

# Preview of the IMPROVE Report V

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**Jenny Hand**

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# Outline of Report

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1. Description of the IMPROVE network
2. Protocol, equipment and analytical changes (UC Davis)
3. Spatial distribution of mass concentrations from IMPROVE and CSN
4. Spatial distribution of reconstructed aerosol extinction from IMPROVE and CSN
5. Spatial variability in monthly mean mass concentrations from IMPROVE and CSN
6. Spatial variability in monthly mean aerosol extinction from IMPROVE and CSN
7. Trend Analysis
8. Urban Excess
9. Regional Haze Rule analysis (Moore and Copeland)
10. Rocky Mountain Atmospheric Nitrogen and Sulfur Species Study (RoMANS)
11. Ammonia sampling (Day)
12. Fine mass biases (Malm)

# Methods

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•We computed regional monthly and annual mean concentrations and mass fractions for:

- Organic Carbon (OC)
- Light Absorbing Carbon (LAC)
- Ammonium Sulfate ( $AS = 1.375 \cdot SO_4^{-2}$ )
- Ammonium Nitrate ( $AN = 1.29 \cdot NO_3^-$ )
- Soil (IMPROVE formulation)
- Sea salt ( $SS = 1.8 \cdot Cl^-$ )
- $dM = FM - RCFM$

where RCFM was computed by summing particulate organic matter ( $POM = 1.8 \cdot OC$ ), LAC, AS, AN, SS, and soil.

• $dM$  can be positive or negative depending on the sampling conditions, artifacts and other assumptions.

# Methods

- Four years of data were investigated (2005-2008). We applied a 50% completeness criteria to the data.
- We grouped 168 IMPROVE sites into 35 previously defined regions, 9 of which include only 1 site, and 7 of which are urban.
- We grouped 176 CSN sites into 32 regions. Eight of the regions had only 1 site.

| Statistic                    | OC   | LAC  | AS   | AN   | Soil  | Sea salt | FM   | RCFM |
|------------------------------|------|------|------|------|-------|----------|------|------|
| <b>Bias<sup>1</sup> (%)</b>  | 8.3  | 5.7  | 7.0  | 17.2 | -31.0 | -62.8    | 18.4 | 0.04 |
| <b>Error<sup>2</sup> (%)</b> | 16.0 | 20.2 | 7.5  | 13.9 | 37.0  | 78.3     | 14.1 | 8.5  |
| <b>r</b>                     | 0.93 | 0.88 | 0.98 | 0.99 | 0.85  | 0.84     | 0.9  | 0.95 |
| <b>IMP/CSN</b>               | 0.93 | 1.0  | 0.96 | 0.92 | 1.6   | 3.2      | 0.88 | 1.0  |

<sup>1</sup> Error = median  $\left( \left| \frac{\bar{X}_i - \bar{Y}_i}{\bar{Y}_i} \right| \right)$ , <sup>2</sup> Bias =  $\frac{1}{N} \sum_i \frac{\bar{X}_i - \bar{Y}_i}{\bar{Y}_i}$ ;  $\bar{X}_i$  and  $\bar{Y}_i$  are the daily data for CSN and IMPROVE concentrations, respectively. The number of data points is given by N.

# Methods

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- Aerosol Light Extinction was computed using a modified original IMPROVE equation:

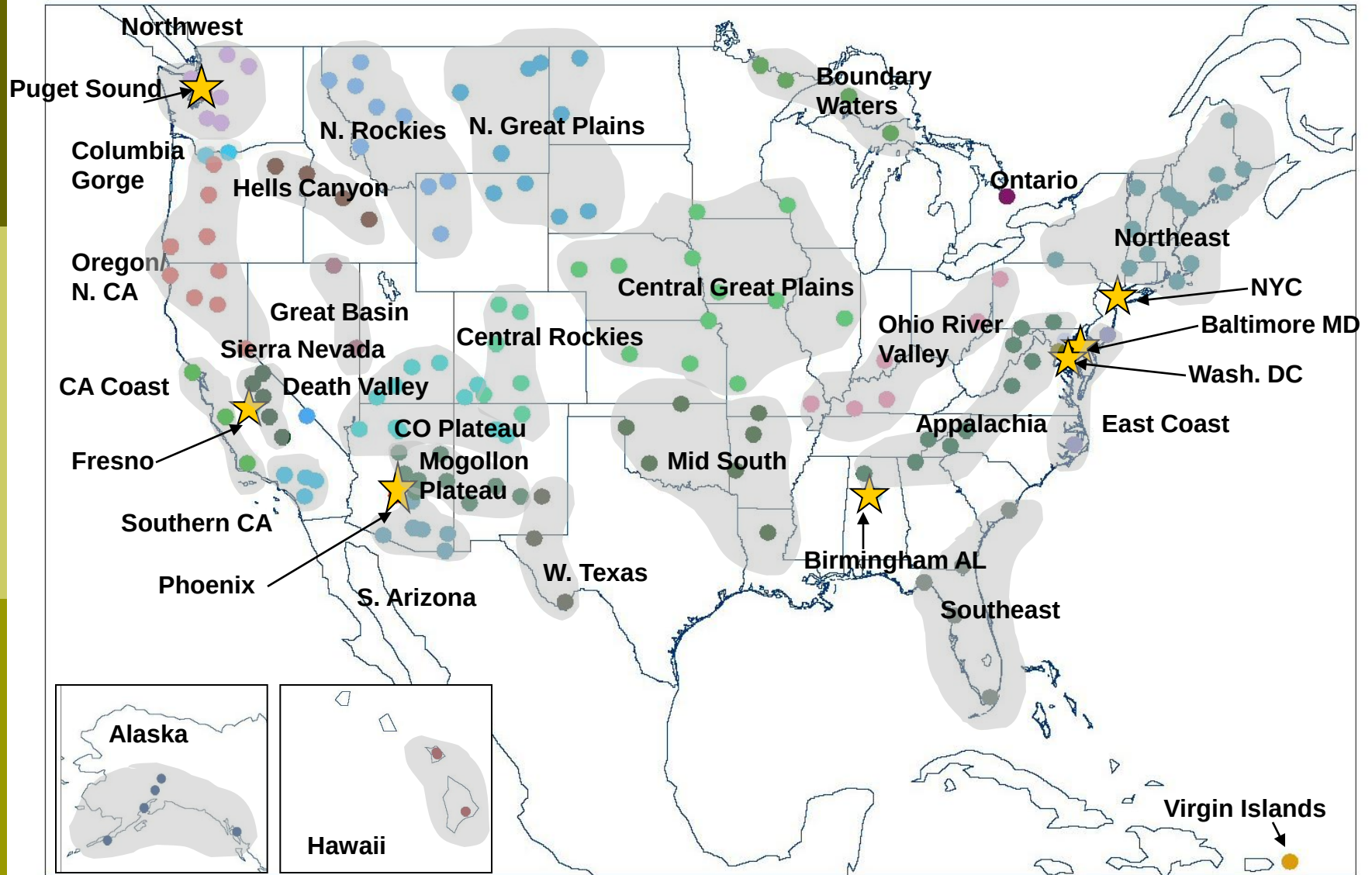
$$\begin{aligned} b_{\text{ext}} = & 3*f(RH)*[\text{ammonium sulfate}] + \\ & 3*f(RH)*[\text{ammonium nitrate}] + \\ & 4*[\text{particulate organic matter}] + \\ & 10*[\text{light absorbing carbon}] + \\ & 1.7*f(RH)_{ss} * [\text{sea salt}] + \\ & 1*\text{Soil} + \\ & 0.6*CM + \\ & \text{Site Specific Rayleigh scattering} \end{aligned}$$

where  $POM = 1.8 * OC$

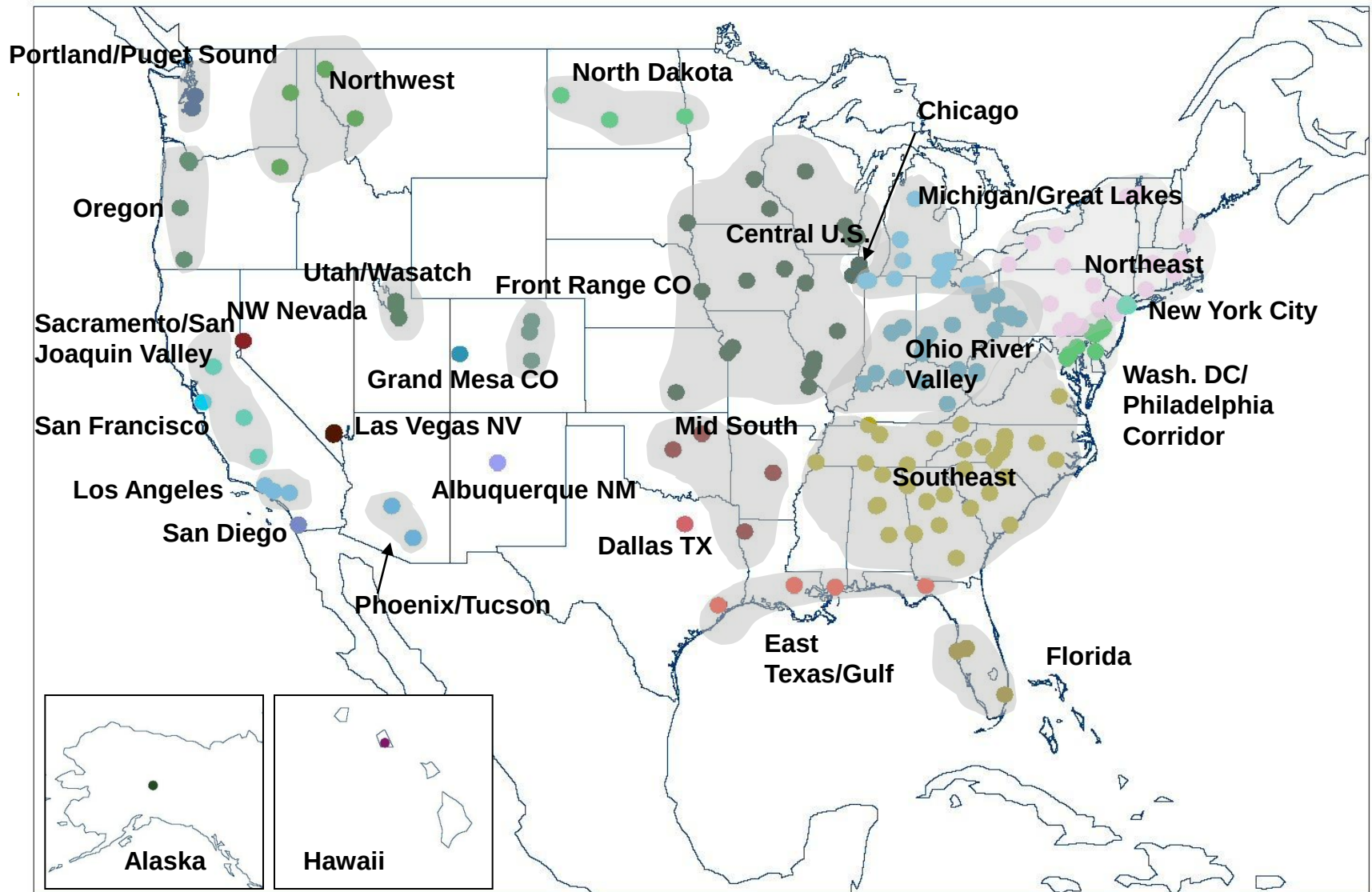
- CSN does not monitor CM, so  $b_{\text{ext}}$  was computed as  $PM_{2.5}$  for CSN.
- dV was computed including CM for IMPROVE

# IMPROVE REGIONS (rural/remote)

★ Urban Sites



# CSN REGIONS (urban/suburban)



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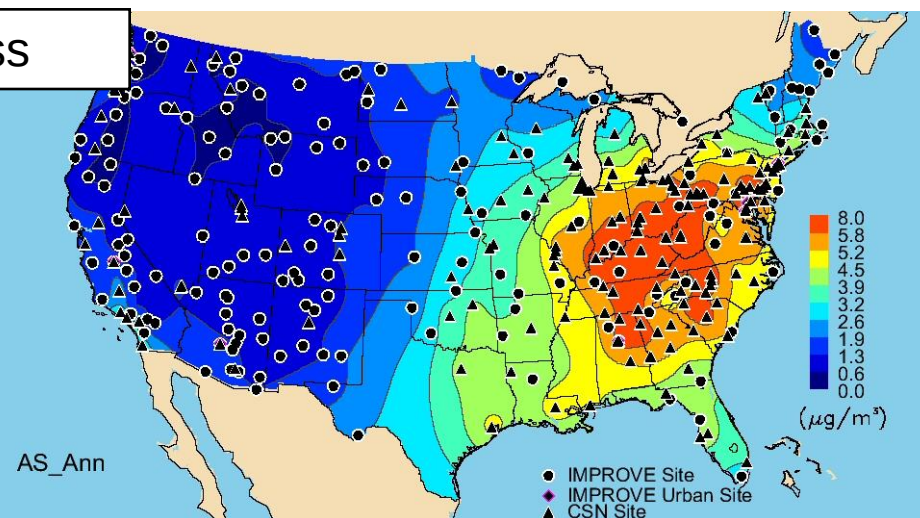
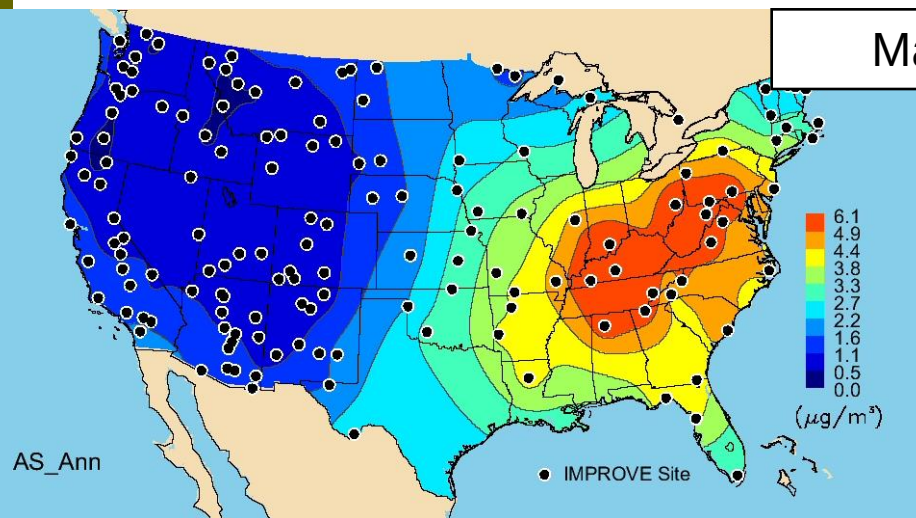
# Spatial Patterns of Mass Concentrations

# Ammonium Sulfate

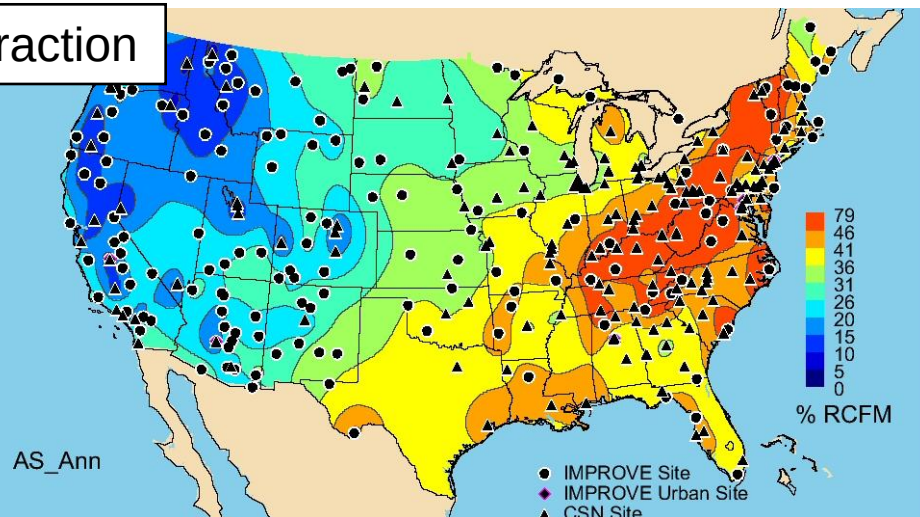
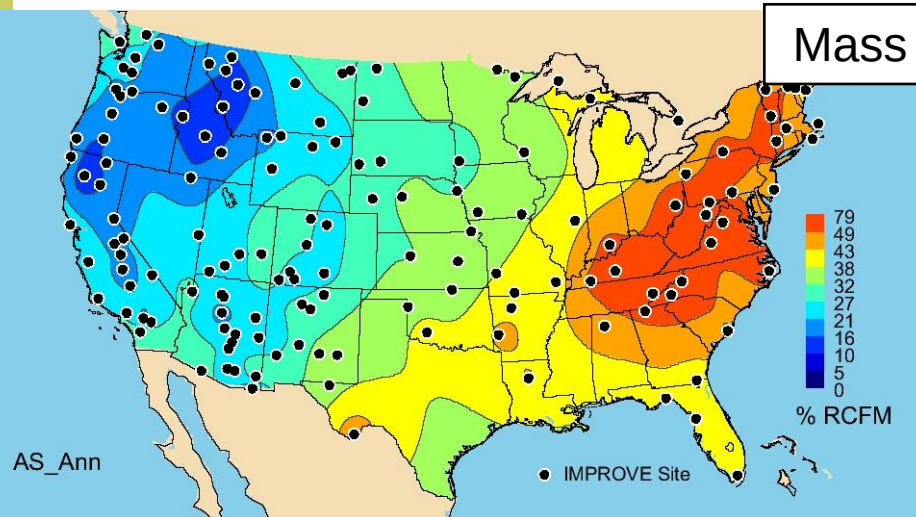
IMPROVE

IMPROVE + CSN

Mass



Mass Fraction

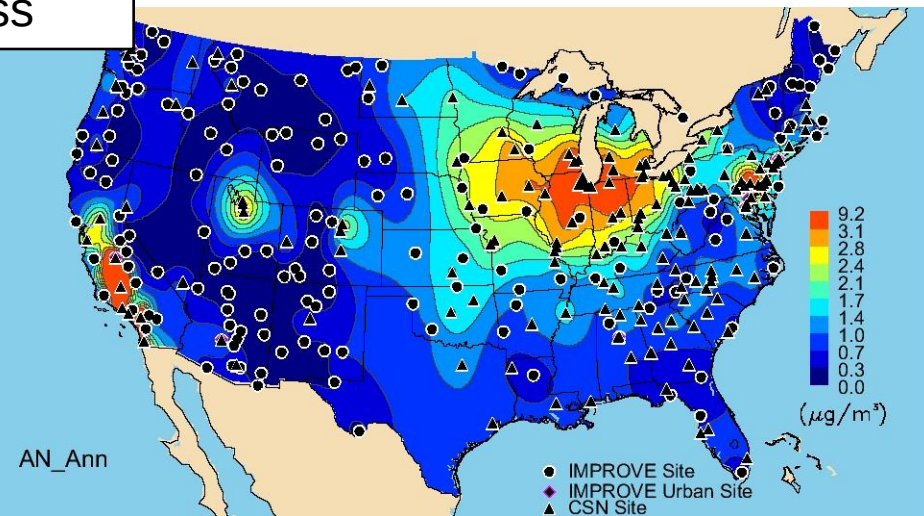
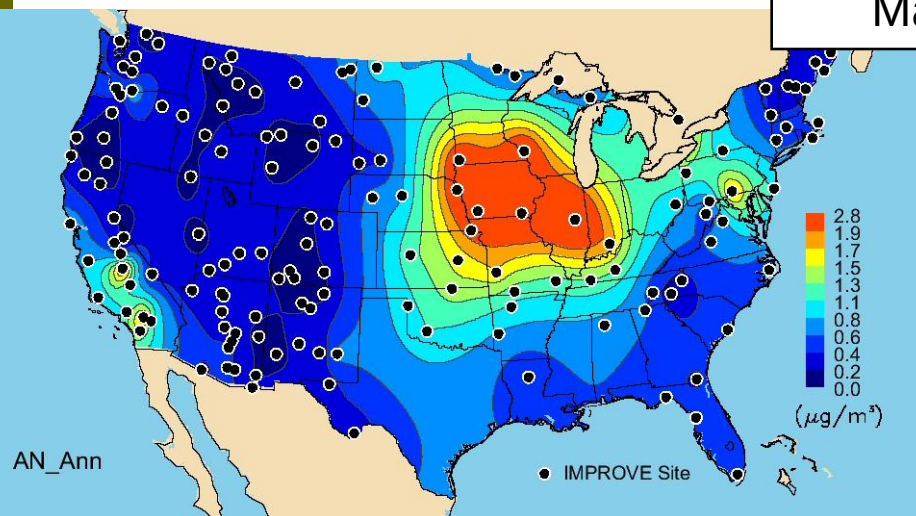


# Ammonium Nitrate

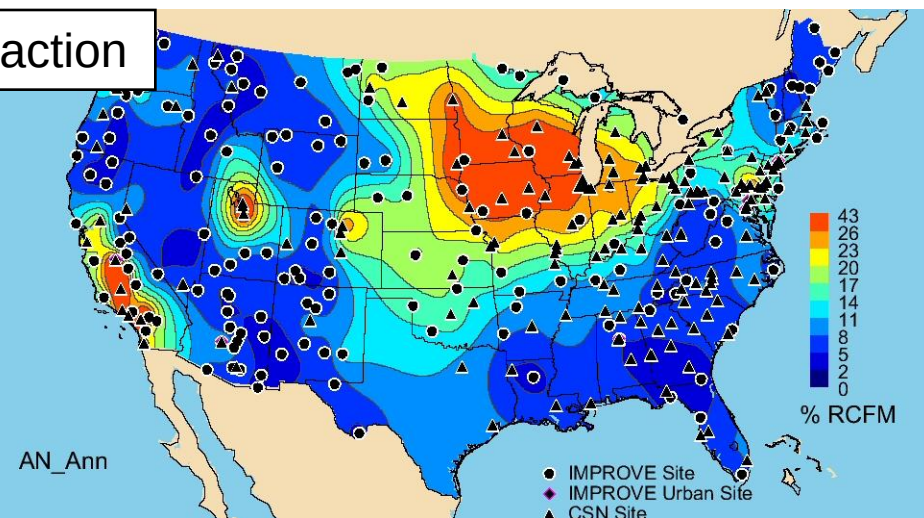
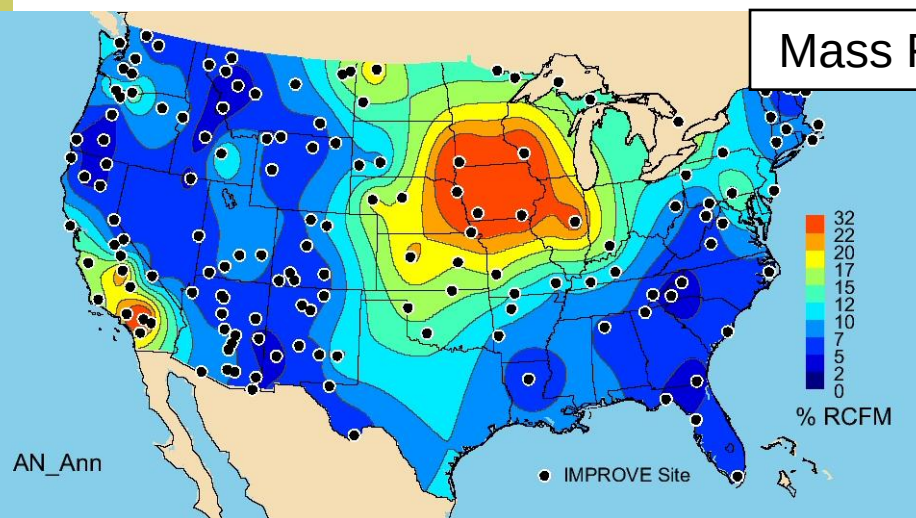
IMPROVE

IMPROVE + CSN

Mass



Mass Fraction

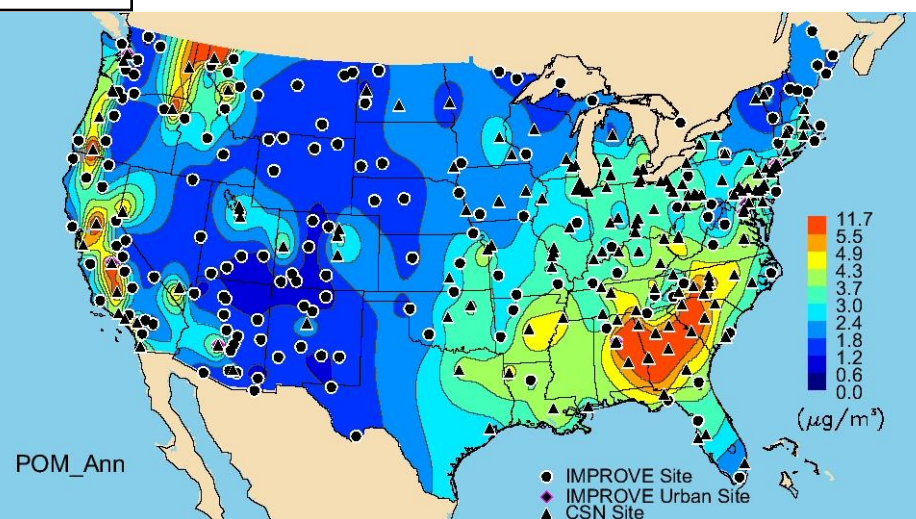
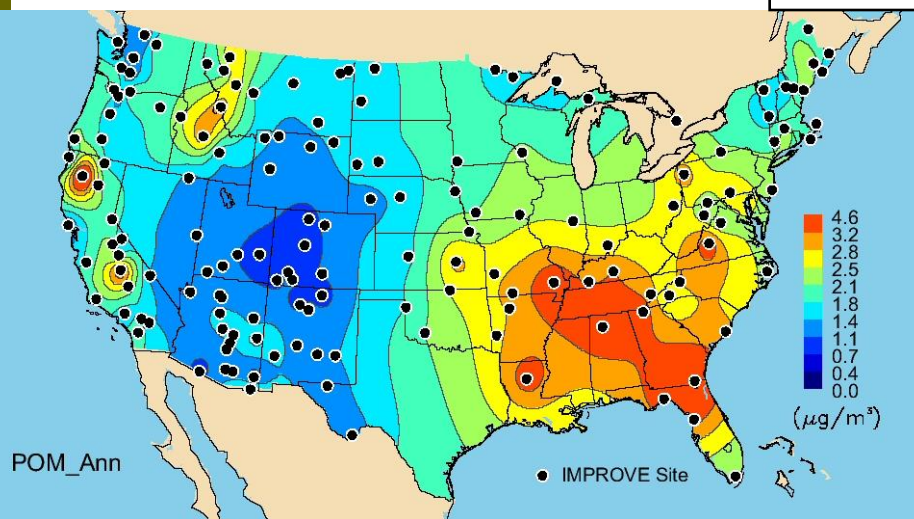


# Particulate Organic Matter

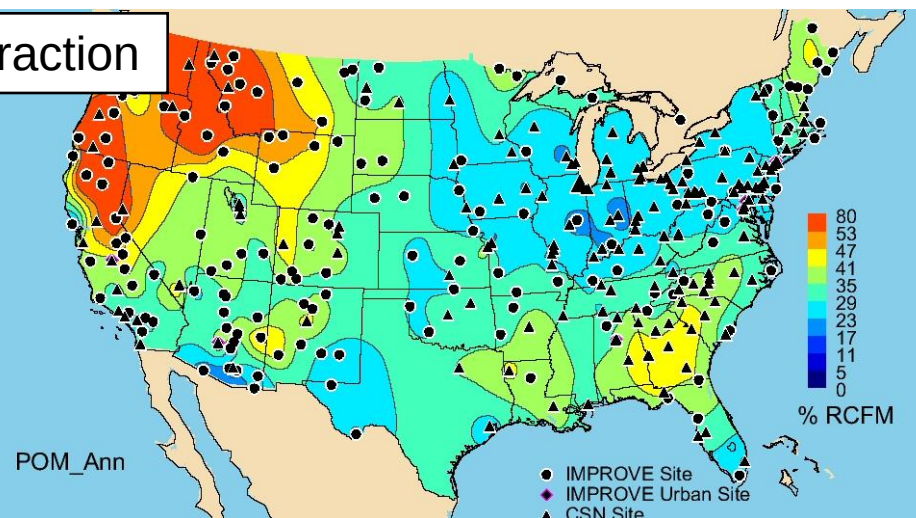
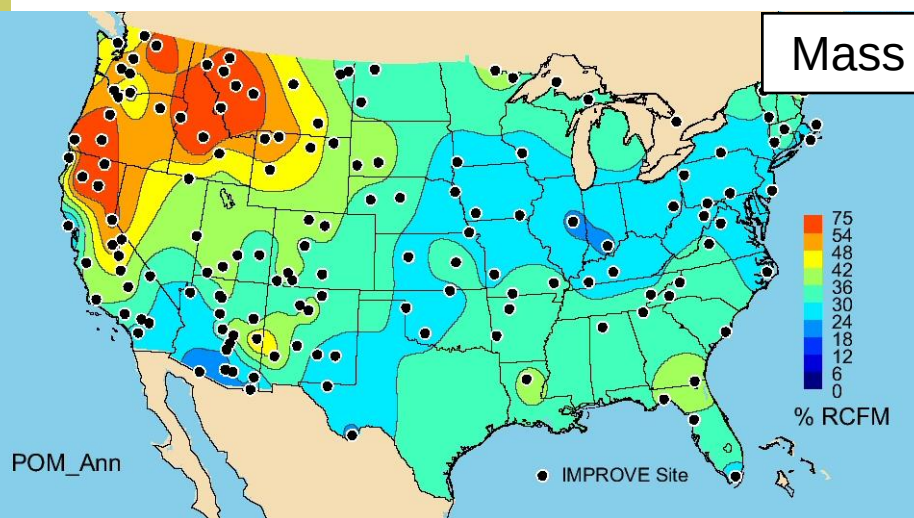
IMPROVE

IMPROVE + CSN

Mass



Mass Fraction

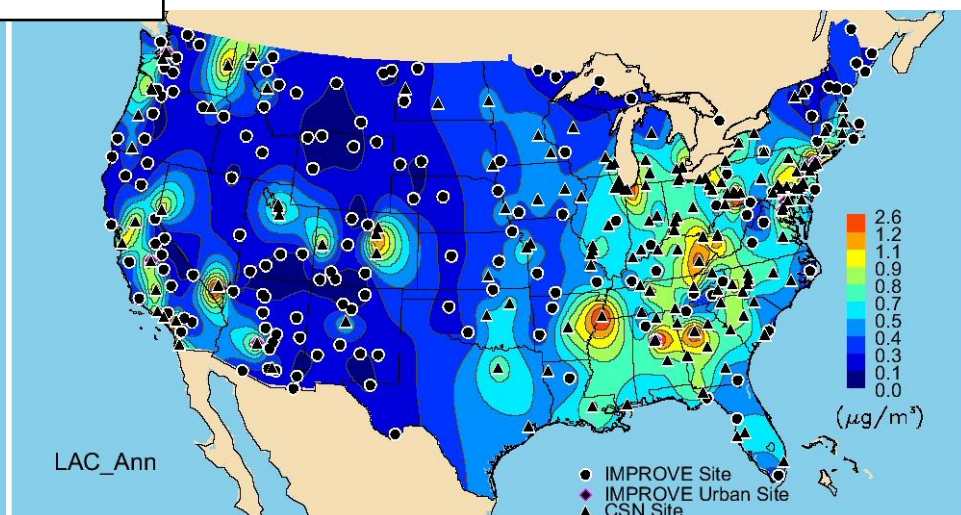
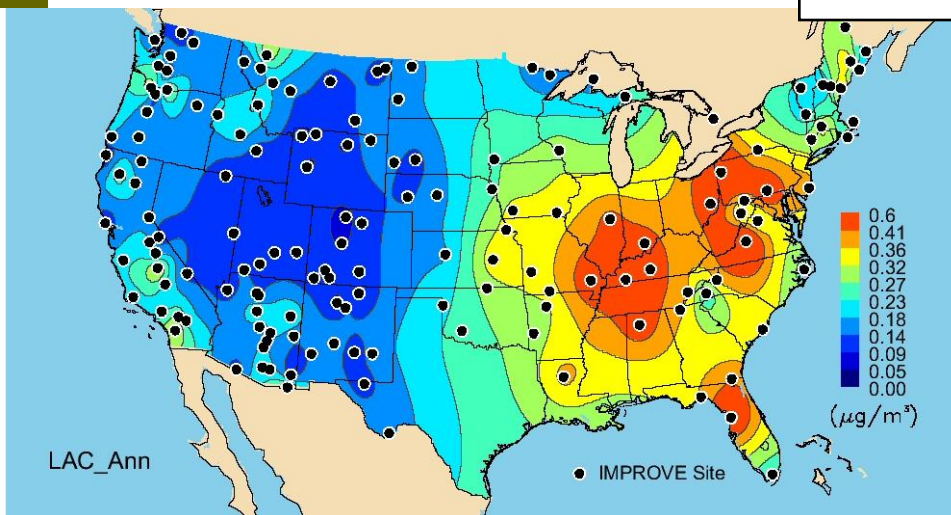


