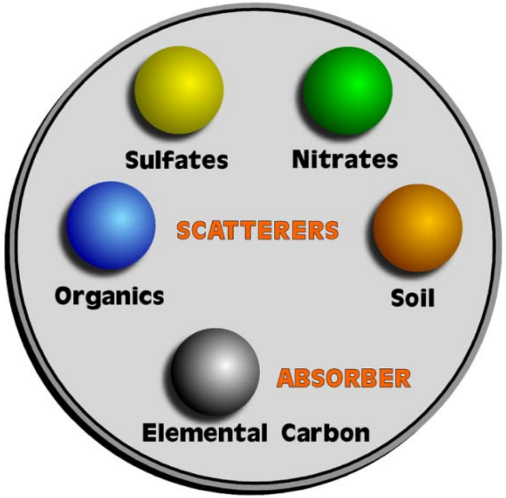
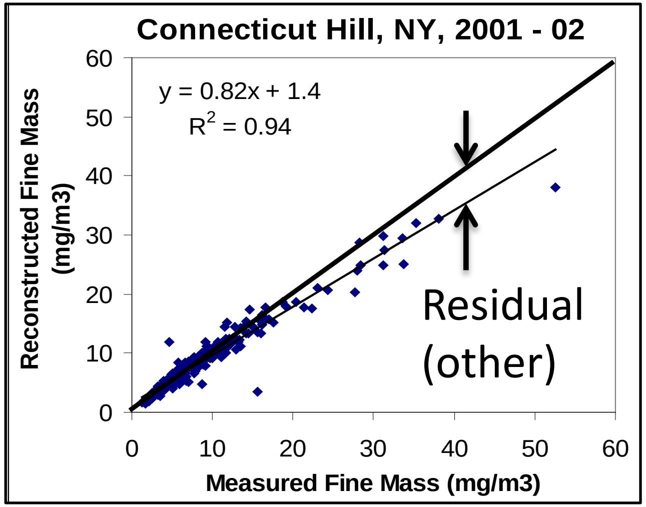
IMPROVE Fine Mass and b_{ext} Reconstruction
Issues, Resolutions and Next Steps

Schichtel, Hand, Prenni, Malm,
Copeland, Vimont, White…….

Fine Particulate Mass Composite Components





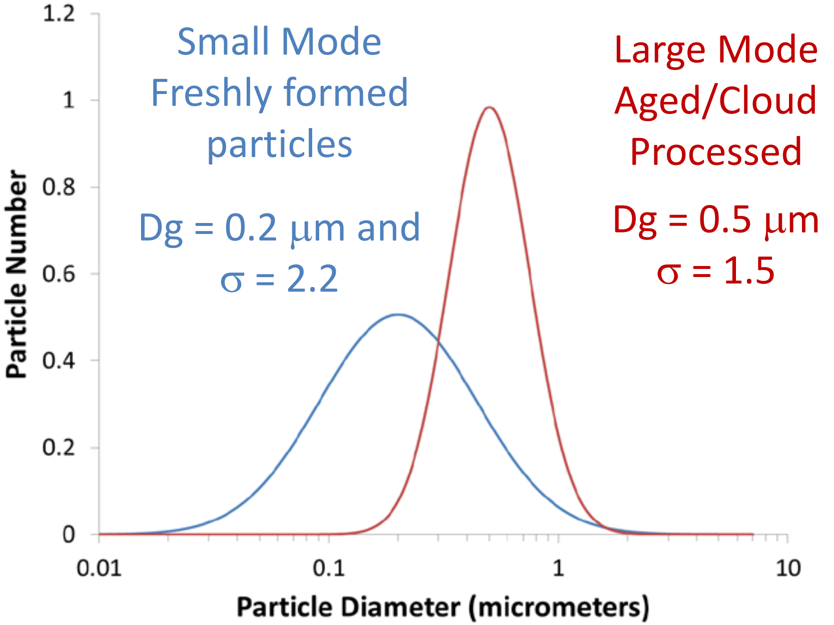
- Ammonium Sulfate = 1.375 * $[SO_4]$
- Ammonium Nitrate = 1.29 * $[NO_3^-]$
- Organics = 1.8 [OC]
- Light Absorbing Carbon = [EC]
- Soil = 2.2[Al]+2.49[Si]+1.63[Ca]+2.42[Fe] +1.94[Ti]
- Sea Salt = 1.8 * [Cl-]
- Carbon multiplier (Roc = 1.8) found through empirical analysis

- RCFM = Sum of aerosol species
- FM = $PM_{2.5}$ Gravimetric Fine Mass
- Residual = Other = Missing Mass = FM-RCFM

IMPROVE Reconstructed Extinction

$$\begin{aligned} b_{ext} = {} & 2.2 \times f_S(RH) \times [Small\ Sulfate] + 4.8 \times f_L(RH) \times [Large\ Sulfate] \\ & + 2.4 \times f_S(RH) \times [Small\ Nitrate] + 5.1 \times f_L(RH) \times [Large\ Nitrate] \\ & + 2.8 \times [Small\ OMC] + 6.1 \times [Large\ OMC] + 10 \times [EC] \\ & + 1 \times [Fine\ Soil] + 1.7 \times f_{SS}(RH) \times [Sea\ Salt] + 0.6 \times [Coarse\ Mass] + Rayleigh \end{aligned}$$

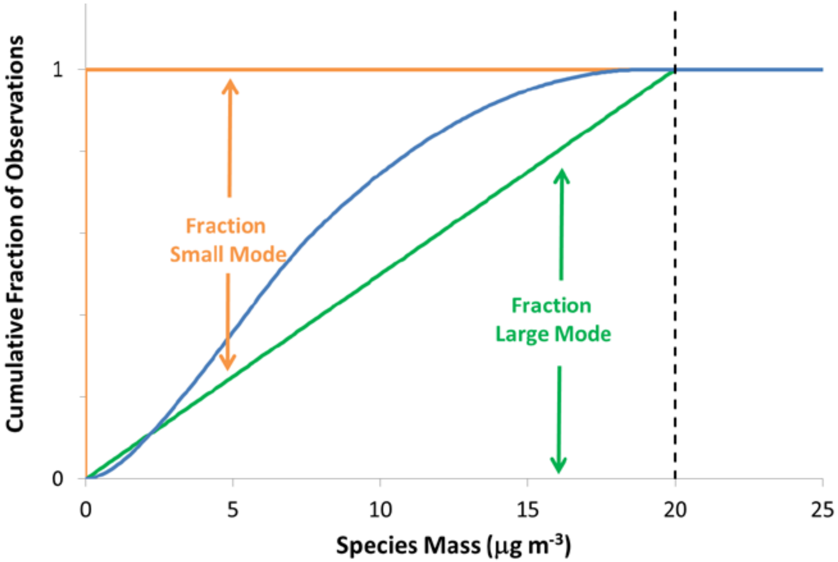
- Aerosols are externally mixed
- Small and large refer to fine particle mass size distribution that have different light scattering properties.
- Assumed that aerosols shift to larger sizes for higher mass concentrations.



