



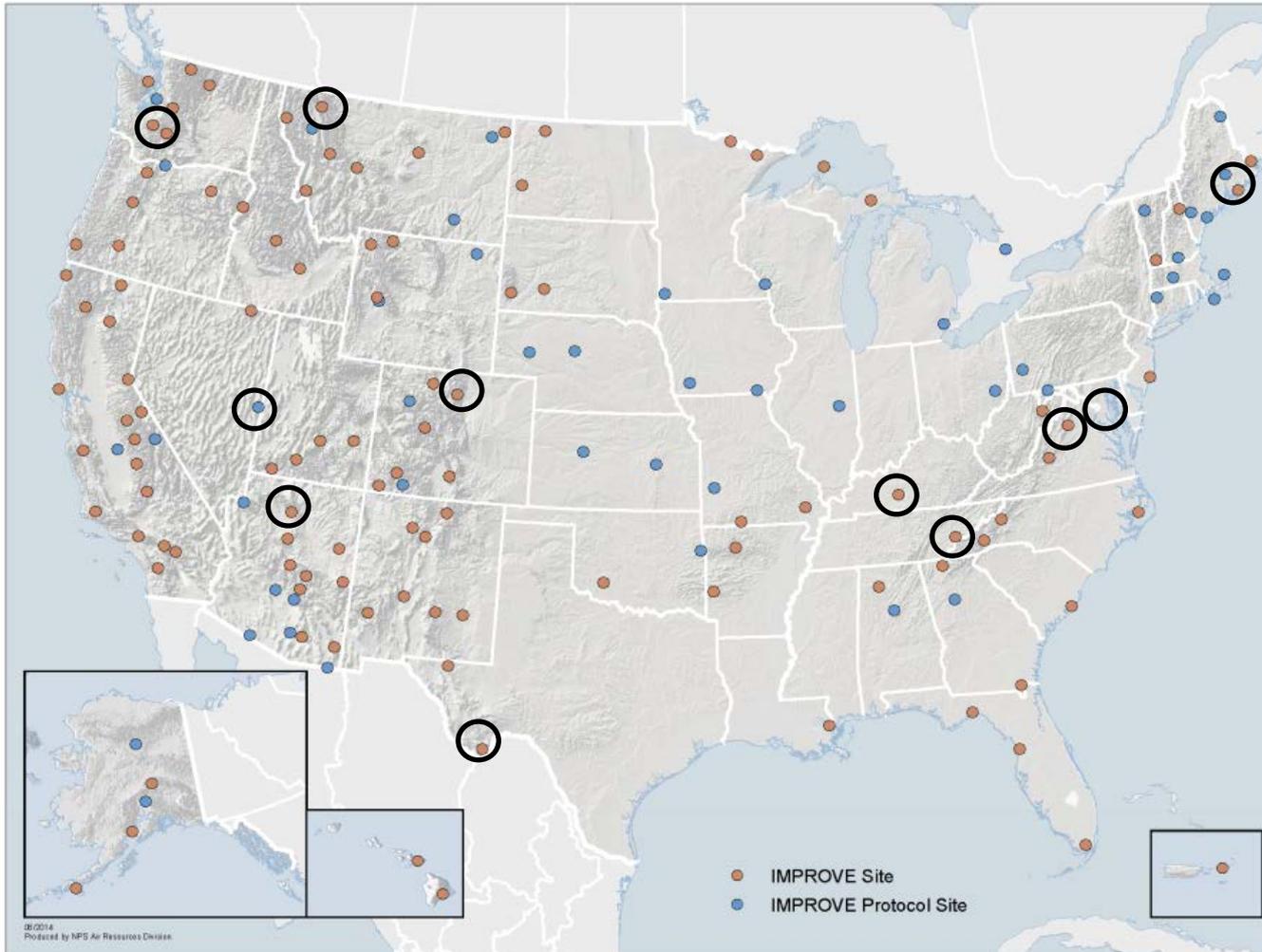
# An Examination of the Current IMPROVE Algorithm

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# IMPROVE Sites with Nephelometers



○ Sites with nephelometers:

- ACAD** – Acadia
- BIBE** – Big Bend
- GLAC** – Glacier
- GRBA** – Great Basin
- GRCA** – Grand Canyon
- GRSM** – Great Smoky
- MACA** – Mammoth Cave
- MORA** – Mount Rainier
- NACA** – National Capital (DC)
- ROMO** – Rocky Mtn
- SHEN** – Shenandoah



## 2<sup>nd</sup> IMPROVE Equation

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$$\begin{aligned} b_{ext} \approx & 2.2 \times f_s(RH) \times [Small\ Sulfate] + 4.8 \times f_L(RH) \times [Large\ Sulfate] \\ & + 2.4 \times f_s(RH) \times [Small\ Nitrate] + 5.1 \times f_L(RH) \times [Large\ Nitrate] \\ & + 2.8 \times [Small\ Organic\ Mass] + 6.1 \times [Large\ Organic\ Mass] \\ & + 1 \times [Fine\ Soil] + 1.7 \times f_{SS}(RH) \times [Sea\ Salt] + 0.6 \times [Coarse\ Mass] \\ & + 10 \times [EC] + Rayleigh\ Scattering\ (site\ specific) + 0.33 \times [NO_2(ppb)] \end{aligned}$$

*Pitchford et al., 2007.*

*Does not depend on gravimetric fine mass.*



## 2<sup>nd</sup> IMPROVE Equation

$$\begin{aligned} b_{ext} \approx & \mathbf{2.2} \times f_s(RH) \times [\mathbf{Small Sulfate}] + \mathbf{4.8} \times f_L(RH) \times [\mathbf{Large Sulfate}] \\ & + \mathbf{2.4} \times f_s(RH) \times [\mathbf{Small Nitrate}] + \mathbf{5.1} \times f_L(RH) \times [\mathbf{Large Nitrate}] \\ & + \mathbf{2.8} \times [\mathbf{Small Organic Mass}] + \mathbf{6.1} \times [\mathbf{Large Organic Mass}] \\ & + \mathbf{1} \times [\mathbf{Fine Soil}] + \mathbf{1.7} \times f_{SS}(RH) \times [\mathbf{Sea Salt}] + \mathbf{0.6} \times [\mathbf{Coarse Mass}] \\ & + \mathbf{10} \times [\mathbf{EC}] + \mathbf{Rayleigh Scattering (site specific)} + \mathbf{0.33} \times [\mathbf{NO}_2(ppb)] \end{aligned}$$

$\alpha$  = dry mass extinction efficiency



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*f(RH) accounts for hygroscopic growth of particles.  
Sulfate and nitrate only.*



## 2<sup>nd</sup> IMPROVE Equation

$$\begin{aligned} b_{ext} \approx & 2.2 \times f_s(RH) \times [\textit{Small Sulfate}] + 4.8 \times f_L(RH) \times [\textit{Large Sulfate}] \\ & + 2.4 \times f_s(RH) \times [\textit{Small Nitrate}] + 5.1 \times f_L(RH) \times [\textit{Large Nitrate}] \\ & + 2.8 \times [\textit{Small Organic Mass}] + 6.1 \times [\textit{Large Organic Mass}] \\ & + 1 \times [\textit{Fine Soil}] + 1.7 \times f_{SS}(RH) \times [\textit{Sea Salt}] + 0.6 \times [\textit{Coarse Mass}] \\ & + 10 \times [EC] + \textit{Rayleigh Scattering (site specific)} + 0.33 \times [NO_2(ppb)] \end{aligned}$$

Large mode mass fraction = [component] / 20  $\mu\text{g m}^{-3}$

Small mode mass fraction = 1 – Large mode mass fraction

Ex. [Sulfate] = 5  $\mu\text{g m}^{-3}$

Large mode = 5  $\mu\text{g m}^{-3}$  / 20  $\mu\text{g m}^{-3}$  = 0.25 (1.25  $\mu\text{g m}^{-3}$ )

Small mode = 1 - 0.25 = 0.75 (3.75  $\mu\text{g m}^{-3}$ )

If the total > 20  $\mu\text{g m}^{-3}$ , all mass is assumed to be in the large mode.



