Review of the IMPROVE Equation for Reconstructing Extinction from Aerosol Measurements

What we will talk about

- Sampling artifacts
- Species composition
- Mass scattering and absorption efficiencies
- Hygroscopicity

Goal is to assess the accuracy and consequences of current assumptions in the formulation of the IMPROVE reconstructed extinction equation in a scientifically defensible way.

What we won’t talk about

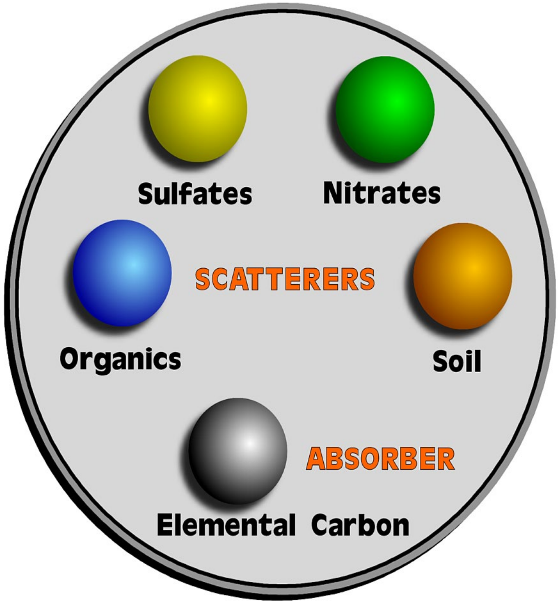
- Effect assumptions have on meeting the reasonable progress goal (glide slope issues)
- f(RH) round-down or cut-off issues
- Weather related issues
- Natural background adjustments

OUTLINE

- Malm
  - Introduction stuff
  - Hygroscopicity
  - Theoretical formulation of mass scattering and absorption efficiencies
  - What does the IMPROVE data tell us
- Hand
  - Measurement issues
  - Chemical composition
  - Literature review of mass scattering and absorption efficiencies
- Malm
  - Summary and recommendations

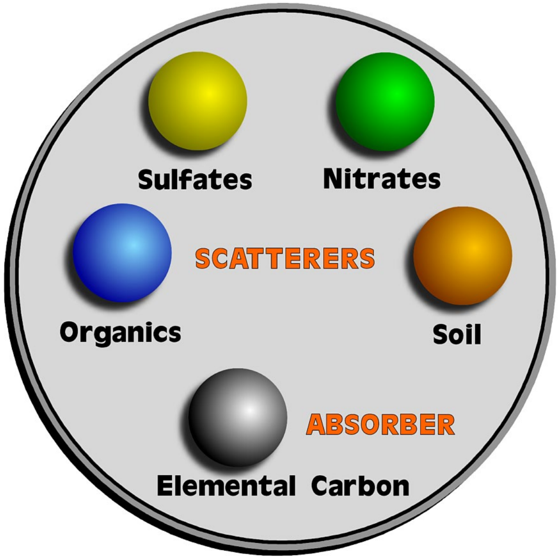
IMPROVE Reconstructed Extinction

$$\begin{aligned} b_{ext}(\mathrm{Mm}^{-1}) = \; & 3.0 * f_{inorg}(rh)\,\mathbf{[(NH_4)_2SO_4] +} \\ & 3.0 * f_{inorg}(rh)\,\mathbf{[NH_4NO_3] +} \\ & 4.0 * f_{OC}(rh)\,\mathbf{[1.4{*}OC] +} \\ & 1.0 * \mathbf{[Soil] +} \\ & 0.6 * \mathbf{[Coarse\ Mass] +} \\ & 10.0 * \mathbf{[Elemental\ Carbon] +} \\ & \quad b_{ray} \end{aligned}$$



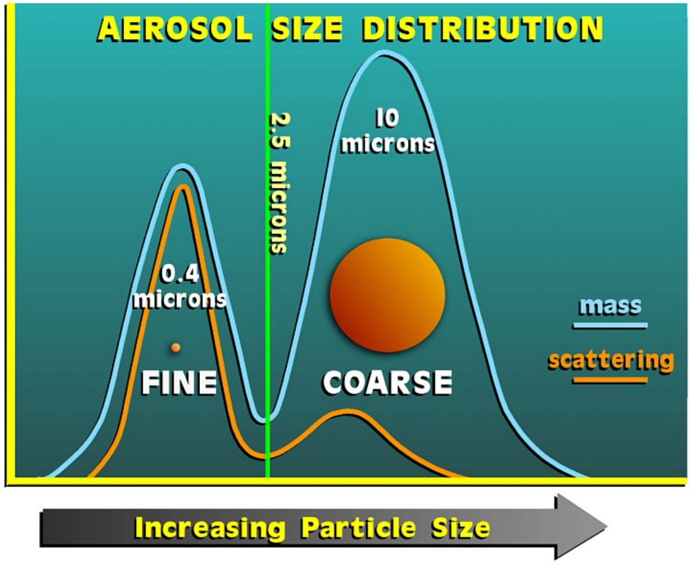
Reconstructed Extinction: Chemical form of Species

$$
\begin{aligned}
b_{ext}(Mm^{-1}) = \; & 3.0 * f_{inorg}(rh)\, [(NH_4)_2SO_4] + \\
& 3.0 * f_{inorg}(rh)\, [NH_4NO_3] + \\
& 4.0 * f_{OC}(rh)\, [1.4*OC] + \\
& 1.0 * [Soil] + \\
& 0.6 * [Coarse\ Mass] + \\
& 10.0 * [Elemental\ Carbon] + \\
& b_{ray}
\end{aligned}
$$



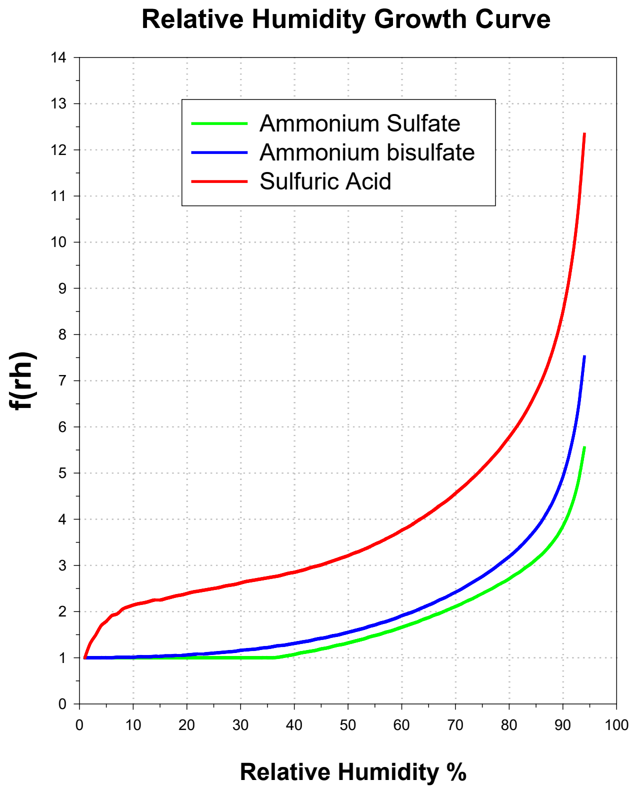
Reconstructed Extinction: Extinction Efficiencies

$$
\begin{aligned}
b_{ext}(Mm^{-1}) = \; & 3.0 * f(rh)\,[(NH_4)_2SO_4] + \\
& 3.0 * f(rh)\,[NH_4NO_3] + \\
& 4.0 * f_{OC}(rh)\,[1.4*OC] + \\
& 1.0 * [Soil] + \\
& 0.6 * [Coarse\ Mass] + \\
& 10.0 * [Elemental\ Carbon] + \\
& b_{ray}
\end{aligned}
$$

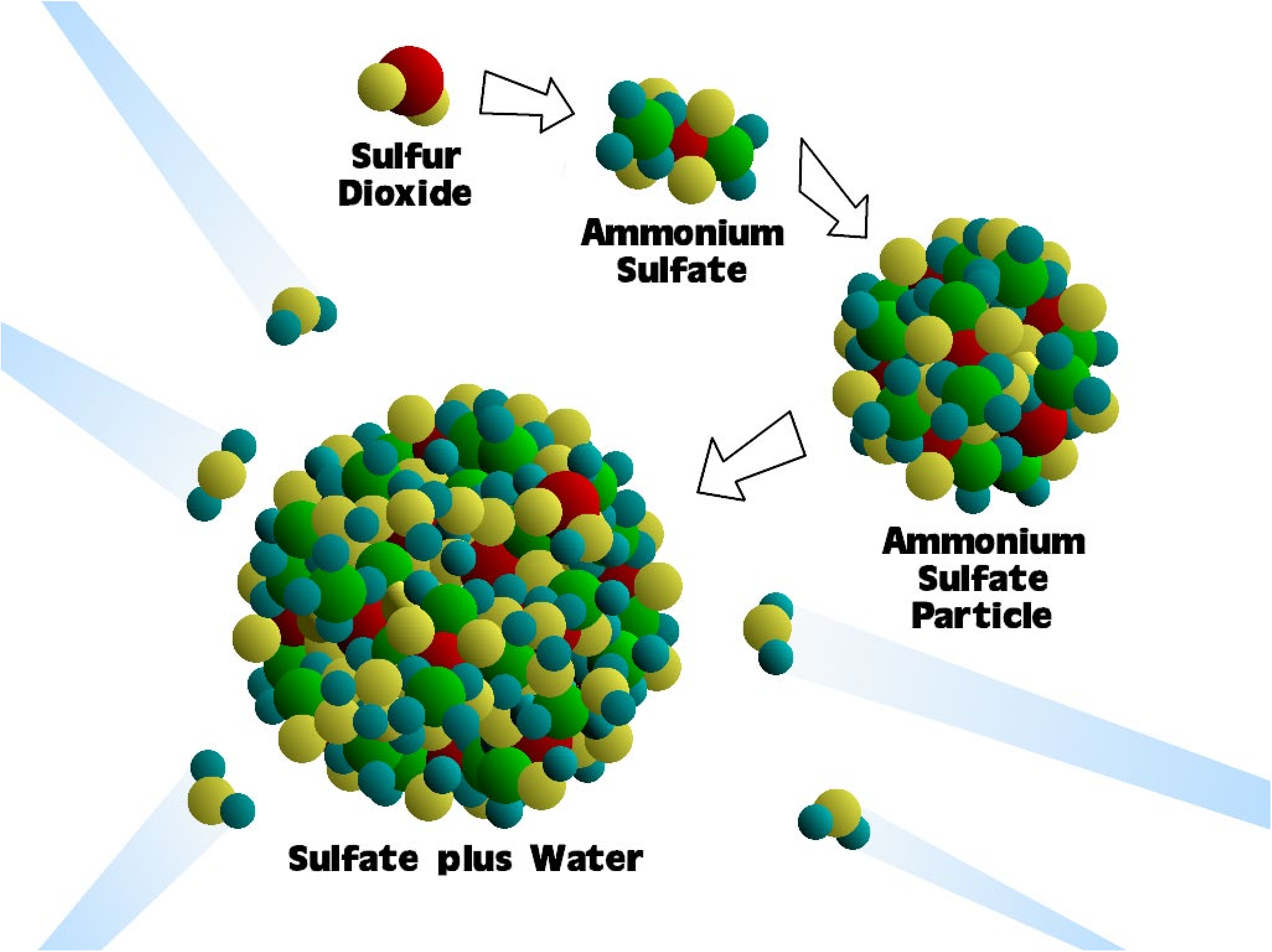


Reconstructed Extinction: Relative Humidity Effects f(rh)

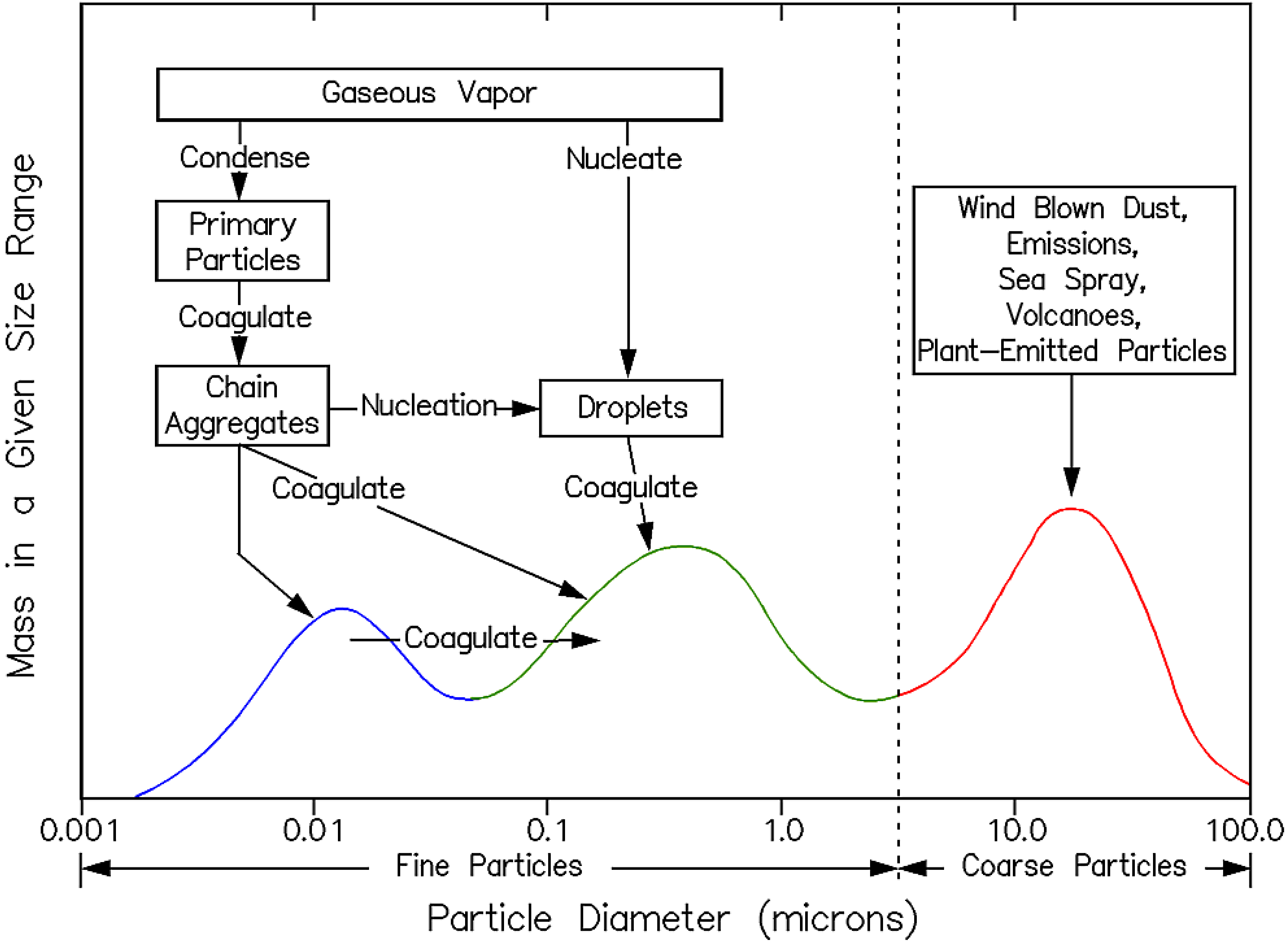
$$\begin{aligned} b_{ext}(Mm^{-1}) = \; & 3.0 * f(rh)\,[(NH_4)_2SO_4] + \\ & 3.0 * f(rh)\,[NH_4NO_3] + \\ & 4.0 * f_{OC}(rh)\,[1.4*OC] + \\ & 1.0 * [\text{Soil}] + \\ & 0.6 * [\text{Coarse Mass}] + \\ & 10.0 * [\text{Elemental Carbon}] + \\ & b_{ray} \end{aligned}$$



Growth of Sulfate

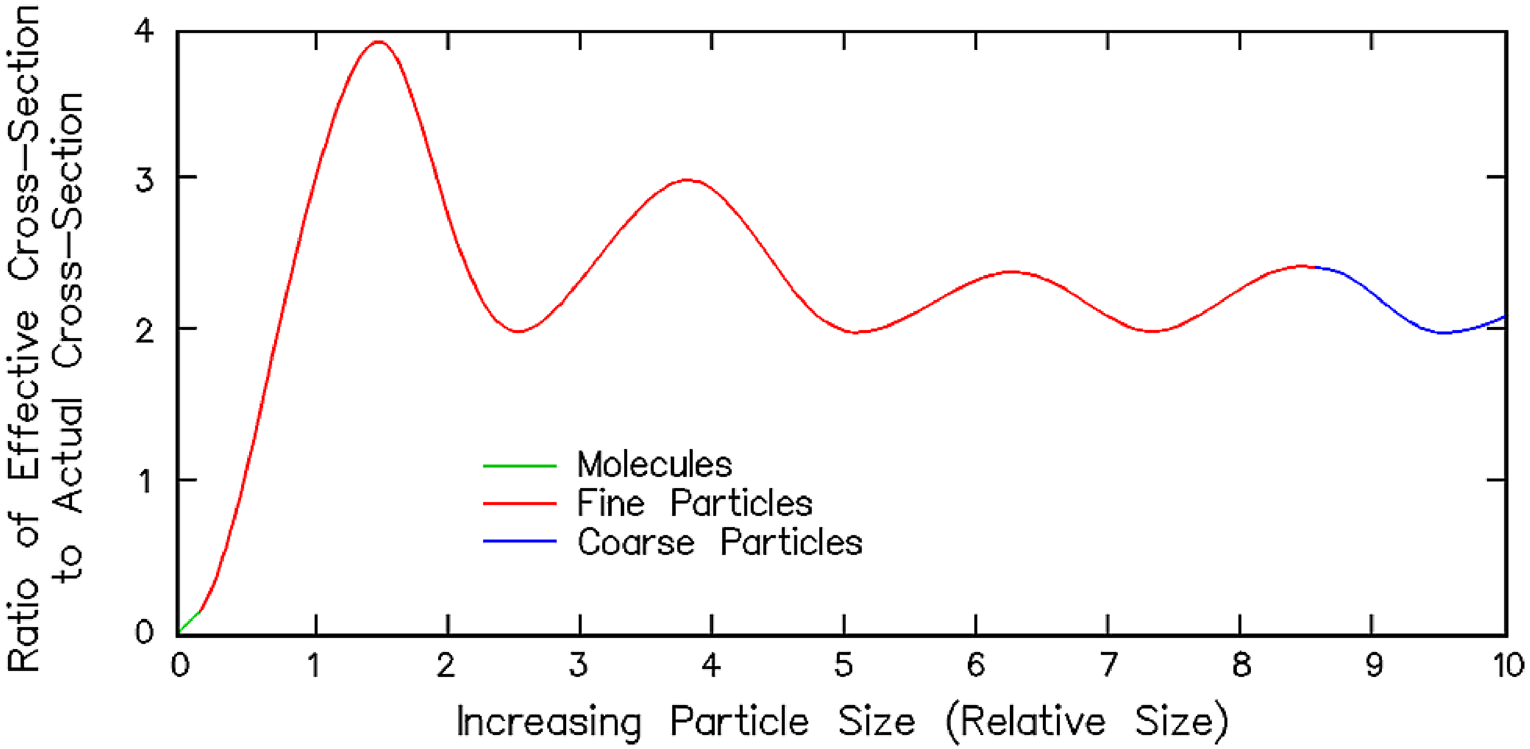


Particle Size Distribution

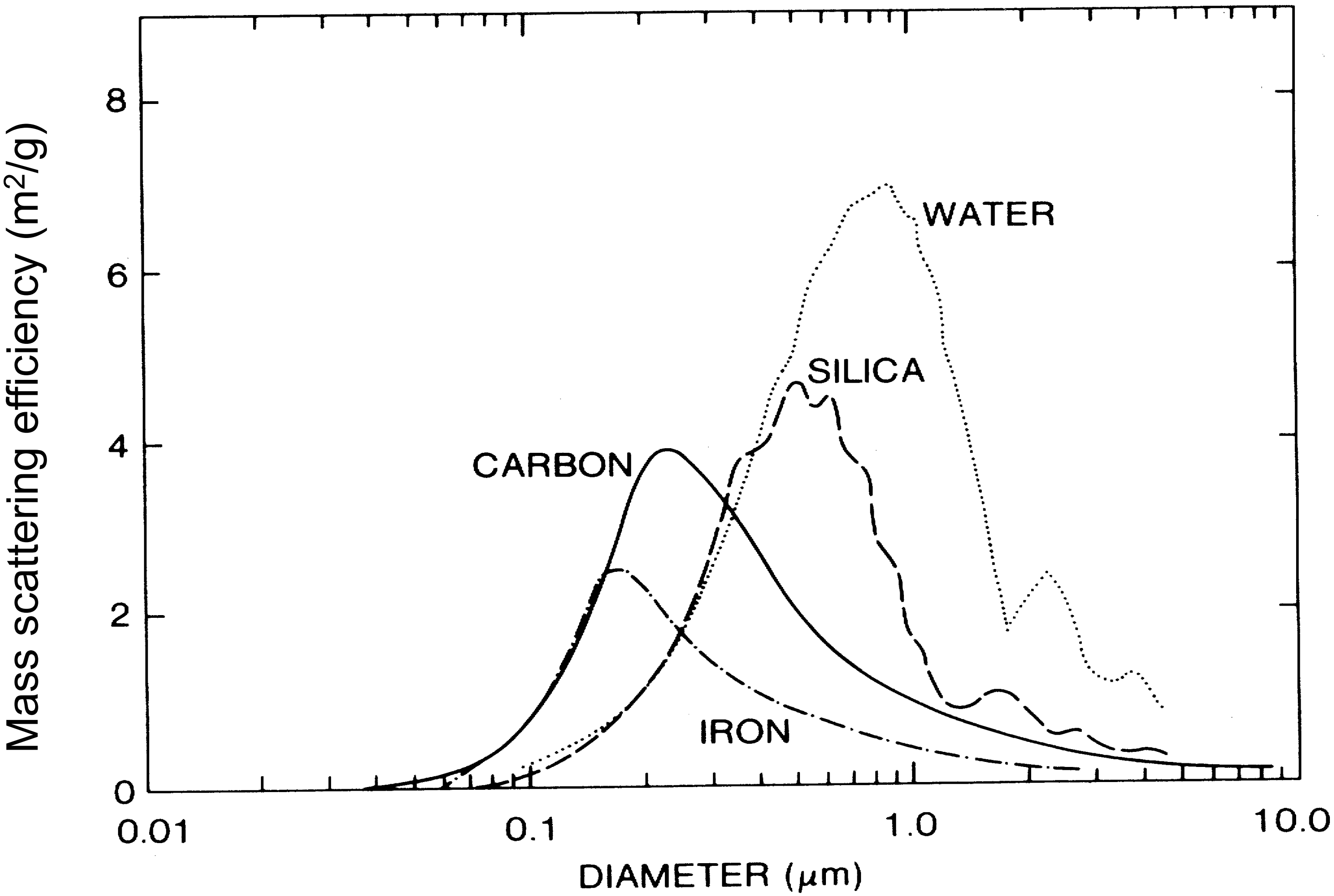


Mathematical description of scattering and absorption

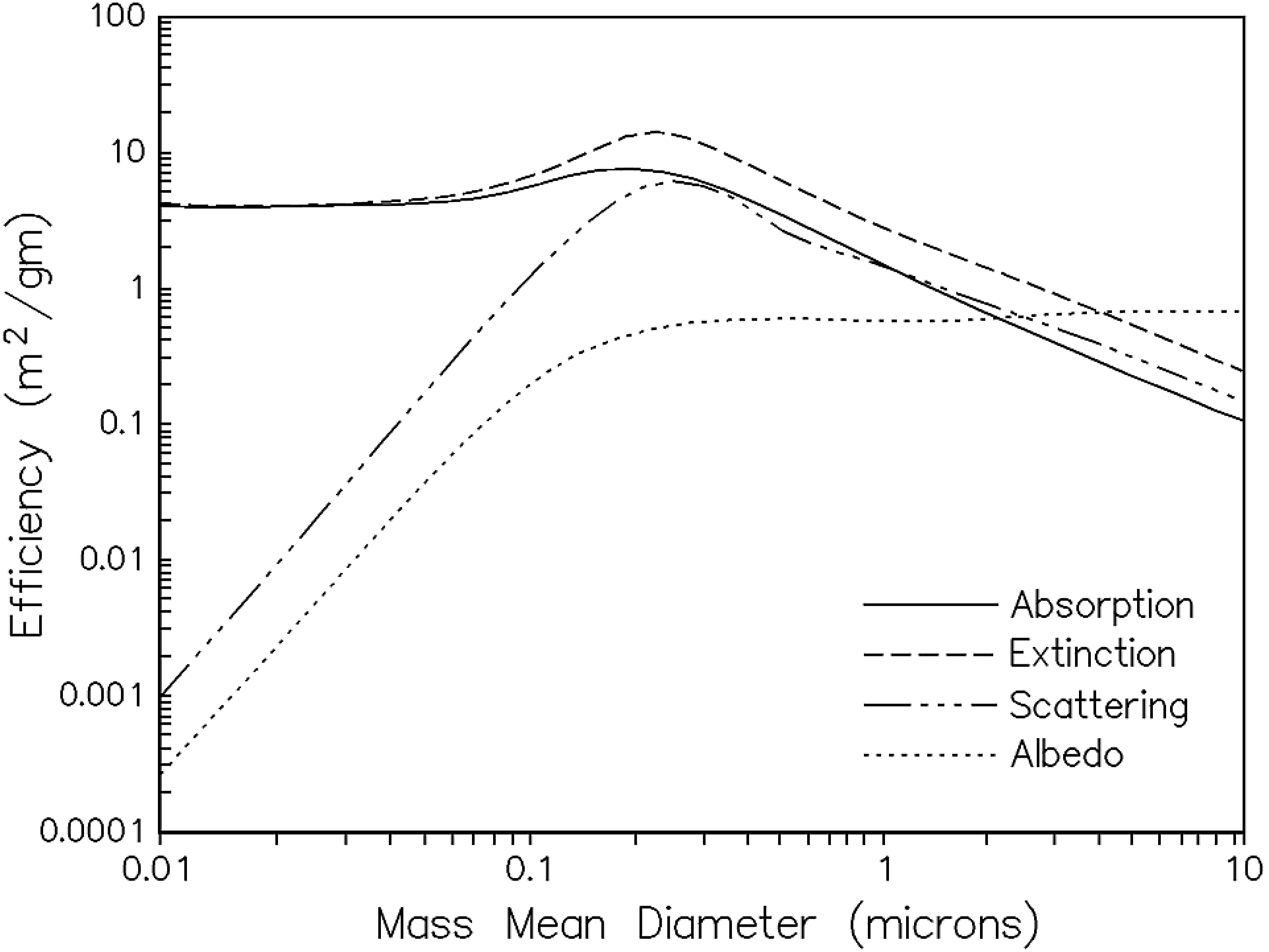
MIE Scattering Efficiency (Q)



Single particle mass scattering efficiency



Carbon Extinction Efficiency



For an aerosol number distribution $f_{N,j}(D_p)$ and complex refractive index $n_j = m + ik$, the light extinction coefficient ($b_{ext,j}$) is computed using:

$$b_{ext,j} = \int_0^\infty \frac{\pi}{4} D_p^2 Q_{ext}(n_j, D_p, \lambda) f_{N,j}(D_p) dD_p$$

The Mie extinction efficiency is given by $Q_{ext}(n_j, D_p, \lambda)$ and is a function of refractive index, particle diameter (D_p), and wavelength (λ).