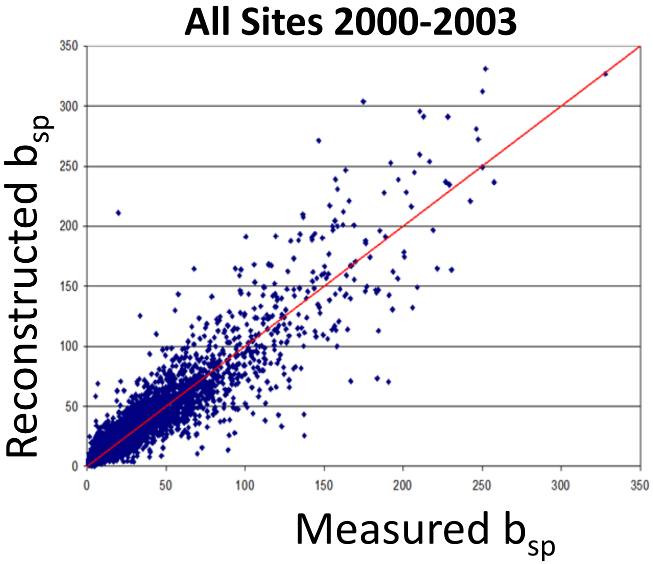
Sulfate, Nitrate and Organics Modes

$$[Large\ Sulfate\ Fraction] = \frac{[Total\ Sulfate]}{20\ \mu\text{g/m}^3}$$

$$[Small\ Sulfate\ Fraction] = 1 - [Large\ Sulfate\ Fraction]$$

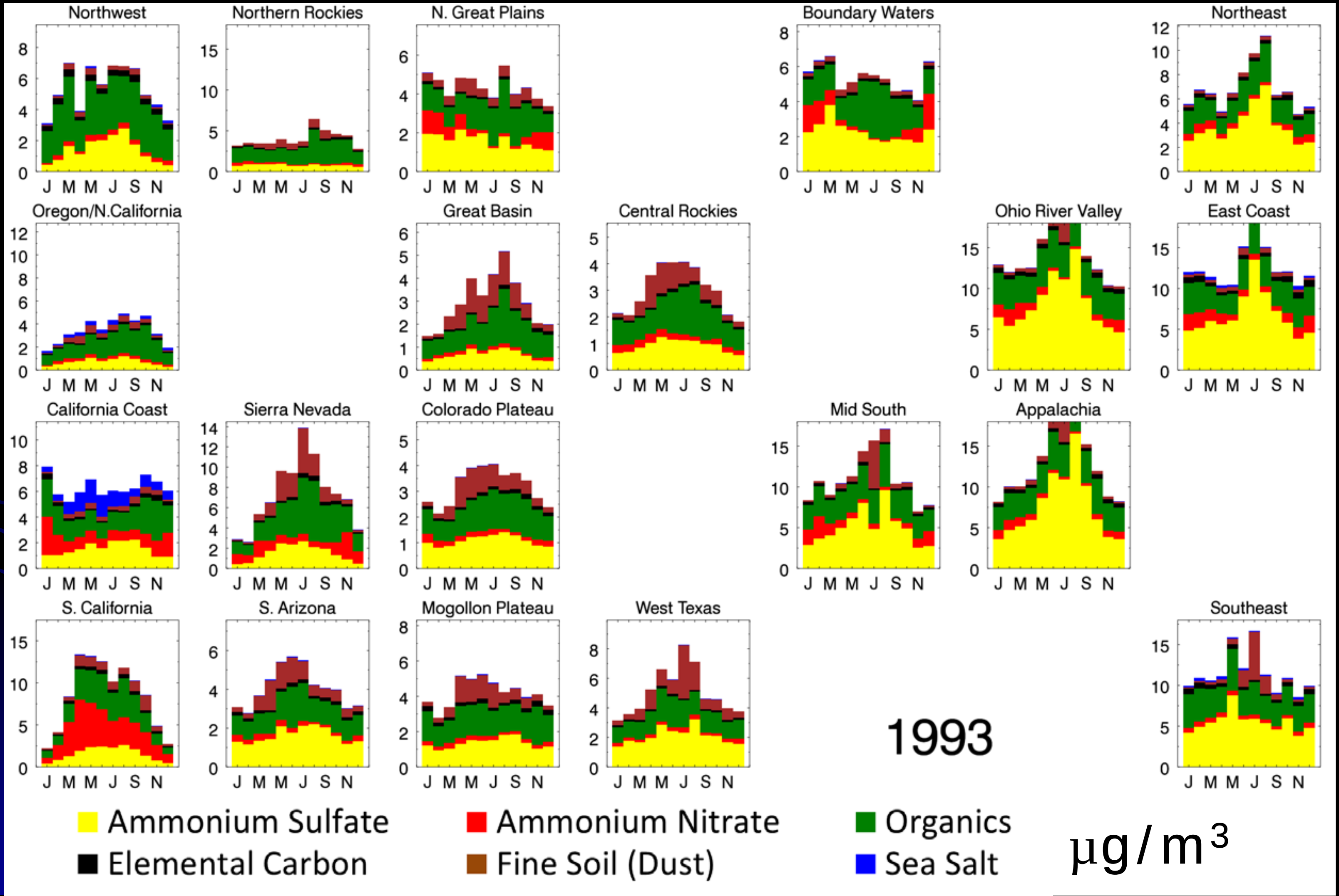


- MSE normalization factor = 20 μg/m^3

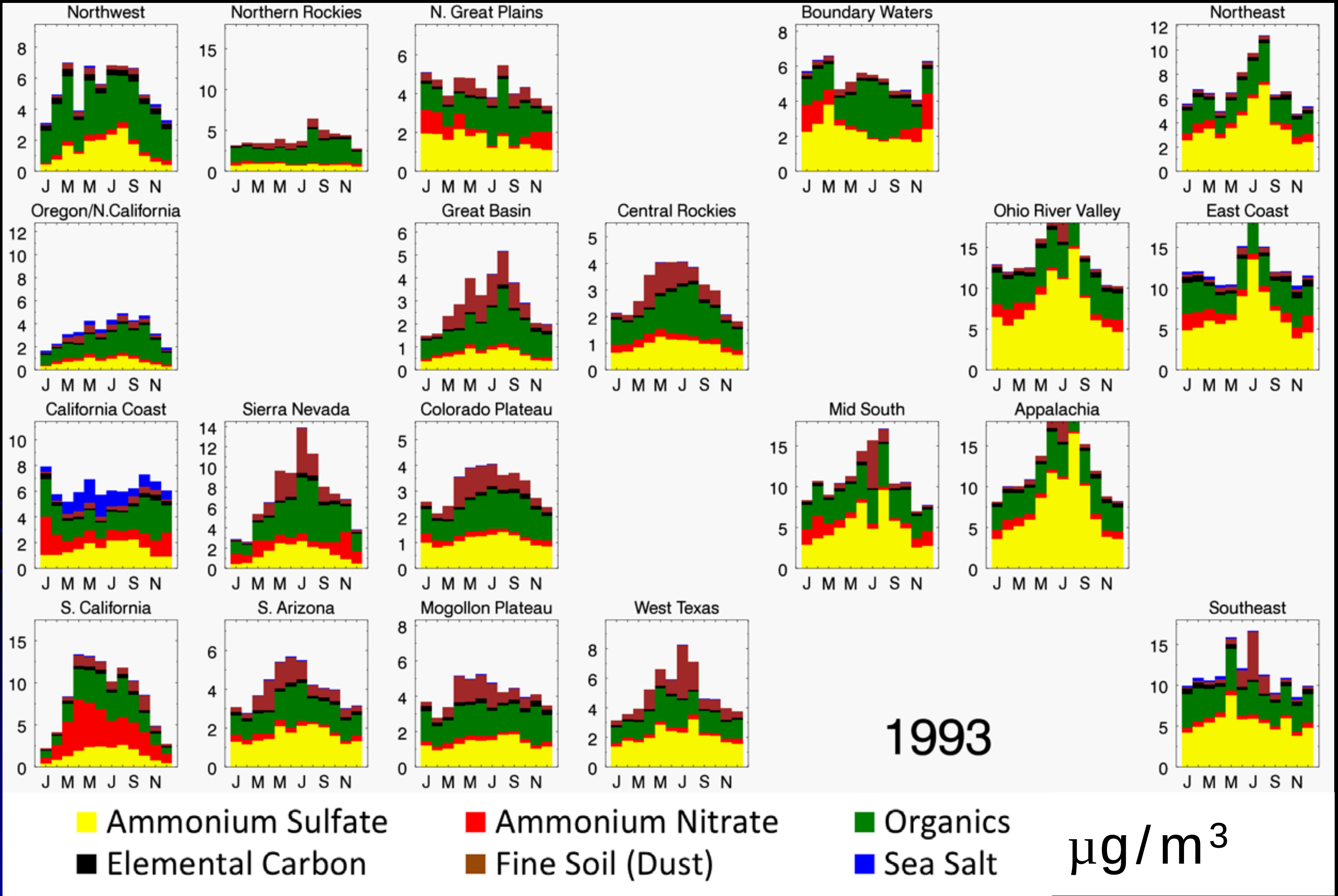


- The value of 20 was found through empirical analyses