# Light Absorbing Carbon

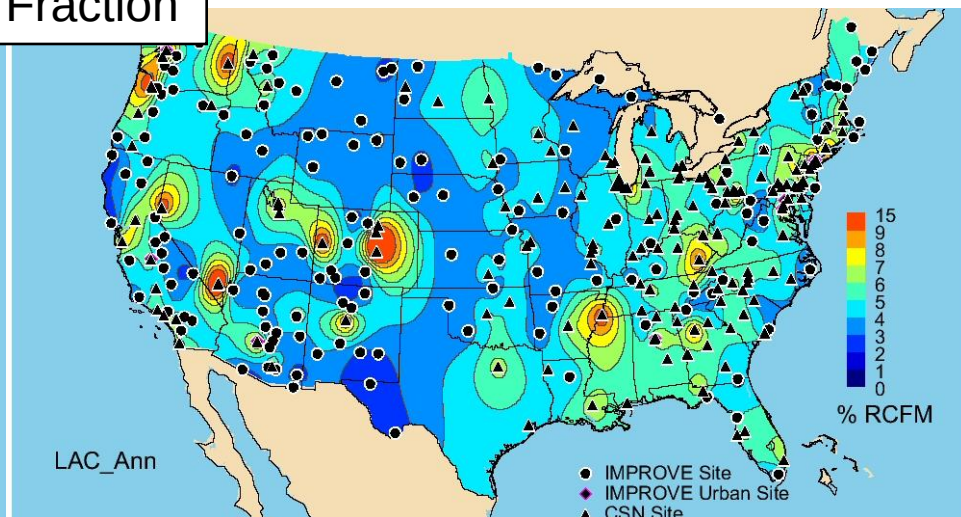
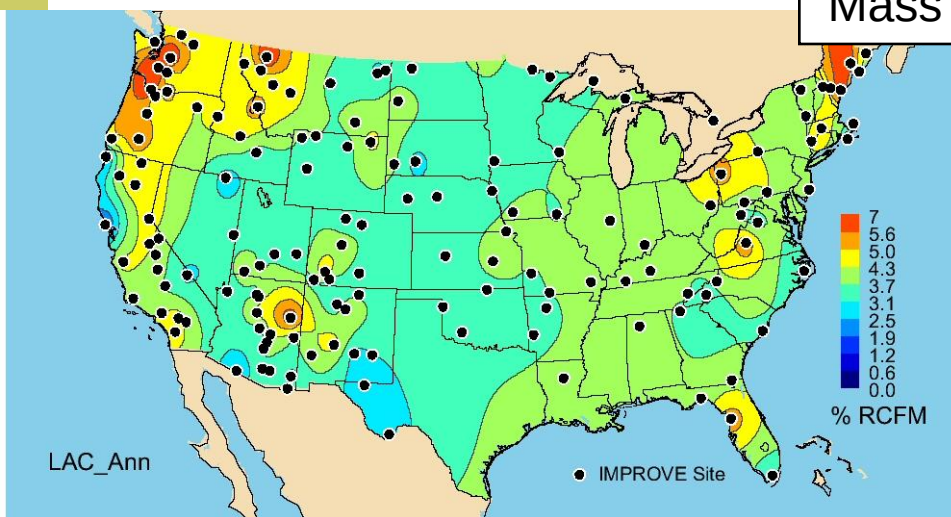
IMPROVE

Mass

IMPROVE + CSN



Mass Fraction

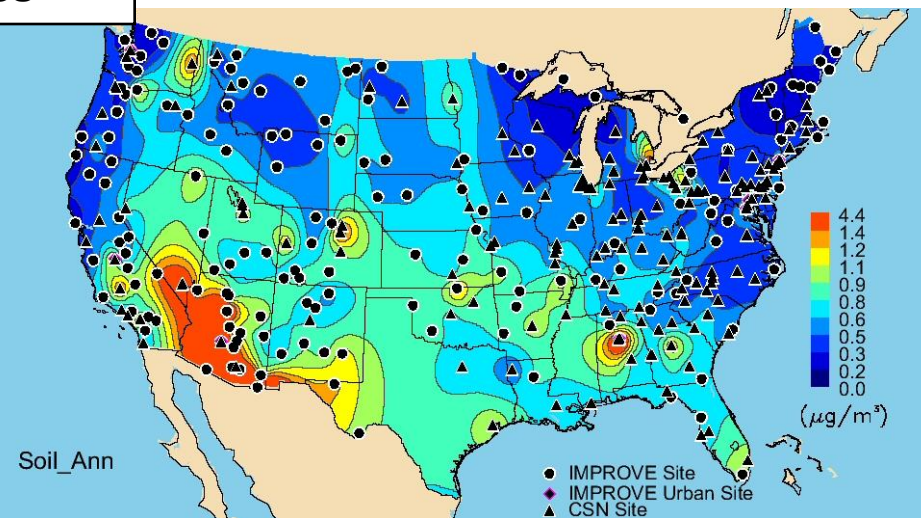
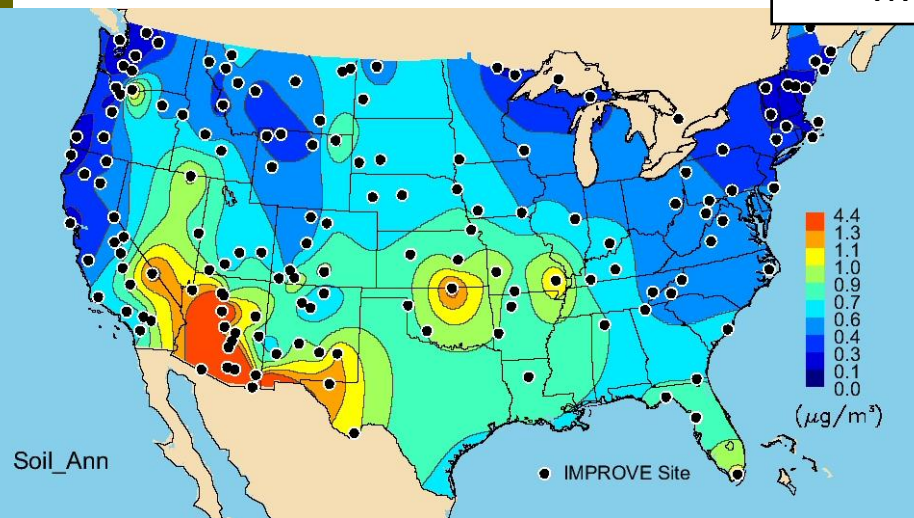


# Soil

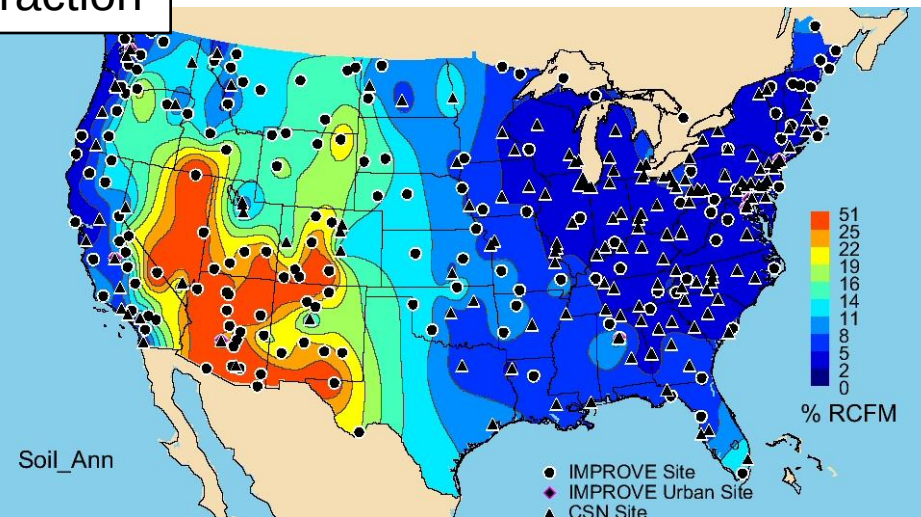
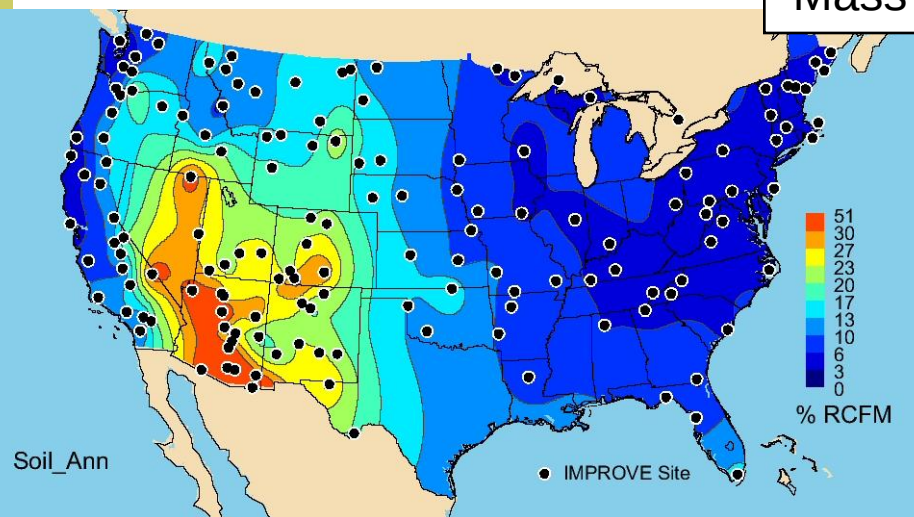
IMPROVE

Mass

IMPROVE + CSN



Mass Fraction

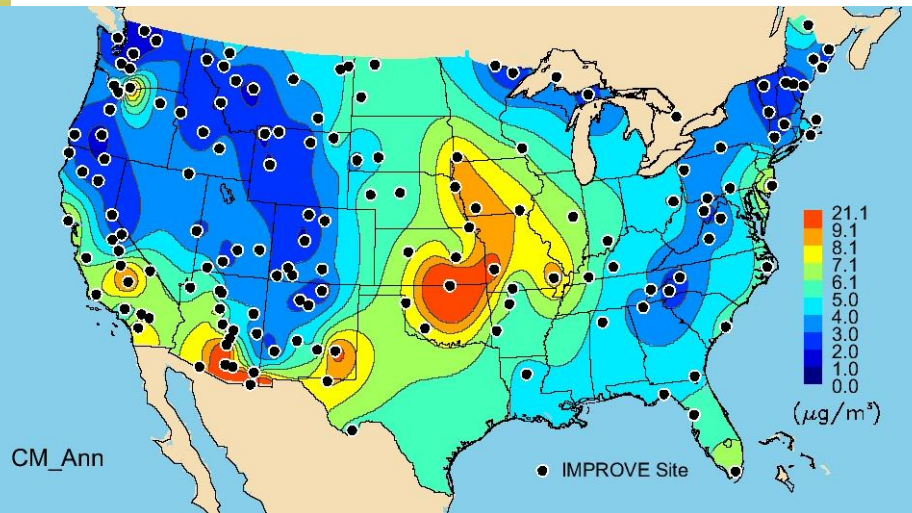
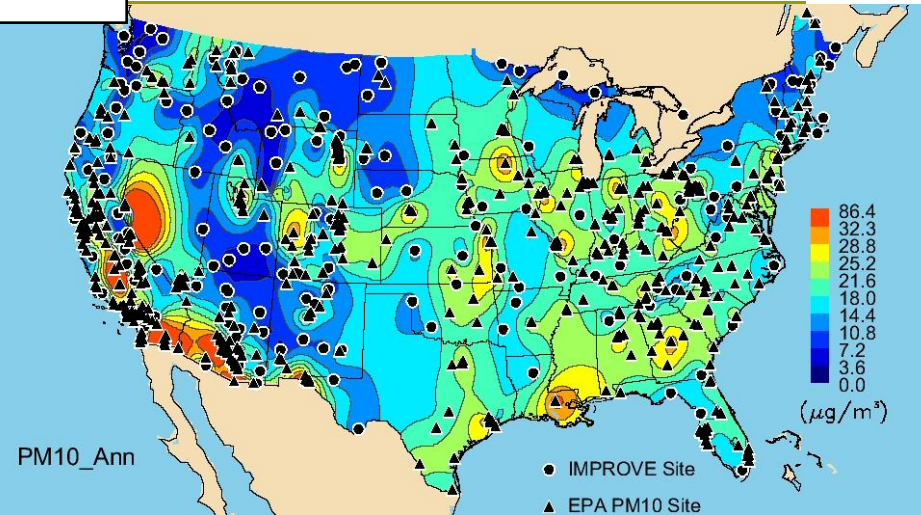
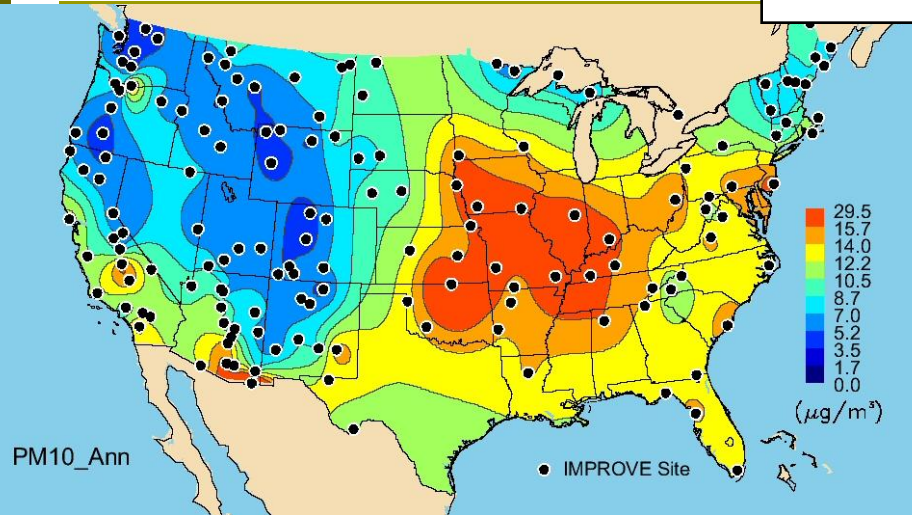


# CM and PM10

IMPROVE

Mass

IMPROVE + EPA

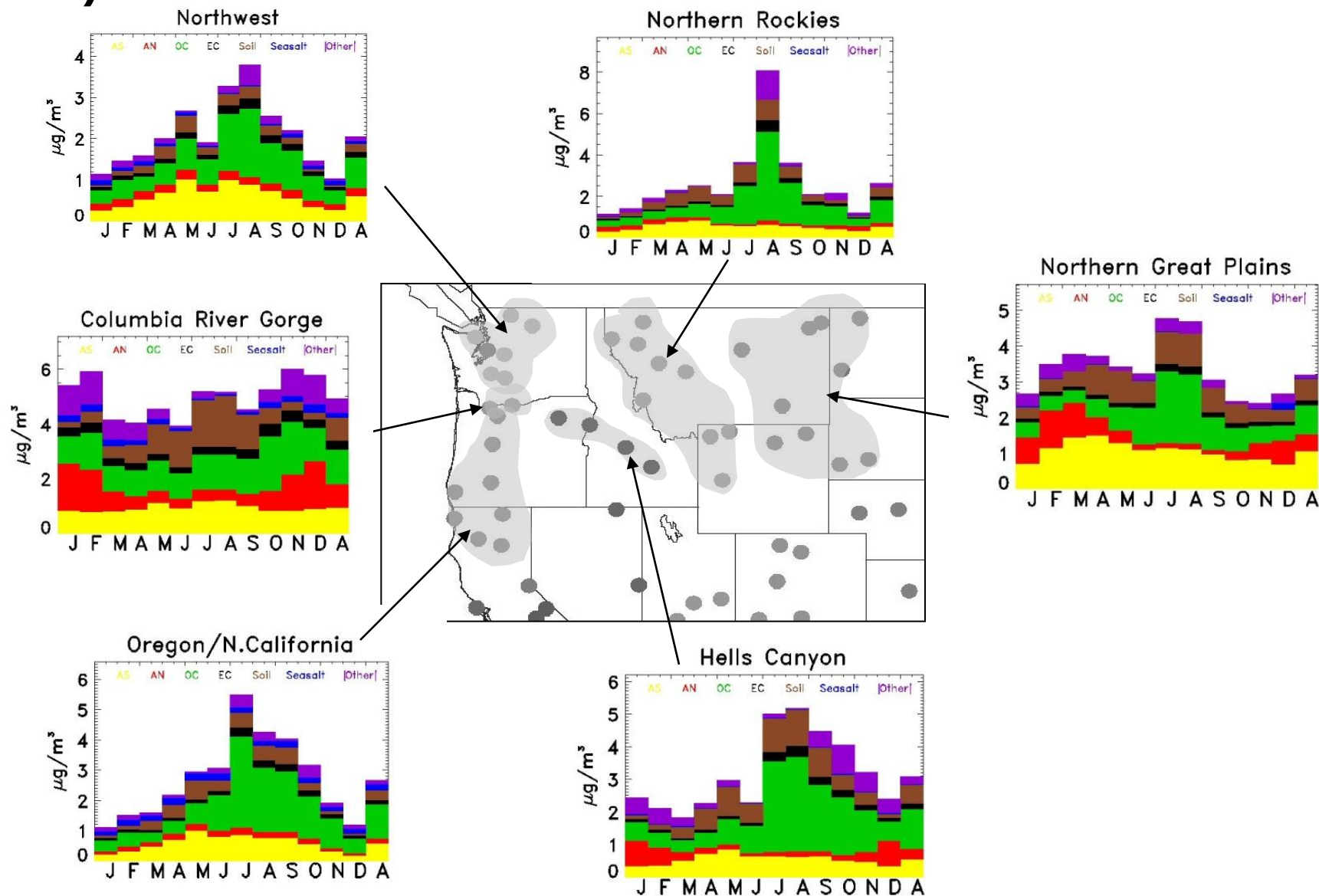


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## Seasonal Patterns of Regional Mass Concentrations

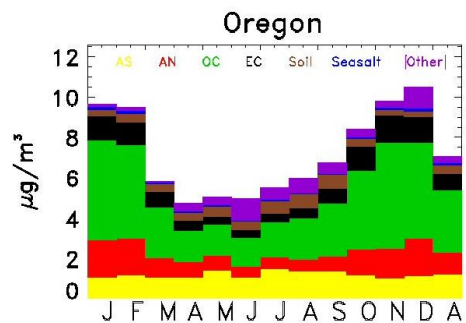
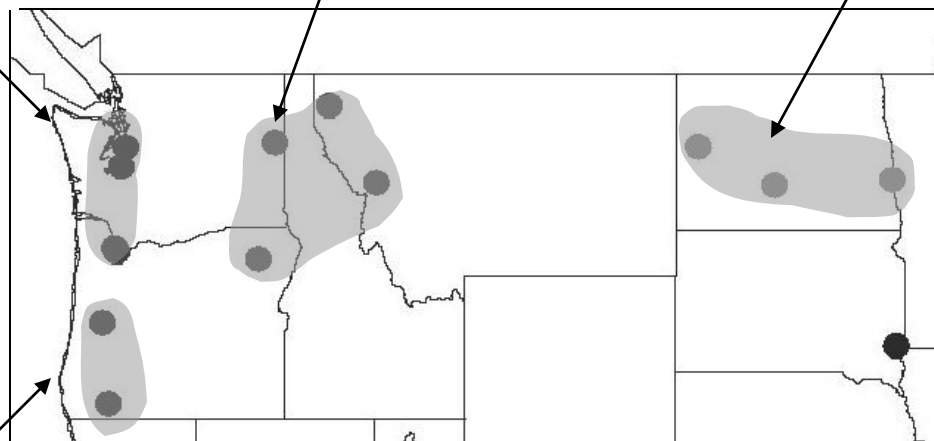
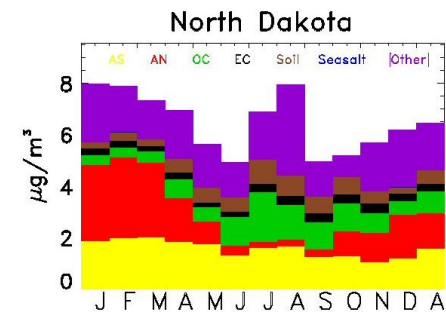
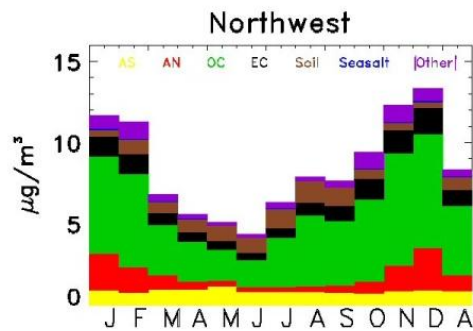
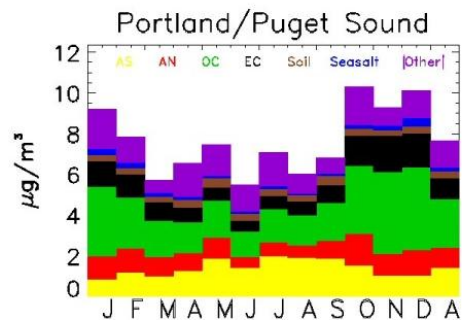
# IMPROVE: Northwest U.S. (rural)

AS AN OC LAC Soil Sea salt |Other|



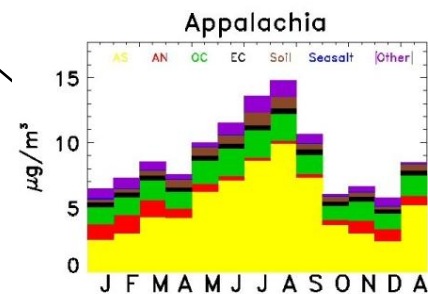
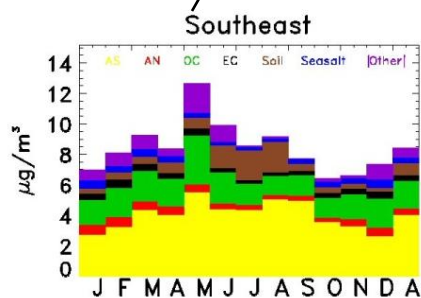
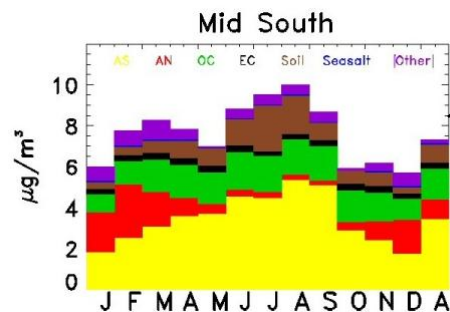
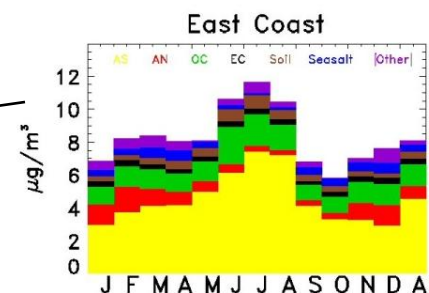
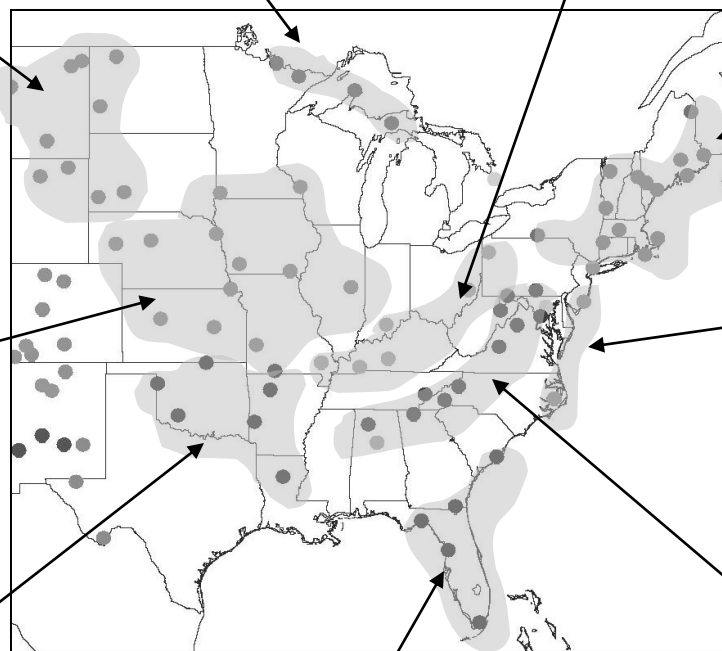
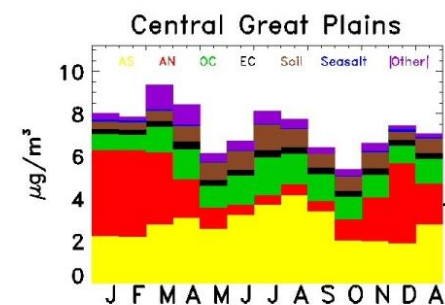
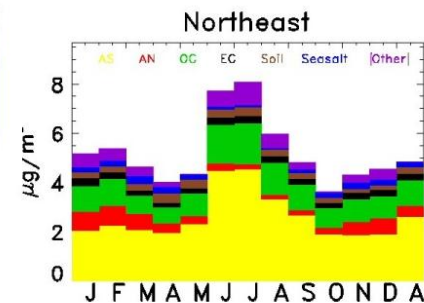
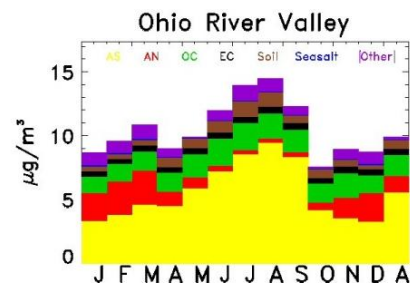
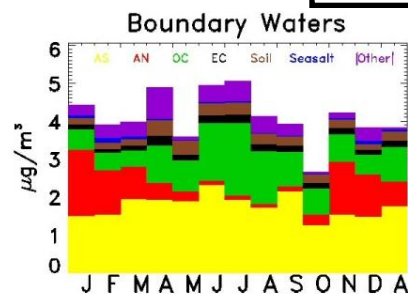
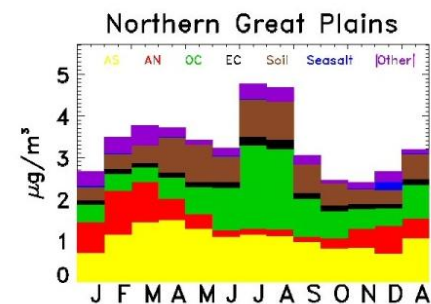
# CSN: Northwest U.S. (urban)

AS AN OC LAC Soil Sea salt |Other|



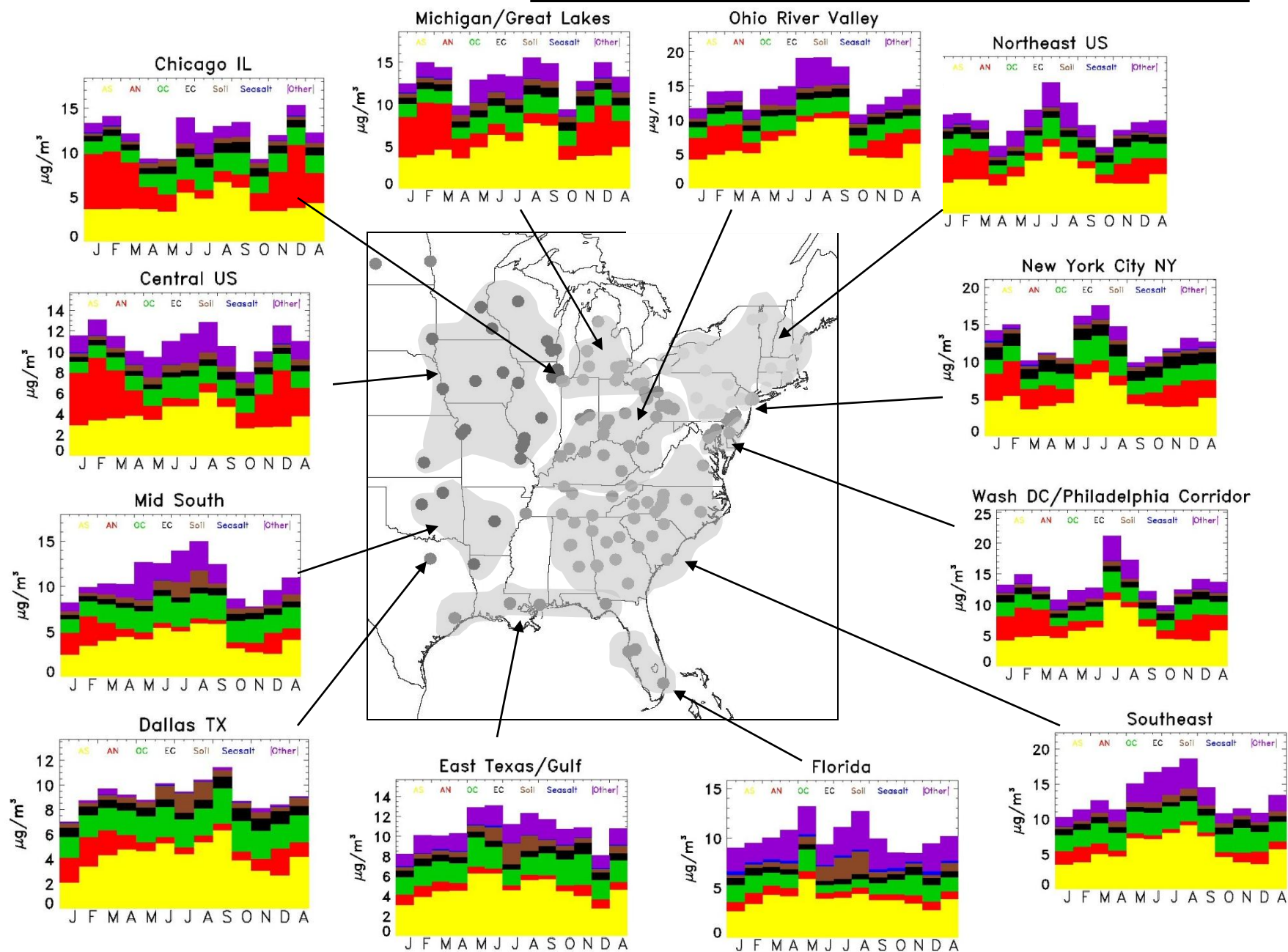
# IMPROVE: Eastern U.S. (rural)