The above equation can be reformulated in terms of aerosol mass size distribution $f_{M,j}(D_p)$

$$b_{ext,j} = \int_0^\infty \alpha_{ext,j}(n_j, D_p, \lambda) f_{M,j}(D_p) dD_p$$

where

$$\alpha_{ext,j} = \frac{3}{2} \frac{Q_{ext}(n_j, D_p, \lambda)}{\rho_j D_p}$$

Normalizing the above equation by mass concentration of species *j* (M_j) allows for the definition of mass extinction efficiency:

$$\alpha_{M,j} = \int_0^\infty \alpha_{ext,j} f'_{M,j}(D_p)\,d(D_p)$$

and

$$b_{ext,j} = \alpha_{M,j} M_j$$

The total extinction is then a linear combination of the product of species mass extinction efficiencies and mass concentrations

$$b_{ext} = \Sigma \alpha_{M,j} M_j$$

This equation also holds for an internally mixed aerosol where the chemical species are mixed in fixed proportions to each other, the index of refraction is not a function of composition or size, and the aerosol density is independent of volume.

Partial Scattering Efficiency

Estimating the change in extinction due to the removal or addition of a single species is different than assigning a fraction of extinction to a chemical species or mixture of species, and is referred to as a “partial mass extinction efficiency” ($\alpha_{ext,part}$):

$$\alpha_{ext,part} = \left(\frac{\partial b_{ext}}{\partial M_j} \right)$$

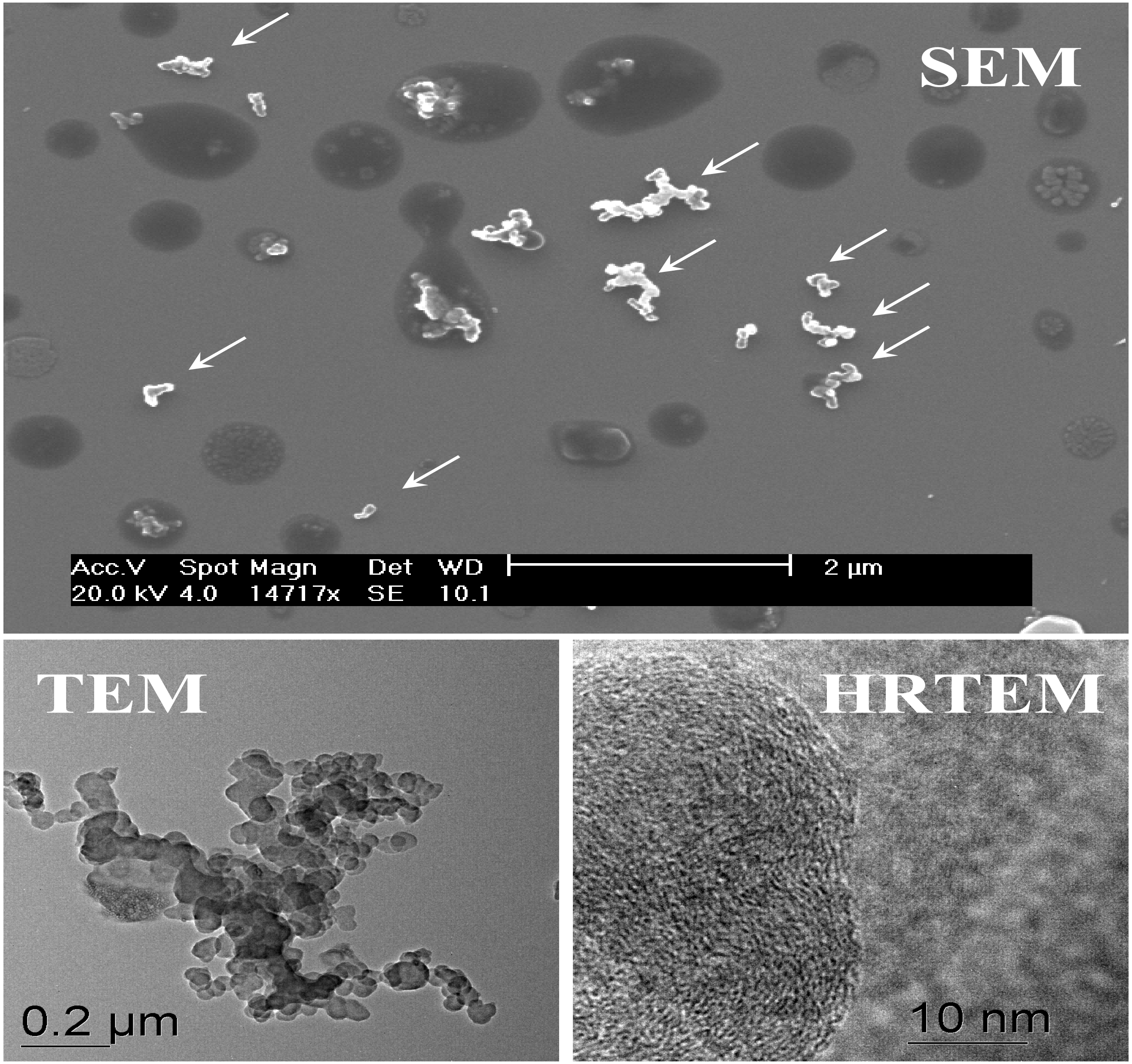
Internal vs External Mixtures

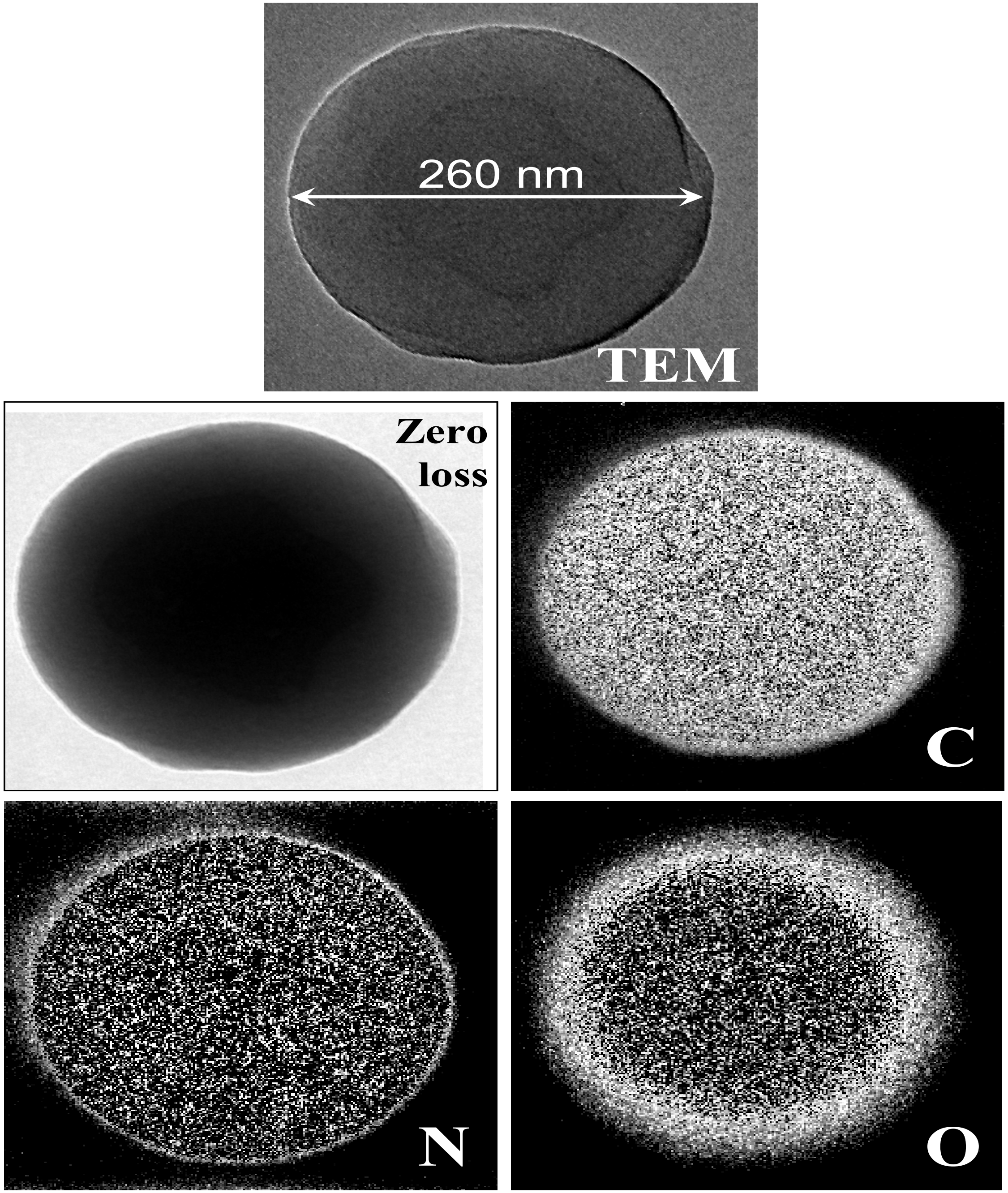
Mass extinction (or scattering) efficiencies are defined as the total aerosol extinction (or scattering) divided by the total aerosol mass.

One model assumes that the aerosol species are mixed externally; the simplest example is a particle composed of a single chemical species such as ammonium sulfate, and for this case the extinction efficiency is referred to as a “mass extinction efficiency”.

Realistically, particles in the atmosphere comprise a variety of inorganic and organic species. These types of particles are referred to as internal mixtures, and their extinction efficiencies are termed “specific mass extinction efficiencies”.

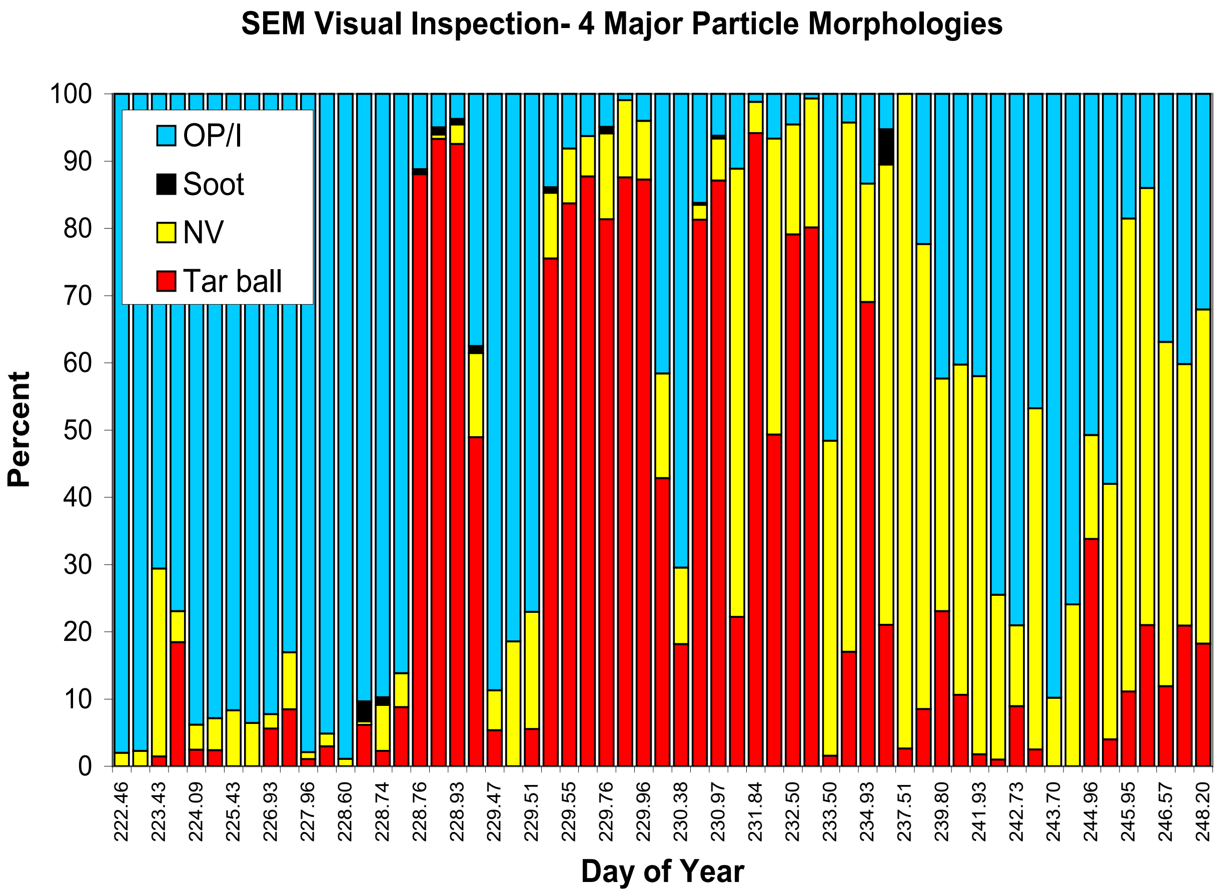
Internally mixed particles can also be externally mixed from other particle populations; the most obvious case would be internally mixed fine mode aerosols externally mixed from coarse mode aerosols.


SEM
Acc.V Spot Magn Det WD
20.0 kV 4.0 14717x SE 10.1
2 µm
TEM
0.2 µm
HRTEM
10 nm


260 nm
TEM
Zero loss
C
N
O

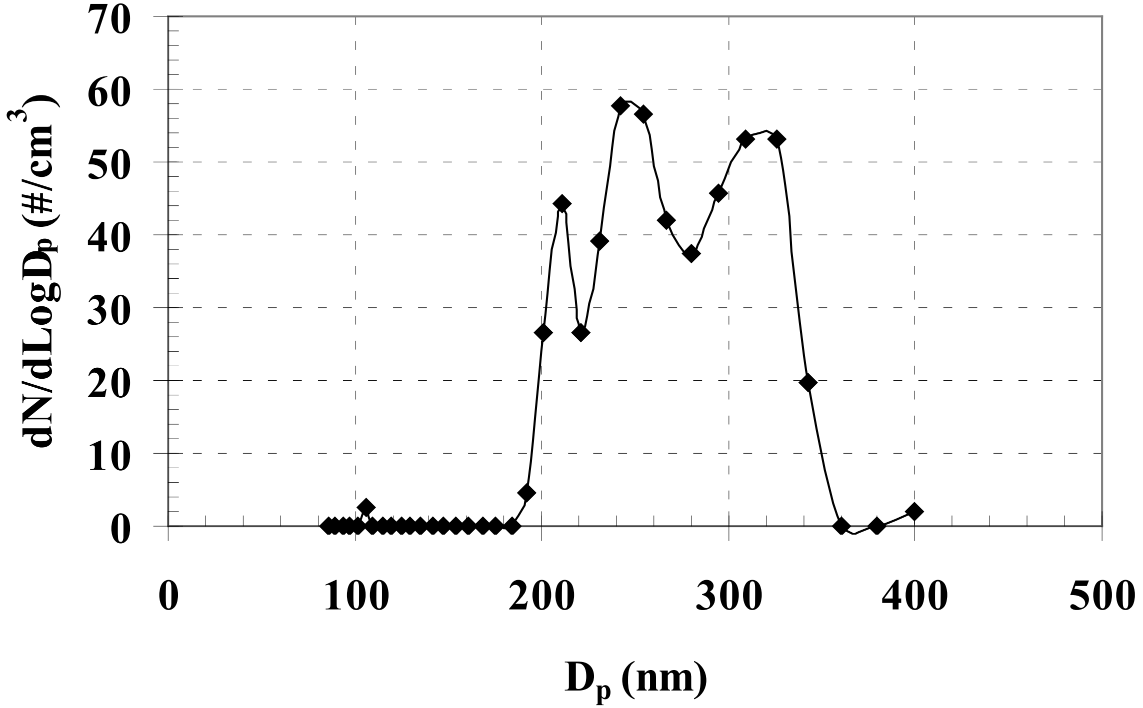
Do we assume an internal or external mixture?

Frequency of occurrence (as percent, %) of four particle types: tar balls, organic with (or without) inclusions (OP/I), non-volatile particles (NV), and soot.


SEM Visual Inspection- 4 Major Particle Morphologies

Yosemite Particle Growth at RH = 88% with D_{dry} = 200 nm

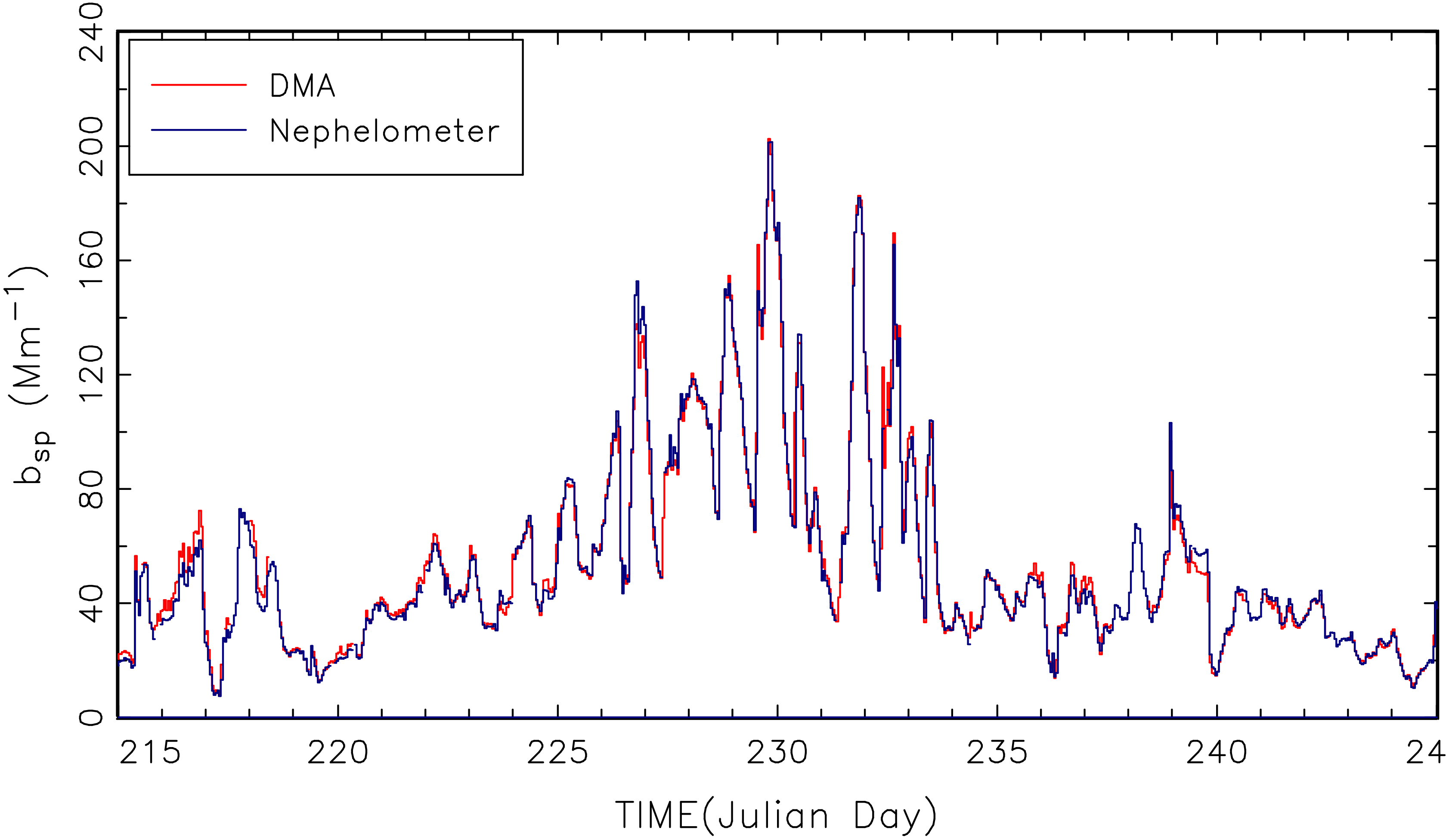
(Composition Data Shows Carbon + Sulfate + Calcium on 2 September 2002)



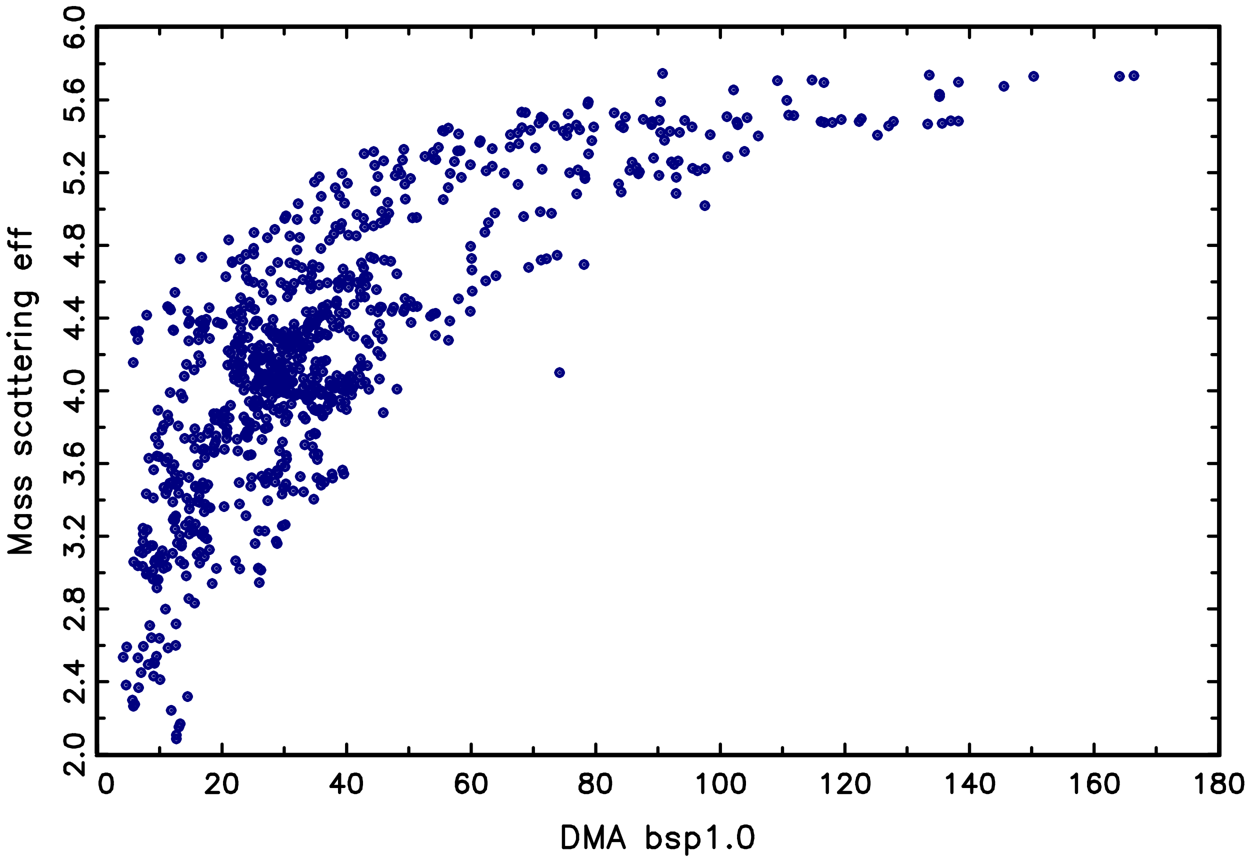
A comparison of measured and modeled scattering and absorption estimates for one special study (Yosemite National Park)