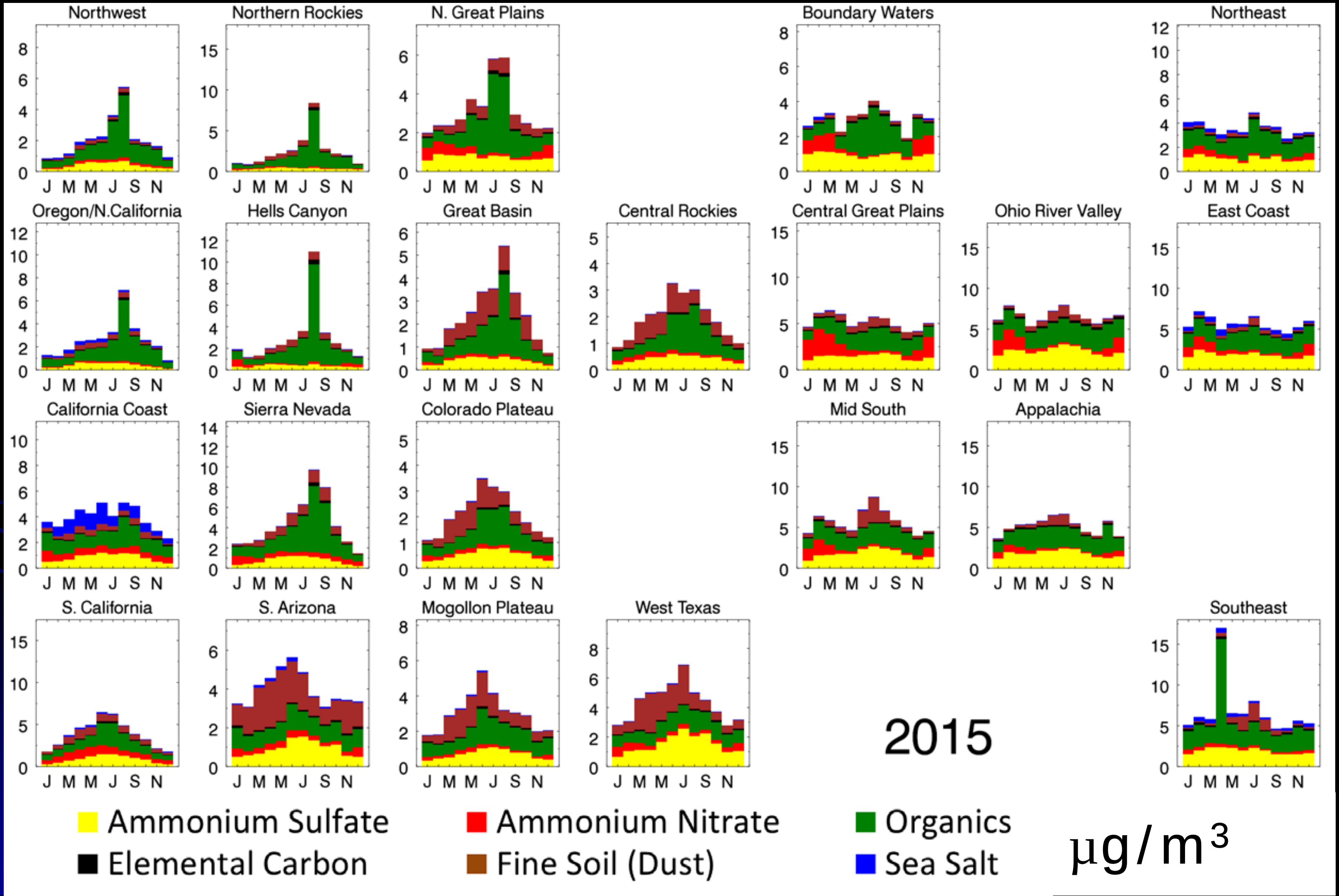
25 Yrs of Seasonal PM2.5 Composition Budgets



25 Yrs of Seasonal PM2.5 Composition Budgets

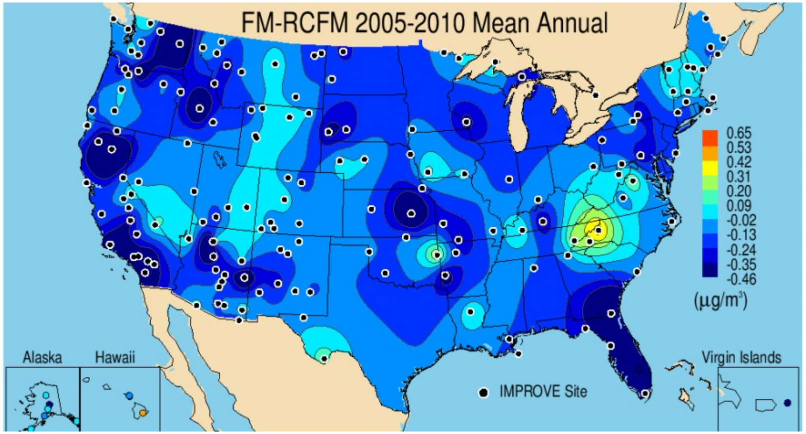


PM2.5 Seasonal Composition, 2014-2016

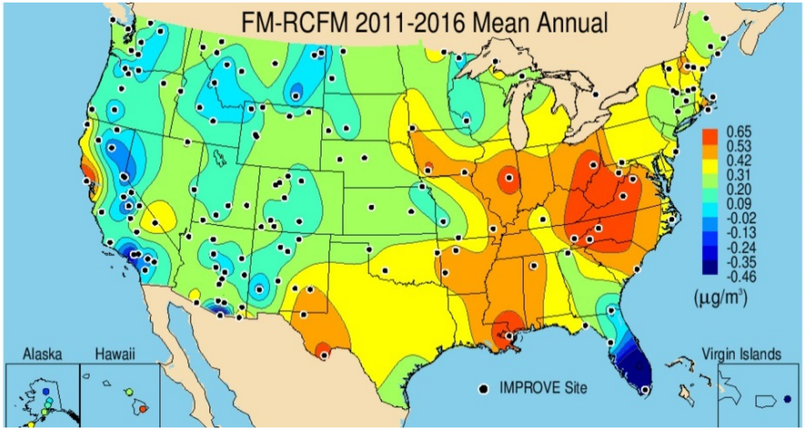


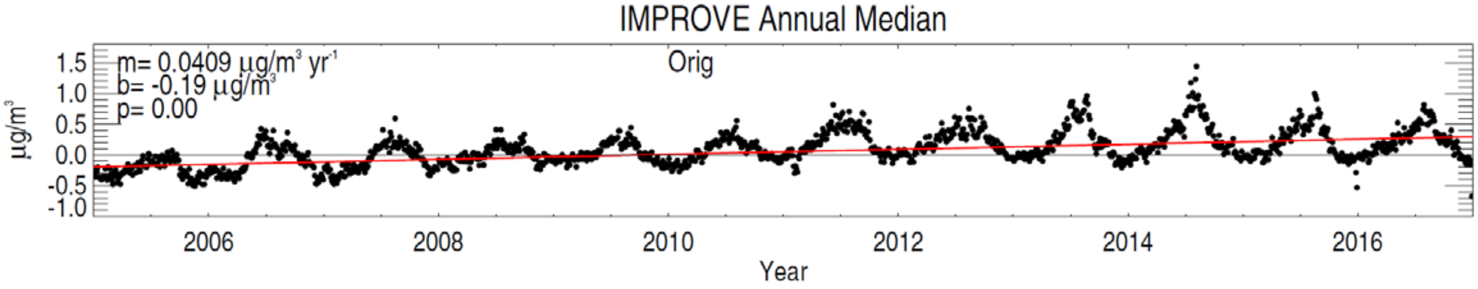
The fine mass residual (FM-RCFM) is increasing

