Some Meandering Thoughts About Marginally Related Air Quality Issues

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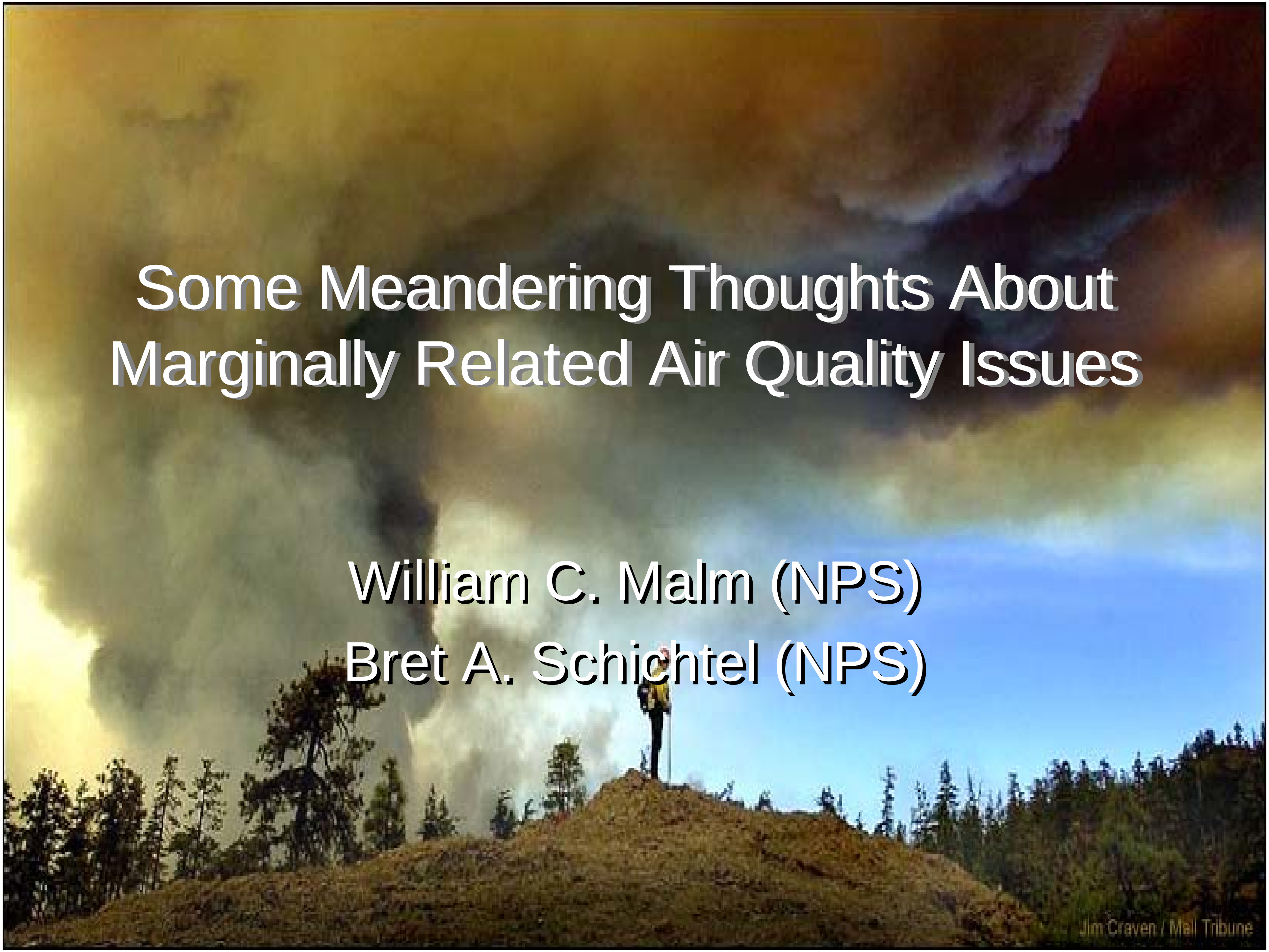


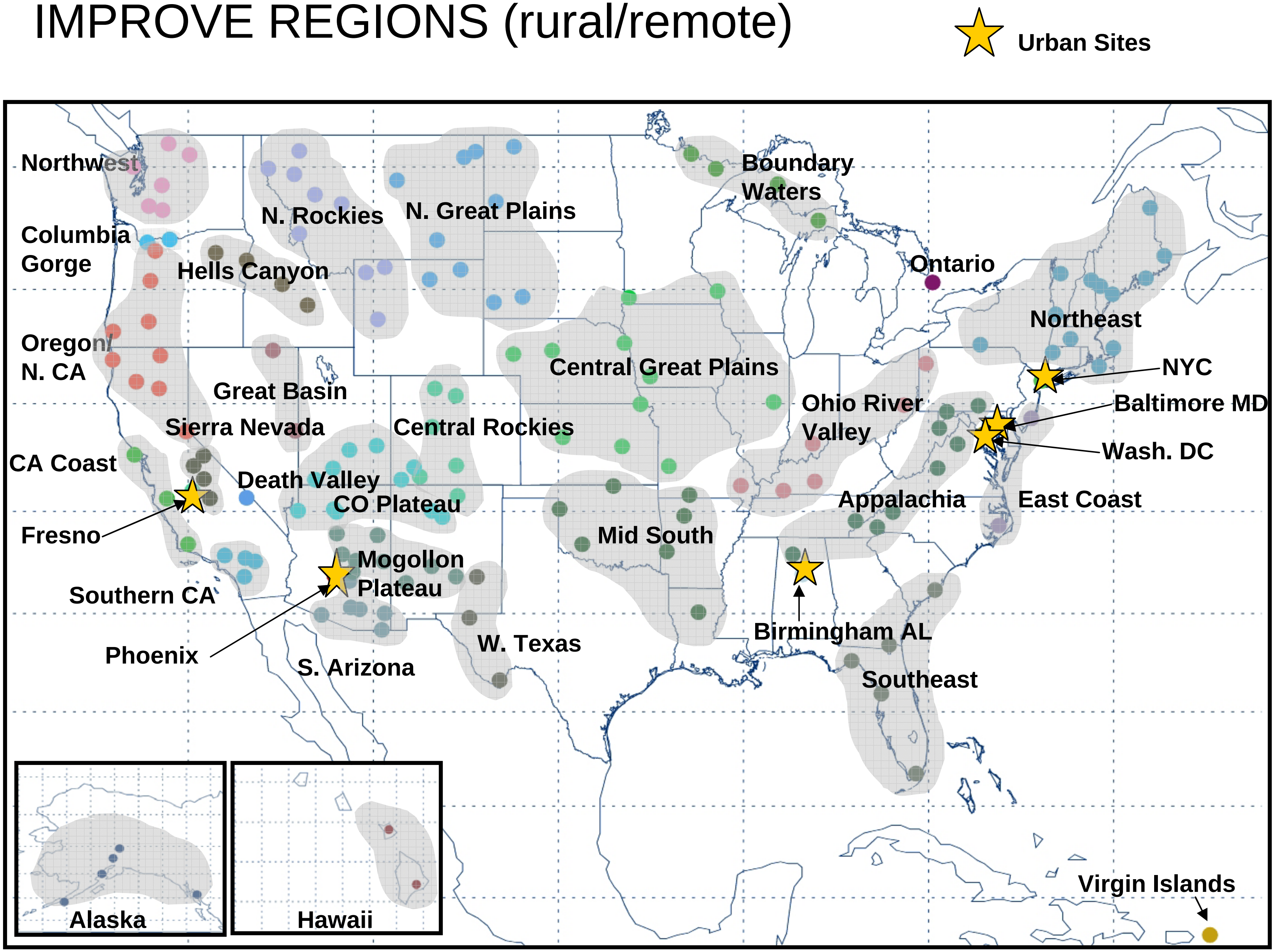
INTRODUCTION

• IMPROVE network operates over 170 mostly remote/rural monitoring sites throughout the United States.

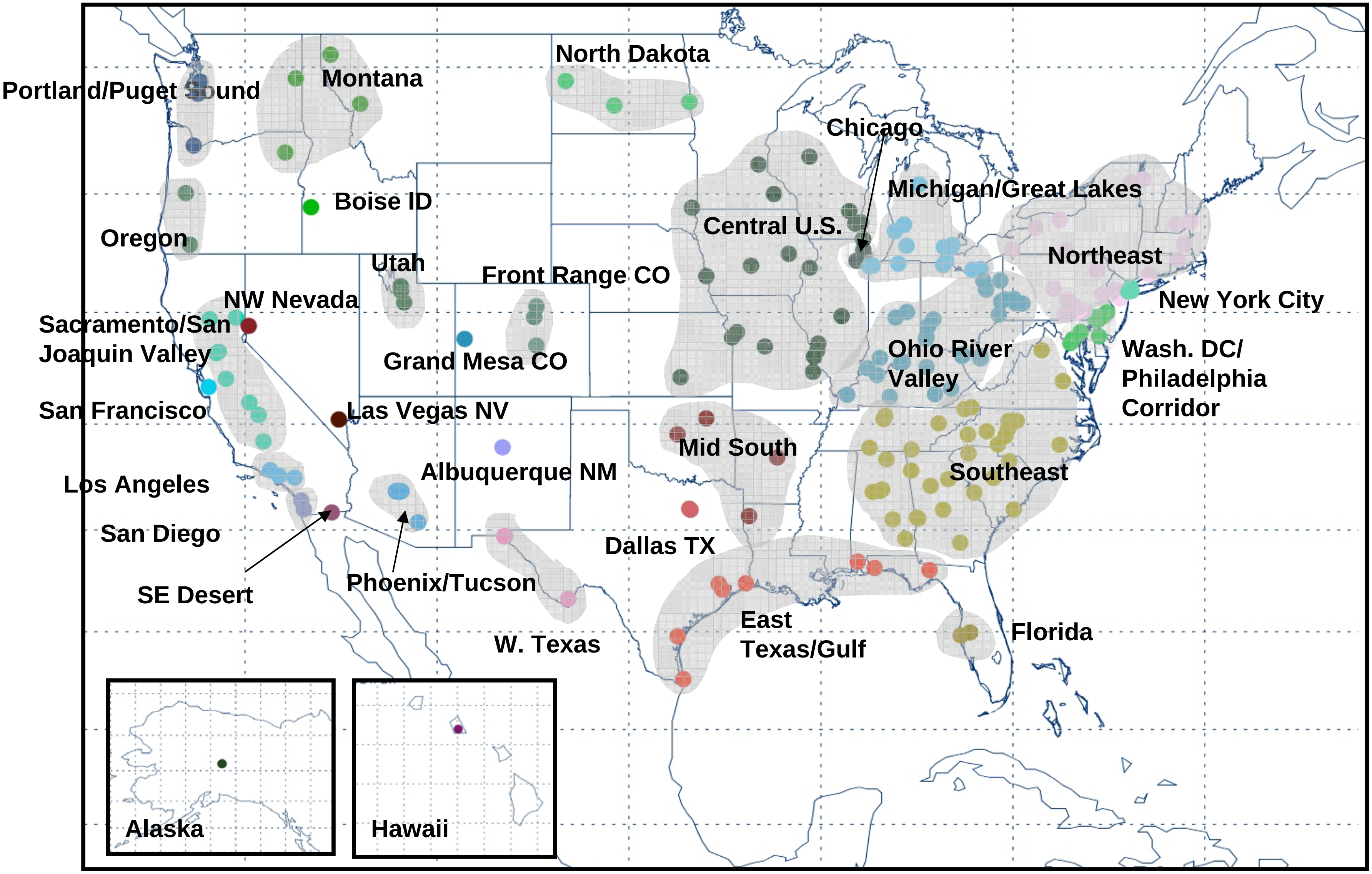
• The Speciated Trends Network (STN), operated by the Environmental Protection Agency, collects $PM_{2.5}$ aerosol data at over 200 urban/suburban monitoring sites.

• By combining data from the IMPROVE and STN networks, the seasonal distribution of key aerosol species can be explored as a function of geographical region, specifically urban and rural locations.

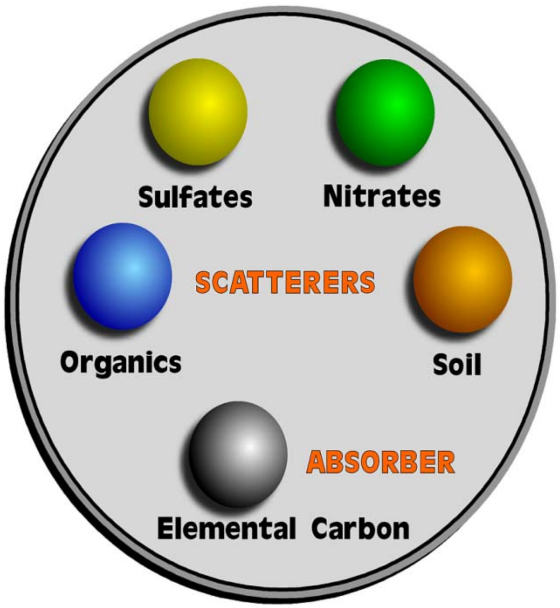
IMPROVE REGIONS (rural/remote)



STN REGIONS (urban/suburban)

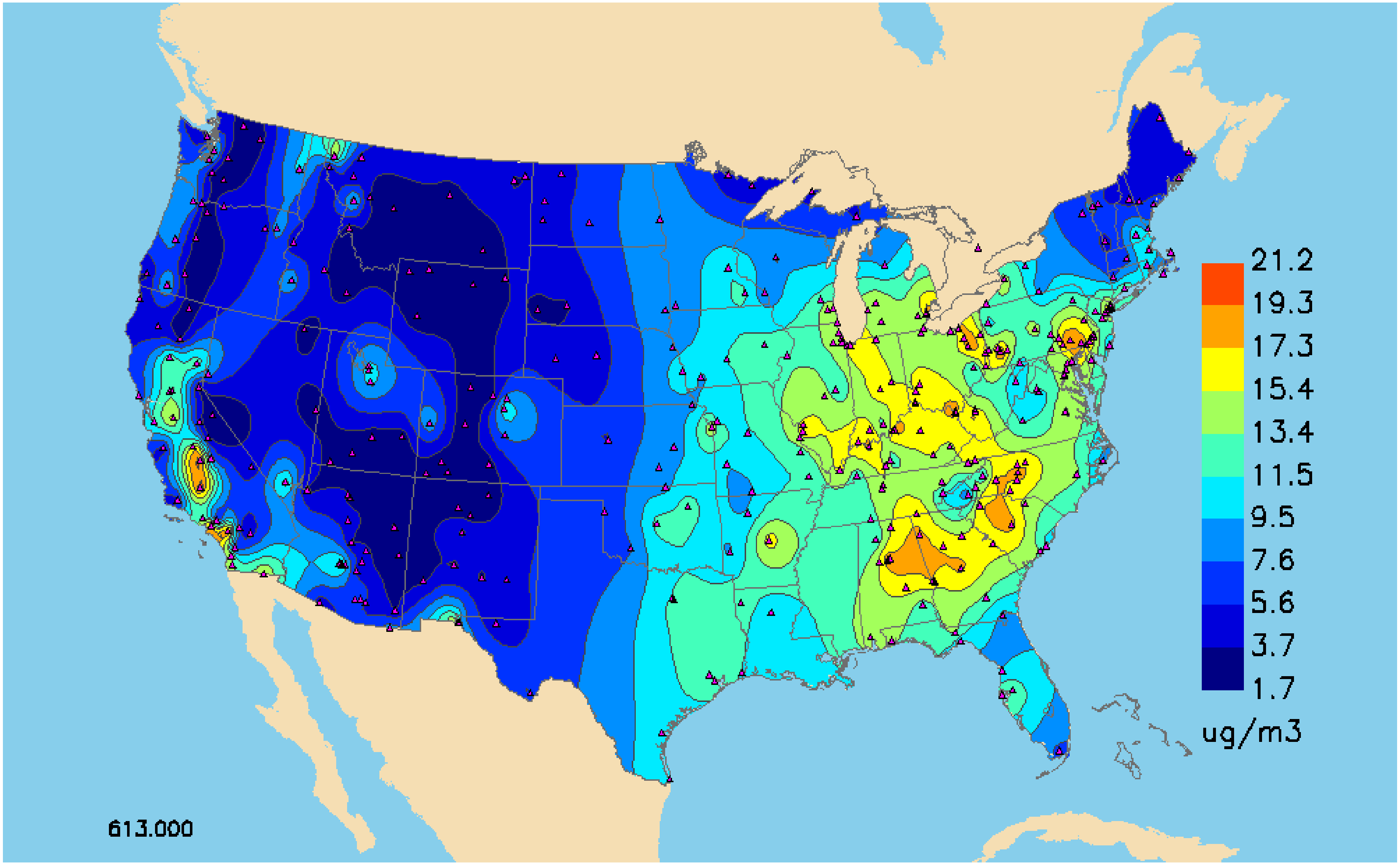


Aerosol Composite Components

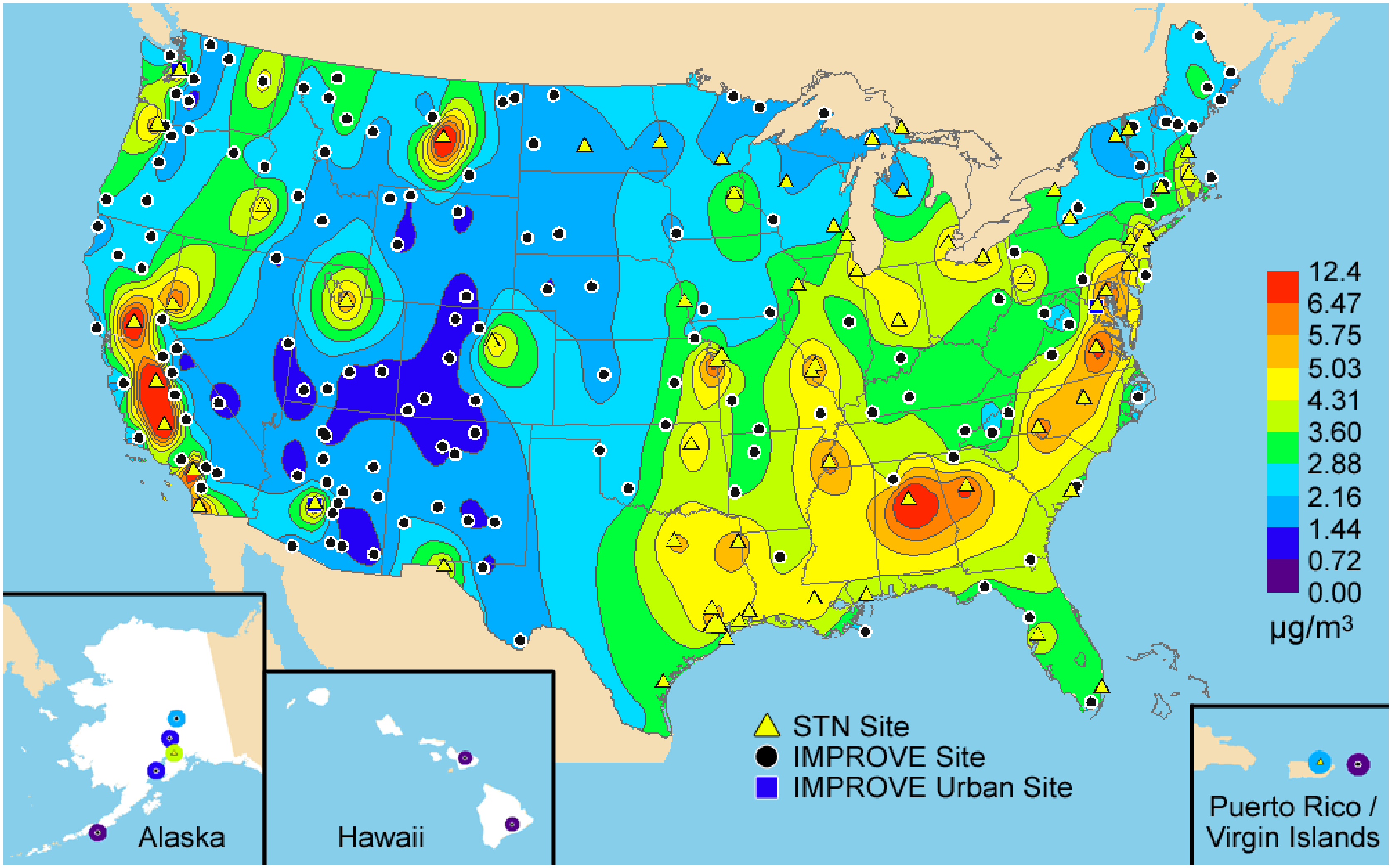


- Ammonium Sulfate = 4.125 * [S]
- Ammonium Nitrate = 1.29 * [NO_3]
- Organics = 1.4 [OC]
- Light Absorbing Carbon = [LAC]
- Soil = 2.2[Al]+2.49[Si]+1.63[Ca]+2.42[Fe] +1.94[Ti]
  - A factor of 1.16 is used for other soil components
- Sea Salt = 1.8 * [Cl-]
- Coarse Mass = PM10 – PM2.5

Gravimetric Fine Mass

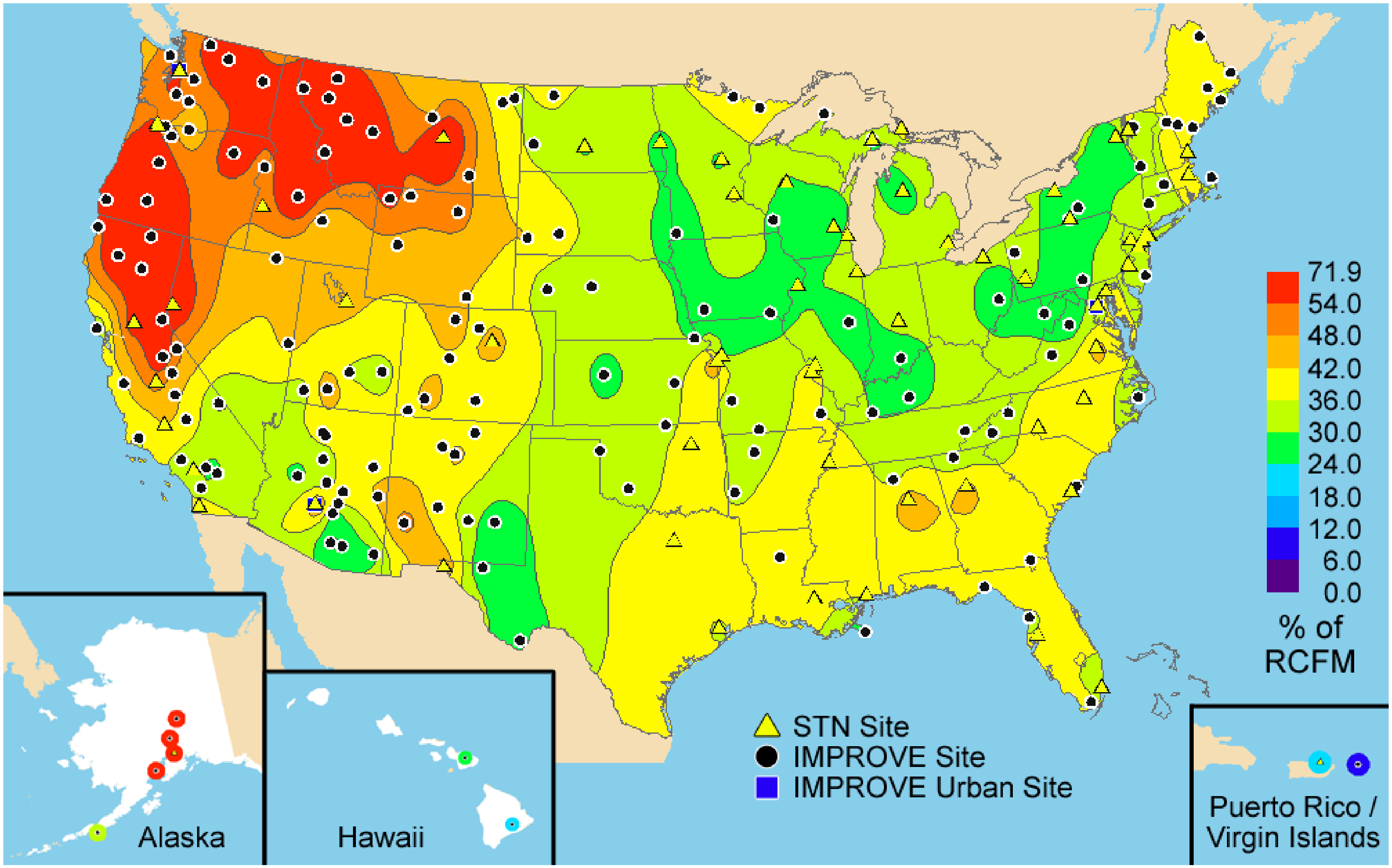


Urban & Rural Annual Organic



IMPROVE monitoring network collects speciated PM2.5 data in rural locations across the United States