Species	Density (g cm^{-3})	Index of Refraction
$(NH_4)_2SO_4$	1.76 (Tang, 1996)	1.53 (Tang, 1996)
Organic Carbon	1.4 (Dick et al., 2000)	1.55 (Stelson, 1990)
Elemental Carbon	2.0 (Seinfeld and Pandis, 1998)	1.8-0.5 (Seinfeld and Pandis, 1998)
$NaNO_3$	2.261 (Tang, 1996)	1.59 (Tang, 1996)
Soil	4 (Based on values reported in Hand and Kreidenweis, 2002)	2 (Based on values reported in Hand and Kreidenweis, 2002)

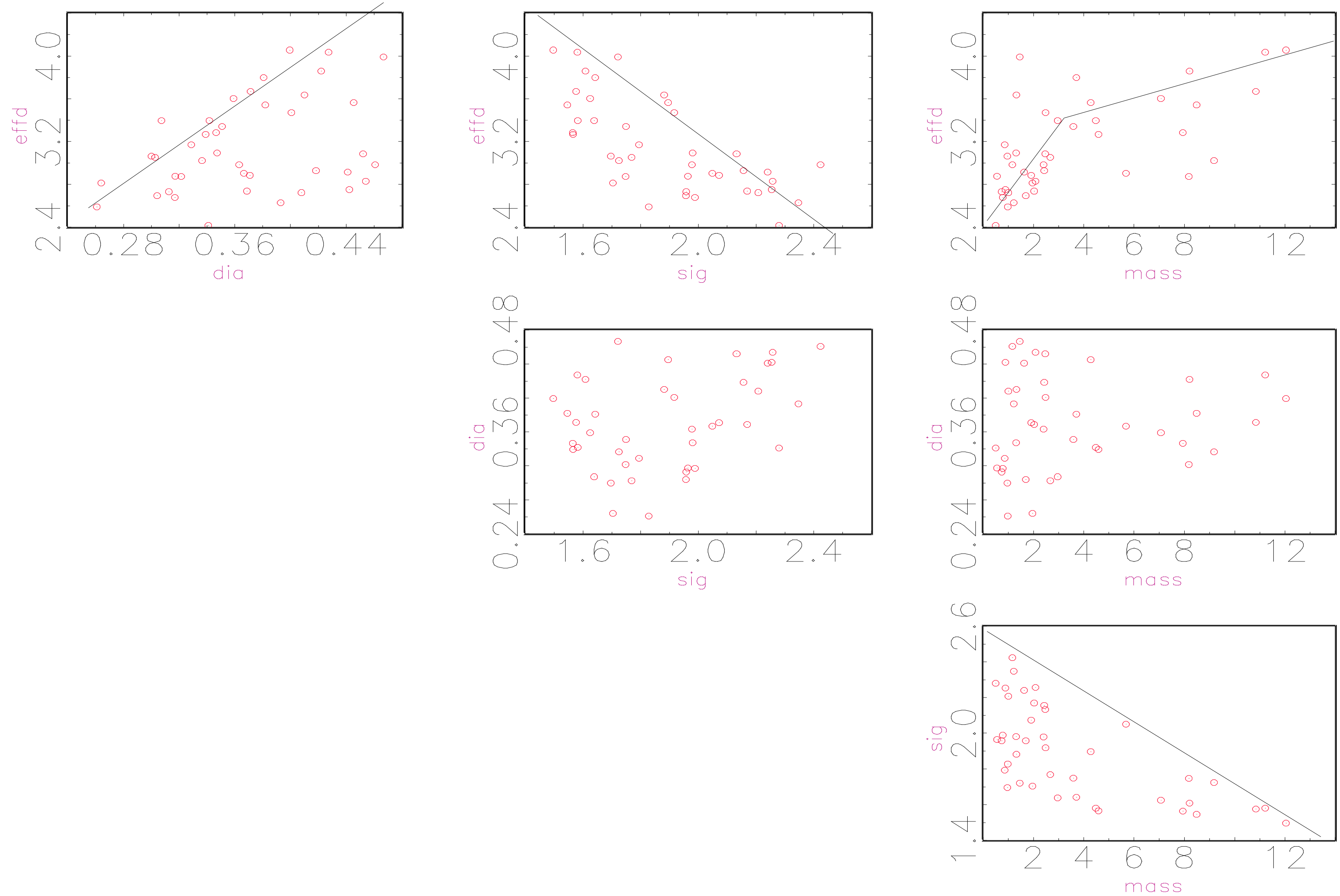
Ambient scattering data compared to internally mixed scattering model with DMA efficiencies and semi-continuous aerosol measurements



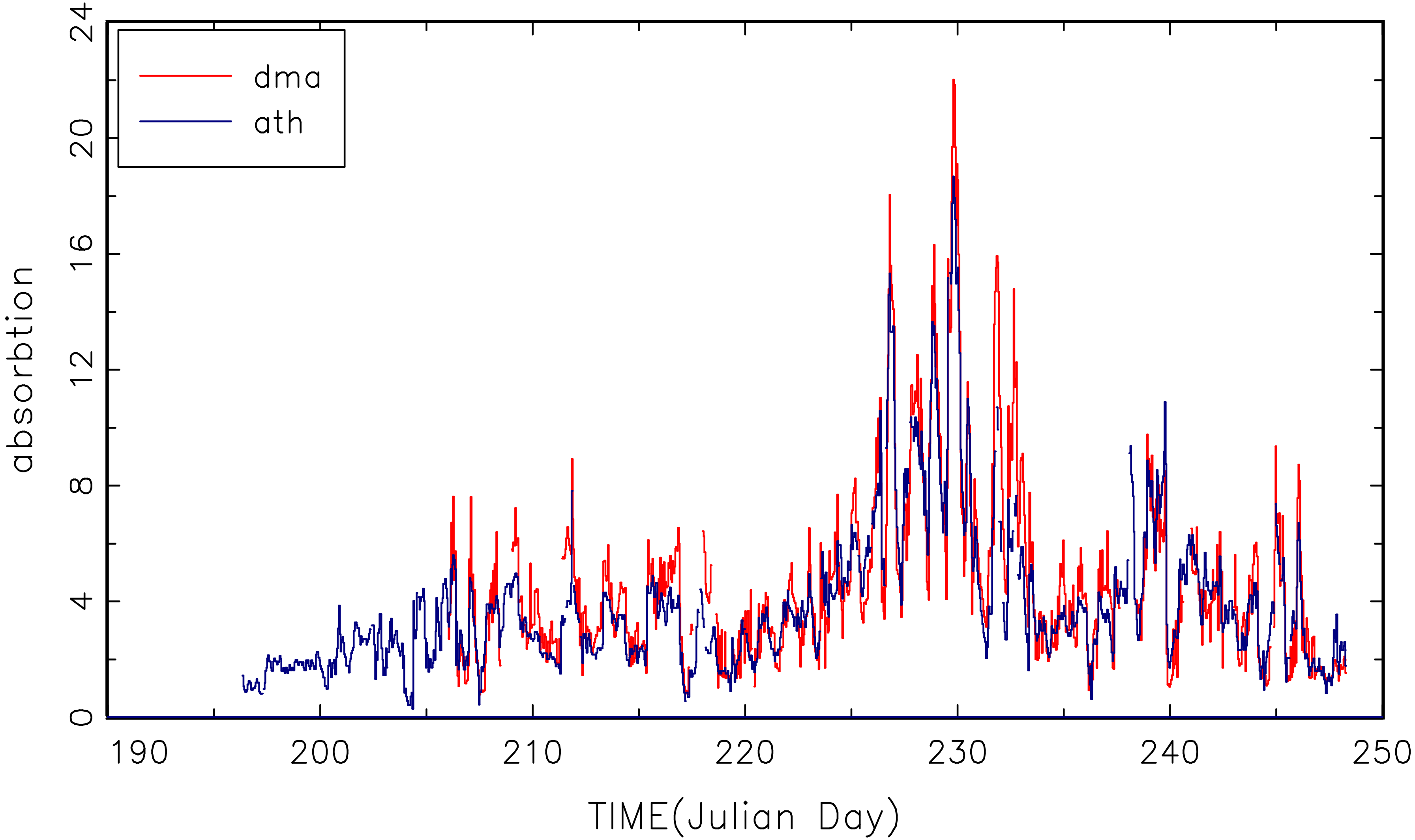
VARIABLE MASS SCATTERING EFFICIENCIES



Multiple Scatter Plot of Size Related Scattering Parameters



Aethalometer data normalized to TOR and absorption estimated from DMA number size distribution measurements



Summary of Optical Variables

Variable	Mean	Std Dev	Minimum	Maximum	Valid
Geometric Mean Diameter	0.33	0.04	0.19	0.43	939
Geometric Std Dev	1.88	0.17	1.51	2.38	939
Real Index of Refraction	1.56	0.01	1.55	1.59	1032
Complex Index of Refraction	0.02	0.01	0.01	0.04	1032
Mass Scattering Efficiency (m^2/g)	4.49	0.76	2.28	5.96	939
Mass Absorption Efficiency (m^2/g)	0.46	0.12	0.16	0.90	939
Derived b_{sp} (Mm^{-1})	48.84	32.47	5.98	202.50	939
Measured b_{sp} (Mm^{-1})	48.14	33.20	6.07	205.65	939
Derived b_{abs} (Mm^{-1})	4.85	3.31	0.79	23.00	939
Measured b_{abs} (Mm^{-1}) (TOR)	3.82	2.56	0.00	18.66	33
Measured b_{abs} (Mm^{-1}) (Ath)	2.83	1.46	0.20	10.10	1218

Apportionment problem with internal mixtures

Suppose:

$V_1=V_2$ and $n_1=n_2$
therefore $b_1=b_2$

$m_1=10$ ug/m^3 $\quad$ $m_2=5$ ug/m^3
$\rho_1= 2$ g/cm^3 $\quad$ $\rho_2= 1$ g/cm^3

$\alpha_1= 3$ m^2/g $\quad$ $\alpha_2=6$ m^2/g

$\alpha_1= \alpha_2(\rho_2/\rho_1)= \alpha_2/2$

Scattering apportionment issues

$b_1=3*10=30\ \mathrm{Mm}^{-1}$
$b_2=6*5=30\ \mathrm{Mm}^{-1}$
$b_{total}=60\ \mathrm{Mm}^{-1}$

$e_1M_1+e_2M_2=e_{mix}M_t$
$60=e_{mix}15$
Therefore:
$e_{mix}=4\ \mathrm{m}^2/\mathrm{g}$

Apportionment problem
$60=4(10+5)=40+20$
2/3 to 1/3 apportionment

Given the specific mass scattering efficiency how do you apportion to species as if they were externally mixed

		Figure 1-A		Figure 1-B	
		species 1	species 2	species 1	species 2
mass	external case	10 μg m^{-3}	5 μg m^{-3}	10 μg m^{-3}	species 2 removed
aerosol type		○	●	○	
species density		2 g cm^{-3}	1 g cm^{-3}	2 g cm^{-3}	
mass scattering efficiency		3 m^{2}g^{-1}	6 m^{2}g^{-1}	3 m^{2}g^{-1}	
particle scattering		30 Mm^{-1}	30 Mm^{-1}	30 Mm^{-1}	
total scattering		60 Mm^{-1}		30 Mm^{-1}	
mass	internal case	15 μg m^{-3}		10 μg m^{-3}	
aerosol type		◍		○	
species density		1.66 g cm^{-3}		2 g cm^{-3}	
specific mass scattering efficiency		4 m^{2}g^{-1}		2 m^{2}g^{-1}	
total scattering		60 Mm^{-1}		20 Mm^{-1}	

continued

$\alpha_{mix}=b_{mix}/M_{mix}$ from measurements

Given α_{mix}, m_1 and m_2 and

$\alpha_{mix}M = \alpha_1 m_1 + \alpha_2 m_2$ where $M=m_1+m_2$

how does one find α_1, and α_2?

$\alpha_1 = \alpha_2(\rho_2/\rho_1) = \alpha_2/2$

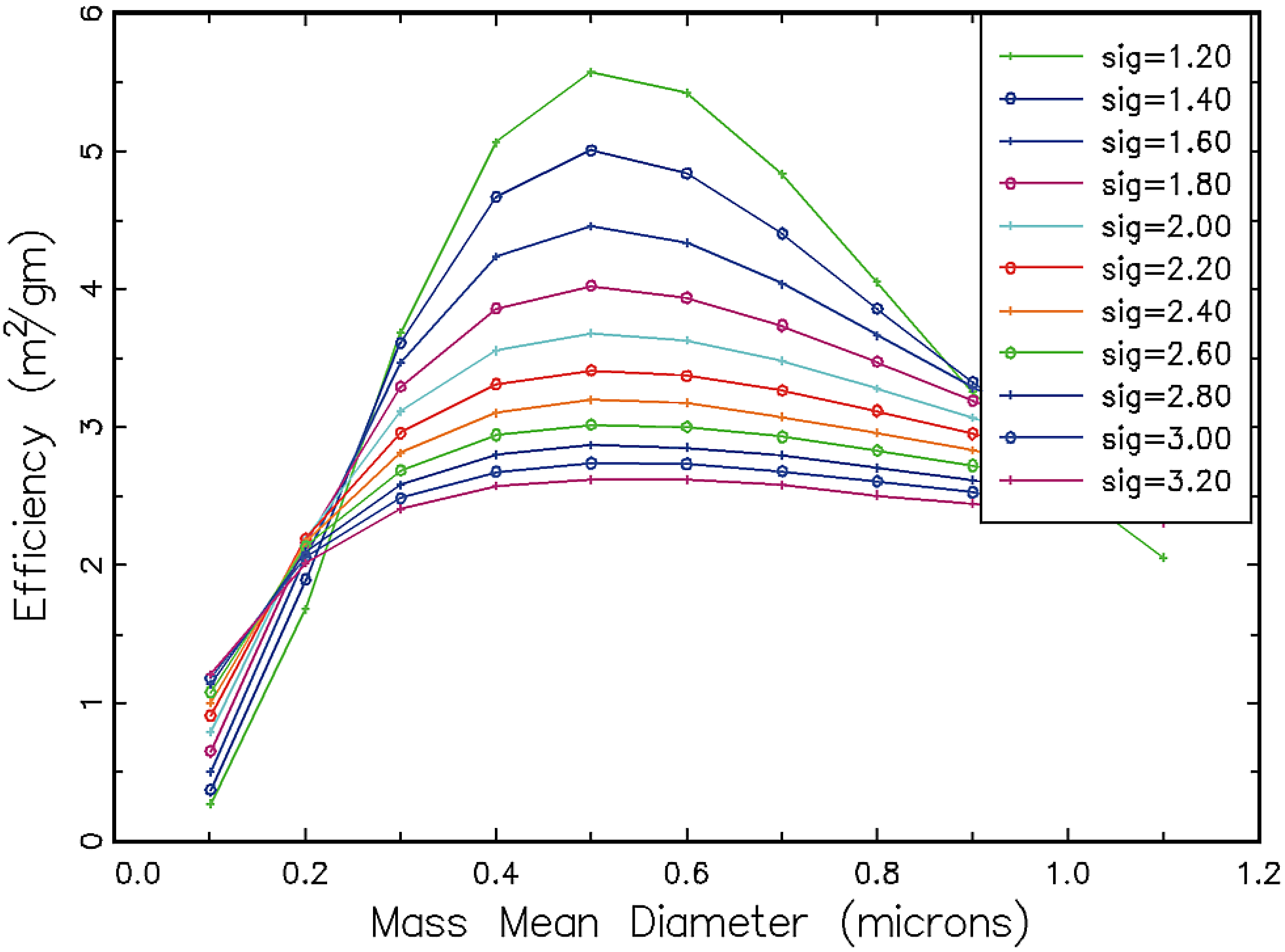
Therefore:

$\alpha_1 = \alpha_{mix}[M/(m_1+2m_2)]$ which gives

$\alpha_1 = 3\ m^2/g$ and $\alpha_2 = 6\ m^2/g$

Therefore the discrepancy is resolved if the specific mass scattering efficiency of the mixed aerosol is prorated to its chemical constituents, based on their relative densities.

Scattering Efficiency as Function of Size



Hygroscopic Aerosols

- *Water uptake by particles in the atmosphere*
- *Aerosol particles grow and scatter more light*
- *Deliquescence - the RH value at which the crystal begins to absorb water and becomes a solution droplet*
- *Hysteresis - water is retained on the particle at RH values lower than predicted by equilibrium*

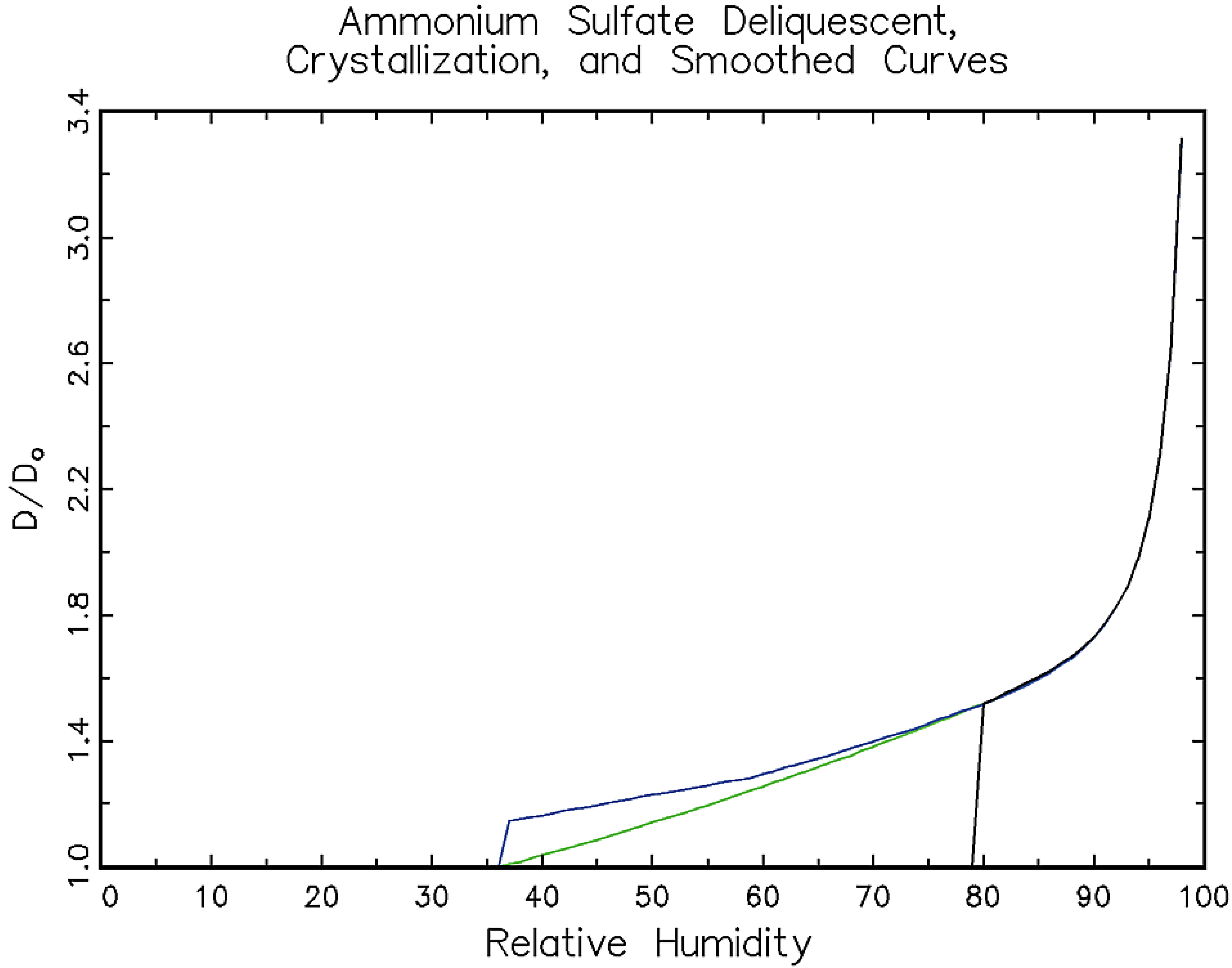
HYGROSCOPICITY ISSUES

$$b_{ext} = e_f(RH)m_f$$

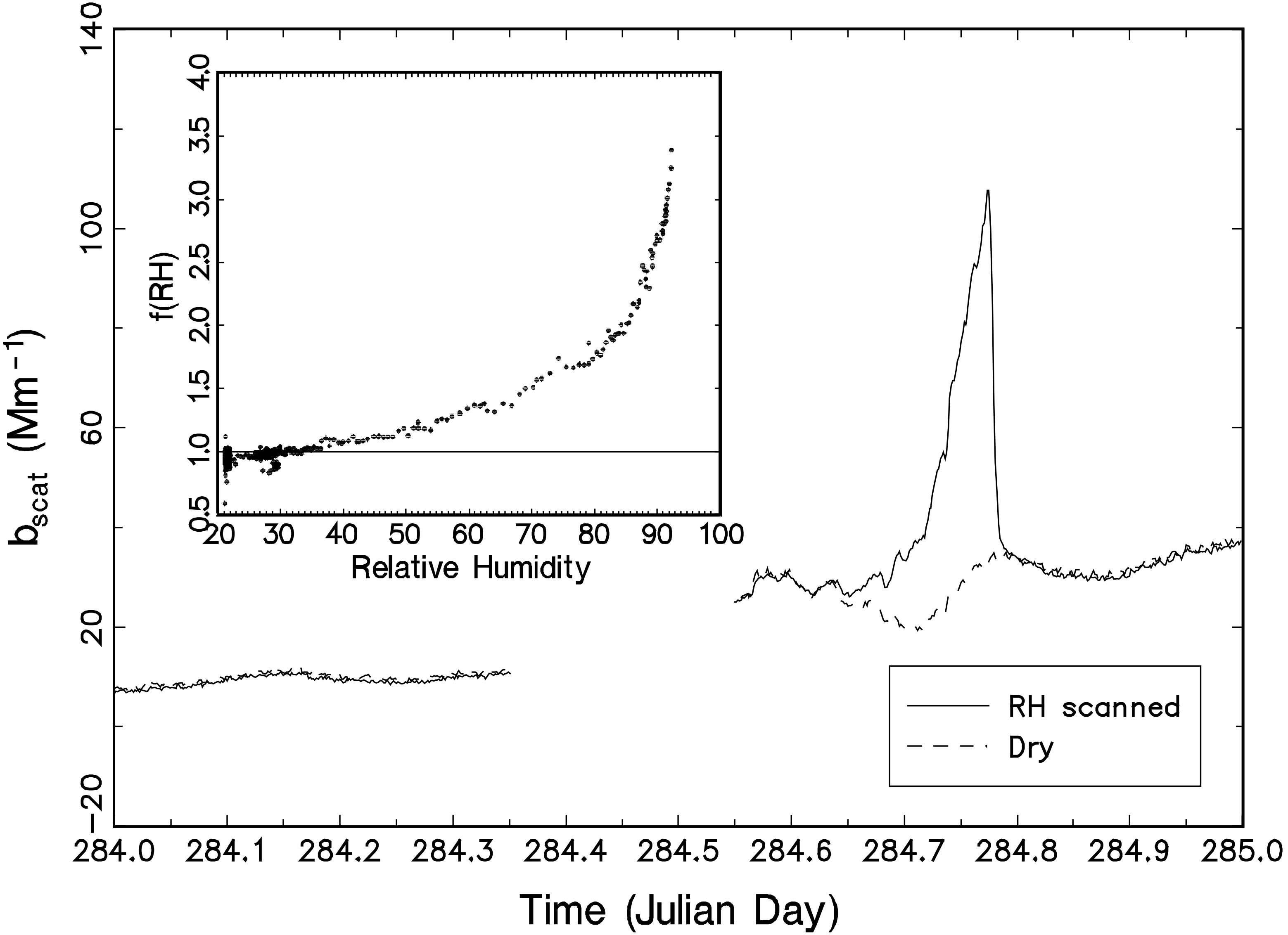
$$b_{ext} = e_f(dry)\left[e_f(RH)/e_f(dry)\right]m_f$$