Annual Mean 2005-2010



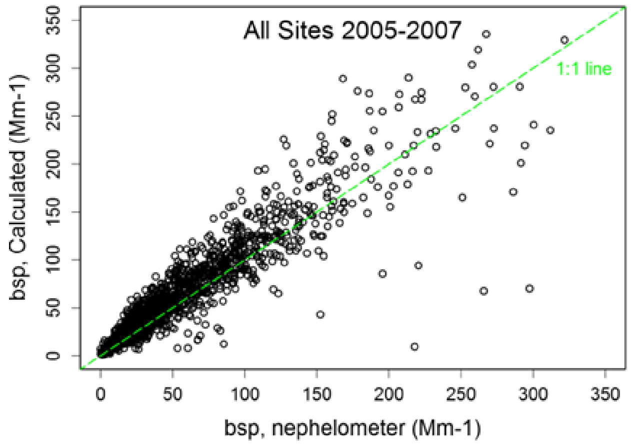
Annual Mean 2011-2016

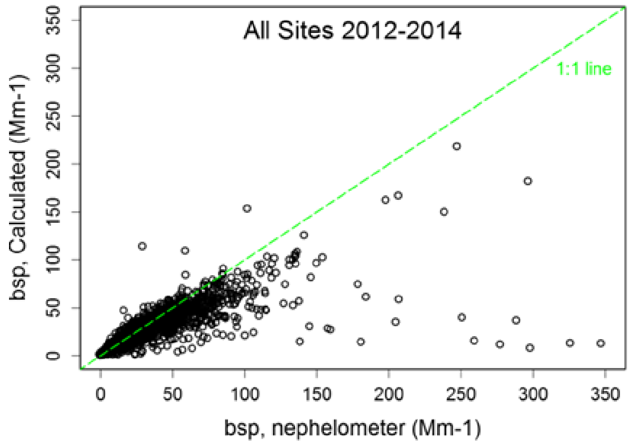




Annual residual increased ~ 0.5 µg m^{-3} from 2005-2016

Reconstructed vs Measured b_{sp}





- Good comparison to the data used to developed the IMPROVE equation
- Systematic overestimation for 2005-2007
- Severe systematic underestimation for 2012 to today

Potential causes of Increased Residual (FM – RCFM)

Some biases known to affect $PM_{2.5}$ Gravimetric Mass and or RCFM*
(+) (FM) Particle Bound Water (PBW: laboratory relative humidity)
(+/-) (RCFM) Organic multiplier (R_{oc} = OM/OC)
(+/-) (RCFM) Dust composition
(+) (RCFM) Sulfur vs sulfate (sulfate neutralization (~30%?); organosulfate)
(-) (FM) Nitrate is lost from Teflon filter (seasonal)
(RCFM) Changes in quartz carbon filter blanks
(FM & RCFM) Semi-volatiles lost on quartz filter (underestimate OC by ~20%, Malm et al., 2011)
(FM & RCFM) Other quartz filter artifacts: evaporation of OC during storage adsorption of VOC gases

*Possible known biases affecting $PM_{2.5}$ measurements (FM) or RCFM.
The impact of the bias on FM is given in the parentheses (negative or positive).

Multiple Linear Regression (MLR):

$$FM - EC - SS = a_o + a_1 AS + a_2 AN + a_3 OC + a_4 dust$$

Where:

FM = $PM_{2.5}$ (gravimetric)
AS = ammonium sulfate ($1.375 * SO_4^{-2}$)
AN = ammonium nitrate ($1.29 * NO_3^-$)
OC = organic carbon
Dust = sum of oxides
SS = sea salt ($1.8 * Cl^-$)

Interpretation:

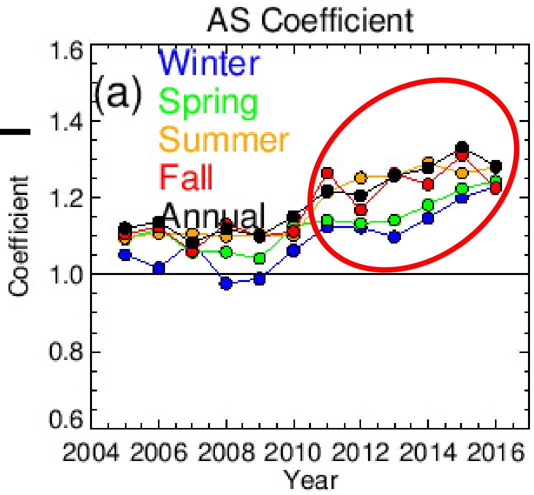
$a_1, a_2, a_4 \sim 1$

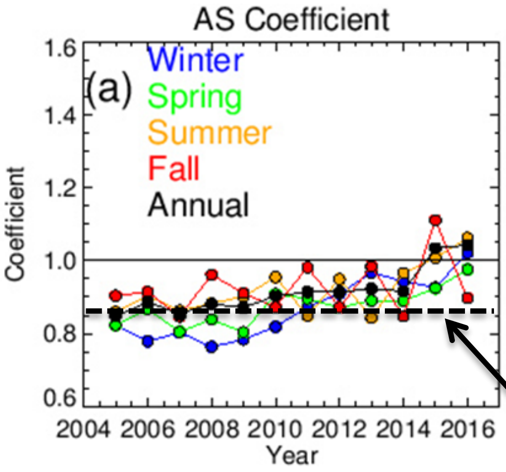
$a_3 = R_{oc}$ *(e.g. OM/OC ratio)*

Excess water on filters after 2011

Ammonium Sulfate Network Median MLR

Original FM: Lab RH issues in 2011





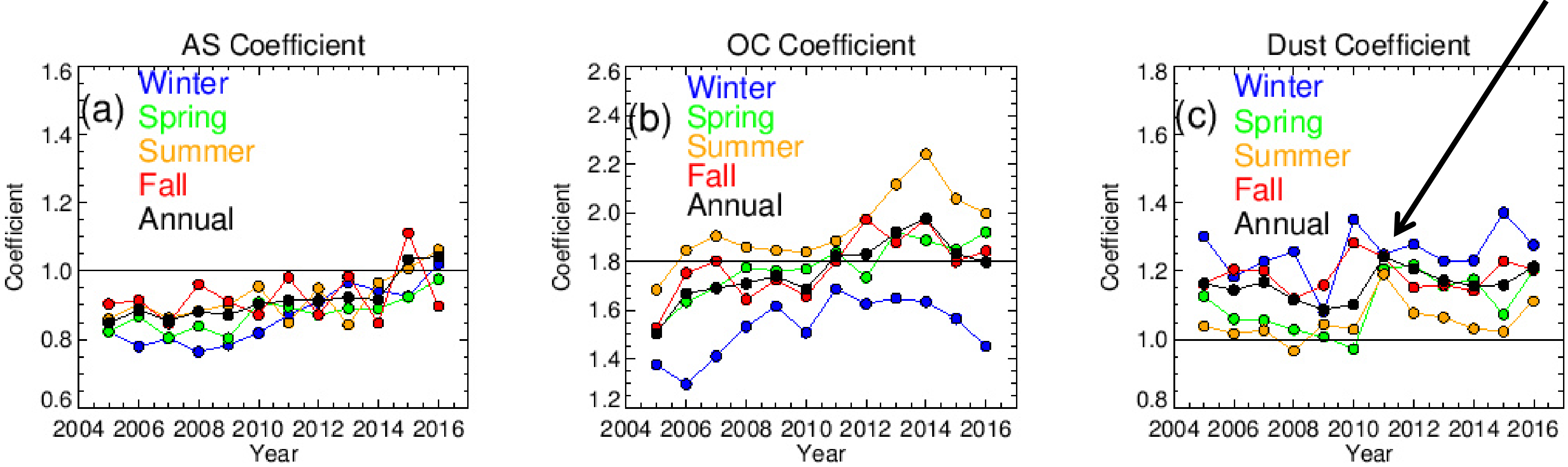
Dry FM: Adjusted FM for PBW

Ammonium bi-sulfate

- AS coefficients > 1 indicating associated water
- The bias was most acute in summer and fall after 2011 when lab RH increased