AS AN OC LAC Soil Sea salt |Other|



# CSN: Eastern U.S.

AS AN OC LAC Soil Sea salt |Other|



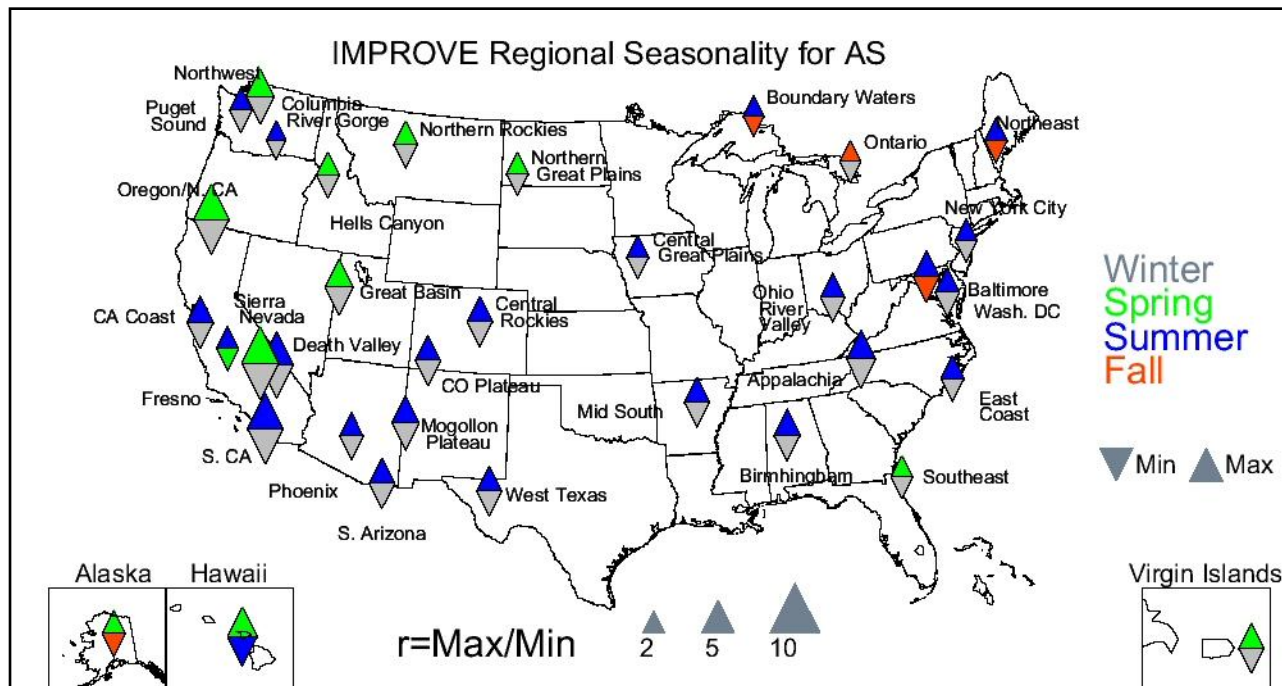
# Seasonal Maps

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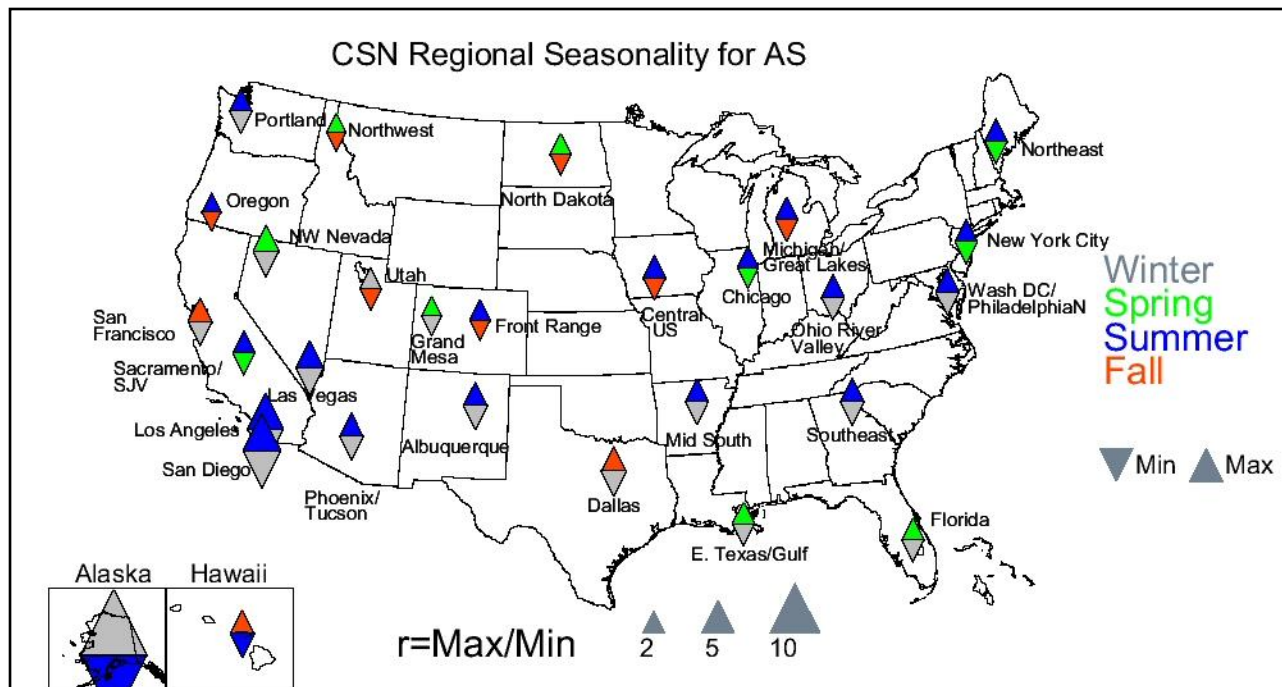
- Determine the month corresponding to the minimum and maximum mean concentration
- Depict seasonality as the ratio of the maximum to minimum concentration

# Seasonality for Ammonium Sulfate

IMPROVE

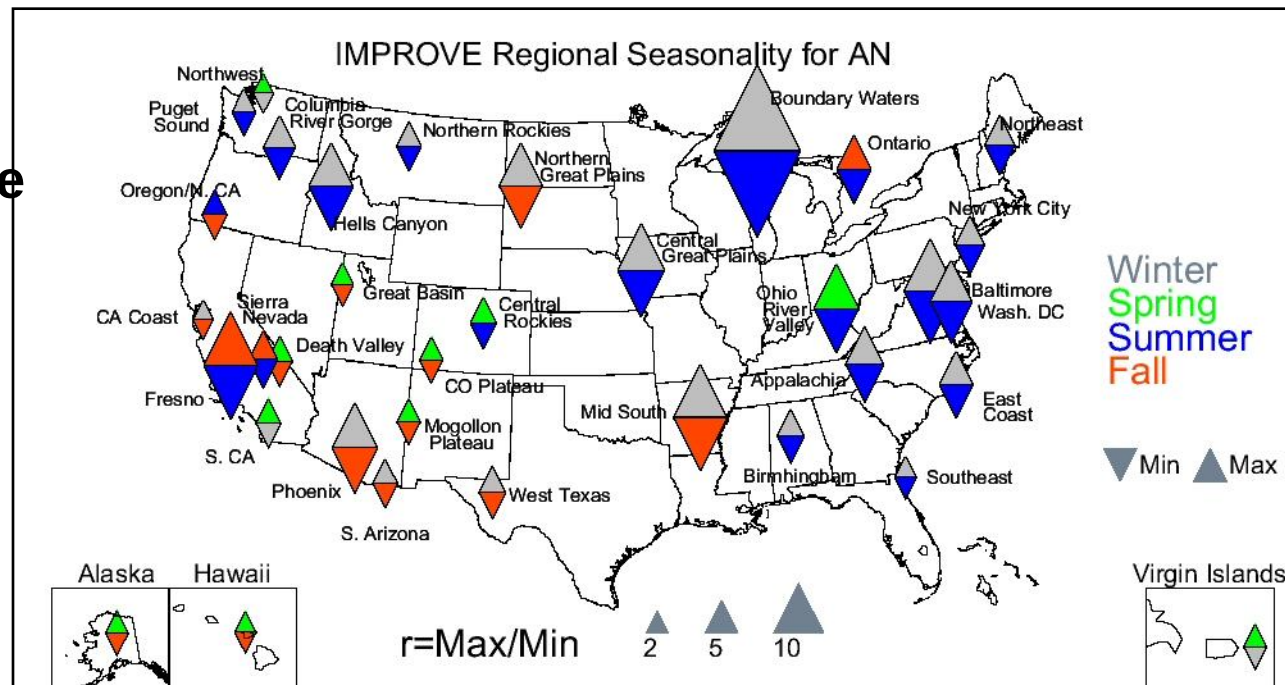


CSN

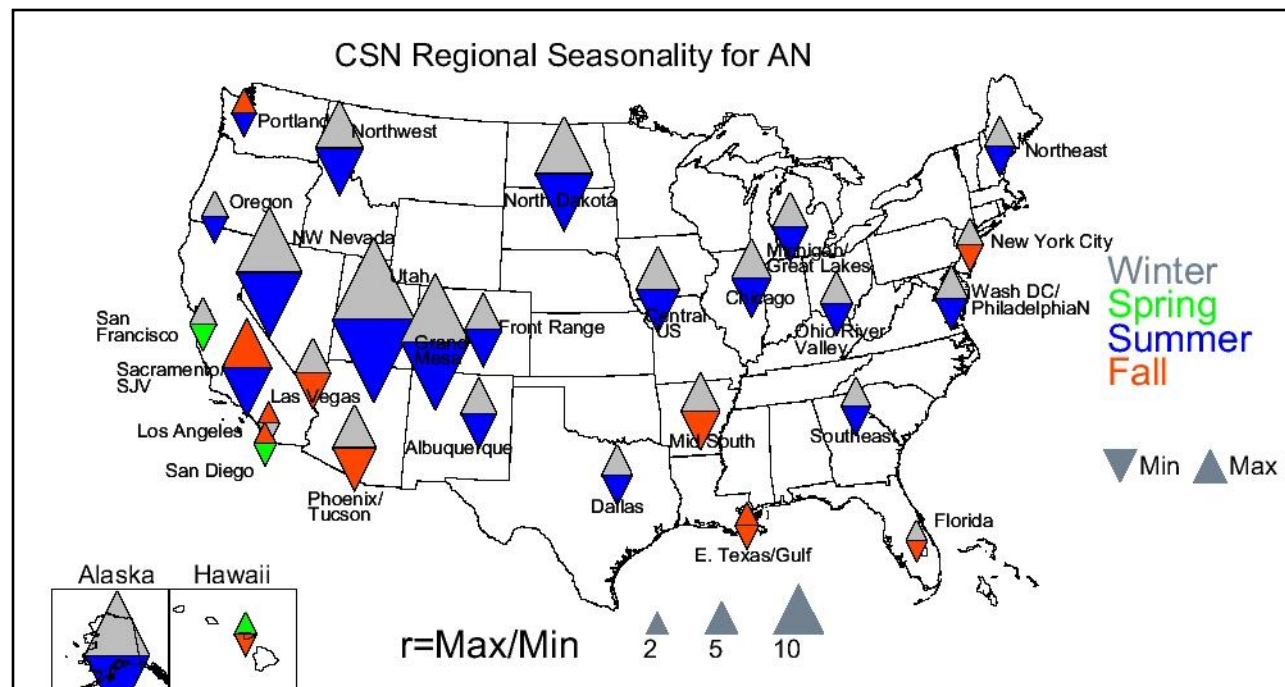


# Seasonality for Ammonium Nitrate

IMPROVE

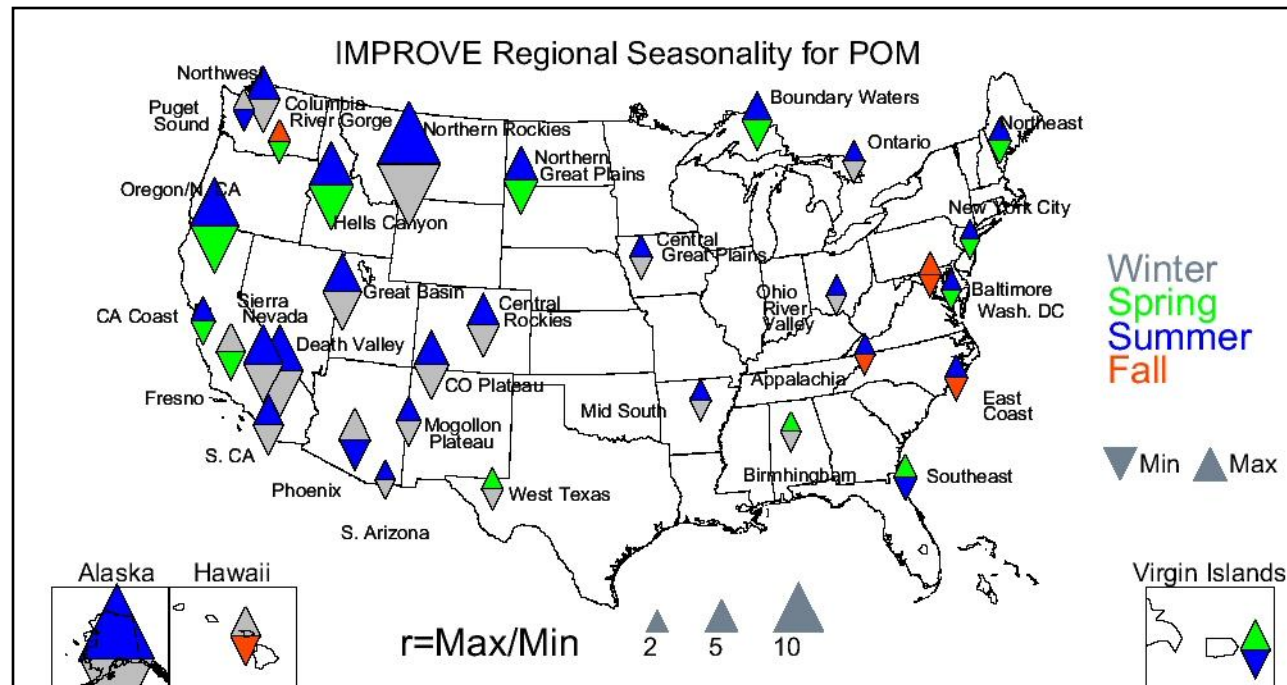


CSN

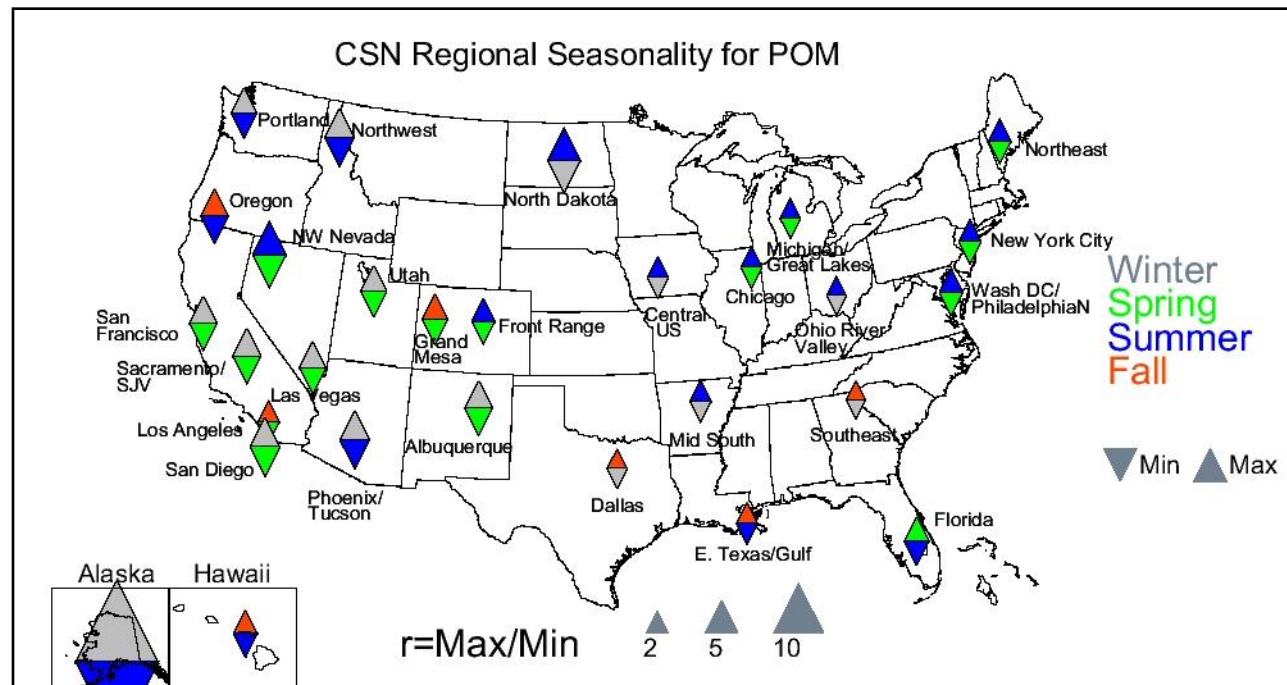


# Seasonality for POM

IMPROVE

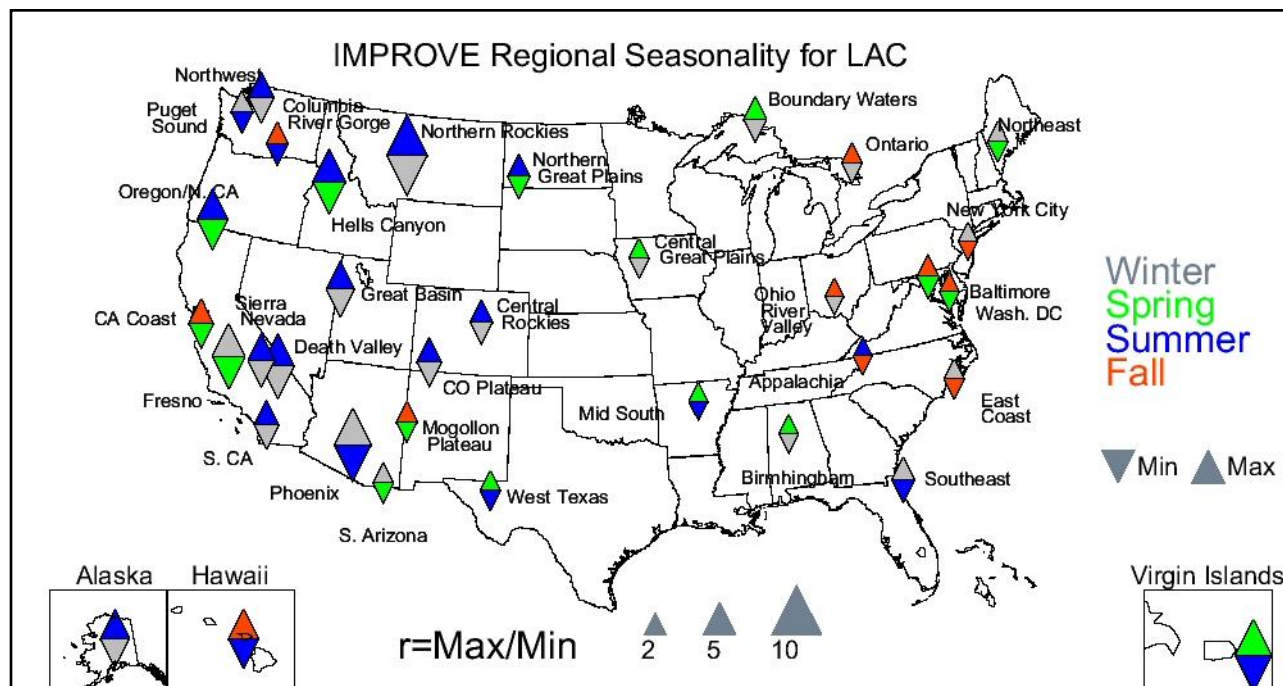


CSN

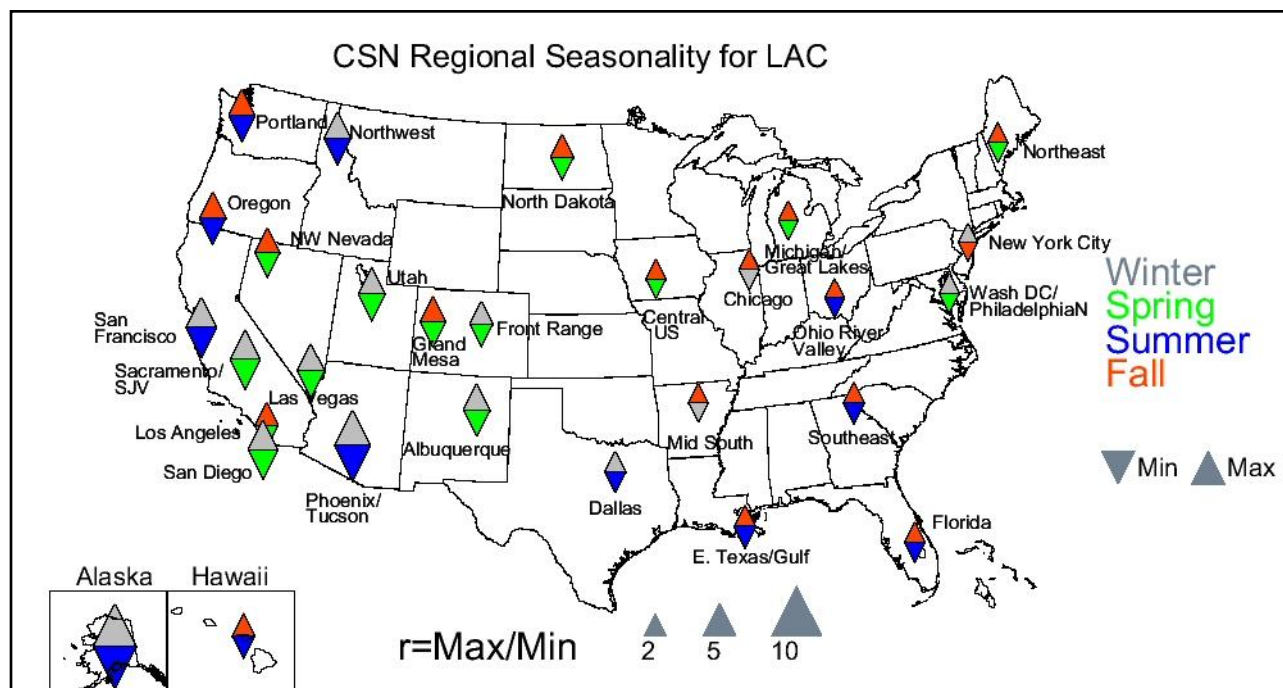


# Seasonality for LAC

IMPROVE

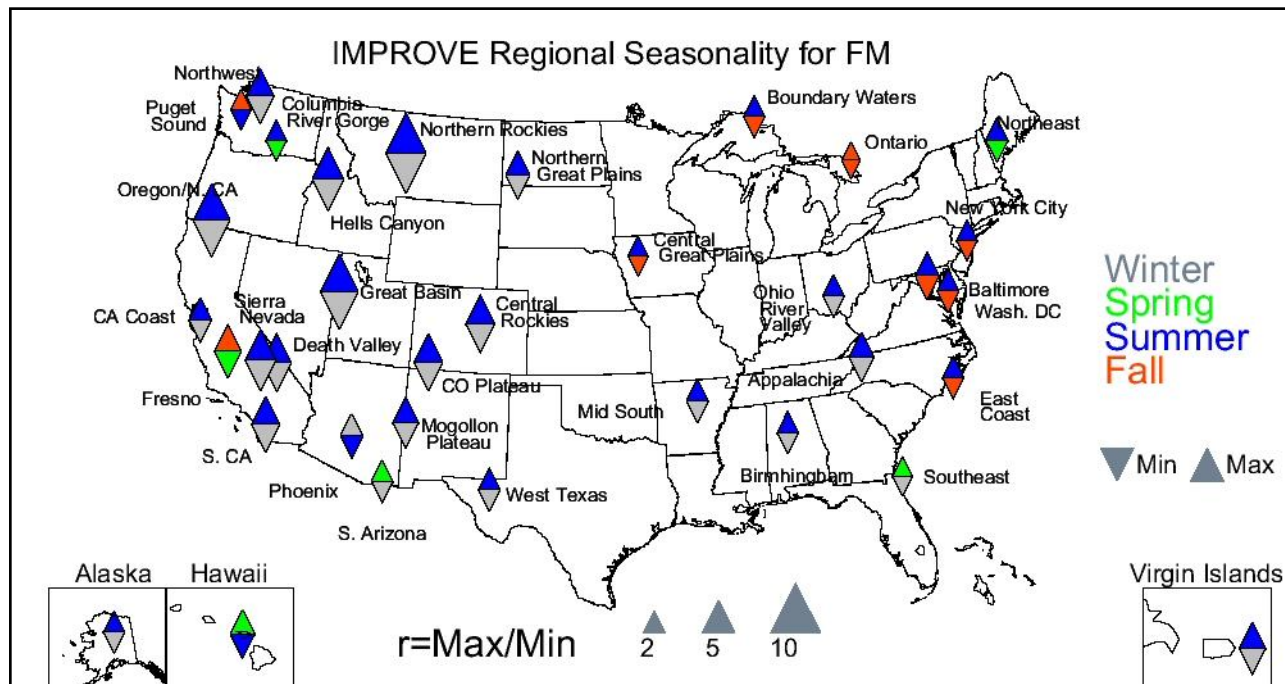


CSN

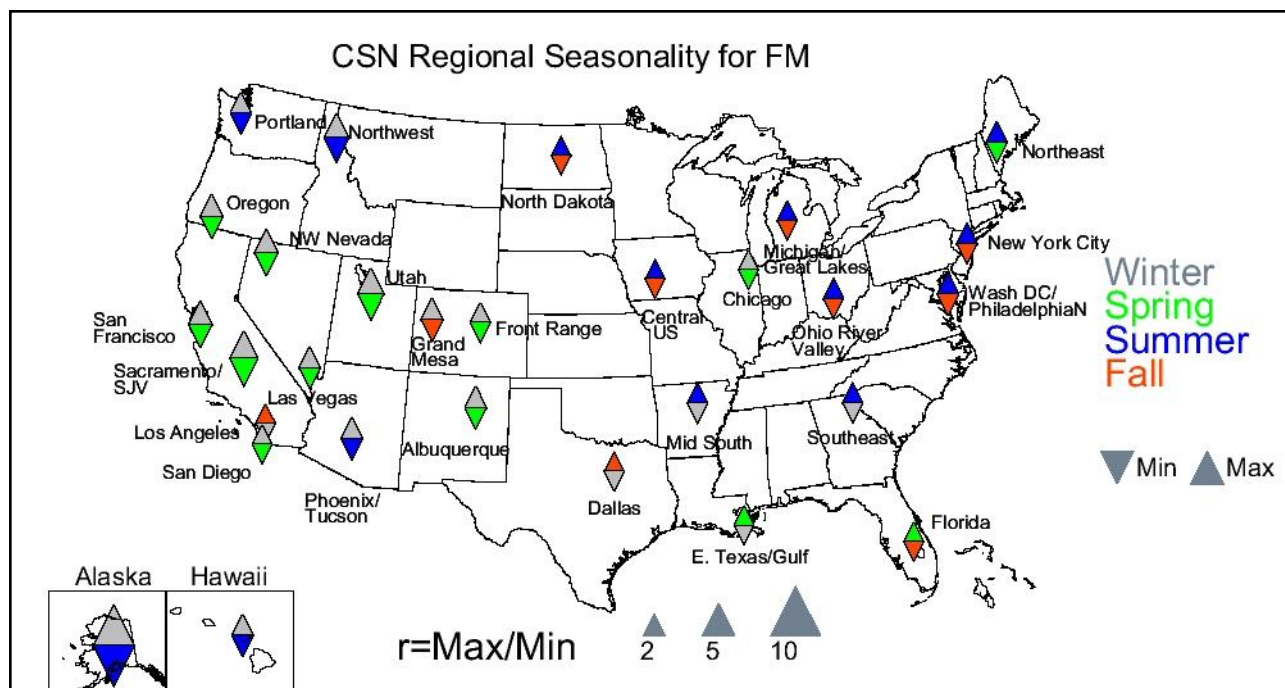


# Seasonality for Fine Mass

IMPROVE

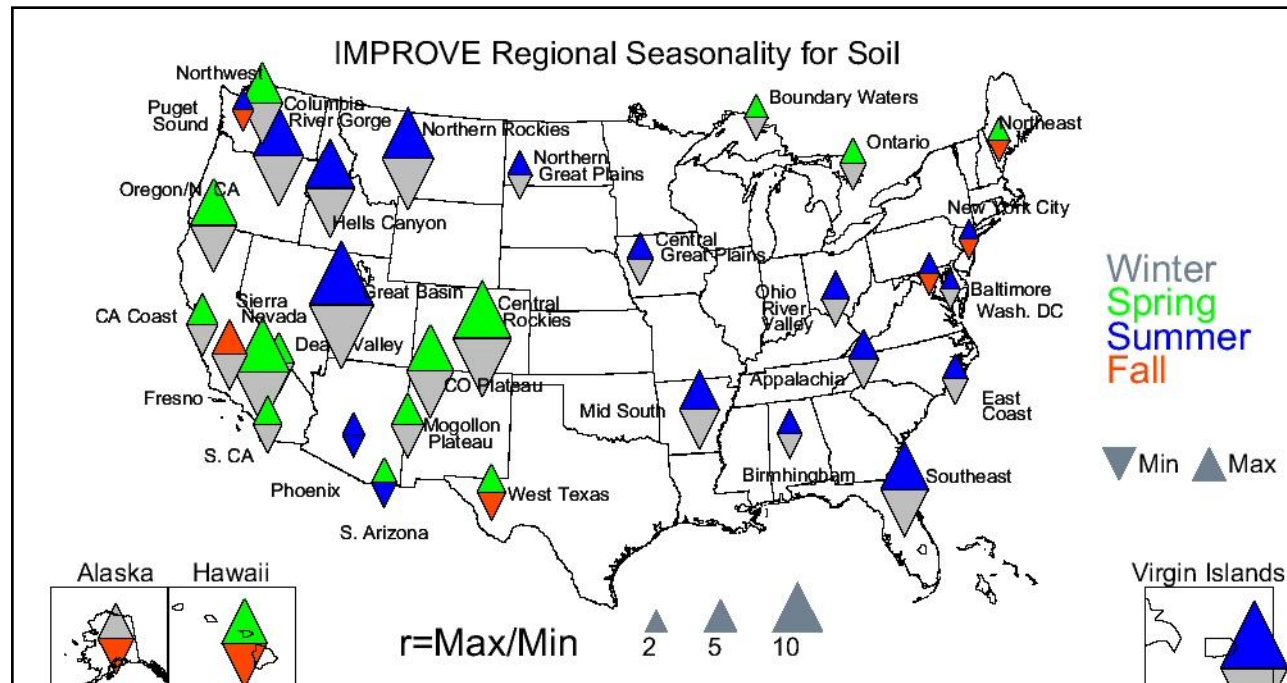


CSN

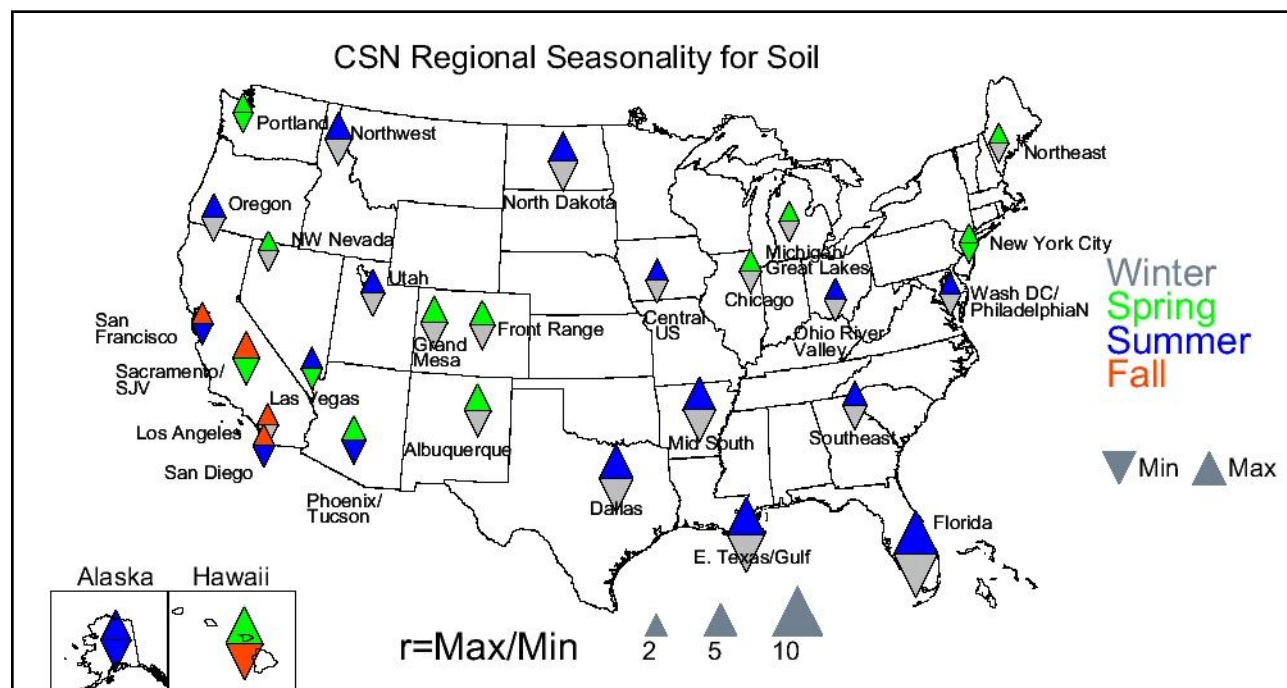


# Seasonality for Soil

IMPROVE



CSN



# Trend Analysis

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- We examined temporal trends in IMPROVE data over the time periods:
  - 1989-2008 (20 year)
  - 2000-2008 (9 year)
- A 50% completeness criteria was applied to data from any given site.
- Species included:
  - Sulfate ion
  - Nitrate ion
  - Organic carbon (OC)
  - Light absorbing carbon (LAC)
  - Total carbon (OC+LAC)
  - Soil
  - Gravimetric fine mass
  - PM10 and Coarse Mass (PM10-PM2.5)

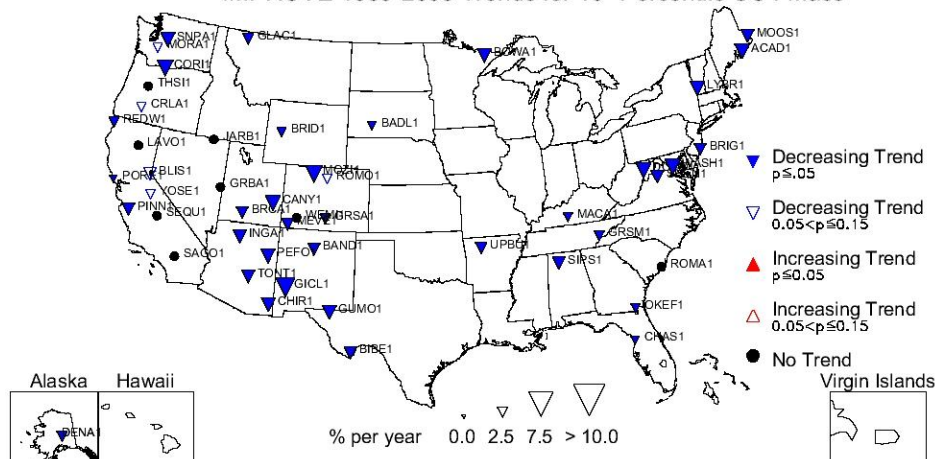
# Trend Analysis

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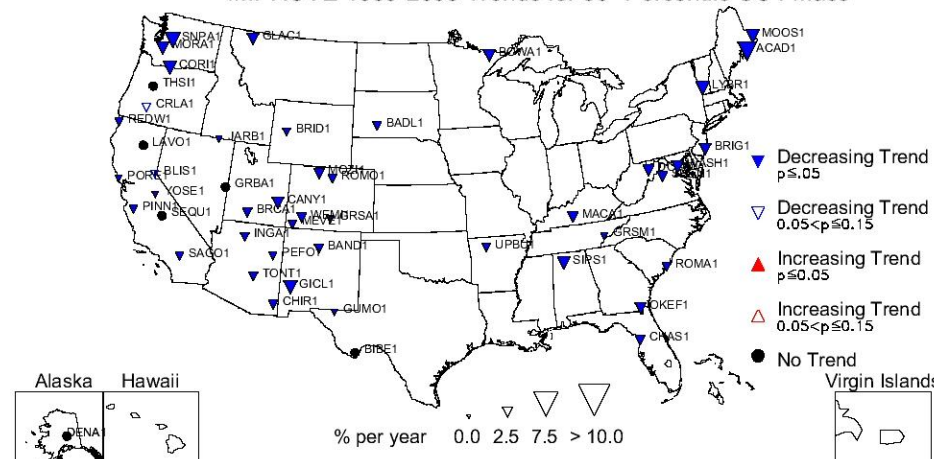
- Trends were computed for 10<sup>th</sup>, 50<sup>th</sup>, 90<sup>th</sup>, Mean, Winter (DJF), Spring (MAM), Summer (JJA) and Fall (SON).
- 70% of the years were required for a given site to be included in the analysis (ranged ~150 sites for 9 yr depending on species, and ~50 sites for 20 yr)
- Theil regression and Kendall's tau statistics were used to compute the slope and the significance, respectively. Theil slope is found by assuming that the true slope is zero and calculating the probability that the estimated slope occurred by chance.
- Significance levels of 0.05 (statistically significant) and 0.15 were used. (A 5 and 15% probability that the differences occurred by chance due to random fluctuations in the time series).

