

# **Review of the IMPROVE Equation for Estimating Ambient Light Extinction Coefficients**

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## **ABSTRACT**

The Interagency Monitoring of Protected Visual Environments (IMPROVE) protocols for reconstructing ambient light extinction from measured aerosol species is the basis for evaluating compliance under the Regional Haze Rule. We review the assumptions involved in computing reconstructed light extinction using the IMPROVE protocol. This review includes examining the biases in the measurements of aerosol composition, the assumed chemical forms of aerosol species, particle hygroscopicity, and assumed mass scattering efficiencies. We present a thorough survey of estimates of mass scattering efficiencies from recent peer-reviewed literature. Furthermore, we use IMPROVE nephelometry and composition data to estimate mass scattering efficiencies using a variety of methods. The current mass scattering efficiencies applied in the IMPROVE equation are then interpreted in the context of this survey and results derived from the IMPROVE data analyses. Finally, a summary of provisional recommendations for refinements to the IMPROVE equation and a discussion of important uncertainties to consider in the assumptions is presented. Although tentative recommendations of refinements to the IMPROVE equation are presented, final refinements to the IMPROVE equation await future discussions of the results presented here.

## **1. Introduction**

The role of aerosols in visibility degradation has been the subject of research for several decades, but recently interest has intensified with attempts to quantify the optical properties of aerosols, especially because of the uncertainties surrounding the role of aerosols in climate change, and because of the need for compliance under the Regional Haze Rule. In most

instances, visibility reduction is primarily due to scattering and absorption by particles. Particle scattering and absorption properties can, with a number of limiting assumptions, be calculated using Mie theory (Mie, 1908; van de Hulst, 1981).

Compliance under the Regional Haze Rule is based on protocols for reconstructing aerosol mass and light extinction ( $b_{ext}$ ) from speciated mass concentrations. Reconstruction equations are used to estimate  $PM_{2.5}$  mass concentrations (for particles with aerodynamic diameters less than 2.5  $\mu m$ ) as well as light extinction coefficients. Dry  $PM_{2.5}$  fine mass is computed using equations 1 and 2:

$$PM_{2.5} = (NH_4)_2SO_4 + NH_4NO_3 + POM + LAC + Soil \quad (1)$$

$$Soil = 2.2Al + 2.49Si + 1.94Ti + 1.63Ca + 2.42Fe \quad (2)$$

where sulfate is assumed to be fully neutralized ammonium sulfate ( $(NH_4)_2SO_4$ ), nitrate is assumed to be in the form of ammonium nitrate ( $NH_4NO_3$ ), and organic carbon is included as particulate organic material (POM), computed by multiplying organic carbon (OC) concentrations by a molecular weight per carbon weight ratio ( $POM = R_{oc} \cdot OC$ ). Light-absorbing carbon is referred to as LAC. We use the term LAC because it is more representative of the optical properties of light-absorbing carbon rather than elemental (EC) or black carbon (BC), although these terms are often used interchangeably in the literature. Fine soil concentrations include the contributions from assumed forms of elemental species (equation 2) (Malm et al., 1994a). Mass concentrations are given in units of  $\mu g m^{-3}$ .

The light extinction coefficient ( $b_{ext}$ ) includes the contributions from light scattering by particles ( $b_{sp}$ ) and gases ( $b_{sg}$ ), and light absorption by particles ( $b_{ap}$ ) and gases ( $b_{ag}$ ):

$$b_{ext} = b_{sp} + b_{ap} + b_{sg} + b_{ag} \quad (3)$$

The only gas in the atmosphere that absorbs visible light is nitrogen dioxide,  $NO_2$ . Absorption by  $NO_2$  at a wavelength of 550 nm is computed as  $b_{ag} = 330[NO_2]$ , where the units of  $b_{ag}$  are  $Mm^{-1}$  ( $Mm^{-1} = 10^{-6} \text{ meters}^{-1}$ ) and the units of  $[NO_2]$  are ppm (Dixon, 1940; Hodkinson, 1966). Light scattering by gases ( $b_{sg}$ ) is described by Rayleigh scattering theory (van de Hulst, 1981). Rayleigh scattering is isotropic and is nearly completely polarized for light scattering at  $90^\circ$  to incoming radiation. Rayleigh scattering is proportional to molecular number density and has a strong spectral dependence ( $\lambda^{-4}$ , where  $\lambda$  is the wavelength of light). Correspondingly,  $b_{sg} = 12 Mm^{-1}$  at sea level and  $\lambda = 550 \text{ nm}$ .

Reconstructed scattering and absorption by particles as formulated in the IMPROVE (Interagency Monitoring of Protected Visual Environments) protocol are given by equations 4 and 5, respectively, assuming an externally mixed aerosol:

$$b_{sp} = 3.0 f(RH)_{AS}[AS] + 3.0 f(RH)_{AN}[AN] + 4.0 R_{OC}[OC] + 1.0 [Soil] + 0.6 [CM] \quad (4)$$

$$b_{ap} = 10.0 [LAC] \quad (5)$$

Estimates of total ambient  $b_{sp}$  in this formulation are in units of  $Mm^{-1}$  and correspond to visible wavelengths ( $\lambda \sim 550 \text{ nm}$ ). This formulation assumes that contributions to total ambient light scattering are from ammonium sulfate (AS), ammonium nitrate (AN), organic carbon (OC), soil, and coarse mass (CM). Each species has a corresponding dry mass scattering or absorption efficiency ( $\alpha$ ) in  $m^2 g^{-1}$ . The terms in the brackets correspond to mass concentrations in  $\mu g m^{-3}$ . Organic carbon mass is multiplied by an organic aerosol mass to organic carbon ratio,  $R_{oc} = 1.4$ , to estimate particulate organic matter. The effects of the uptake of water as a function of relative humidity (RH) by hygroscopic species is estimated by the  $f(RH)$  factor.

The formulation of the equations used in the IMPROVE reconstructions (equations 1–5), requires a number of assumptions. Each assumption has associated uncertainties that obviously

will have consequences for reconstructed extinction, albeit to varying degrees. The purpose of this report is to evaluate or comment on each assumption, and when possible, suggest refinements. Refinements of many of the assumptions are not suggested at this time because data do not currently exist to support modifications, or they would require further measurements to characterize. Suggested refinements do include increasing the  $R_{oc}$  factor used to compute particulate organic matter and modifying the  $f(RH)$  factor to reflect some water associated with particles below a relative humidity of 40%. Mass scattering efficiencies for ammonium sulfate and POM may also be adjusted to reflect current data. The assumptions and some related questions are listed below, along with the section in which they are discussed. Although estimating uncertainties and their combined effects on extinction from the assumptions described in the following sections is important, it is beyond the scope of this report.

- Section 2. Sampling biases: definitions and descriptions of their effects on nitrate (2.1), ammonium (2.2), carbonaceous aerosols (2.3), and elemental and coarse mass (2.4).
- Section 3. Chemical forms of species: multiplier used to compute particulate organic matter from organic carbon (3.1), nitrate as ammonium nitrate (3.2), sulfate as ammonium sulfate (3.3), soil composition (3.4), coarse mass speciation (3.5), and sea salt (3.6).
- Section 4. Hygroscopic growth curves and scattering enhancement curves ( $f(RH)$ ): hygroscopicity of species, assumed growth curves, and relative humidity ranges.
- Section 5. Mass scattering efficiencies: theoretical discussion of mass scattering efficiencies (5.1), review of methods used for deriving efficiencies (5.2), survey of reported efficiencies (5.3), and derived values using IMPROVE data (5.4).

- Section 6. Suggested refinements of IMPROVE equation and summary of comparisons of reconstructed and measured extinction using new equation.

## 2. Sampling Biases

Before investigating the assumptions involved for each species included in the IMPROVE equation, it is of interest to review any sampling issues or uncertainties related to the measurements of these species. The IMPROVE network utilizes four separate sampling modules to characterize the  $PM_{2.5}$  aerosol composition and total mass. Module A is equipped with Teflon<sup>®</sup> filters used for analysis of gravimetric  $PM_{2.5}$  mass by gravimetry and elemental composition by X-ray fluorescence (XRF). In module B, nylon filters are used to collect particles for ion analysis using ion chromatography (IC). The module is preceded by a denuder designed to capture acidic gases. Module C incorporates quartz filters for use in quantifying organic and light-absorbing carbon by thermal optical reflectance (Chow et al., 1993), and module D uses Teflon<sup>®</sup> filters to collect particles for gravimetric  $PM_{10}$  total mass measurements.

Sampling artifacts, or biases, are not uncommon with filter sampling. An artifact is defined as any increase or decrease in the material being sampled that results in a positive or negative bias in the ambient concentration measured. Artifacts can occur due to contamination issues (contamination of the filter medium or of the cassettes during transport) or adsorption of gases on the filter medium during sampling or transportation and handling. These types of artifacts are considered positive. Negative sampling artifacts arise from volatilization of gases from disassociated particles on the filter or during handling after collection (McDade et al., 2004). Sampling biases affect aerosol species differently depending on the volatility of the particles being measured and the sampling technique being used; therefore applying corrections for sampling biases is not always straightforward.

Corrections of IMPROVE data due to sampling artifacts have been applied as part of the routine IMPROVE methodology since the beginning of the network. We will briefly review the methodology IMPROVE applies for artifact correction and then discuss recent research about artifacts that are associated with specific species, such as nitrate, ammonium, and carbonaceous aerosols.