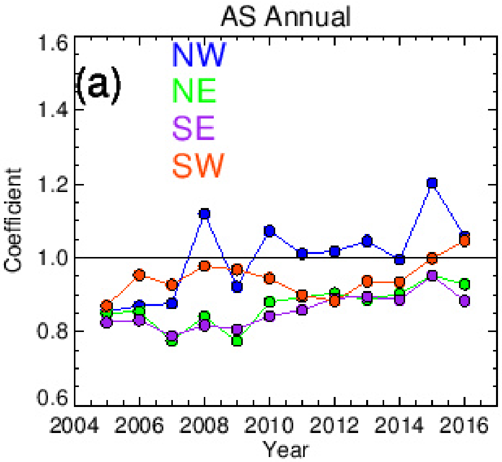
- Using dry FM in the regression reduced AS coeff. to 1 or less
- Coefficients increased in time
  - more neutralized aerosol
  - error in the drying method

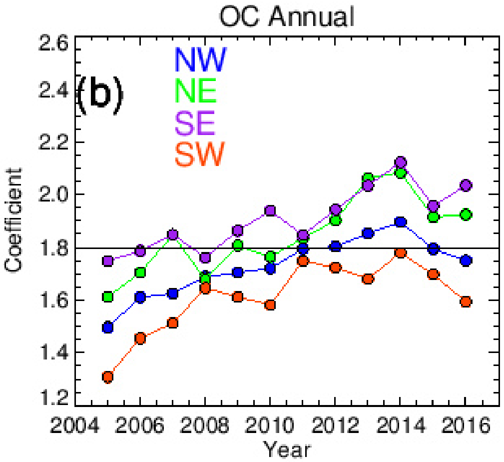
Network Median MLR Results (Dry FM) by Season

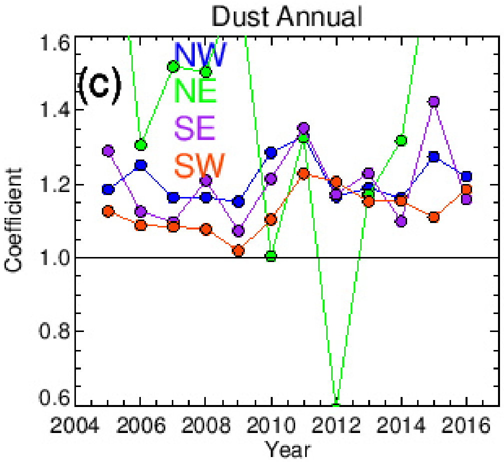

New XRF system

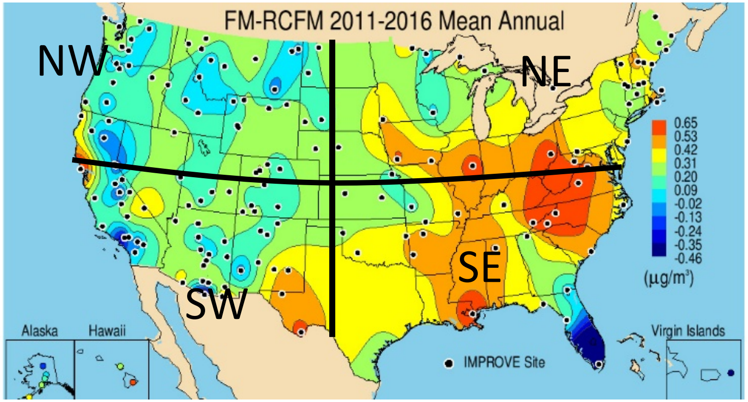
- Regression analysis suggests
  - Roc factor is increasing with time
  - Roc is seasonal with high summer values ~2 and lower winter values ~1.6
  - Soil is underestimated by 15-20%

Network Median MLR Results (Dry FM) by Region









Regions split at 40°N and -100°W

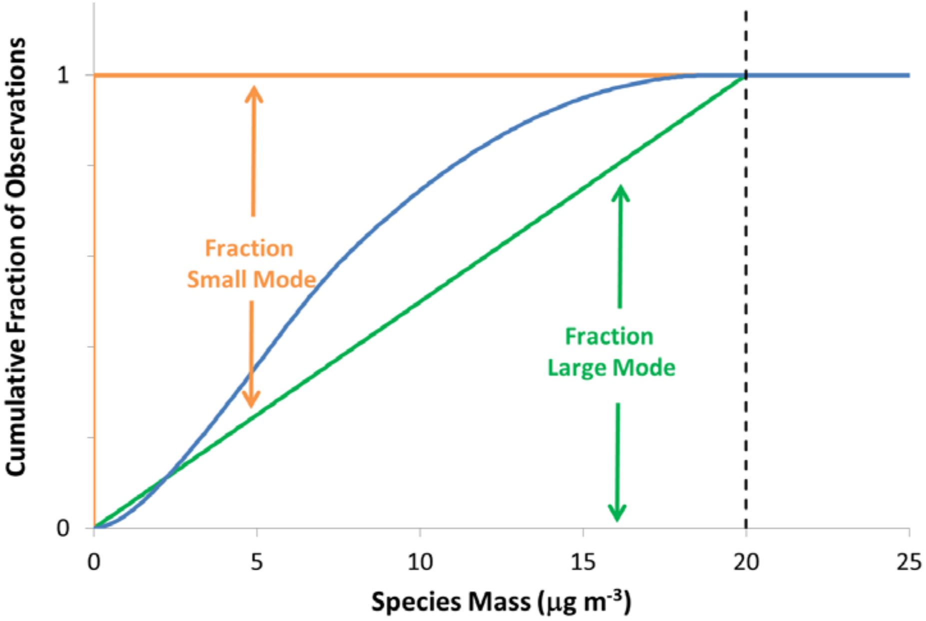
- Regression analysis suggests
  - Sulfate maybe more acidic in the east than the west
  - Roc is larger in the east than west
  - Soil composition regionality is smaller than noise

IMPROVE Reconstructed Extinction

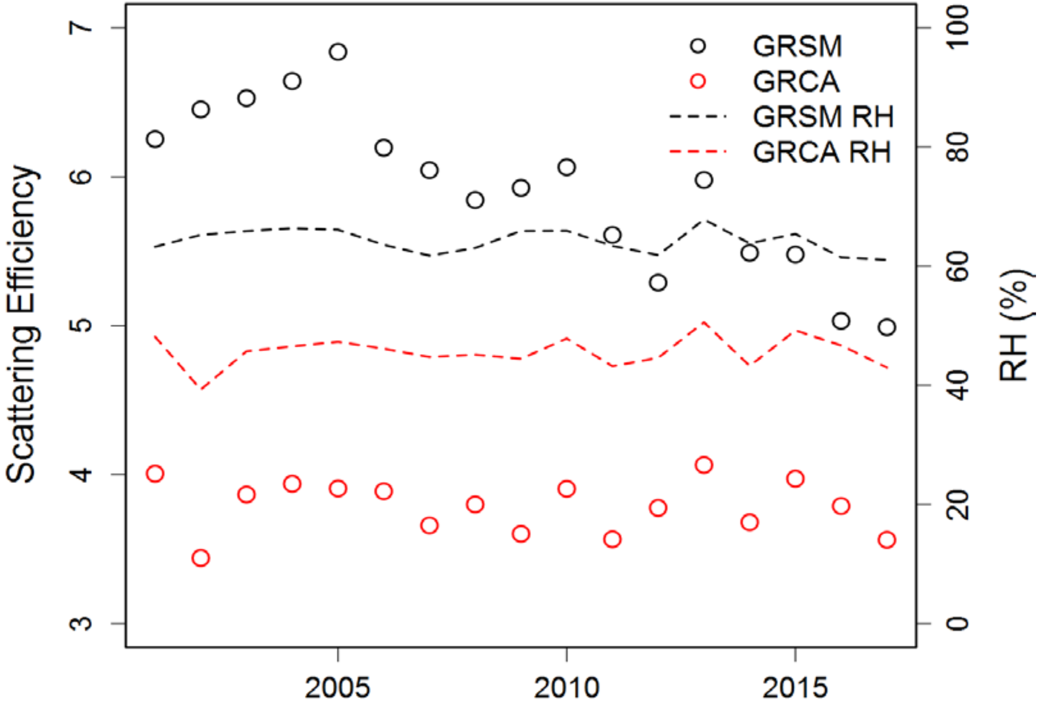
$$\begin{aligned} b_{ext} = {} & 2.2 \times f_s(RH) \times [Small\ Sulfate] + 4.8 \times f_L(RH) \times [Large\ Sulfate] \\ & + 2.4 \times f_s(RH) \times [Small\ Nitrate] + 5.1 \times f_L(RH) \times [Large\ Nitrate] \\ & + 2.8 \times [Small\ OMC] + 6.1 \times [Large\ OMC] + 10 \times [EC] \\ & + 1 \times [Fine\ Soil] + 1.7 \times f_{SS}(RH) \times [Sea\ Salt] + 0.6 \times [Coarse\ Mass] + Rayleigh \end{aligned}$$