# 20 Year Sulfate Trends

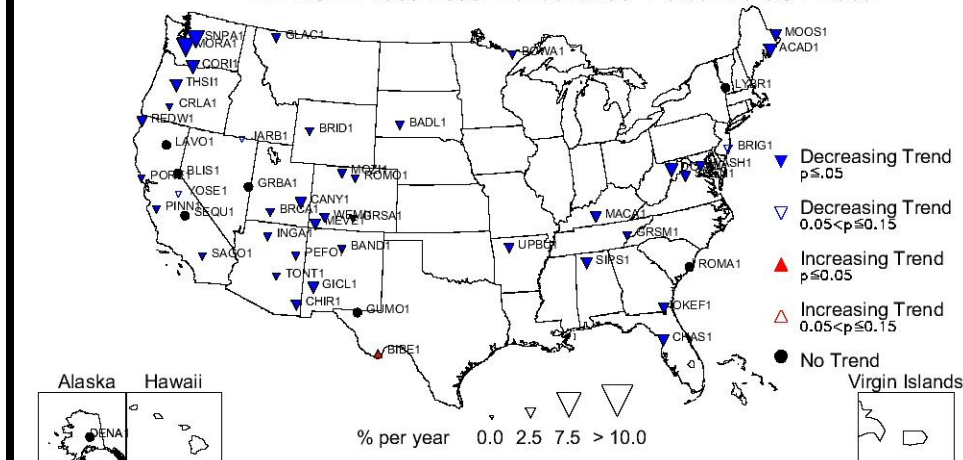
IMPROVE 1989-2008 Trends for 10<sup>th</sup> Percentile SO<sub>4</sub> Mass



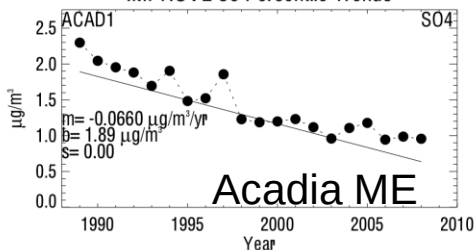
IMPROVE 1989-2008 Trends for 50<sup>th</sup> Percentile SO<sub>4</sub> Mass



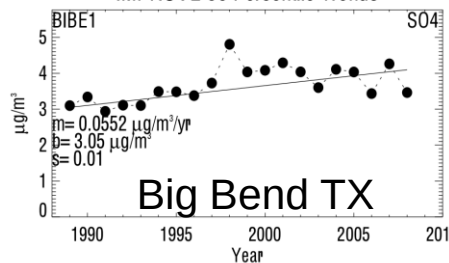
IMPROVE 1989-2008 Trends for 90<sup>th</sup> Percentile SO<sub>4</sub> Mass



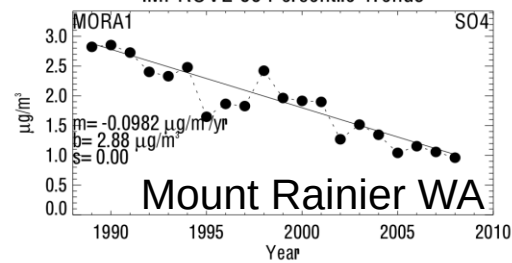
IMPROVE 50 Percentile Trends



IMPROVE 90 Percentile Trends

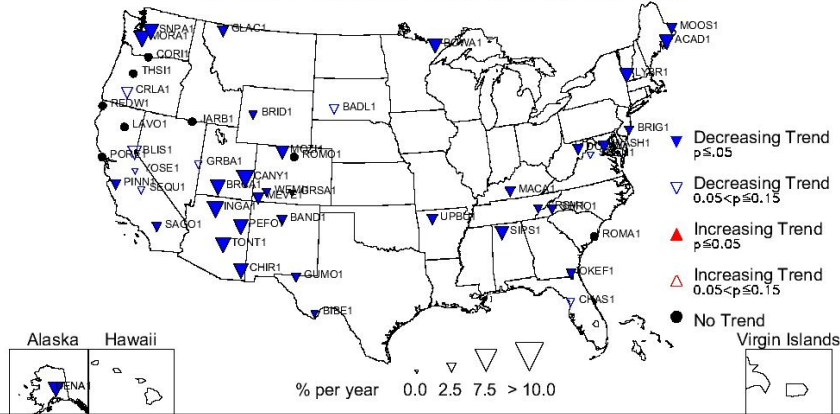


IMPROVE 90 Percentile Trends

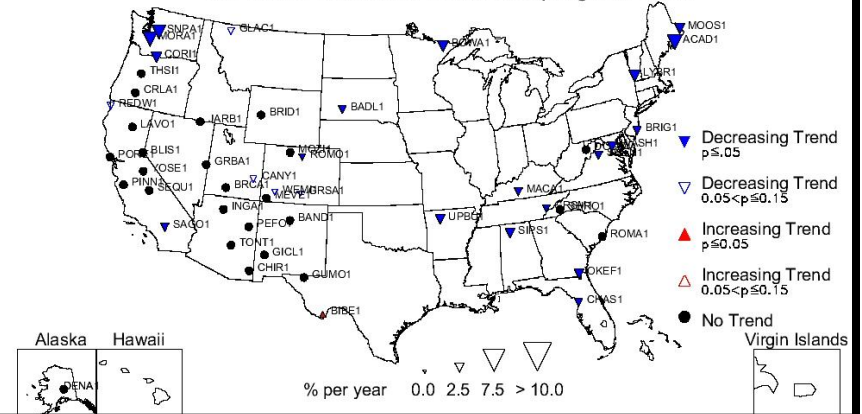


# 20 Year Sulfate Trends

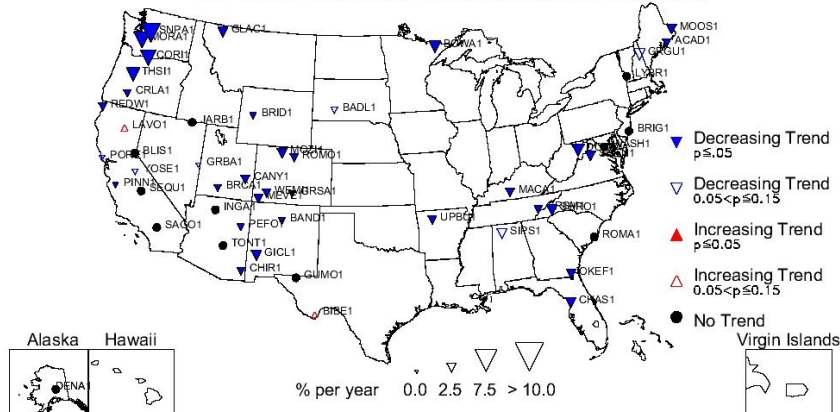
IMPROVE 1989-2008 Trends for Winter SO<sub>4</sub> Mass



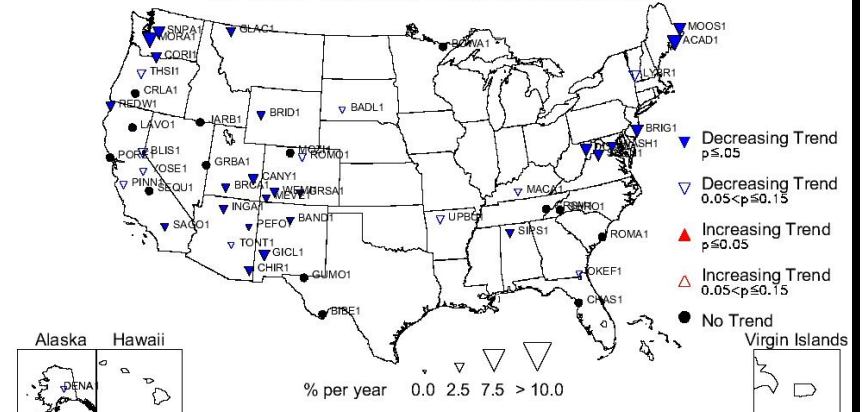
IMPROVE 1989-2008 Trends for Spring SO<sub>4</sub> Mass



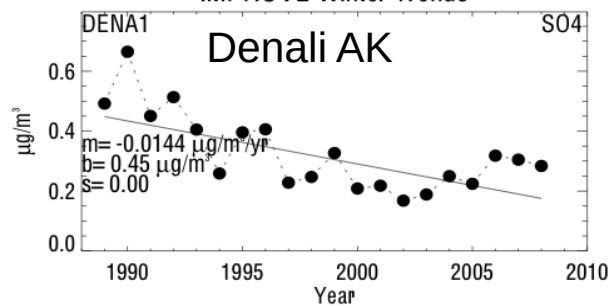
IMPROVE 1989-2008 Trends for Summer SO<sub>4</sub> Mass



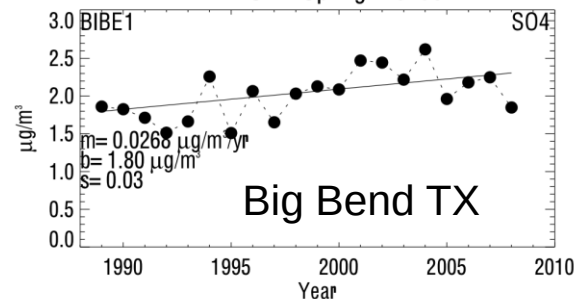
IMPROVE 1989-2008 Trends for Fall SO<sub>4</sub> Mass



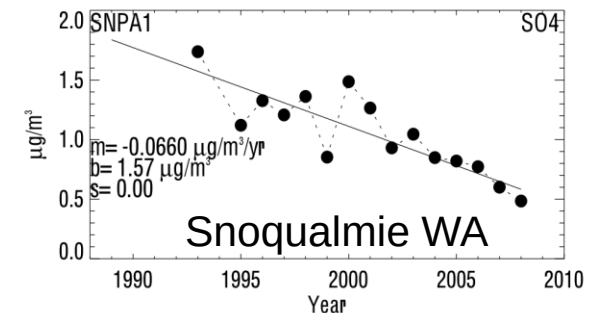
IMPROVE Winter Trends



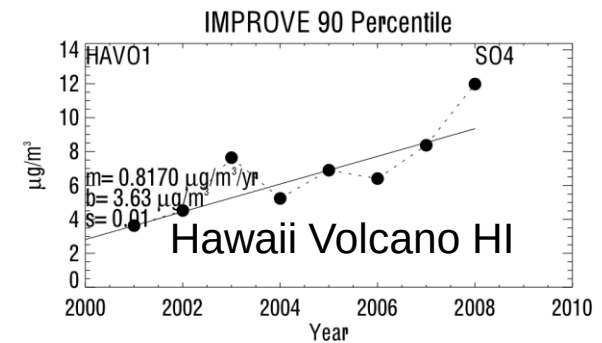
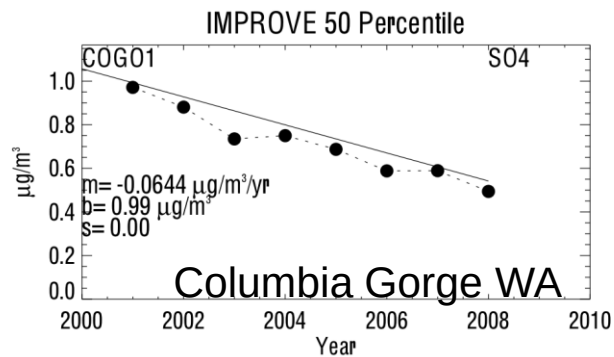
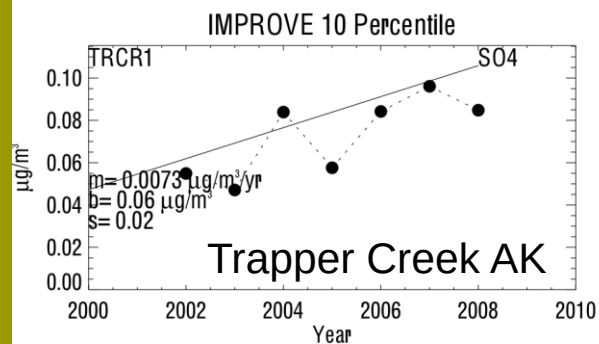
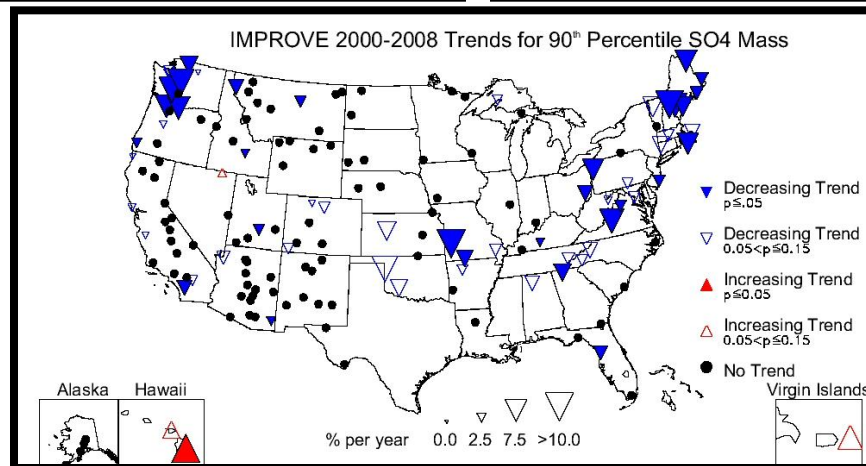
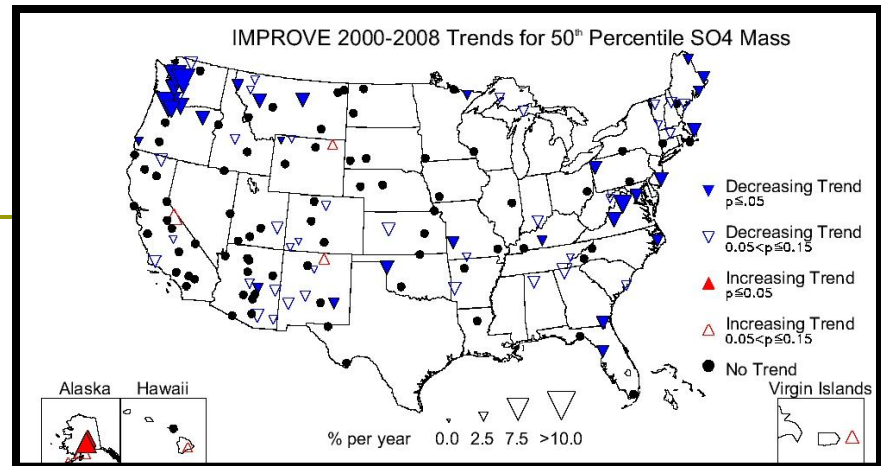
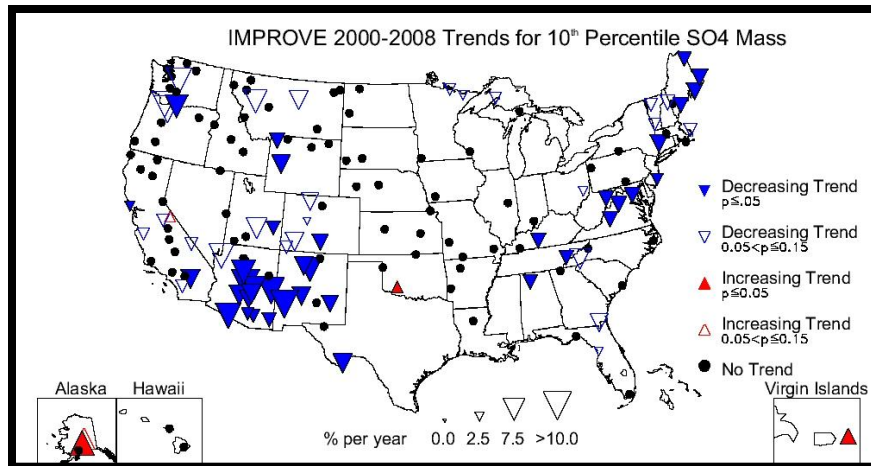
IMPROVE Spring Trends



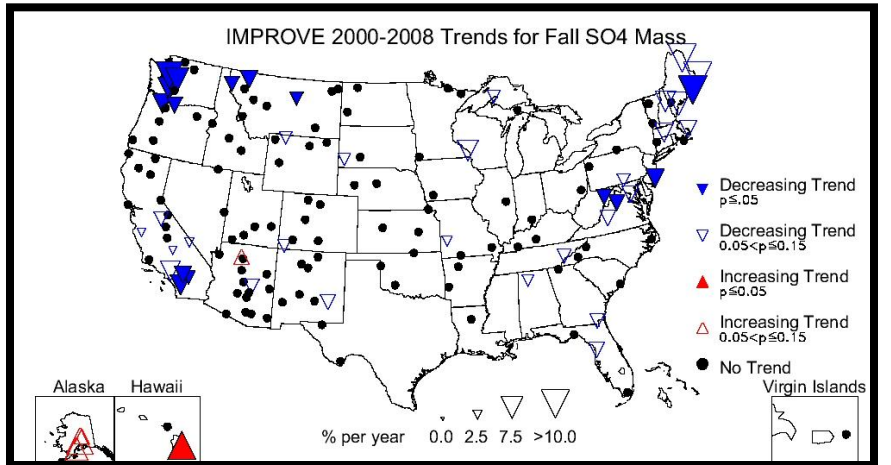
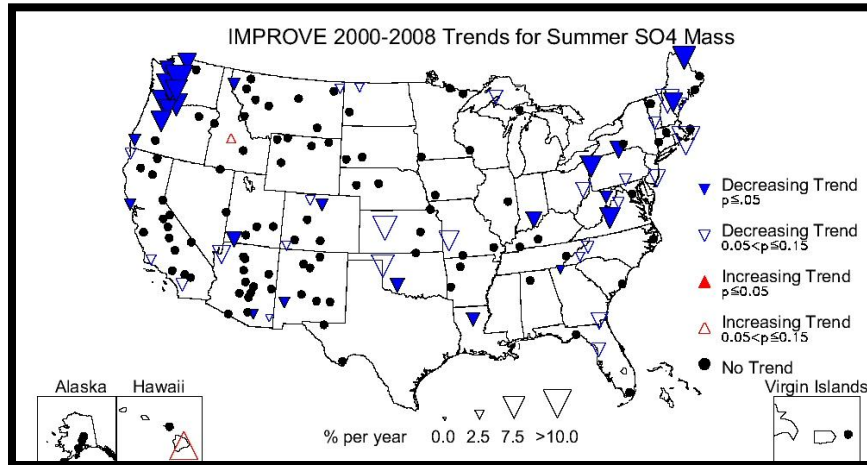
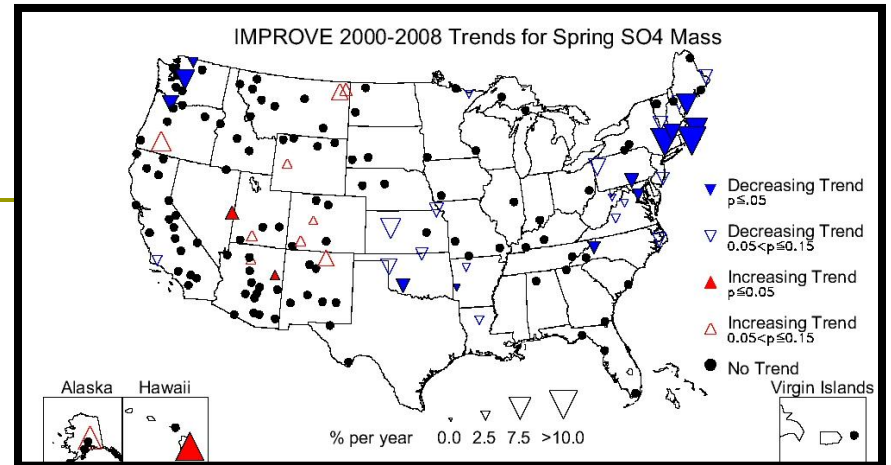
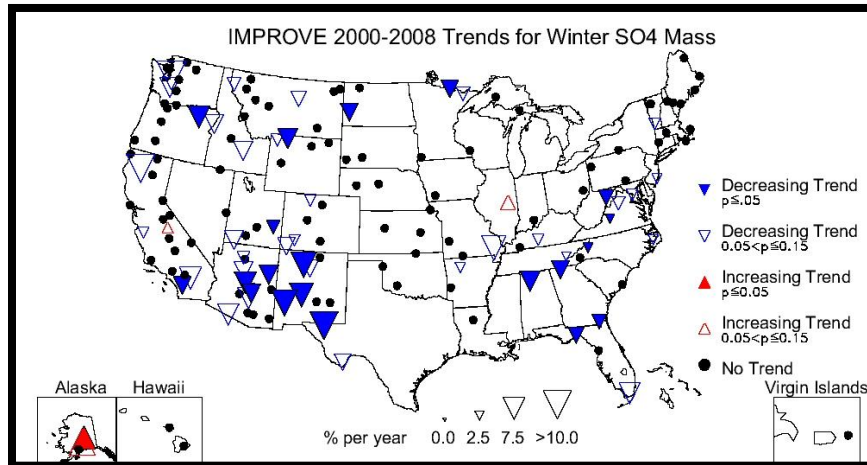
IMPROVE Summer Trends



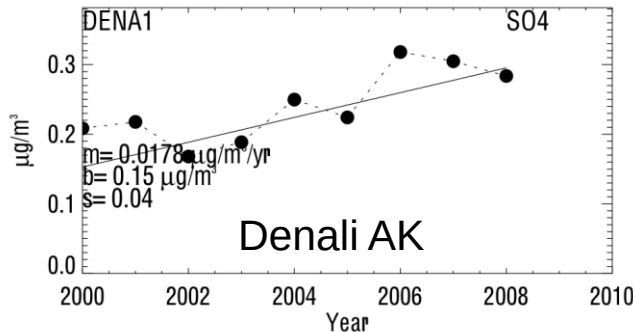
# 9 Year Sulfate Trends



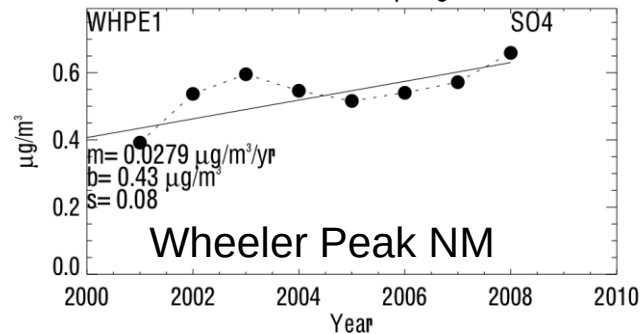
# 9 Year Sulfate Trends



IMPROVE Winter



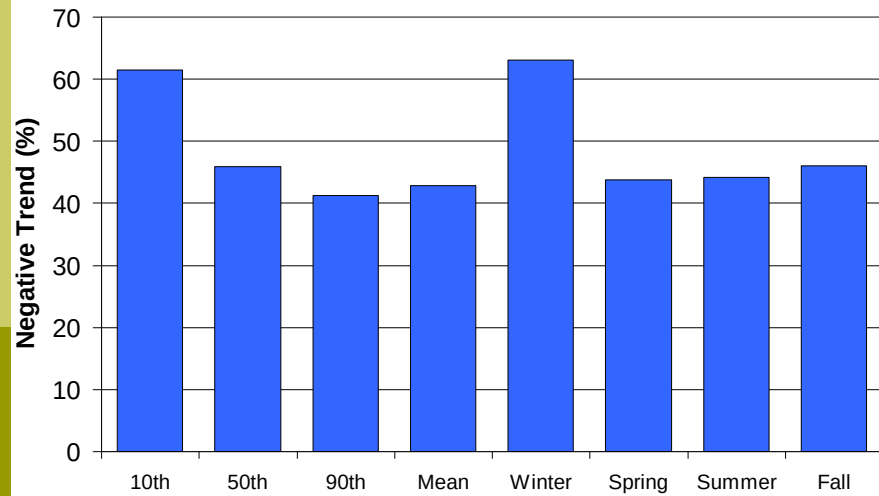
IMPROVE Spring



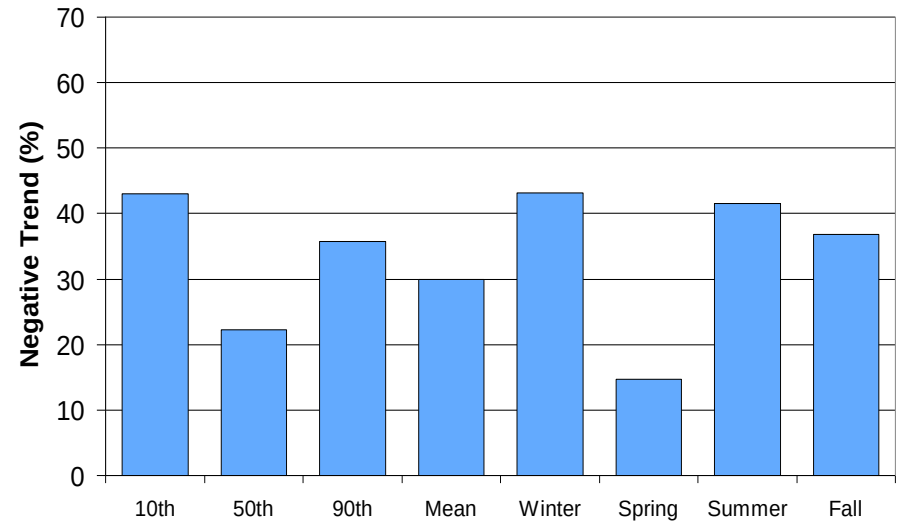
# 9 Year vs 20 Year Sulfate Trends

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**Sulfate Twenty Year Overall Trend (1989-2008)**



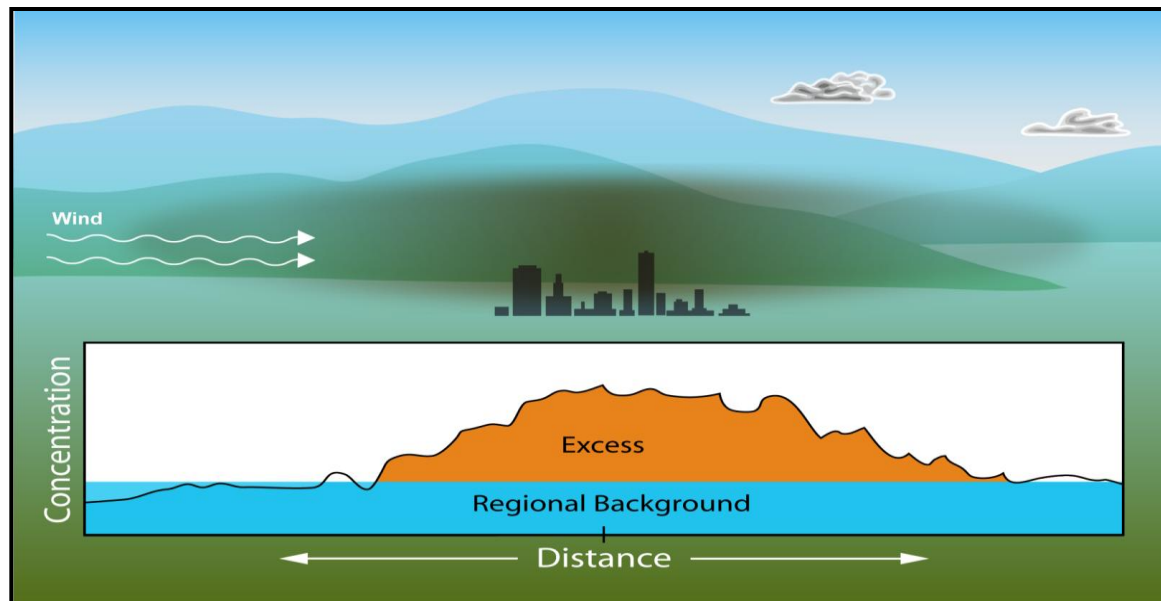
**Sulfate Nine Year Overall Trend (2000-2008)**



# Urban Excess

Computed the ratio and difference in urban and rural concentrations by using the CSN data and the interpolated IMPROVE concentration at the CSN site.

Ratios and differences were also computed using data only; mean rural concentrations were computed using IMPROVE data from sites within 300 km of a CSN site.