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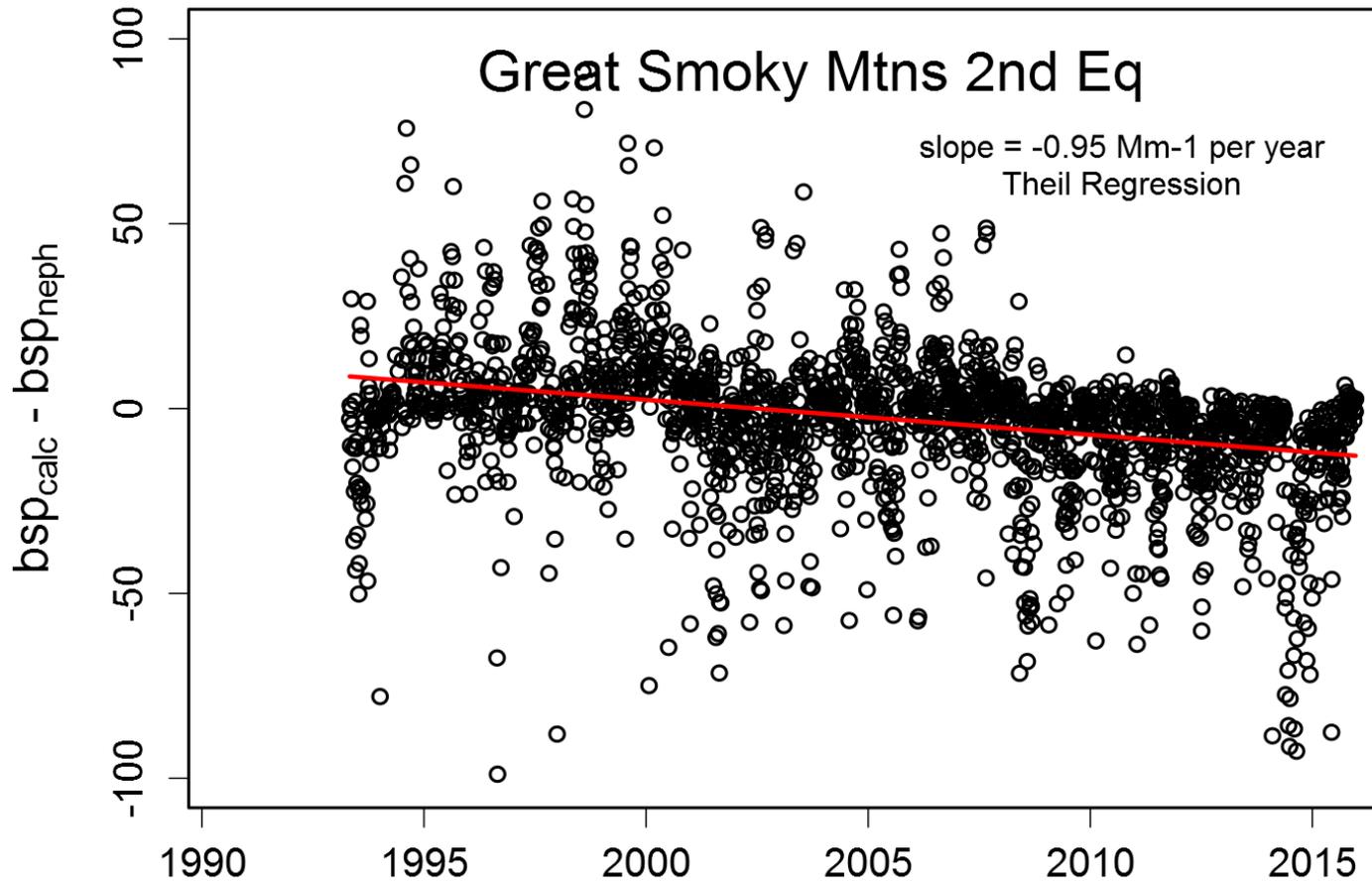
**Compare calculated scattering to measurements from nephelometer.**

- Remove EC contribution to extinction
- Remove Rayleigh Scattering term
- Remove NO<sub>2</sub> absorption
- calculated coarse mass =  $0.5 \times 0.6 \times [Coarse\ Mass]$   
    ➔ Account for truncation error in nephelometer





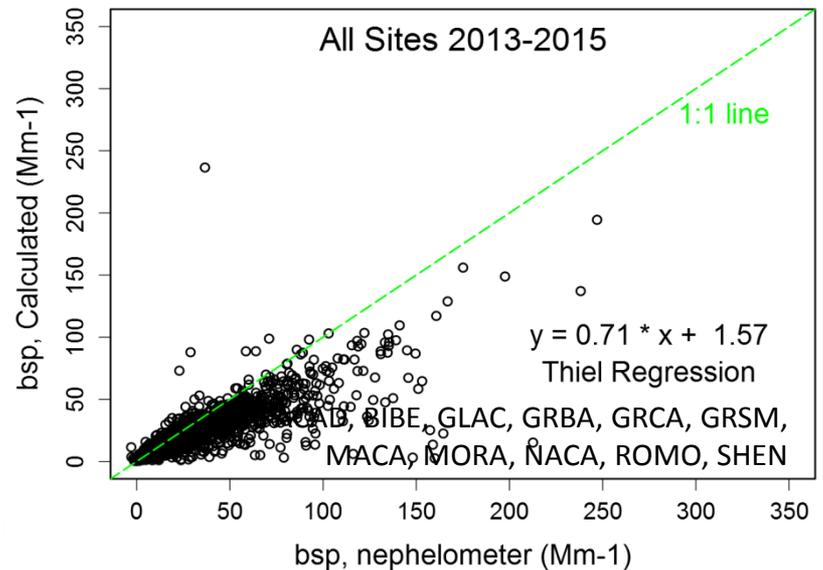
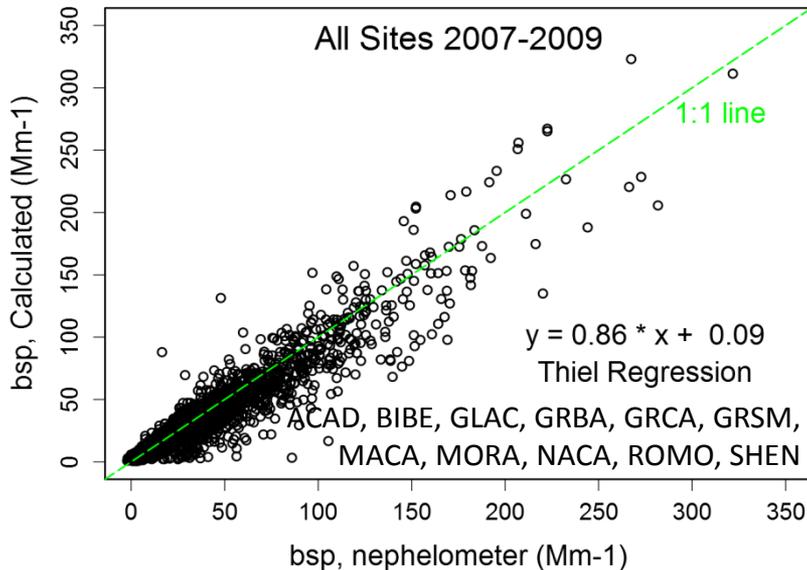
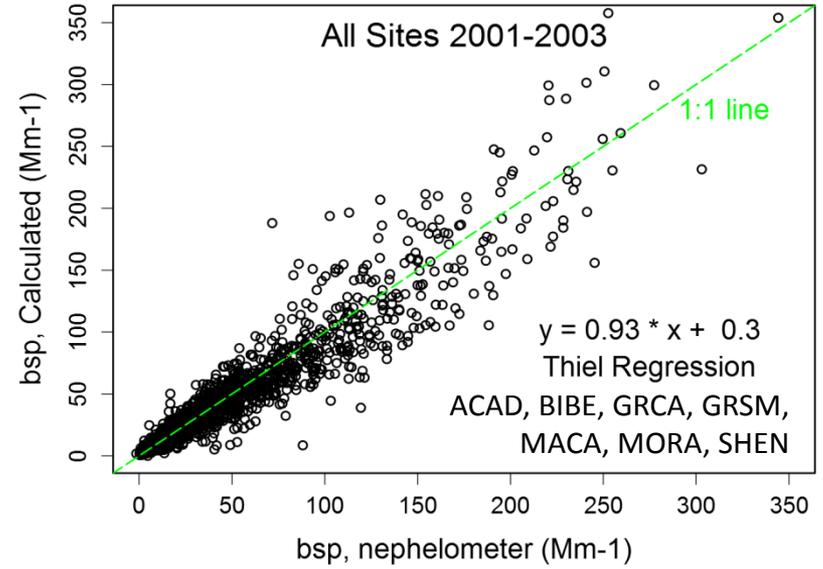
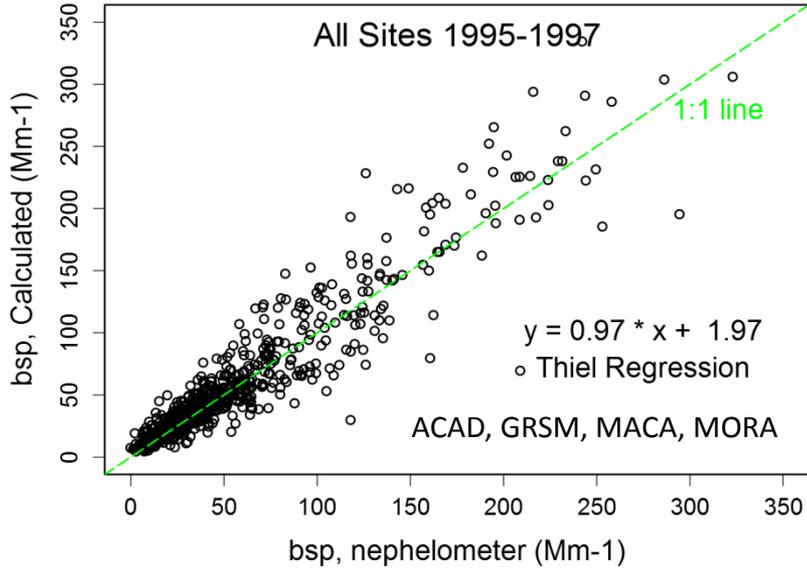
# GRSM over time



Decreasing at 8 of 11 parks (not GRBA, GRCA, & ROMO).