$$b_{ext} = e_f(dry)f(RH)m_f$$

Ammonium Sulfate D/D_o Curves

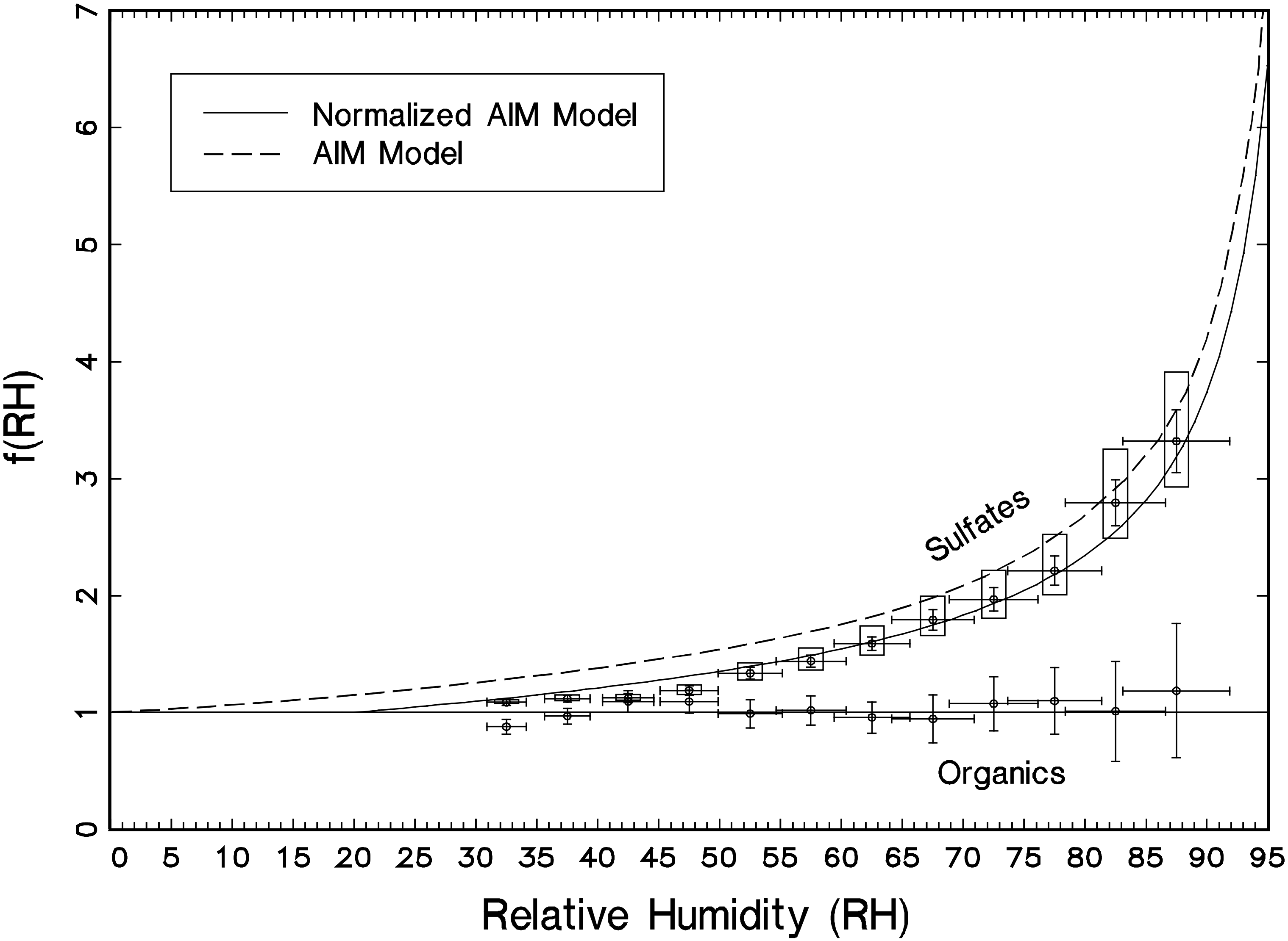


Dry and Wet Nephelometer Measurements

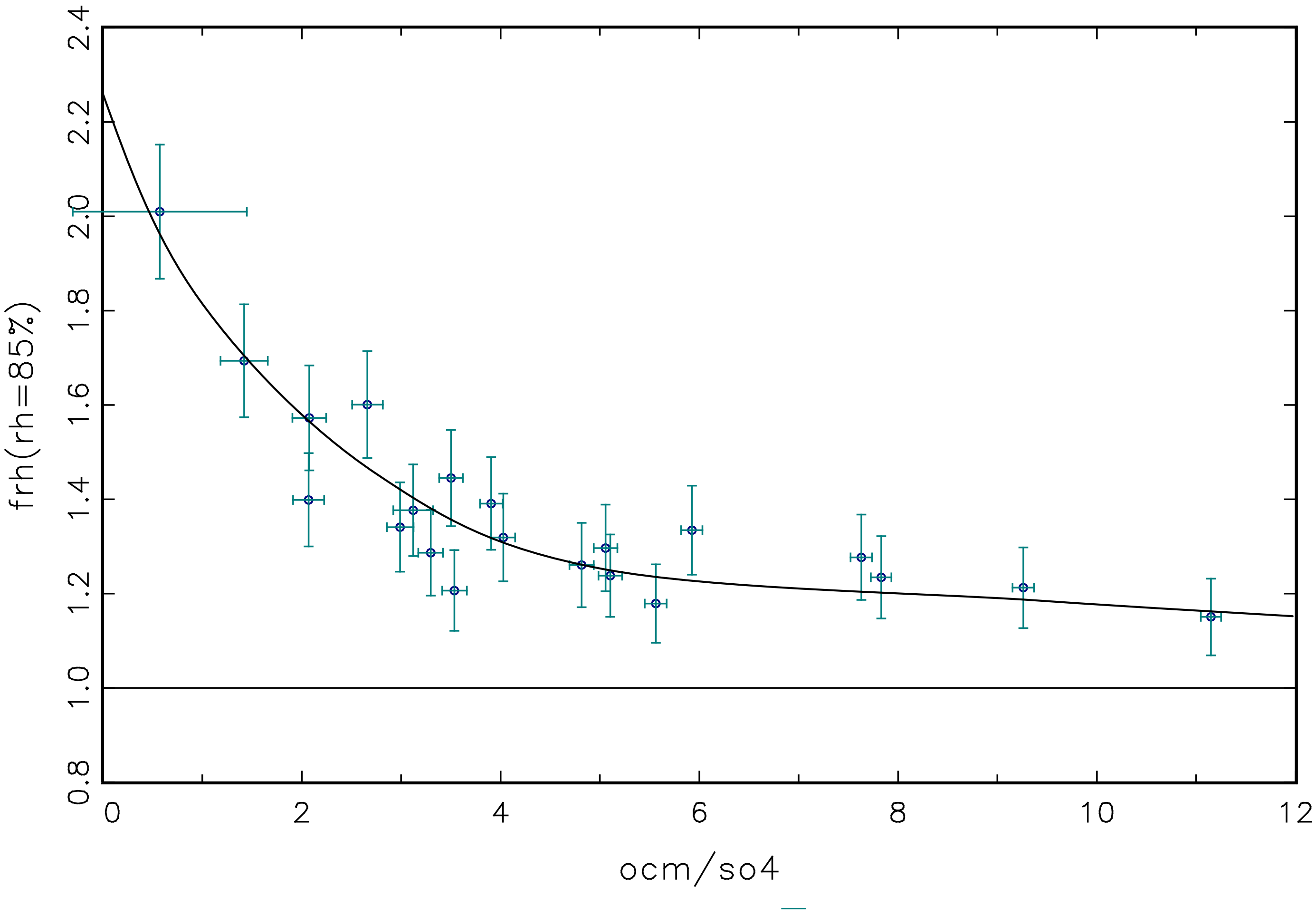


Statistical Estimate of f(RH) Curves

$$b_{scat,water}(RH) = a_o + a_1[Ammoniated \quad SO_4] + a_2[OMC] + ... + a_n[Other\ Species]$$



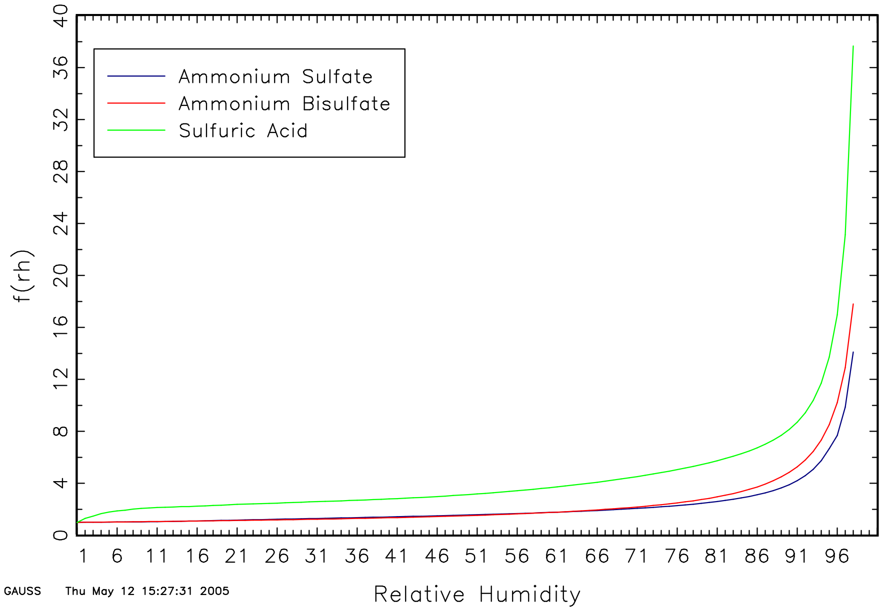
ORGANIC HYGROSCOPICITY



WHAT f(RH) CURVE SHOULD BE USED FOR INORGANICS AND ORGANICS?

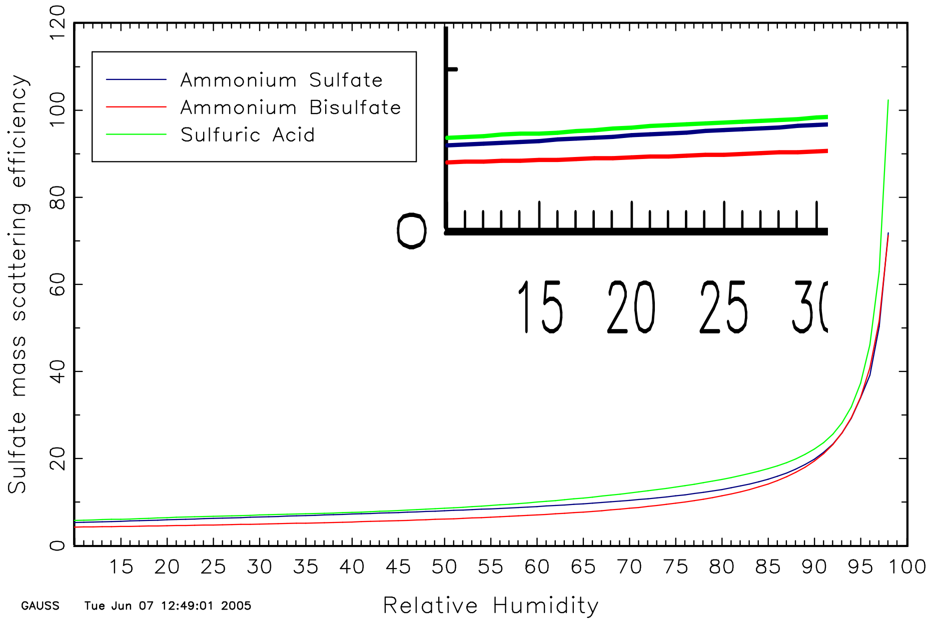
GAUSS Thu May 12 15:14:37 2005

f(RH) curves d_g=0.4 sig=1.9



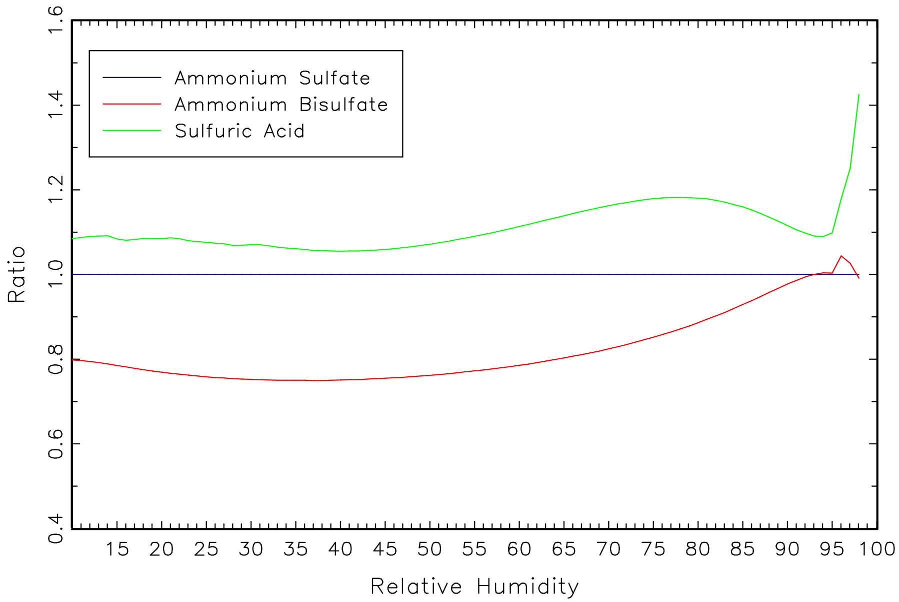
GAUSS Thu May 12 15:25:40 2005

Sulfate mass scattering efficiency



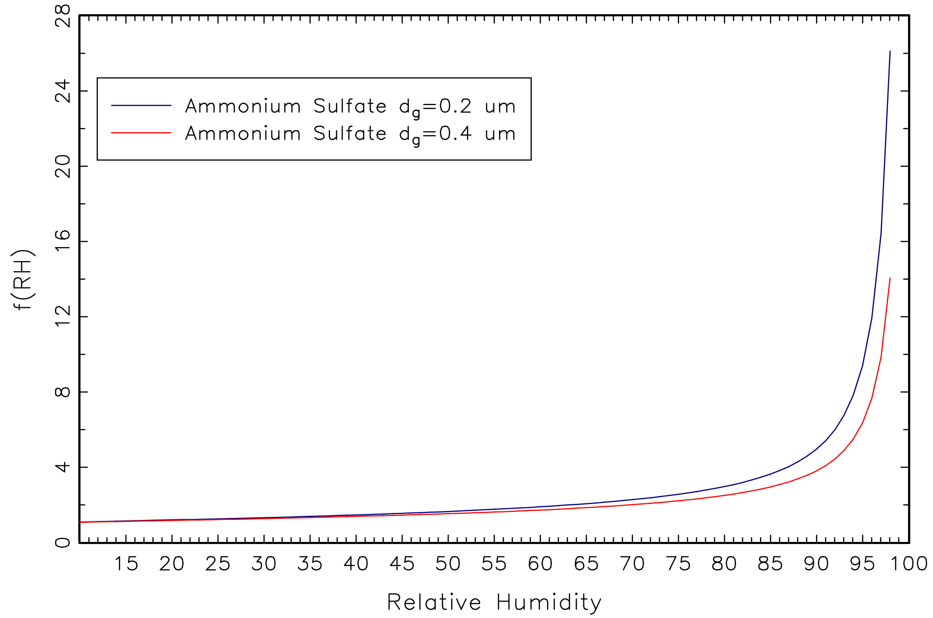
GAUSS Thu May 12 15:27:31 2005

Normalized to Ammonium Sulfate



GAUSS Tue Jun 07 12:49:01 2005

Difference in size assumptions



RECOMMENDATION

- Develop and use a new f(RH) curve that allows for aerosol growth below 40% RH
- f(RH) for organics = 1 (possible 1.1-1.2 at 85% RH)

MASS SCATTERING EFFICIENCIES

An exploration of the IMPROVE database

Three different approaches for developing mass scattering efficiencies from ambient measured scattering and aerosol concentrations (22 Sites with co-located nephelometers and aerosol samplers)

Method 1

A regression utilizing the following equation:

$$b_{sp}=a_o+a_1 f(RH)[(NH_4)_2SO_4]+a_2 f(RH)[NH_4NO_3] + a_3[POM] + a_4[soil + CM] + a_5[sea\ salt]$$

METHOD 2

Assume the fine mode is an internal mixture of ammonium sulfate, ammonium nitrate, and organic material (1.8*OC) and that:

$$b_{mix,dry} = \alpha_{mix} M_{mix} = \alpha_{inorg}\,[(NH_4)_2SO_4 + NH_4NO_3] + 1.21\,\alpha_{inorg}\,[POM]$$

Measured b_{mix} is estimated using:

$$b_{mix} = b_{open} - b_{CM} - b_{soil} - b_{SS}$$

Ambient b_{mix} is estimated using:

$$b_{mix\_est} = (3.0)f(RH\,[(NH_4)_2SO_4 + NH_4NO_3] + 3.63[POM]$$

Form a regression model $b_{mix}=a_1 b_{mix\_est}$ and

$$\alpha_{inorg}=a_1 3.0 \text{ and } \alpha_{pom}=a_1 3.63$$

METHOD 3

Mass weighted approach:

$$SCF = \frac{b_{mix}}{b_{mix\_est}} = \frac{b_{open} - b_{CM} - b_{soil} - b_{SS}}{3.0 f(RH)[(NH_4)_2SO_4 + NH_4NO_3] + 3.63[POM]}$$

$SCF = a_o + a_1[M_{mix}]$ (Thiel regression)

$$b'_{mix\_est} = SCF'\{3.0f(RH)[(NH_4)_2SO_4 + NH_4NO_3] + 3.63[POM]\}$$

$\alpha'_{inorg} = 3.0 \cdot SCF'$ and $\alpha'_{org} = 3.63 \cdot SCF'$.

EXAMPLE

SUMMARY STATISTICS FOR ACADIA NATIONAL PARK

Variable (ug/m^3)	Mean	Std Dev	Minimum	Maximum	Valid	Missing
CM	2.76	2.80	-0.38	41.99	604	33
FM	5.63	5.06	0.61	45.58	621	16
AS	2.72	2.99	0.30	28.37	628	9
AN	0.37	0.40	0.01	3.30	620	17
POM	1.73	1.40	0.07	17.18	624	13
LAC	0.22	0.16	-0.01	1.13	624	13
Soil	0.26	0.32	0.00	4.34	628	9
Sea Salt	0.06	0.26	0.00	3.01	637	0
RH (%)	67.41	12.65	30.41	89.78	600	37
b_{sp} (Mm^{-1})	21.07	25.09	2.38	235.13	277	360
N (b_{sp})	18.01	7.37	1.00	24.00	637	0
f(RH)$_{amb,new}$	2.38	0.62	1.32	4.26	600	37
f(RH)$_{chamb,new}$	1.83	0.42	1.05	3.67	637	0
f(RH)$_{amb,old}$	2.15	0.61	1.01	3.65	600	37
f(RH)	1.66	0.41	1.00	3.29	637	0

SUMMARY STATISTICS FOR OPTICAL VARIABLES USING IMPROVE EQUATION

Variable	Mean	Std Dev	Minimum	Maximum	Valid
b_{sp}	21.36	25.46	2.38	235.13	267
b_{sp_recon}	24.32	24.34	3.74	217.90	267
b_{mix}	20.17	25.26	0.74	234.37	267
b_{mix_est}	23.13	24.07	3.30	217.14	267
b_{sp}(AS)	14.14	19.55	1.75	184.85	267
b_{sp}(AN)	2.45	3.18	0.19	27.76	267
b_{sp}(POM)	6.54	4.69	0.79	29.95	267
b_{sp}(Soil)	0.29	0.24	0.01	2.27	267
b_{sp}(CM)	1.72	1.94	-0.21	25.19	267
b_{sp}(SS)	0.05	0.23	0.00	2.80	267
b_{sp}(soil+CM)	2.01	2.04	-0.02	25.80	267
b_{ap}	2.30	1.56	0.43	11.27	267
$b_{sp}(H_2O)$	8.51	11.76	0.85	112.63	267

RESULTS FOR ACADIA

Acadia NP METHOD 1

Variable	Coefficient (a_i)	Standard Error	Derived Mass Scattering Efficiency (m^2 g^{-1})
AS	1.13	0.03	3.38
AN	0.88	0.12	2.65
POM	0.60	0.09	2.17
CM+Soil	-0.39	0.17	-0.23
Sea salt	5.32	1.56	5.32

Results for METHOD 2 Regression	
a_1 coefficient	0.95
Standard error in a_1	0.01
α_{inorg} (m^2 g^{-1})	2.84
α_{org} (m^2 g^{-1})	3.43

Typically gives the best fit between measured and estimated scattering – right answer for wrong reason!

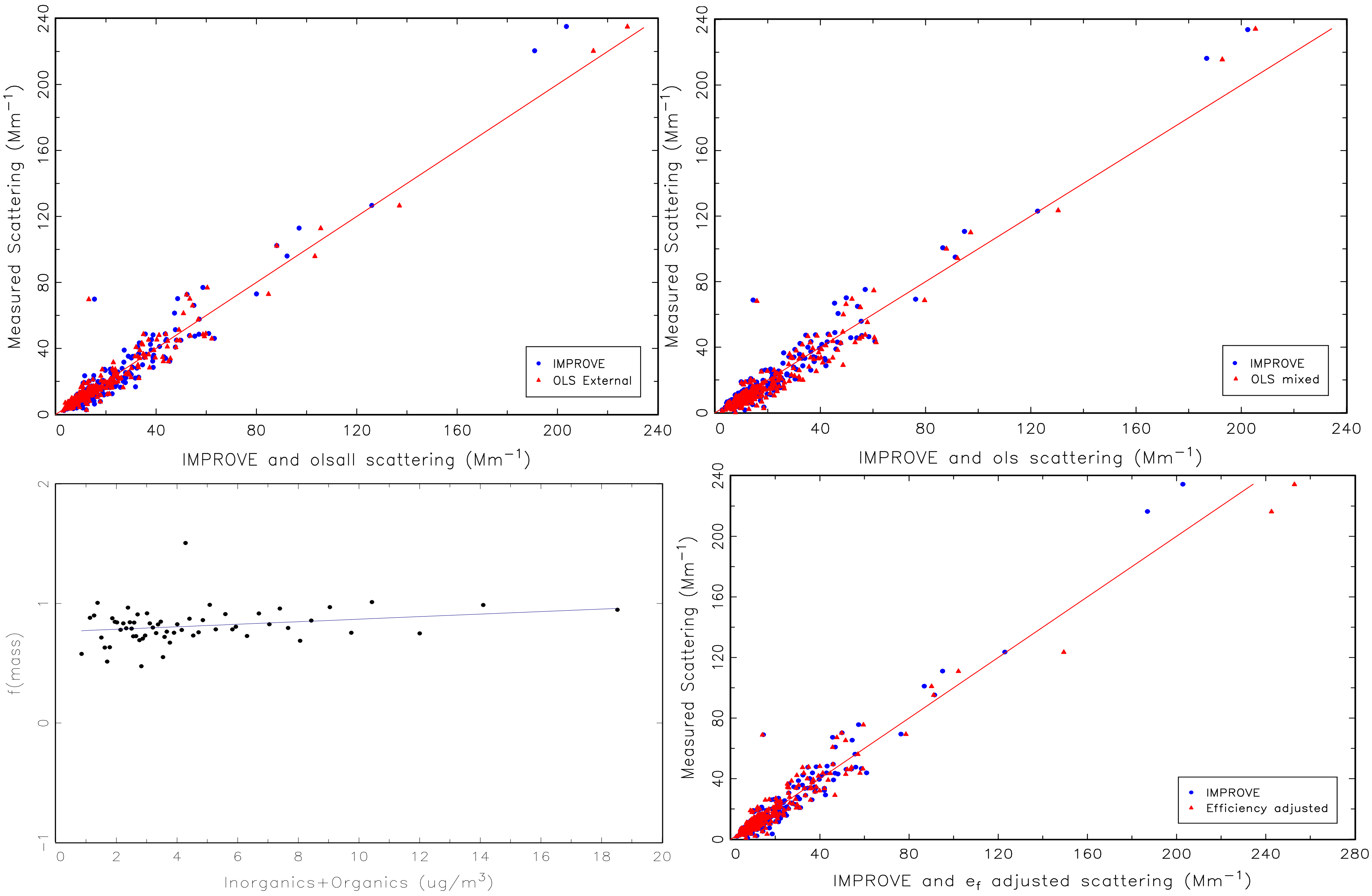
METHOD 3

METHOD 3 Theil Regression results (SCF)	
Intercept	**0.76**
Slope	**0.011**
Significance	**0.08**