# Urban Excess

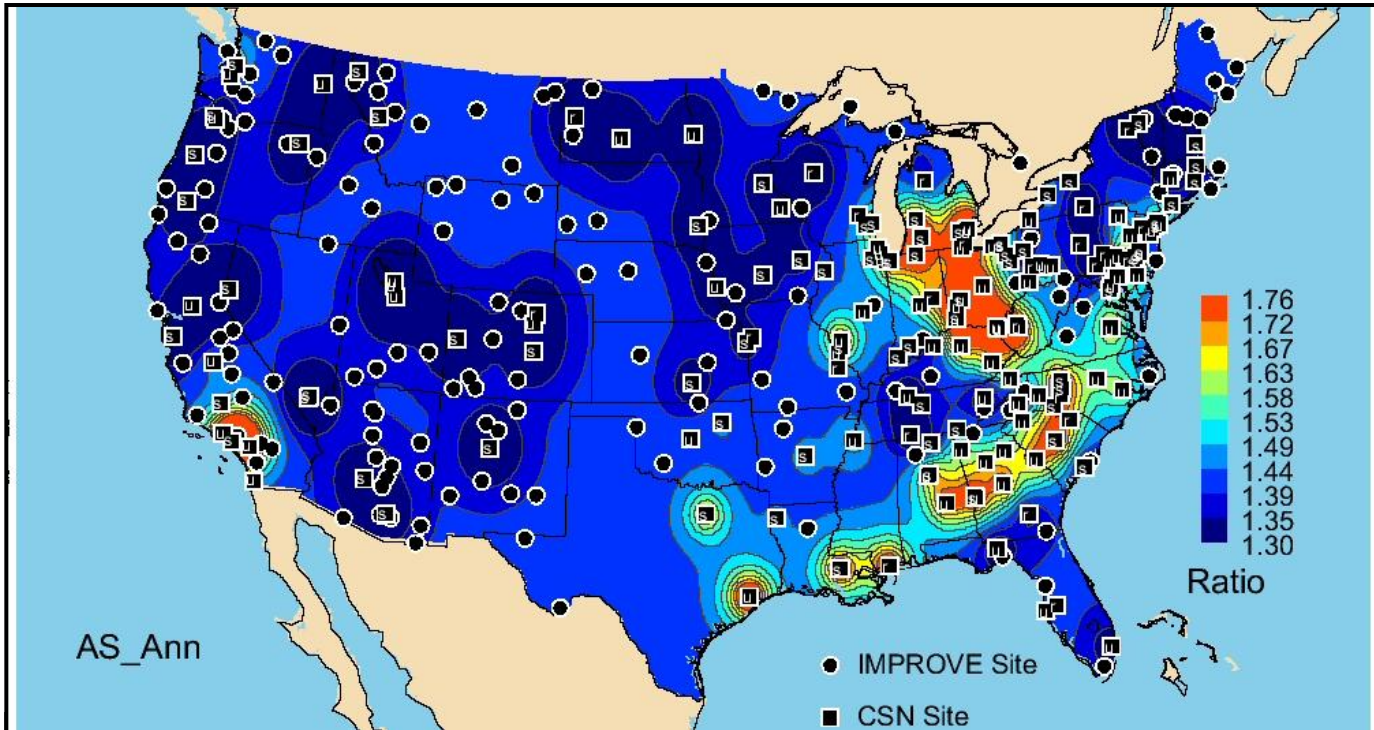
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## Caveats:

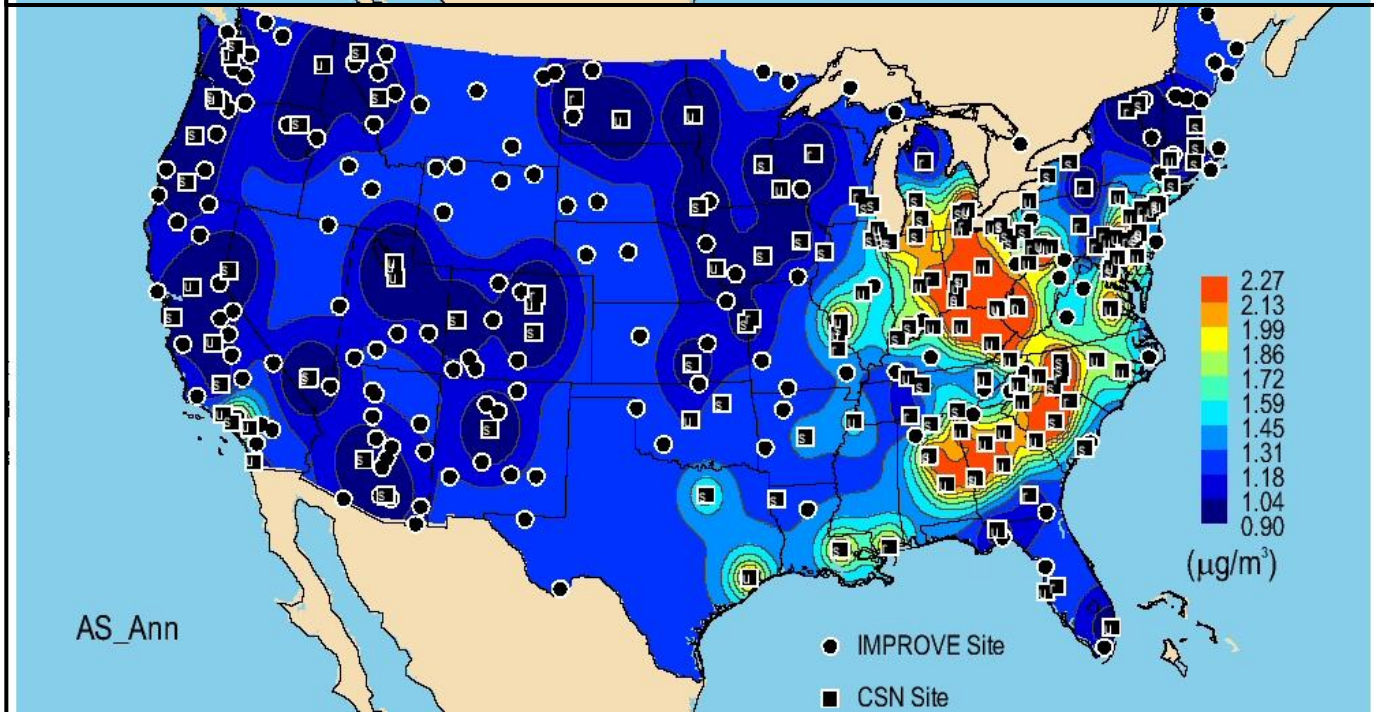
- The urban excess results should be interpreted as semi-quantitative.
- No elevation corrections have been applied. Many remote IMPROVE sites are located at high elevation and could be above the boundary layer.
- Isopleths should not be strictly interpreted, they serve to guide the eye in observing patterns. Site locations for both networks are not regularly spaced; regions with high site density from only one network could affect the derived results (e.g. eastern U.S.).

# Ammonium Sulfate

Urban/Rural

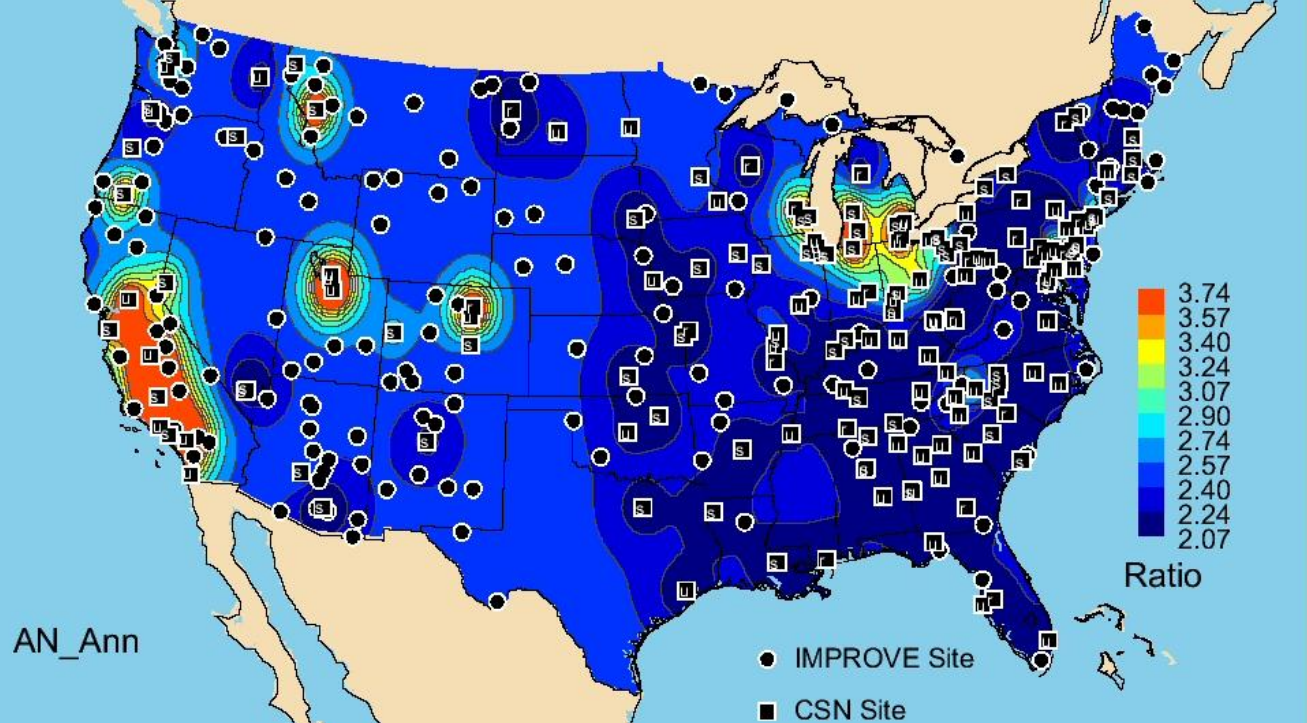


Urban-Rural

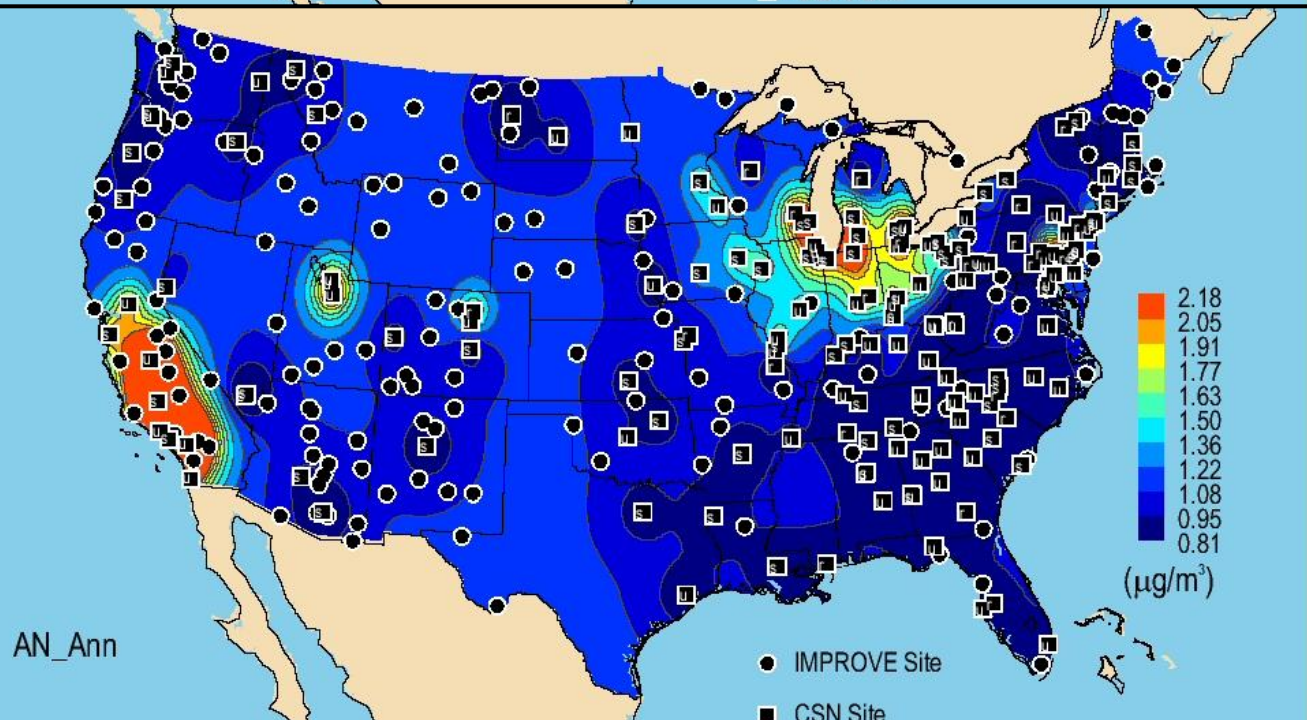


Ammonium  
Nitrate

Urban/Rural



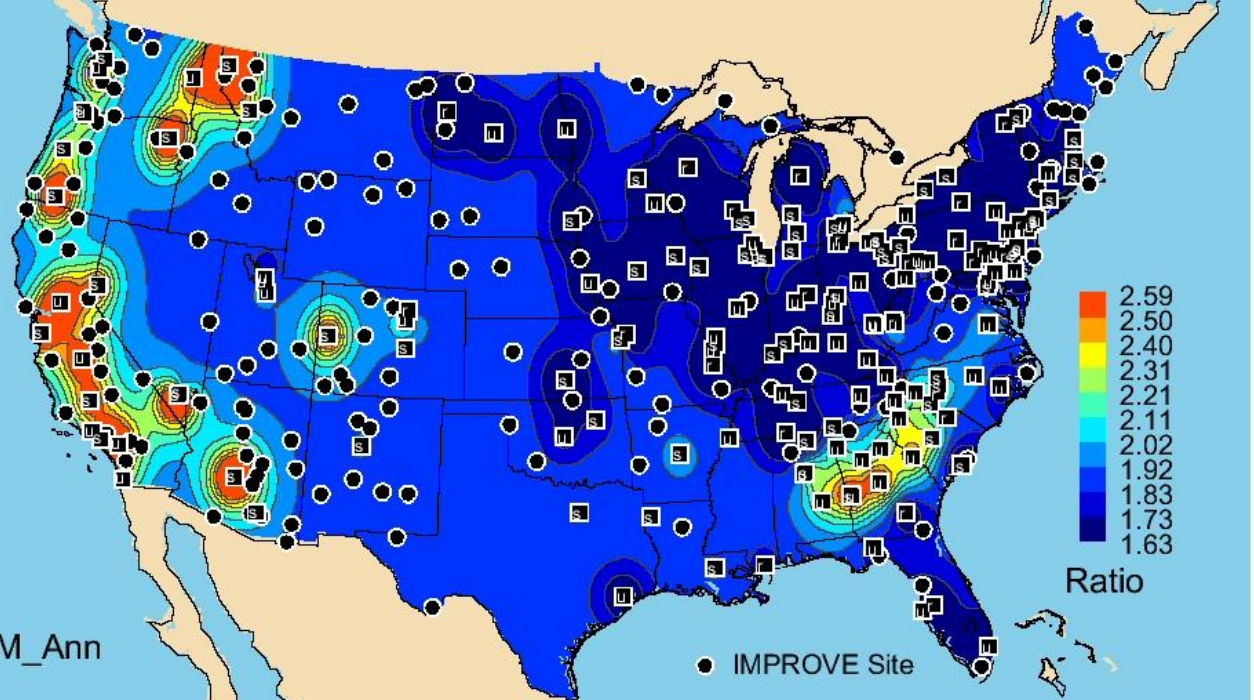
Urban-Rural



POM

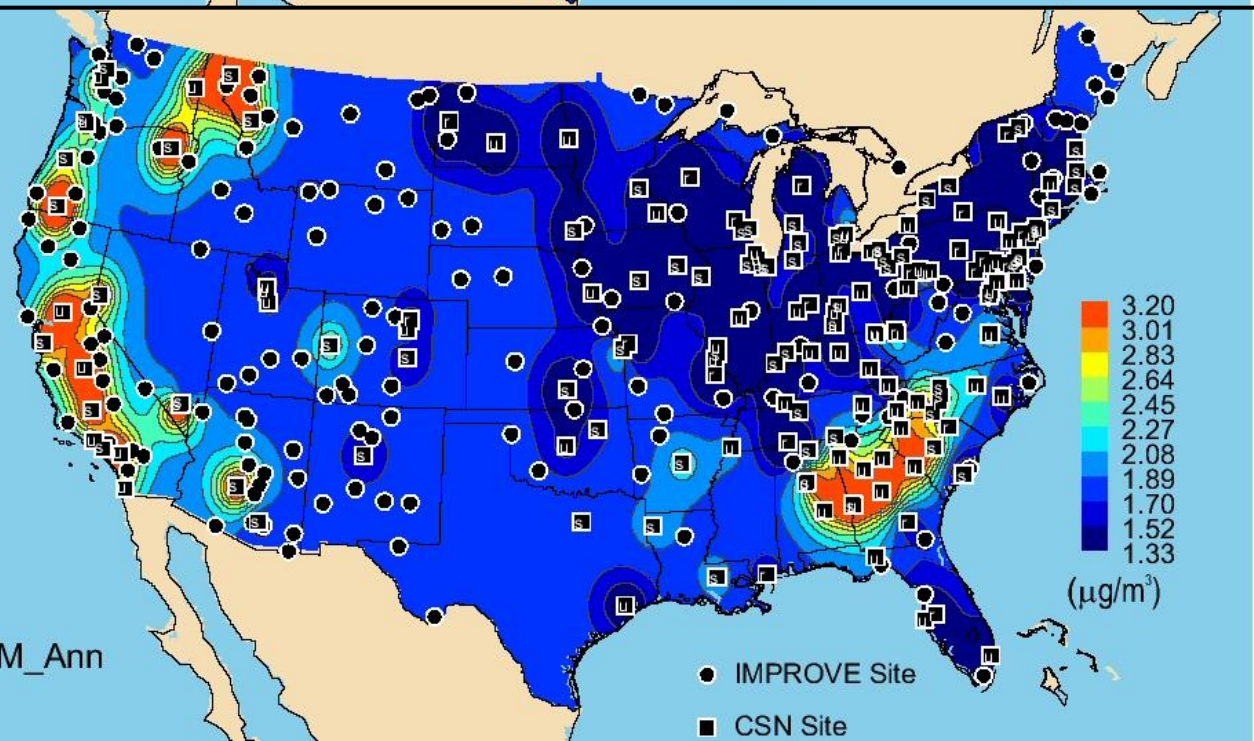
Urban/Rural

POM\_Ann



Urban-Rural

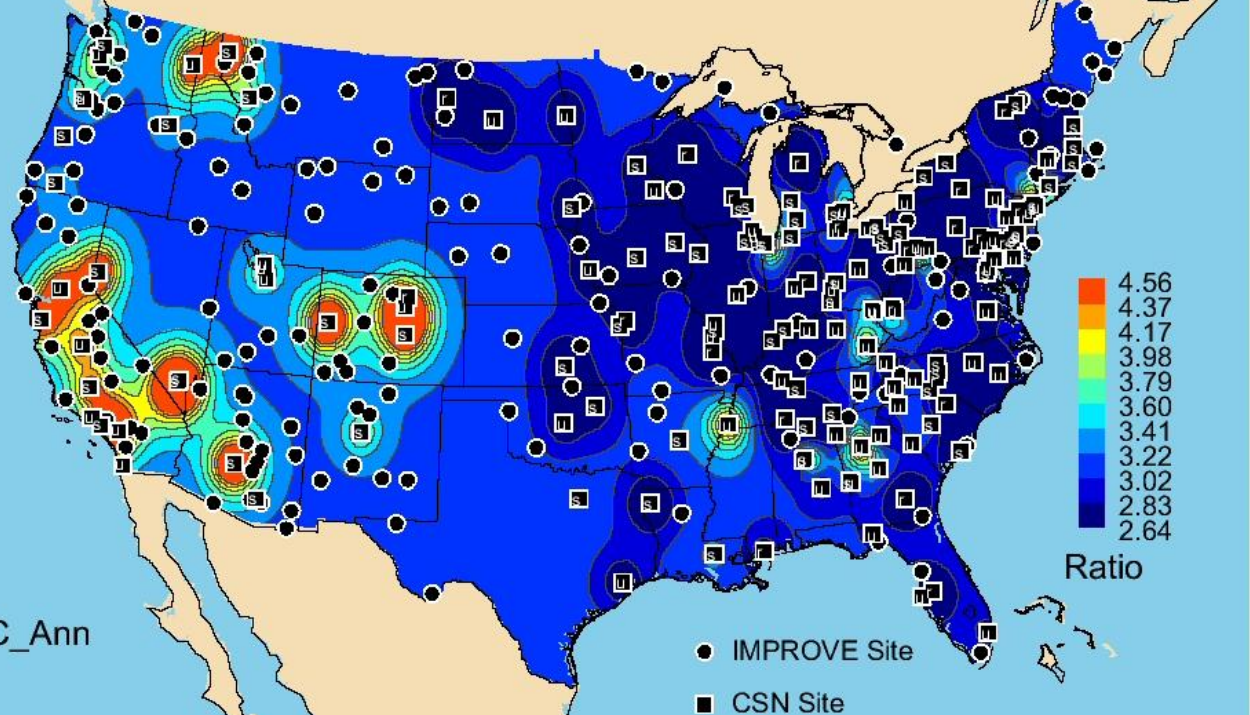
POM\_Ann



LAC

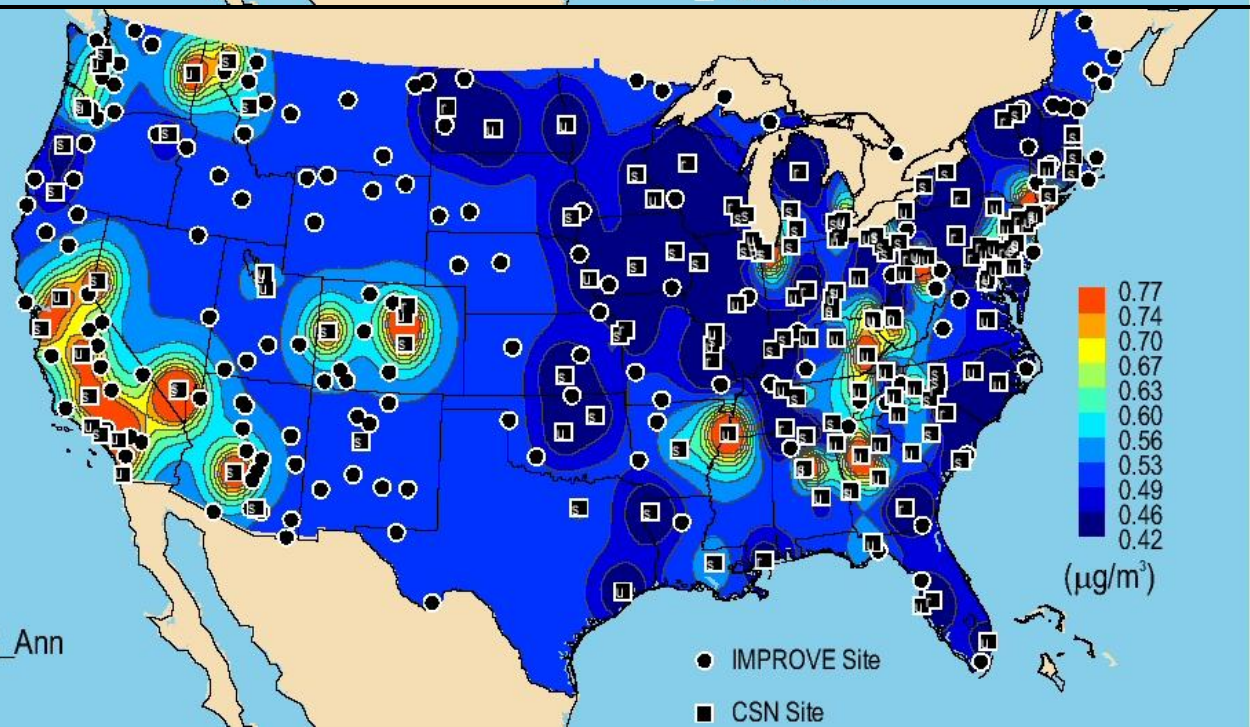
Urban/Rural

LAC\_Ann



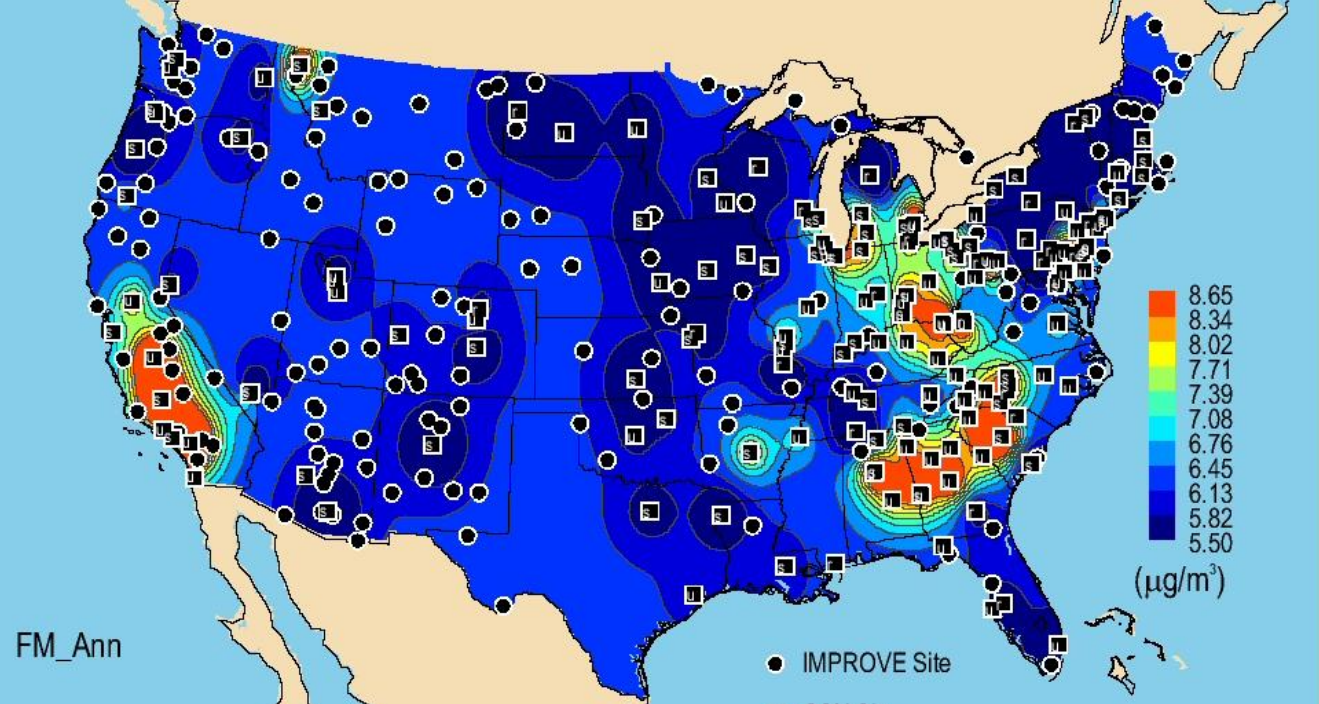
Urban-Rural

LAC\_Ann

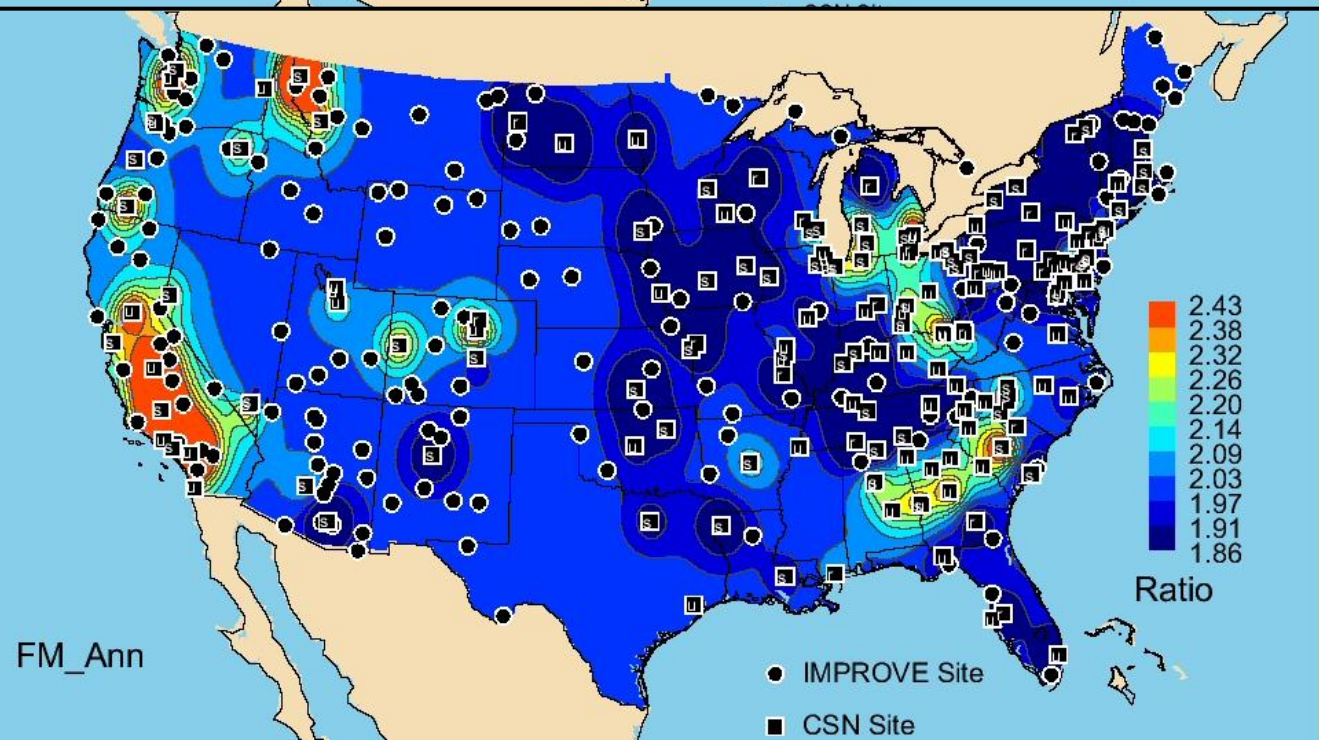


Fine Mass

Urban/Rural



Urban-Rural

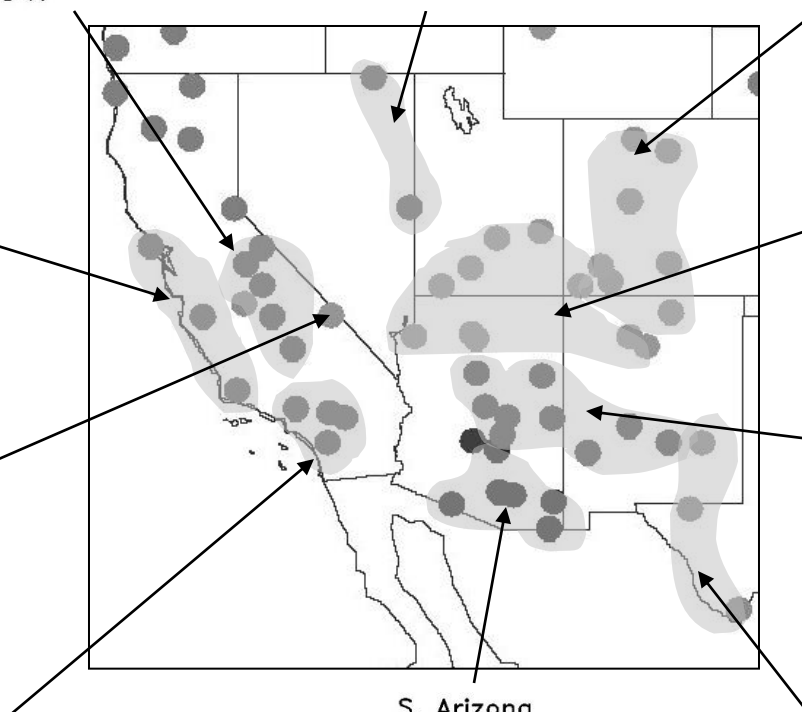
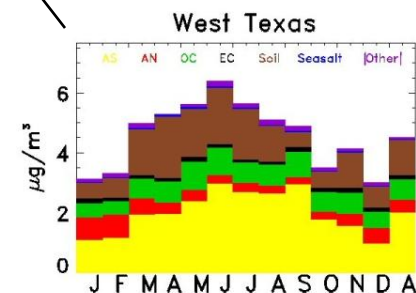
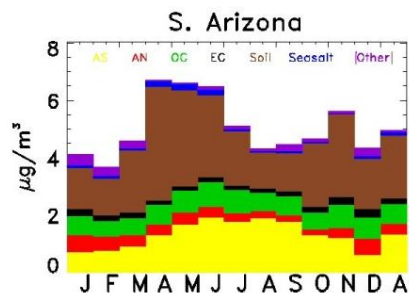
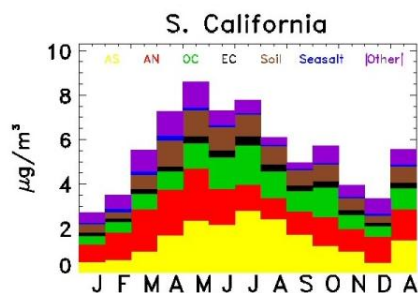
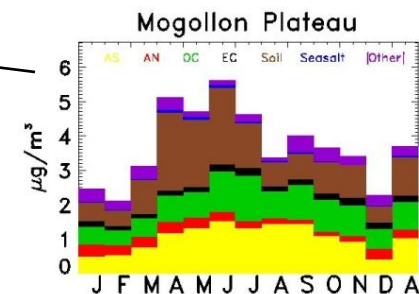
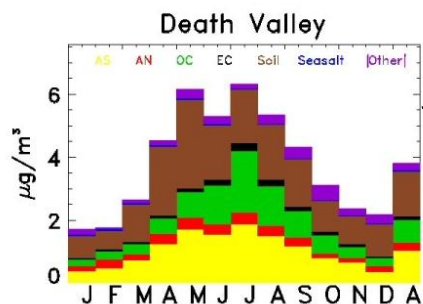
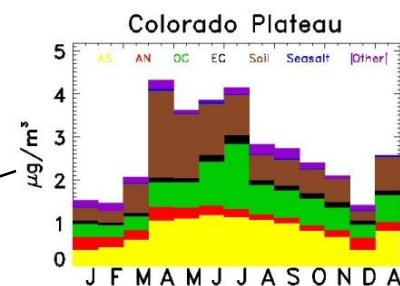
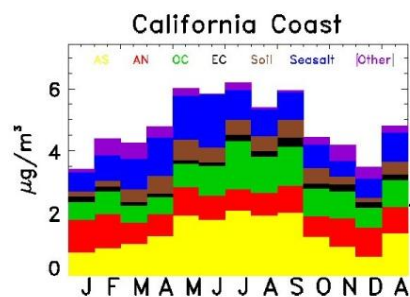
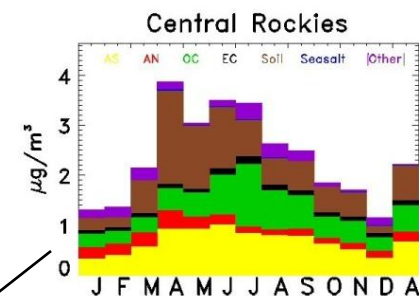
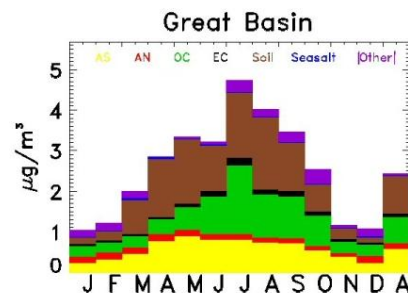
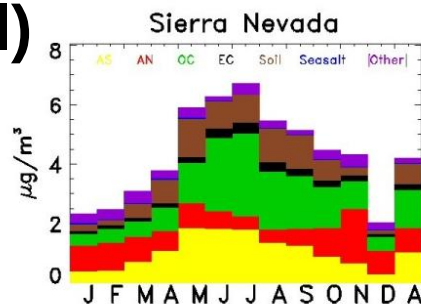