# Relationship between Measured & Reconstructed Scattering has Changed over Time.

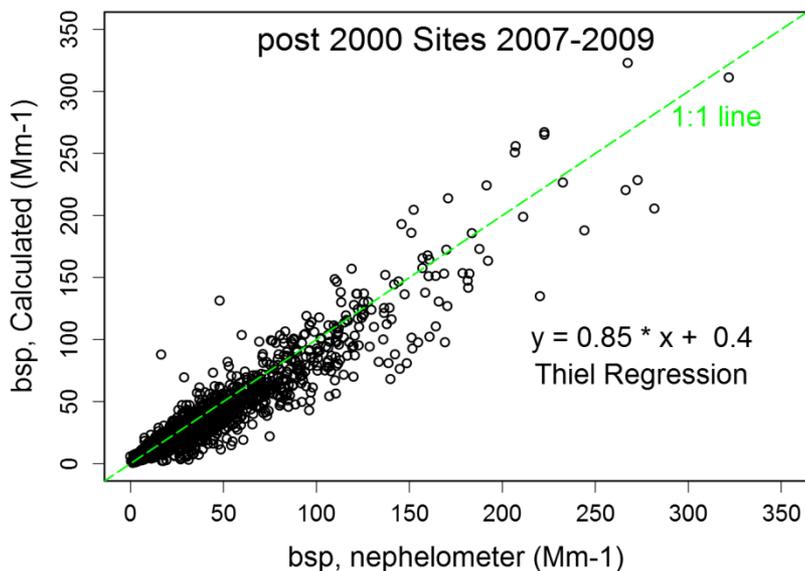


IMPROVE

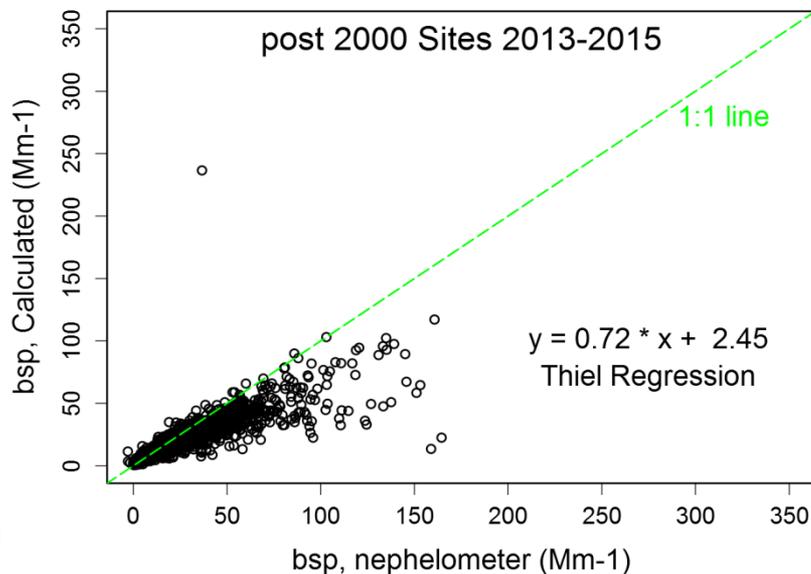
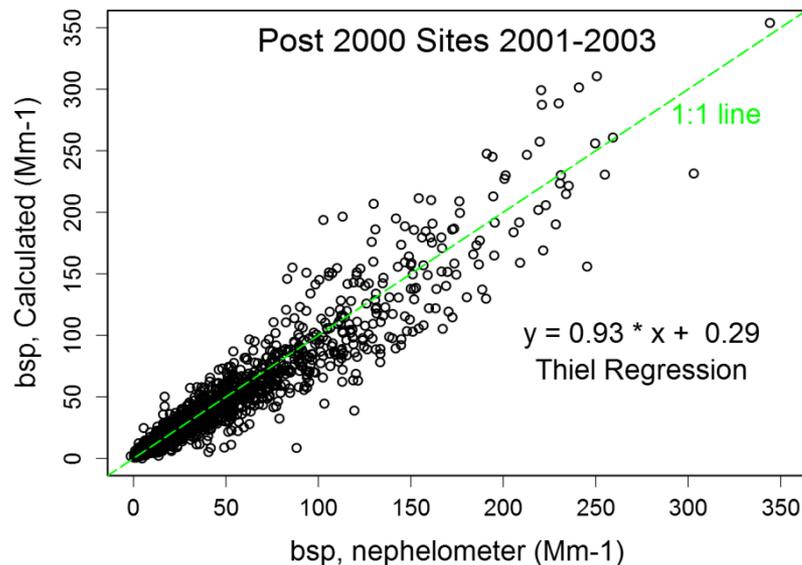


# Limiting to Continuous Records (7 sites)

Trend remains when limiting to sites that have data throughout the time period:  
ACAD, BIBE, GRCA, GRSM,  
MACA, MORA, SHEN

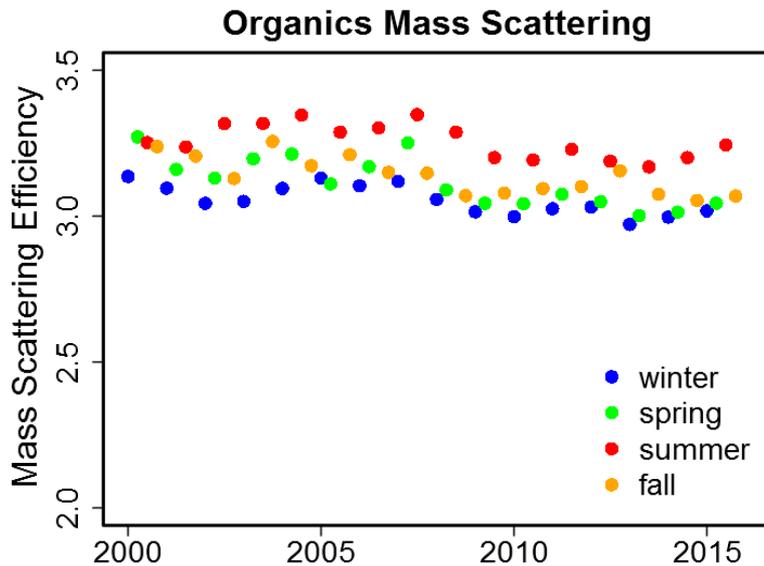
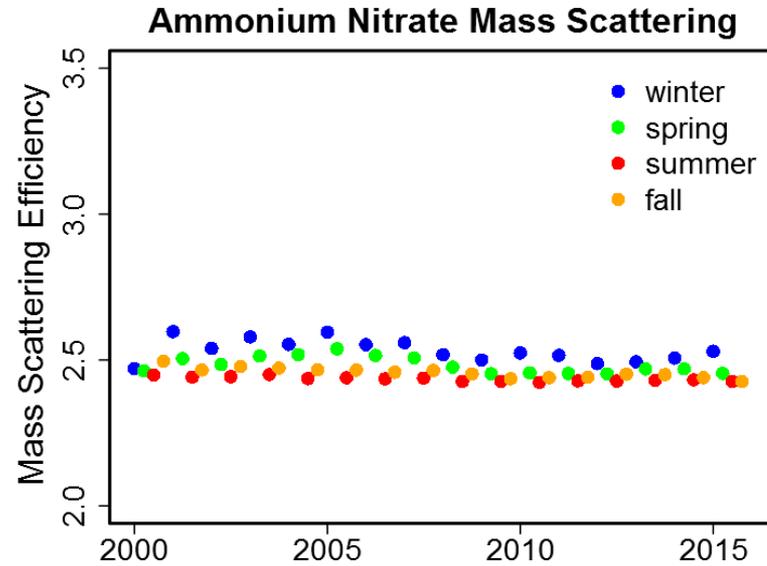
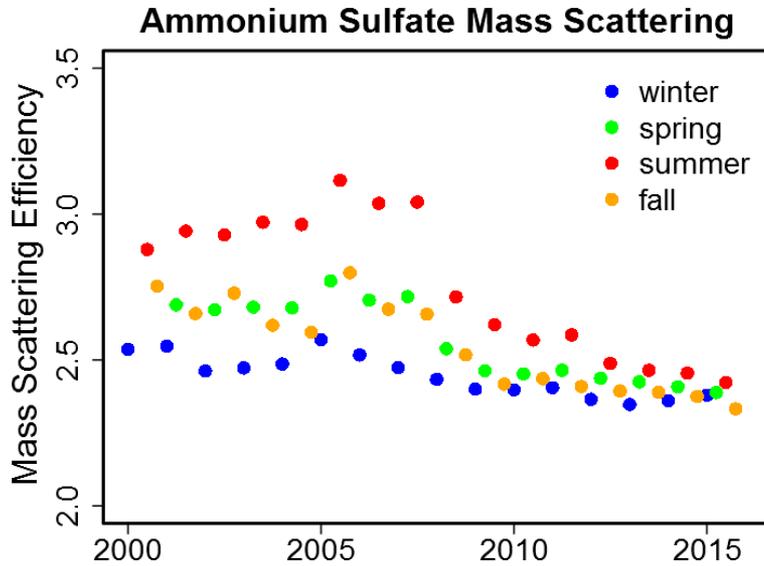