Dynamic field blanks for both Teflon<sup>®</sup> and nylon filters are collected at all of the sites. These filters are treated like network filters in that they are placed in the sampler, but no sample air is drawn through them. Concentrations on Teflon<sup>®</sup> field blanks are statistically insignificant, so no corrections are made for measurements on Teflon<sup>®</sup> filters. The concentrations measured on the nylon filter field blanks are subtracted from the measured filters. Monthly median artifact corrections are applied to the data since the change in IMPROVE data processing from seasonal to monthly in June 2002. These corrections are applied separately for each ion. Analysis of artifacts on the nylon filter suggests that sulfate ion artifacts are typically less than 10% of the ambient concentration, and nitrate artifacts range between 10–20% (McDade et al. 2004). Further discussion of nitrate artifacts, including discussions on denuder efficiency, will be presented in the next section.

Quartz field blanks are also collected at all of the sites, but quartz after-filters are collected at six sites only. The after-filters are placed behind the primary quartz filter and are designed to capture organic gases (positive artifact). Negative artifacts for carbonaceous aerosols are assumed to be insignificant compared to positive artifacts, although other studies suggest negative artifacts (volatilization) can be important (Turpin et al., 2000). Concentrations from the after-filters from the subset of sites are used to correct for positive artifacts from data at all of the sites. Monthly median values are also used for quartz filters, and each fraction of organic carbon

has a separate artifact correction. Typical artifacts for organic carbon can correspond to half of the reported ambient concentration (McDade et al., 2004). A more in-depth discussion of carbonaceous aerosol artifacts will be reviewed in section 2.3.

### ***2.1. Nitrate Sampling Issues***

The nylon filters in module B are used for analysis of particulate nitrate because the nitrate ion is retained by the filter when ammonium nitrate dissociates under conditions of high temperature and low relative humidity. Preceding the filter is an annular denuder coated with  $\text{Na}_2\text{CO}_3$  and glycerin to remove gaseous nitric acid that would otherwise be retained by the nylon filter. The denuders are serviced once per year during annual maintenance. A positive artifact could occur due to degradation of efficiency of the denuder with time, allowing nitric acid to be collected on the nylon filter. Therefore characterizing the efficiency of the denuders has been a topic of recent study (Ashbaugh et al., 2004; Yu et al., 2005a). Daily samples were collected for four consecutive weeks during different times of the year at IMPROVE sites representing areas with significant seasonal nitrate contributions to fine mass (Brigantine National Wildlife Refuge NJ, Grand Canyon National Park AZ, San Geronio Wilderness CA, and Bondville IL). At each site a combination of IMPROVE ion modules with different denuder configurations were operated. The denuder configurations were designed to compare freshly coated denuders to denuders that had been previously exposed to high levels of nitric acid. The combination also represented different coating options: from the typical IMPROVE coating, to no coating. One module was operated with no denuder at all. For all the sites, no differences in nitrate concentrations were observed due to the different denuder configurations. The denuder configuration used regularly as a part of the IMPROVE network was found to be efficiently removing  $\text{HNO}_3$  (Ashbaugh et al., 2004).

As part of the same study, the extraction efficiency of nitrate from the nylon filter was investigated (Yu et al., 2005a). Typically, basic solutions (i.e., sodium bicarbonate) are used to extract nitrate on nylon filters; however, this leads to interference from  $\text{Na}^+$  ions during ion chromatography. Instead, the use of deionized water for extraction of nylon filters has been investigated. Data from the study described above suggest that deionized water extraction with ultrasonification efficiently extracts nitrate and sulfate ions from nylon filters (Yu et al., 2005a) and successfully avoids issues of  $\text{Na}^+$  and  $\text{NH}_4^+$  interference during IC analysis.

While the previous discussions suggest that nitrate measurements and artifacts from denuder-nylon filter configurations are fairly well understood, the effects of nitrate loss on Teflon<sup>®</sup> filters remain a sampling issue and have important implications for measurements of fine mass concentrations by gravimetry. Hering and Cass (1999) investigated the effects of nitrate loss from the Federal Reference Method (FRM) measurements of  $\text{PM}_{2.5}$  mass on Teflon<sup>®</sup> filters. They found that nitrate concentrations were 28% lower on Teflon<sup>®</sup> filters compared to nylon filters. Ammonium nitrate particles are volatile and disassociate to form nitric acid gas and ammonia gas, and this reaction is very sensitive to temperature, pressure, and relative humidity. Changes in these parameters during sampling can cause significant losses of nitrate and ammonium from the sampling media, as Teflon<sup>®</sup> filters do not retain nitric acid as nylon filters do. Correcting mass concentrations for lost nitrate is impossible because knowledge of the history of the equilibrium of ammonium nitrate/nitric acid and ammonia gases at the temperature, pressure, and relative humidity that the filter substrate experienced during the sampling period is required. Diurnal and seasonal trends in nitrate loss were observed by Hering and Cass (1999), as well as Ashbaugh and Eldred (2004) who performed a similar study. The implications for the negative artifact of sampling volatile particles on Teflon<sup>®</sup> filters are obvious.



Under-reporting nitrate concentrations results in an overemphasis of nonvolatile species such as dust and sulfate. Specific to this report, comparisons of reconstructed fine mass using the IMPROVE equation and gravimetric fine mass could be highly affected by significant underestimations of nitrate due to the volatilization of ammonium nitrate from the Teflon<sup>®</sup> filter used for gravimetric analysis.

## **2.2. *Ammonium Sampling Issues***

Although ammonium is not routinely analyzed at IMPROVE, it is important to review the sampling issues related to ammonium to understand measurements made during special studies and by other researchers. The effects of ammonium loss from filter media were studied as part of the nitrate loss study described above (Yu et al., 2005b). Losses of ammonium are affected by sample location (urban versus rural), meteorological sampling conditions (e.g., relative humidity, temperature), chemical composition of the sampled aerosol, and gas-to-particle partitioning. Volatilization of ammonium nitrate can lead to ammonium loss from filter media, as can reaction of ammonium nitrate with strong acids. Also, when ammonium nitrate is captured by the nylon filter, nitrate is bound by the filter but ammonium can volatilize. Two filter pack configurations were designed to study ammonium loss: denuded nylon-nylon (N-N) and denuded Teflon<sup>®</sup>-nylon (T-N). Ammonium loss from nylon filters was observed at the four sites where measurements were performed (ranging from ~ 10% to 52%), suggesting a single nylon filter is not sufficient for capturing ammonium nitrate. Results from the N-N and T-N filter pack systems suggest that the T-N configuration is as good as, or better than, the N-N configuration for ammonium retention (Yu et al., 2005b). Applying a correction factor for the negative bias in ammonium would require estimates of ammonium loss at each site, which is a difficult task. Understanding the sampling biases for ammonium is very important, especially during special studies when

$\text{NH}_4^+$  is measured, because its concentrations are very useful in predicting the chemical form of aerosol species, which reduces the uncertainty in reconstructed fine mass and light extinction.

### **2.3. *Carbonaceous Aerosol Sampling Issues***

Understanding sampling biases for carbonaceous aerosols is important for accurately quantifying the concentrations of organic and light-absorbing carbon and has been the focus of several studies. Before we discuss the sampling issues related to quantifying the concentrations of carbonaceous aerosols, we provide a brief review of the analytical technique used by the IMPROVE network. The Desert Research Institute (DRI) thermal/optical reflectance (TOR) technique used for IMPROVE (Chow et al., 1993) is one of the thermal methods available to analyze carbonaceous aerosols (also referred to as evolved gas analysis). Typically, for thermal methods the sample filter is heated in a step-wise manner in different atmospheres (i.e., oxygen or helium) and the volatilized carbon from the filter is detected. For each temperature regime a carbon concentration is determined, with the lower temperature concentrations summed for organic carbon (O1, O2, O3, O4, and OP) and the highest temperature regime corresponding to what is typically referred to as elemental or light-absorbing carbon (E1, E2, and E3). A more representative nomenclature would refer to this high temperature carbon as refractory carbon; because of its low volatility it does not evolve without oxidants at lower temperatures. The pyrolysis of organic carbon on the filter as the temperature is increased can contribute to the concentrations of refractory carbon. To account for this effect, the filter is monitored by the reflectance (or transmittance, as is used in thermal optical transmittance methods) of laser light, which decreases when the filter darkens due to pyrolysis. Once oxygen is introduced into the chamber, the pyrolyzed carbon combusts, the filter lightens, and the laser light returns to its original intensity. After this point, the amount of carbon measured is associated with refractory (light-absorbing) carbon. The split between organic and light-absorbing carbon is based on the

conditions for which this process occurs and is dependent on refractory properties of both pyrolyzed and light-absorbing carbon. Huebert and Charlson (2000) discuss several of the uncertainties associated with thermally defined carbonaceous aerosols, especially pointing out that as these methods differ from one laboratory to another (e.g., temperatures regimes, rate of temperature changes, carrier gases in the chamber), making it very difficult to compare results. In section 5.3 we will discuss in more detail the issues related to the definitions of OC and LAC by this method.