Urban & Rural Annual Organic Carbon Fraction

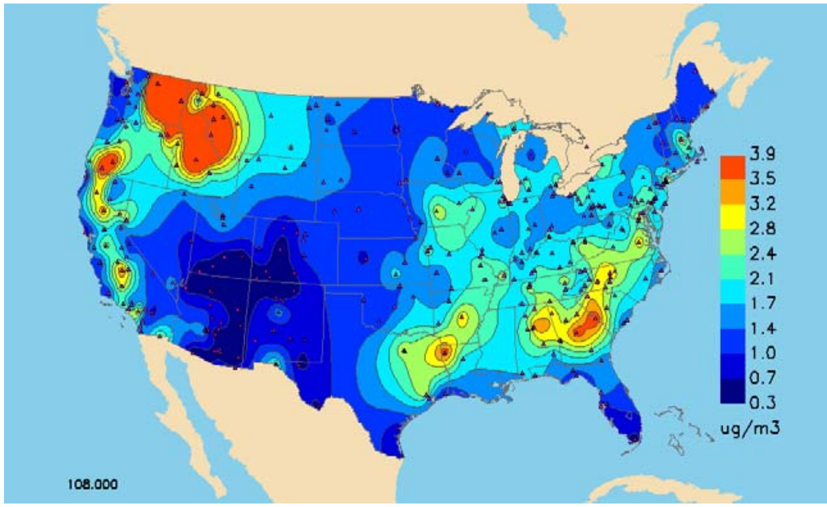


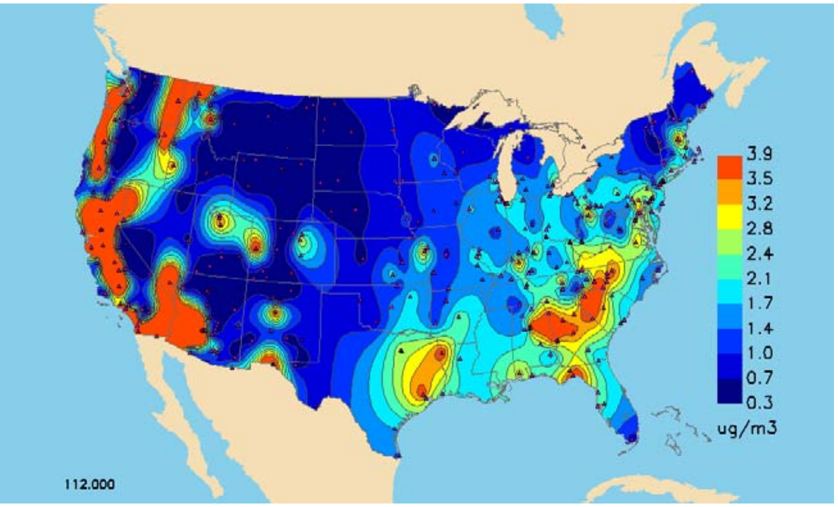
Spatial Patterns: IMPROVE/STN (monthly mean, μg m^{-3})

Aug

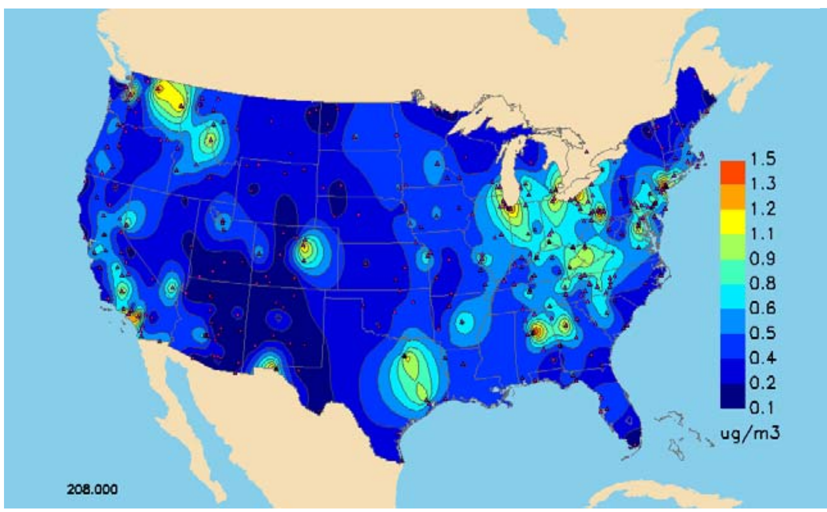
Dec

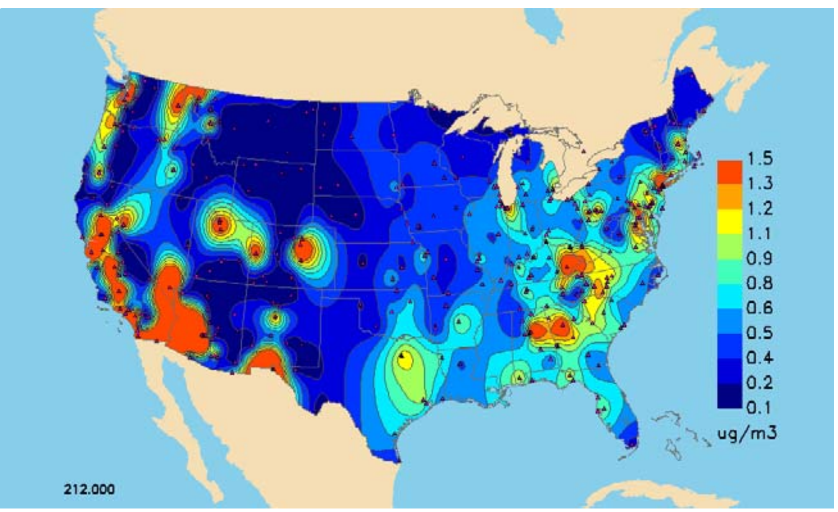
OC





LAC



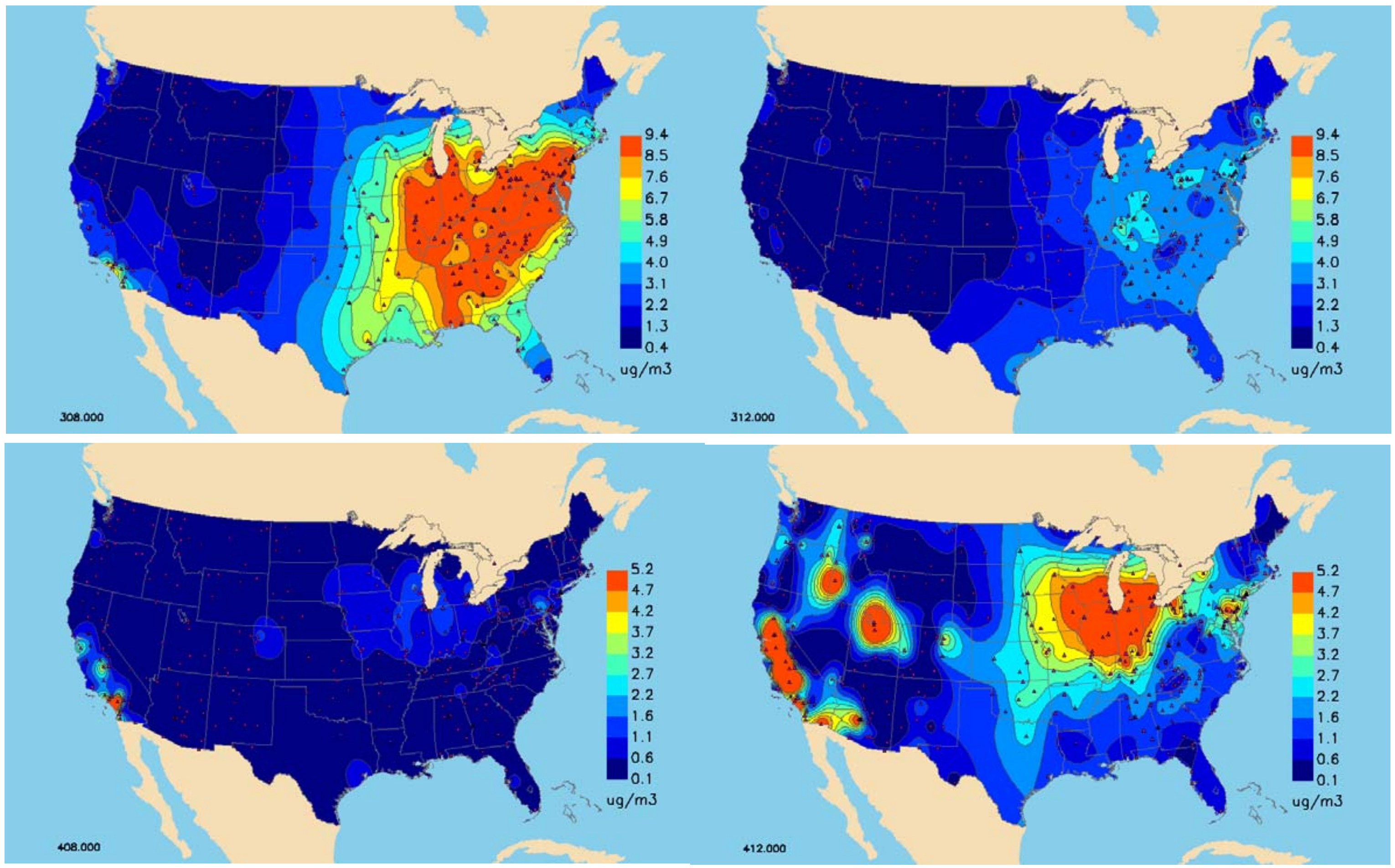


Spatial Patterns: IMPROVE/STN (monthly mean, $\mu g\ m^{-3}$)

Aug | Dec

Ammonium Sulfate

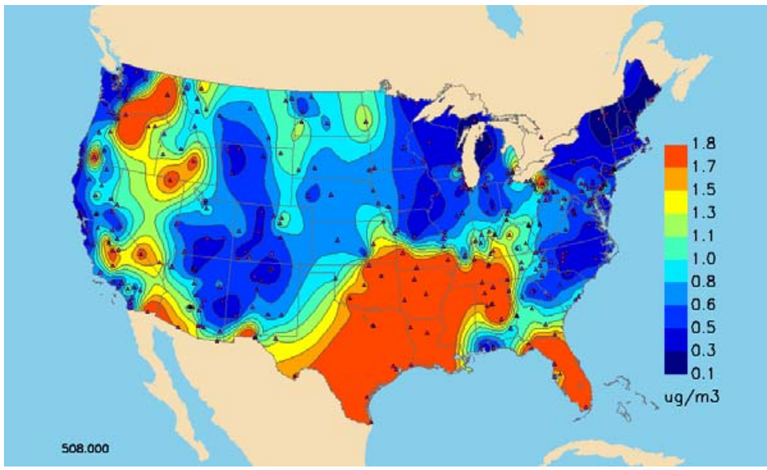
Ammonium Nitrate



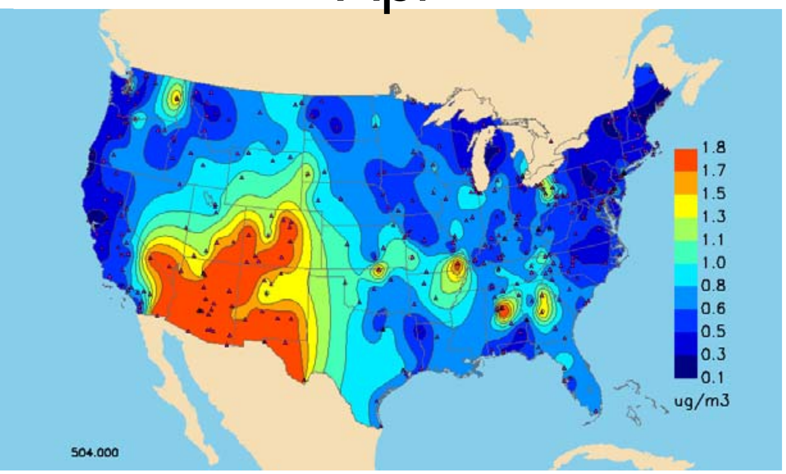
Spatial Patterns: IMPROVE/STN (monthly mean, $\mu g\ m^{-3}$)