WPROVE





# Mass Scattering Efficiencies Decrease due to Reduced Aerosol Mass



Ex. Sulfate Scattering Efficiency

$$2.2 \times f_s(RH) \times [\textit{Small Sulfate}] + 4.8 \times f_L(RH) \times [\textit{Large Sulfate}]$$

Mass Scattering Efficiency =

fraction small  $\times$  small mode scattering efficiency +  
fraction large  $\times$  large mode scattering efficiency



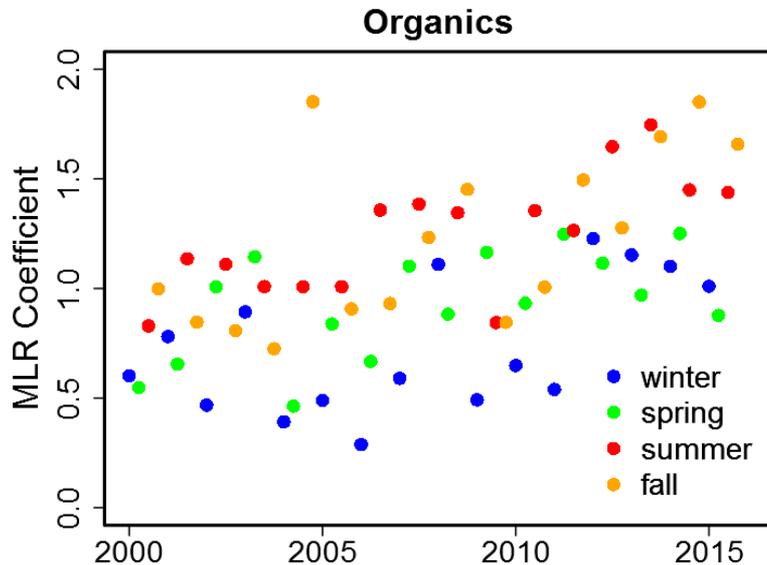
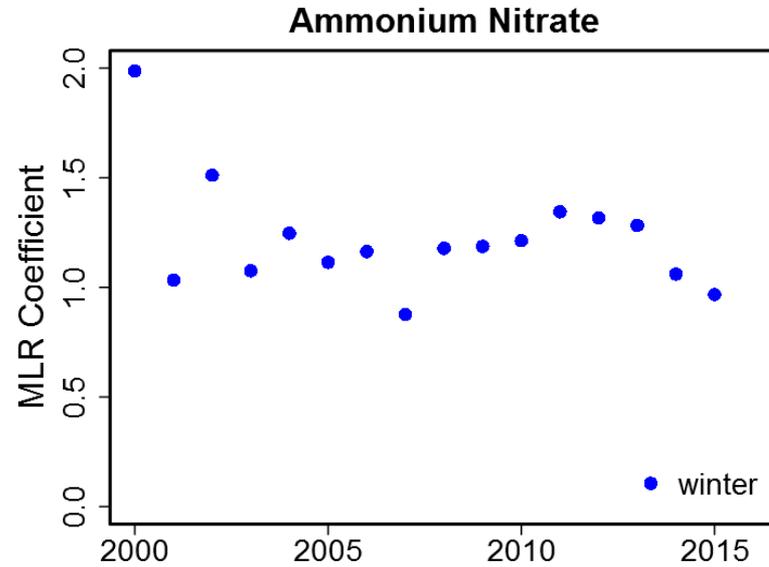
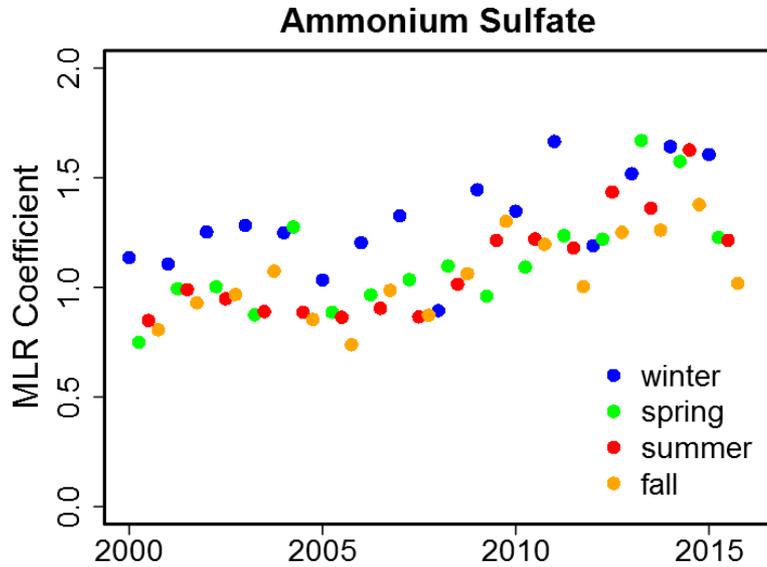
# Multiple Linear Regression

$$y = c_0 + c_1 \times AS + c_2 \times AN + c_3 \times Org$$

- $y = bsp_{Meas} - ([\text{Fine Soil}] + 1.7 \times f_{SS}(\text{RH}) \times [\text{Sea Salt}] + 0.5 \times 0.6 \times [\text{Coarse Mass}])$
- $AS = 2.2 \times f_s(\text{RH}) \times [\text{Small Sulfate}] + 4.8 \times f_L(\text{RH}) \times [\text{Large Sulfate}]$
- $AN = 2.4 \times f_s(\text{RH}) \times [\text{Small Nitrate}] + 5.1 \times f_L(\text{RH}) \times [\text{Large Nitrate}]$
- $Org = 2.8 \times [\text{Small OMC}] + 6.1 \times [\text{Large OMC}]$
- Solve for coefficients ( $c_1, c_2, c_3$ ) each season.
  - Limits [0, 2]



# Multiple Linear Regression Results



Sulfate → Increasing

Winter Nitrate → ~stable

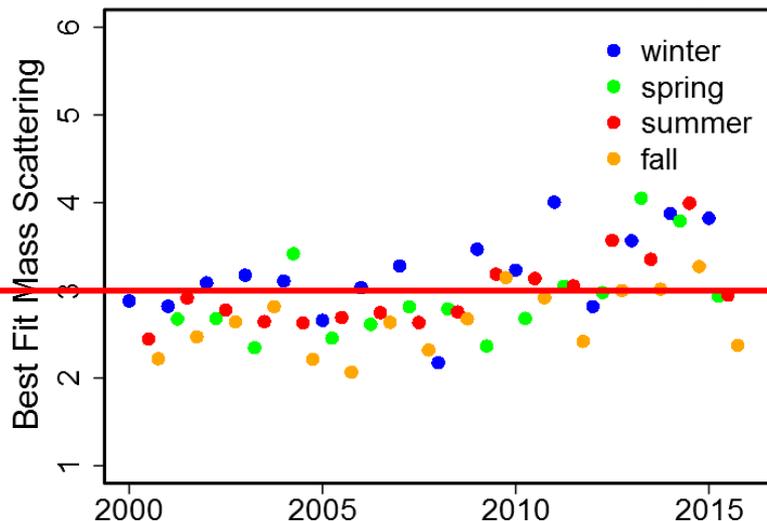
Organics → scatter with seasonal increases