Turpin et al. (2000) review the difficulties inherent in measuring particulate organic carbon. Interference from gaseous and condensable organics can result in sampling errors due to interactions with the filter media. Positive artifacts arise from adsorption of organic gases onto the filter, and negative artifacts occur due to volatilization of particulate organics. They report artifact contributions to organic carbon mass ranging from -80% to +50%. Positive and negative artifacts occur simultaneously, which makes correcting for them difficult. Subramanian et al. (2004) utilized several sampling approaches in an attempt to estimate these artifacts. Depending on the types of denuders and filter configurations, they found that positive artifacts could be eliminated, or that artifacts may depend on sampling duration, and probably also depend on sampling location. Huebert and Charlson (2000) state that systematic errors on the order of  $\pm 80\%$  are possible using thermal methods.

The IMPROVE network assumes negative artifacts are insignificant and only corrects for positive artifacts that are estimated from quartz after-filters collected at six sites (Chiricahua AZ, Grand Canyon AZ, Yosemite CA, Okefenokee GA, and Mount Rainier WA) (McDade et al., 2004). The after-filters are placed directly behind the primary quartz filter. Quartz filter field blanks are collected at every site and are only used for identification of problems. Field blank

filters and the after-filters have similar concentrations; however, the after-filters are used because they are exposed to the same air sample as the primary filter. Artifacts are determined separately for each fraction of organic and light-absorbing carbon from TOR analyses. McDade et al. (2004) evaluate the artifacts for O<sub>3</sub> and E<sub>2</sub>, the more prominent fractions of OC and LAC. The O<sub>3</sub> artifact represents nearly half of the reported ambient concentration, and the E<sub>2</sub> artifact decreased to less than 10% of ambient concentrations after the IMPROVE sampler switched to version 2 in 2000. Although some spatial and seasonal differences are observed in the artifact estimates (the Okefenokee site has higher artifacts than the other sites, and summer appears to have higher O<sub>3</sub> and E<sub>2</sub> artifacts than winter), the same median artifact value is applied to the entire network. Based on studies performed at the University of California, Davis, it appears that the positive artifact is due to saturation of the quartz filter from exposure to ambient organic acids in the atmosphere, and would probably affect all filters sent to the field similarly. These results are substantiated by Subramanian et al (2004) who found that quartz after-filters provided a robust estimate of positive artifacts for sampling durations of 24 hours, long enough for equilibrium to be achieved. However, if some volatile organic compounds are being lost from the primary filter to the after filter, this correction could be too large.

#### ***2.4. Issues Related to Elemental Species and Coarse Mass***

An X-ray fluorescence (XRF) technique is used to determine concentrations of trace elements with atomic mass number (Z) from 11 to 82 (Na-Pb). White et al. (2004) report on the uncertainties and detection limits for trace elements. Lower Z elements (e.g., Na, Mg) have much higher minimum detection limits (White, personal communication), and therefore detectable amounts of those elements can be much more difficult to obtain. Other uncertainties in trace elements, especially those corresponding to coarse mode aerosols, arise due to uncertainties in the flow rates of the samplers. The size cut of the cyclone used to collect and separate PM<sub>2.5</sub>

aerosols is very sensitive to the flow rate of the sampler. Variations in the flow rate (e.g., due to clogged inlets) can have significant impacts on the size range of aerosols being collected and termed “fine”. This issue can be important when interpreting fine mass versus coarse mass because the soil contribution in the IMPROVE equation typically corresponds to the tail of coarse mode mineral aerosols. The size distribution of the coarse mode aerosols can vary significantly, as shown by Hand et al. (2002). Over a four-month study in Big Bend National Park, the volume mean diameter of the coarse mode ranged from  $\sim 2 \mu\text{m}$  to  $5 \mu\text{m}$ . The tail of this mode that is measured as part of the  $\text{PM}_{2.5}$  mass is obviously sensitive to the size distribution statistics of the coarse mode aerosols, which complicates any correction that may be applied to data with flow rate issues. The interpretation of coarse soil as fine soil has important consequences for reconstructed mass as well as reconstructed light extinction because the applied optical properties are significantly different for each mode (as will be seen in section 5).

### **3. Chemical Form of Species in the IMPROVE Equation**

Aerosol species included in the reconstructed mass and IMPROVE reconstructed extinction equation are assumed to be in specific chemical forms and size ranges. In this section we investigate whether these assumptions are appropriate. In particular we investigate the speciation of POM, sulfate, soil, nitrate, coarse mass, and sea salt.

#### **3.1. *Particulate Organic Material (POM)***

Accurate estimates of particulate organic material (POM) are required in order to compute  $\text{PM}_{2.5}$  mass closure and to estimate optical properties such as light scattering. Estimating the contributions of organic carbon aerosol to mass or scattering requires an estimate of the total mass associated with organic carbon. The organic carbon multiplier ( $R_{oc}$ ) used to estimate particulate organic material (POM) is an estimate of the average molecular weight per carbon weight for organic carbon aerosol and takes into account contributions from other

elements associated with the organic matter, such as N, O, and H. It is highly spatially and temporally variable. It is impossible to determine which and how many elements are associated with POM without knowing the chemical formula of the organic compound, and it is common for ~ 20–40 % of organic aerosol mass to remain unidentified (Turpin and Lim, 2001).

Because the organic compounds that compose POM are largely unknown, the approach for taking into account other elements in POM mass has been to apply an average multiplier. As Turpin and Lim (2001) review, the often-used value of 1.4 dates back to samples collected in Pasadena CA in the early 1970s and 1980s (Grosjean and Friedlander, 1975; White and Roberts, 1977; Van Vaeck and Van Cauwenberghe, 1978; Countess et al., 1980; Japar et al., 1984). More recently, Turpin and Lim (2001) have reviewed several estimates of  $R_{oc}$  in terms of the types of compounds known to compose POM, and that review will not be repeated here. However, to summarize their findings, they recommend a factor of  $1.6 \pm 0.2$  for urban organic aerosols, a factor of  $2.1 \pm 0.2$  for non-urban organic aerosols, and values ranging from 2.2 to 2.6 for samples with impacts from biomass burning. Russell (2003) used Fourier Transform Infrared (FTIR) spectroscopy to estimate POM from the number of carbon bonds present and the molecular mass of each functional group associated with the carbon bonds. Over 90% of  $R_{oc}$  from estimates from samples in northeastern Asia and the Caribbean were between 1.2 and 1.6, with mean values below 1.4. Values of  $R_{oc}$  like those reported by Turpin and Lim (2001) and Russell (2003) are derived using techniques that depend on the functional groups and molecular compounds of organic carbon aerosols. El-Zanan et al. (2005) used solvent extractions from archived IMPROVE filters at five sites to directly measure POM mass and carbon content and derive an average  $R_{oc}$  of 1.92 (range of 1.58–2.58). They also used a mass balance approach to estimate the  $R_{oc}$  ratio using the IMPROVE data that resulted in an average value of 2.07 across the

IMPROVE network. Other types of methods result in similar findings. Reconstruction of fine mass and light scattering coefficients allow estimates of  $R_{oc}$  to be derived, as was done in a two-month study in Yosemite National Park by Malm et al. (2005a) where POM dominated the fine mass. They found that an  $R_{oc}$  factor of approximately 1.8 allowed for closure in fine mass and light scattering coefficients for periods that encompassed both pristine conditions as well as the impacts of biomass burning and regional haze. Poirot and Husar (2004) found better agreement between measured and reconstructed fine mass by applying an  $R_{oc}$  factor of 1.8 during a biomass burning event in the New England and mid-Atlantic state regions. However, Day et al. (2005) sampled fresh biomass smoke in a burn chamber and found  $R_{oc}$  values near 1.0.

Previous investigators have attempted to estimate  $R_{oc}$  from comparisons of gravimetric and reconstructed mass; however, a number of issues arise with this type of analysis. These issues originate from the uncertainties in the assumptions involved in the formulation of reconstructed mass and have been discussed in the literature (Andrews et al., 2000; Rees et al., 2004; Tanner et al., 2004; El-Zanan et al., 2005); therefore they will be mentioned only briefly here. Some of the uncertainties inherent in reconstructed mass equations include the assumed form of aerosol species. For example, sulfate is typically assumed to be in the form of fully neutralized ammonium sulfate, although in reality the form of sulfate could be different (more acidic). Nitrate is assumed to be in the form of ammonium nitrate, and as we will show later, this assumption may be inappropriate under certain conditions. Water may be retained by hygroscopic species on the filters used to determine gravimetric  $PM_{2.5}$  mass. Soil mass requires an assumption of soil composition as defined by equation 2, and OC concentrations may be affected by sampling artifacts and analytical issues regarding the method-dependent definitions of organic and light-absorbing carbon. El-Zanan et al. (2005) performed sensitivity studies

related to these issues and found that values of  $R_{oc}$  varied between 1.74 and 2.2, although they believe the lower values are not realistic. They also found higher values of  $R_{oc}$  determined from mass balance methods in the summer (2.33) compared to the winter (1.87).

The approach implemented here for estimating  $R_{oc}$  from IMPROVE data applies an ordinary least square (OLS) multiple-linear regression (MLR) analysis using:

$$PM_{2.5,i} = a_1[(NH_4)_2SO_4]_i + a_2[NH_4NO_3]_i + a_3[OC]_i + a_4[LAC]_i + a_5[soil]_i + a_6[sea\ salt]_i \quad (6)$$

The results of the regression analysis for each site are presented in Appendix 1, including a statistical summary of gravimetric mass and aerosol species mass concentrations (minimum, maximum, mean, and standard deviation). Also presented for each site is the fractional contribution of each species to gravimetric mass, and a comparison between reconstructed and gravimetric mass. The statistically significant (95% level) regression coefficients for each site are reported in Table 1, with the mean and standard deviation of the coefficients listed in the final two rows. If the mass for each species (other than POM) is accurately estimated and the regression is unbiased, then the regression coefficient for a given species should equal 1. The regression coefficient for POM corresponds to the  $R_{oc}$  factor. Scatter plots of gravimetric and reconstructed mass are presented in Appendix 1. Reconstructed mass has been computed using equation 1 and using the regression coefficients derived from equation 6.