Soil

Aug

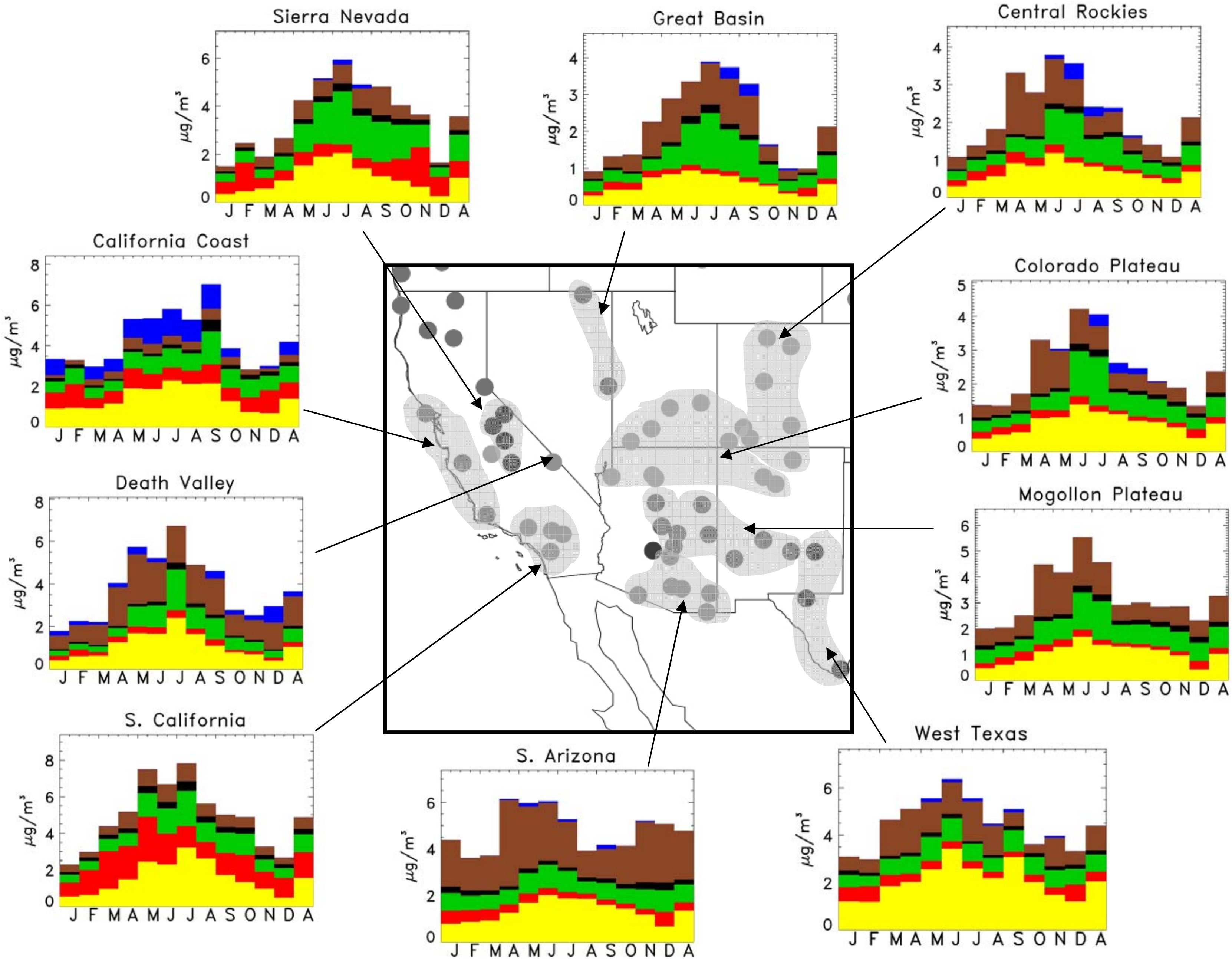


Apr



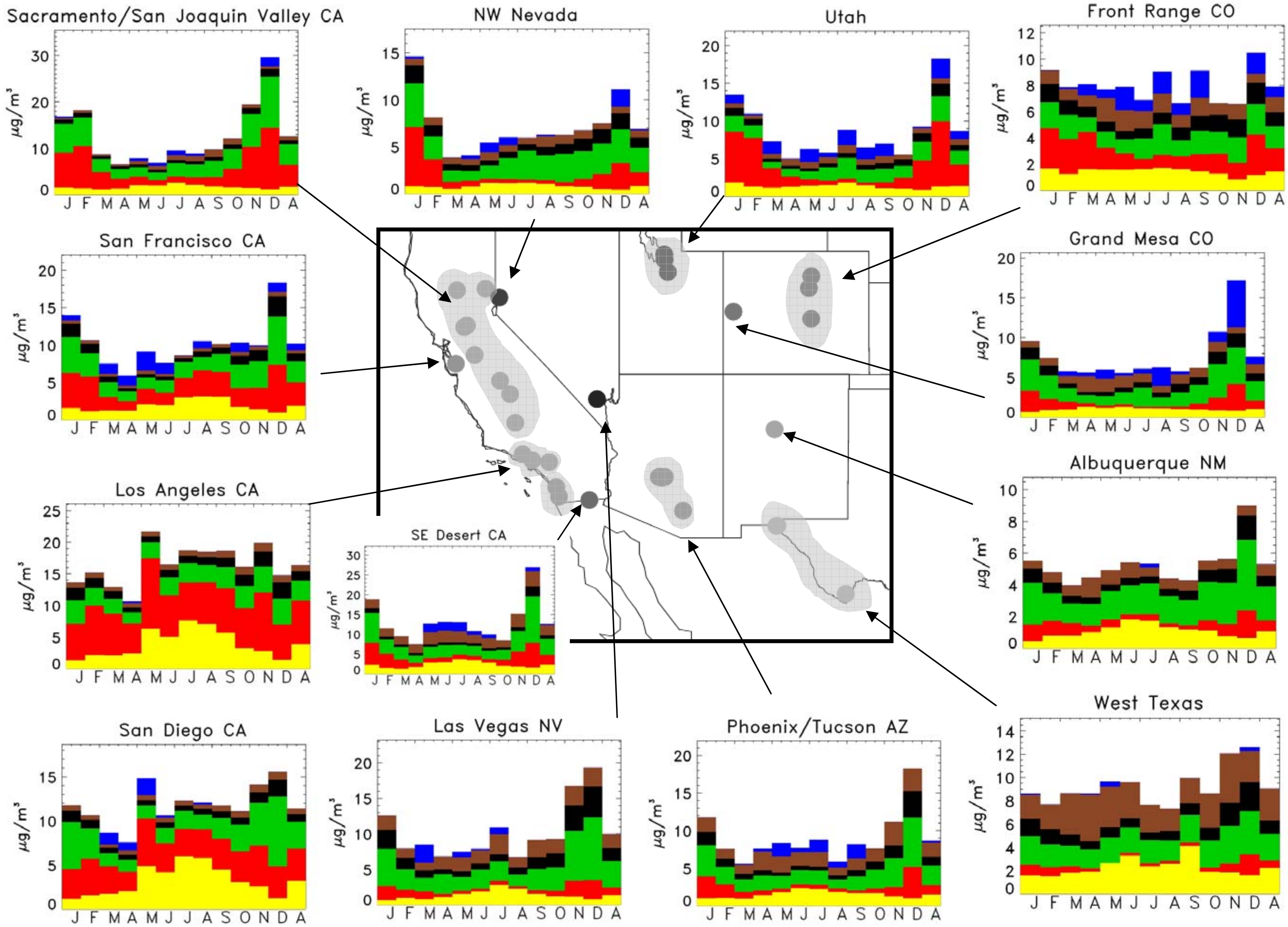
IMPROVE: Southwest U.S. Region

AS AN OC LAC Soil Other



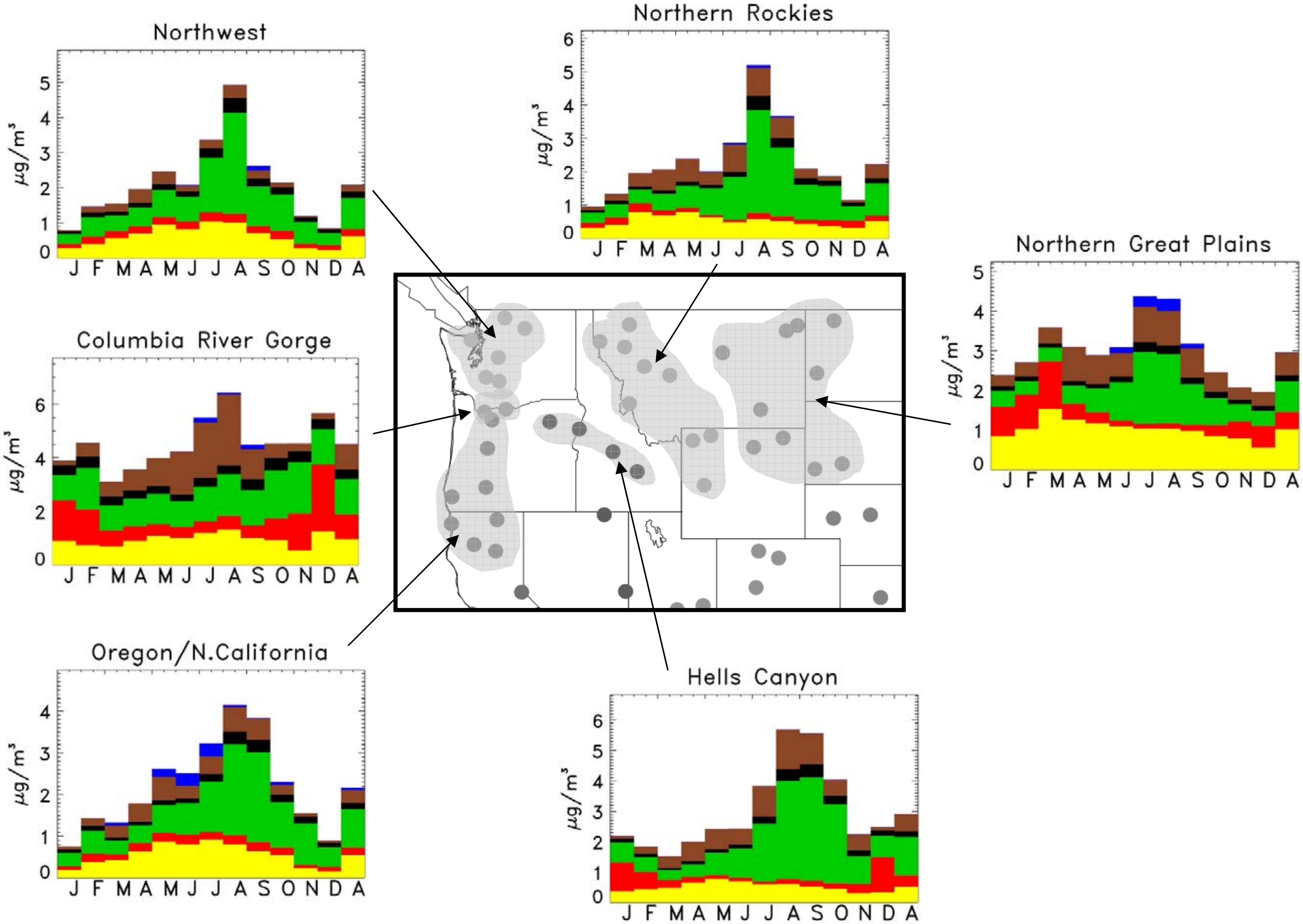
STN: Southwest U.S. Region

AS AN OC LAC Soil Other



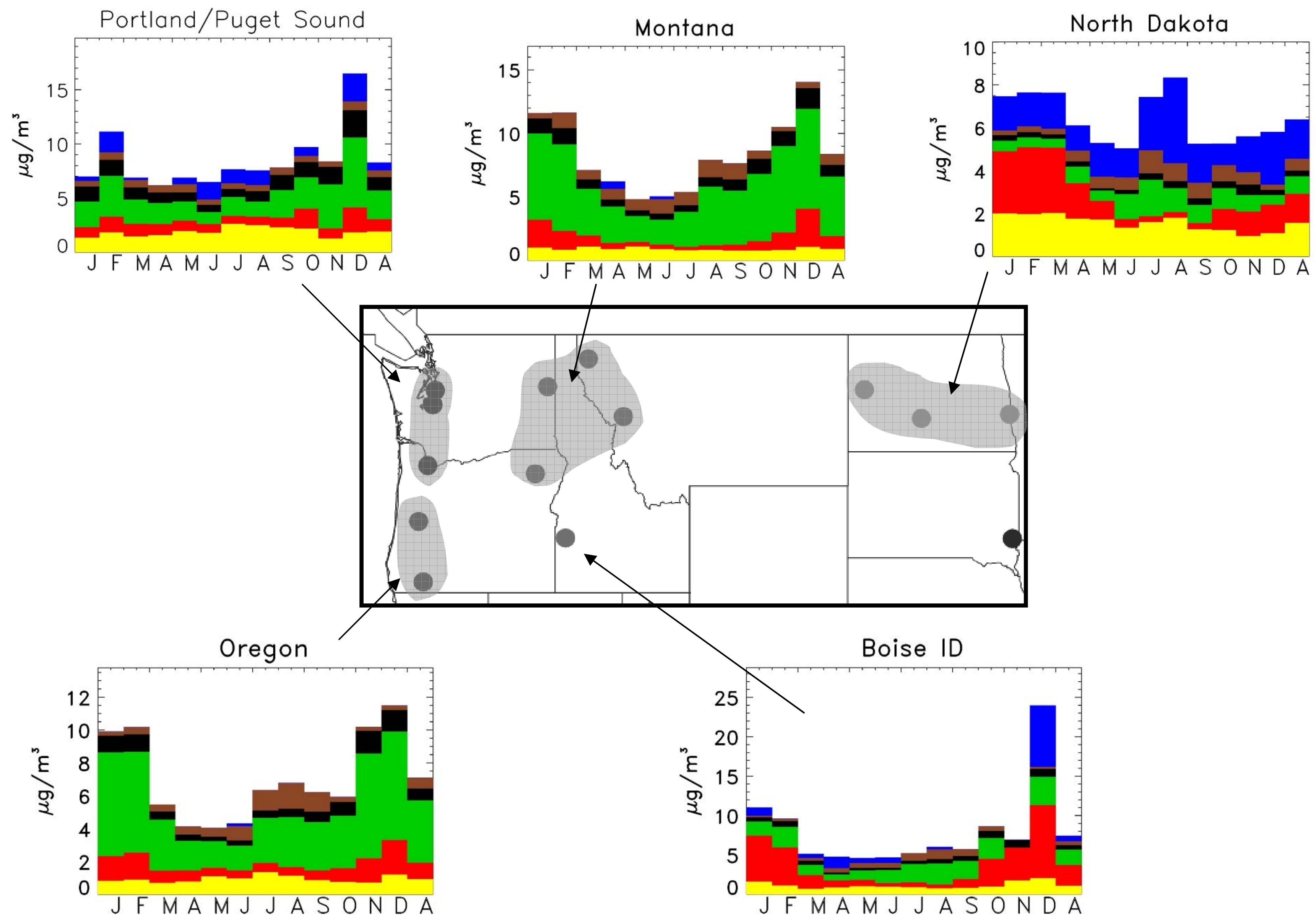
IMPROVE: Northwest U.S. Region

AS AN OC LAC Soil Other

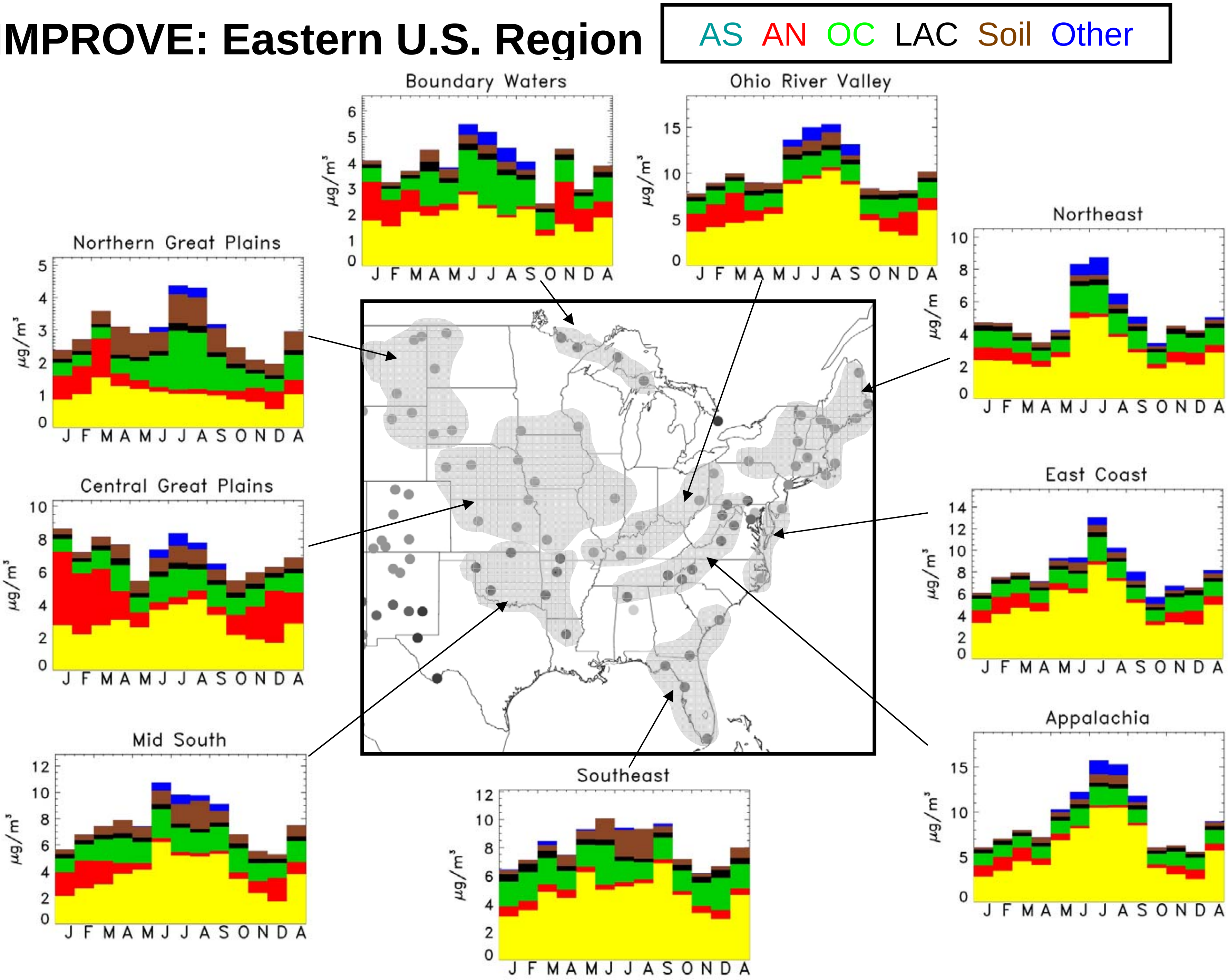


STN: Northwest U.S. Region

AS AN OC LAC Soil Other

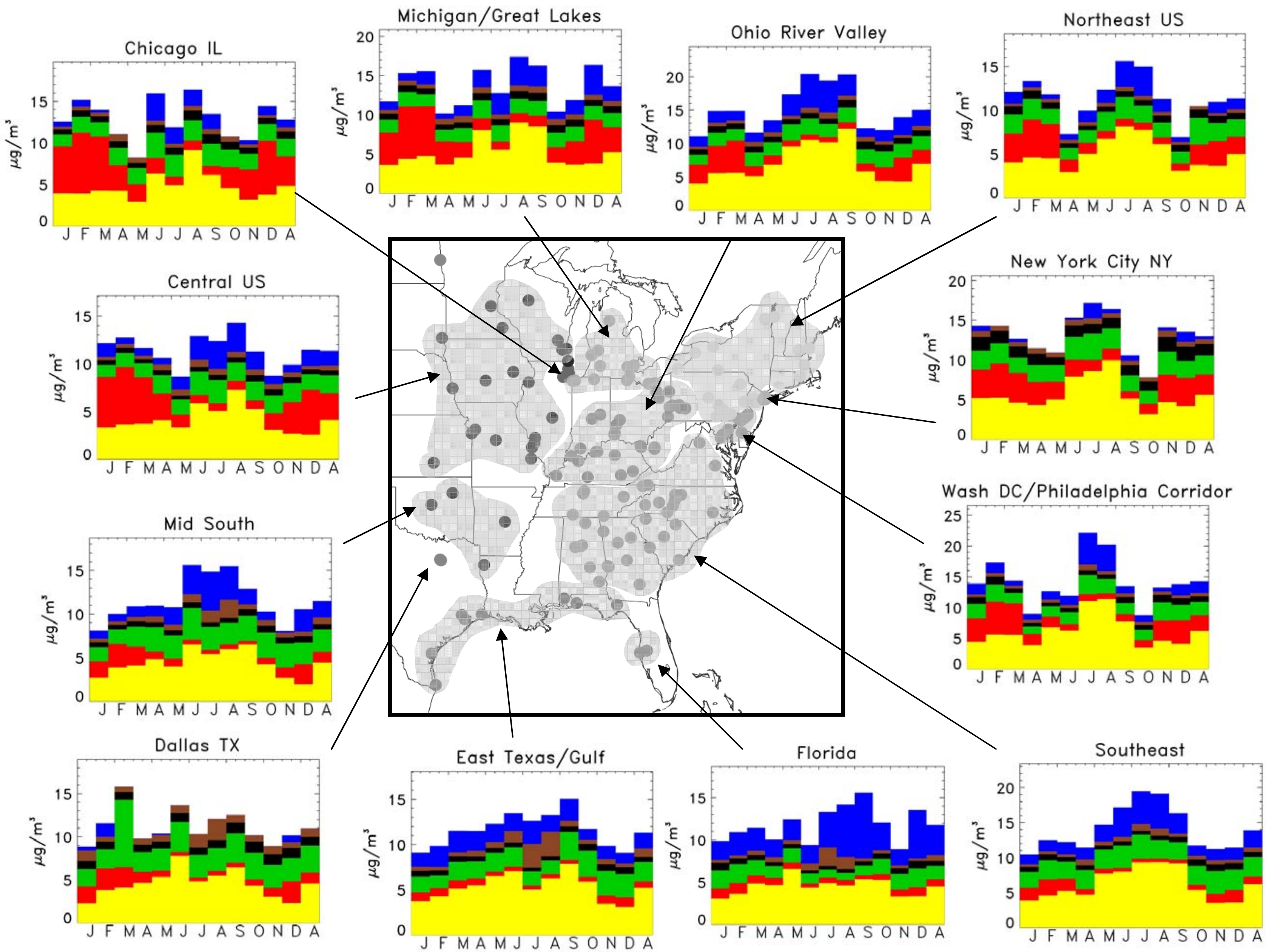


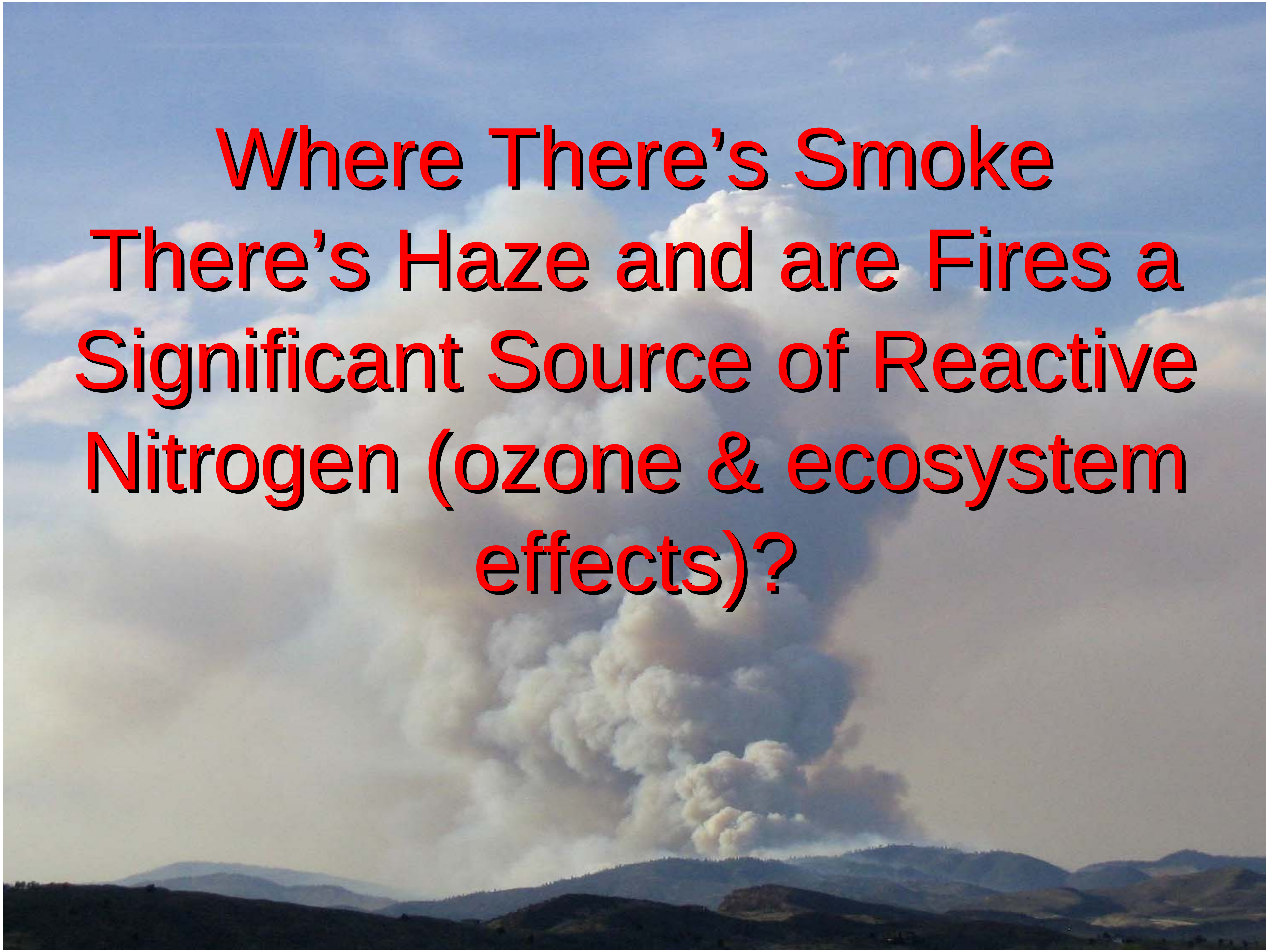
IMPROVE: Eastern U.S. Region



STN: Eastern U.S. Region

AS AN OC LAC Soil Other



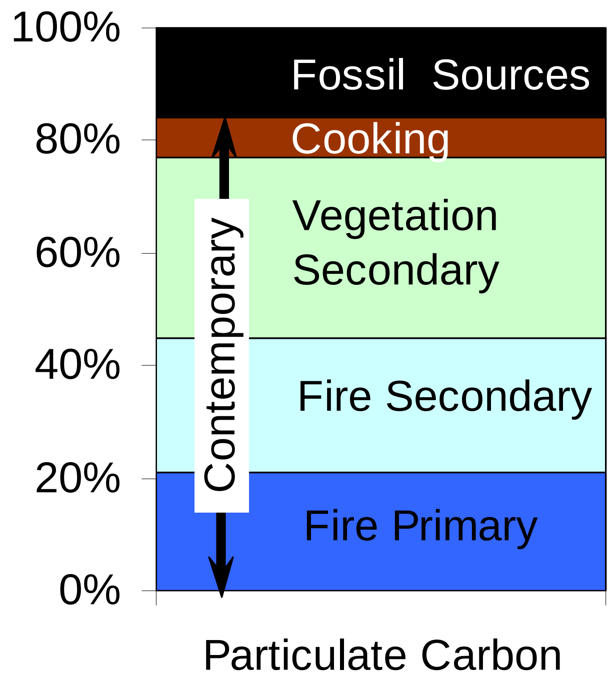

Where There’s Smoke There’s Haze and are Fires a Significant Source of Reactive Nitrogen (ozone & ecosystem effects)?

What have we recently learned?

Smoke Management Needs for Air Quality Regulations

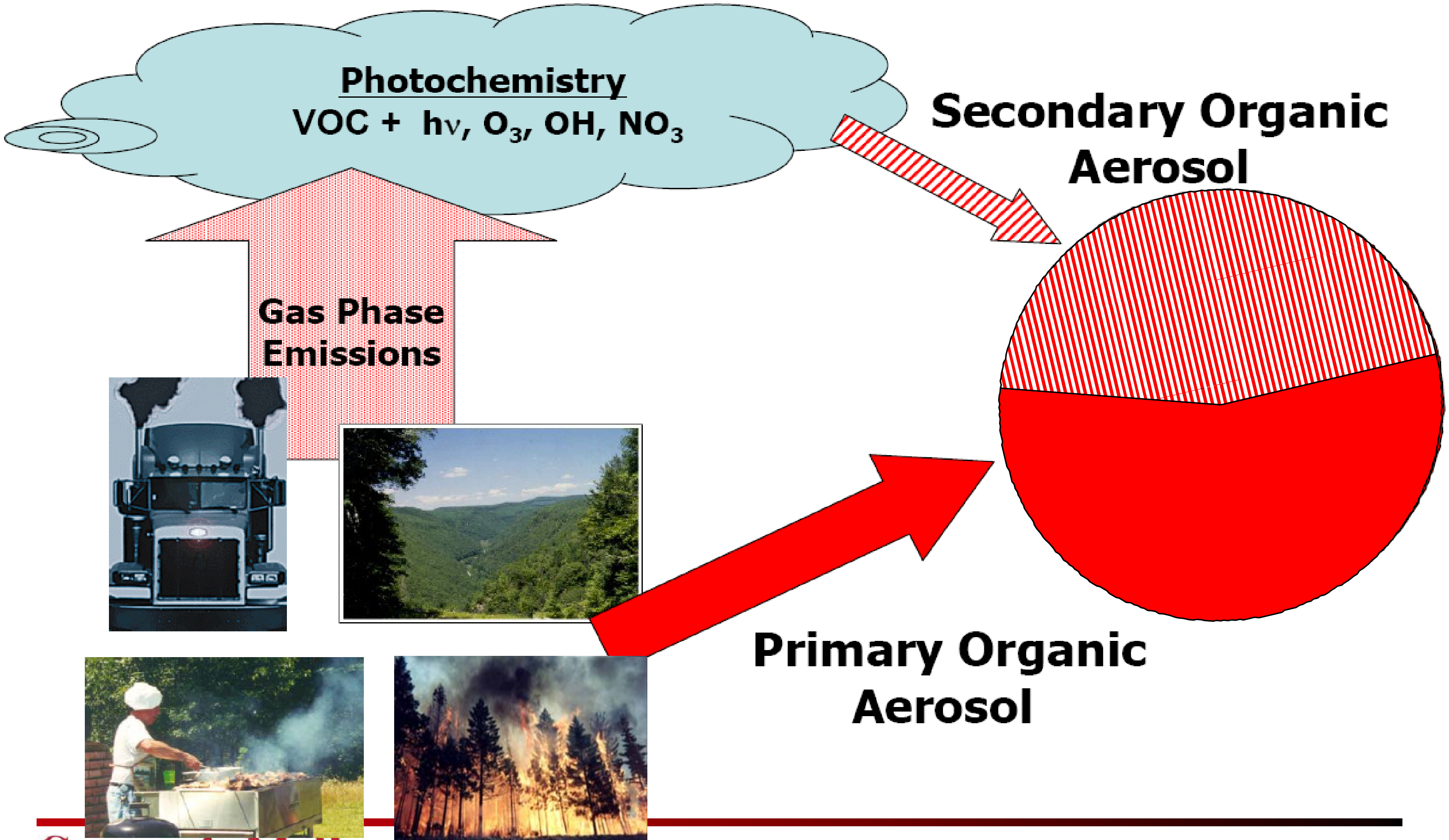
- **Develop an unambiguous <u>routine</u> and <u>cost effective</u> methodology for apportioning primary and secondary carbonaceous compounds in PM2.5 RETROSPECTIVELY to prescribed, wildfire, agricultural fire, and residential wood burning activities**
  - Daily contributions needed for Haze Rule to properly estimate natural contribution and contribution to worst 20% haze days
  - Annual and daily contributions needed for PM2.5 and PM10 NAAQS
  - Long term retrospective analysis needed to assess successes of smoke management policies
- **Similar needs for ozone and reactive nitrogen deposition issues**