**For sulfate, are coefficients simply offsetting decrease in dry mass scattering efficiency?**

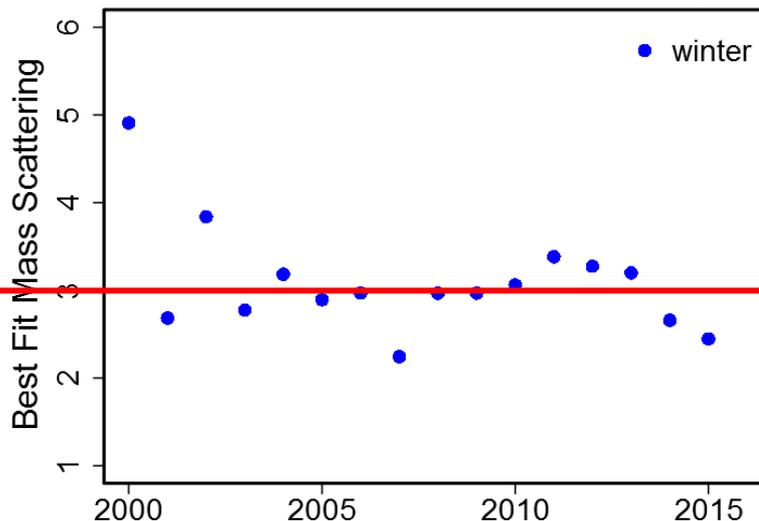


# MLR Coeff $\times$ Mass Scattering Efficiency

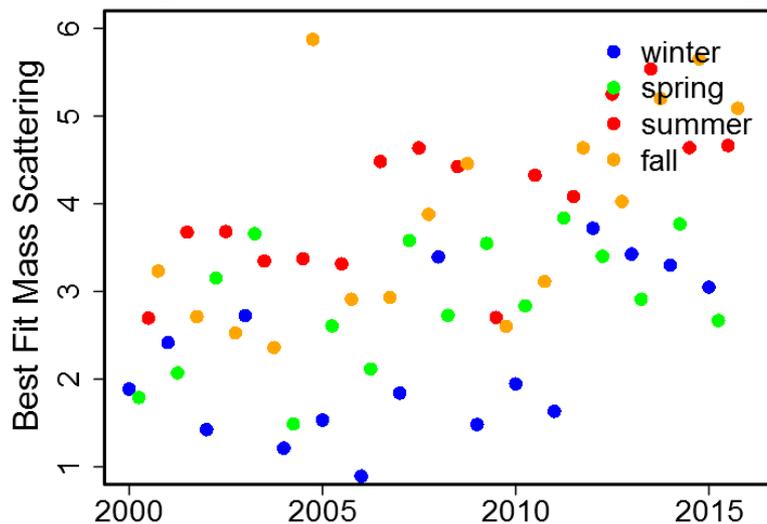
AS: MLR Coeff \* Mass Scattering



AN: MLR Coeff \* Mass Scattering



Organics: MLR Coeff \* Mass Scattering



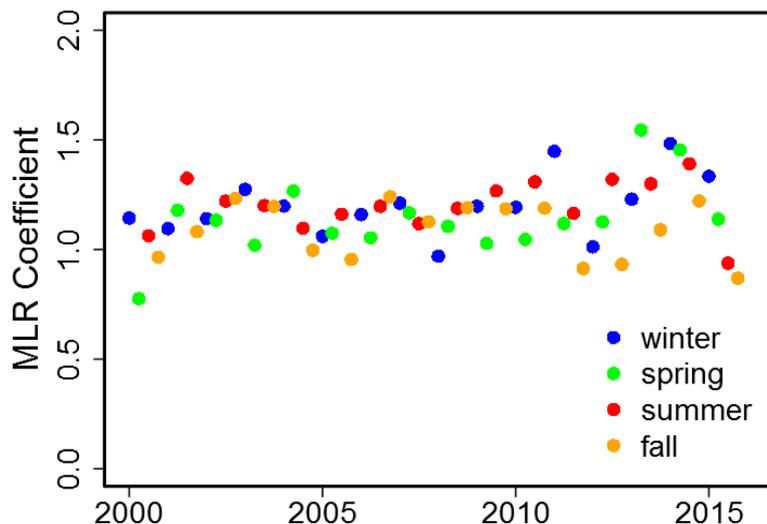
AS and winter AN = “best fit” mass scattering efficiency  $\sim 3 \text{ m}^2/\text{g}$ , as was used in the 1<sup>st</sup> IMPROVE Equation.

Scatter in organics.

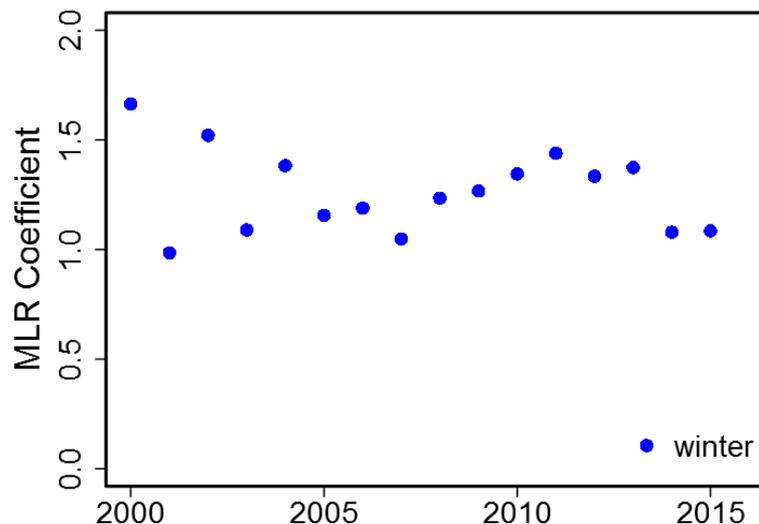


# MLR – 1<sup>st</sup> IMPROVE Equation

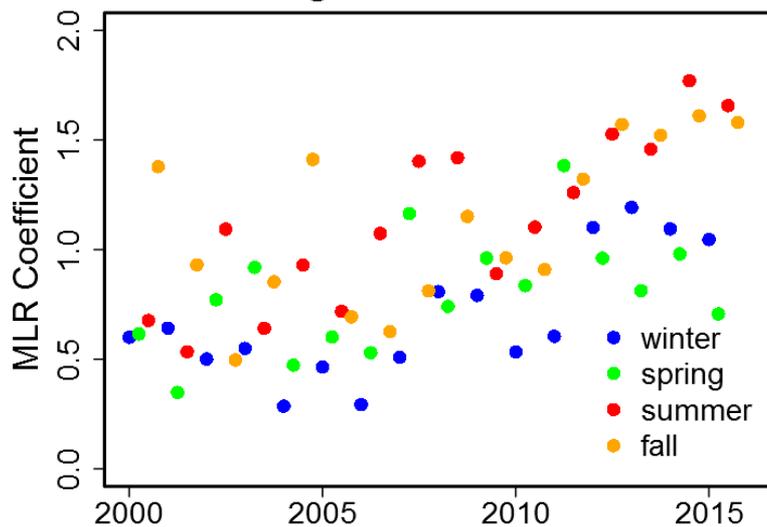
### Ammonium Sulfate Coefficients



### Ammonium Nitrate Coefficients



### Organic Coefficients



AS and winter AN reasonably stable.

Scatter in organics, with seasonal increases.

\*Roc = 1.8



# Revised Approach

- Assume 1<sup>st</sup> IMPROVE Equation provides reasonable estimates for ammonium sulfate and ammonium nitrate.
- Focus on organics
  - Organics contribution to light scattering =

$$[\text{OC}] \times R_{\text{oc}} \times \alpha \times f(\text{RH})_{\text{org}}$$

Measured organic carbon concentration from IMPROVE.

Organic mass to organic carbon ratio.  
IMPROVE 1 = 1.4  
IMPROVE 2 = 1.8

Organic dry mass scattering efficiency.

Change in scattering due to increasing RH. Assumed to be 1 for organics.



# Revised Approach: [OC] and $\alpha$

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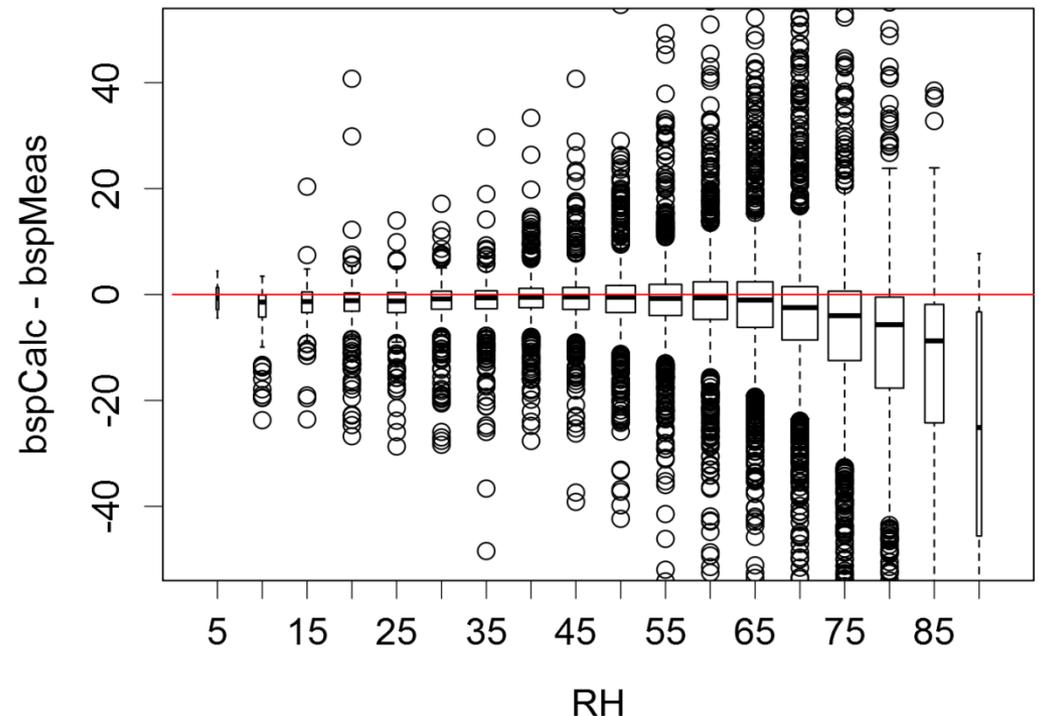
$$[\text{OC}] \times \text{Roc} \times \alpha \times f(\text{RH})_{\text{Org}}$$

- Assume [OC] measurements are accurate.
- Select a value for  $\alpha$ :
  - 1st IMPROVE = 4 m<sup>2</sup>/g
  - 2nd IMPROVE = ~3.2 m<sup>2</sup>/g
  - From regression,  $\alpha_{\text{Org}} = \mathbf{3.6 \text{ m}^2/\text{g} \text{ (median)}}$



# Revised Approach: $f(\text{RH})$

- Measurements suggest  $f(\text{RH})_{\text{Org}} > 1$  for BSOA.
  - e.g. Quinn et al., 2005, Varutbangkul et al., 2006, Prenni et al., 2007, Duplissy et al., 2008, Wex et al., 2009, Alfarra et al., 2013, Attwood et al., 2014, Lowenthal et al., 2015, Brock et al., 2016, Zhao et al., 2016
- Calculated values under-predict measured light scattering at high RH.