**Table 1. Statistically significant (95%) regression coefficients using the ordinary least square multiple-linear regression analysis (equation 6). Site code is in the first column. The remaining columns correspond to coefficients associated with ammonium sulfate (AS), ammonium nitrate (AN), particulate organic matter (POM), light absorbing carbon (LAC), soil, and sea salt, respectively. Insignificant coefficients are replaced with “.”.**

Site	AS	AN	POM	LAC	Soil	Sea Salt
ACAD	1.23	.	1.85	.	1.40	1.02
ADPI	1.23	0.49	1.67	.	1.68	.
AGTI	1.05	0.67	1.63	.	1.09	.
AREN	1.08	0.80	1.70	2.36	0.50	.
BADL	1.14	0.65	1.98	.	1.06	.
BALD	1.29	0.75	1.76	.	1.18	.
BAND	1.21	0.54	1.52	.	1.12	.



BIBE	1.08	0.74	1.84	.	1.02	.
BLIS	1.25	0.54	1.74	.	1.06	.
BLMO	1.00	1.09	1.27	.	1.09	.
BOAP	1.18	0.68	1.71	0.65	1.30	.
BOND	0.98	1.01	1.28	.	1.17	.
BOWA	1.18	0.84	1.88	.	1.32	.
BRCA	1.25	0.50	1.40	1.16	1.41	.
BRET	1.16	0.70	1.53	.	1.51	.
BRID	1.31	.	1.73	.	1.22	.
BRIG	1.08	0.54	1.99	.	1.18	0.95
BRLA	0.97	.	1.91	.	1.52	.
BRMA	1.04	.	1.42	.	1.10	.
CABA	1.17	0.56	1.16	2.52	1.10	1.19
CABI	1.46	.	2.05	.	1.19	.
CACO	1.25	0.51	1.62	.	1.31	0.82
CACR	1.11	0.50	1.67	.	1.06	.
CADI	1.22	0.63	1.40	2.77	1.05	.
CANY	1.10	0.55	1.74	.	1.21	.
CAPI	1.04	0.50	2.07	.	1.21	.
CEBL	1.11	1.14	2.07	.	1.11	.
CHAS	1.17	.	1.44	0.90	0.99	0.59
CHER	1.11	0.98	1.43	.	1.57	.
CHIR	1.28	0.79	1.36	1.59	1.15	0.88
CLPE	1.25	.	1.71	.	1.38	.
COGO	1.10	0.57	1.63	.	1.10	.
COHI	1.21	0.63	1.92	.	1.68	.
COHU	1.01	0.33	1.71	.	1.16	.
CORI	1.33	0.60	1.59	.	1.14	0.95
CRES	1.00	0.98	2.16	.	1.14	.
CRLA	1.68	.	1.68	0.48	1.10	1.10
CRMO	1.40	0.71	1.96	.	1.25	.
DENA	1.39	.	1.89	.	0.85	1.13
DEVA	1.05	0.70	1.65	.	1.25	.
DOME	0.95	0.81	1.77	.	1.36	.
DOSO	1.16	.	1.58	.	1.00	.
ELDO	1.13	0.82	1.44	.	1.05	.
ELLI	1.07	0.97	2.07	.	1.10	.
EVER	1.00	.	1.44	4.40	1.20	.
FLAT	1.33	.	1.74	.	1.23	.
FOPE	1.10	0.49	2.06	.	1.27	.
GAMO	1.20	.	1.66	.	1.29	.
GICL	1.22	1.79	1.54	.	1.09	.
GLAC	1.16	0.93	1.58	1.43	1.17	.
GRBA	1.45	0.58	1.70	.	1.35	.
GRCA	1.29	.	1.36	4.66	1.27	.
GRGU	1.10	.	1.65	3.90	0.99	.
GRII	1.04	0.96	1.73	.	1.34	.

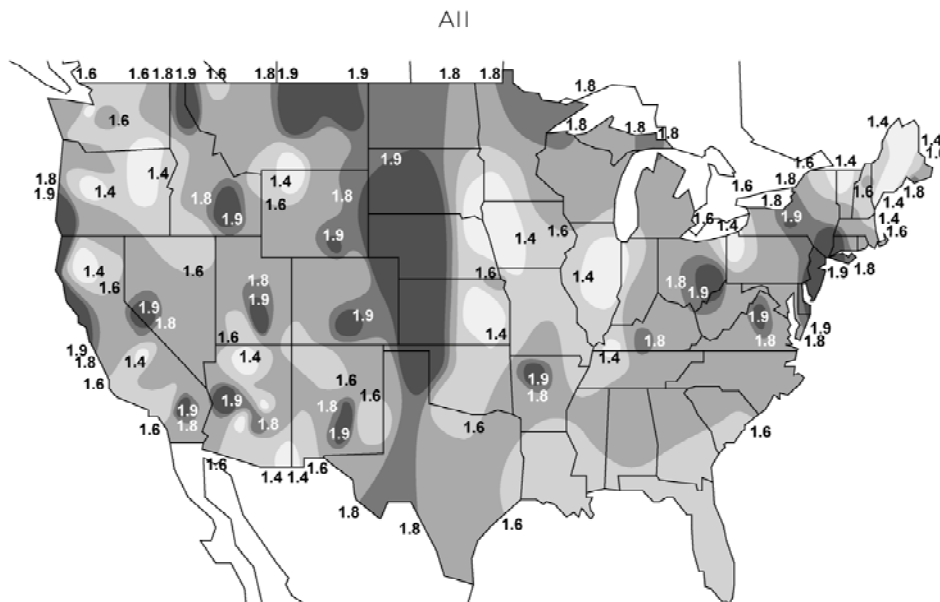
GRSA	1.34	.	1.98	.	1.16	.
GRSM	1.23	.	1.71	.	1.02	.
GUMO	1.14	.	1.66	.	1.02	1.96
HALE	1.01	2.05	1.45	.	0.97	.
HAVO	1.61	.	1.45	.	1.15	.
HECA	1.01	0.69	1.52	.	1.29	.
HEGL	1.09	0.69	1.75	.	1.19	.
HILL	1.36	.	2.04	.	1.42	.
HOOV	1.37	.	2.08	.	1.59	.
IKBA	1.12	0.33	1.86	.	1.61	.
INGA	1.12	.	1.36	.	1.27	.
ISLE	1.00	0.82	1.67	.	0.72	0.51
JARB	1.23	0.99	1.49	.	1.29	.
JARI	1.22	0.52	1.66	1.39	0.73	.
JOSH	1.25	0.74	2.00	.	1.03	.
KAIS	1.11	1.03	1.81	.	1.27	.
KALM	2.25	.	2.16	.	1.64	.
LABE	0.86	1.48	1.72	.	1.41	0.85
LASU	1.10	1.01	1.54	.	1.03	.
LAVO	1.52	0.43	1.41	1.42	1.17	.
LIGO	1.24	.	1.75	.	1.07	.
LIVO	1.26	0.73	1.79	.	1.17	.
LOST	1.16	0.93	1.80	.	1.37	.
LYBR	1.10	0.37	1.63	.	1.02	.
MACA	1.01	0.22	1.81	.	1.08	.
MELA	1.08	0.80	1.84	.	1.16	.
MEVE	1.32	1.27	1.45	.	1.00	.
MING	1.27	0.85	1.45	.	1.14	.
MKGO	1.39	0.66	1.38	.	0.40	.
MOHO	1.36	.	1.77	.	1.11	1.23
MOMO	1.08	.	2.04	.	1.35	.
MONT	1.48	.	1.74	11.08	2.21	.
MOOS	1.13	0.62	1.66	0.68	1.50	1.04
MORA	1.30	0.76	1.59	1.55	0.90	1.14
MOZI	1.25	.	1.70	.	1.11	.
NEBR	1.21	0.66	2.06	.	1.20	.
NOAB	0.82	.	1.26	4.98	1.30	.
NOCA	1.62	.	1.48	.	1.09	1.60
NOCH	.	.	1.71	.	2.64	.
OKEF	1.12	.	1.44	2.51	1.01	0.62
OLTO	1.15	0.97	1.29	0.97	1.01	0.66
OLYM	1.15	0.96	1.73	.	1.36	0.80
PASA	1.54	.	1.53	.	1.21	2.85
PEFO	1.35	0.77	1.76	2.13	1.18	.
PHOE	1.28	0.68	1.29	0.78	1.13	.
PINN	1.32	0.64	1.66	0.89	1.28	1.15
PMRF	1.22	0.54	1.36	.	1.02	.