Sources Contributing to Particulate Carbon

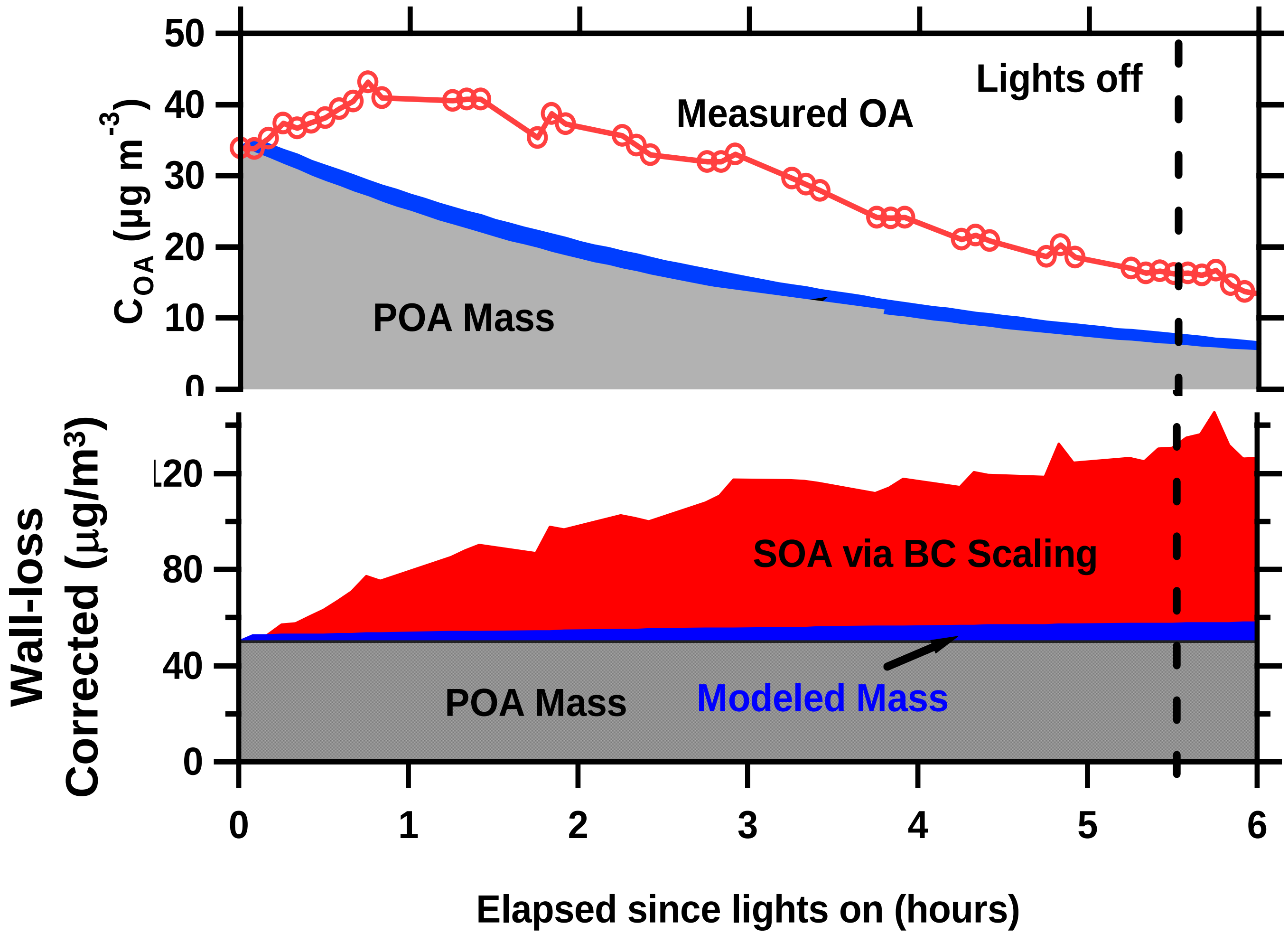


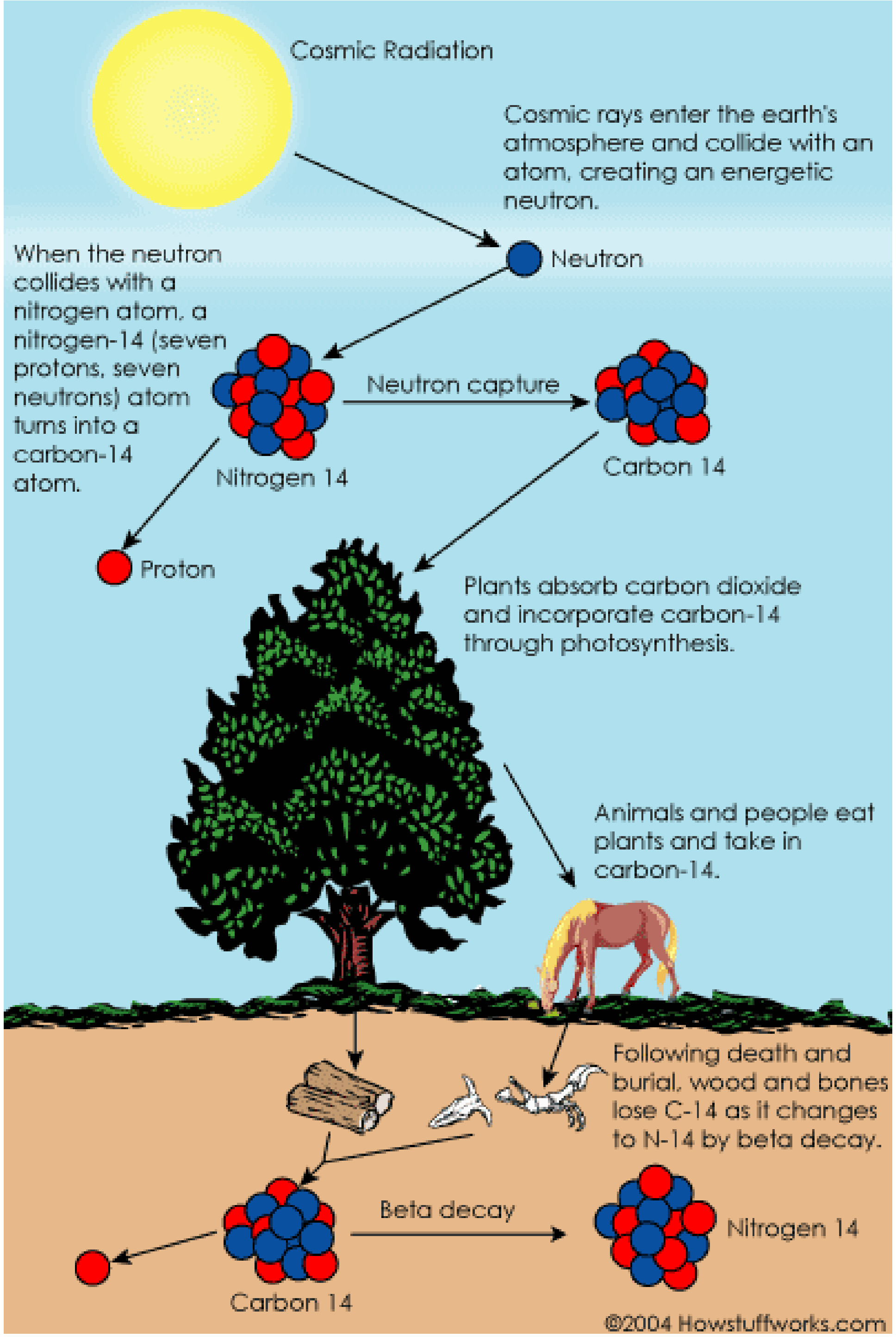
- A large fraction of ambient particulate carbon is secondary organic carbon (SOC) formed from emitted organic gases
- Source can be divided into a contemporary or fossil fraction
- Contemporary or biogenic carbon source include
  - Fires, SOC from vegetation, cooking, pollen, HULIS and others
- Fossil or “old” carbon arises from burning of fossil fuels

Sources of Organic Aerosol (OA)



Aging Rapidly Creates Lots of SOA

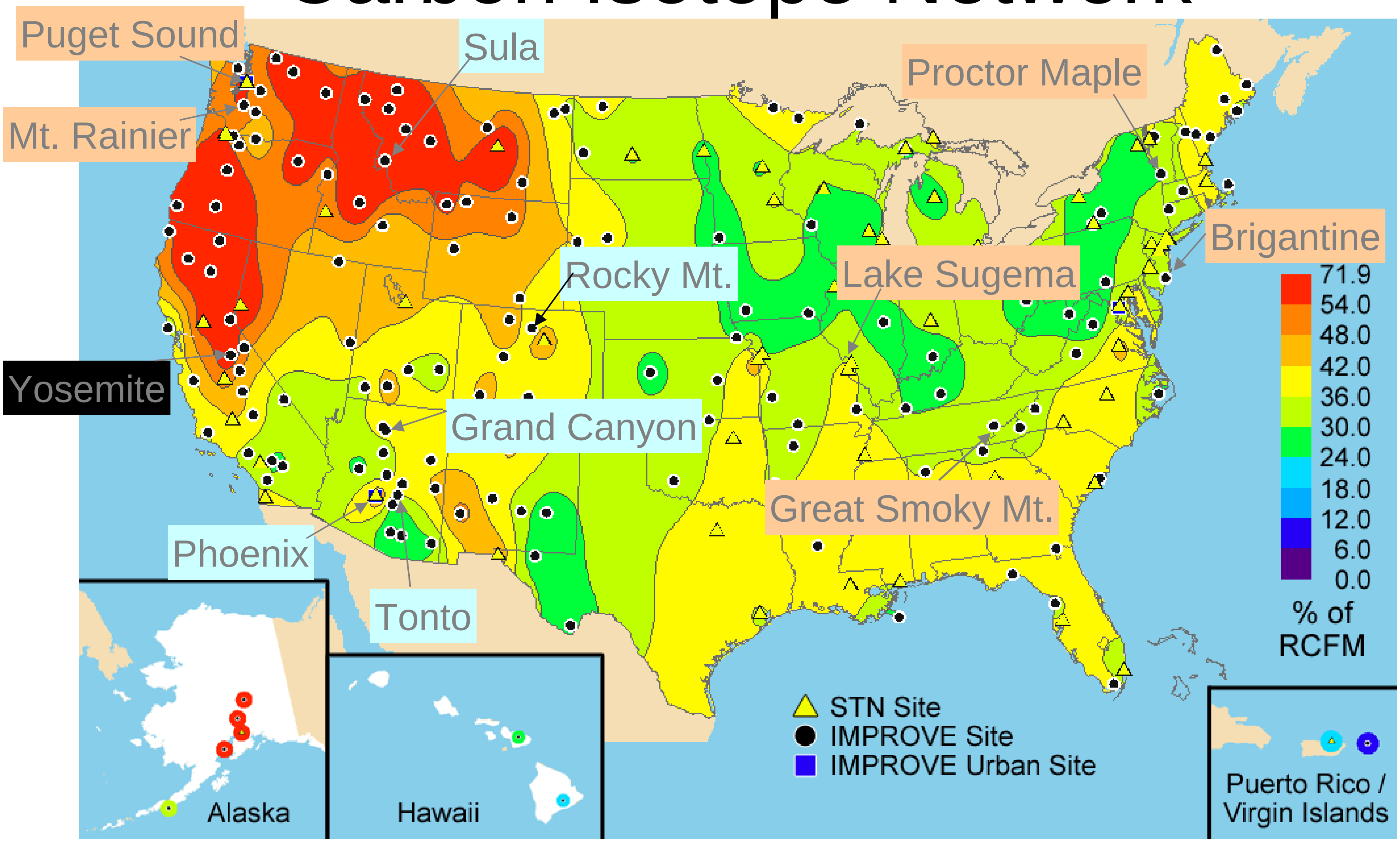




Radiocarbon Isotope (Carbon-14)

- The ratio of ^{14}C to ^{12}C in the air and in all living things is nearly constant
- ^{14}C half life ~ 5700 years
- Fossil carbon, e.g. oil, coal and gas, has no C-14
- $^{14}C/^{12}C$ can distinguish between fossil and contemporary (fires, cooking, road dust, pollen) in particulate carbon samples

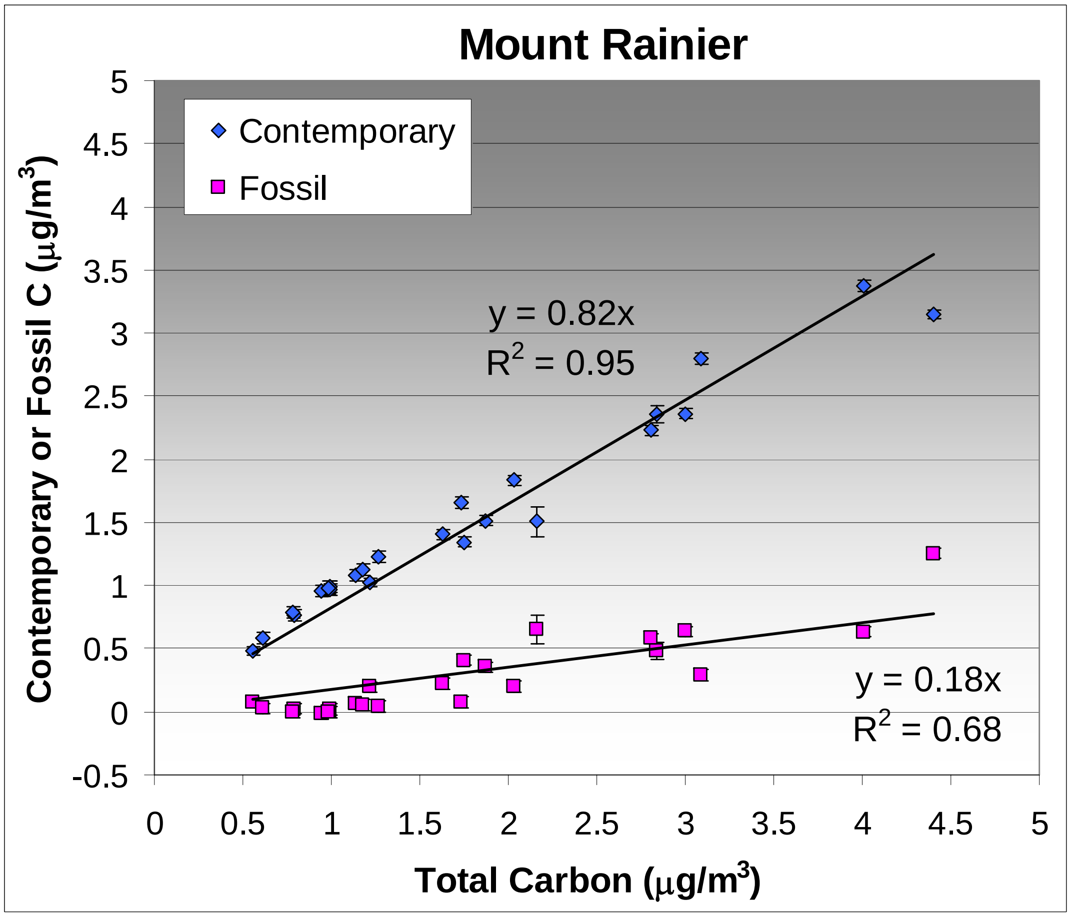
Carbon Isotope Network



Six day PM2.5 samples

- Summer: Jun – Aug '04; Winter: Dec '04 – Feb '05
- Summer: Jun – Aug '05; Winter: Dec '05 – Feb '06
- Summer: Jul – Aug '02

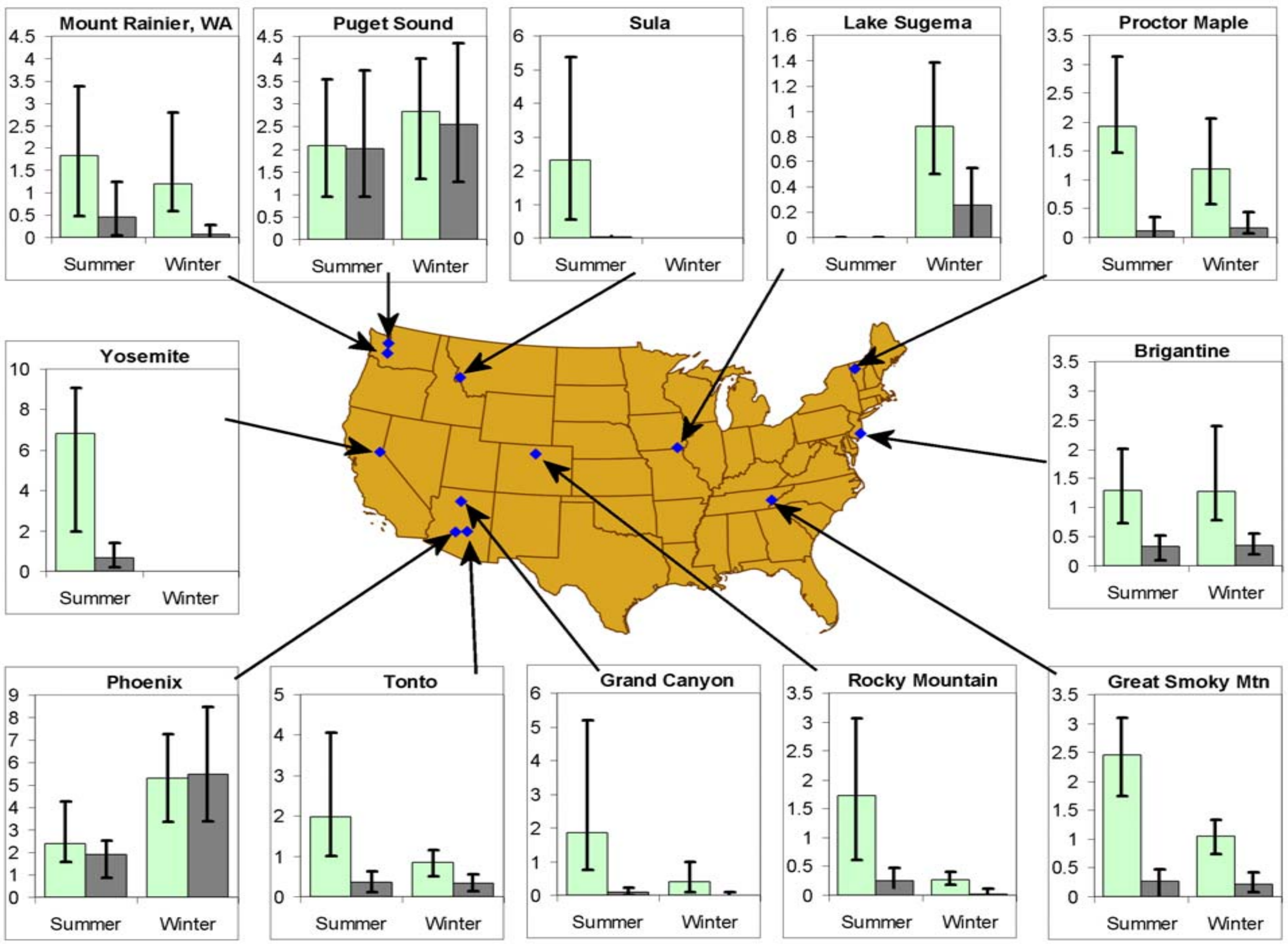
Contemporary (Biogenic) Vs Fossil Carbon



$$f_M = \frac{\left(C_{14}/C\right)_{Sample}}{\left(C_{14}/C\right)^{Biogenic}_{AD1950}}$$

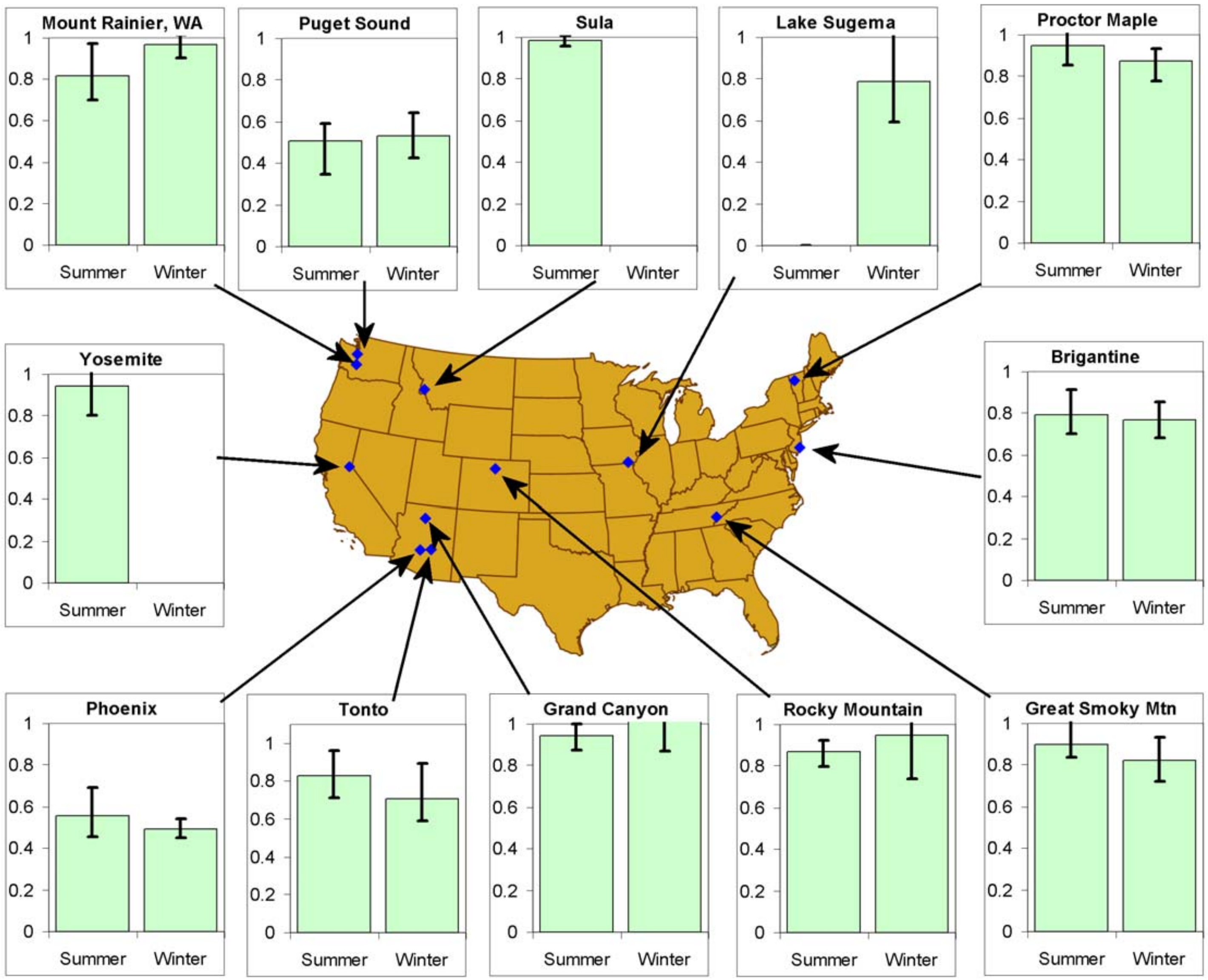
- C_{14} half life ~5000 yr
- f_M = 0 for fossil C
- f_M ~ 1.08 for biogenic C
- Fraction Contemporary = f_M/1.08
- Samples corrected for positive organic artifact on filters

Seasonal Contemporary and Fossil C ($\mu g/m^3$)



The error bars represent the range in six day concentrations

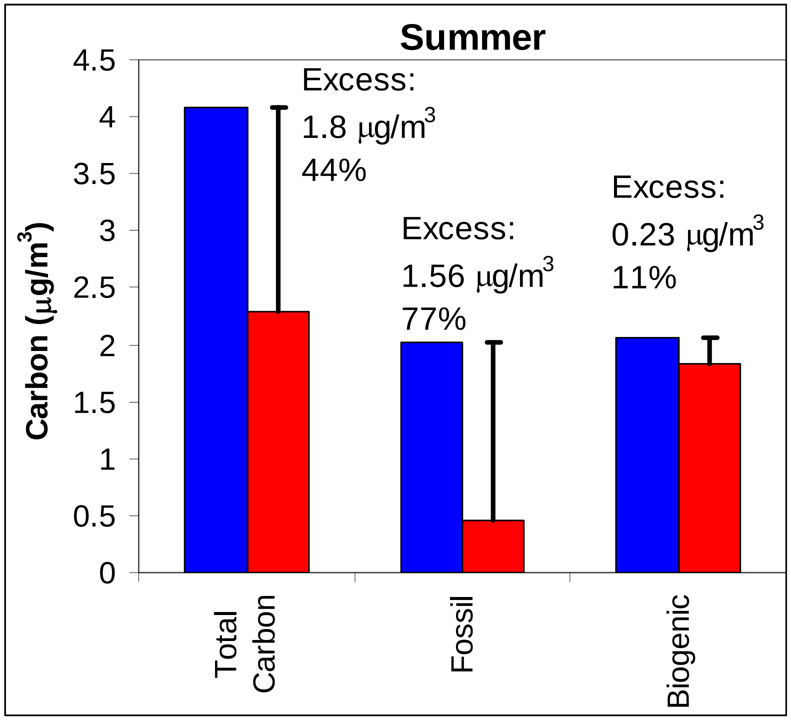
Seasonal Fraction Contemporary

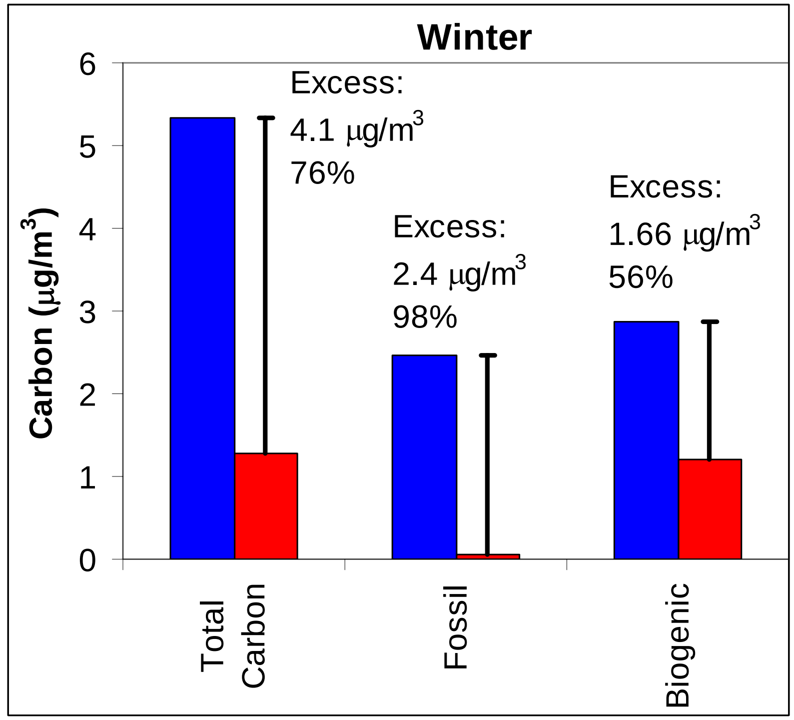


The error bars represent the fraction contemporary range

Urban Excess

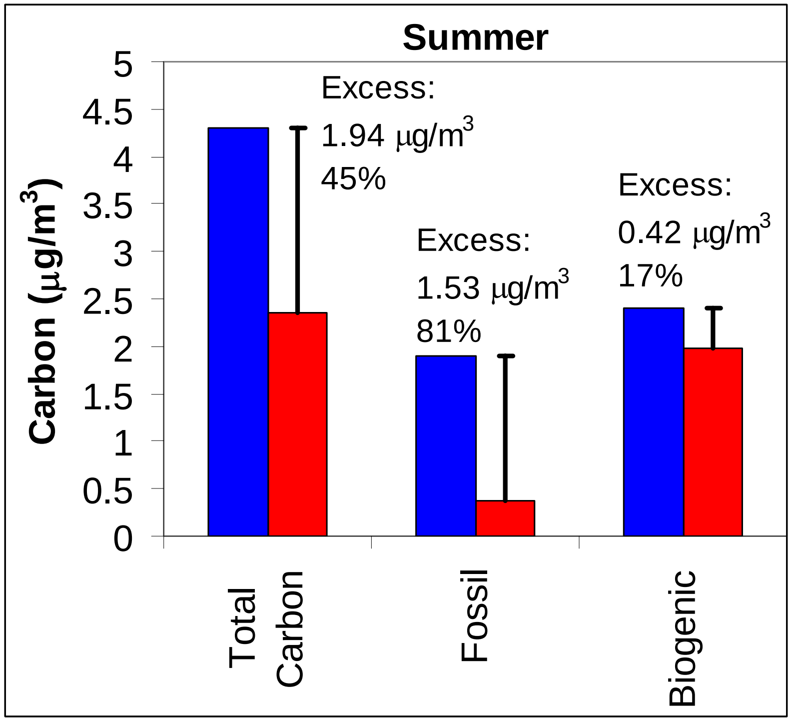
Puget Sound, WA (Blue) - Mount Rainier, WA (Red)