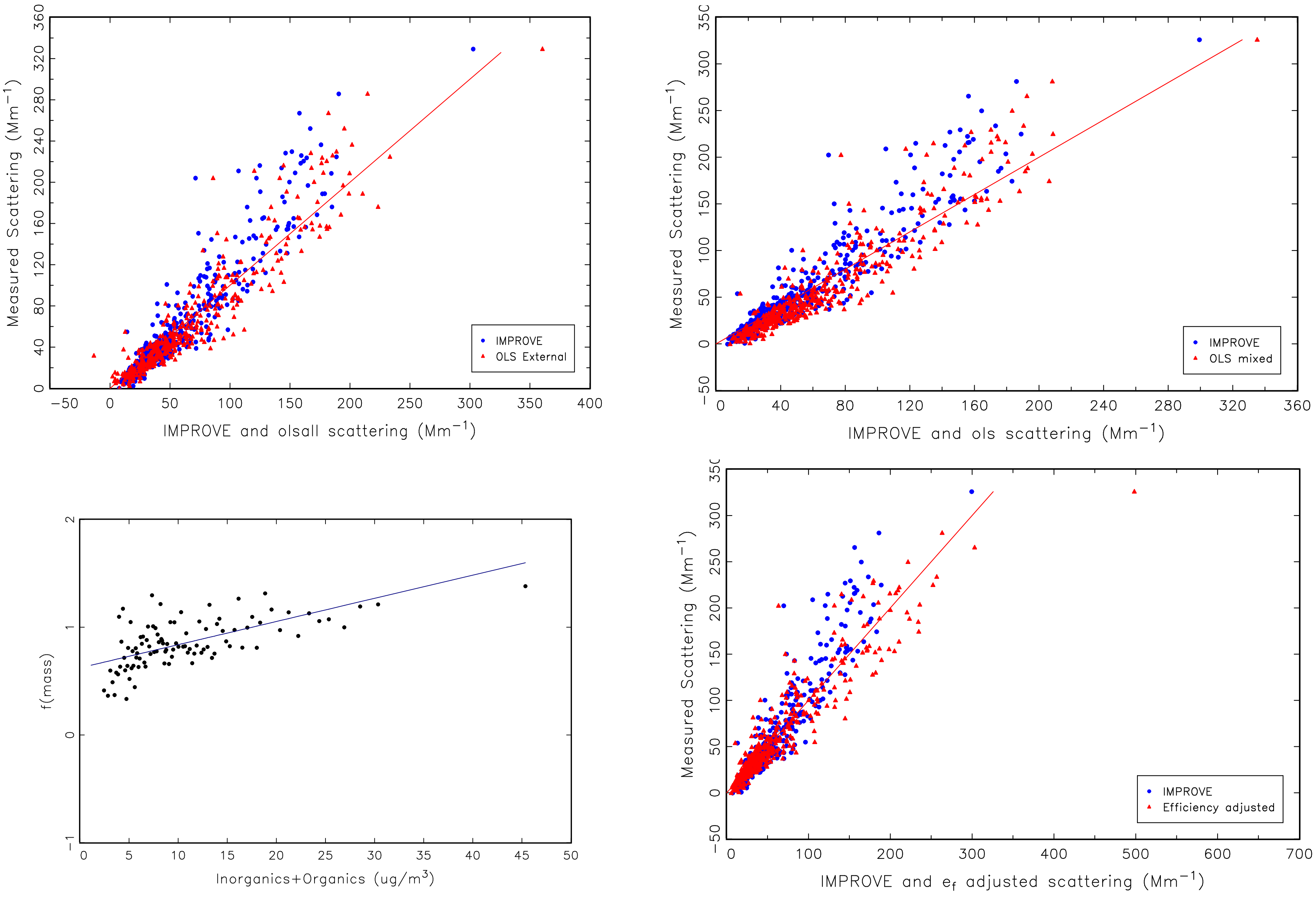
Acadia NP			
Specific Scattering Efficiency ($m^2\ g^{-1}$)	**Lower**	**Mean**	**Upper**
Inorganics (α_{inorg})	**2.33**	**2.44**	**2.58**
Organics (α_{org})	**2.82**	**2.95**	**3.13**

ACADIA NP					
Variable	**Mean**	**Std Dev**	**Minimum**	**Maximum**	**Valid**
SCF	**0.81**	**0.29**	**0.08**	**3.98**	**267**
$\alpha_{inorg}\ (m^2\ g^{-1})$	**2.44**	**0.13**	**2.31**	**3.40**	**617**
$\alpha_{org}(m^2\ g^{-1})$	**2.95**	**0.16**	**2.79**	**4.12**	**617**

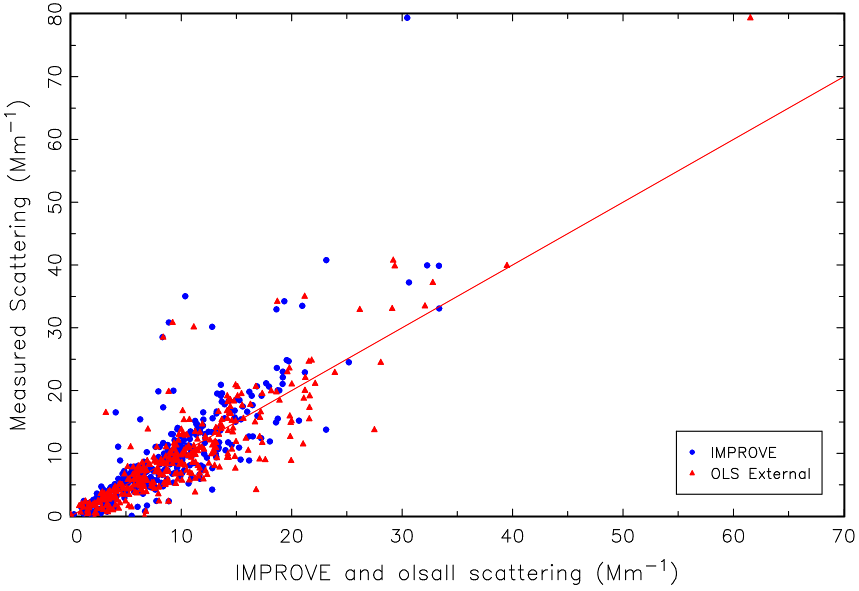
Method 1, 2, and 3 for Acadia National Park

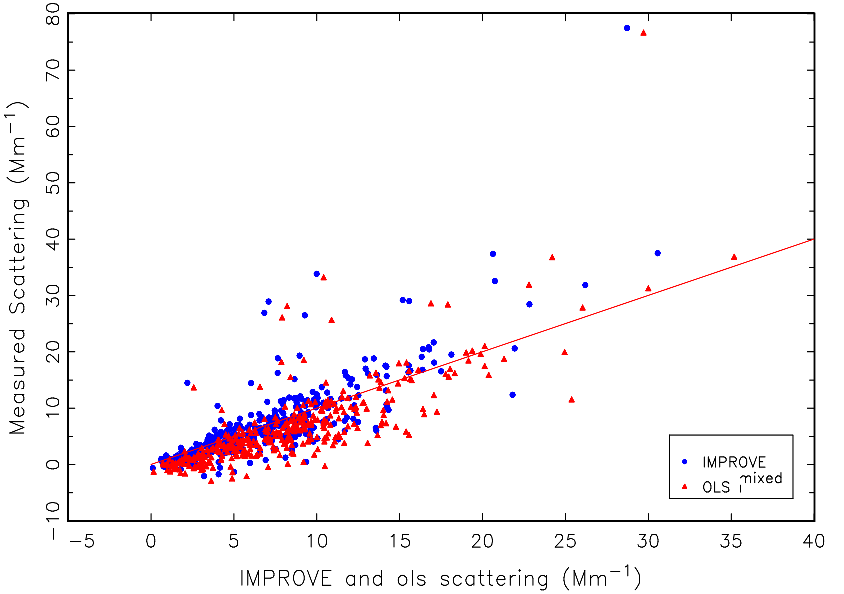


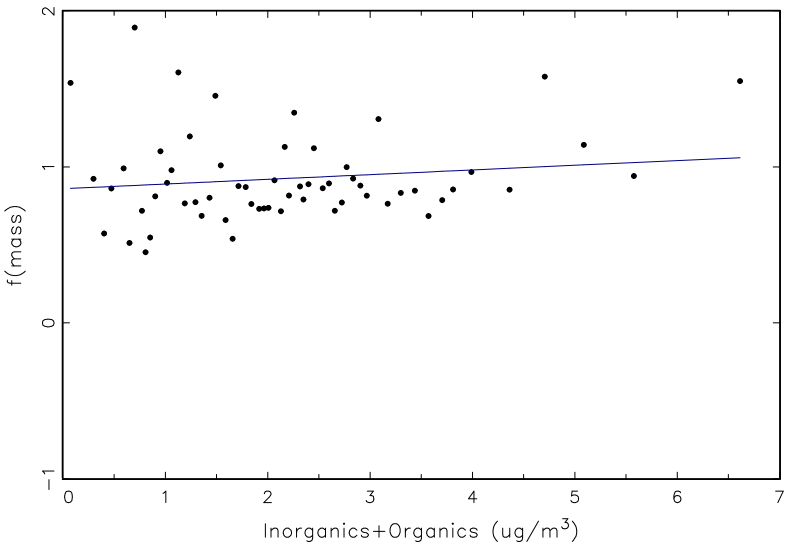
Method 1, 2, and 3 for Great Smoky National Park

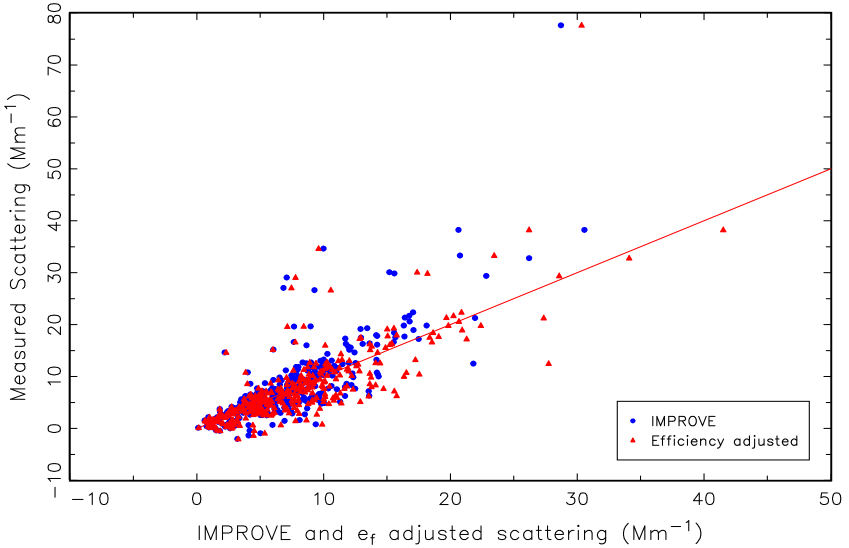


Method 1, 2, and 3 for Grand Canyon National Park

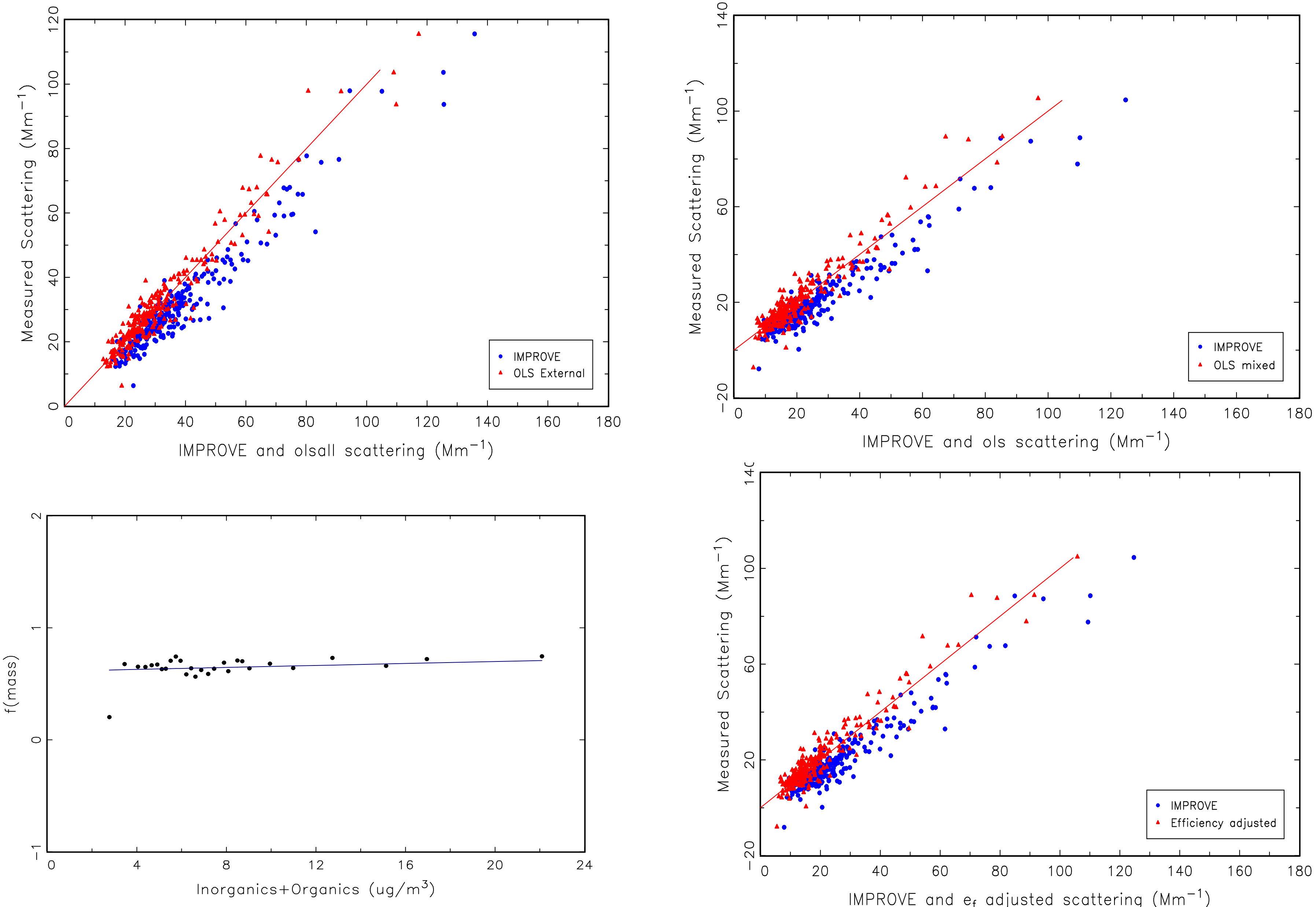




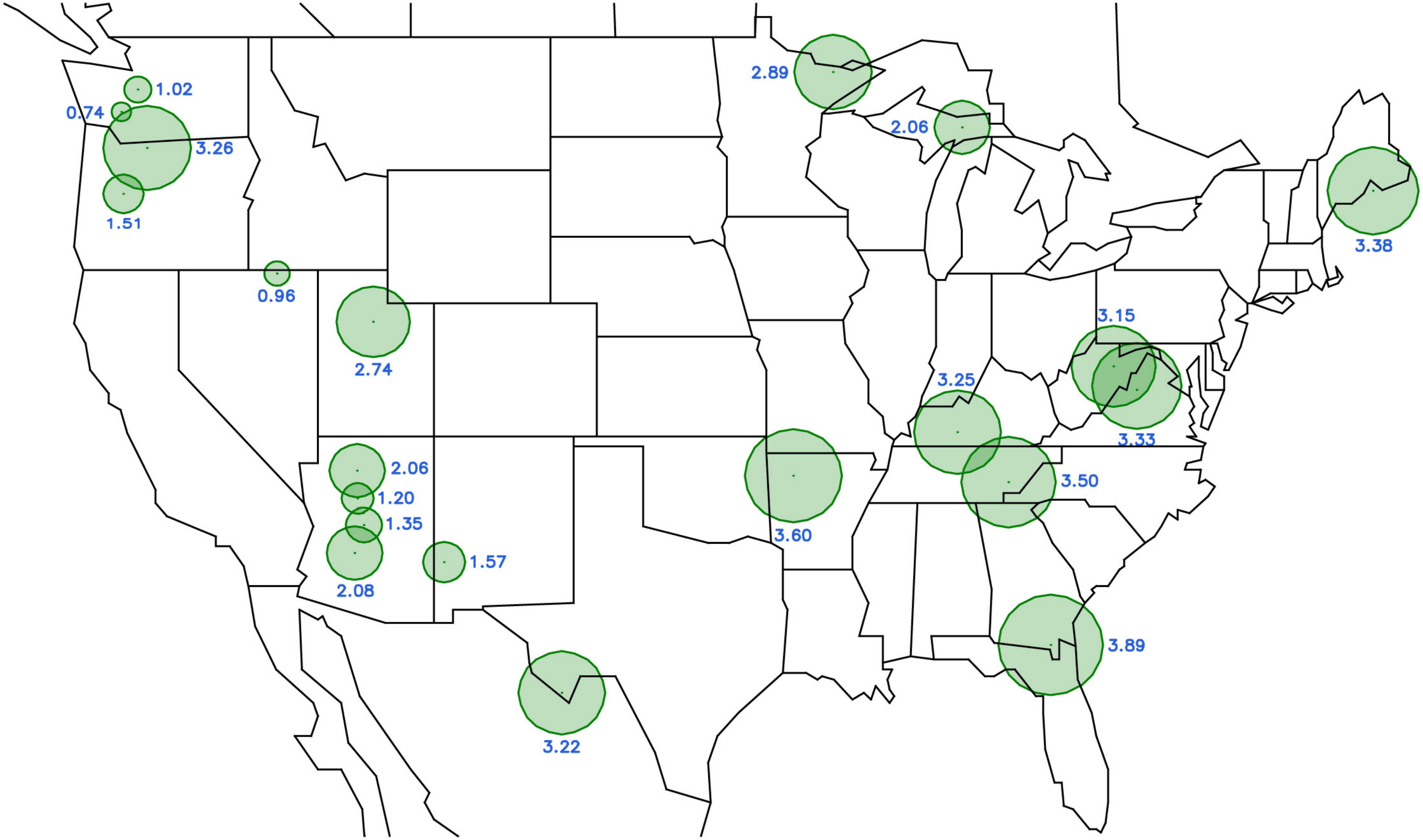




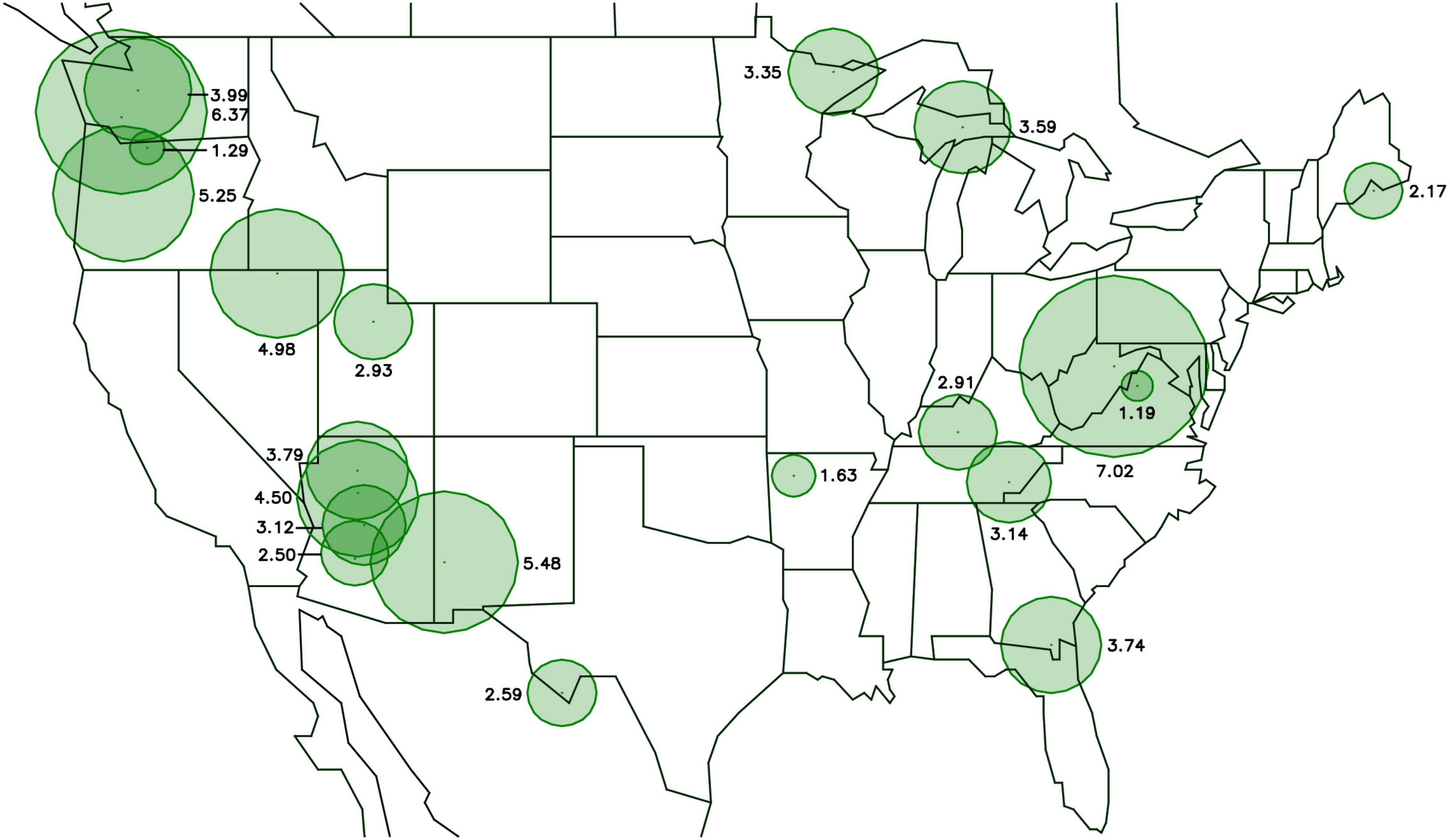
Method 1, 2, and 3 for Phoenix National Park



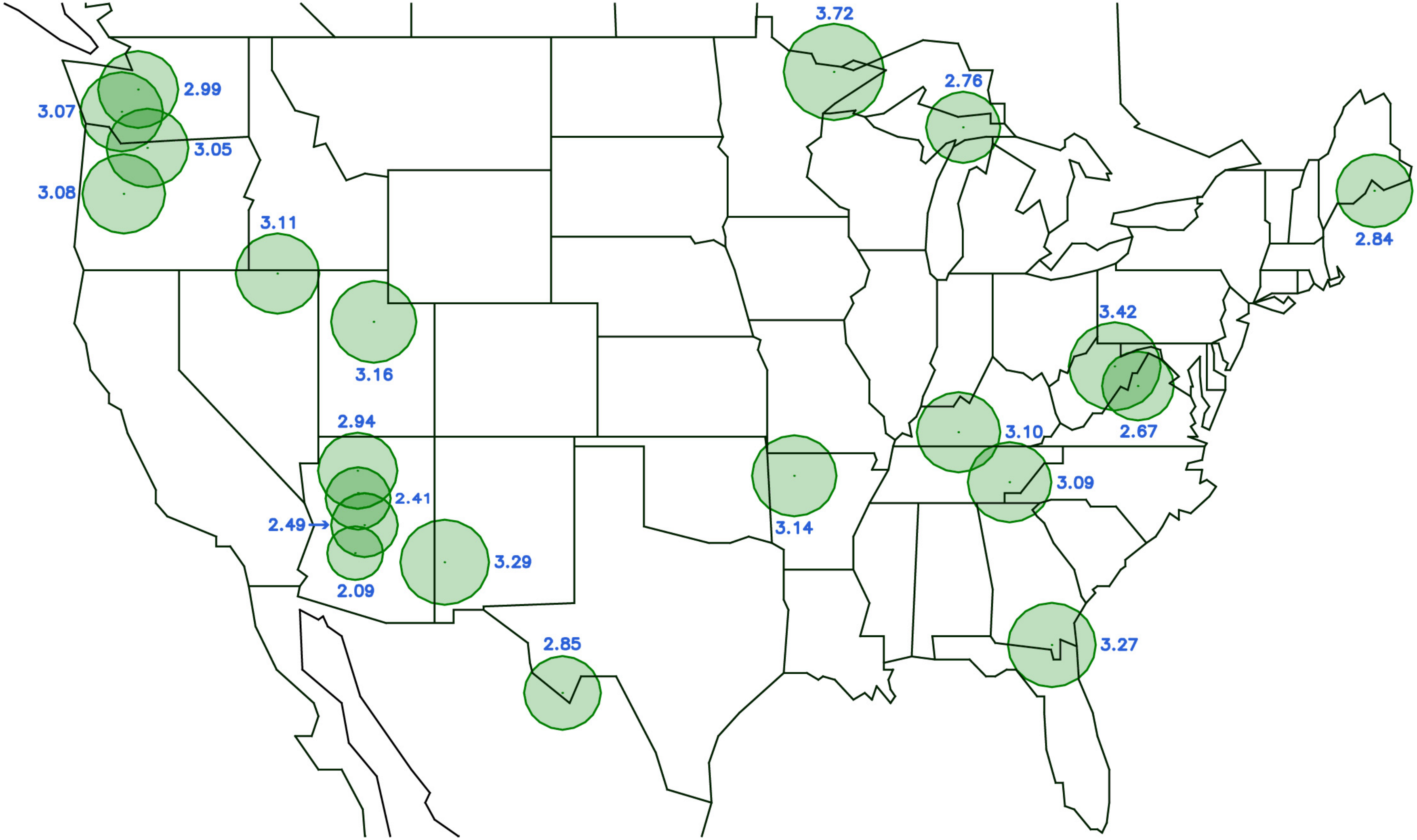
Method 1: SO_4


1.02
0.74
3.26
1.51
0.96
2.74
2.06
1.20
1.35
2.08
1.57
3.22
3.60
2.89
2.06
3.25
3.50
3.15
3.33
3.89
3.38