- Assumes that fraction of large particles is proportional to the species mass
- The proportionality constant (MSE normalization factor) = 1/20

Large Sulfate Frac = $\dfrac{Sulfate}{20\ \mu g/m^3}$



Sulfate scattering: GRSM and GRCA

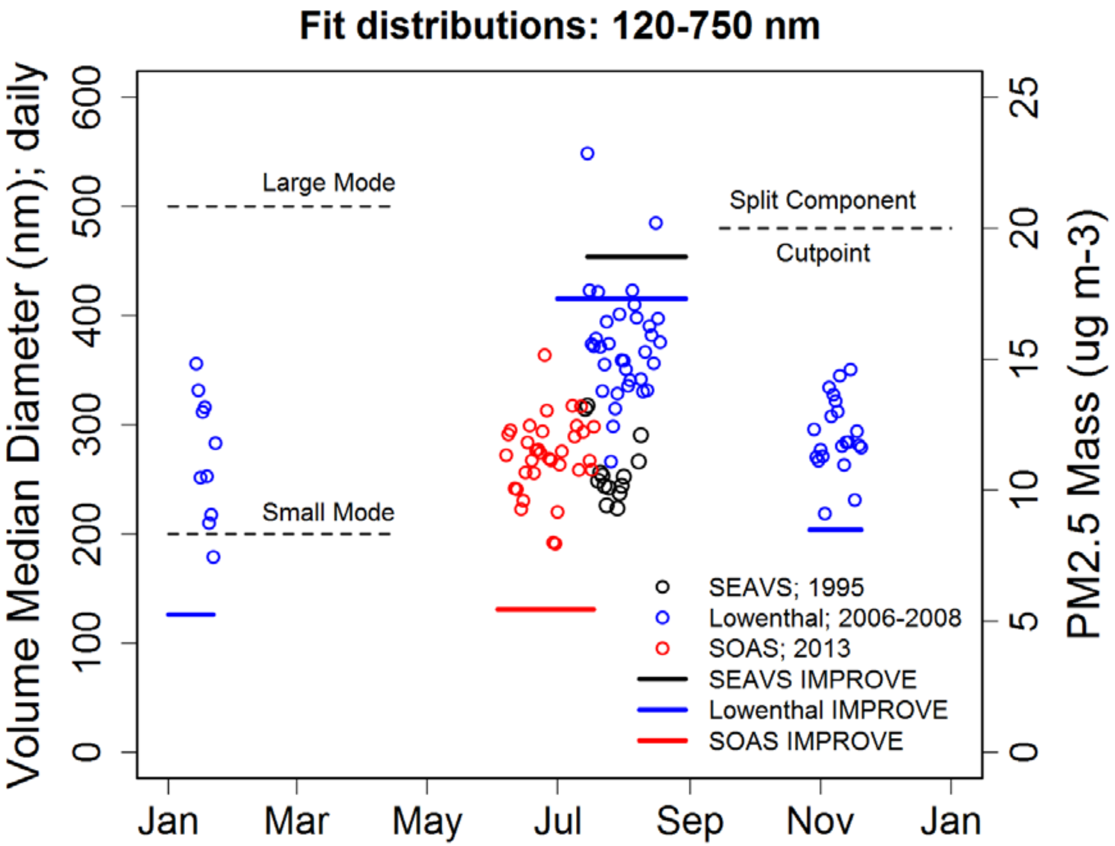


- IMPROVE Equation predicts sulfate scattering efficiencies trending down in the eastern US due to decreased sulfate.
- Constant in the west where sulfate has been more const.
- Assumption is that lower masses ➔ less aged aerosol ➔ more aerosol is in smaller mode, which is less efficient at scattering visible light.

Is scattering efficiency proportion to mass?

- Many studies have shown a relationship between scattering efficiency and mass over short periods (not space)
- No study has looked at the dependence over years with trending aerosol concentrations, but we can:
  - Great Smoky Mountains aerosol size measurements
    - SEAVS (Hand). 1995. Optical size distributions.
    - Lowenthal et al. 2006-2008. SMPS.
    - SOAS (Russell). 2013. SMPS.
  - Analysis
    - Lognormal distributions were fit to aerosol volume data.
    - Distributions fit with a single mode.
    - Data were limited to identical size range (120 – 750 nm).

GRSM size distribution fits



- No long term trend in size.
- Size distributions NOT dependent on long term trends in aerosol mass.
- Some correlation of aerosol mass and diameter in 2006-2008.
  - Could be seasonal effect

Focus on the MSE Normalization Factor of 20

$$[Large\ Sulfate] = \frac{[Total\ Sulfate]}{20} \times [Total\ Sulfate]$$

- A constant normalization factor implies that changes in size distribution are caused by changes in concentrations
- Concentrations and size distribution are more likely correlated and driven by aging processes
  - Less aged aerosol -> smaller concentrations and size distributions
  - More aged / cloud processed aerosol -> larger conc. and size distributions
- The size distributions and scattering efficiency's should be dependent on the relative concentrations at a given site/year

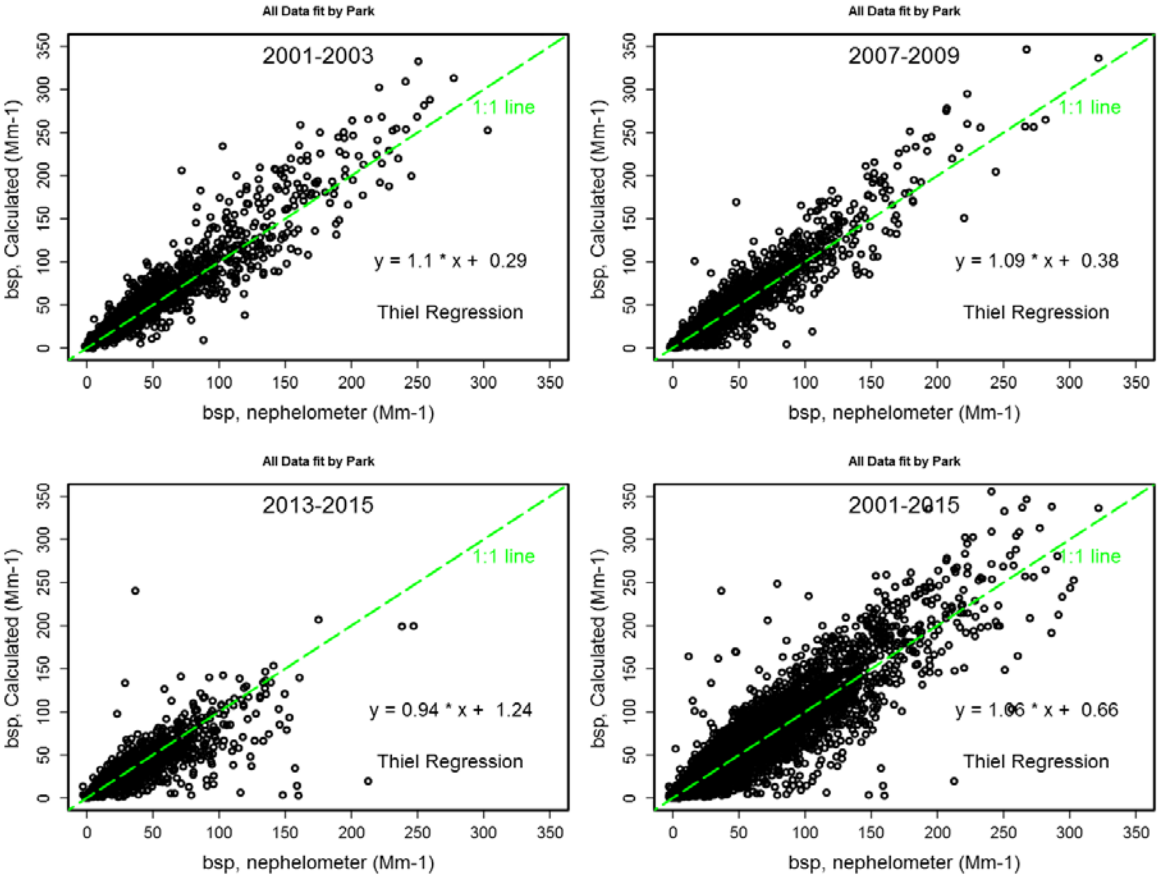
Focus on the MSE Normalization Factor of 20

$$[Large\ Sulfate] = \frac{[Total\ Sulfate]}{MSE\ Norm\ Frac} \times [Total\ Sulfate]$$