# Extras

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# IMPROVE: Southwest U.S. (rural)

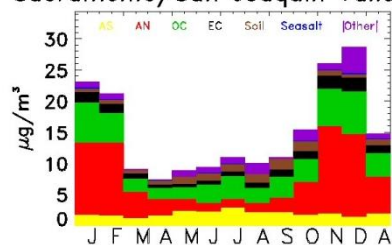
AS AN OC LAC Soil Sea salt |Other|



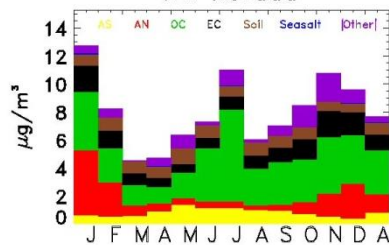
# CSN: Southwest U.S. (urban)

AS AN OC LAC Soil Seasalt |Other|

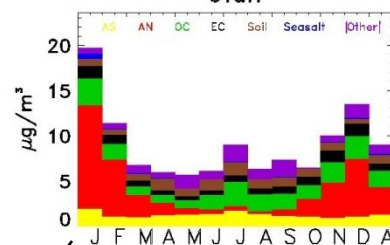
Sacramento/San Joaquin Valley CA



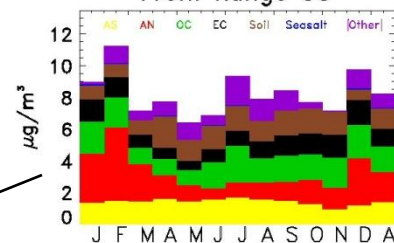
NW Nevada



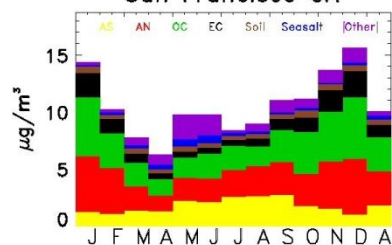
Utah



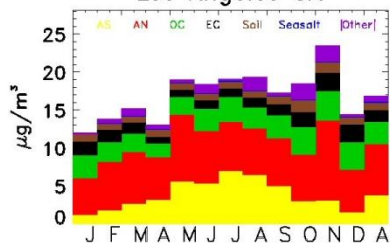
Front Range CO



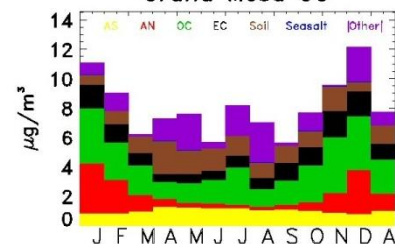
San Francisco CA



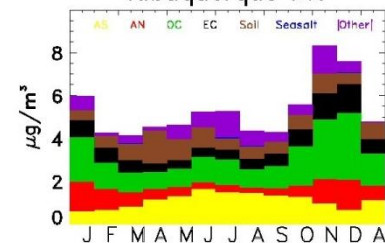
Los Angeles CA



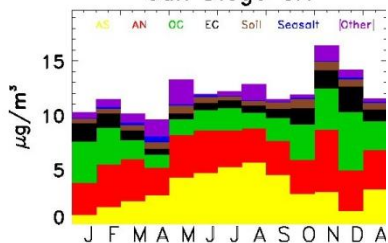
Grand Mesa CO



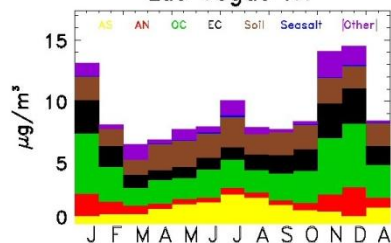
Albuquerque NM



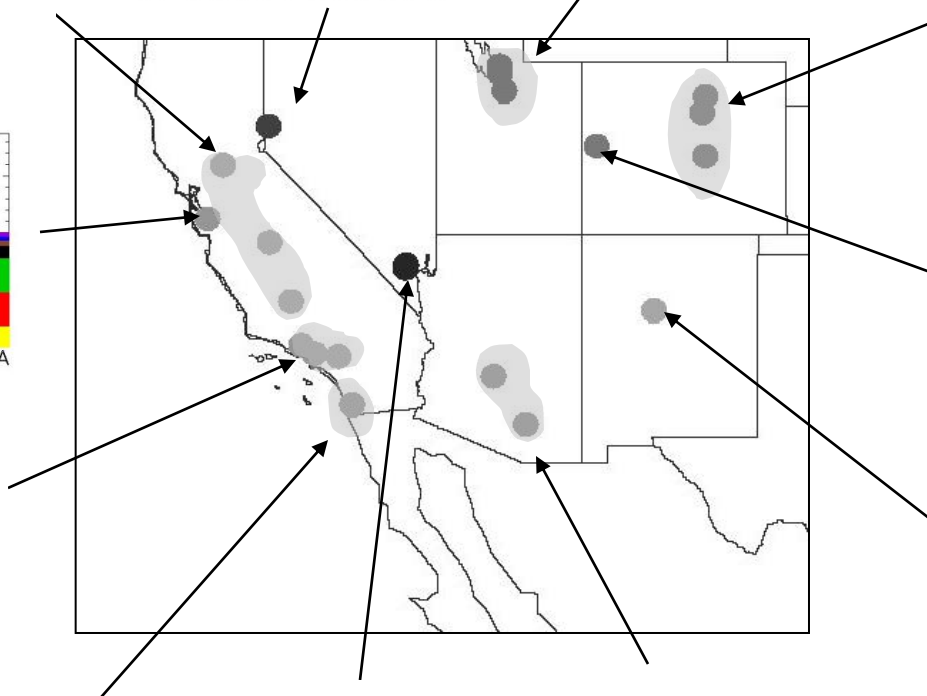
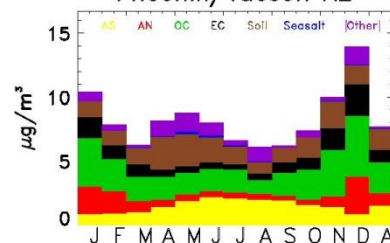
San Diego CA



Las Vegas NV



Phoenix/Tucson AZ



# IMPROVE and CSN Carbon (2)

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## Major Differences:

CSN does not subtract positive artifacts associated with quartz filter sampling  
IMPROVE sampler has a higher face velocity (11 times) compares to Met One Sass sampler  
NIOSH and IMPROVE carbon analysis protocols are different

## Analysis:

Data from 12 urban monitoring sites with collocated IMPROVE and CSN samplers from 2005-2006

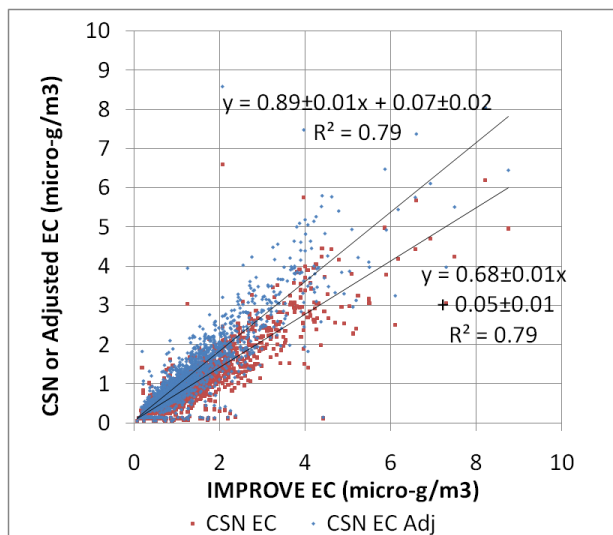
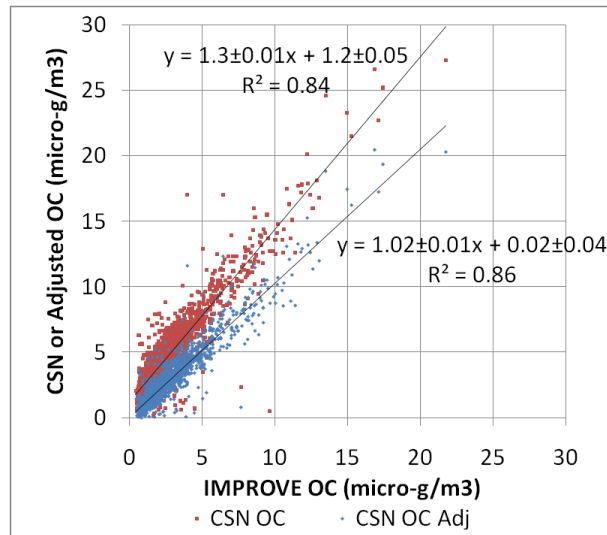
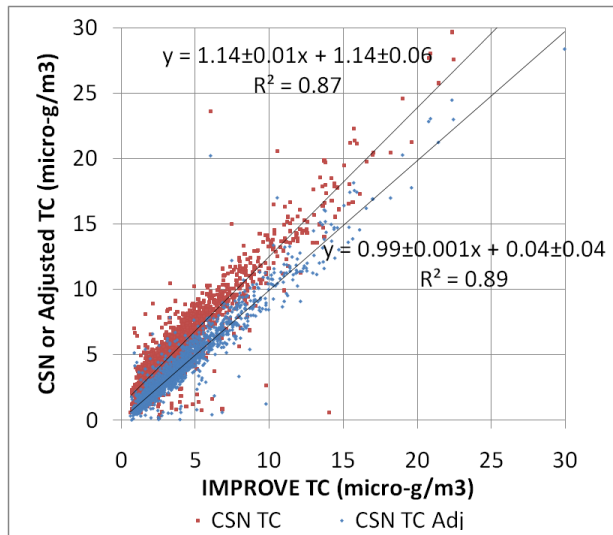
CSN **total carbon** concentrations are systematically higher than IMPROVE TC:

- additive bias interpreted as the positive artifact for uncorrected CSN data
- multiplicative bias interpreted as a negative organic carbon artifact associated with the loss of semivolatile OC from the filter.

IMPROVE **LAC** concentration are systematically higher than CSN LAC:

- Multiplicative bias: mainly analytical and probably due to the fact that the NIOSH TOT method results in lower LAC and higher OC concentrations compared to IMPROVE TOR method.
- No additive bias was observed, consistent with no LAC measured on IMPROVE back up filters
- Essentially increase CSN LAC by 30%

# IMPROVE and CSN Carbon (3)



The CSN and IMPROVE TC, OC and EC concentrations for all collocated IMPROVE and CSN samplers that collected data in 2005 and 2006. The red data points are for the reported CSN carbon concentrations and the blue data points are for the adjusted CSN carbon concentrations.

# IMPROVE/CSN Comparisons

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- Current IMPROVE Report IV (Nov 2006) details the comparisons of data between collocated IMPROVE and CSN sites
- Annual averages for 6 collocated sites in 2002
- Annual averages for 5 collocated sites in 2003

|                                          | <b>PM<sub>2.5</sub></b> | <b>AS</b> | <b>AN</b> | <b>OC</b> | <b>LAC</b> | <b>Soil</b> |
|------------------------------------------|-------------------------|-----------|-----------|-----------|------------|-------------|
| Average IMPROVE ( $\mu\text{g m}^{-3}$ ) | 9.1                     | 3.3       | 1.1       | 4.0       | 0.6        | 1.4         |
| Average CSN ( $\mu\text{g m}^{-3}$ )     | 9.2                     | 3.2       | 1.0       | 4.1       | 0.5        | 0.9         |
| Error (%)                                | 8.3                     | 5.5       | 13.2      | 16.0      | 15.9       | 35.5        |
| Bias (%)                                 | 1.3                     | -0.6      | -0.5*     | -0.8*     | -10.4*     | -30.8*      |

\* IMPROVE is higher

# IMPROVE and CSN Carbon (1)

Table 2. The negative multiplicative artifact (M) and the monthly positive additive organic artifact (a) used to convert the CSN carbon concentrations to IMPROVE. The units for the positive artifacts are  $\mu\text{g}/\text{m}^3$  and  $b_{\text{OC}}$  is unitless.

$$\text{EC}_{\text{adj}} = 1.3 \cdot \text{EC}$$

$$\text{OC}_{\text{adj}} = ((\text{OC} - 0.3 \cdot \text{EC}) - a) / M$$

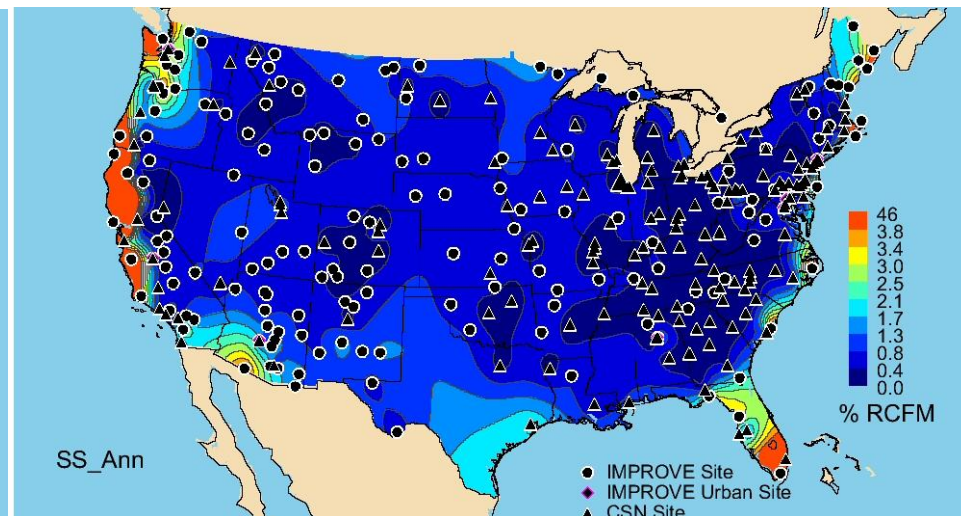
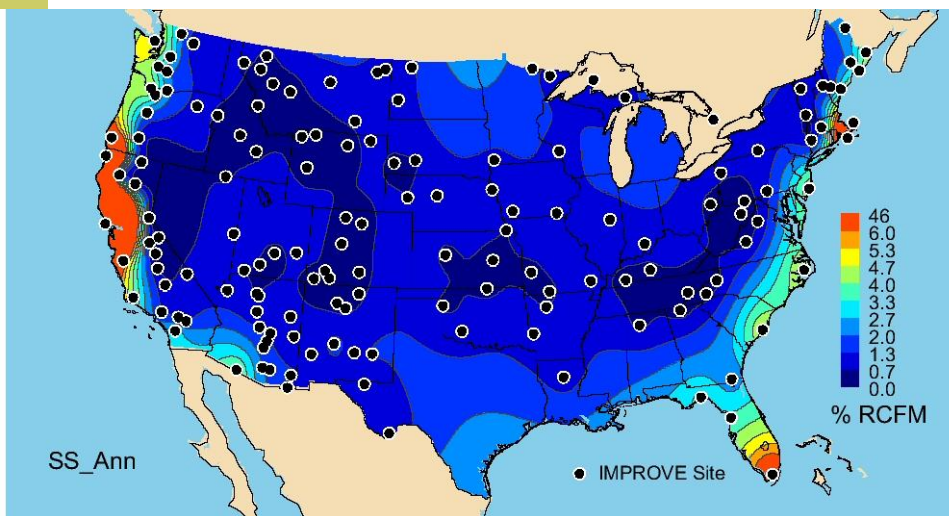
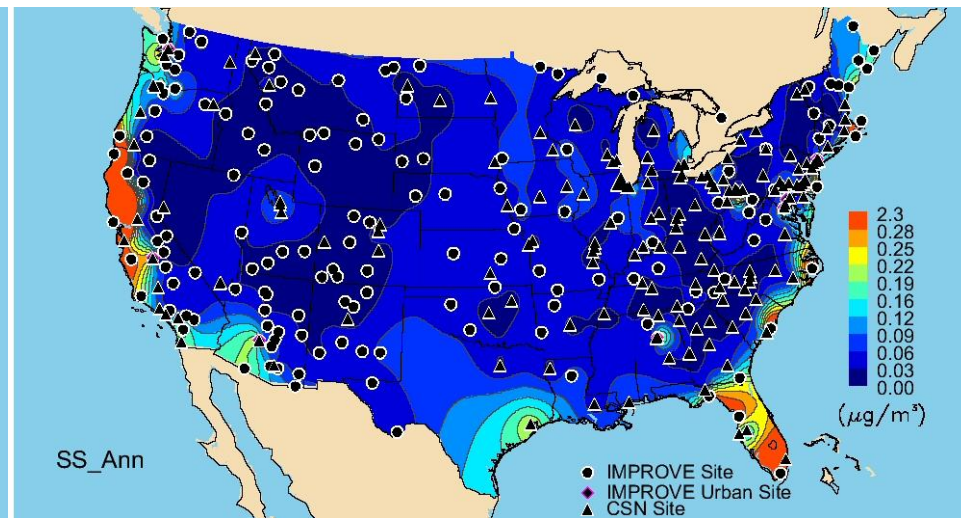
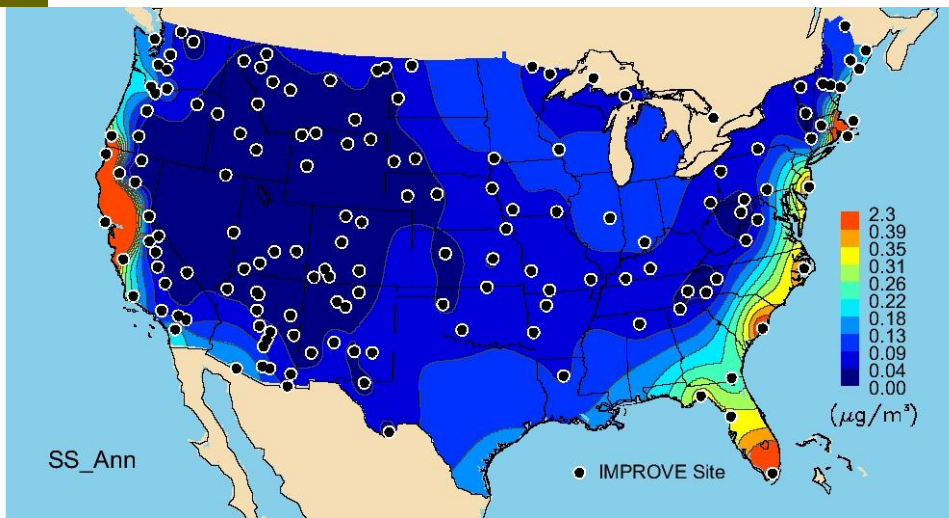
|                        | MetOne | Anderson | URG  | R&P-2300 | R&P-2025 |
|------------------------|--------|----------|------|----------|----------|
| <b>M</b>               | 1.2    | 1.2      | 1.1  | 1.1      | 1.1      |
| <b>a<sub>Jan</sub></b> | 1.1    | 0.92     | 0.24 | 1.2      | 0.24     |
| <b>a<sub>Feb</sub></b> | 1.3    | 1.1      | 0.27 | 1.4      | 0.27     |
| <b>a<sub>Mar</sub></b> | 1.2    | 1.0      | 0.26 | 1.4      | 0.26     |
| <b>a<sub>Apr</sub></b> | 1.4    | 1.2      | 0.29 | 1.5      | 0.29     |
| <b>a<sub>May</sub></b> | 1.6    | 1.3      | 0.33 | 1.7      | 0.33     |
| <b>a<sub>Jun</sub></b> | 1.7    | 1.4      | 0.35 | 1.8      | 0.35     |
| <b>a<sub>Jul</sub></b> | 1.8    | 1.5      | 0.38 | 2.0      | 0.38     |
| <b>a<sub>Aug</sub></b> | 1.9    | 1.6      | 0.41 | 2.1      | 0.41     |
| <b>a<sub>Sep</sub></b> | 1.5    | 1.2      | 0.31 | 1.6      | 0.31     |
| <b>a<sub>Oct</sub></b> | 1.2    | 0.90     | 0.23 | 1.2      | 0.23     |
| <b>a<sub>Nov</sub></b> | 1.0    | 0.85     | 0.22 | 1.1      | 0.22     |
| <b>a<sub>Dec</sub></b> | 1.1    | 0.89     | 0.23 | 1.2      | 0.23     |

# IMPROVE and CSN

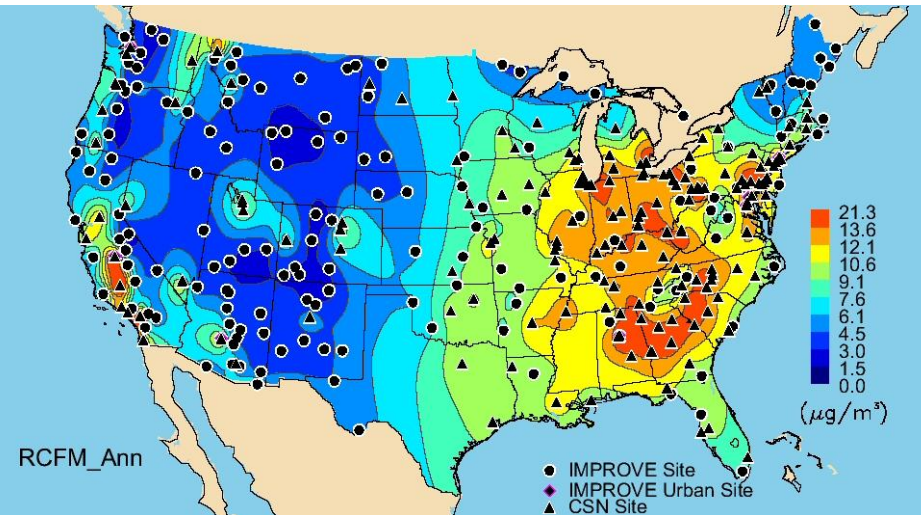
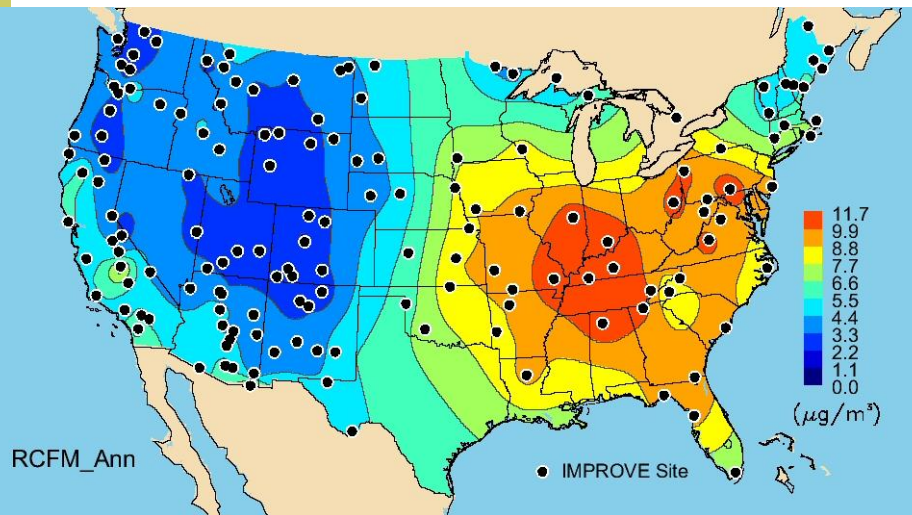
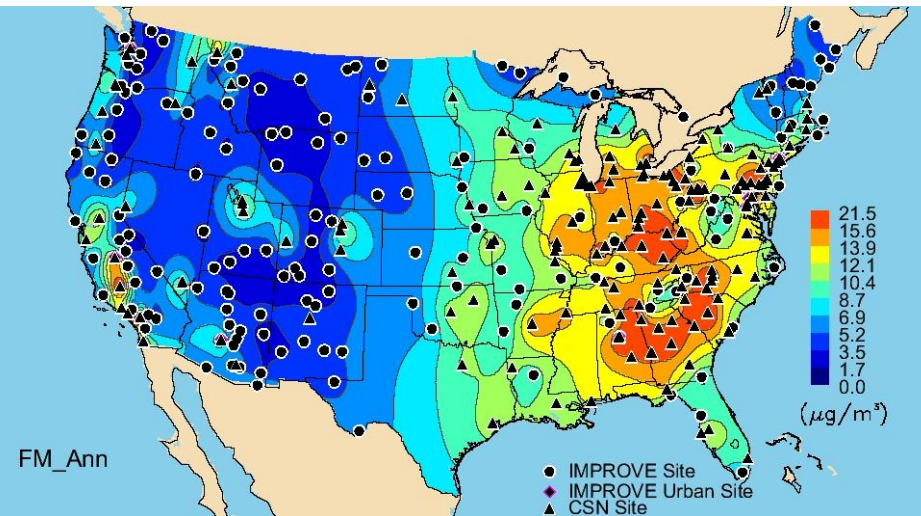
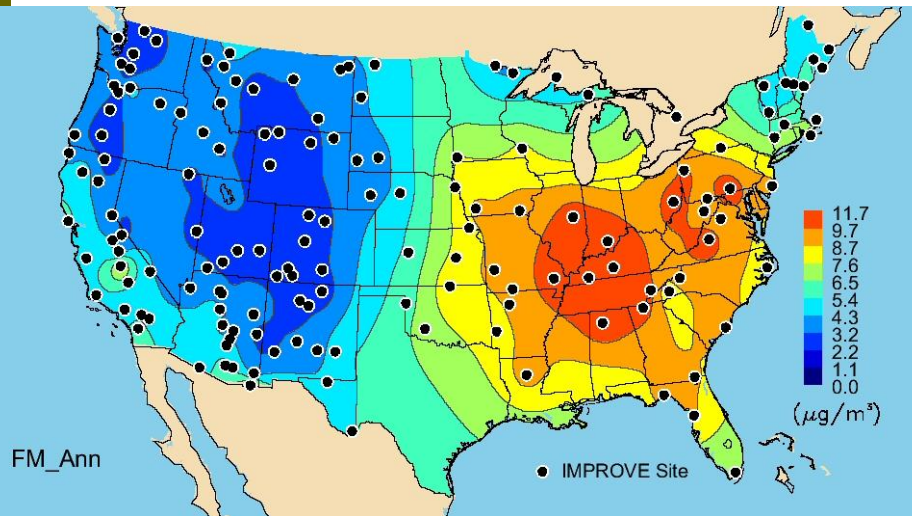
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- The IMPROVE and CSN networks operate a similar 1-in-3 (or 1-in-6) day sampling schedule during which  $PM_{2.5}$  aerosols are collected for analyses of speciated composition.
- Similar chemical analyses are employed by both networks to determine gravimetric  $PM_{2.5}$  mass, inorganic species and mineral species.
- Carbon: IMPROVE uses thermal optical reflectance (TOR) and CSN uses thermal optical transmission (TOT), both of which are known to produce similar total carbon concentrations but different splits between organic carbon (OC) and light absorbing carbon (LAC).
- IMPROVE regularly blank corrects carbon data, CSN does not. We applied blank corrections to CSN OC and LAC data to account for both positive and negative artifacts.