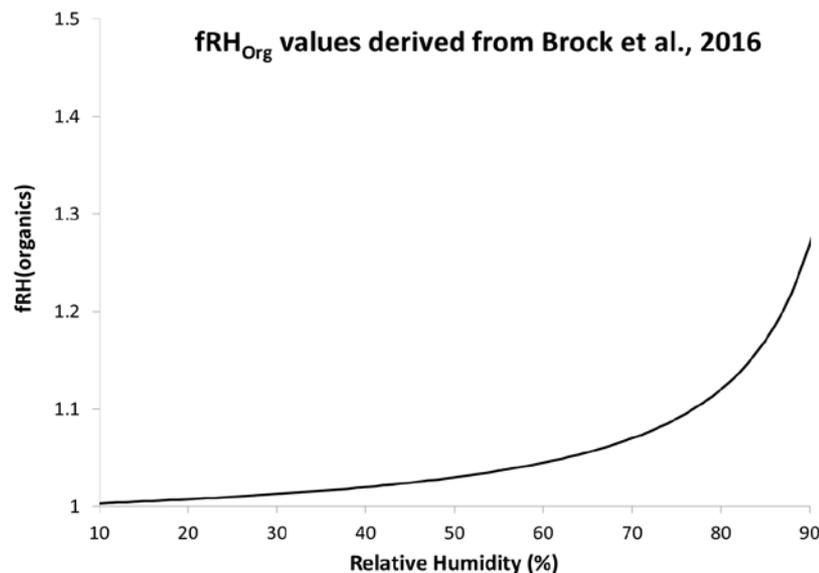
# Revised Approach (f(RH))

$$[\text{OC}] \times \text{Roc} \times \alpha \times \mathbf{f(\text{RH})}_{\text{org}}$$

- Brock et al. (2016) examined hygroscopicity during SENEX & SEAC<sup>4</sup>RS field campaigns in 2013.
- Developed a parameterization for f(RH):

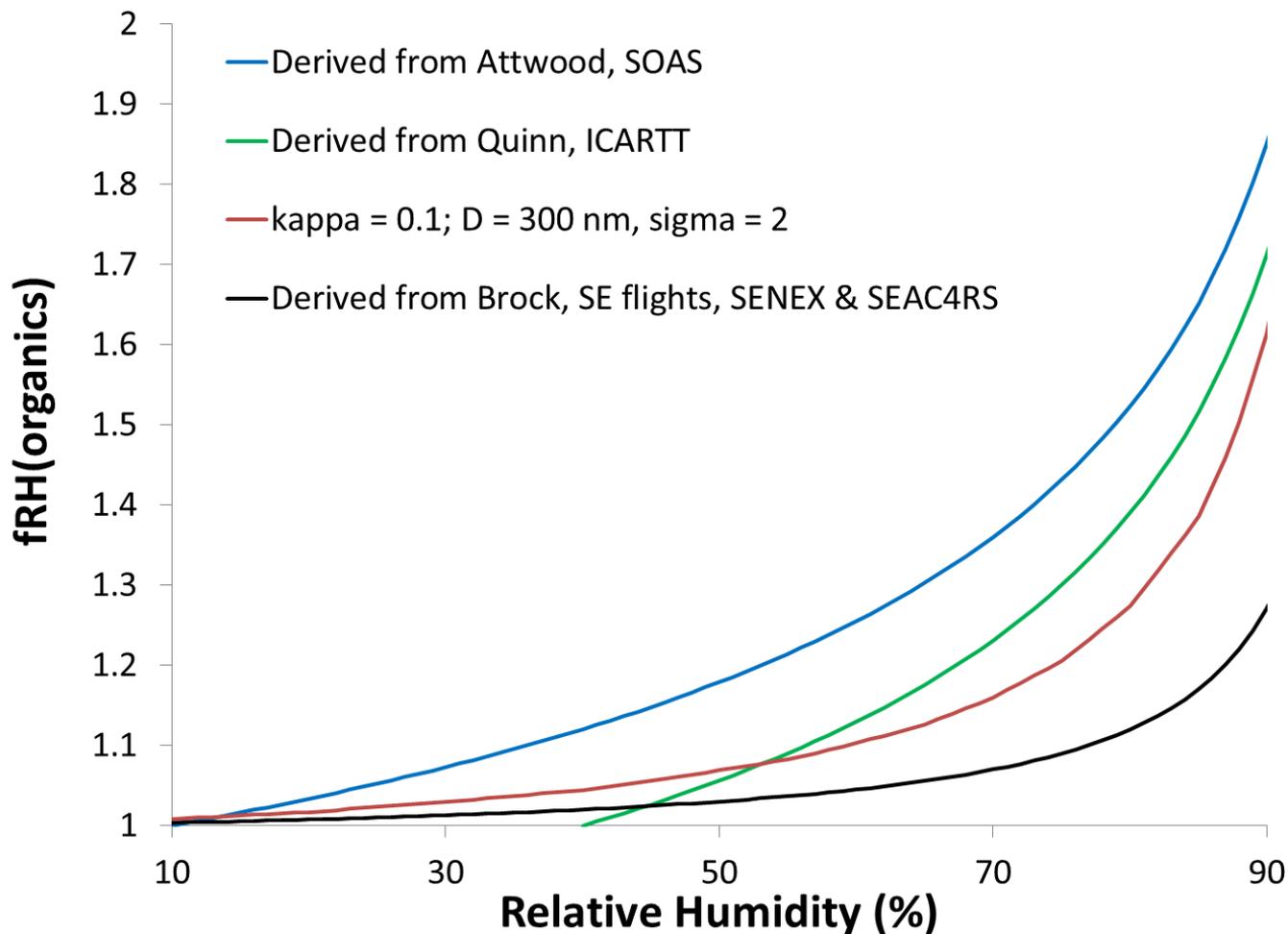
$$f(\text{RH}) \cong 1 + \kappa_{\text{ext}} \frac{\text{RH}}{100 - \text{RH}}$$

- Extrapolate composition/  
RH-dependent  
measurements:  $\kappa_{\text{ext}} = 0.030$





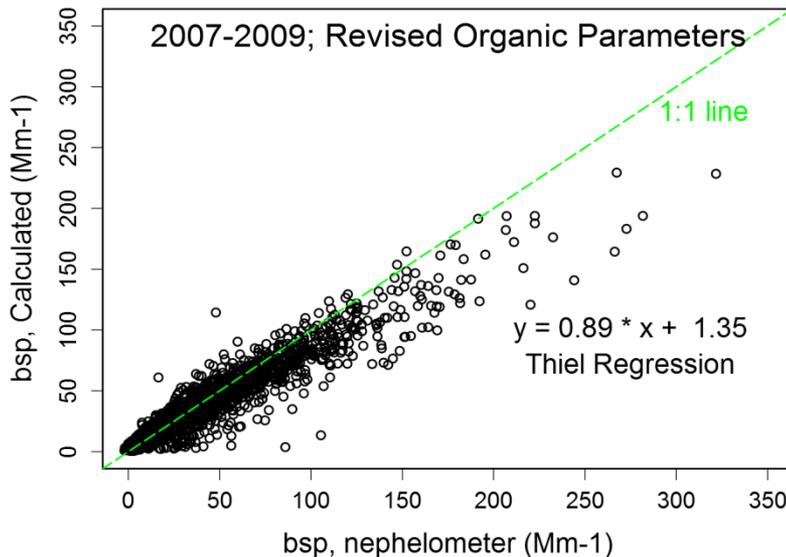
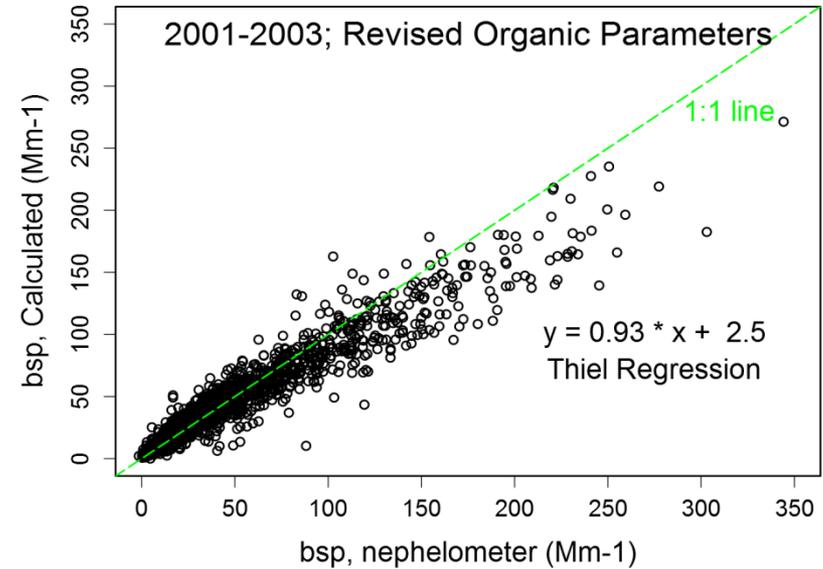
# Comparison to other $f(\text{RH})_{\text{Org}}$ values