- The size distributions and scattering efficiency's should be dependent on the relative NOT absolute concentrations at a given site/year
- Regression and data analysis showed that the best fit between reconstructed and measured light scatter occurred with

MSE Norm Factor = 95th percentile concentration at each site, year and species

Measured vs Calculated for all Parks



- MSE normalization factor = 95th %-ile
- At all parks, overall better agreement.
- Temporal trend still apparent.
  - Did not account for findings from the RCFM analysis

RCFM - Conclusions

- Uncontrolled laboratory RH since 2011 has likely increased the relative water on the filters resulting in increased bias
  - The new RH controlled weighting chamber will fix this
- Ammoniated sulfate appears to be moving from ammonium bi-sulfate in early 2000’s to ammonium sulfate today
  - East is more acid than west
  - Current assumption of ammonium sulfate is good, but the ammoniated sulfate mass and scatter likely overestimated in early years
- Fine soil maybe underestimated by 15-20%
  - Any revised IMPROVE equation should include the increased soil
  - This should have minimal impacts on RHR metrics

RCFM - Carbonaceous Conclusions

- Roc appears to vary by season and region
  - Higher Roc in the summer ~2, than winter ~1.6
  - Higher Roc in the East ~2 than West ~1.8
- Some indication that Roc has increased since 2011, especially in summer (varies regionally), Why?
  - Emissions/chemistry changes? (See Bill's presentation)
  - Analytical issues?

- Any revised IMPROVE equation should account for
  - Roc Seasonal variations
  - Roc Long-term trends
  - Possibly Roc regional variations

Reconstructed b_{ext} - Summary

- Associated with large decreases in FM (especially sulfate), the reconstructed b_{ext} is now significantly underestimated in the eastern US
- Size distributions are correlated to mass concentrations but not caused by mass concentrations
- The mass scattering efficiency (MSE) should be dependent on the relative concentration not the absolute concentration, e.g. the 95th %-ile for a given site, species

- Next steps
  - Publish reconstructed FM and bext findings
  - Develop potential IMPROVE equation III that incorporates new findings
    - Evaluate impact of the revised equation on RHR metrics and trends
      - Will increase reconstructed b_{ext} thus remove some “current” progress
      - May shift some days that are considered most impaired
      - May increase perceived benefit from future source reductions
    - Any new equation should incorporate any changes to carbonaceous aerosol measurements

- Questions?

Multiple Linear Regression

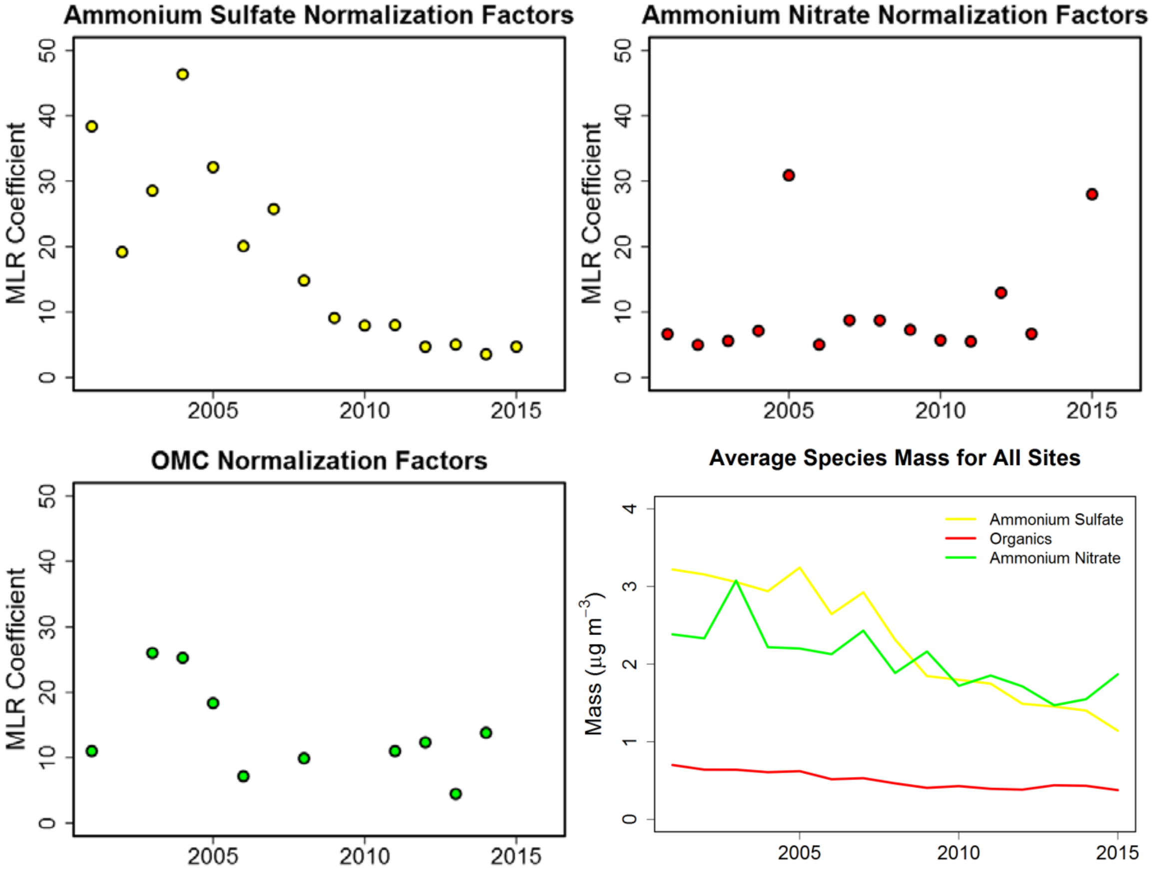
$$
\begin{aligned}
b_{sp}^{*} &= bsp_{Meas} - [SOIL] - 1.7 \times fRH_{SS} \times [SS] - 0.6 \times 0.5 \times [CM] \\
AS &= 2.2 \times fRH_{s} \times [ammSO_4]_{s} + 4.8 \times fRH_{l} \times [ammSO_4]_{l} \\
&= 2.2 \times fRH_{s} \times \left(1 - \frac{[ammSO_4]}{x}\right) \times [ammSO_4] + \\
&\qquad 4.8 \times fRH_{l} \times \frac{[ammSO_4]}{x} \times [ammSO_4] \\
&= \underbrace{2.2 \times fRH_{s} \times [ammSO_4]}_{\text{Move to } b_{sp}^{*} \text{ term.}} + \frac{1}{x} \underbrace{\times [ammSO_4]^{2} \times (4.8 \times fRH_{l} - 2.2 \times fRH_{s})}_{\text{AS}}
\end{aligned}
$$

Repeat for $ammNO_3$ and OMC.