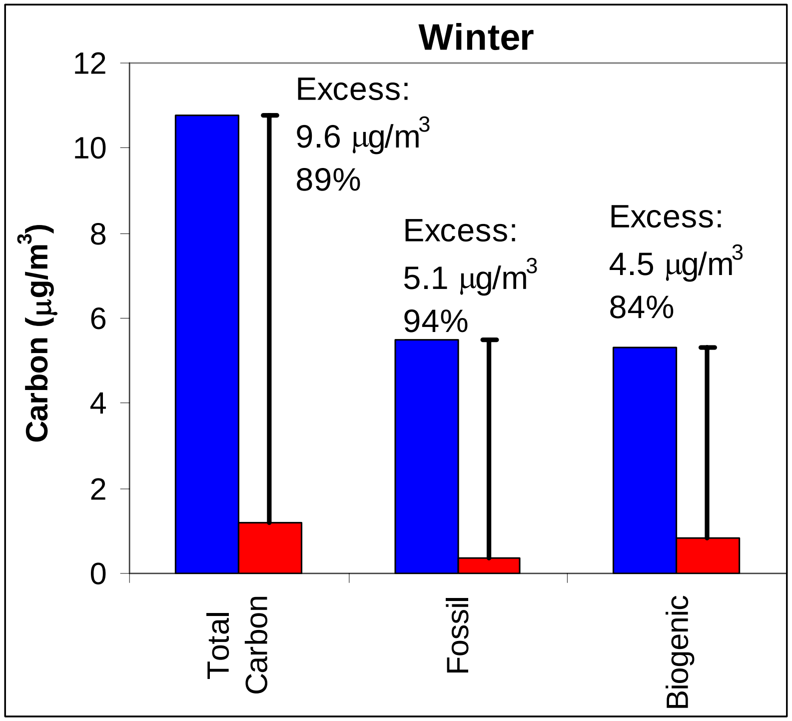




- Puget Sound fossil carbon is primarily due to local sources during winter and summer
- Summer biogenic carbon is regionally distributed
- ~40% of the winter urban excess is biogenic carbon
  - Not all biogenic carbon is “natural”

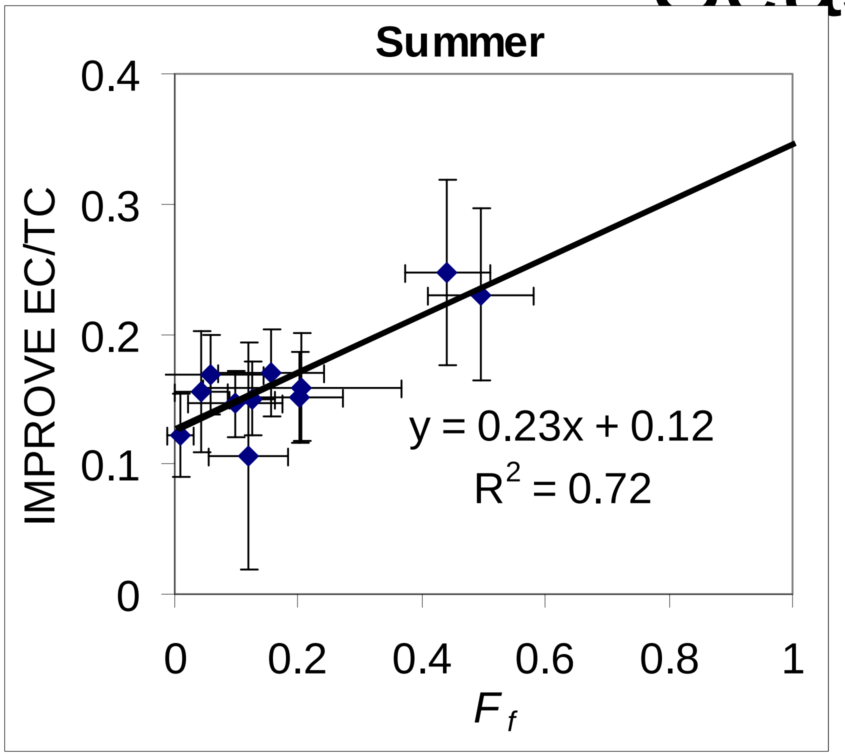
Urban Excess
Phoenix, AZ (Blue) – Tonto, AZ (Red)

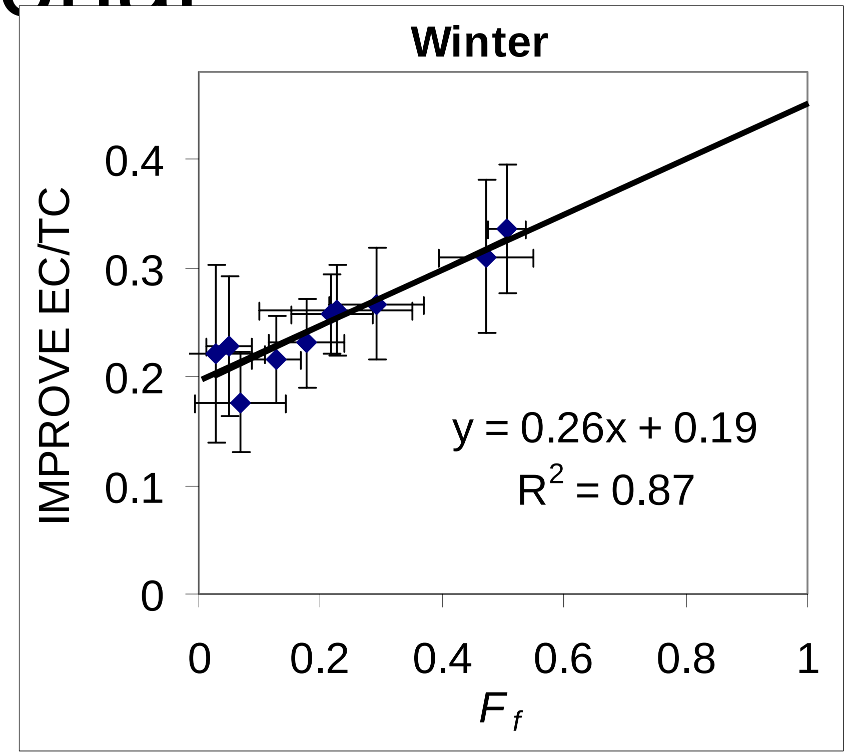




- Phoenix fossil carbon is primarily due to local sources during winter and summer
- Summer biogenic carbon is regionally distributed
- About half of the winter urban excess is biogenic carbon
  - Not all biogenic carbon is “natural”

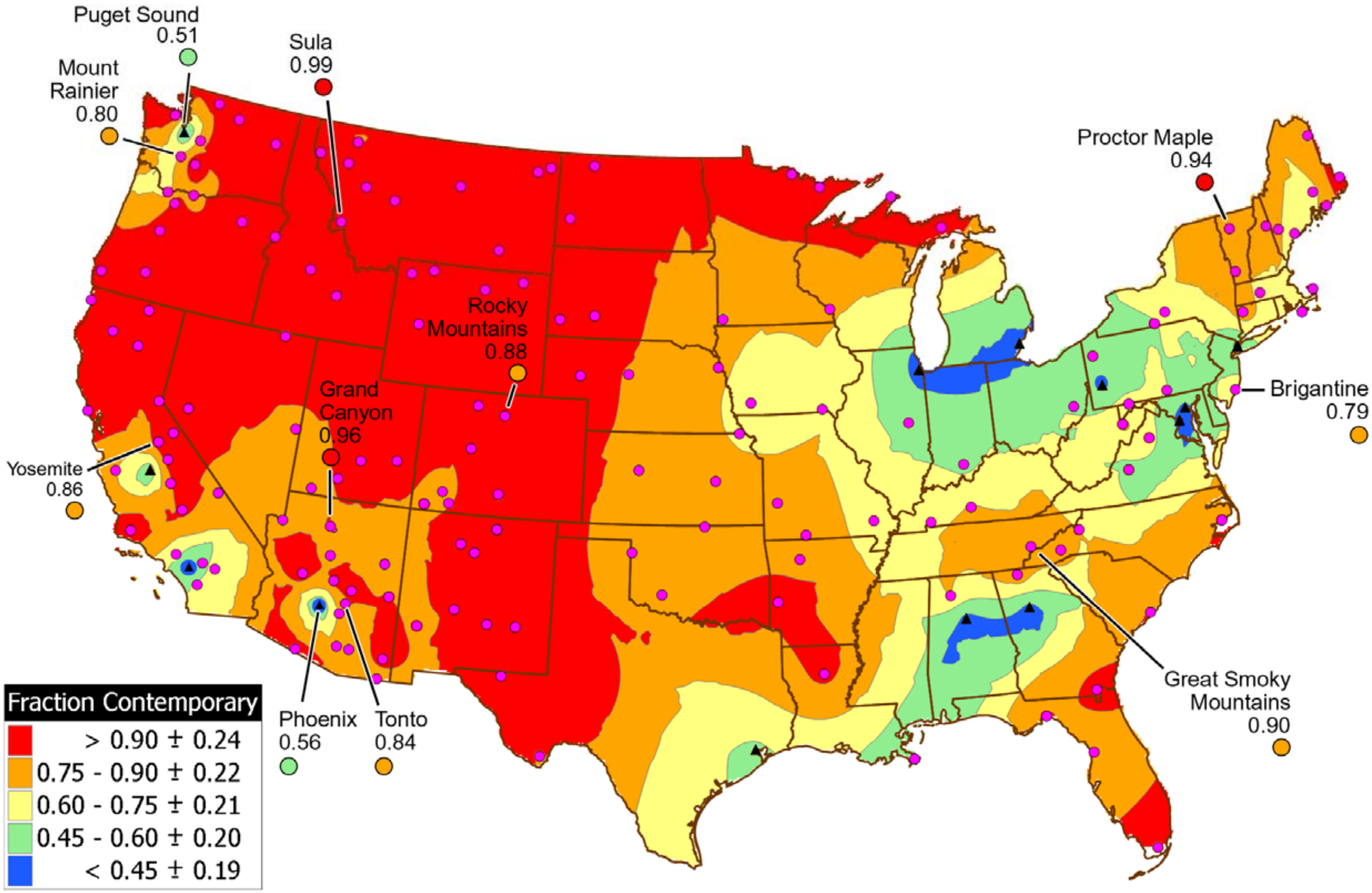
Fraction Biogenic Vs EC/TC - Seasonal





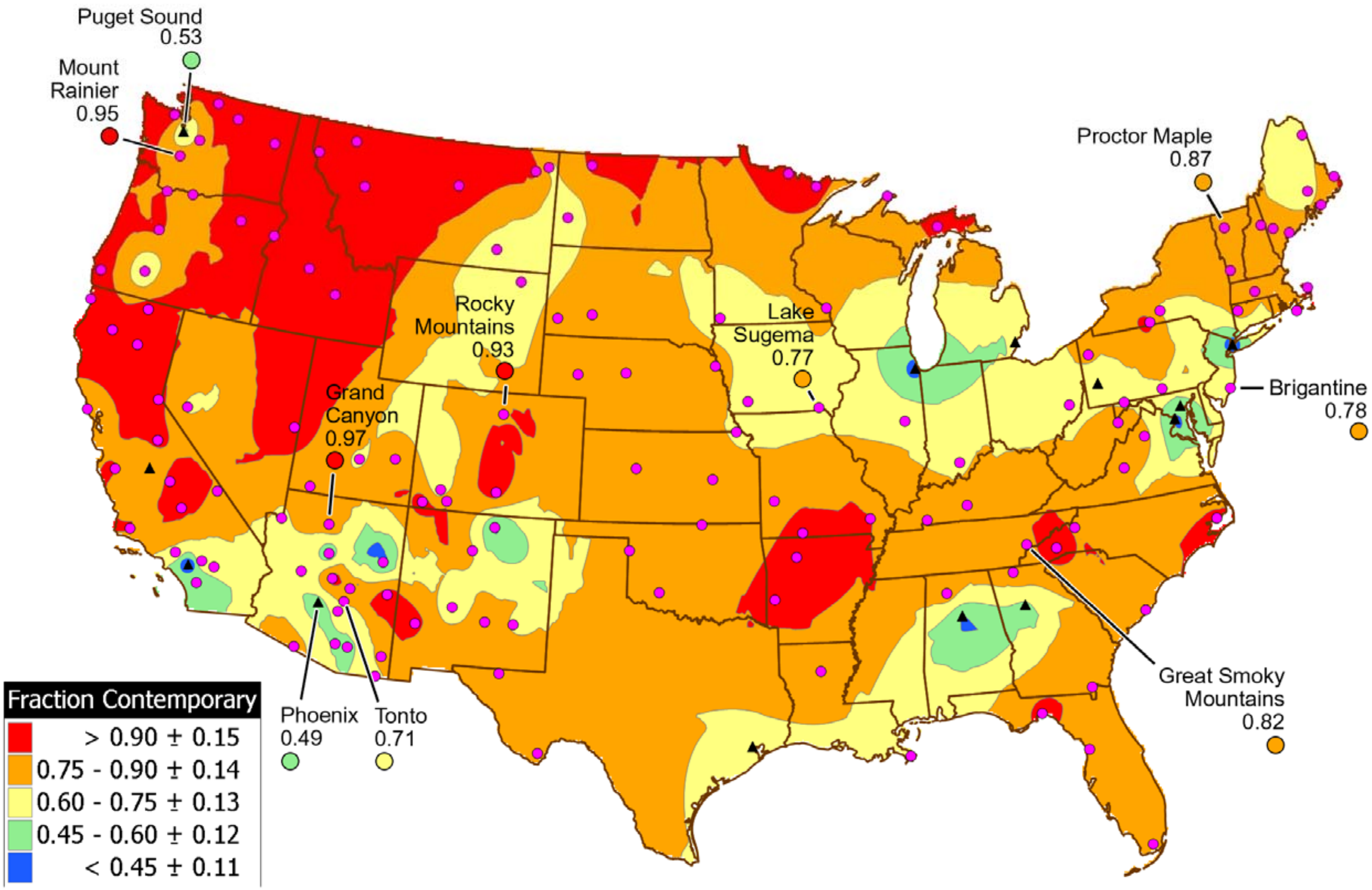
- Summer EC/TC
  - Fossil ~ 0.36
  - Biogenic ~ 0.12
- Winter EC/TC
  - Fossil ~ 0.45
  - Biogenic ~ 0.19

Fraction Biogenic - Summer 2004-05



The summer (June-August) IMPROVE carbon data were partitioned into fossil and biogenic carbon using the derived fossil and biogenic EC/TC ratios

Fraction Biogenic - Winter 2004-06



The summer (December - February) IMPROVE carbon data were partitioned into fossil and biogenic carbon using the derived fossil and biogenic EC/TC ratios

Estimating Secondary Organic Carbon (SOC)

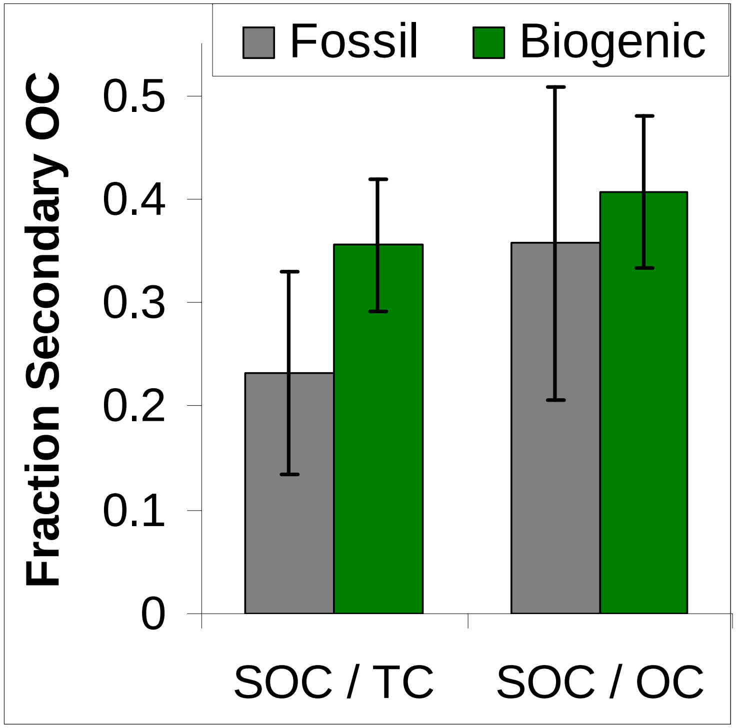
- Assume:
  - All elemental carbon is primary
  - Winter organic carbon is primary (PC)
  - Summer organic carbon is primary + secondary

$$\left(\frac{SOC}{PC}\right)_{Summer} = \frac{(EC/TC)_{Winter}}{(EC/TC)_{Summer}} - 1$$

$$\left(\frac{SOC}{TC}\right)_{Summer} = \frac{1}{(PC/SOC+1)}$$

$$\left(\frac{SOC}{OC}\right)_{Summer} = \frac{(SOC/TC)_{Summer}}{1-(EC/TC)_{Summer}} - 1$$

Contribution of Secondary Organic Carbon during the Summer

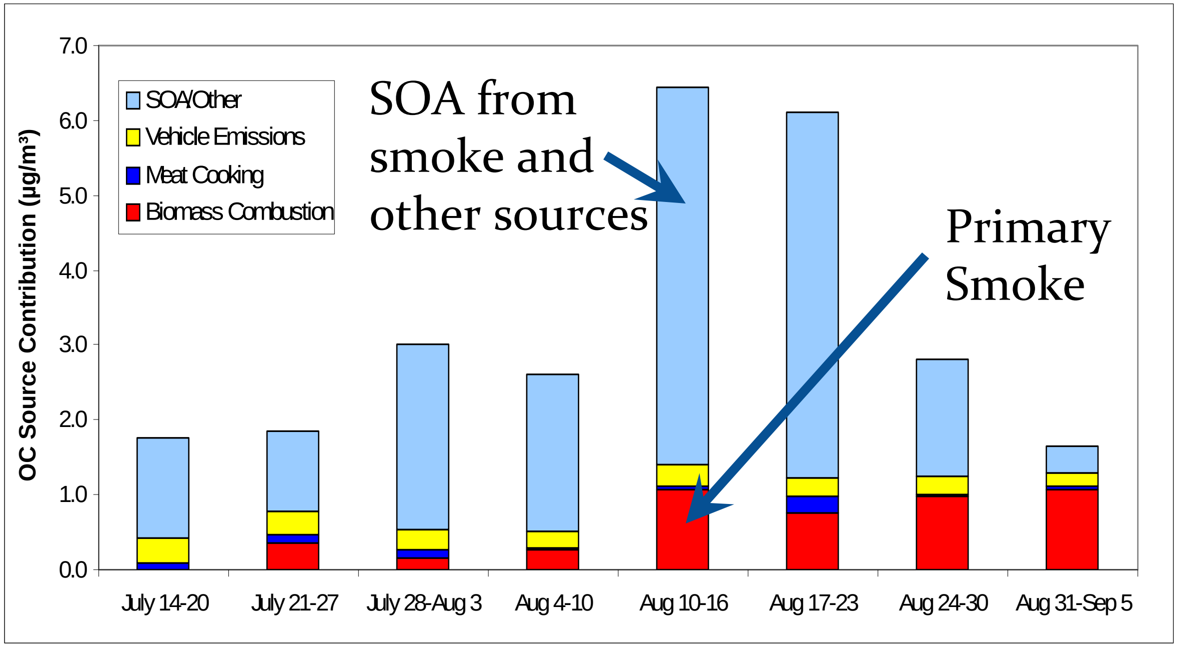


	Secondary TC	Secondary OC
Biogenic	36% (6.4)	41% (7.3)
Fossil	23% (10)	36% (15)

- Assumes all winter organic carbon is primary
  - Underestimates the summer secondary particulate carbon
- Assumes that a similar mix of sources contribute to the particulate carbon in the summer and winter.
  - Impact on estimate is unknown

Contributions from Biomass Burning

Smoke Impacting Yosemite NP Summer 2002



Biomass burning can have significant **primary** and **secondary** particulate carbon contributions

- Biogenic carbon accounts for
  - 80-95% of the total carbon at the rural sites
  - 70-80% of total carbon at near urban sites
  - 50% of total carbon at urban sites
- Little seasonality and total variation in fraction modern carbon
- Urban fossil carbon is primarily due to local sources during the winter and summer
- Summer biogenic carbon is regionally distributed
- 40-50% of the winter urban excess is biogenic carbon
  - Not all biogenic carbon is “natural”

- 42% or more of the summertime organic carbon is secondary
- 32% or more of the summertime fossil carbon is secondary

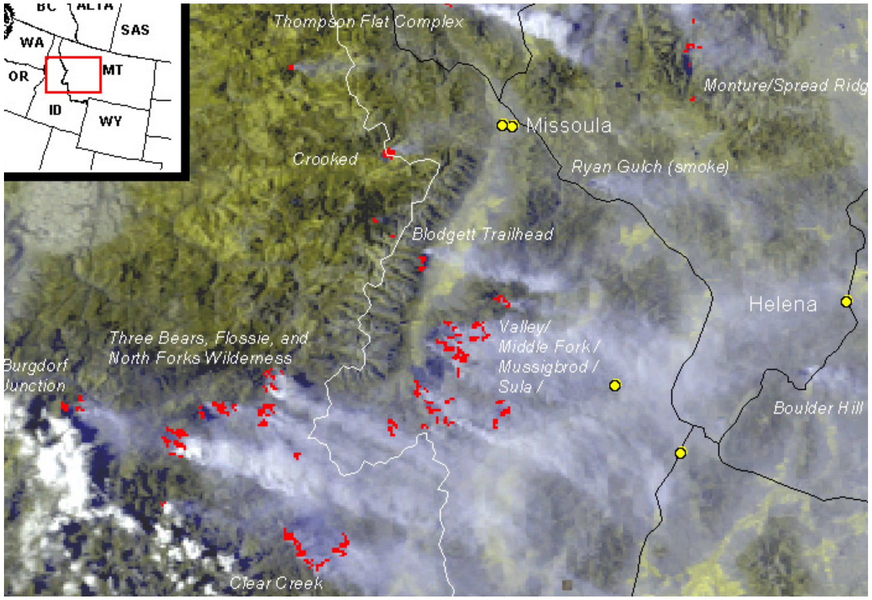
Sources of Carbon

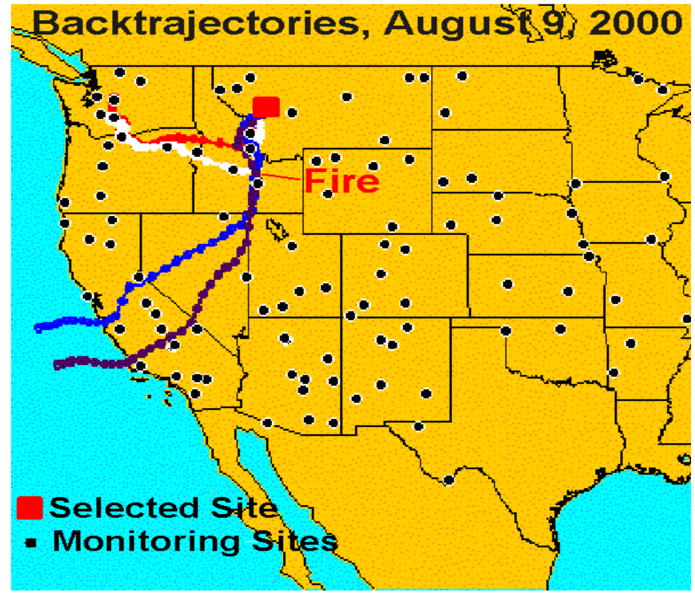
	Primary	Secondary
Biogenic	• Smoke - **<u>Wildfire</u>**, Agriculture and residential wood & open burning • Pollen • Soil • Cooking	• Smoke - **<u>Wildfire</u>**, Agriculture and residential wood & open burning • Vegetation
Fossil	• Combustion – **<u>Mobile</u> (Automobile, Diesel)** – **<u>Off Road Mobil</u>** – Oil/gas – Coal (power generation, industry)	• Combustion –**<u>Mobile</u> (Automobile, Diesel)** – **<u>Off Road Mobil</u>** – Oil/gas – Coal (power generation, industry) • Evaporative loss of

Other Effects Associated with fire emissions

- NOx emissions?
- NH3 emissions?
- VOC emissions?