PORE	1.28	0.74	1.93	.	1.26	1.04
PRIS	0.93	1.00	1.30	.	1.19	0.62
PUSO	1.23	0.76	1.35	0.82	1.07	1.21
QUCI	1.30	0.64	1.95	.	0.40	.
QURE	1.05	0.28	1.63	2.12	0.87	.
QUVA	1.17	0.79	2.00	.	1.37	.
RAFA	1.39	0.95	1.57	.	0.96	1.20
REDW	1.23	1.59	2.16	.	1.25	0.92
ROMA	1.19	.	1.60	.	1.20	0.91
ROMO	1.27	.	1.71	.	1.34	.
SACR	1.30	0.97	1.45	.	1.55	2.80
SAFO	1.08	0.99	1.63	.	0.80	.
SAGA	1.12	0.60	1.57	.	0.91	.
SAGO	1.00	0.91	1.27	.	1.07	1.46
SAGU	1.25	0.26	1.50	1.29	1.26	.
SAMA	1.17	.	1.58	.	1.42	.
SAPE	1.08	.	1.57	.	1.23	.
SAWE	1.30	.	1.50	.	1.29	.
SAWT	1.84	.	1.74	.	1.20	.
SENE	1.16	0.70	1.81	.	0.72	.
SEQU	1.29	0.91	1.35	2.93	0.98	.
SHEN	1.11	.	1.97	.	0.87	.
SHRO	1.22	.	1.74	.	1.10	.
SIAN	1.10	0.38	1.37	2.25	1.37	.
SIKE	1.18	.	1.53	.	1.15	.
SIME	1.43	.	1.28	.	1.32	1.16
SIPS	1.04	.	1.69	.	1.04	.
SNPA	1.33	0.64	1.71	.	1.23	1.23
SPOK	1.24	0.71	1.66	.	1.28	.
STAR	1.61	.	1.11	.	1.70	.
SULA	1.58	.	1.63	.	1.15	.
SWAN	1.13	.	1.75	.	1.33	.
SYCA	1.43	0.44	1.59	.	1.10	.
TALL	1.05	0.84	1.12	3.34	1.51	.
THBA	1.00	0.77	1.84	.	1.04	.
THRO	1.13	0.81	1.85	.	1.01	.
THSI	1.75	.	1.28	.	1.52	.
TONT	1.17	0.67	1.92	.	1.09	.
TRCR	1.59	.	1.91	.	0.62	.
TRIN	2.08	.	1.16	.	1.15	1.03
TUXE	2.20	.	1.91	3.09	0.62	1.05
ULBE	0.98	0.91	1.99	.	1.17	.
UPBU	1.10	0.67	1.94	.	0.88	.
VIIS	0.75	2.34	1.44	.	1.31	.
VILA	1.07	1.02	1.27	.	0.80	.
VOYA	1.22	1.01	1.83	.	1.32	0.89
WASH	1.16	0.82	1.70	0.87	1.04	0.82

WEMI	1.41	.	1.68	.	1.21	.
WHIT	1.23	1.04	2.19	.	1.23	.
WHPA	1.13	0.96	1.57	.	1.09	.
WHPE	1.05	.	1.66	0.87	1.31	.
WHRI	1.32	.	1.74	.	1.27	.
WICA	1.06	0.55	1.93	.	1.17	.
WIMO	1.23	0.80	1.55	.	1.18	.
YELL	1.12	0.62	1.54	2.57	1.30	.
YOSE	1.15	0.74	1.68	.	1.26	0.99
ZION	1.34	0.64	1.63	.	1.28	.
<b>Avg</b>	1.22	0.78	1.66	2.28	1.18	1.12
<b>Std Dev</b>	0.22	0.32	0.24	2.00	0.26	0.51

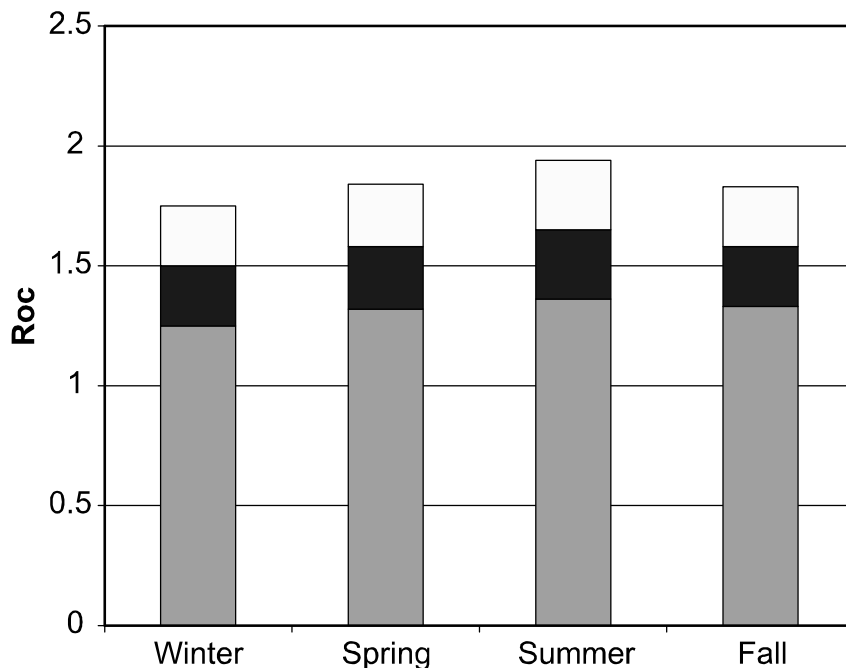
The mean value of  $R_{oc}$  derived from equation 6 (see Table 1) is shown as a summary in Figure 1. There are clear spatial trends in the  $R_{oc}$  factor. The highest coefficients of 1.8–2.0+ are just east of the Rocky Mountain range and may be reflective of wild and prescribed fire activity to the west of this region. Both Malm et al (2005a) and Poirot and Husar (2004) derived  $R_{oc}$  factors near 1.8 at sites with air masses influenced by aged biomass smoke, and higher  $R_{oc}$  values corresponding to biomass burning were reported by Turpin and Lim (2001). Three of the four sites in Alaska (not shown) also have coefficients near 1.9, with the exception of Simeonof National Wildlife Refuge on the Alaskan peninsula. Other remote locations have  $R_{oc}$  values near 1.8. Coefficients ranging from 1.6 to 1.8 are found around most of the United States, with distinct regions having coefficients less than 1.6. Regions in the Northwest, interior Midwest, and Northeast are this category.

**Figure 1. Mean value of  $R_{oc}$  multiplier derived from an ordinary least square multi-linear regression analysis (equation 6).**



The average coefficient over all sites is  $R_{oc} = 1.66 \pm 0.24$ , with all 158 sites having significantly valid coefficients. On a seasonal basis the coefficients do not vary significantly, as seen by the mean and standard deviation values presented in Figure 2. The mean summer value ( $R_{oc} \sim 1.7$ ) is near the average value of 1.66, while the lowest values were derived during winter ( $R_{oc} \sim 1.5$ ). Some seasonality in  $R_{oc}$  is expected, with higher values in summer due to photochemical reactions from warmer temperatures and higher solar insolation. Results from these analyses suggest that the existing  $R_{oc}$  value of 1.4 in the IMPROVE equation is probably too low. Based on estimates reported from other studies and the analysis performed here, we recommend a  $R_{oc}$  value in the range of 1.7–1.8.

**Figure 2.** Mean seasonal values of  $R_{oc}$  for all sites. Standard deviations are also shown as upper and lower bars.



### 3.2. Nitrate

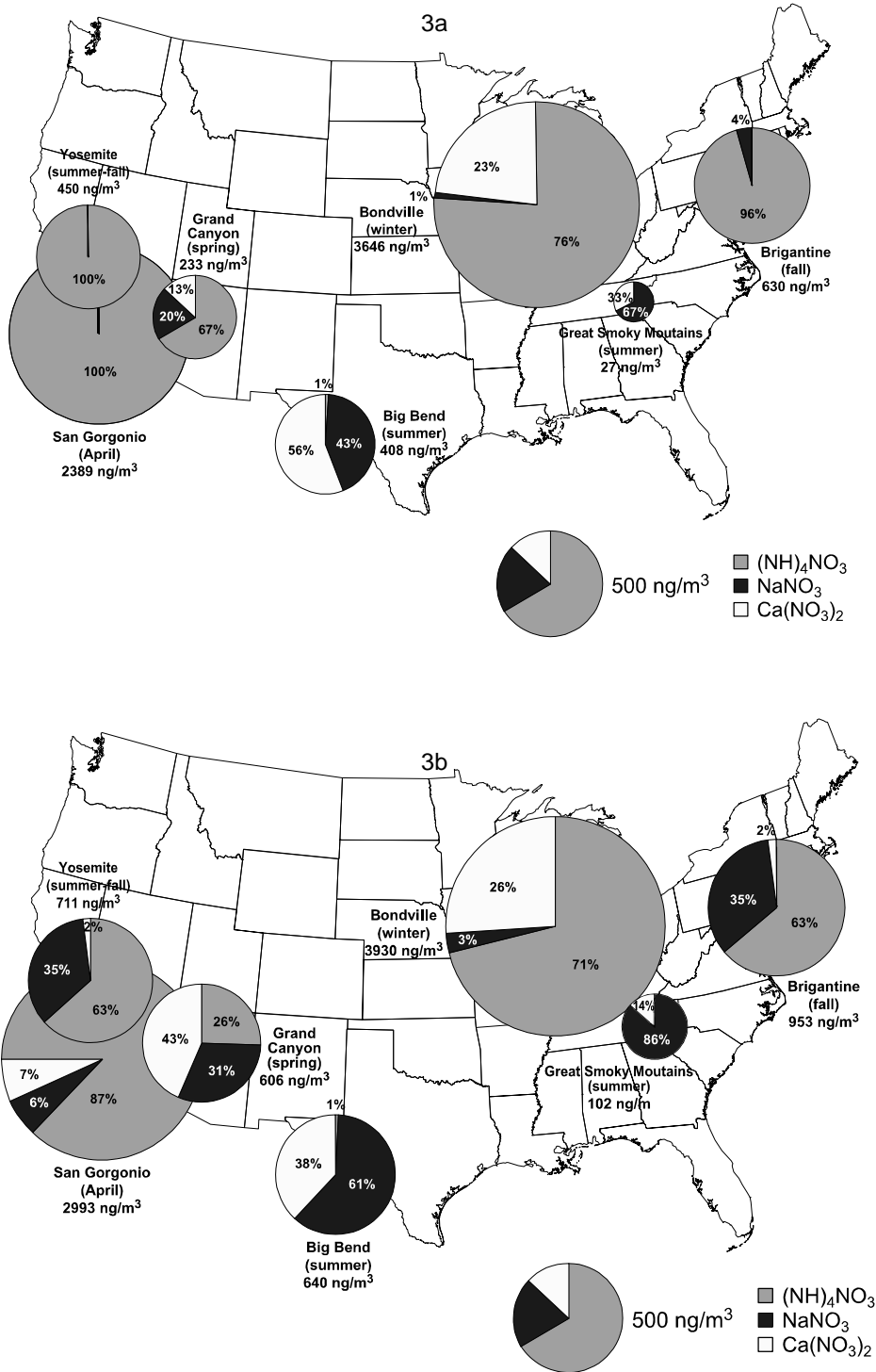
Nitrate is an important seasonal contributor to particulate matter at many locations in the United States. Nitrate is assumed to be present in the fine mode as ammonium nitrate; however, it can be present in the coarse mode also. Field studies at several IMPROVE monitoring sites investigated the speciation and size of aerosol nitrate using a size-resolved impactor (MOUDI), and have shown that nitrate is often present as coarse mode nitrate. Lee et al. (2004a) computed the speciation of nitrate by first calculating leftover ammonium from  $(\text{NH}_4)_2\text{SO}_4$ . Excess ammonium is then associated with nitrate as  $\text{NH}_4\text{NO}_3$ , and any excess nitrate not associated with ammonium is determined. Sodium is first combined with  $\text{Cl}^-$  as sea salt, and any excess sodium