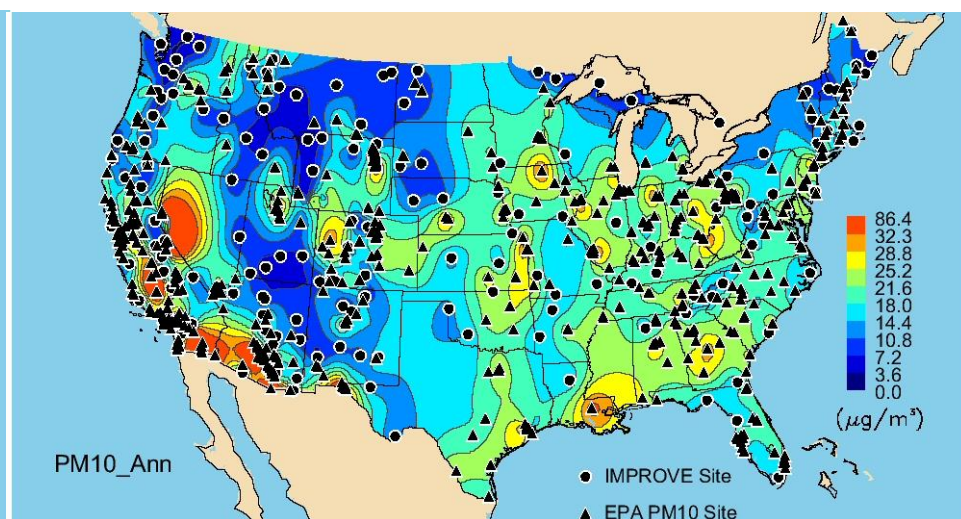
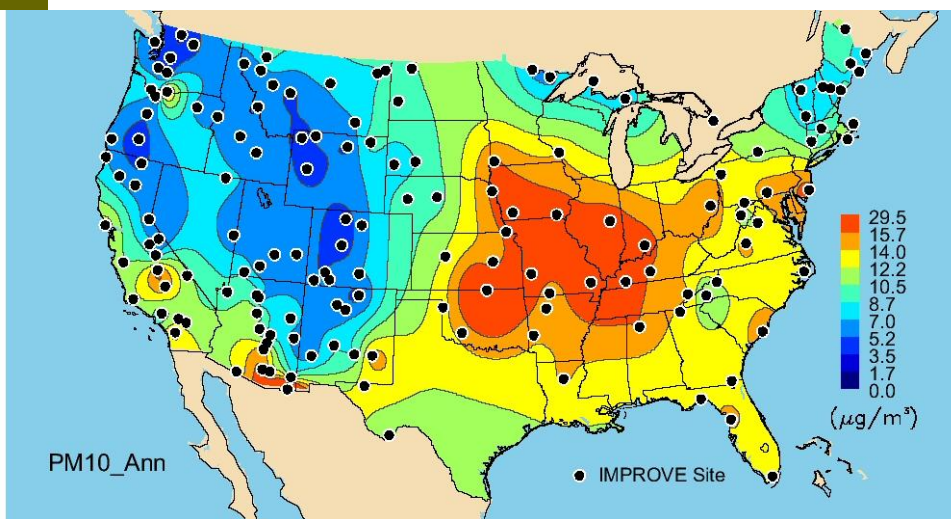
# Sea salt



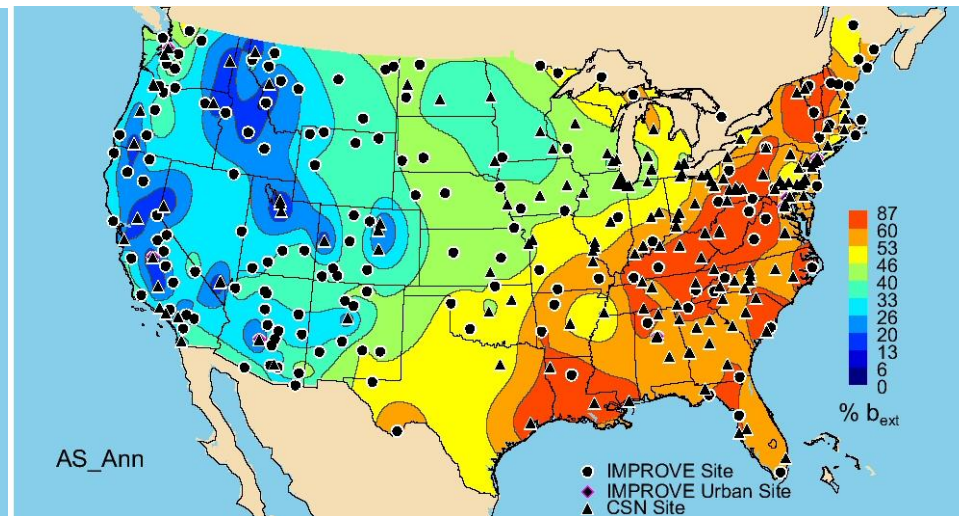
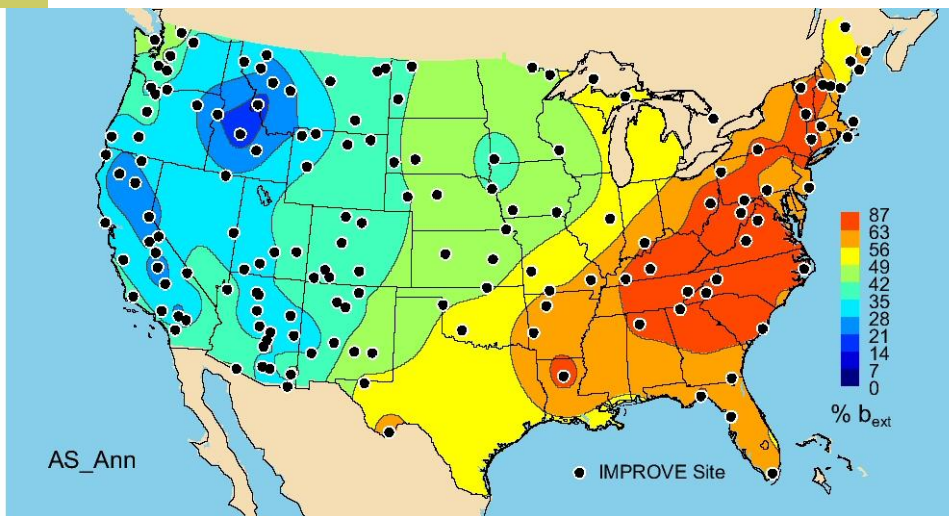
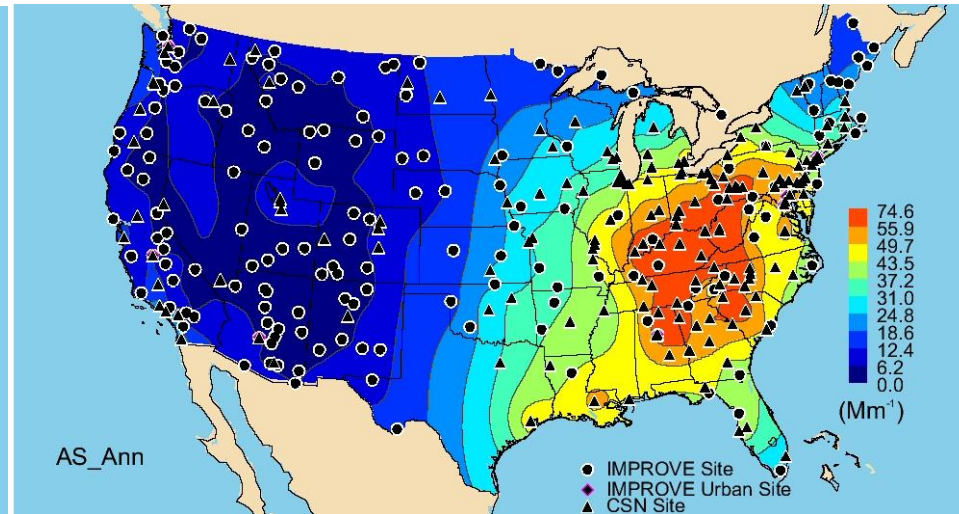
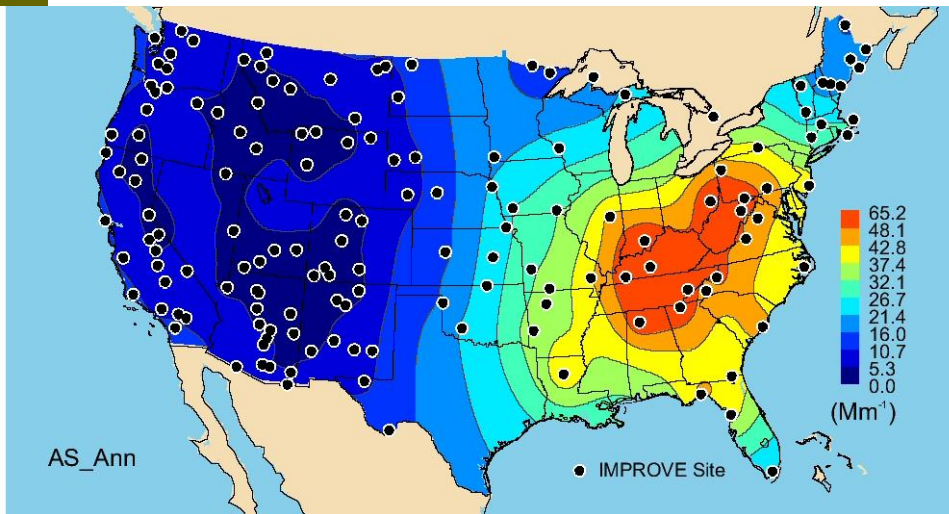
# Gravimetric Fine Mass and Reconstructed Fine Mass



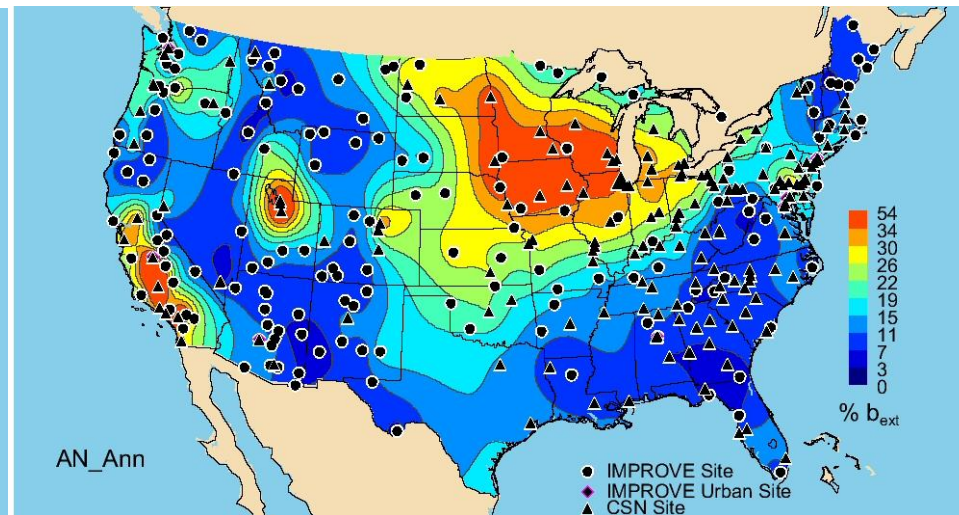
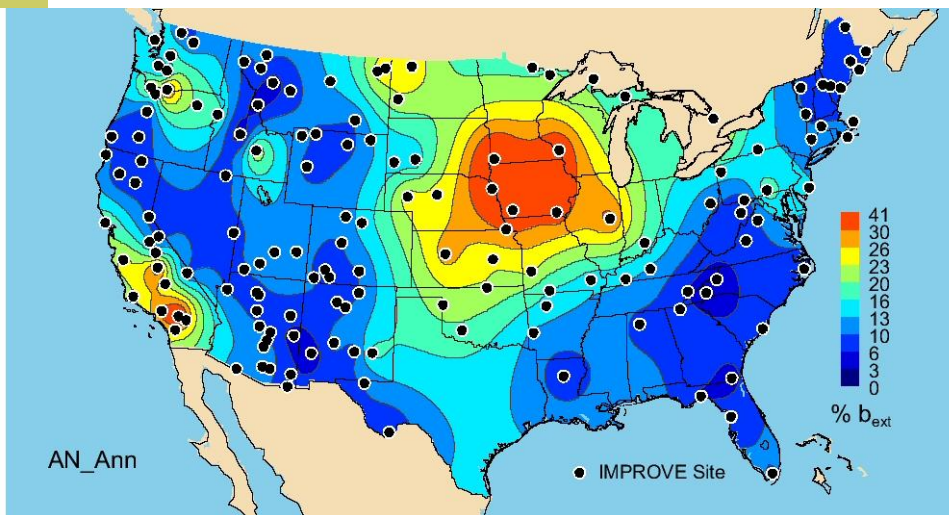
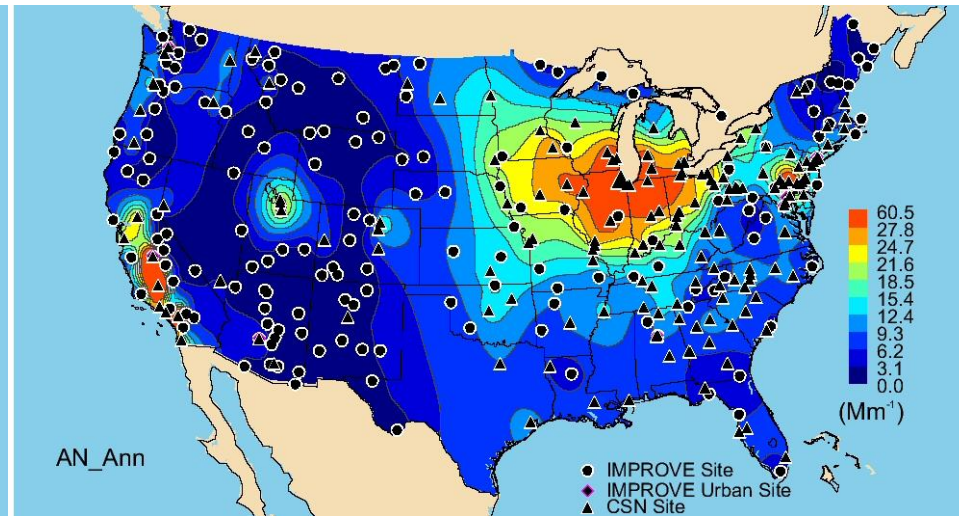
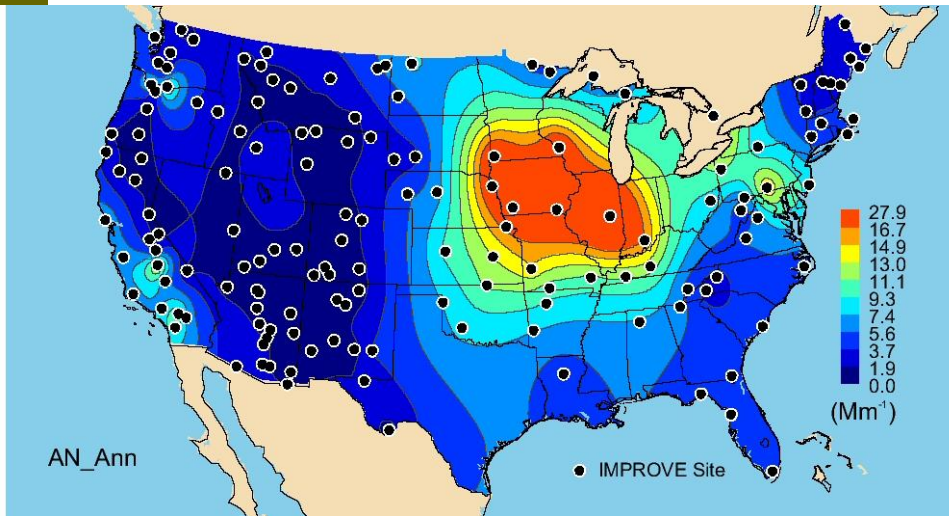
# PM10



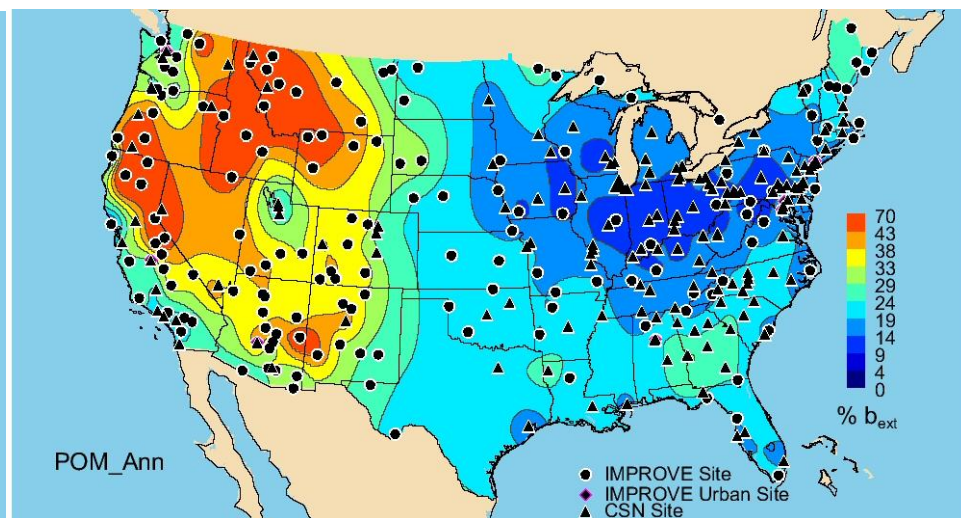
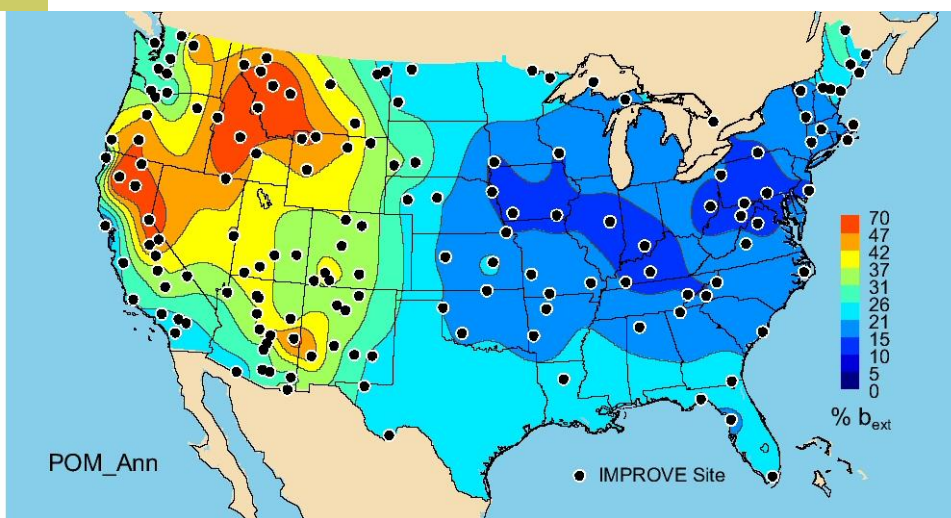
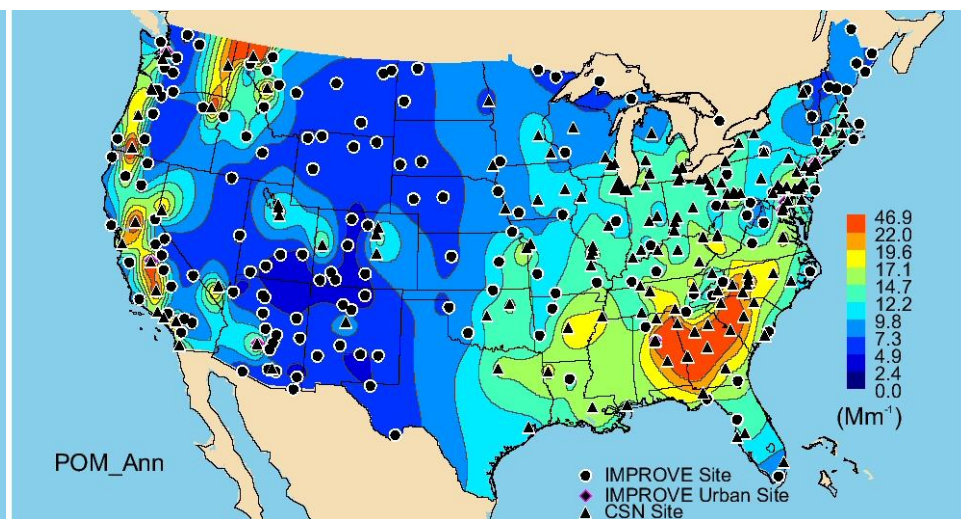
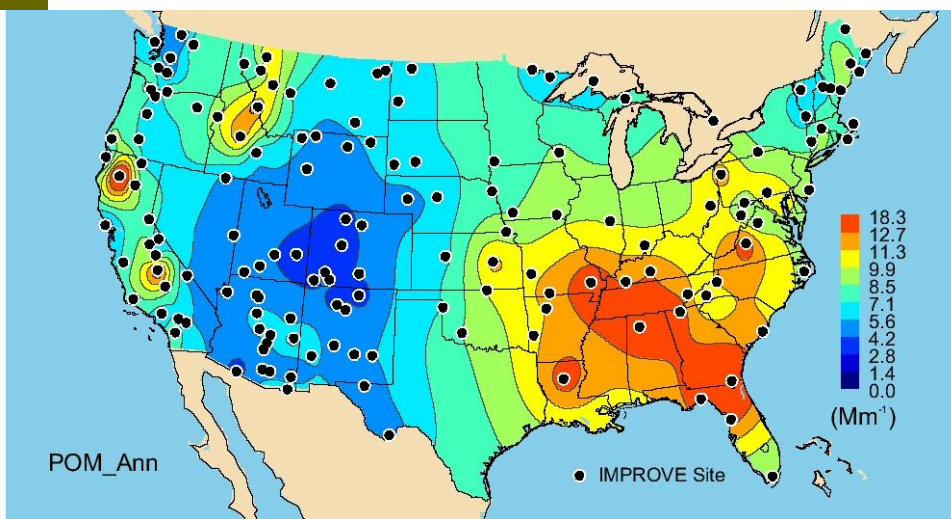
## Ammonium Sulfate Annual bext



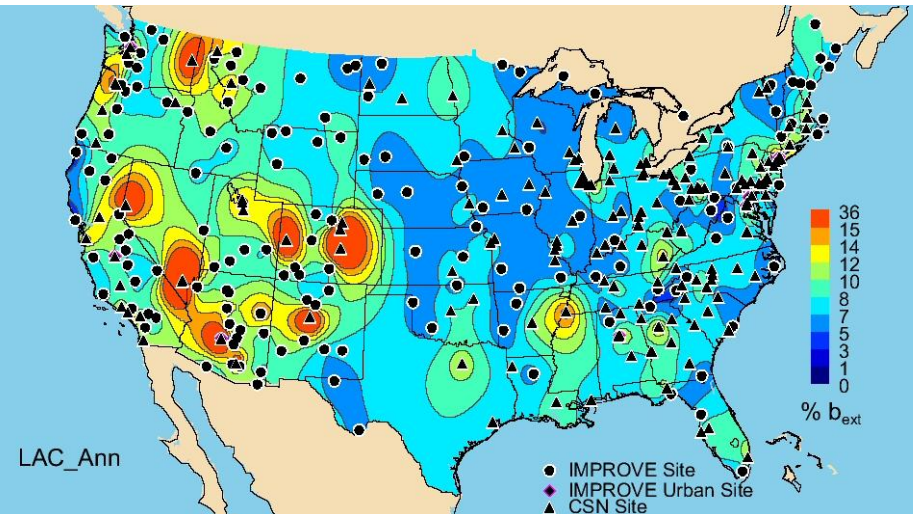
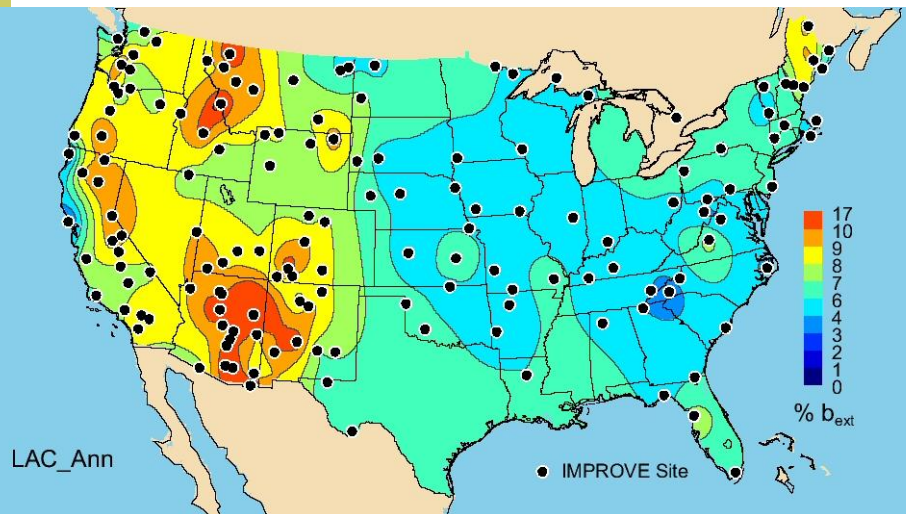
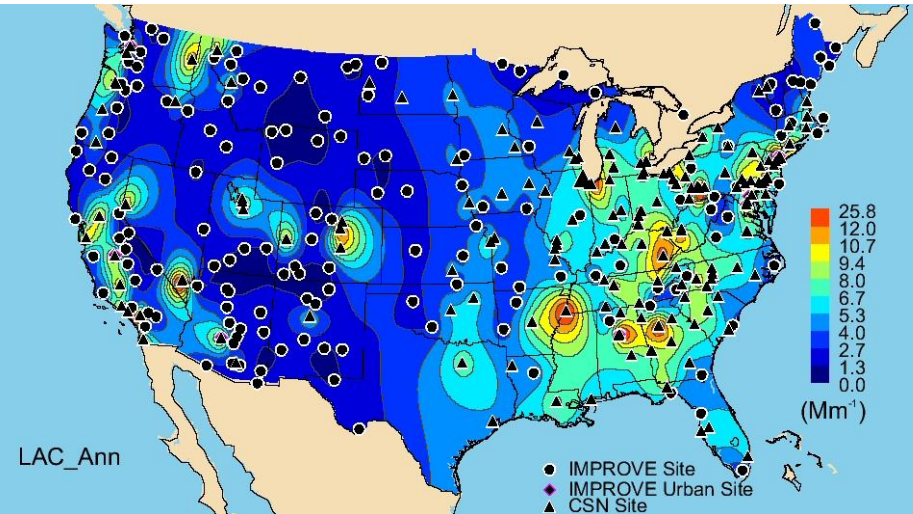
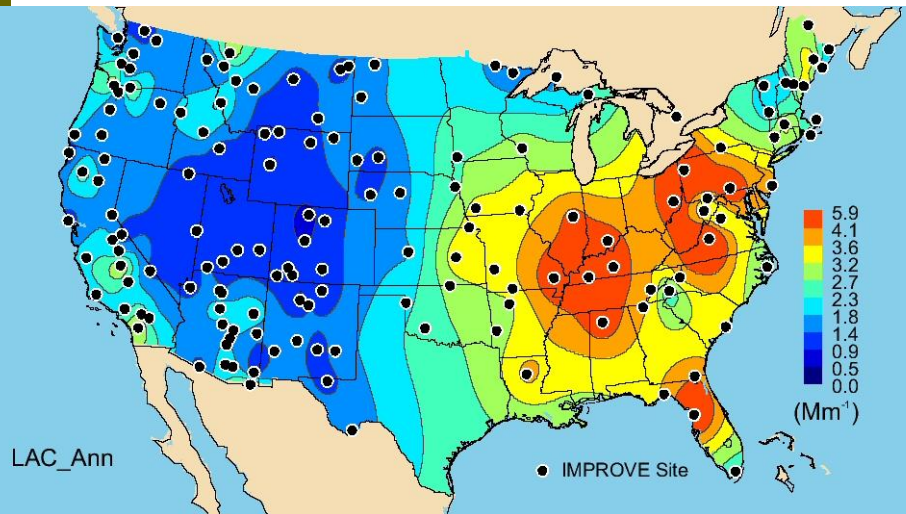
# Ammonium Nitrate Annual bext



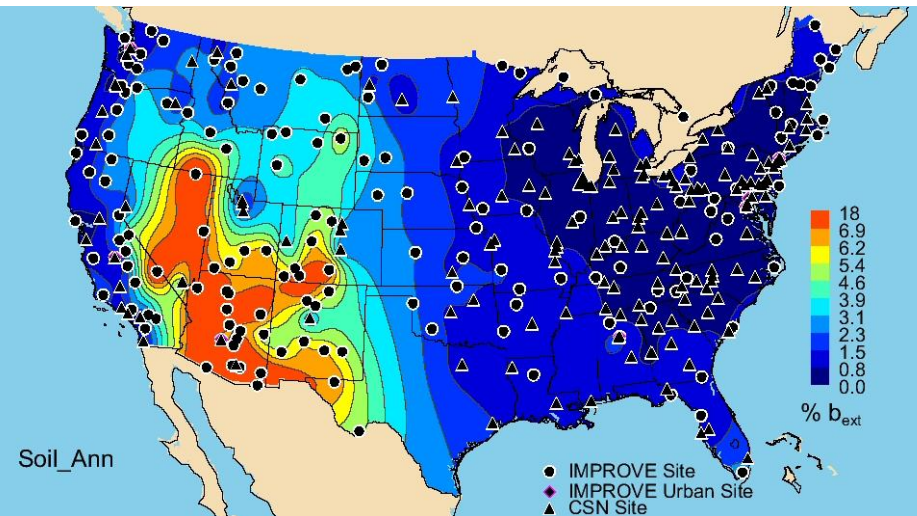
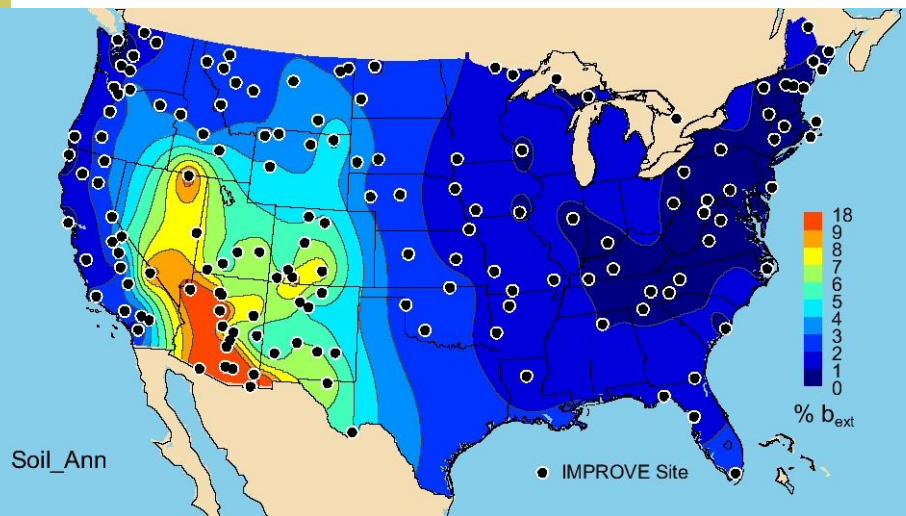
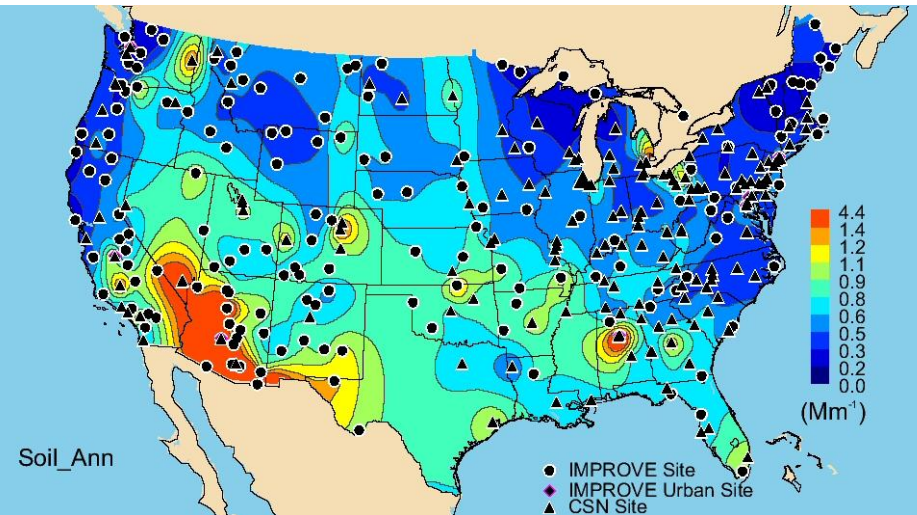
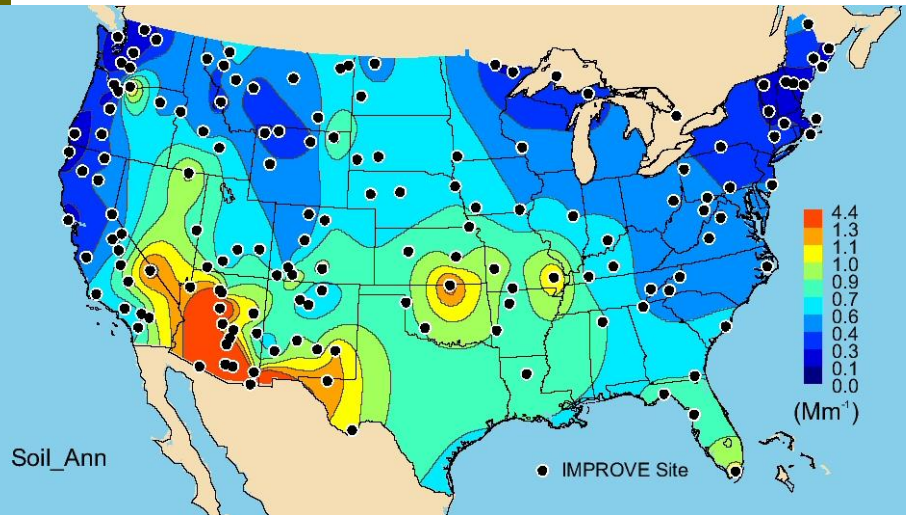
## Particulate Organic Matter Annual bext