Northern Rockies Wildfire Impacts





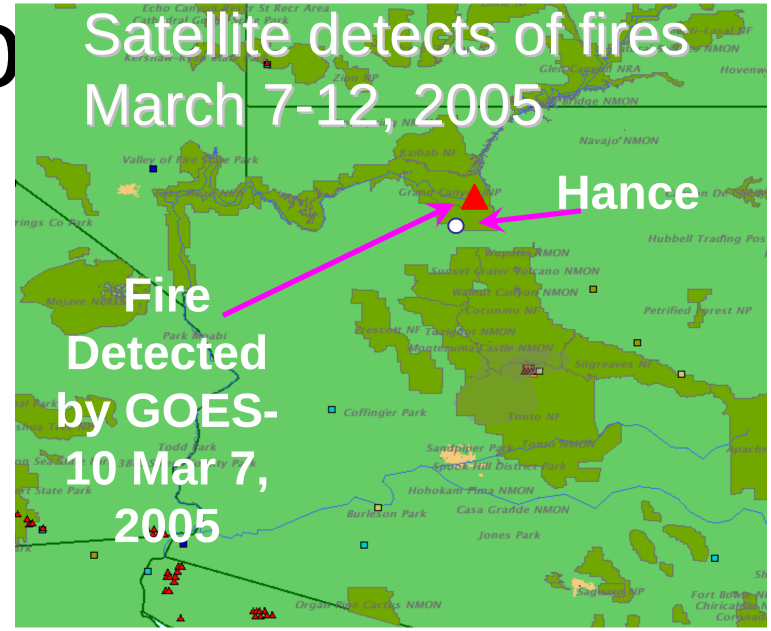
MONT1 8/9/2000 Fine Mass Composition

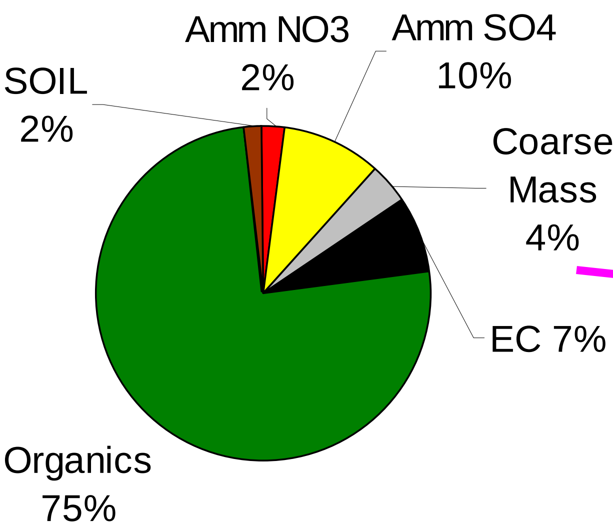
NH4NO3	1.06 ug/m3	0.9 %
(NH4)2SO4	0.25 ug/m3	0.2 %
OMC	108.0 ug/m3	92.9 %
EC	6.57 ug/m3	5.7 %
SOIL	0.36 ug/m3	0.3 %

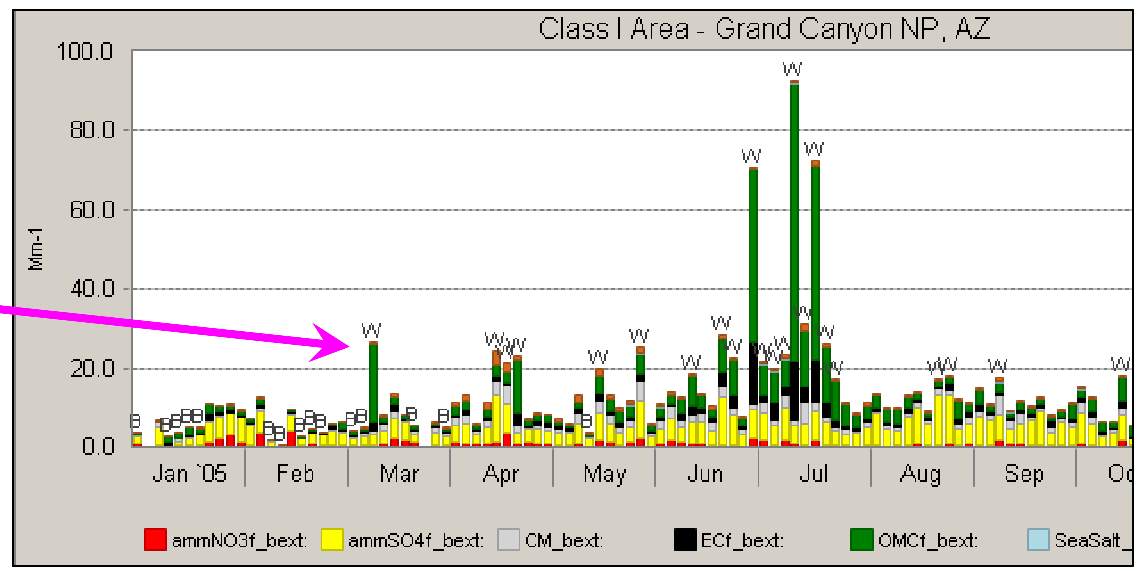
Total: 116.2 ug/m3

Prescribed Fire in the Grand

yo







Agricultural Fires

California Field

Oregon grass seed

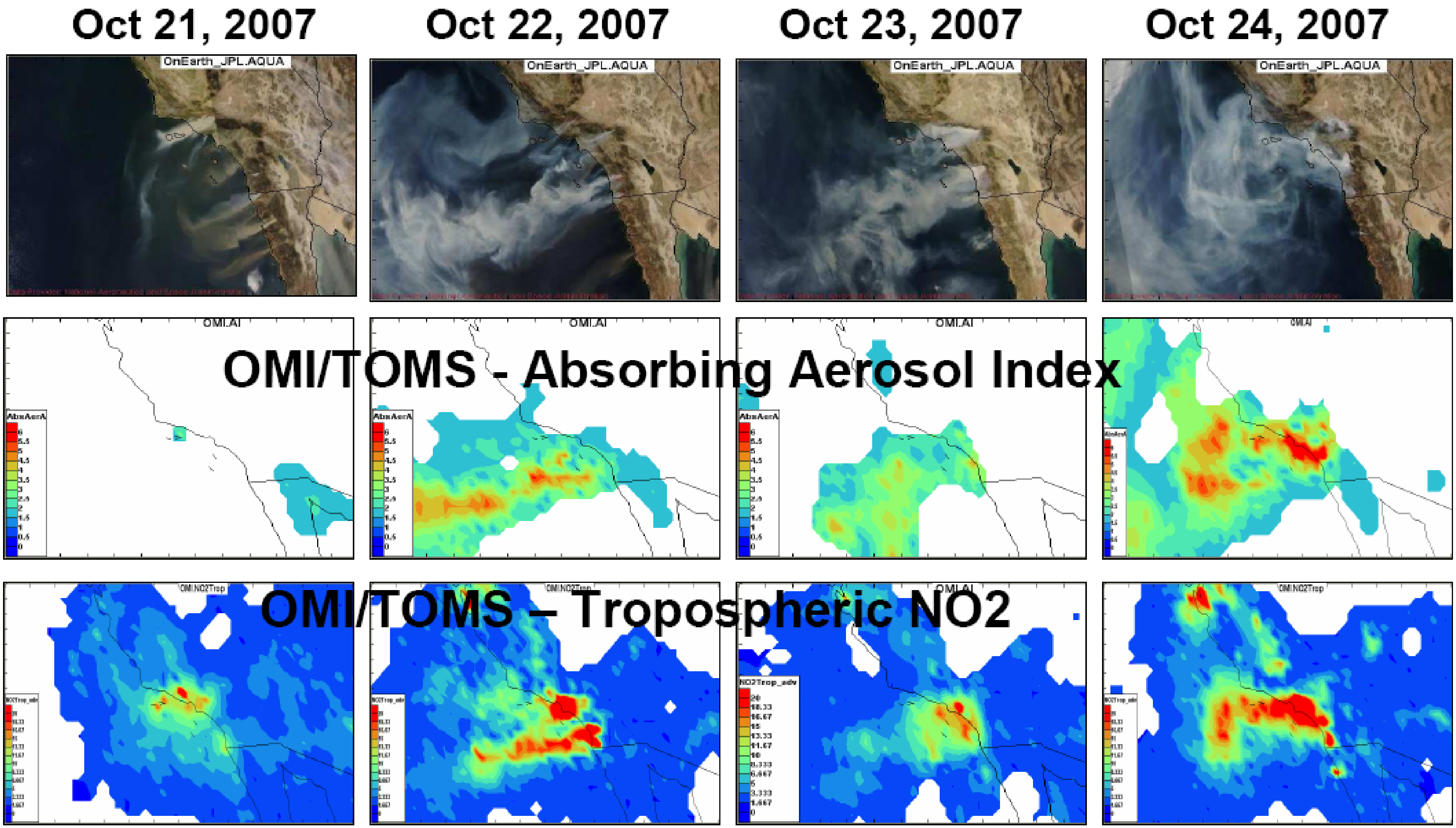
Idaho field burning

Wheat Field in Little Rock Arkansas

Are fires a significant source of Reactive Nitrogen?

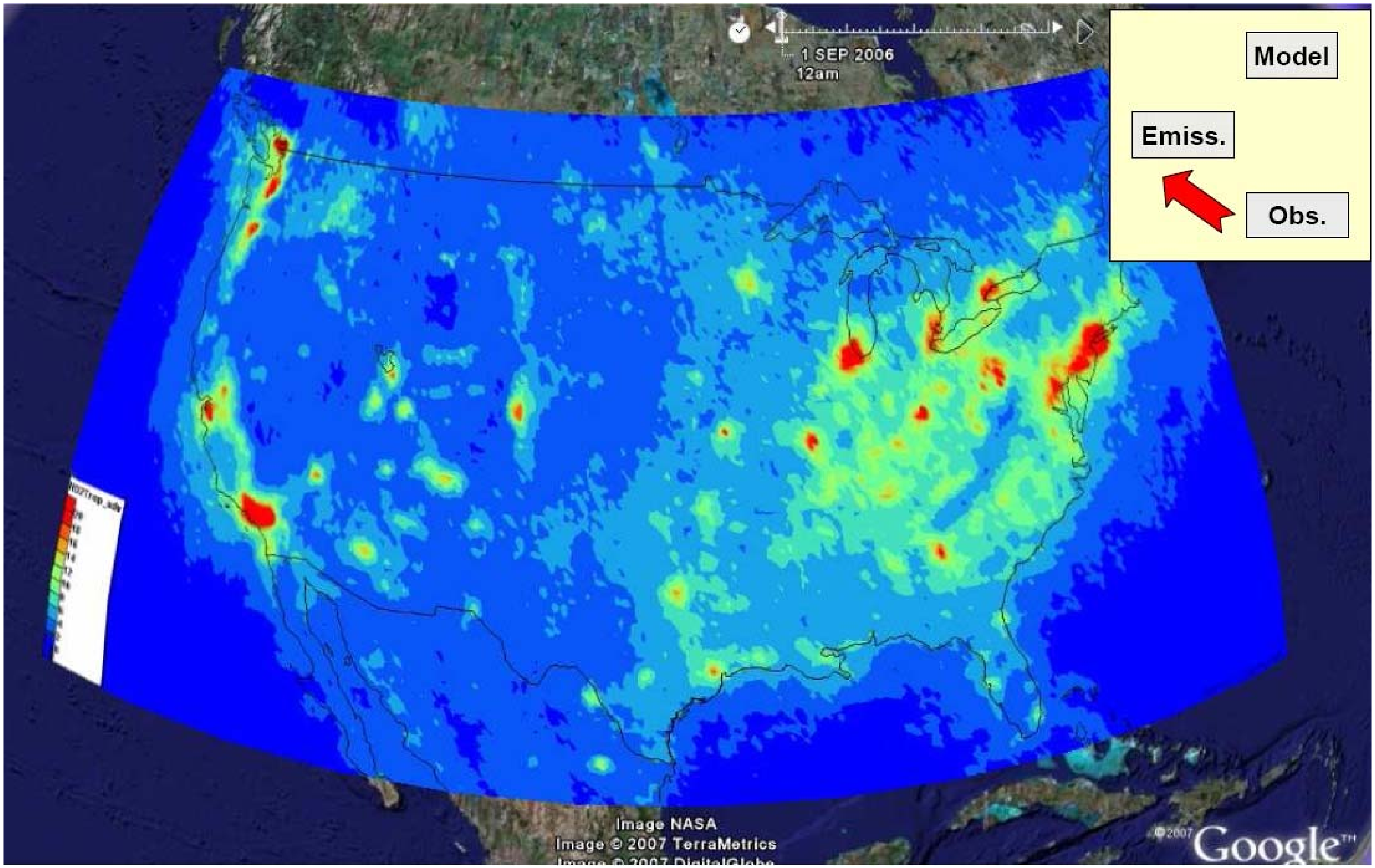
- 2002 WRAP emission inventory estimates small NO_x and NH_3 emission rates, < 2%.
- Is this right?

Southern California Fires



Husar et al., 2007

Tropospheric NO_2 from Space
OMI sensor on the AURA satellite platform

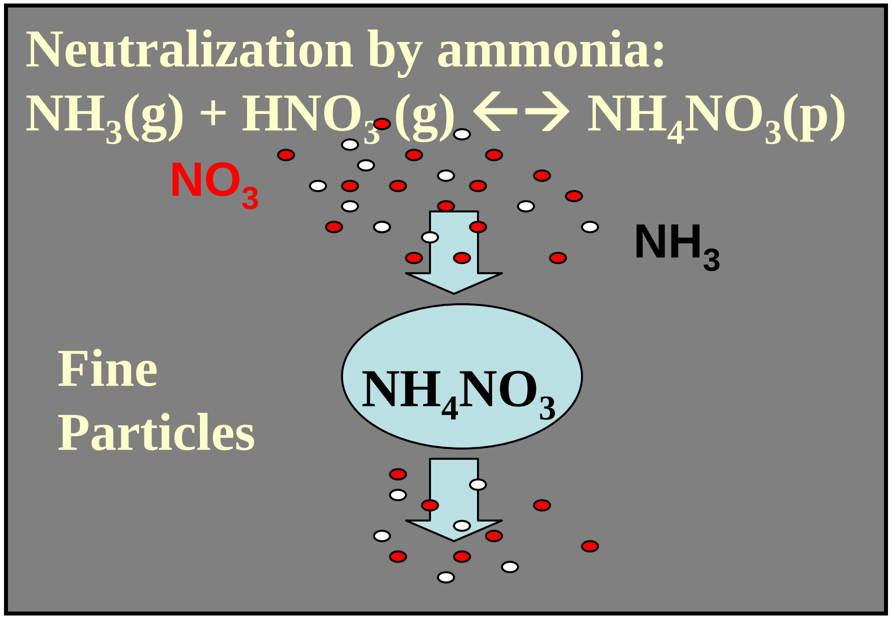


- Average Tropospheric NO_2 Concentrations (Husar et al, 2007)

Why Concern Over Ammonia?

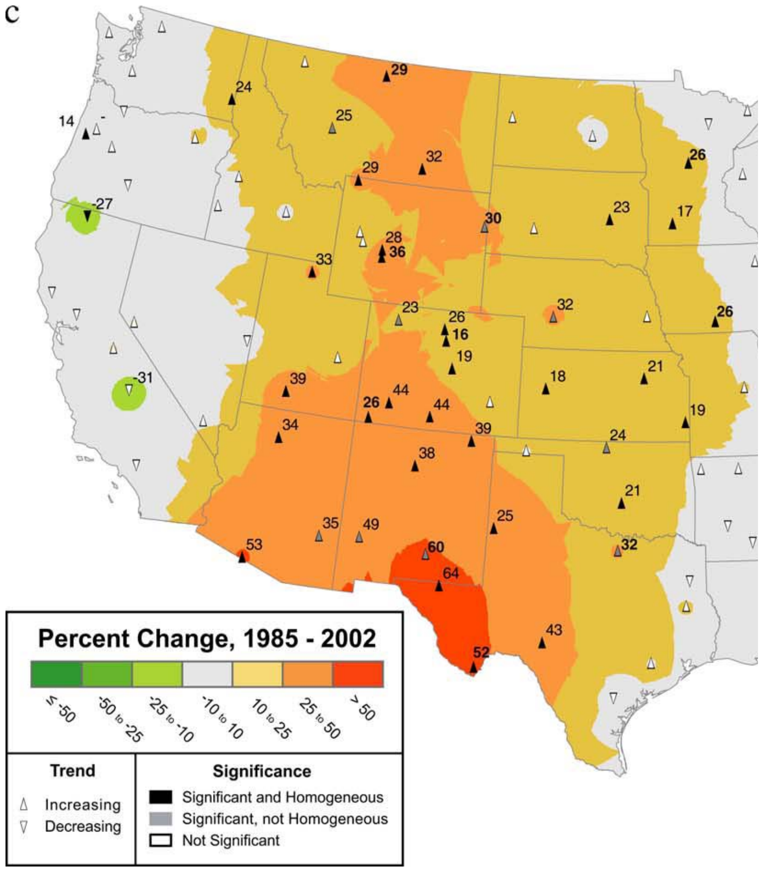
- Direct response of a basic gas neutralizing acidity in particles and gases. (neutralization of acidic sulfate aerosols – reaction with nitric acid vapor – reactions with organic salts)
- Response of PM formation can be dislocated from where ammonia reduction first took place.
- Ammonia deposition via cloud uptake and subsequent rain, dry deposition in the gas vs particle phase have vastly different time scales that leads to different lifetimes and particle response
- Large ecosystem effects (releases H^+, consumes O_2 and releases NO_2)

Atmospheric Nitrogen

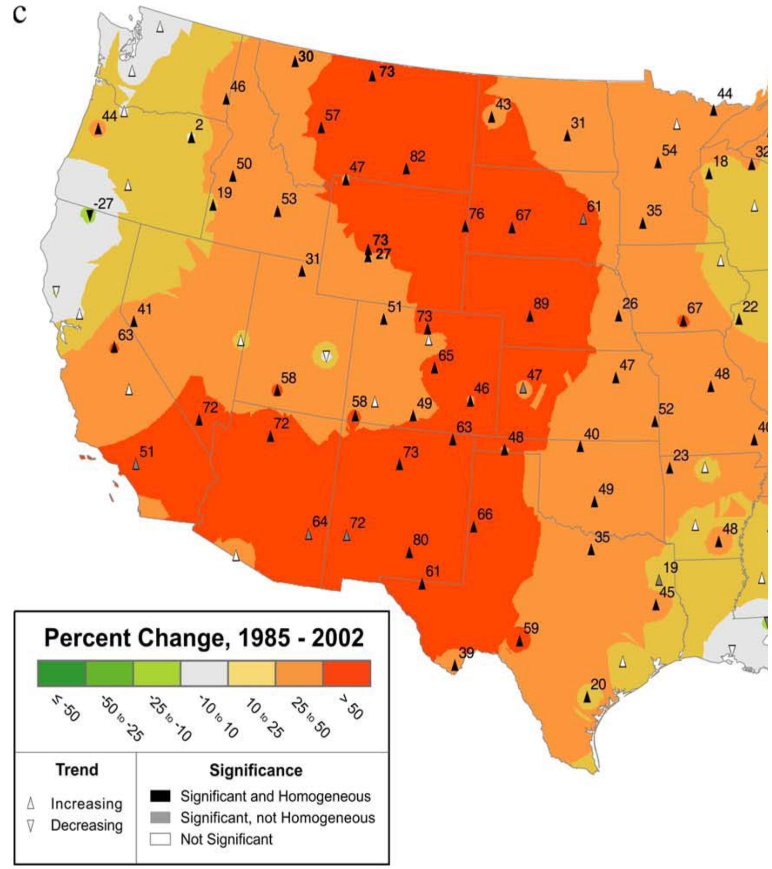


- **Nitrates are generally formed from the oxidation of NOx to nitric acid gas HNO_3**
- **Nitric acid is neutralized by NH_3 forming particulate nitrates**
- **OZONE!**

Are Fires Contributing to the Increasing Wet Nitrogen Deposition?