is combined with excess nitrate ( $\text{NaNO}_3$ ). If additional nitrate is left over, it is associated with crustal compounds such as  $\text{Ca}^{+2}$  or  $\text{Mg}^{+2}$  ( $\text{Ca}(\text{NO}_3)_2$  or  $\text{Mg}(\text{NO}_3)_2$ ).

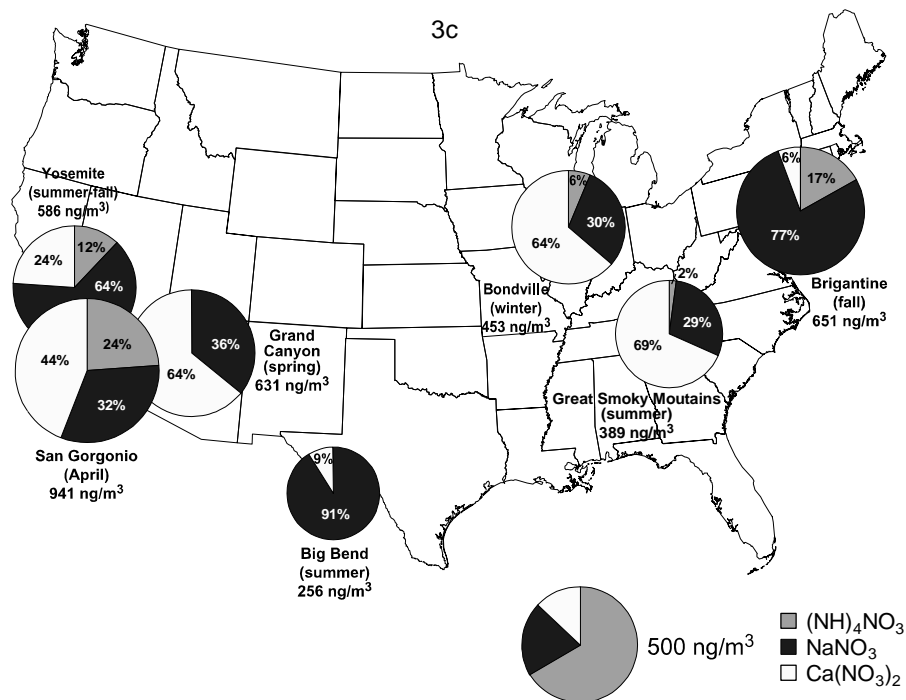
$\text{NH}_4\text{NO}_3$  forms from the reaction of gas phase ammonia and nitric acid and is more favorable in regions with high ammonia and nitric acid concentrations and low sulfate concentrations. The equilibrium reaction producing aerosol-phase  $\text{NH}_4\text{NO}_3$  is sensitive to small changes in temperature and relative humidity that can shift the equilibrium to the gas phase. However, the reaction of gas phase nitric acid with sea salt or calcium carbonate is not an equilibrium reaction and results in nitrate being transferred to the aerosol phase and associated with coarse mode particles.

Two estimates of fine mode nitrate for the three forms discussed above have been computed by summing the nitrate in the MOUDI size bins corresponding to  $D_p < 1$  and  $D_p < 3.2$   $\mu\text{m}$  (although the MOUDI does not have a 2.5  $\mu\text{m}$  size bin, we assume that the fine mode corresponding to  $D_p < 3.2$   $\mu\text{m}$  most closely represents the IMPROVE  $\text{PM}_{2.5}$  measurement). Fine mode nitrate estimates are presented in Figures 3a and 3b, respectively. Coarse mode nitrate is computed in a similar manner for  $D_p > 1$   $\mu\text{m}$  and is presented in Figure 3c. The size of the pie charts in Figure 3 represents the total nitrate concentration in that size range (a doubling of the pie size corresponds to 8 times the concentration), and the total nitrate concentration in that size mode is listed beside its chart.

Figure 3. (a) Fine mode ( $D_p < 1 \mu\text{m}$ ) nitrate speciation of  $\text{NH}_4\text{NO}_3$ ,  $\text{NaNO}_3$  and  $\text{Ca}(\text{NO}_3)_2$  at several IMPROVE sites. The size of the pie chart reflects the magnitude of the concentration of total nitrate in this size mode, which is listed under each chart. (b) Same as (a) but for  $D_p < 3.2 \mu\text{m}$ . (c) Same as (a) but for coarse mode ( $D_p > 1 \mu\text{m}$ ).







The data presented in Figure 3a demonstrate that fine mode ( $D_p < 1 \mu\text{m}$ ) nitrate is not always speciated as ammonium nitrate. For example, during summer in Big Bend National Park TX, only 1% of fine mode nitrate was in the form of ammonium nitrate, and during winter in Bondville IL, ammonium nitrate accounted for 76% of the nitrate species in the fine mode while  $\text{Ca}(\text{NO}_3)_2$  accounted for 24%, even though the fine mode total nitrate concentrations in Bondville are considerably higher than the other sites. During spring in the Grand Canyon National Park AZ,  $\text{NH}_4\text{NO}_3$  was 67% of fine mode nitrate, and during summer at Great Smoky Mountains National Park TN, it was only 33%. However, in both San Gorgonio National Park CA (spring), and Yosemite National Park CA (summer), the fine mode nitrate was completely speciated as ammonium nitrate, and in Brigantine NJ (autumn), it was nearly all ammonium nitrate (96%). For the sites where ammonium nitrate was not the dominant form of nitrate in the fine mode, the contribution of nitrate ion to  $\text{PM}_{2.5}$  mass concentration was less than  $\sim 20\%$ .

Coarse mode speciation of nitrate at these sites (see Figure 3c) reflects the reaction pathways of nitric acid with mineral aerosols discussed earlier. For example, at several of the sites (Brigantine NJ, Yosemite National Park CA, and Big Bend National Park TX) coarse mode nitrate was associated with sea salt as  $\text{NaNO}_3$ . At Big Bend National Park TX, nitrate had replaced  $\text{Cl}^-$  in sea salt ( $\text{NaNO}_3$ ) (Lee et al., 2004a) and MOUDI impactor data showed that nitrate and sodium had similar size distributions. However, at other sites nitrate was associated with crustal material ( $\text{Ca}(\text{NO}_3)_2$ ) (Bondville IL, Great Smoky Mountains National Park TN, and Grand Canyon National Park AZ).

At many of the sites, the nitrate concentrations in the coarse mode were higher than in the fine mode. For example, data from the Grand Canyon National Park (spring) indicates that concentrations of nitrate in the coarse mode were almost three times higher than nitrate in the fine mode, and roughly 14 times higher in Great Smoky Mountains National Park. Nitrate concentrations at Yosemite National Park were comparable for both modes, similarly for Brigantine NJ. The only sites where fine mode nitrate mass was considerably higher than coarse mode nitrate mass were Bondville IL and San Geronio CA.