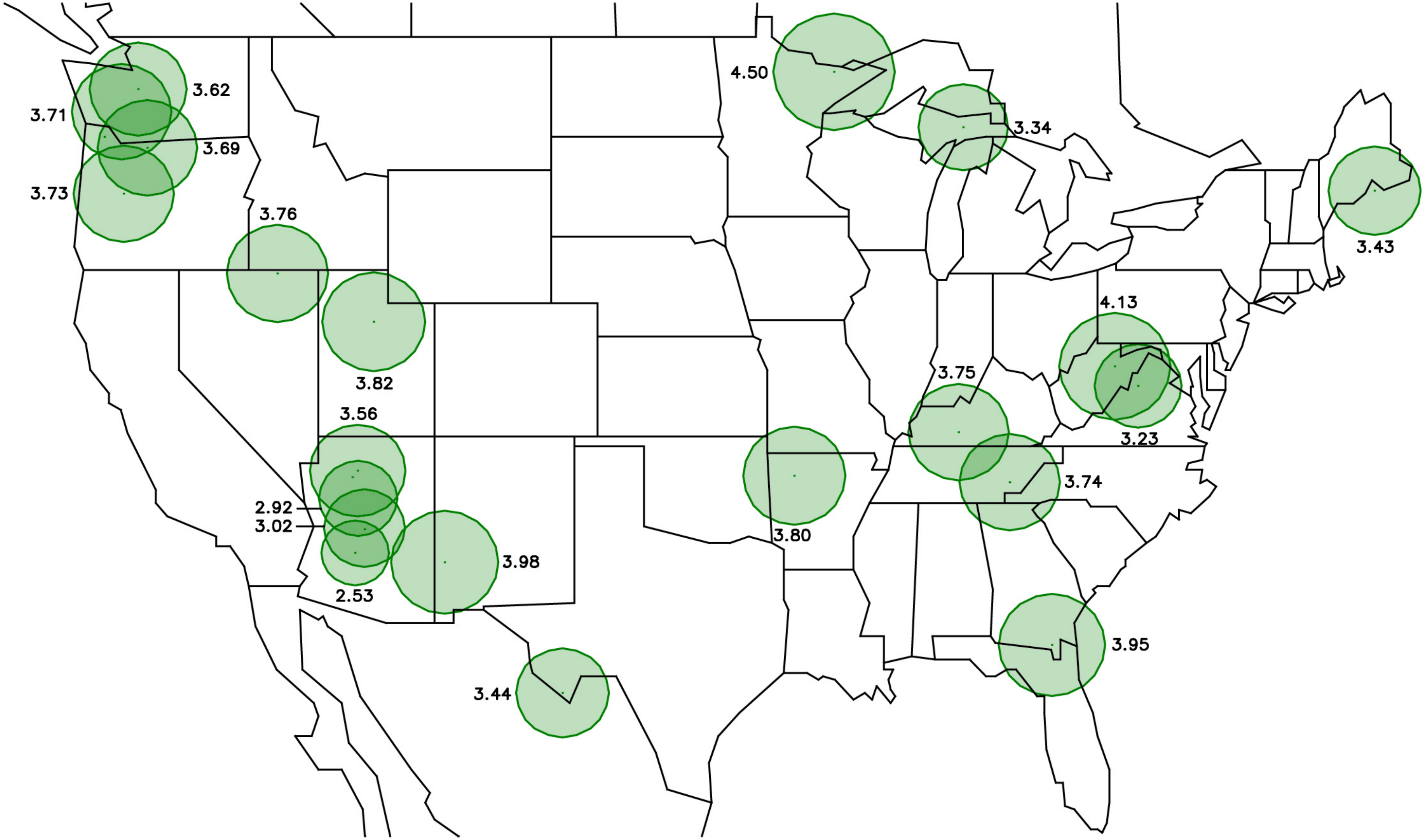
Method 1: POM


3.35
3.99
6.37
3.59
1.29
2.17
5.25
4.98
2.93
2.91
1.19
3.79
1.63
7.02
4.50
3.12
3.14
2.50
5.48
3.74
2.59

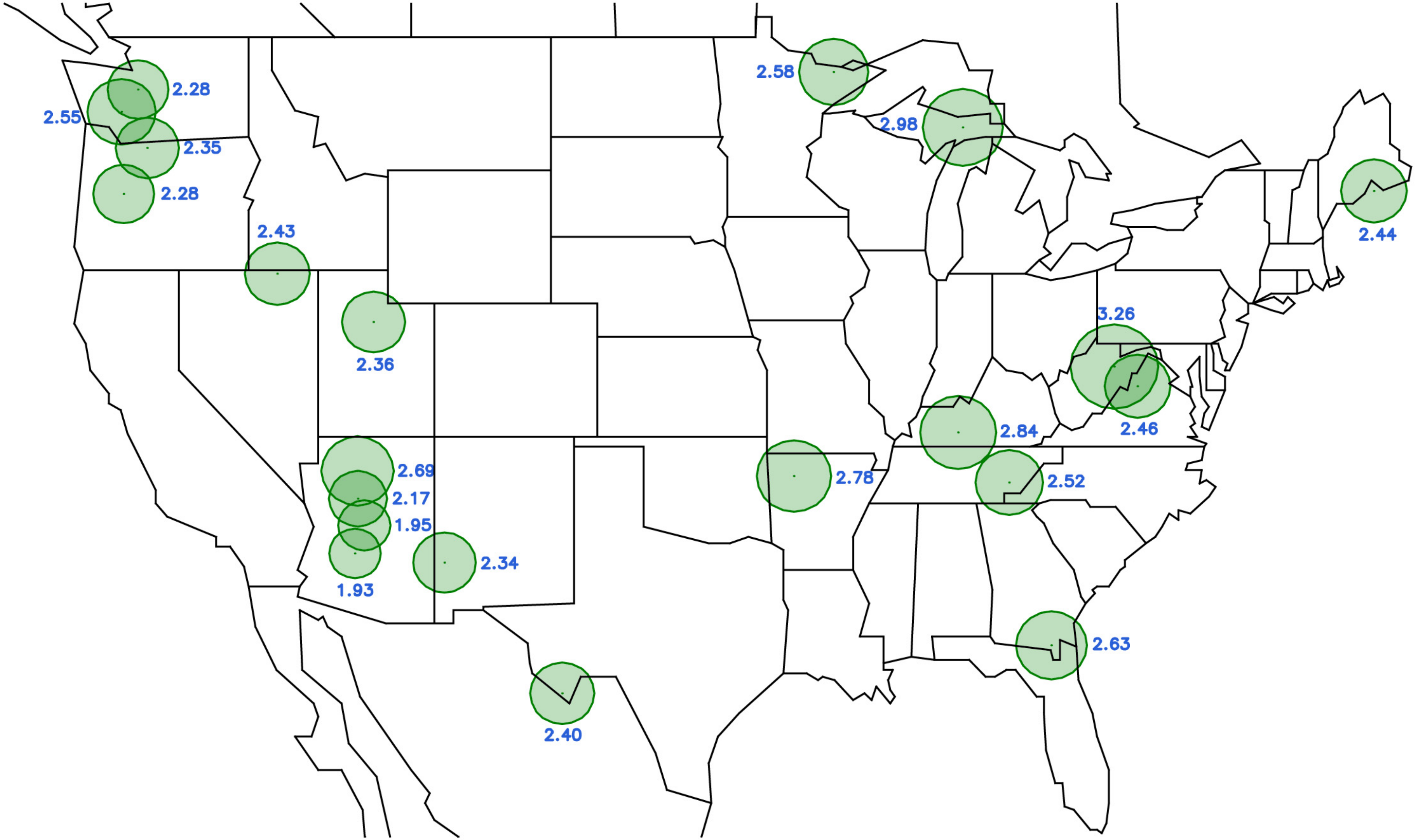
Method 2: Inorganics



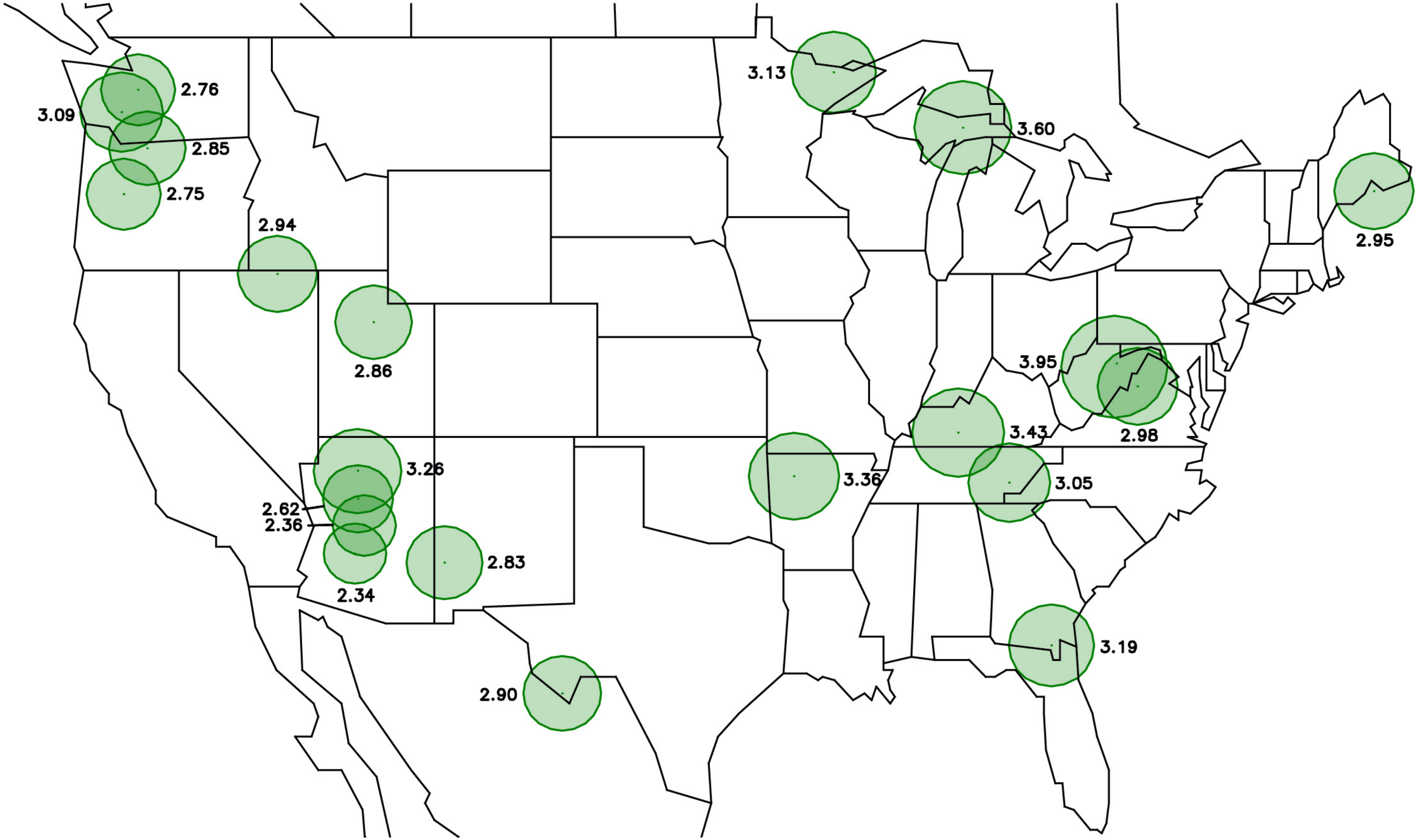
Method 2: POM


4.50
3.62
3.71
3.34
3.69
3.73
3.43
3.76
4.13
3.82
3.75
3.56
3.23
2.92
3.02
3.74
3.80
3.98
2.53
3.95
3.44

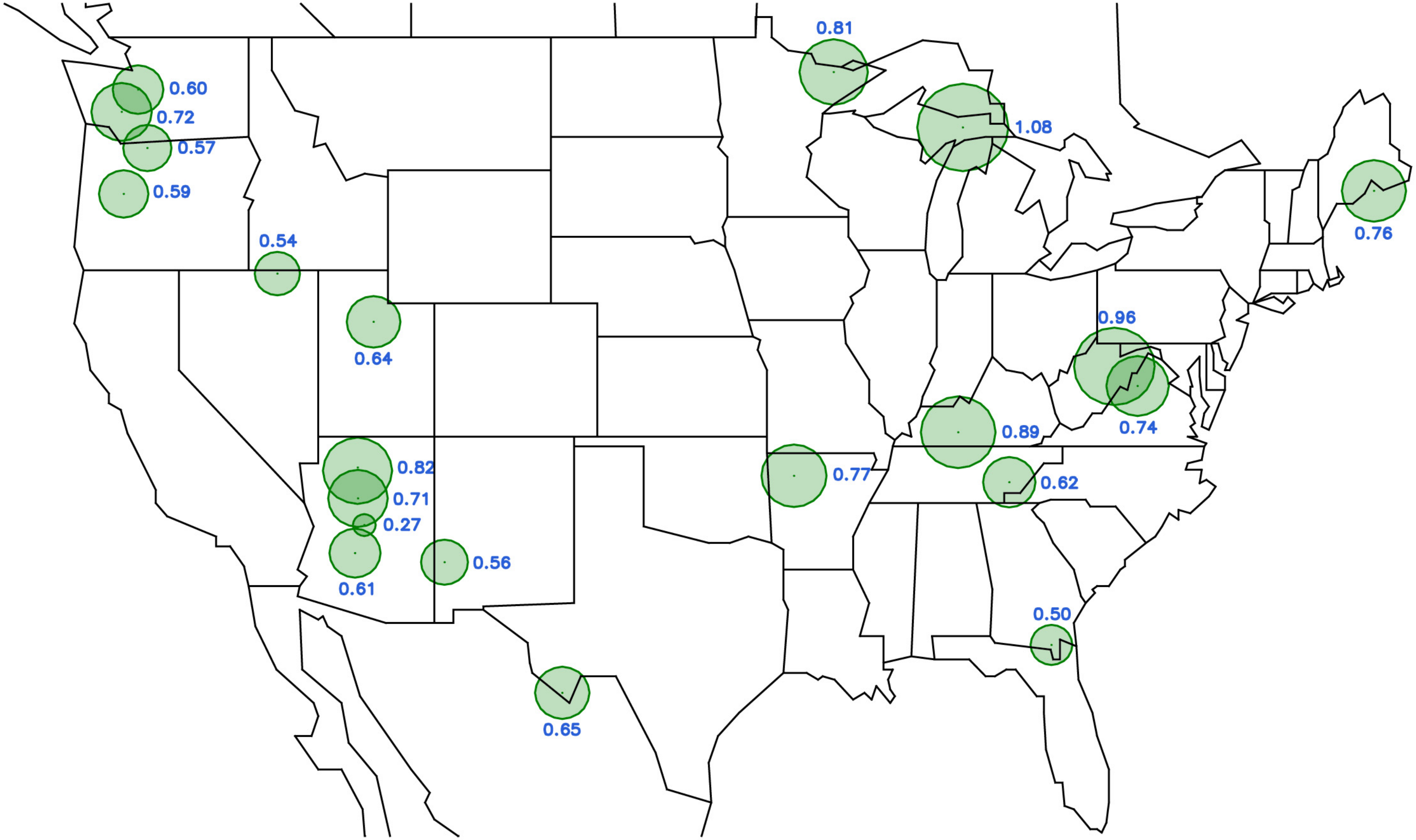
Method 3: Inorganics



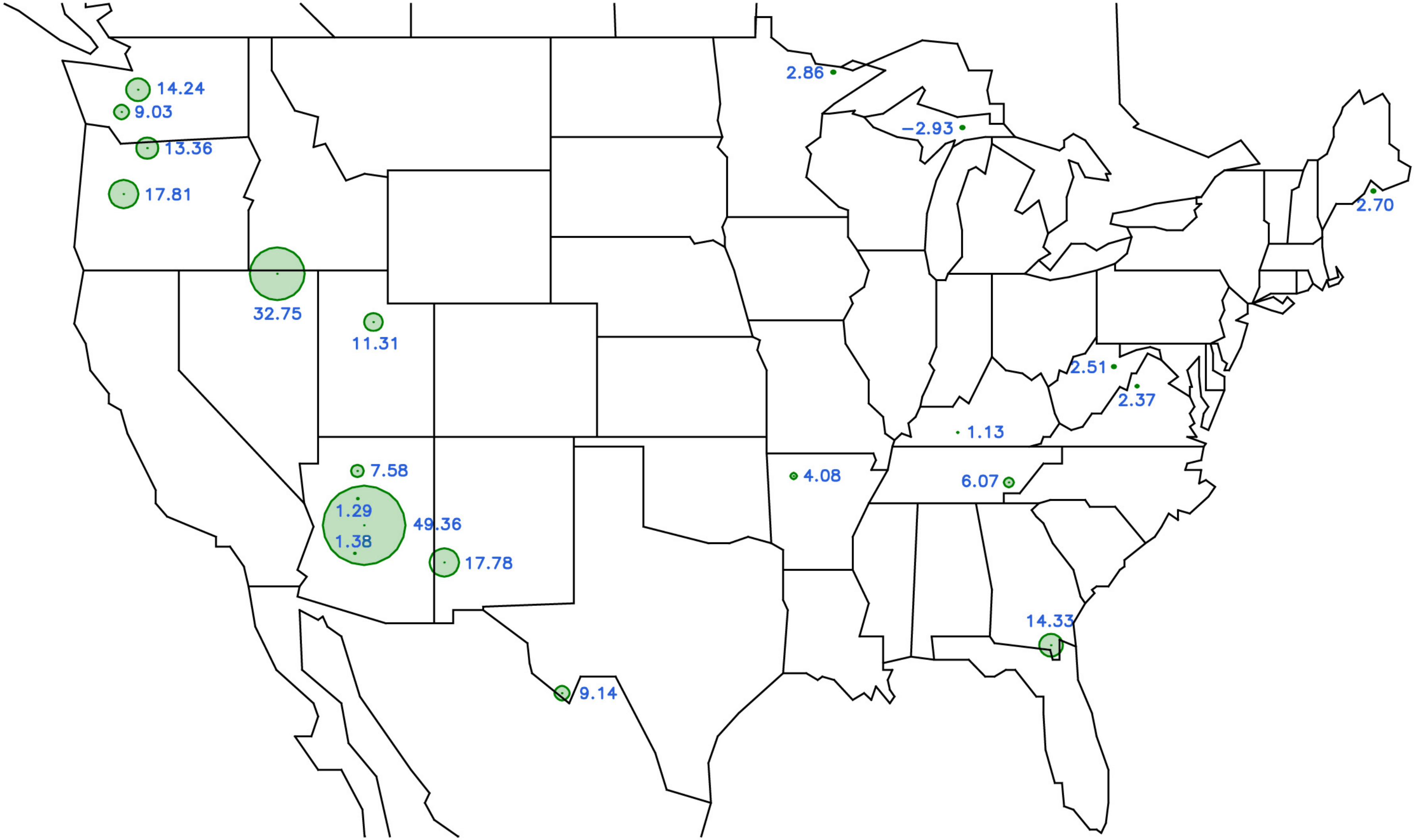
Method 3: POM


2.76
3.09
2.85
2.75
2.94
2.86
3.26
2.62
2.36
2.34
2.83
2.90
3.13
3.60
2.95
3.95
2.98
3.43
3.05
3.36
3.19

Method 3: Intercept



Percent Change in Efficiency in Doubling of Mass

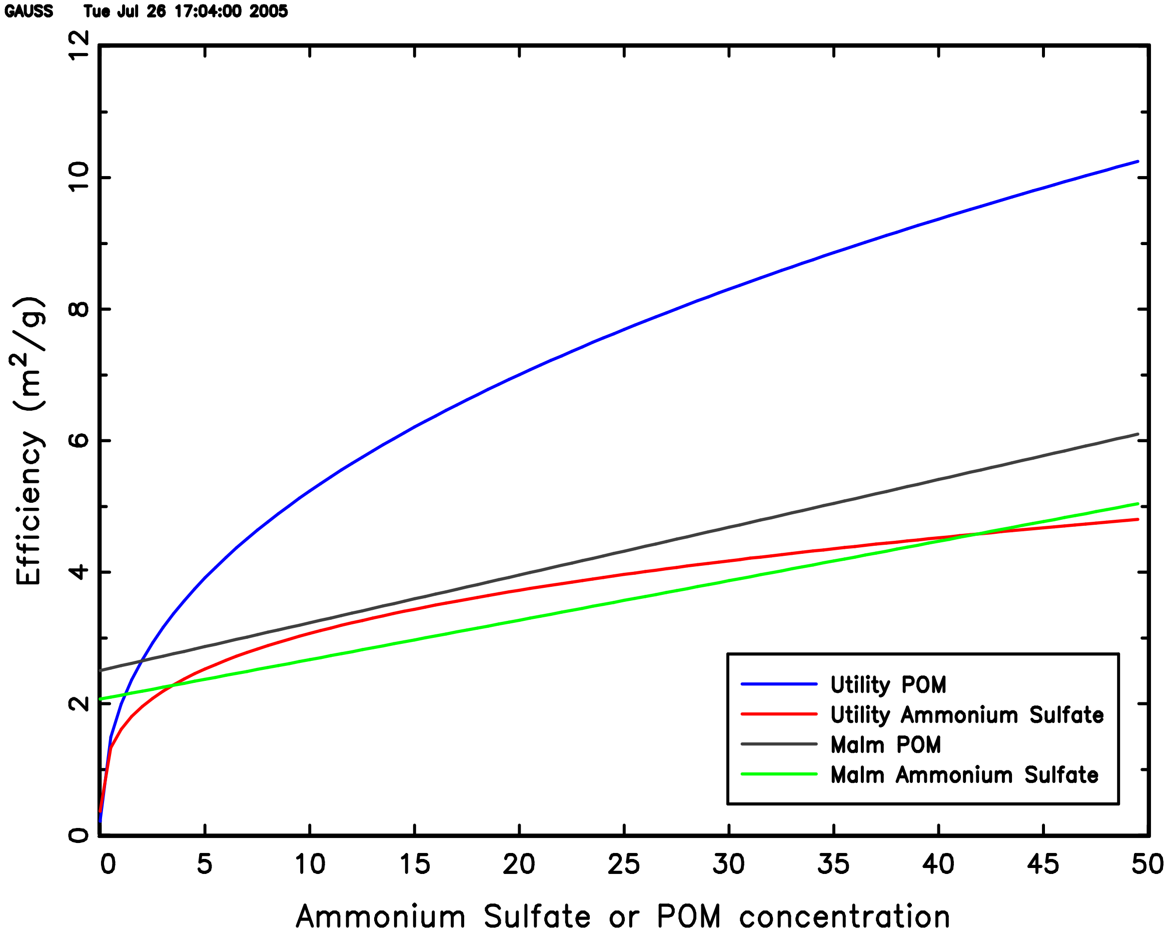


Literature Review

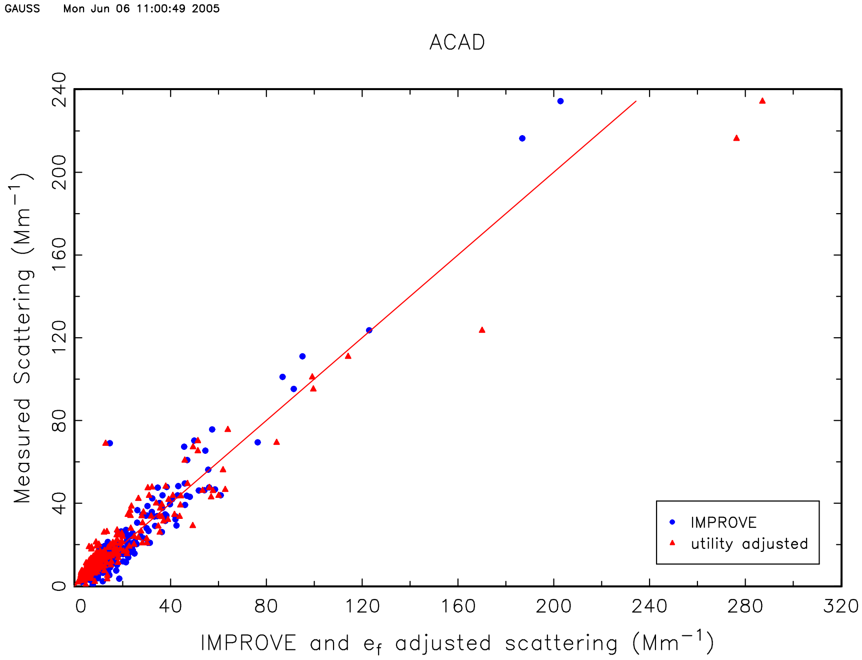
Utility Recommended Mass Scattering Efficiencies