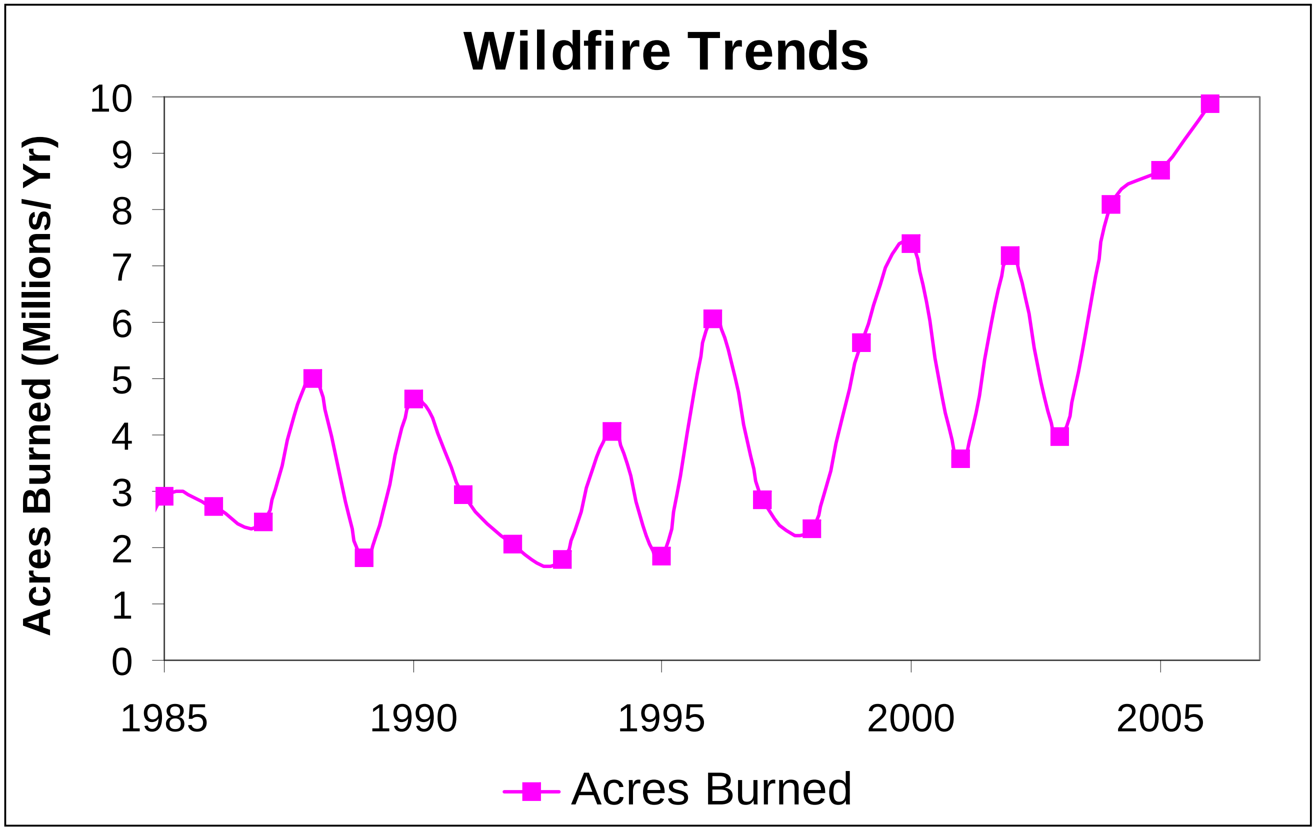


Wet nitrate concentration deposition trends

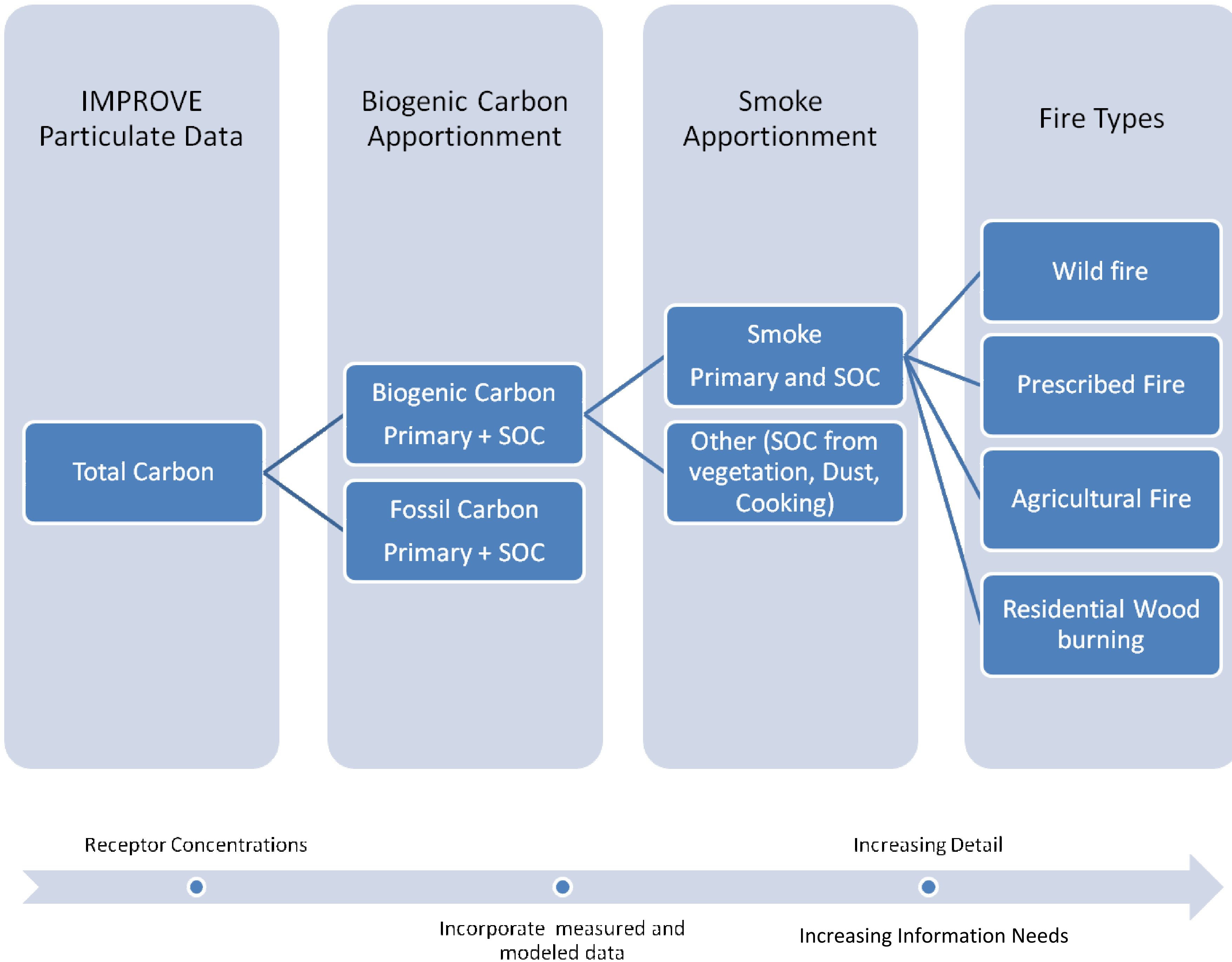


Wet ammonium concentration deposition trends

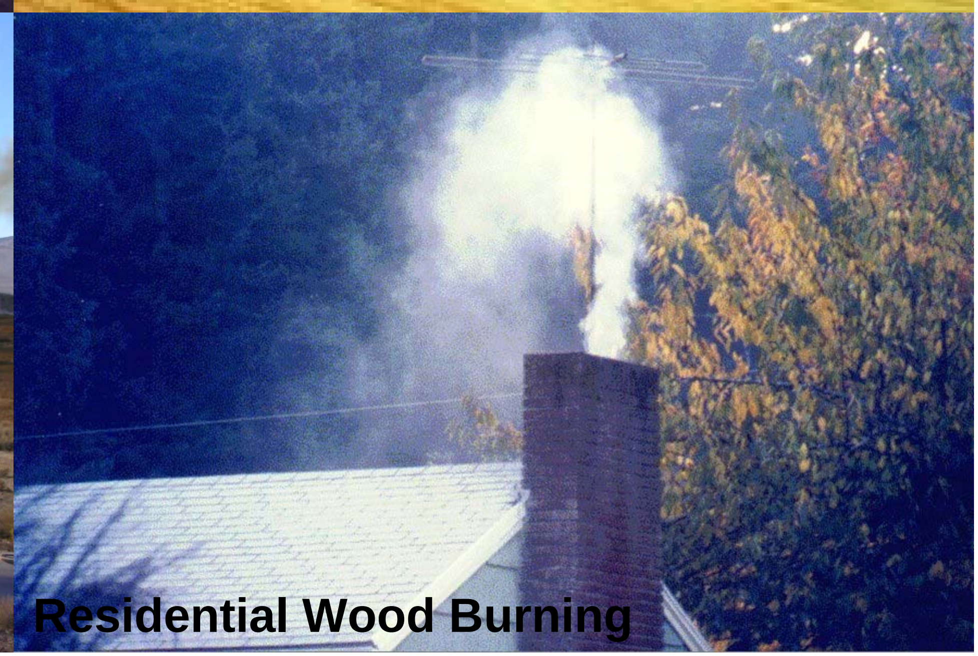
Are Fires Contributing to the Increasing Wet Nitrogen Deposition?



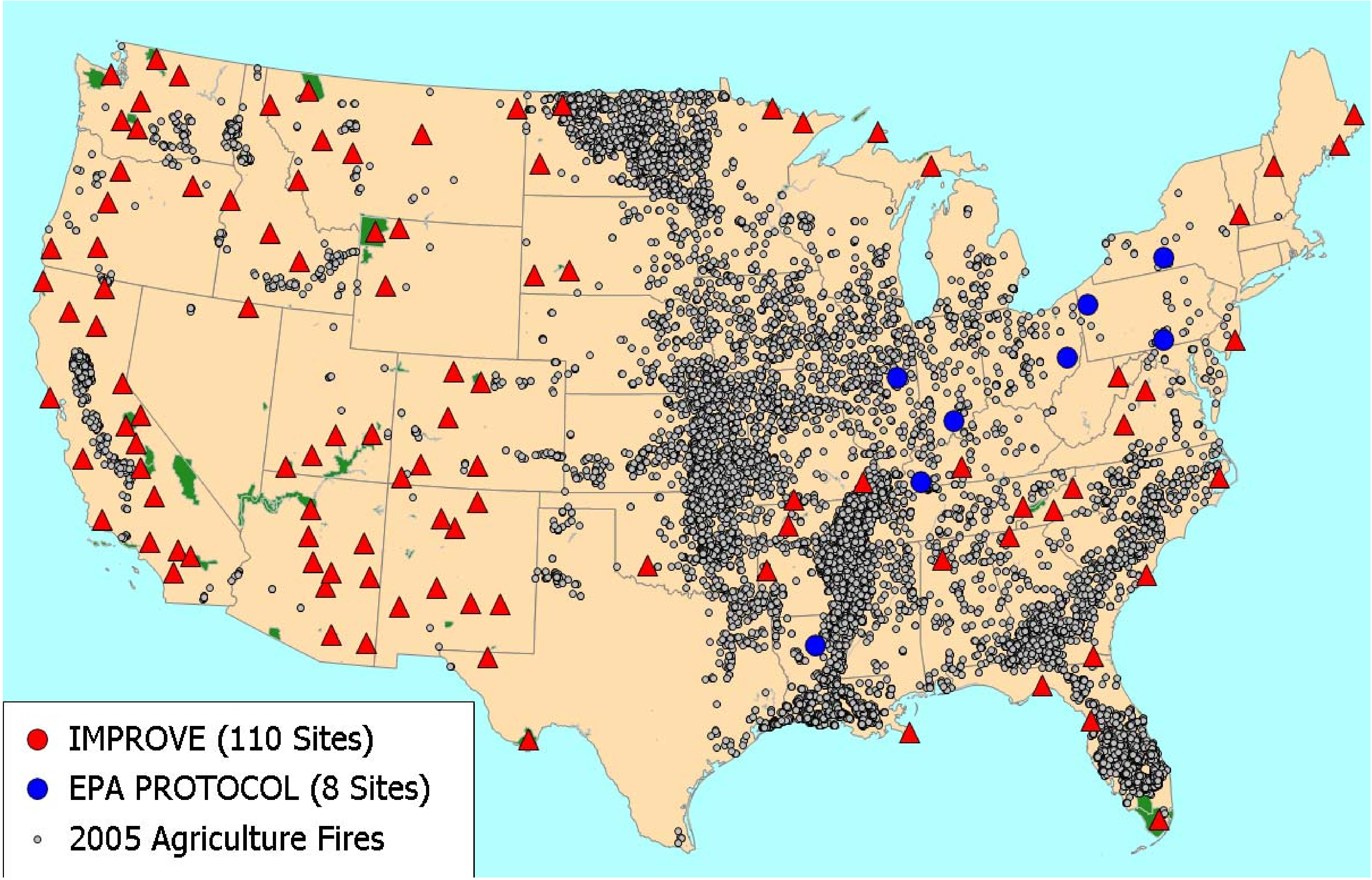
Fires emit reactive nitrogen and the acres burned throughout the western United states has been trending upward since 1995


IMPROVE Particulate Data
Biogenic Carbon Apportionment
Smoke Apportionment
Fire Types
Total Carbon
Biogenic Carbon Primary + SOC
Fossil Carbon Primary + SOC
Smoke Primary and SOC
Other (SOC from vegetation, Dust, Cooking)
Wild fire
Prescribed Fire
Agricultural Fire
Residential Wood burning
Receptor Concentrations
Incorporate measured and modeled data
Increasing Detail
Increasing Information Needs

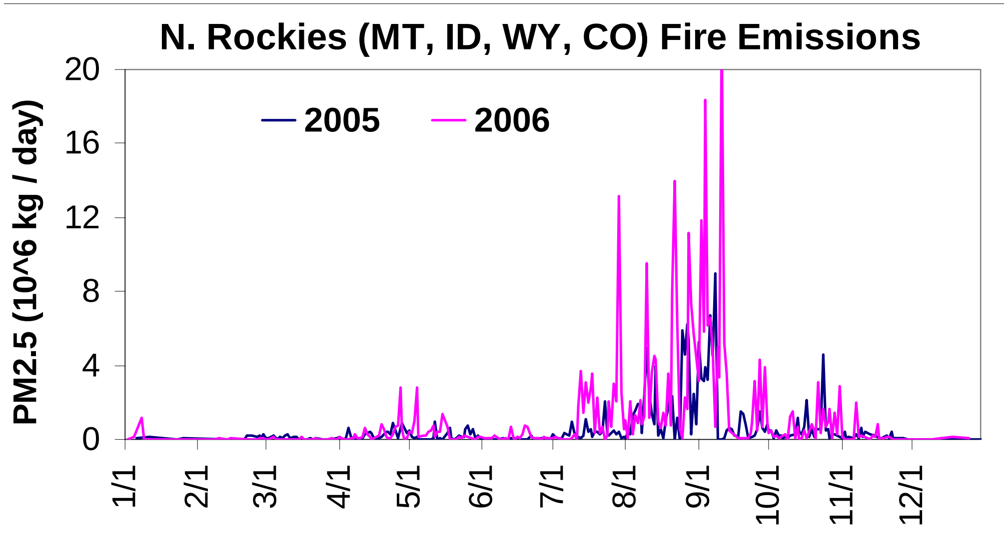
Contribution of Fires to Particulate



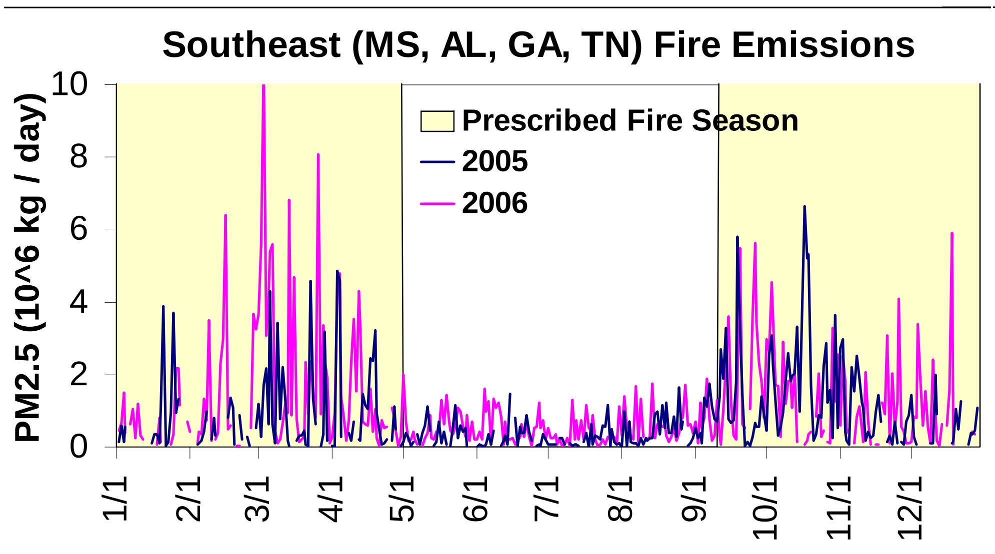
2005 Agricultural Fires

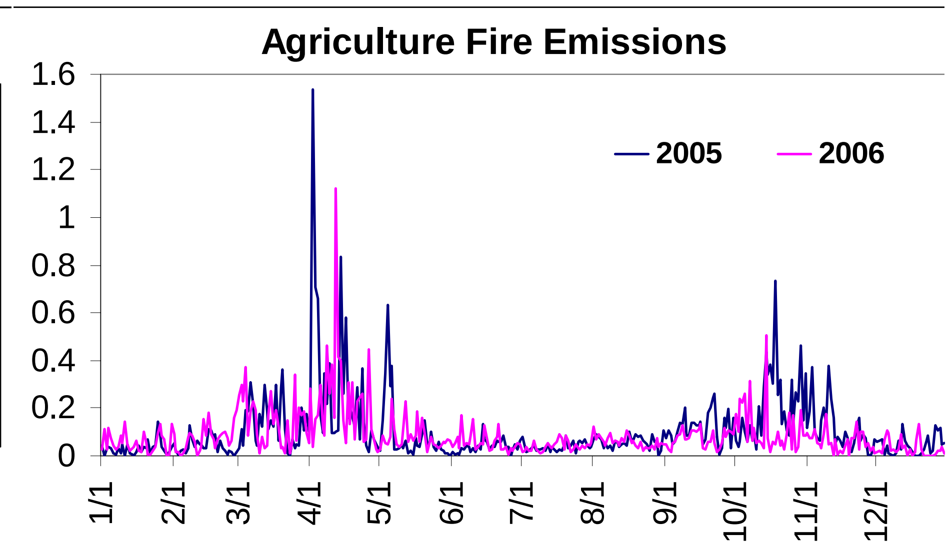


Fire Emission Seasons and geography



- Wildfires occur predominately in the west during June – September
- Prescribed and agricultural fires occur in cool months
- Prescribed fire is prevalent in the southeast





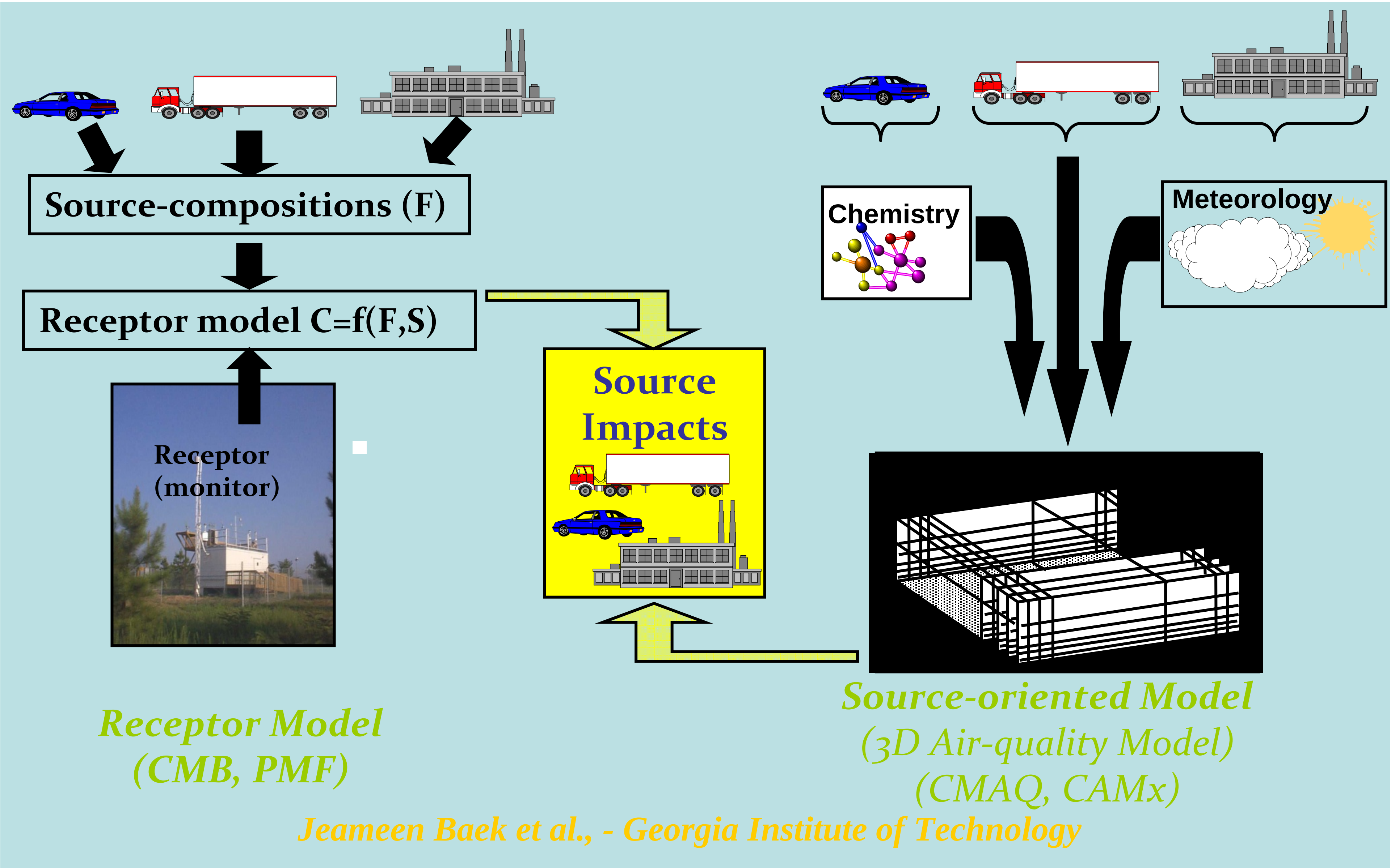
Smoke Management Needs for Air Quality Regulations

- **Develop an unambiguous <u>routine</u> and <u>cost effective</u> methodology for apportioning primary and secondary carbonaceous compounds in PM2.5 RETROSPECTIVELY to prescribed, wildfire, agricultural fire, and residential wood burning activities**
  - Daily contributions needed for Haze Rule to properly estimate natural contribution and contribution to worst 20% haze days
  - Annual and daily contributions needed for PM2.5 and PM10 NAAQS
  - Long term data needed to assess successes of smoke management policies
- **Similar needs for ozone and reactive nitrogen deposition issues**

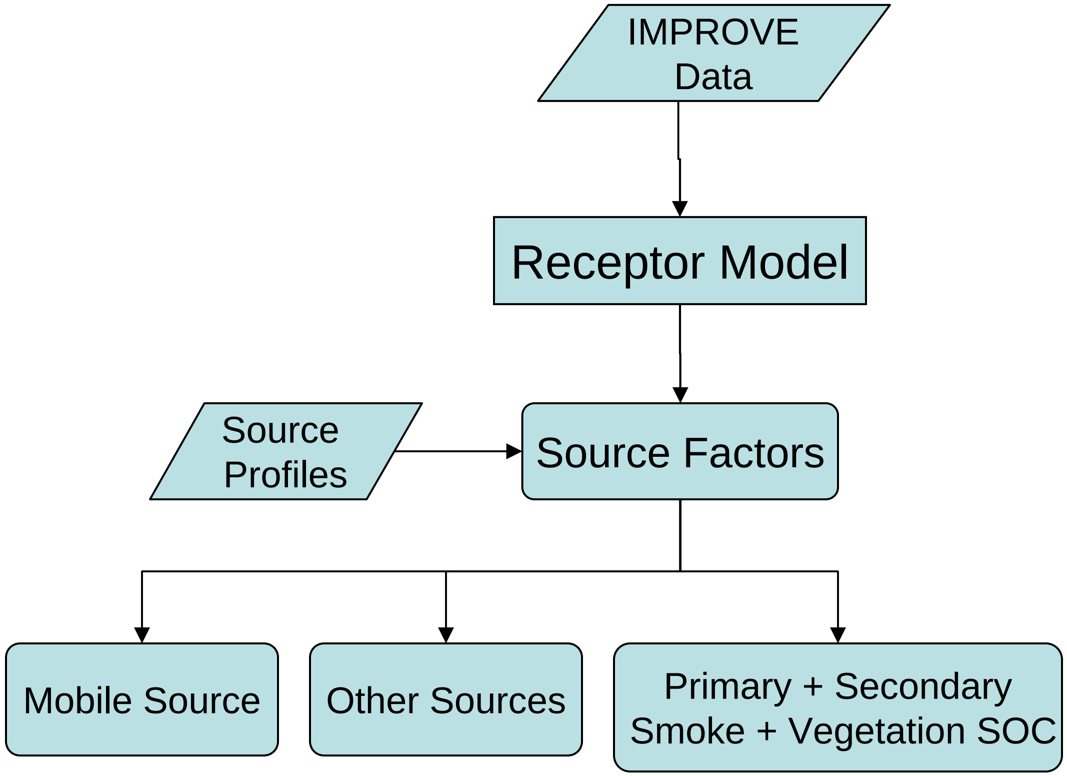
Developing a Retrospective Smoke Apportionment System

- Source apportionment system to estimate the contribution of primary and secondary smoke from different types of fire
  - Primary Smoke
    - Cheap and easy smoke markers species (Levoglucosan) measurements methods applicable in routine monitoring programs
    - Smoke source profiles for agricultural and wildland fuel types
  - Secondary Smoke and Smoke Types
    - Hybrid source apportionment model - Statistical model for integrating deterministic modeling results and measured data