The two estimates of fine mode nitrate for  $D_p < 1 \mu\text{m}$  and  $D_p < 3.2 \mu\text{m}$  in Figures 3a and 3b, respectively, were computed to demonstrate the importance of the size cut of the impactor on the interpretation of nitrate speciation. For example, shifting the fine mode cutpoint from  $1 \mu\text{m}$  to  $3.2 \mu\text{m}$  for data from the Brigantine NJ site results in the speciation of nitrate changing from predominantly  $\text{NH}_4\text{NO}_3$  (96%), to 63%  $\text{NH}_4\text{NO}_3$  and 35%  $\text{NaNO}_3$  because more of the coarse mode tail is being included (see Figures 3a–3c). Similar behaviors are observed at Grand Canyon National Park AZ, Big Bend National Park TX, and Great Smoky Mountains National Park TN,

where the speciation of fine mode nitrate changes significantly because of the inclusion of coarse mode nitrate mass.

Determining or predicting the form of nitrate is not straightforward; it depends on meteorological parameters such as temperature and relative humidity, as well as the presence and acidity of other species such as sulfate. Also, the amount of coarse mode nitrate being attributed to the fine mode also depends on the cutpoint of the impactor, which depends on the accuracy of the flow rate. However, for data gathered at the sites shown in Figures 3a–3c, when fine mode total nitrate concentrations were roughly greater than  $0.5 \mu\text{g m}^{-3}$ , ammonium nitrate contributed over 70% of the observed total nitrate in the fine mode. Obviously, the form of nitrate is very important in accurately accounting for contributions of nitrate to fine mass and to light extinction—optical properties of fine mode ammonium nitrate (as well as hygroscopic properties) are quite different than coarse mode sodium nitrate or calcium nitrate. Accurately estimating the speciation of nitrate would require measurements of fine mode ammonium and speciation of coarse mass. Because these measurements are not currently available at all sites, and based on the previous discussion that suggests higher levels of nitrate in the fine mode are probably associated with  $\text{NH}_4\text{NO}_3$ , we recommend that nitrate remains in the form of ammonium nitrate in the IMPROVE formulation.

### **3.3. Sulfate**

Elemental sulfur and the sulfate ion are measured as part of the IMPROVE network. To assess the contributions of sulfate to fine mass or light extinction, the molecular form of sulfate must be known. The IMPROVE algorithm assumes that sulfate is in the form of fully ammoniated sulfate  $((\text{NH}_4)_2\text{SO}_4)$ . The molecular form of sulfate depends on its degree of neutralization, for which routine measurements of the ammonium ion are required. The

IMPROVE network does not measure the  $\text{NH}_4^+$  ion, and as discussed in section 2.2, there are inherent sampling issues with respect to ammonium measurements. The molar ratio of ammonium to sulfate ranges from 2 for fully neutralized ammonium sulfate to 0 for sulfuric acid. Many authors have shown that aerosol sulfate acidity can vary temporally and spatially. More acidic aerosols have been measured at many locations around the United States (Gebhart et al., 1994; Liu et al., 1996; Day et al., 1997; Lowenthal et al., 2000; Lefer and Talbot, 2001; Quinn et al., 2002a; Chu et al., 2004; Hogrefe et al., 2004; Schwab et al., 2004; Tanner et al., 2004; Zhang et al., 2005). Special studies at IMPROVE sites have also demonstrated variability. At the Great Smoky Mountains National Park during the summer of 1995 (Southeastern Aerosol and Visibility Study, SEAVS), ammonium to sulfate molar ratios of 1.1 were observed (Hand et al., 2000). During the Big Bend Regional Aerosol and Visibility Observational (BRAVO) study at Big Bend National Park, Lee et al. (2004a) found ammonium to sulfate molar ratios of 1.54 on average. On average, fully neutralized ammonium sulfate was measured at Yosemite National Park during the summer of 2002 (Malm et al., 2005a). Seasonal and spatial variations in aerosol acidity complicate recommendations of a single form of ammoniated sulfate, and regular measurements of the  $\text{NH}_4^+$  ion at IMPROVE sites do not exist.

The coefficient ( $a_1$ ) multiplying ammonium sulfate in the regression model described in section 3.1 provides some indication of the role of sulfate in reconstructed fine mass. A coefficient greater than 1 suggests that water mass retained on the gravimetric filter is associated with sulfate, because ammonium sulfate is assumed in the regression and it has the highest molecular weight of any ammoniated sulfate species. Gravimetric fine mass is measured from Teflon<sup>®</sup> filters that are weighed at a relative humidity of ~ 40%; therefore an acidic sulfate (or other) species could be responsible for retained water on the filter. The amount of residual water

on the filter is a function of the relative humidity at which the filter is weighed and the RH history to which the aerosol is exposed. Issues related to water on the filter cannot be avoided because acidic sulfate species retain water to very low relative humidity. On average, the MLR coefficient associated with sulfate was greater than 1 at almost all of the IMPROVE sites (see Table 1). Others have found similar results; for example, Andrews et al. (2000) suggested that up to half of the discrepancy between measured and reconstructed fine mass could be accounted for by water uptake on the Teflon<sup>®</sup> filter by sulfate species during the SEAVS study in Great Smoky Mountains National Park. As previously stated, it is impossible to know the form of sulfate to assume in the IMPROVE equation because ammonium is not measured; therefore we recommend that ammonium sulfate remain as the form of sulfate IMPROVE equation.

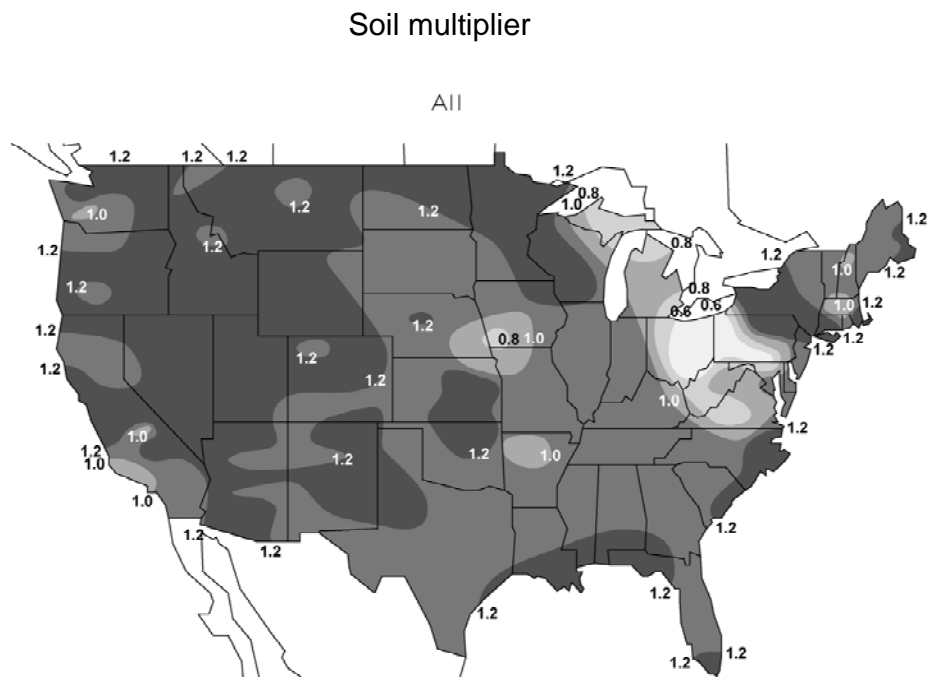
#### **3.4. *Soil Composition***

The composition of soil varies as a function of soil taxonomy at a given location. Soil taxonomy charts show variability across the United States with soil type, with the southwestern United States differing from the eastern United States, and many finer differentiations beyond that. Soil composition can also vary due to long-range intercontinental and transcontinental transport. Several studies have shown that contributions of Asian dust to U.S. fine soil concentrations can be significant episodically, affecting aerosol concentrations and mineralogy across the United States (VanCuren and Cahill, 2002; Jaffe et al., 2003; VanCuren, 2003). Transport of North African dust to the United States occurs regularly, affecting aerosol concentrations in the Virgin Islands, the eastern and southeastern United States (Perry et al., 1997), and even as far west as Big Bend National Park (Hand et al., 2002). Due to the spatial and temporal variability in dust sources, it is very difficult to characterize an appropriate aerosol soil composition for each measurement site. Soil mass concentrations are therefore estimated by a general method that sums the oxides of elements that are typically associated with soil ( $\text{Al}_2\text{O}_3$ ,

SiO<sub>2</sub>, CaO, K<sub>2</sub>O, FeO, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>), with a correction for other compounds such as MgO and Na<sub>2</sub>O, H<sub>2</sub>O and carbonates (Malm et al., 1994a).

Elemental concentrations are multiplied by factors that represent the mass concentrations of the oxide forms. Several corrections are also made. Molar concentrations of iron are assumed to be equally abundant in the forms of FeO and Fe<sub>2</sub>O<sub>3</sub>. Potassium has a non-soil contribution from biomass smoke, so the soil potassium is estimated by using Fe as a surrogate, or  $[K] = 0.6[Fe]$ . The formula for computing soil concentration is given in equation 2 and has been divided by 0.86 to account for other compounds. Results from the multiple linear regression technique described in section 3.1 (see Table 1 and Figure 4) suggest that, on average for all the IMPROVE sites, the soil composition is being underestimated by roughly 20%. Spatial variability is observed in the soil coefficient from the MLR method, with soil concentrations in the western United States being underestimated more than the Midwest and eastern United States. An area of the country from Michigan south through the Ohio River Valley appears to have overestimated soil concentrations by 10–30 %. Although the results from the MLR method suggest an underestimation of soil mass on average, the lack of measurements of soil composition around the United States and the additional complication of contributions of long-range (Mexico, Asia, and Africa) soil at many U.S. sites do not allow for suggestions for refinements to the soil formula at this time.