Regression: $b_{sp}^{*} = c_1 \times AS + c_2 \times AN + c_3 \times OMC$

Normalization Factors: $ammSO_4 = \frac{1}{c_1}$; $ammNO_3 = \frac{1}{c_2}$; $OMC = \frac{1}{c_3}$

Regression Results: MSE normalization factor decreasing, especially for ammonium sulfate

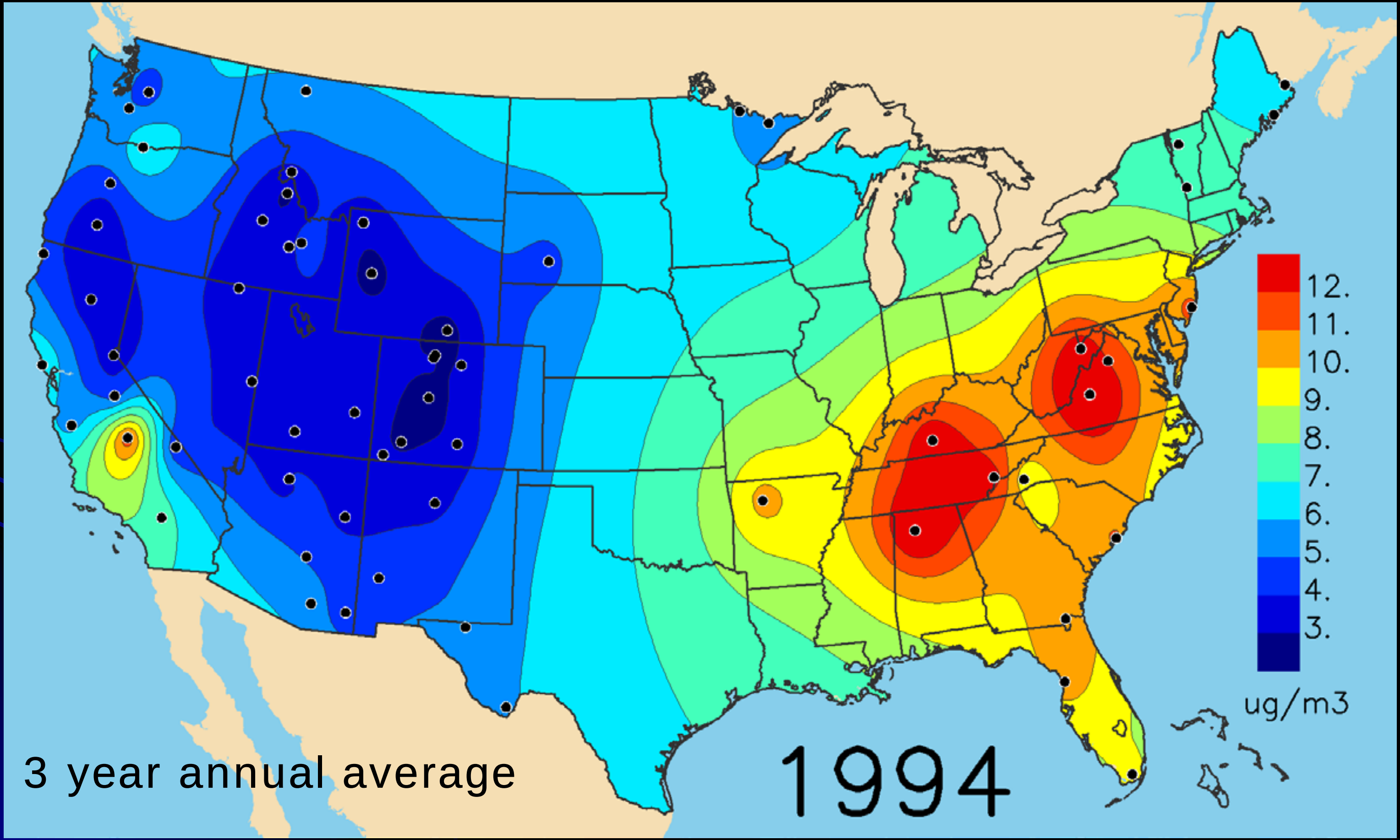


Best fit MLR coefficients are ~ 95th percentile conc for each species each year.

Extinction

- Study Sheds New **Light** on **Extinction** of Dinosaurs

Changes in Fine Particulate Matter in the Rural US over the past 22 years



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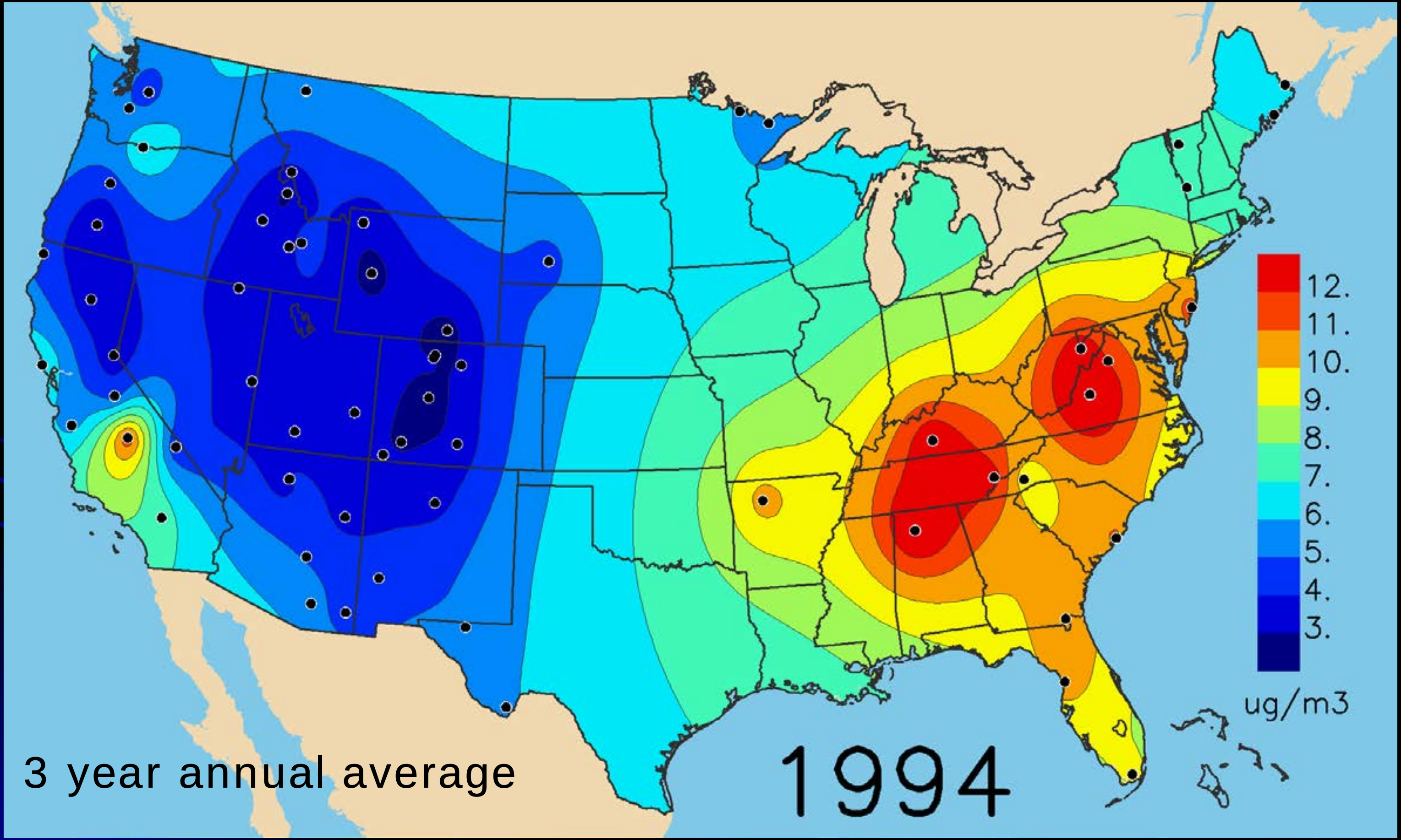

Interagency Monitoring of Protected Visual Environments (IMPROVE)

- Objectives
  - Support Regional Haze Rule by providing haze monitoring representing all visibility-protected CIA
  - Establish current visibility and aerosol conditions;
  - Document long-term trends for assessing progress towards the national visibility goal for CIA & as required by the Regional Haze Rule
  - Identify chemical species and emission sources responsible for existing man-made visibility impairment