Hybrid Source Apportionment Model

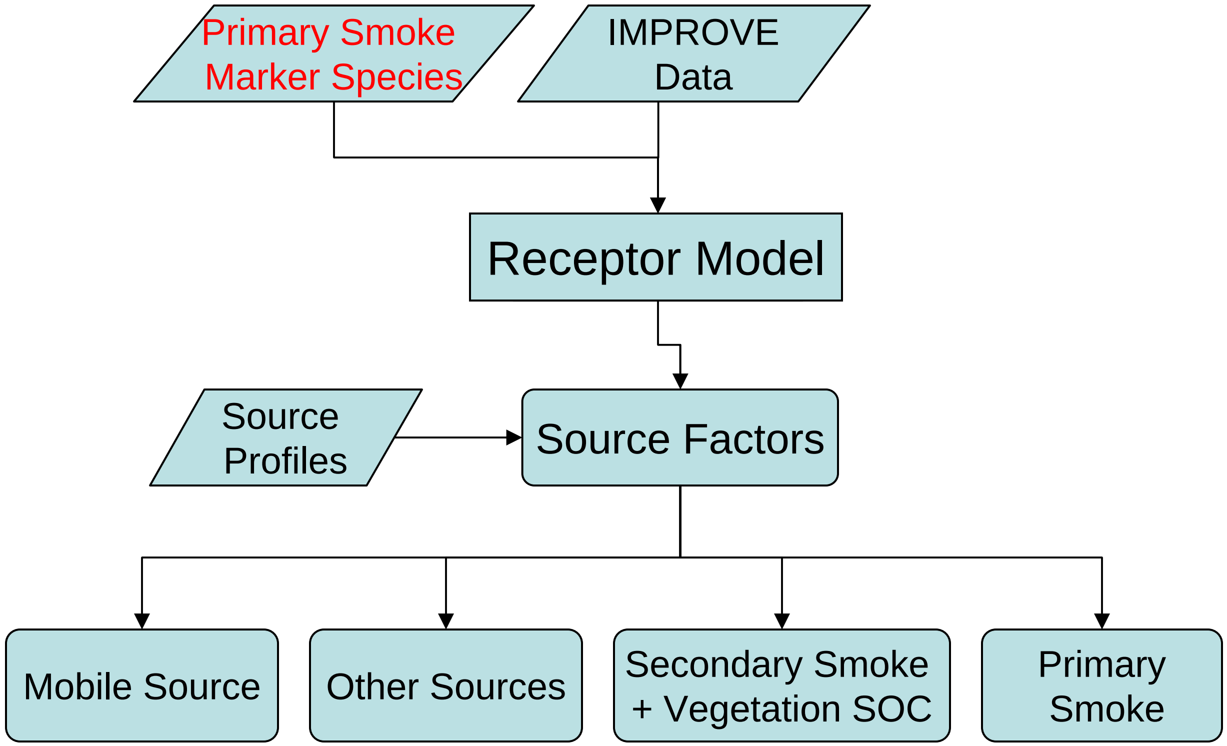


Smoke Apportion: Receptor Modeling



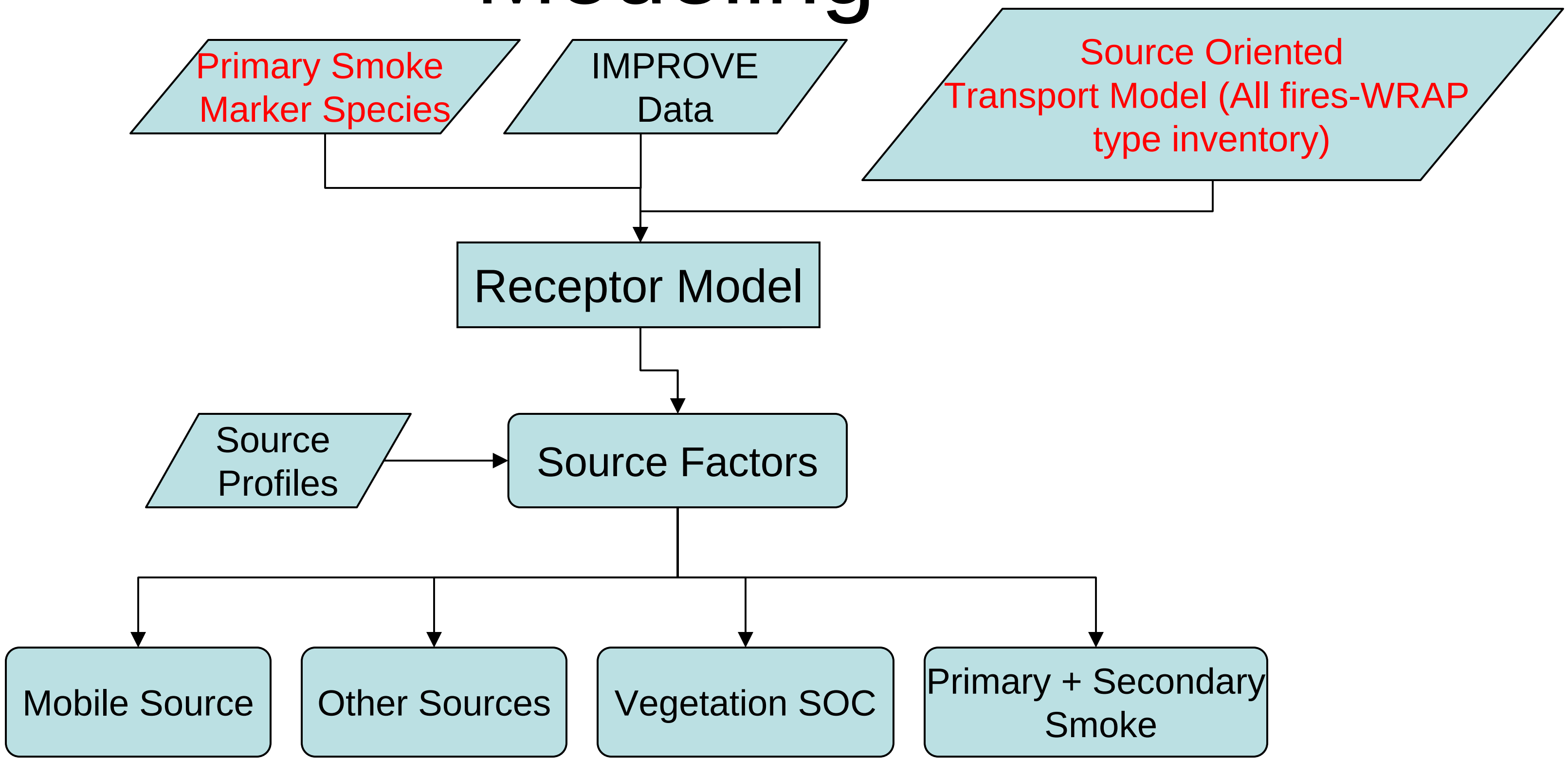
- PMF type models with IMPROVE data retrieves a smoke/SOA factor – dominate contributor to contemporary carbon in rural areas

Smoke Apportion: Receptor Modeling



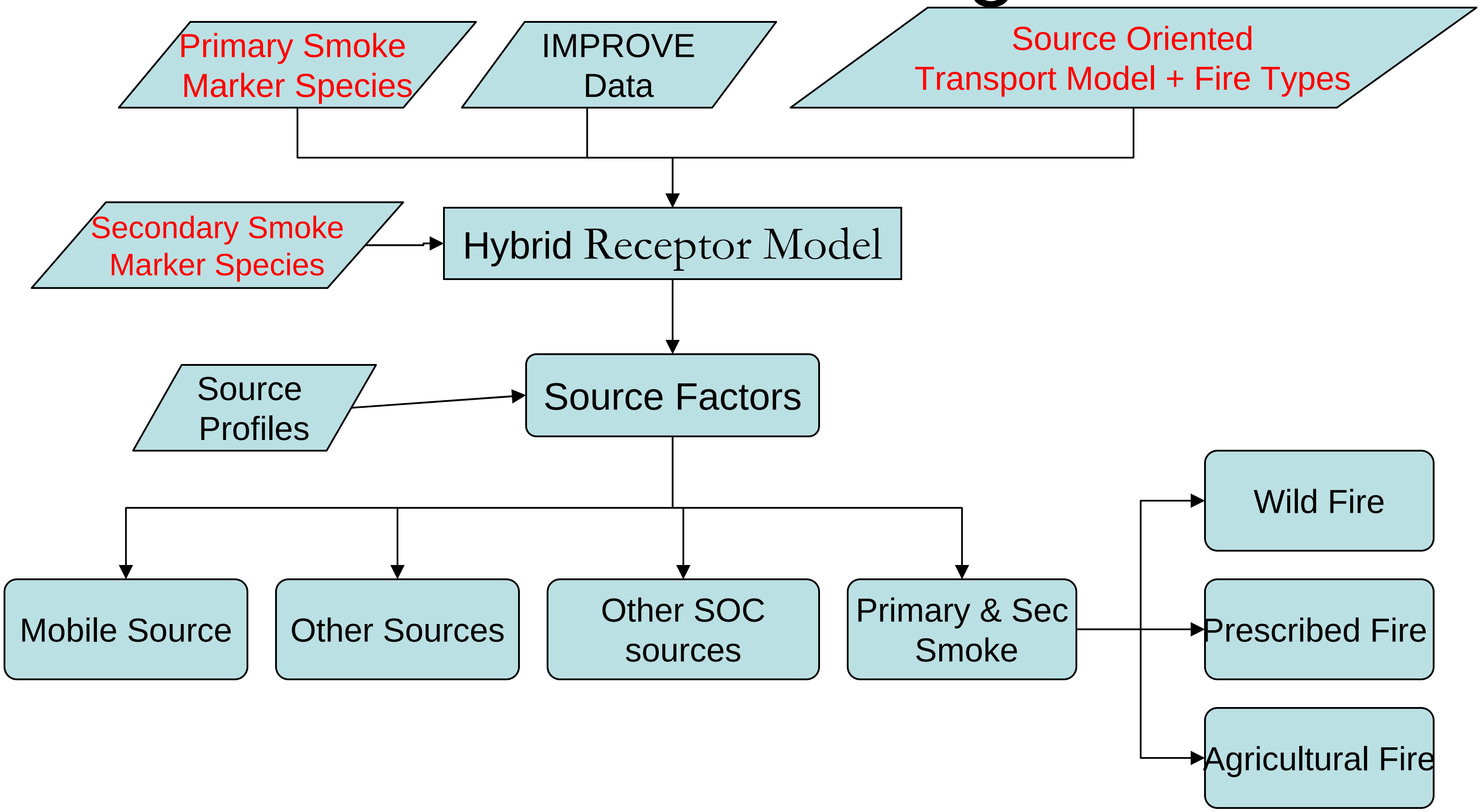
- Addition of primary smoke marker species allows the separation of primary smoke from SOC

Smoke Apportion: Hybrid Receptor Modeling



- Addition and incorporation of prior source attribution results in a hybrid receptor model can separate both primary and secondary smoke from other sources

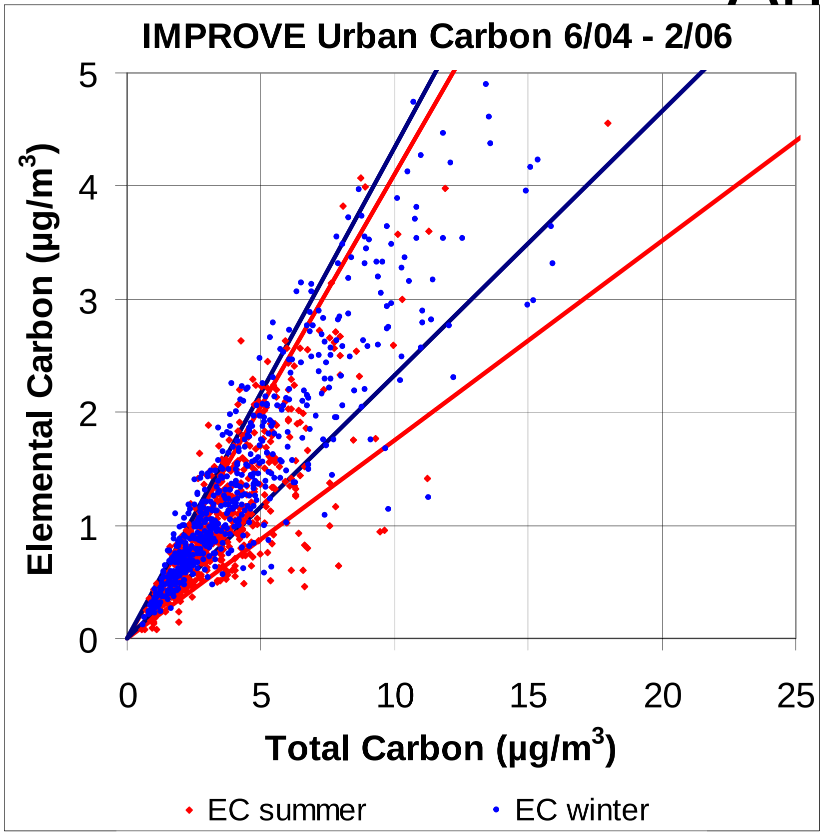
Smoke Apportion: Hybrid Receptor Modeling

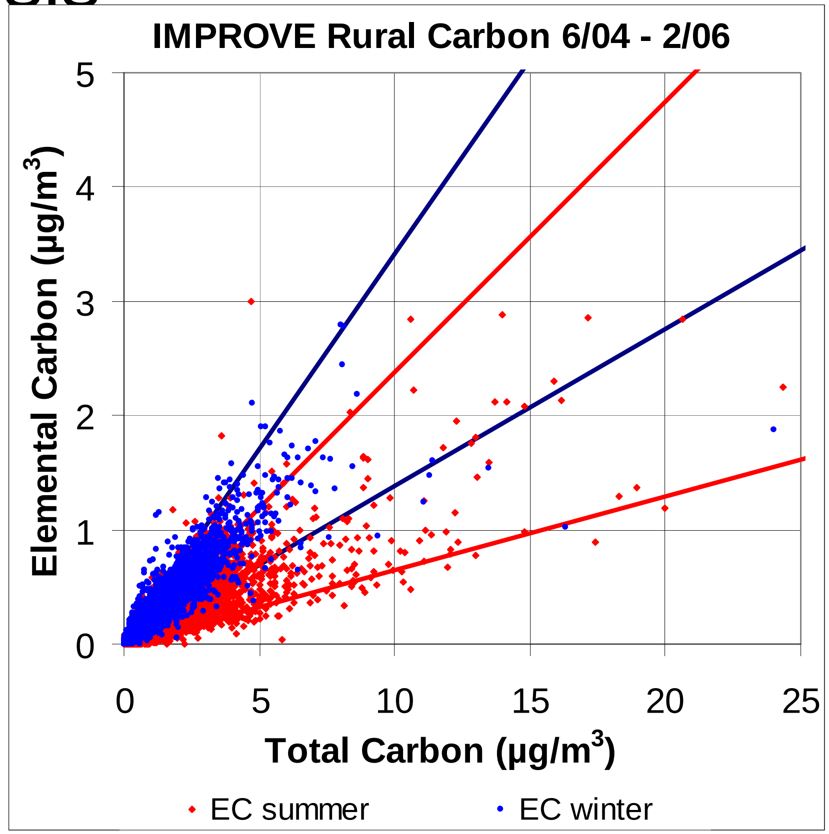


- By tagging the prior source attributions by the fire type and the fire location, the contributions of fire can be apportioned to specific fire types and locations


Clouds do not constitute
visibility impairment!

EC/TC Ratios from IMPROVE Data Edge Analysis



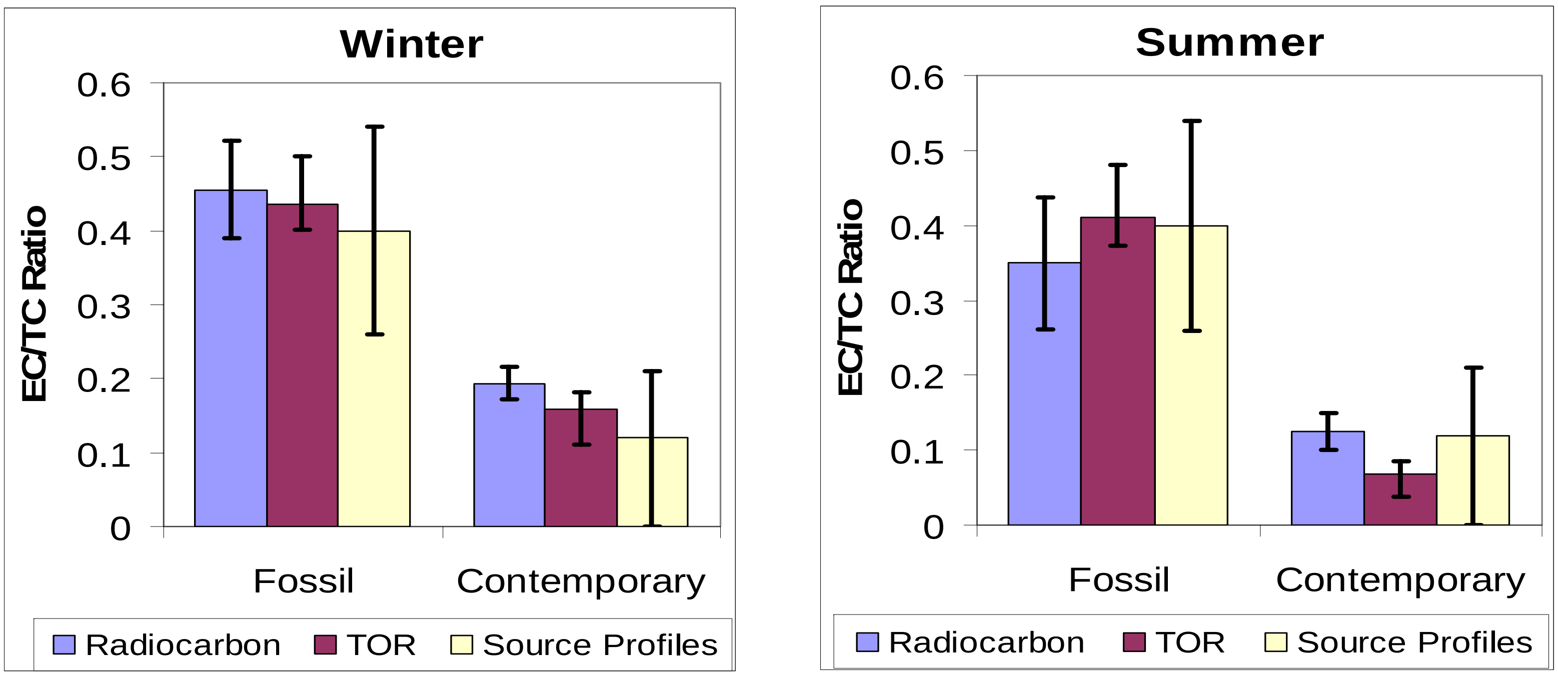


- Urban 90th %-ile edge ~ Fossil EC/TC
  - Summer – 0.41
  - Winter – 0.44
- Rural 10th %-ile edge ~ Biogenic EC/TC
  - Summer – 0.065
  - Winter – 0.14

Measured Primary EC/TC Ratios

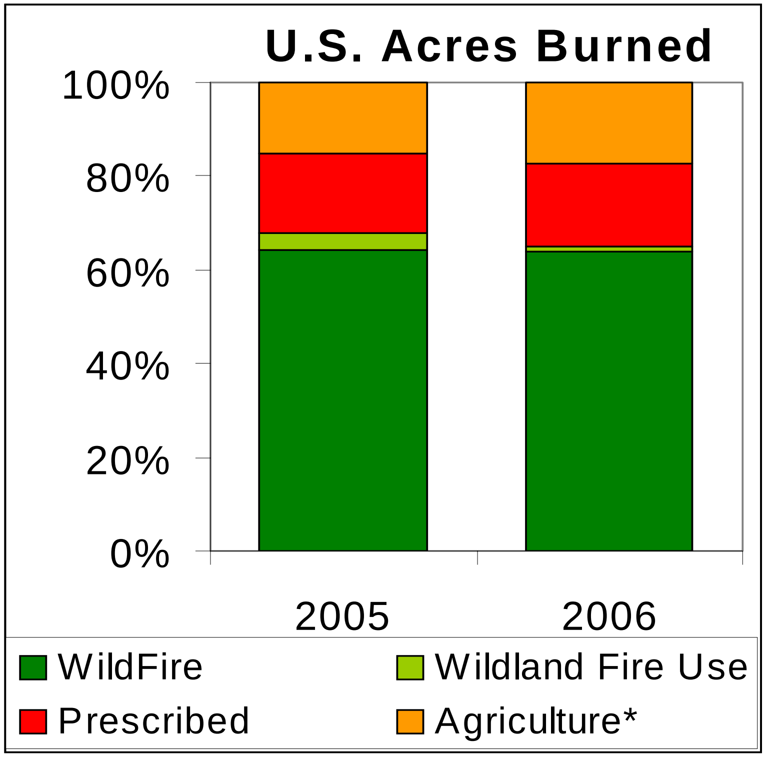
- Mobile Sources – Fossil Carbon
  - Adjusted Roadside: EC/TC = 0.39 (Chow et al., 2004)
  - 1996 Sepulveda. CA tunnel study: EC/TC = 0.57 (Gillies et al., 2001)
  - Light duty vehicle: EC/TC = 0.3 (Cadle et al., 1997)
  - Heavy Duty Diesel: EC/TC = 0.63 (Lowenthal et al. 1994)
- Wood Smoke – Biogenic Carbon (McDonald et al., 2000)
  - Softwood in fireplace: EC/TC = 0.2
  - Hardwood in fireplace: EC/TC = 0.1
  - Hardwood in woodstove: EC/TC = 0.11
  - Texas grass and soft and hardwood: EC/TC = 0.2 (Chow et al., 2004)
- Cooking
  - EC/TC = 0.1 (Chow et al., 2004)
- Secondary organic aerosol
  - EC/TC = 0

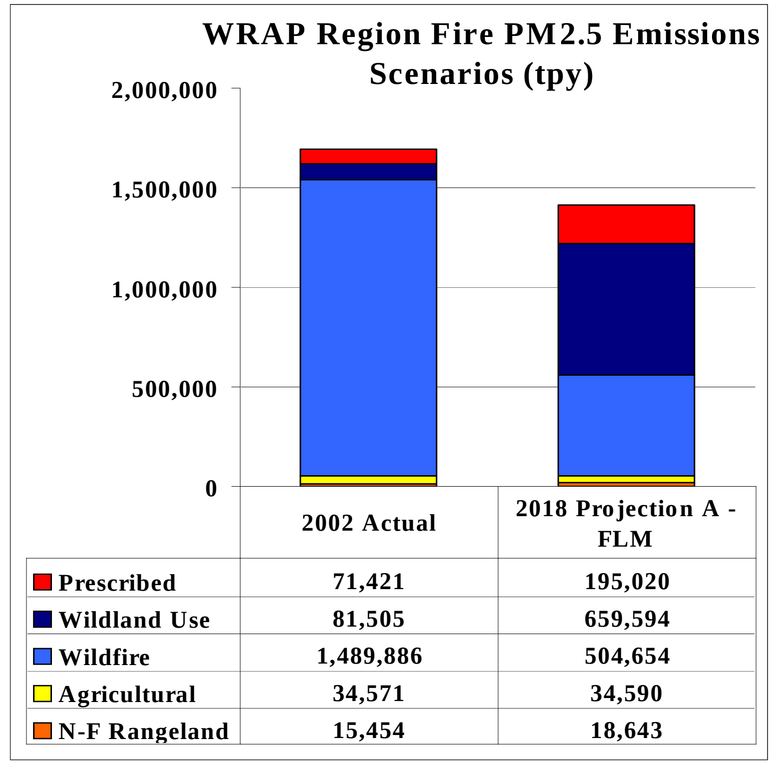
Comparison of EC/TC estimates



- Projected fossil and biogenic EC/TC ratios are in line with other estimates
  - Summer Fossil EC/TC ratio is on low side
- Literature summer EC/TC higher than C 12/14 and EC/TC edge analyses
  - Literature examined primary aerosol
- Fossil and Biogenic EC/TC is smaller in the summer than the winter indicating some summertime SOA formation for both

Emissions from Different Fire Types





- Wildfire and wildland fire use, “Natural fires”, are the largest sources of smoke, especially in the western United States.