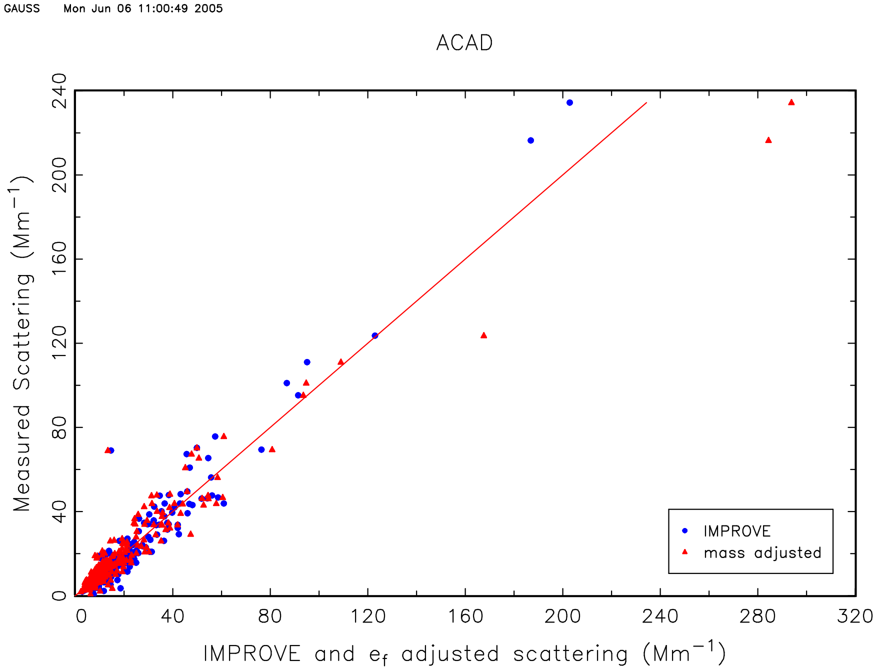
$\alpha=1.61*[(NH_4)_2SO_4 + NH_4NO_3]^{1.28}+1.99*POM^{1.42}$ (Utility)

$\alpha_{inorg}=3(0.7+.02*M_{mix})$ and $\alpha_{POM}=3.63(0.7+.02*M_{mix})$ (IMPROVE)

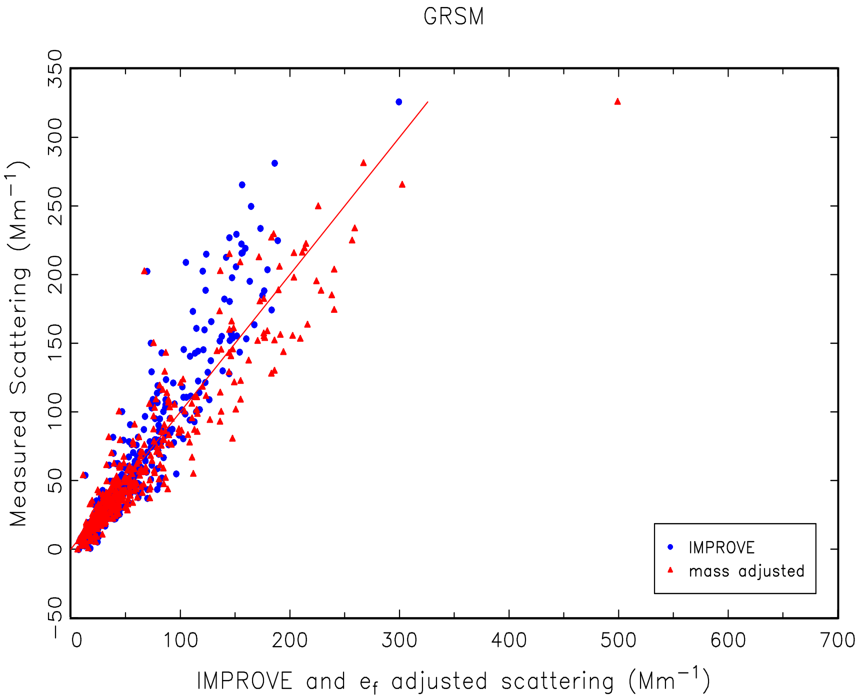


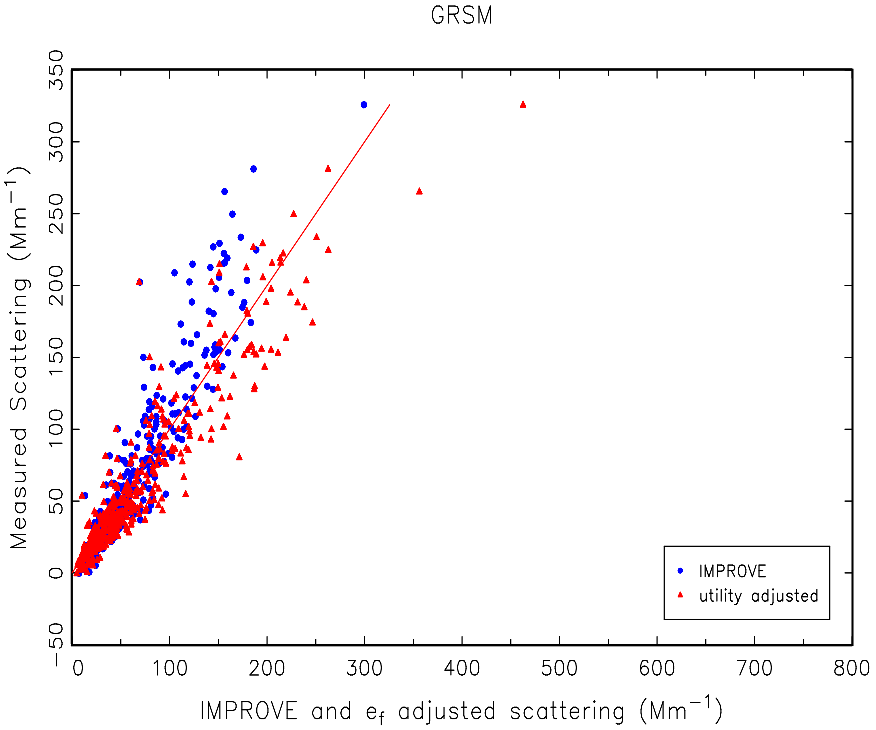
Comparison of Utility and Mass adjusted (ACADIA)



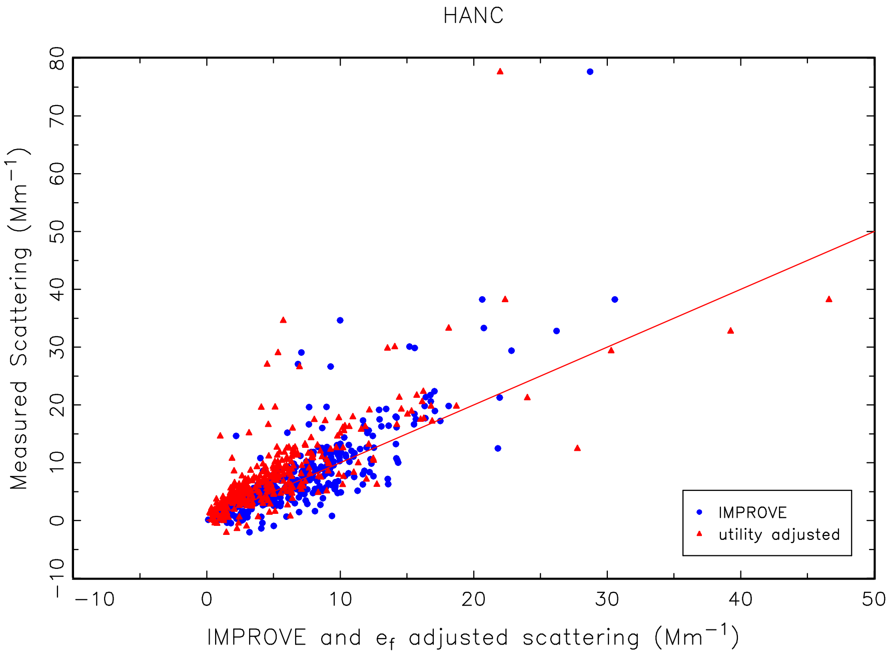


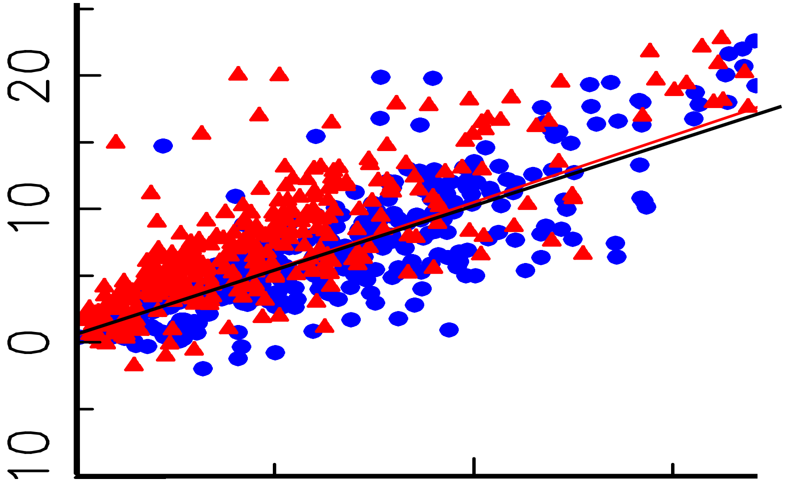
Comparison of Utility and Mass adjusted (GREAT SMOKY)

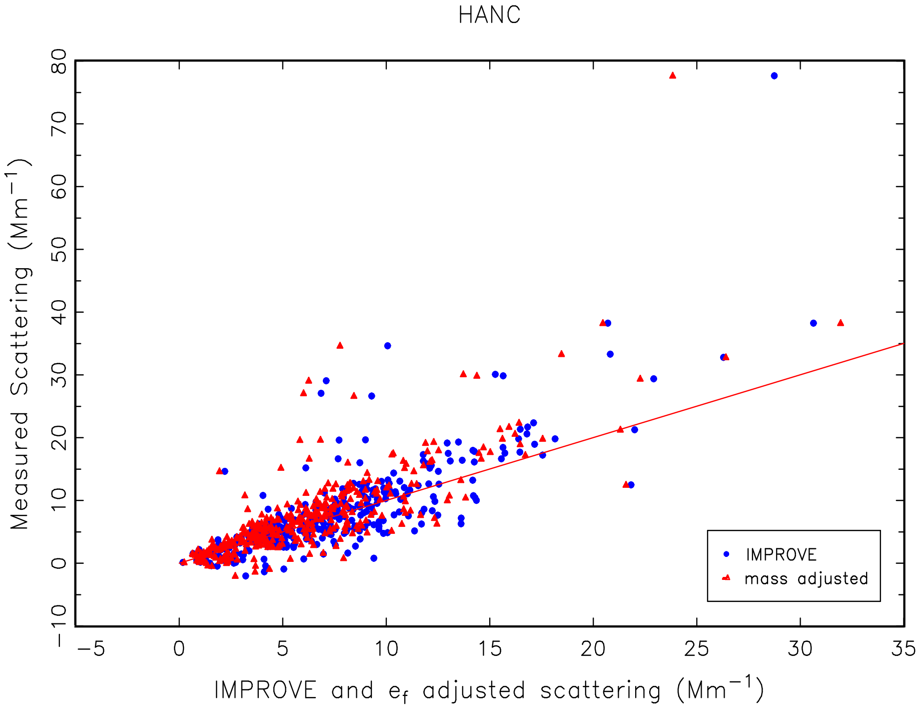




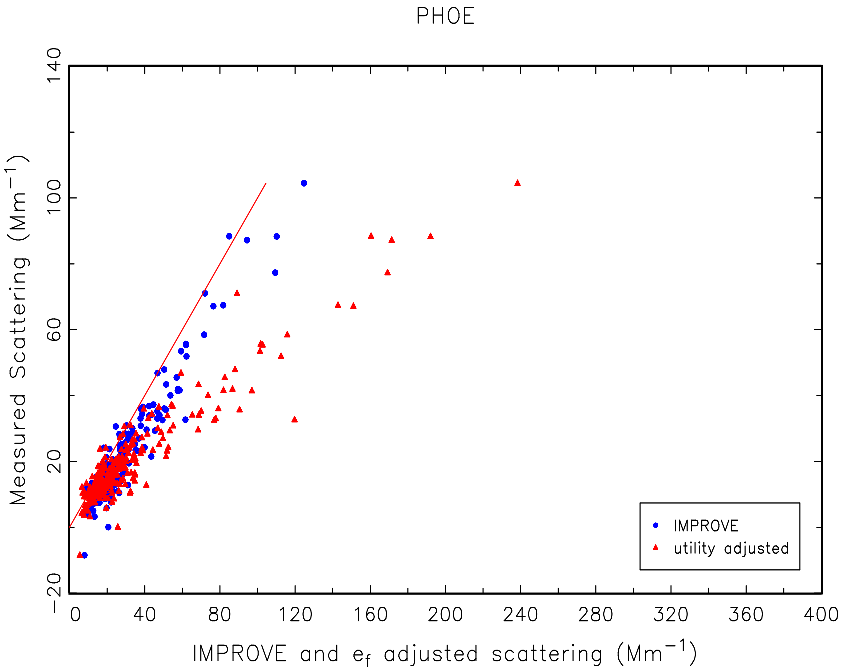
Comparison of Utility and Mass adjusted (GRAND CANYON)

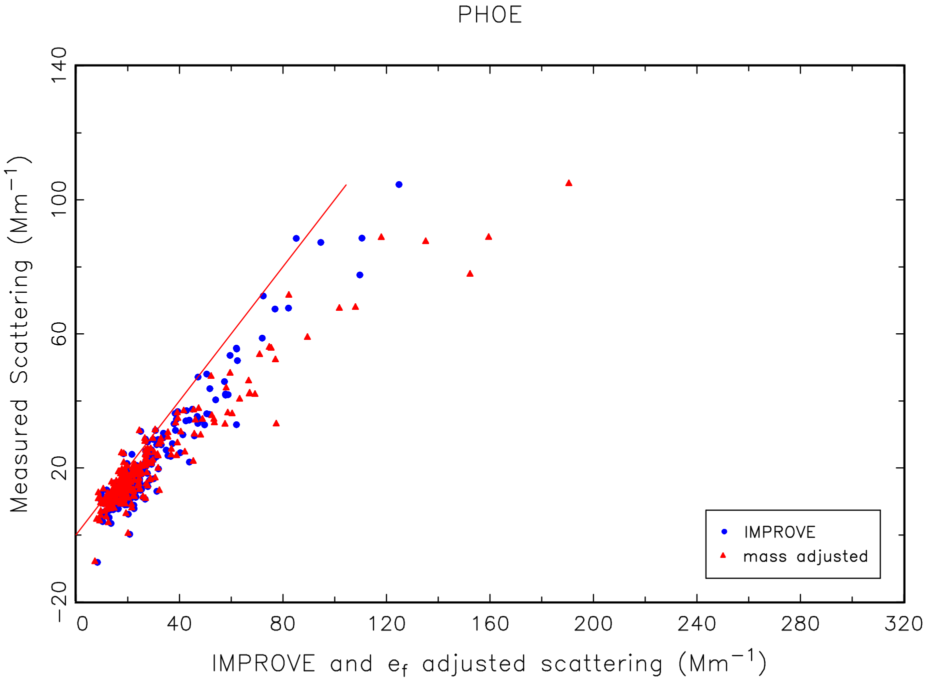




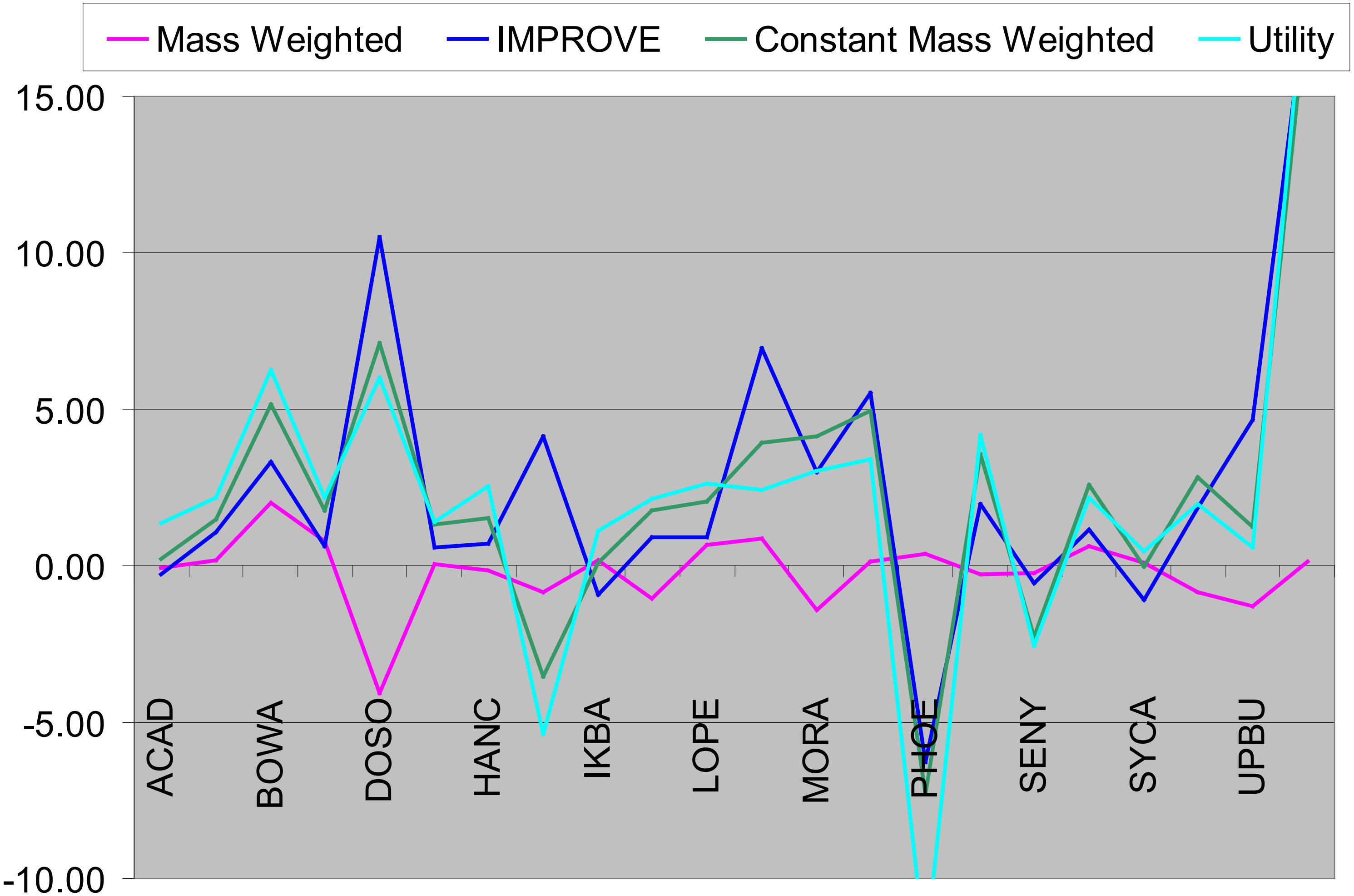


Comparison of Utility and Mass adjusted (PHOENIX)

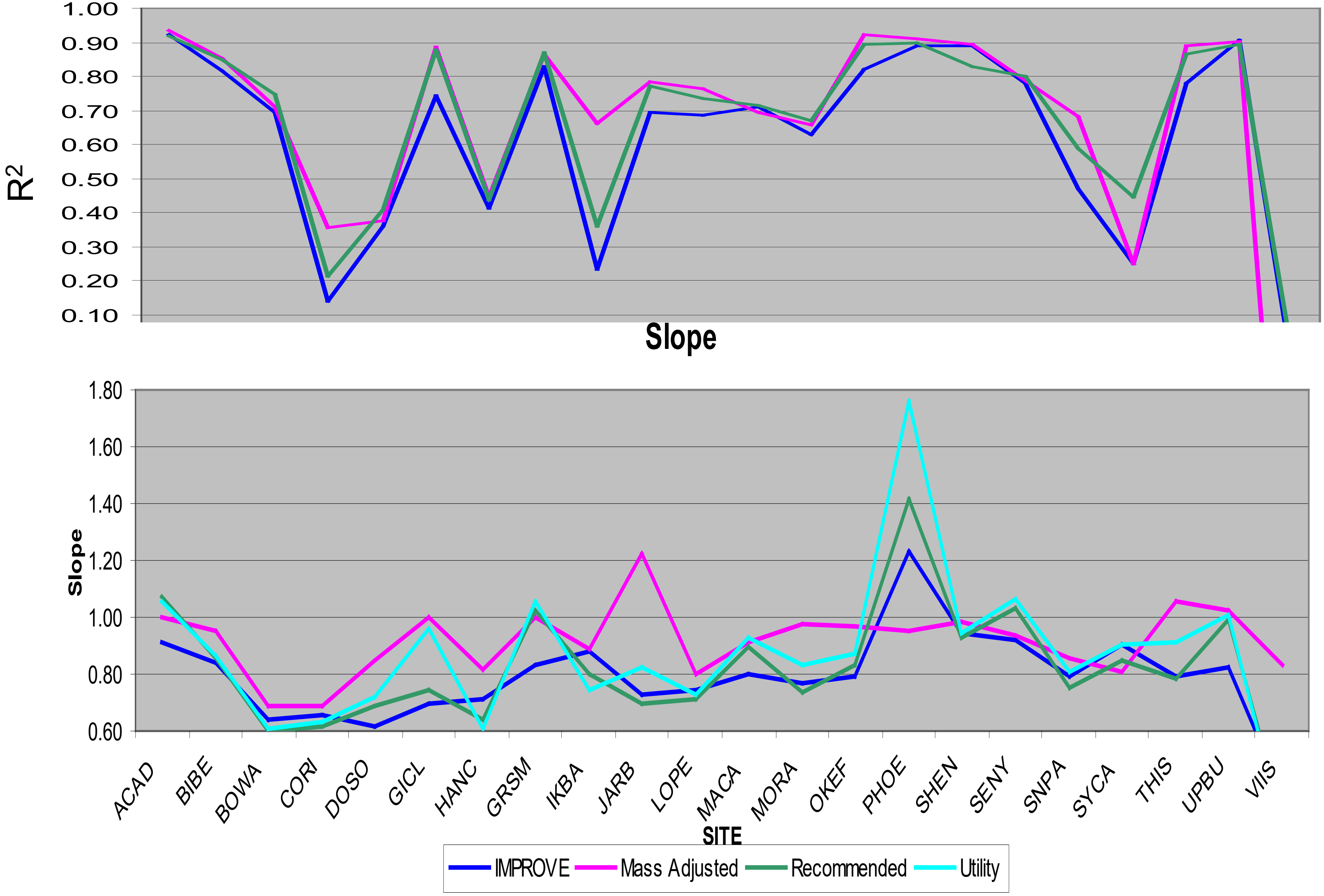




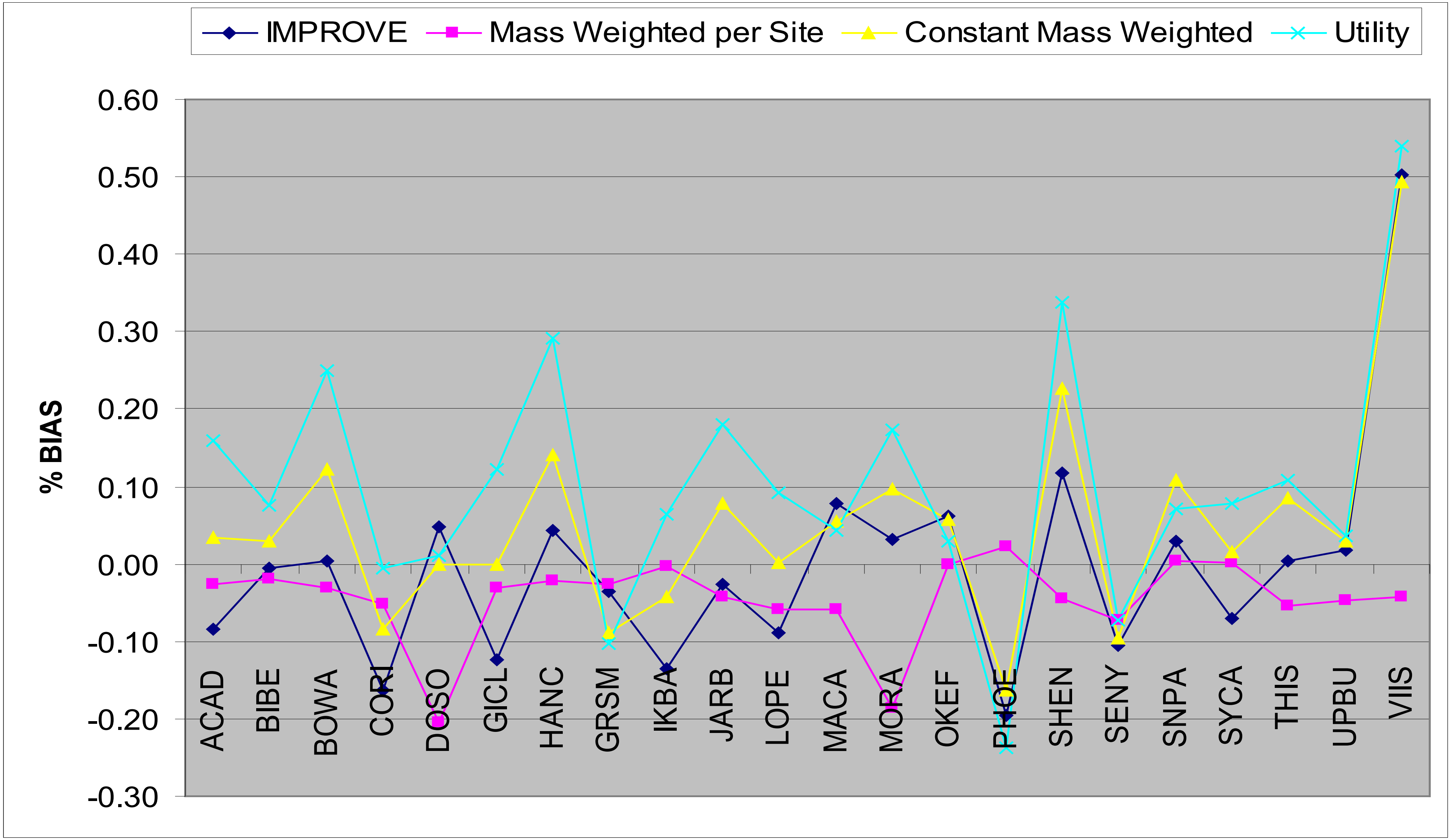
AVERAGE BIAS



OLS Regression of $b_{mix\_measured}$ vs $b_{estimated}$



% Median Bias



IMPROVE
Mass Weighted per Site
Constant Mass Weighted
Utility
% BIAS
0.60
0.50
0.40
0.30
0.20
0.10
0.00
-0.10
-0.20
-0.30
ACAD
BIBE
BOWA
CORI
DOSO
GICL
HANC
GRSM
IKBA
JARB
LOPE
MACA
MORA
OKEF
PHOE
SHEN
SENY
SNPA
SYCA
THIS
UPBU
VIIS