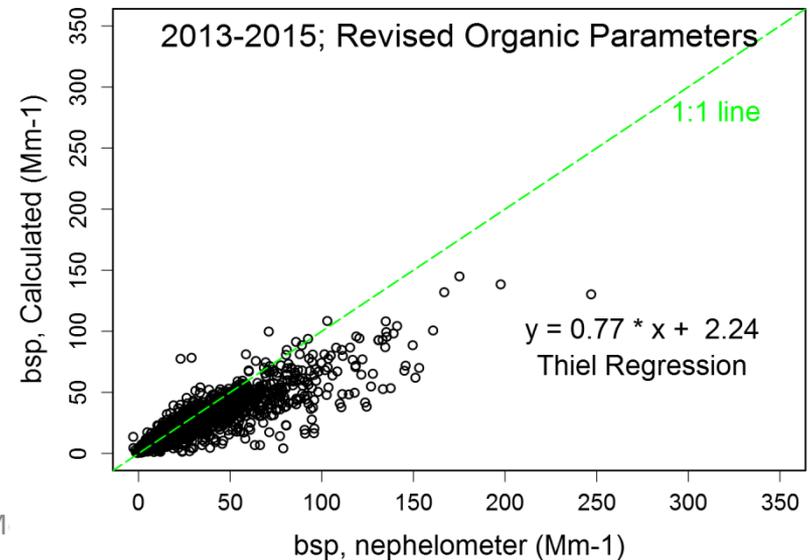


# Trends are still observed between measured & calculated bsp.

- Incorporate  $\alpha = 3.6$   $\text{m}^2/\text{g}$  for organics, and  $f(\text{RH})$  values from Brock et al. (2016).



PROVE M



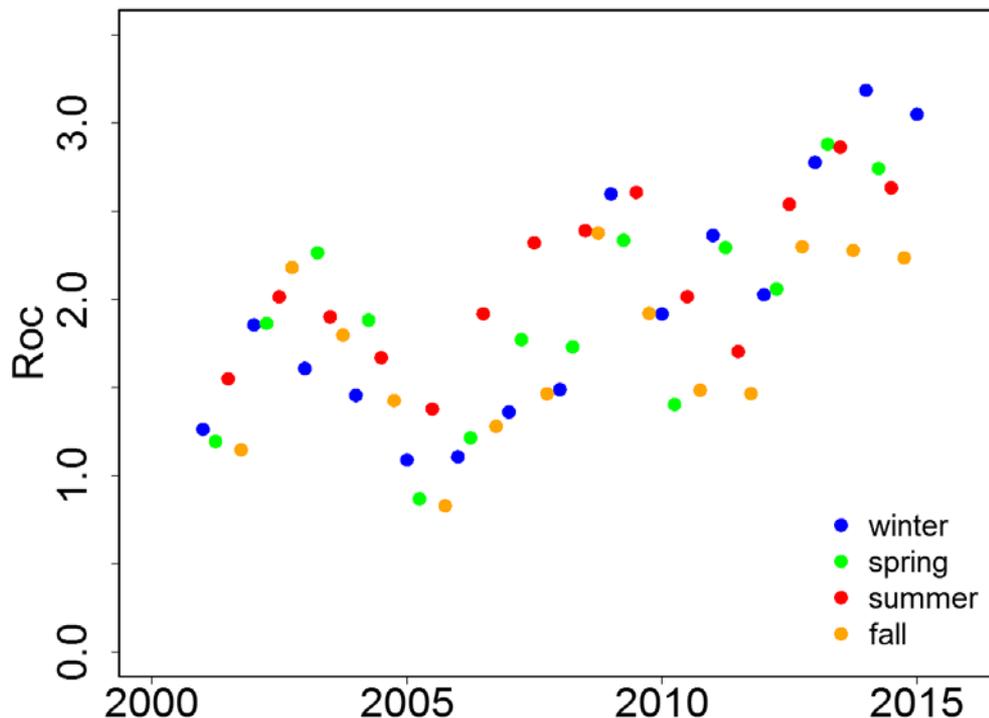


# Revised Approach: Roc

$$[\text{OC}] \times \mathbf{Roc} \times \alpha \times f(\text{RH})_{\text{Org}}$$

- Using  $\alpha = 3.6 \text{ m}^2/\text{g}$  for organics, and  $f(\text{RH})$  values from Brock et al. (2016), solve for Roc over time.

Roc; Revised Equation; Brock fRH



Derived values show trend in Roc values.

Consistent with values from the literature, but the range is greater than has been observed.

Increase comes more from the eastern sites.

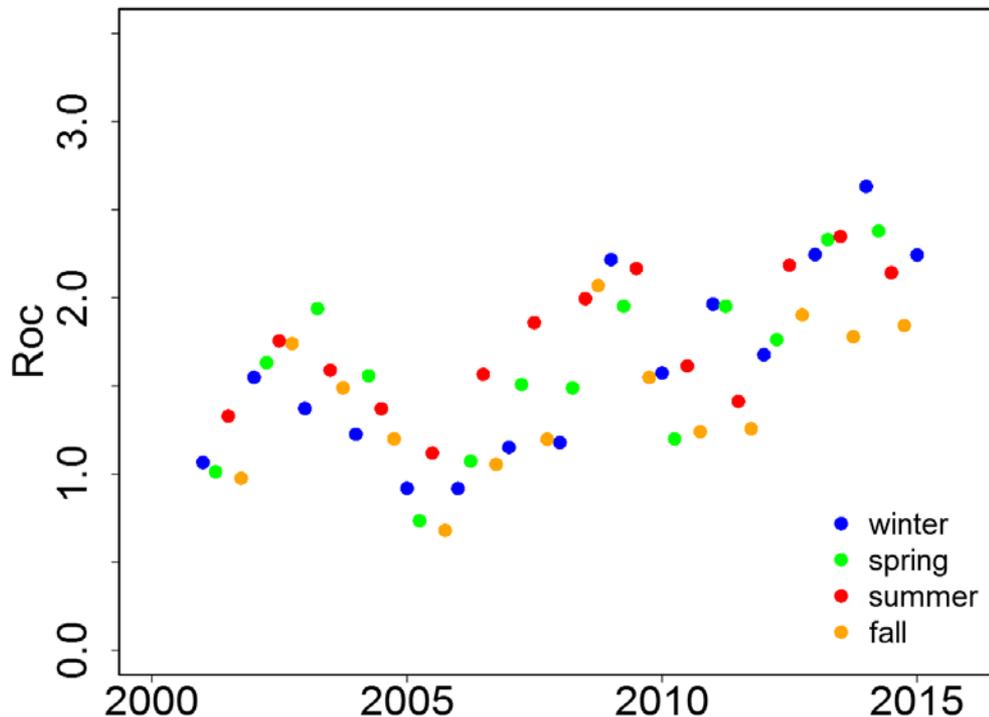


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$$[\text{OC}] \times \mathbf{Roc} \times \alpha \times f(\text{RH})_{\text{Org}}$$

- Using  $\alpha = 3.6 \text{ m}^2/\text{g}$  for organics, and  $f(\text{RH})$  values from Attwood et al. (2014), solve for Roc over time.

