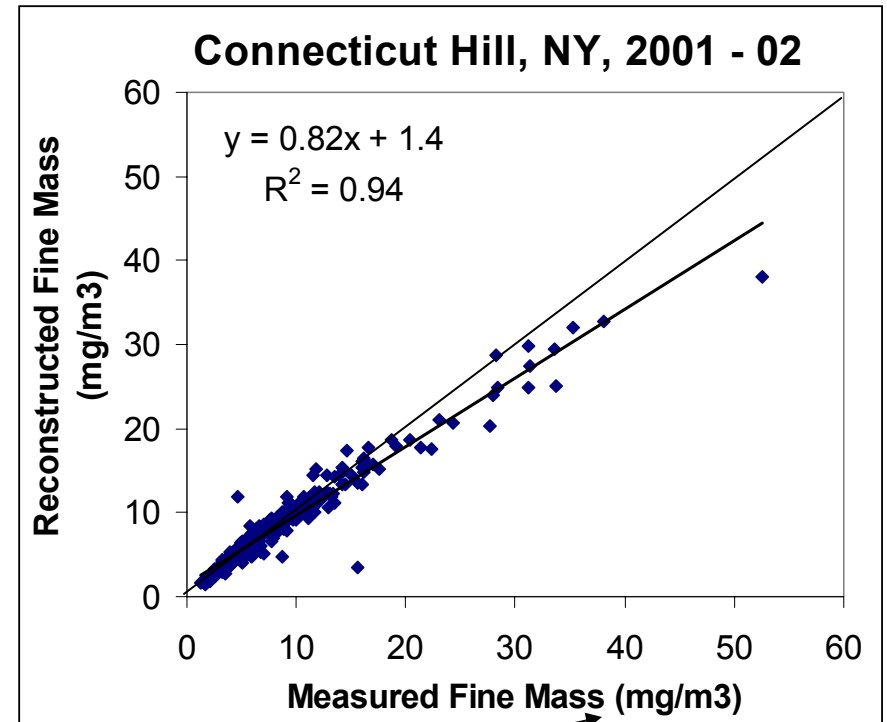
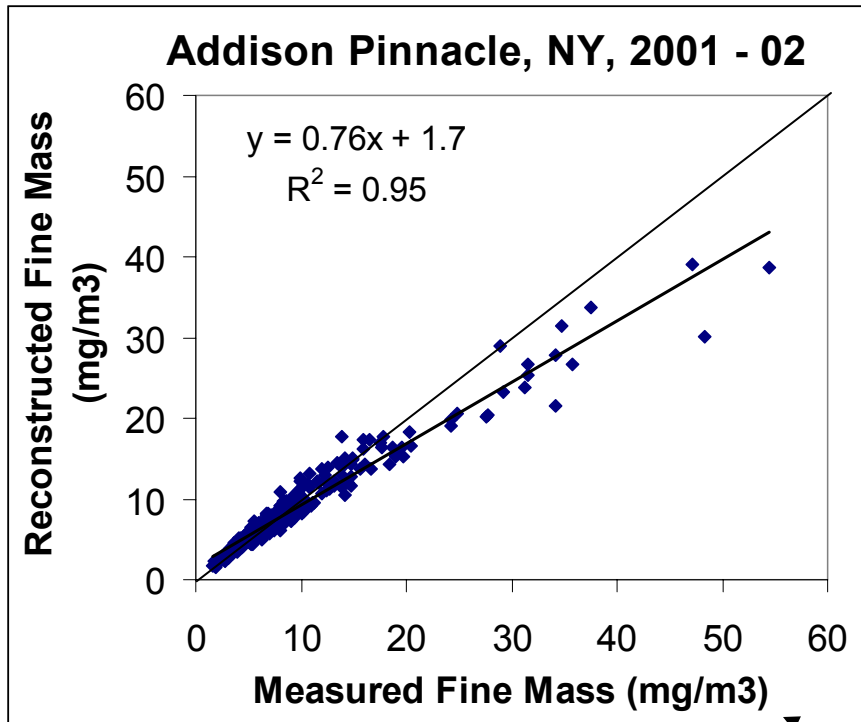
Module	Filter	Size	Variable	Analysis
A	Teflon	PM2.5	mass	gravimetric
			Na-Mn	Proton Induced X-Ray Emission
			Fe-Pb	X-ray Fluorescence
			total H	Proton Elastic Scattering
			optical absorption	Hybrid Integrating Plate/Sphere
B	Nylon	PM2.5	sulfate, nitrate	Ion Chromatography
C	Quartz	PM2.5	OC, EC in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



$\mu\text{g}/\text{m}^3$

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