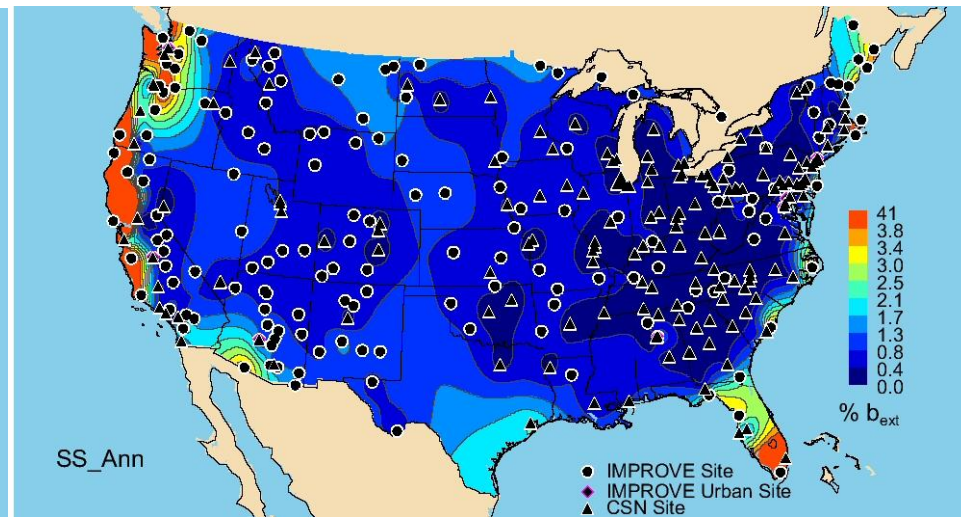
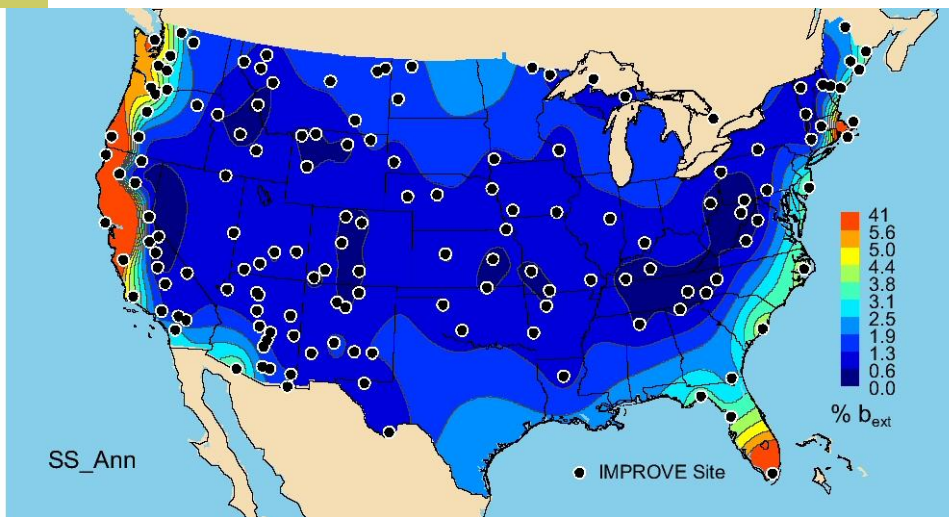
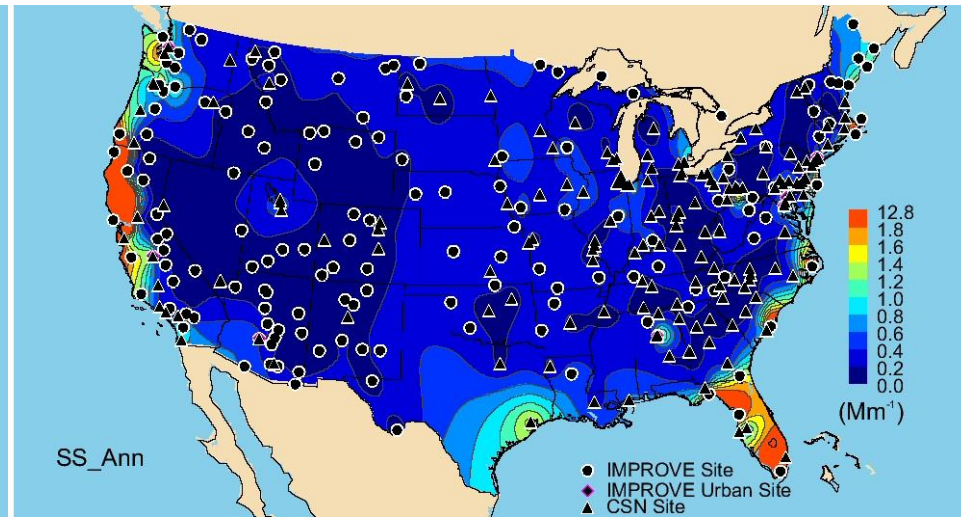
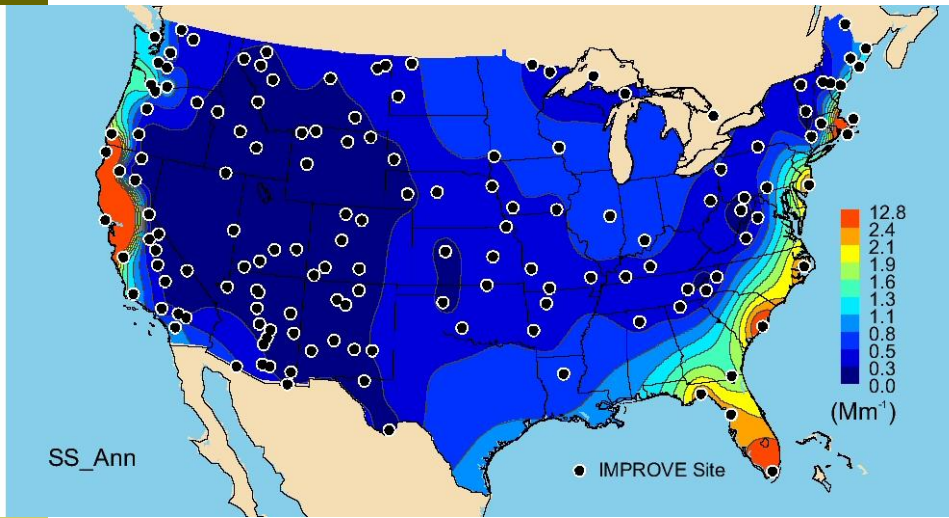
# Light Absorbing Carbon Annual bext



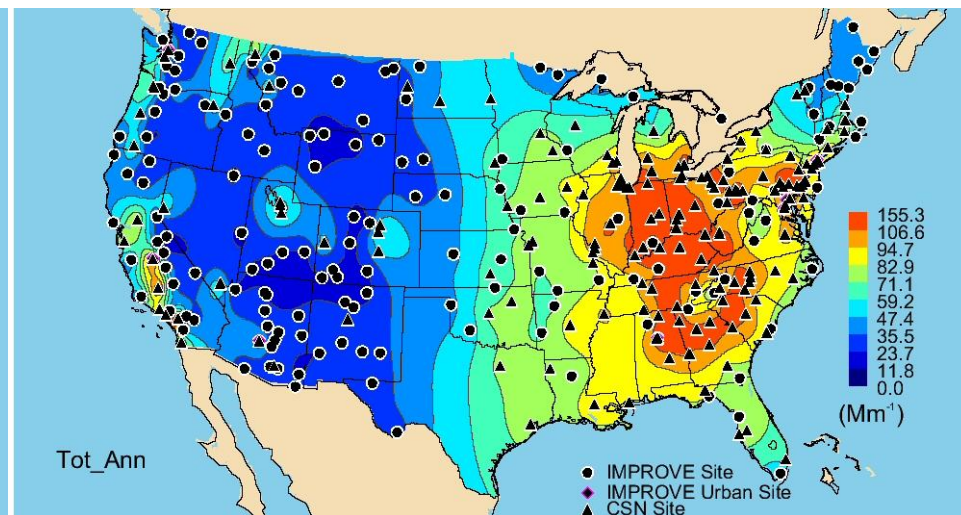
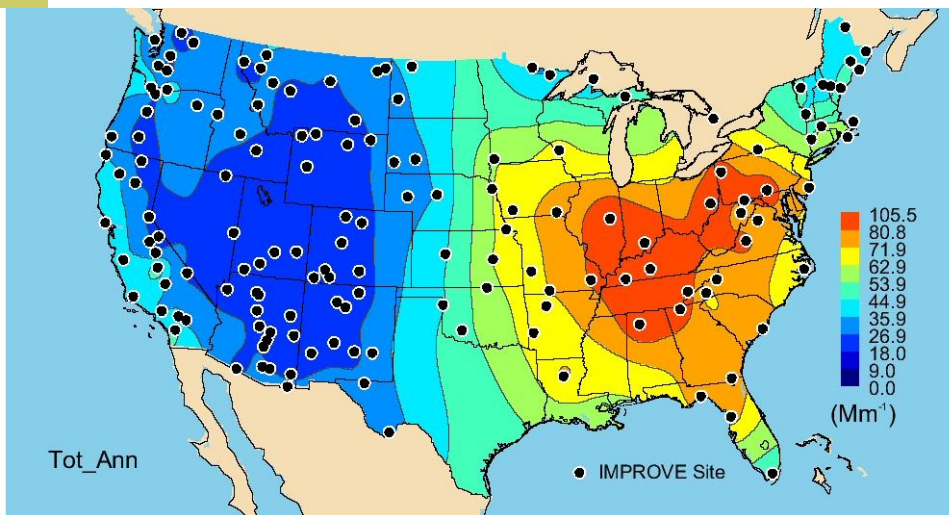
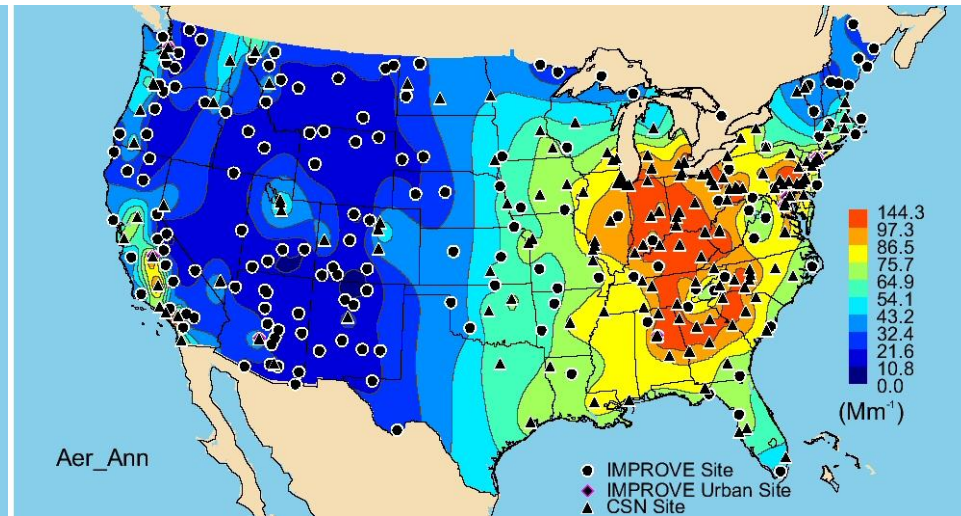
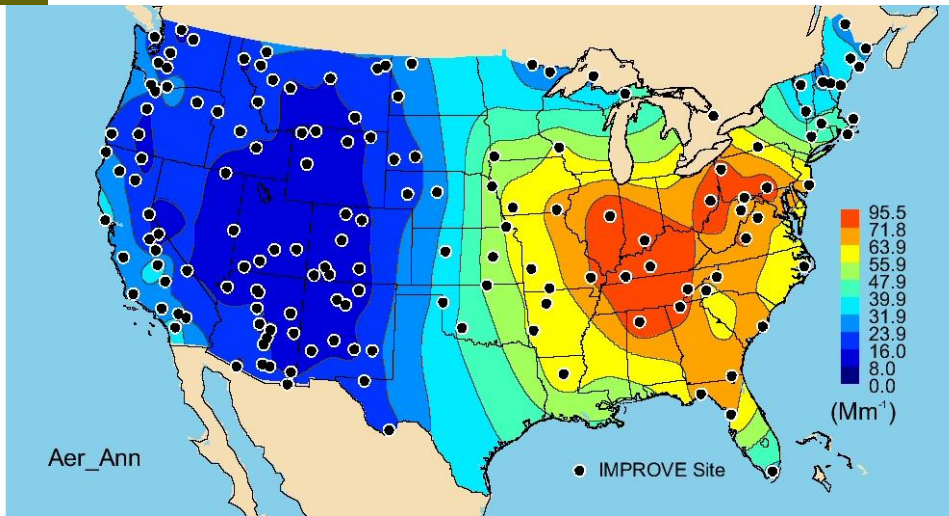
# Soil Annual bext



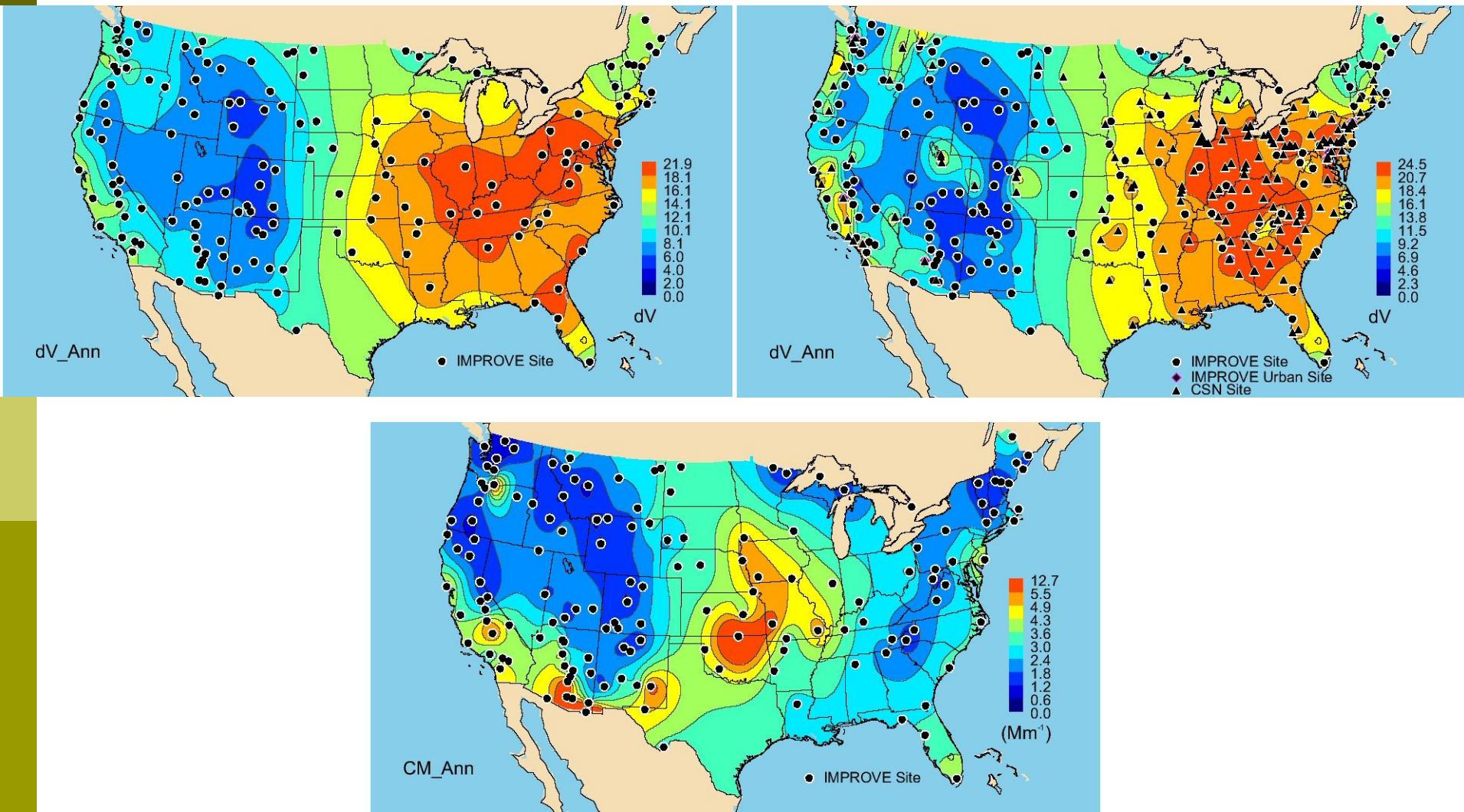
## Sea salt Annual bext



# Aerosol Annual bext

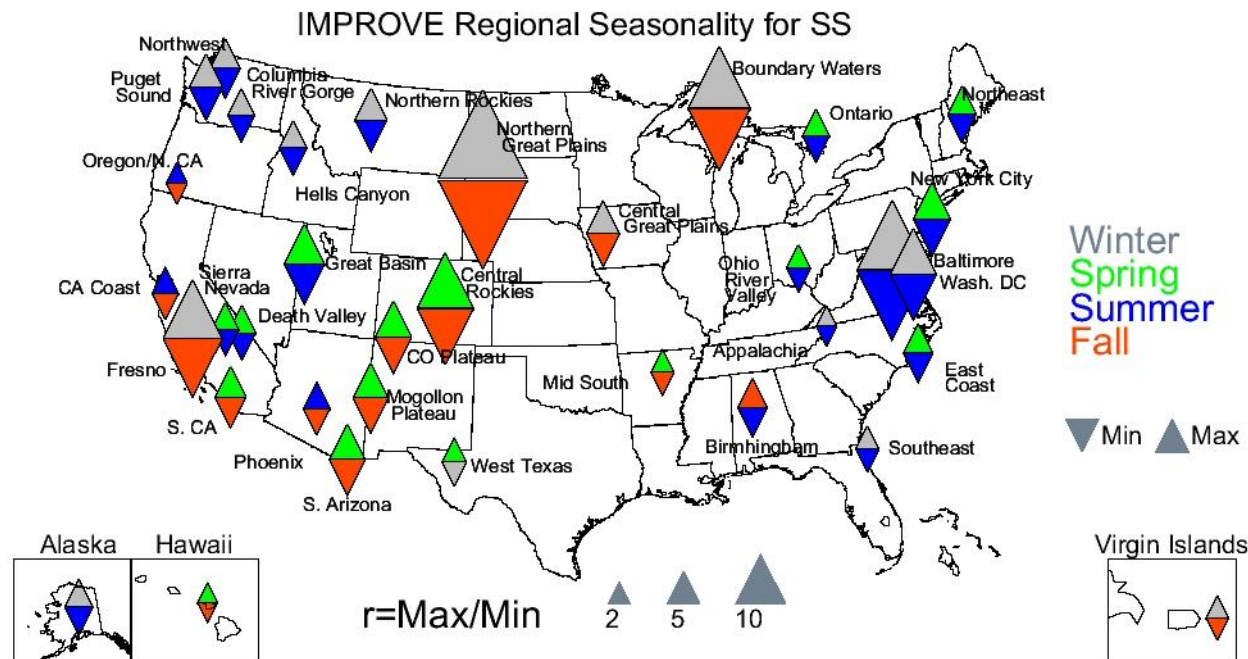


## Deciview and Coarse Mass Annual bext

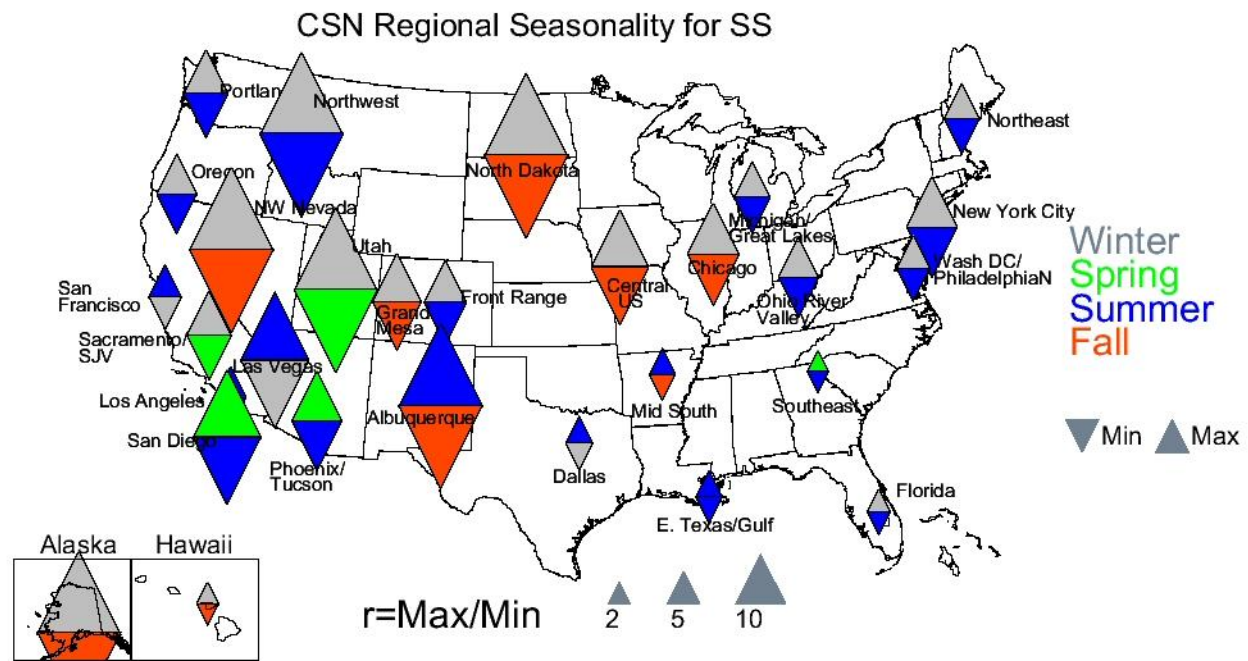


# Seasonality for Sea salt

IMPROVE

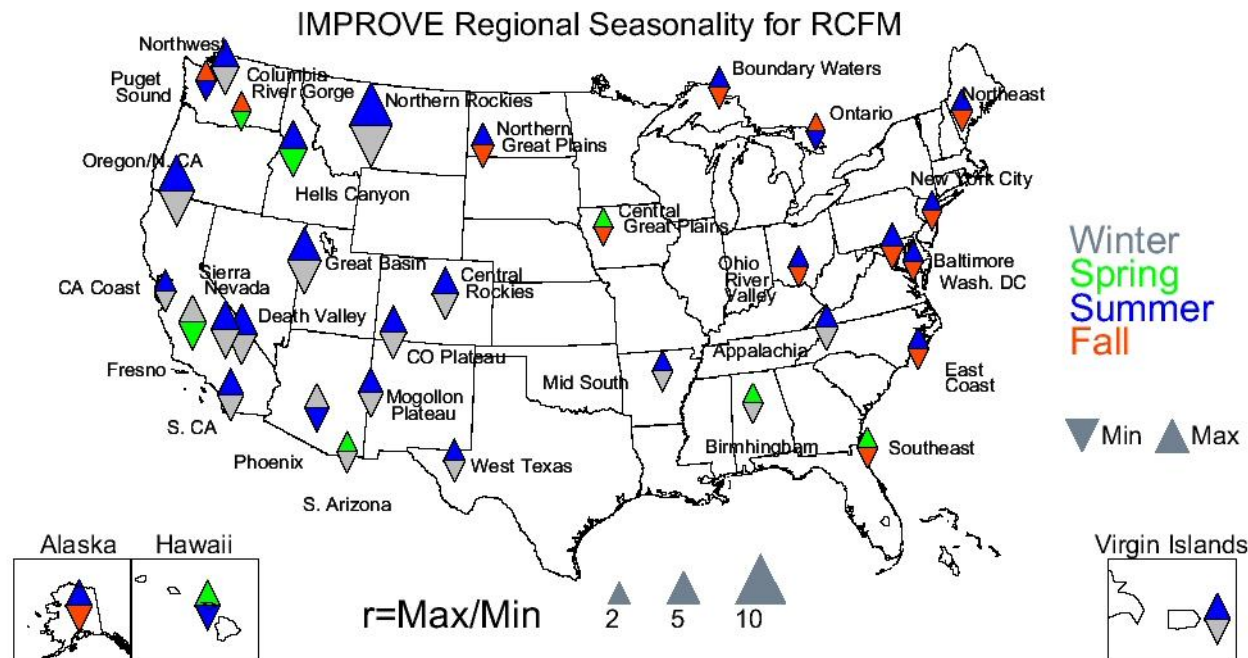


CSN

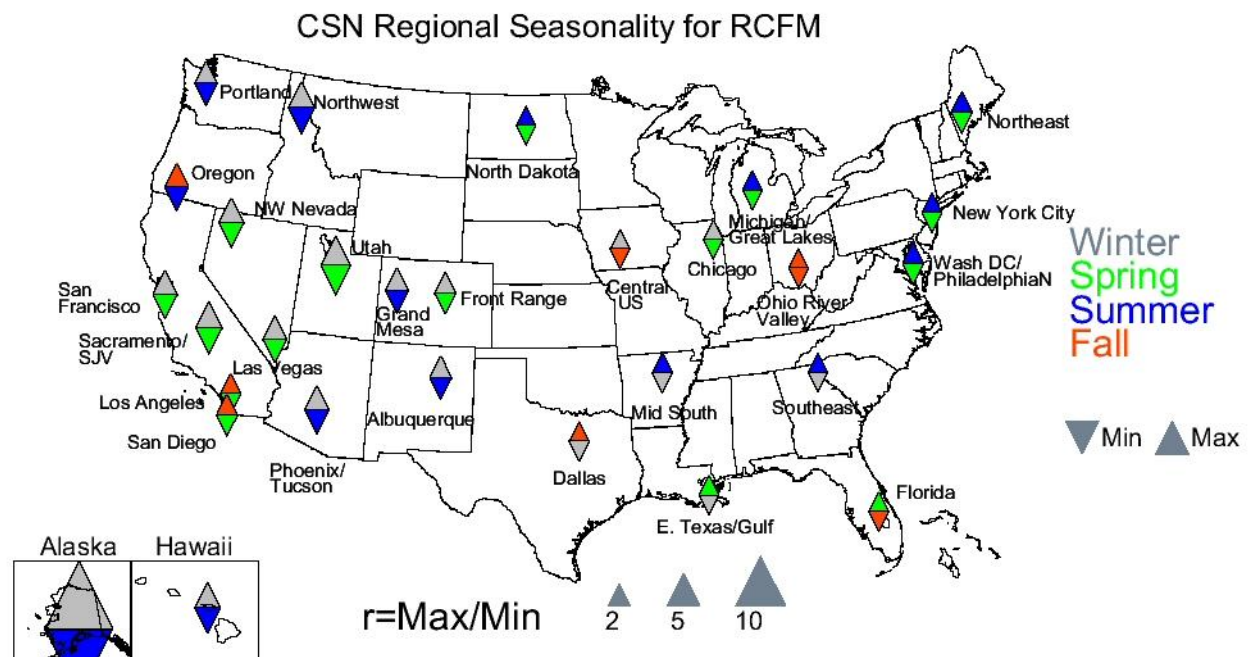


# Seasonality for RCFM

IMPROVE

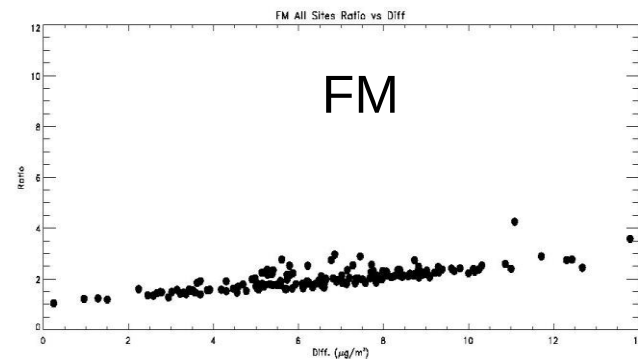
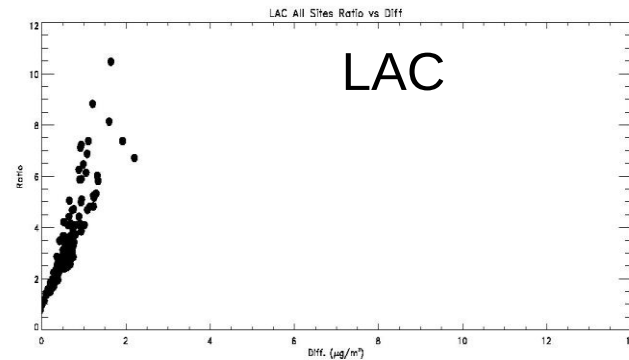
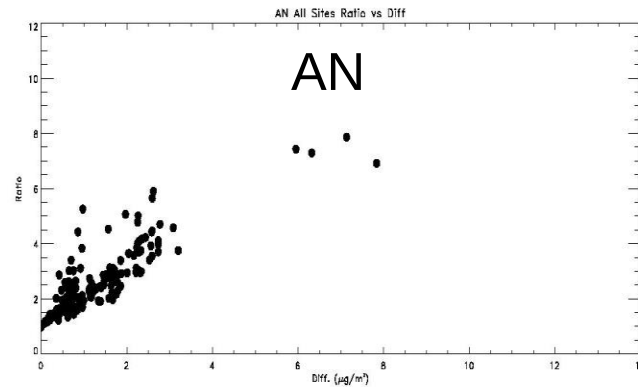
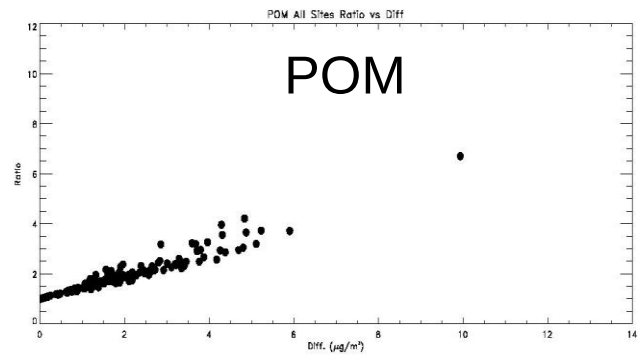
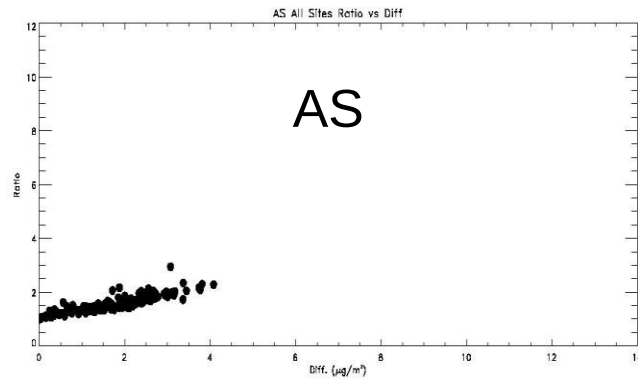


CSN



# Urban Excess

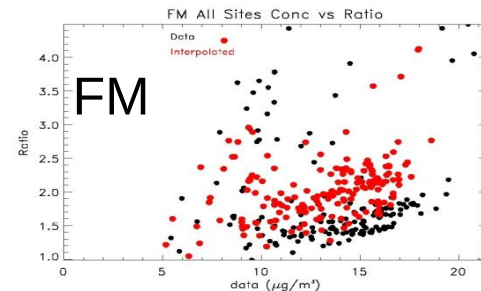
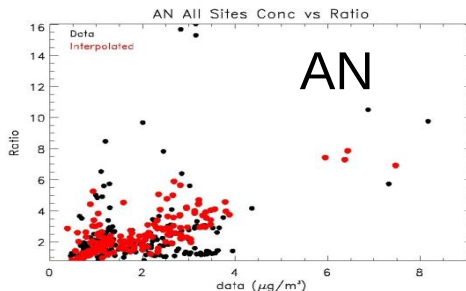
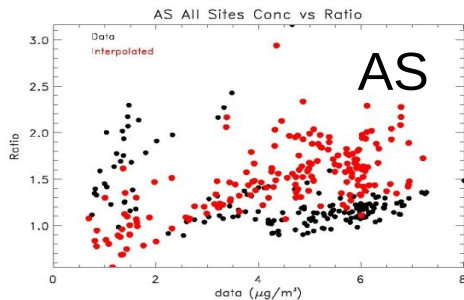
Urban/Rural



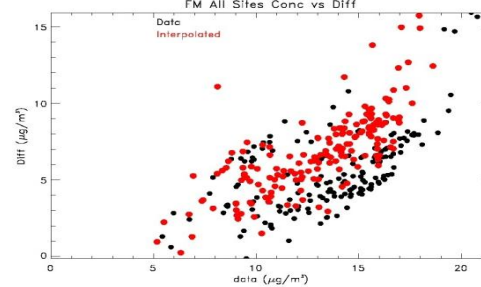
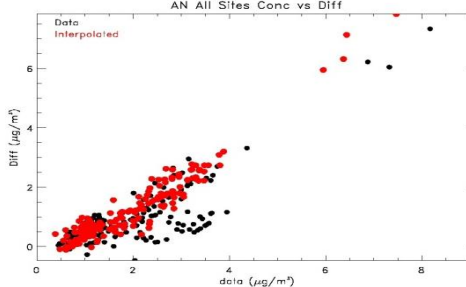
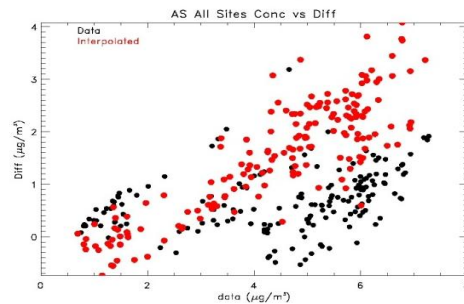
Urban-Rural

# Urban Excess

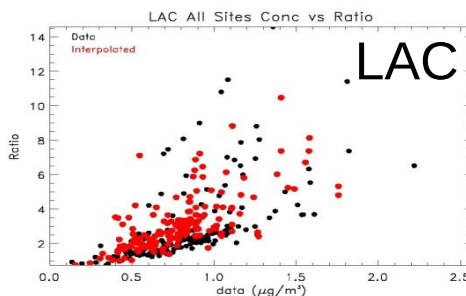
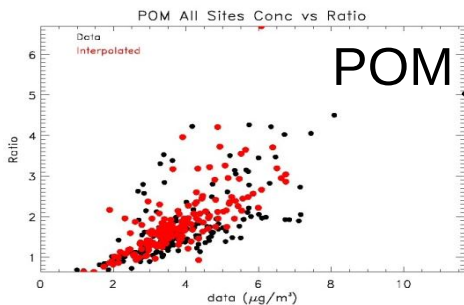
Ratio



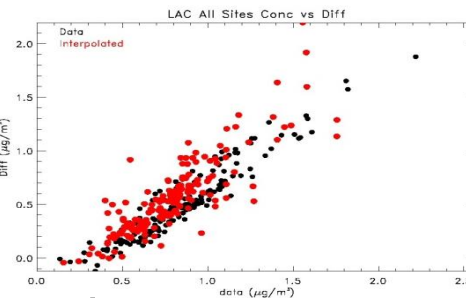
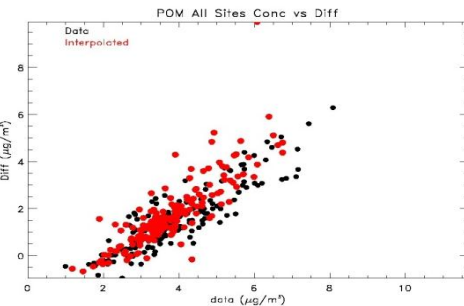
Diff



Ratio



Diff



Concentration