Roc; Revised Equation; Attwood fRH

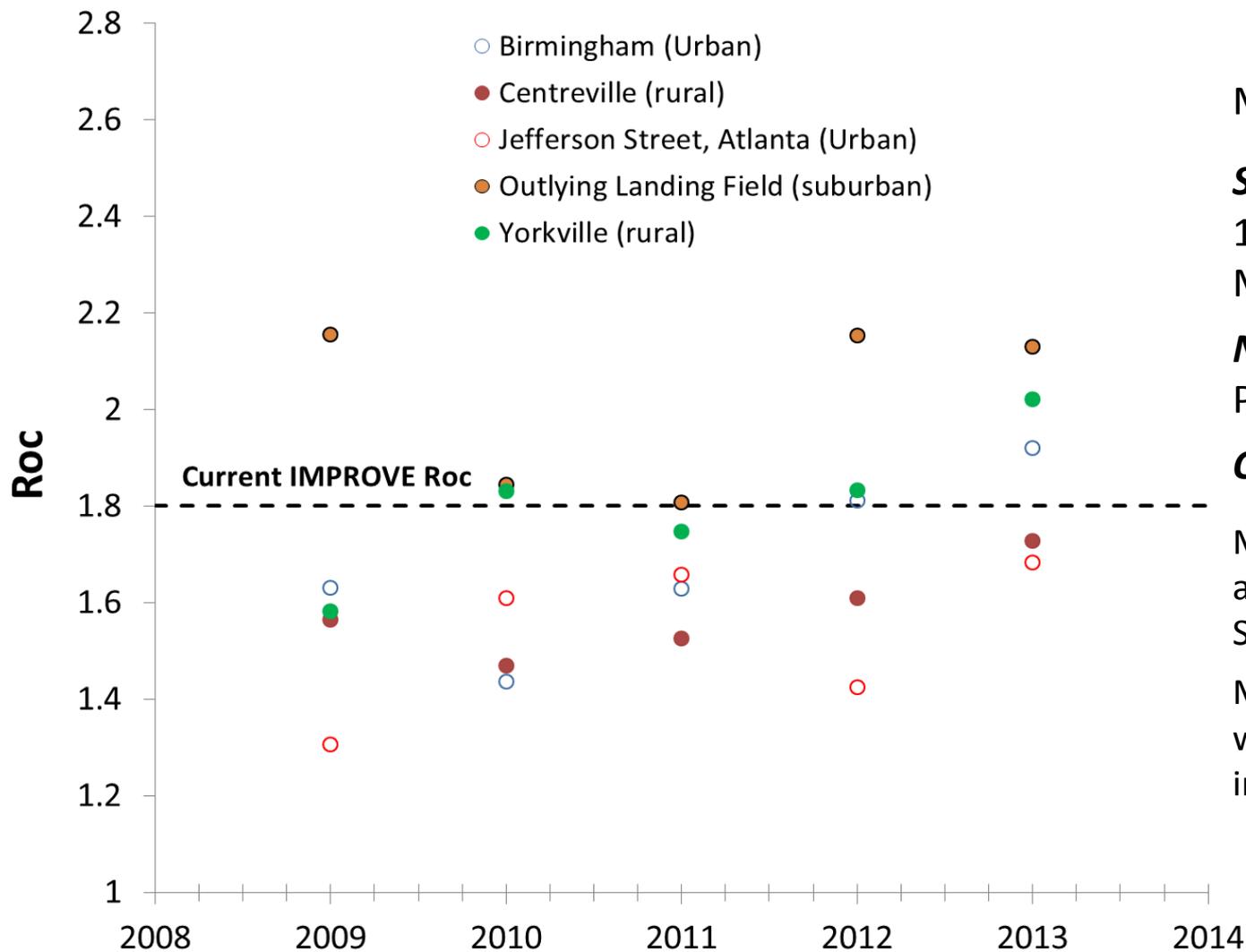


A more hygroscopic aerosol leads to tighter range in Roc.

In all cases, Roc is accounting for ALL changes over time. Other factors likely play a role.



# Blanchard et al., 2016. SEARCH Network



Mass Balance Approach:

$$\text{Sum} = 1.28 \cdot \text{SO}_4 + 1.15 \cdot \text{NO}_3 + 1.25 \cdot \text{NH}_4 + \text{MMO} + \text{EC} + \text{OC} + \text{Cl} + \text{Na}$$

$$\text{Non-measured (NM)} = \text{PM}_{2.5} \text{ mass} - \text{Sum}$$

$$\text{OM}^* = \text{OC} + \text{NM}$$

Major metal oxides (MMO) are computed according to SEARCH convention

Multipliers are averages for water associated with inorganic species





# Summary

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- There is a trend in the relationship between measured and reconstructed light scattering.
- Calculated  $b_{sp}$  now underpredicts measured  $b_{sp}$ .
- Disagreement is partly due to shift to lower mass scattering efficiency for ammonium sulfate
- Although it does not affect the trend with time,  $f(RH)_{Org}$  should be considered.
- A changing Roc may also play a role in this trend.



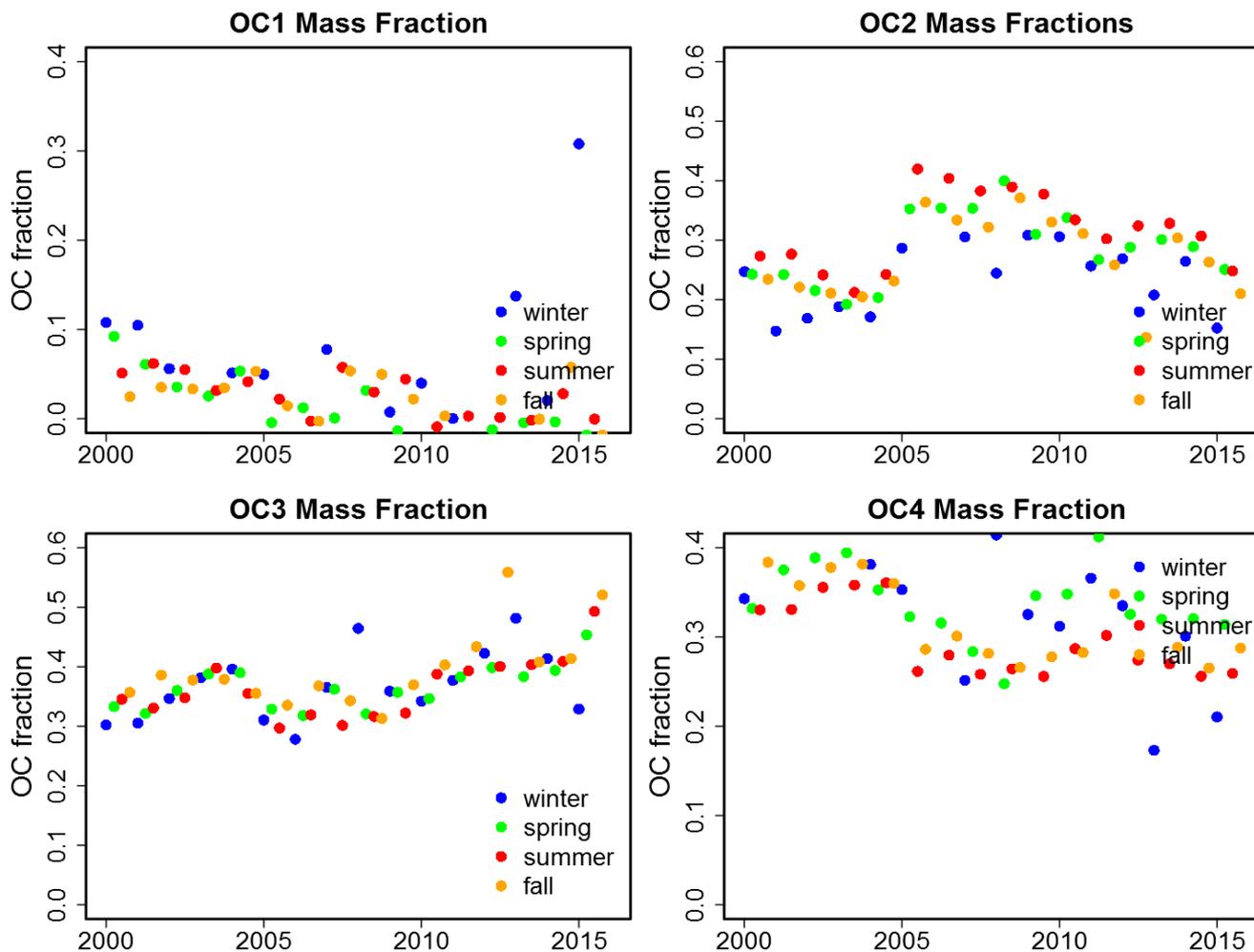
# EXTRAS

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# Revised Approach: Roc

$$[\text{OC}] \times \mathbf{Roc} \times \alpha \times f(\text{RH})_{\text{Org}}$$





# 1<sup>st</sup> IMPROVE Equation

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$$b_{ext} \approx 3 \times f(RH) \times [Sulfate] + 3 \times f(RH) \times [Nitrate] + \\ 4 \times [Organic Mass] + 1 \times [Fine Soil] + \\ 0.6 \times [Coarse Mass] + 10 \times [EC] + 10$$

*Malm et al., 1994*

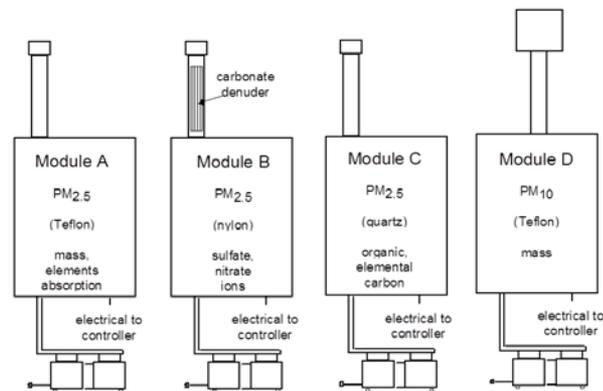


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Aerosol concentrations come from IMPROVE measurements.





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**f(RH) accounts for change in scattering due to changes in ambient RH.**

**Organics are assumed to not take up water.**

**Rayleigh Scattering  
(10 Mm<sup>-1</sup>)**

An arrow points from the text "Rayleigh Scattering (10 Mm<sup>-1</sup>)" to the constant "10" in the equation above.



## 2<sup>nd</sup> IMPROVE Equation

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*Pitchford et al., 2007* developed a revised IMPROVE algorithm that reduced bias for high and low light extinction regimes and was more consistent with atmospheric literature.



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