POSSIBLE CHANGES TO THE IMPROVE EQUATION

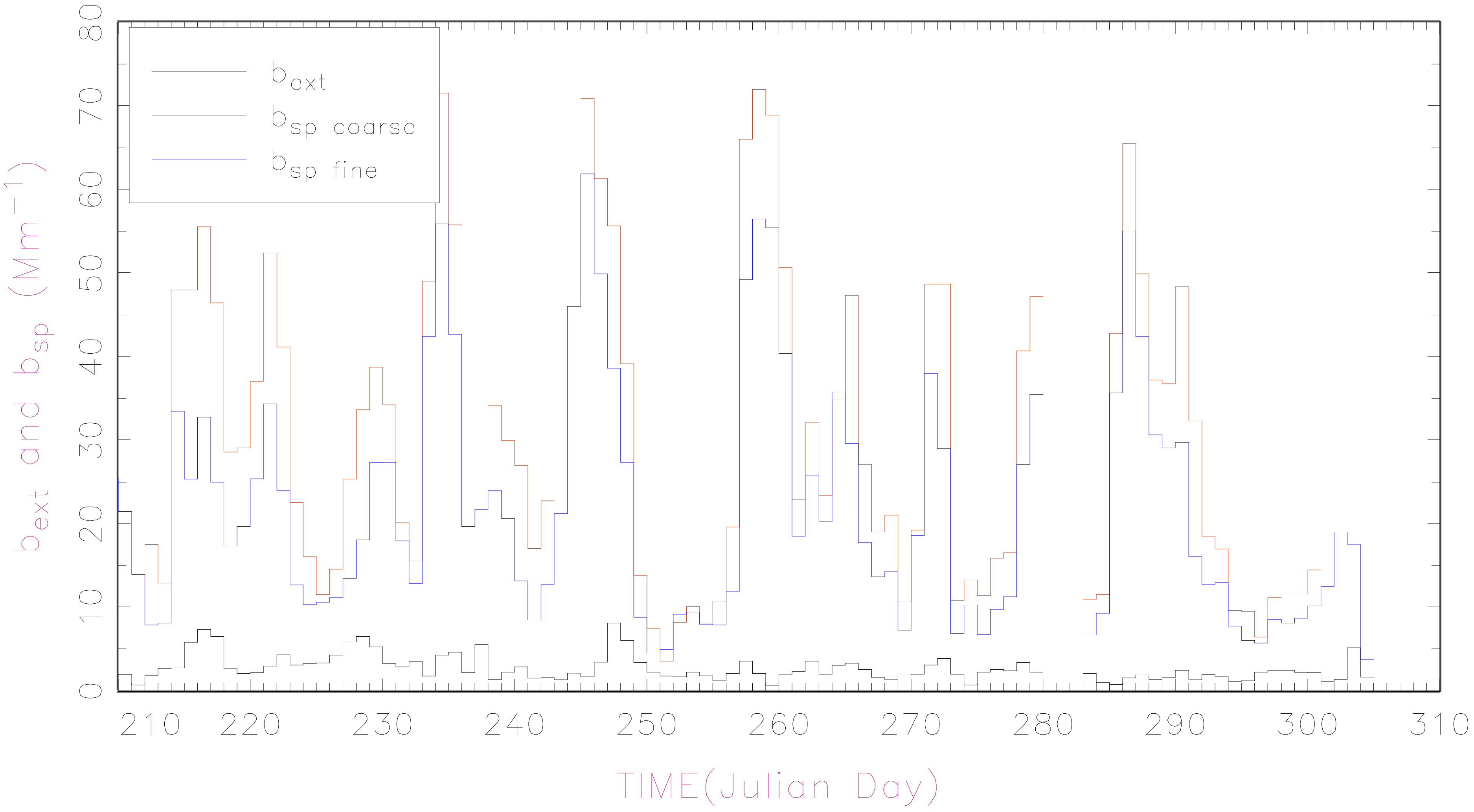
- Elements of equation that stay the same:
  - Sulfate as ammonium sulfate/nitrate as ammonium nitrate
  - Estimate of soil concentration as is
  - b_{abs}=10.0*LAC
  - b_{soil}=1.0*Soil
  - b_{cm}=0.6*CM
- Elements of equation that can be changed:
  - POM=1.8*OC
  - New f(RH) curve with continuous growth below 40% RH for inorganics and f(RH)=1 for POM – (could be 1.1-1.2 at 85%RH)
  - Include sea salt as 1.8*Cl^- and develop an associated f(RH)
  - Include NO_2 absorption
  - Adjust mass scattering efficiencies of sulfate and nitrate
    - α_{inorg}=2.5 m^2/g and α_{pom}=3.0 m^2/g – constant for all mass loadings
    - $\alpha_{inorg}=3(0.7+.02*M_{mix})$ and $\alpha_{POM}=3.63(0.7+.02*M_{mix})$
    - Adjust α differently across US

ADDITIONAL RECOMMENDATIONS

- Ammonium should be measured
- Coarse mass should be speciated
- Change cut point from 2.5 to 1.0 um
- Better measurement/estimation of absorption and scattering from LAC

DISCUSSION?

Extinction, Fine and Coarse Particle Scattering (Optical Measurements)



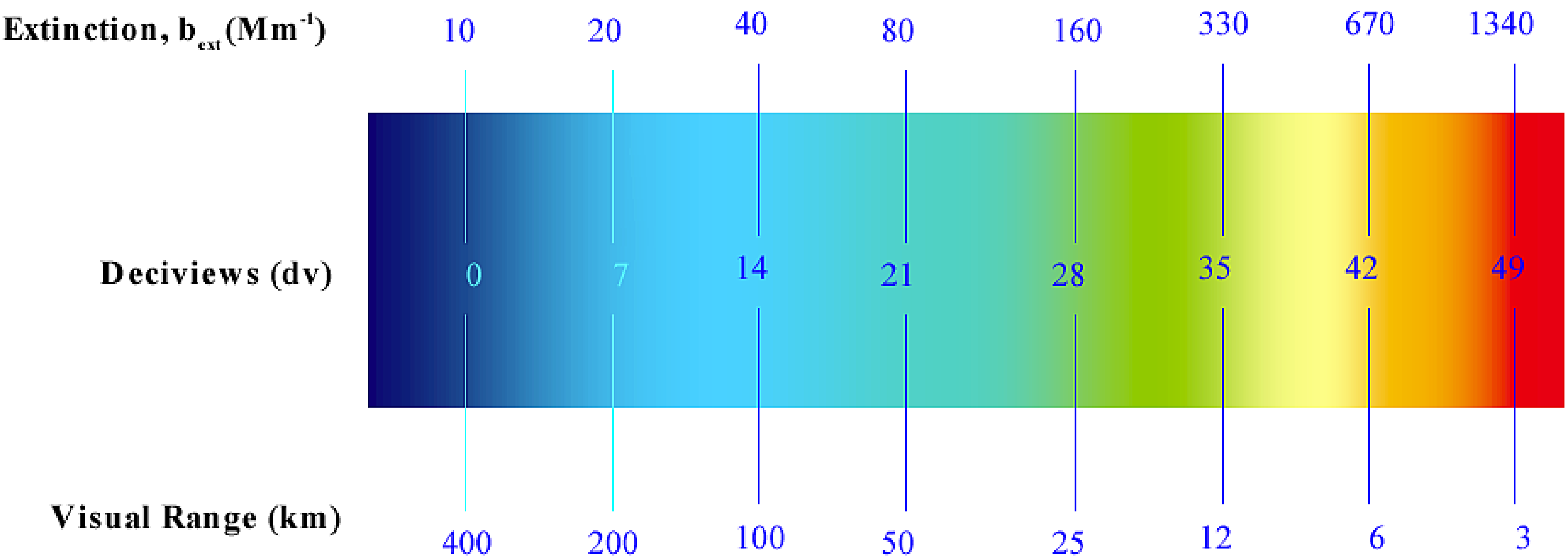
For an atmosphere completely free of aerosols consisting only of gases (Rayleigh Atmosphere) at 5000 ft elevation the rate of light loss is:

1% per kilometer : 0.01 km^{-1}

or in Megameters 10.0 Mm^{-1}

Visibility Metrics

- **Apparent contrast: $C_r = C_o e^{-b_{ext} r}$**
- **Visual Range: $vr = 3912 / b_{ext}$**
- **decView: $dv = 10 \ln(b_{ext}/10)$**



Mean Central Rocky Mt. Summer Visibility
150 km

Mean Appalachian Summer Visibility
23 km

One Approximation for Estimating b_{ext}

$$b_{ext} = (e_{sf})f_s(RH)[Ammoniated\ SO_4] + (e_{nf})f_n(RH)[NH_4NO_3]$$

$$+(e_{ocmf})\,f_{ocm}(RH)[OMC] + (e_{soilf})[SOIL]$$

$$(e_{sc})f_s(RH)[Ammoniated\ SO_4] + (e_{nc})f_n(RH)[NH_4NO_3]$$

$$+(e_{ocmc})\,f_{ocm}(RH)[OMC] + (e_{soilc})[SOIL] + 10[lacf + lacc].$$

IMPROVE equation for estimating extinction for purposes of tracking progress

$$
\begin{aligned}
b_{ext} = {} & (e_{sf})f_s(RH)[(NH_4)_2\mathrm{SO}_4] + (e_{nf})f_n(RH)[NH_4NO_3] \\
& + (e_{ocmf})\,f_{ocm}(RH)[OMC] + (e_{soilf})[SOIL] \\
& (e_c)[Coarse\ \mathrm{Mass}] + (e_{lacf})[lacf]
\end{aligned}
$$

Concentrations are 24 hr averages

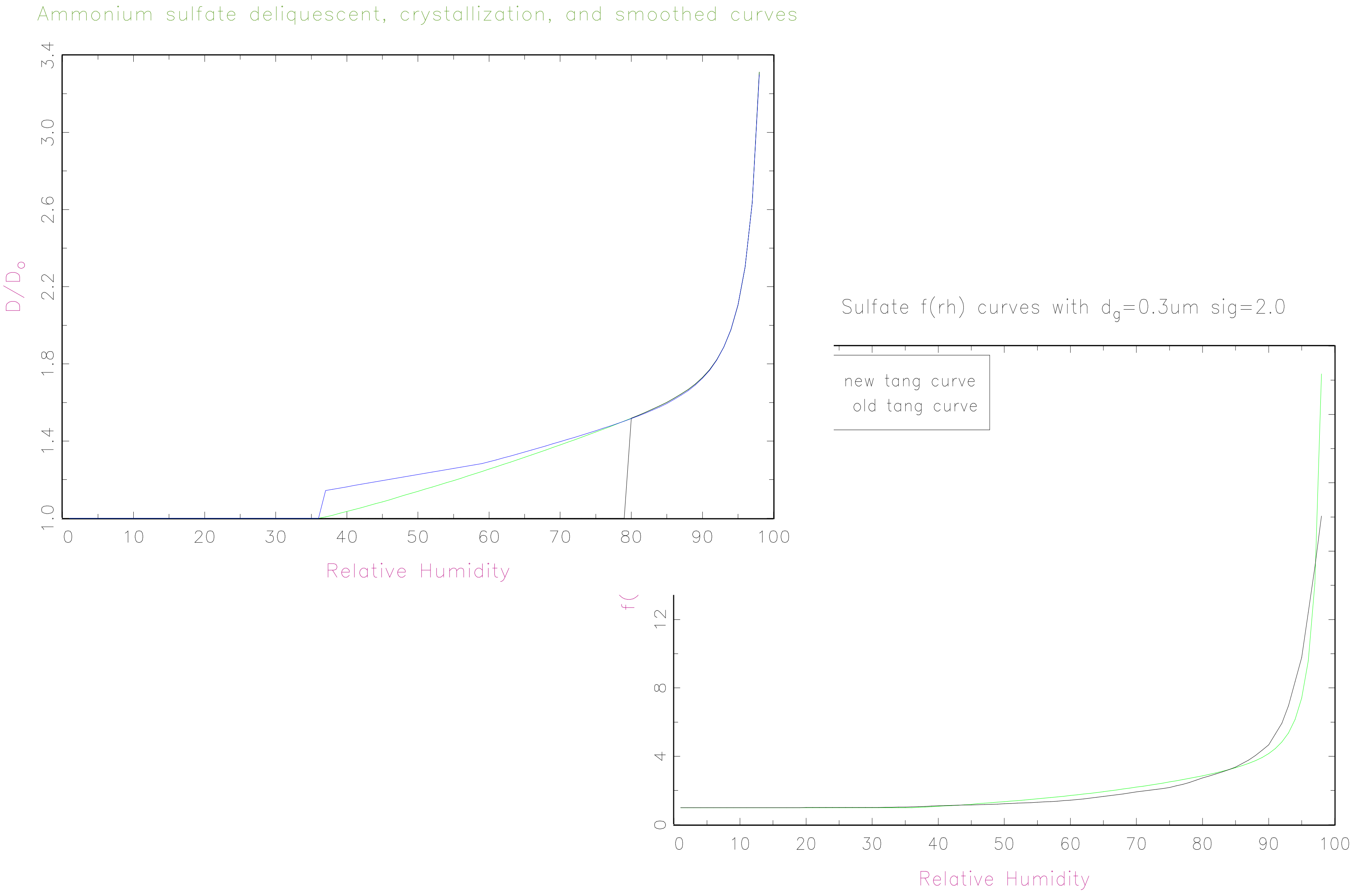
Some technical issues concerning estimating extinction from measured aerosol species

- Issues
  - Internal vs external mixture?
  - Chemical form of species?
  - Constant mass scattering efficiencies?
  - What species are hygroscopic ?
  - Form of f(RH) curves?
  - Coarse mass composition?
  - Sampling issues?

IMPROVE equation for estimating extinction for purposes of tracking progress

$$
\begin{aligned}
b_{ext} &= (e_{sf})f_{s}(RH)[(NH_4)_2\mathrm{SO}_4] + (e_{nf})f_{n}(RH)[NH_4NO_3] \\
&\quad + (e_{ocmf})\,f_{ocm}(RH)[OMC] + (e_{soilf})[SOIL] \\
&\quad (e_{c})[Coarse\ \mathrm{Mass}] + (e_{lacf})[lacf]
\end{aligned}
$$

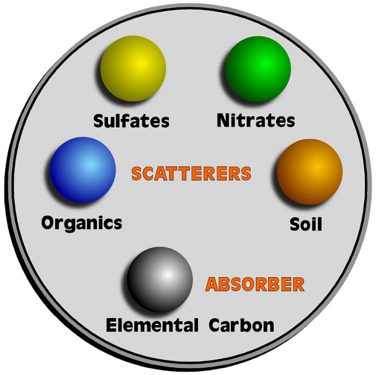
Concentrations are 24 hr averages



Ammonium sulfate deliquescent, crystallization, and smoothed curves

Sulfate f(rh) curves with d_g=0.3um sig=2.0

IMPROVE Aerosol Species Equations



Species	Equation
Ammonium sulfate	$[\text{Sulfate}]_A = 4.125[S]_{PIXE}$ $[\text{Sulfate}]_B = 1.375[SO4]_{IC}$
Ammonium nitrate	$[\text{Nitrate}]_B = 1.29[NO_3]_{IC}$
Organic	$[OMC]_C = 1.40([OCLT]_{TOR} + [OCHT]_{TOR})$ $[OMH]_A = 11.0([H]_{PESA} - 0.25[S]_{PIXE})$
Light absorbing carbon	$[LAC]_C = [ECLT]_{TOR} + [ECHT]_{TOR}$
Fine soil	$[\text{Fine Soil}]_A = 2.20[Al]_{PIXE} + 2.49[Si]_{PIXE} + 1.63[Ca]_{PIXE} + 2.42[Fe]_{PIXE} + 1.94[Ti]_{PIXE}$
Reconstructed Fine Mass	$RCFM = [\text{Sulfate}]_A + [\text{Nitrate}]_B + [OMC]_C + [LAC]_C + [\text{Fine Soil}]_A$
Coarse mass	$[CM] = [PM_{10}]_D - [PM_{2.5}]_A$

PESA - Proton Elastic Scattering
PIXE - Particle Induced X-ray Emission
TOR - Thermal Optical Reflectance
IC - Ion Chromatography

ALL METHOD 1 RESULTS

Site	**AS**	**AS Std Err**	**AN**	**AN Std Err**	**POM**	**POM Std Err**	**CM + Soil**	**CM+Soil Std Err**	**Sea Salt**	**Sea Salt Std Err**
ACAD	3.38	0.08	2.65	0.35	2.17	0.33	-0.23	0.10	5.32	1.56
BIBE	3.22	0.09	2.71	0.70	2.59	0.26	0.32	0.02	29.69	47.39
BOWA	2.89	0.54	6.05	0.39	3.35	1.67	-0.57	0.36	2.78	7.57
CORI	3.26	0.36	11.60	0.56	1.29	0.39	0.00	0.08	-0.96	0.75
DOSO	3.15	0.73	9.90	3.38	7.02	3.01	-1.95	1.03	0.00	0.00
GICL	1.57	0.17	1.54	1.33	5.48	0.09	0.16	0.04	-5.08	35.29
HANC	2.06	0.29	10.87	0.78	3.79	0.24	0.08	0.06	6.29	123.60
GRSM	3.50	0.08	4.57	0.71	3.14	0.39	-0.88	0.21	-556.61	346.55
IKBA	1.35	0.35	2.31	0.60	3.12	0.32	0.55	0.02	-21.31	15.28
JARB	0.96	0.51	3.33	0.38	4.98	0.23	0.27	0.06	7.49	29.61
LOPE	2.74	0.36	4.95	0.17	2.93	0.29	0.18	0.08	1.62	39.35
MACA	3.25	0.17	4.47	0.28	2.91	0.63	-0.28	0.33	-178.36	790.62
MORA	0.74	2.91	-8.75	13.82	6.37	2.24	1.50	1.22	38.67	35.10
OKEF	3.89	0.54	0.09	4.16	3.74	1.47	0.01	0.56	0.00	0.00
PHOE	2.08	0.21	2.85	0.16	2.50	0.09	0.30	0.02	1.25	2.92
SHEN	3.33	0.21	4.29	0.88	1.19	1.03	-0.35	0.40	0.00	0.00
SENY	2.06	0.22	4.23	0.29	3.59	0.82	0.64	0.56	235.66	490.61
SNPA	1.02	2.04	10.05	3.00	3.99	1.34	0.07	0.49	-404.37	1389.96
SYCA	1.20	0.33	6.13	0.90	4.50	0.17	0.22	0.02	0.00	12.24
THIS	1.51	0.44	2.97	0.96	5.25	0.23	-0.06	0.09	0.68	8.75
UPBU	3.60	0.13	4.82	0.50	1.63	0.62	0.21	0.15	-374.66	679.08
VIIS	3.97	0.28	6.24	1.23	-3.64	0.92	0.85	0.04	2.41	0.27
Average	2.49	0.50	4.45	1.62	3.27	0.76	0.05	0.27	-54.98	184.39
Std Dev	1.05		4.26		2.17		0.66		174.24	

METHOD 2 RESULTS

Site	α_{inorg} $(m^2\,g^{-1})$	α_{org} $(m^2\,g^{-1})$
ACAD	2.84	3.43
BIBE	2.85	3.44
BOWA	3.72	4.50
CORI	3.05	3.69
DOSO	3.42	4.13
GICL	3.29	3.98
HANC	2.94	3.56
GRSM	3.09	3.74
IKBA	2.49	3.02
JARB	3.11	3.76
LOPE	3.16	3.82
MACA	3.10	3.75
MORA	3.07	3.71
OKEF	3.27	3.95
PHOE	2.09	2.53
SHEN	2.67	3.23
SENY	2.76	3.34
SNPA	2.99	3.62
SYCA	2.41	2.92
THIS	3.08	3.73
UPBU	3.14	3.80
VIIS	5.82	7.04
Average	2.98	3.60
Std Dev	0.70	0.85

THIEL REGRESSION FOR METHOD 3

Site	**Intercept**	**slope**	**t-value**	**% change**
ACAD	0.763	0.011	0.078	2.70
BIBE	0.647	0.033	0.000	9.14
BOWA	0.810	0.012	0.573	2.86
CORI	0.574	0.044	0.000	13.36
DOSO	0.960	0.012	0.066	2.51
GICL	0.559	0.060	0.000	17.78
HANC	0.820	0.034	0.152	7.58
GRSM	0.625	0.020	0.000	6.07
IKBA	0.273	0.133	0.000	49.36
JARB	0.540	0.131	0.003	32.75
LOPE	0.639	0.041	0.001	11.31
MACA	0.886	0.005	0.136	1.13
MORA	0.716	0.036	0.086	9.03
OKEF	0.497	0.042	0.000	14.33
PHOE	0.607	0.004	0.086	1.38
SHEN	0.742	0.009	0.080	2.37
SENY	1.080	-0.015	0.115	-2.93
SNPA	0.604	0.050	0.015	14.24
SYCA	0.706	0.005	0.652	1.29
THIS	0.588	0.064	0.001	17.81
UPBU	0.774	0.016	0.002	4.08
VIIS	3.009	-0.356	0.000	-31.01
Average	0.686	0.036		10.39
Std Dev	0.52	0.09		14.71

METHOD 3 RESULTS

	α_{inorg} $(m^2\ g^{-1})$	**α_{inorg} $(m^2\ g^{-1})$**	**α_{inorg} $(m^2\ g^{-1})$**	**α_{org} $(m^2\ g^{-1})$**	**α_{org} $(m^2\ g^{-1})$**	**α_{org} $(m^2\ g^{-1})$**	**PERCENT CHANGE α_{inorg} & α_{org}**
Site	**Lower**	**Mean**	**Upper**	**Lower**	**Mean**	**Upper**	
ACAD	2.34	2.44	2.68	2.83	2.95	3.24	14.60
BIBE	2.08	2.40	2.90	2.52	2.90	3.51	39.63
BOWA	2.47	2.58	2.81	2.99	3.13	3.41	13.75
CORI	1.91	2.35	3.17	2.31	2.85	3.84	65.91
DOSO	3.00	3.26	3.75	3.63	3.95	4.54	25.03
GICL	1.85	2.34	3.72	2.24	2.83	4.50	101.19
HANC	2.52	2.69	2.96	3.05	3.26	3.59	17.77
GRSM	2.09	2.52	3.32	2.53	3.05	4.02	59.14
IKBA	1.24	1.95	2.96	1.51	2.36	3.58	137.54
JARB	1.83	2.43	3.70	2.22	2.94	4.48	102.15
LOPE	2.08	2.36	2.86	2.52	2.86	3.46	37.09
MACA	2.73	2.84	3.01	3.30	3.43	3.64	10.25
MORA	2.22	2.55	3.07	2.69	3.09	3.71	38.07
OKEF	1.98	2.63	3.64	2.39	3.19	4.40	84.26
PHOE	1.87	1.93	2.07	2.26	2.34	2.51	10.73
SHEN	2.54	2.98	3.18	3.08	3.60	3.84	24.92
SENY	2.30	2.46	2.75	2.78	2.98	3.32	19.56
SNPA	1.92	2.28	2.87	2.32	2.76	3.47	49.56
SYCA	2.14	2.17	2.22	2.59	2.62	2.68	3.71
THIS	1.83	2.28	3.17	2.21	2.75	3.83	73.26
UPBU	2.46	2.78	3.27	2.98	3.36	3.95	32.46
VIIS	4.77	6.87	8.04	5.77	8.31	9.73	68.69
Average	2.28	2.69	3.28	2.76	3.25	3.97	43.74
Std Dev	2.34	2.44	2.68	2.83	2.95	3.24	14.60

Change in color of carbon aerosol due to particle growth