**Figure 4. Mean values of the soil coefficient from an ordinary least square multi-linear regression analysis (equation 6).**



### 3.5. *Coarse Mass*

Coarse mass is the difference between  $PM_{10}$  and  $PM_{2.5}$  mass concentrations measured gravimetrically and is not routinely analyzed for speciation; therefore the IMPROVE equation treats all of coarse material as non-hygroscopic dust. A few short-term special studies at national parks during which coarse mass speciation and aerosol mass size distributions were measured have shown that coarse mass consists of a substantial amount ( $\sim 40\text{--}50\%$ ) of carbonaceous material and inorganic salts such as calcium and sodium nitrate (Malm and Day, 2000; Hand, 2001; Lee et al., 2004a,b). To investigate the speciation of coarse mass, a coarse particle speciation network was initiated at nine IMPROVE sites in 2003. Sites were selected to be representative of the continental United States and were operated according to IMPROVE

protocol analytic procedures for a period of one year, with additional A, B, and C modules operating with PM<sub>10</sub> inlets. Preliminary results from one year of data from the sites suggest that over 50% of coarse mass is soil (as defined by the IMPROVE soil equation), with soil contributions higher in the western than eastern half of the country. Particulate organic material is the next highest contributor (15–35%) with fairly homogeneous spatial distribution. Nitrate is next highest contributor (5–15%), probably associated with sea salt on the coast and dust in the inner and western areas of the country. Sulfate is a minor contributor to coarse mass, although at coastal regions in the Northeast it averaged up to 10%, probably related to sea salt. The optical, physical, chemical, and hygroscopic properties of coarse mode aerosols can vary significantly depending on the composition and size distribution of coarse mass, and could have important implications to total scattering, because in some remote areas contributions to total scattering from the coarse mode scattering could be comparable to fine mode contributions. For example, there were several periods during the BRAVO study in Big Bend National Park when up to 80% of total scattering was attributable to the coarse mode (Hand, 2001; Hand et al., 2002).

Several special studies at IMPROVE sites have suggested that the coarse mode aerosol composition can affect the fine mode mass because often the tail of the coarse mode is measured as part of the fine mode. For example, during the BRAVO study at Big Bend National Park, size-segregated MOUDI impactor measurements (Lee et al., 2004a), as well as particle size distribution measurements (Hand et al., 2002), suggested that a 1  $\mu\text{m}$  aerodynamic diameter was a much more realistic separation between the fine and coarse mode. Similar results were found in Yosemite National Park, San Geronio CA, Grand Canyon AZ, Brigantine NJ, and Great Smoky Mountains National Park (Lee et al., 2004b). The use of a PM<sub>2.5</sub> size cut for IMPROVE samplers results in a substantial fraction of the tail of the coarse mode distribution in fine mode samples,



and this can vary significantly with an variable sampler flow rate that affects the size cut of the cyclone. The implications can be important for understanding the hygroscopicity, optical properties, mixing, and trends of fine mode aerosols.

### **3.6. *Sea Salt***

Although contributions from sea salt to coarse mass (and indirectly to fine mass) are not included in the IMPROVE reconstruction equation, sea salt can be a significant fraction of the fine mass at many coastal locations, (e.g., the Virgin Islands), as well as contribute significantly to light scattering (e.g., Quinn et al., 2001, 2002b, 2004). Sea salt concentrations are typically computed from sea salt markers like the sodium ion, chloride ion, or combination of ions (Quinn et al. 2001). Difficulties in computing sea salt from data from the IMPROVE network arise because positive ions are not analyzed; therefore sodium ion (the strongest indicator of sea salt) data are not available. Elemental sodium data are available from XRF analyses; however sensitivity issues regarding poor detection of Na result in large uncertainties corresponding to Na from XRF (White et al., 2004). Issues also arise when using the chloride ion or chlorine to estimate sea salt because reaction of gaseous nitric acid with sea salt produces sodium nitrate particles and the release of gaseous HCl. The depletion of chloride during this reaction results in an underestimation of sea salt when using chloride to compute it.

For non-coastal sites the inclusion of sea salt is not expected to have a considerable impact on reconstructed light scattering, so underestimating the contribution at those sites is not significant. However, Lowenthal and Kumar (2003) found that including sea salt (computed using Na and Cl) to reconstructed fine mass at Point Reyes CA increased reconstructed fine mass by 30% on average. Because sea salt is hygroscopic, the added effects of water mass to light scattering in coastal higher RH environments could be important also. Recent work by Lowenthal and Kumar (2005) suggests the possibility of using strontium as a surrogate for sea

salt. Investigations into this possibility are ongoing. The elemental abundance of strontium varies depending on the type of soil (Siefert et al., 1999) and estimates of Sr-derived sea salt depend on accurate estimates of its crustal abundance in relation to other elements. Because many IMPROVE sites have been shown to be influenced by long-range transport of Asian and north African dust (e.g., Perry et al., 1997; VanCuren and Cahill, 2002; Jaffe et al., 2003; VanCuren, 2003; Hand et al., 2004; Jaffe et al., 2005) as well as local dust sources, it is very important that the contributions to Sr from dust sources versus sea salt be accurately characterized, as both can be very important contributors to light scattering. For example, in Barbados (near the Virgin Islands), Li et al. (1996) found that for a 10-year mean, dust contributed 56% to light scattering, compared to 33% by sea salt.

The MLR analysis in section 3.1 and summarized in Table 1 included sea salt as  $1.6 \cdot \text{Cl}^-$  ( $\text{NaCl}$ ). This analysis suggests that east and west coastal sites underestimate sea salt mass by about 10% on average even with some chloride depletion. We recommend that sea salt be included in the reconstructed fine mass equation as  $1.8 \cdot \text{Cl}^-$  (sea salt is 55%  $\text{Cl}^-$  by weight as defined by the composition of sea water by Seinfeld and Pandis, 1998) because of the uncertainties related to sodium measurements. Interestingly, the ratio of the 1.8 and 1.6 factors is 1.12, similar to the average regression coefficient for sea salt, so perhaps some of the underestimate was related to the sea salt multiplication factor. The contributions of sea salt to the light extinction equation (including its hygroscopic properties) should also be included.

#### **4. Hygroscopic Growth**

The hygroscopicity of atmospheric aerosols is an important characteristic that determines how a particle will behave in a changing relative humidity (RH) environment. Soluble particles will uptake water, resulting in increased mass and particle size, both of which determine how efficiently particles scatter light, as well as their atmospheric lifetimes. A pure salt particle (e.g.,

ammonium sulfate) exposed to increasing RH will undergo an abrupt change from a solid particle to a droplet at a particular relative humidity (referred to as deliquescence) that is specific to its chemical composition. Above this point the particle continues to grow exponentially. As the RH decreases, the solution droplet will lose water by evaporation and remain in a metastable supersaturated state until it effloresces and returns to a solid particle at a lower RH than that at which it deliquesced. The metastable state can exist for indefinite periods of time. This behavior is also referred to as hysteresis because the particle follows a different path of growth and evaporation.

Although extensive laboratory studies have been performed to characterize the hysteresis behavior of hygroscopic aerosols of known composition (e.g., Tang and Munkelwitz, 1994; Tang, 1996), many field studies have also been performed to understand the relationship between the hygroscopic, optical, and chemical properties of ambient aerosols. These types of measurements are typically performed by a few different methods. Tandem differential mobility analyzers (TDMA) arranged in series allow for the selection of a single particle size in the first DMA (typically a dry size). The particle size is measured in the second DMA after it has been exposed to increased (or decreased) relative humidity in a conditioner that separates the two DMAs. Growth factors ( $D/D_o$ ) are derived from these measurements as a ratio of a humidified particle diameter ( $D$ ) to the initial dry particle diameter ( $D_o$ ) as a function of relative humidity. This technique has been employed in many field studies, several of which are reviewed by Cocker et al. (2001). The results of most of these studies suggest the presence of particle modes with varying degrees of solubility and hygroscopic characteristics (“more” or “less” hygroscopic modes), reflecting the varying chemical composition and mixing properties of the aerosols. Bimodal growth of urban aerosols have been shown to have a less hygroscopic mode with  $D/D_o$

ranging from 1.0 to 1.4 (for RH ~ 80–90%), and a more hygroscopic mode with  $D/D_o = 1.1–1.8$  (e.g., Zhang et al., 1993; Busch et al., 1999; Ferron et al., 1999). Carrico et al. (2005) observed monomodal, bimodal, and trimodal growth profiles at Yosemite National Park. They found an inverse relationship between the mass fraction of POM and hygroscopicity, and found that the growth factors were significantly lower than expected for ionic components of the aerosol composition, especially during periods dominated by biomass smoke.

Another technique for characterizing particle growth utilizes optical particle counters that measure aerosol size distributions at changing relative humidities. During the Southeastern Aerosol and Visibility Study (SEAVS), Kreisberg et al. (2001) used a relative-humidity-moderated differential mobility optical particle size spectrometer (RH-DMOPSS) to measure dry and humidified particle size distributions. Hand et al. (2000) used a relative-humidity-controlled optical particle counter to obtain both dry and humidified size distributions. Size distributions statistics (such as geometric mean diameter and integrated volume concentrations) for both the wet and dry distributions are used to construct diameter growth curves ( $D/D_o$ ). This method differs from the TDMA method in that  $D/D_o$  curves are determined for an integrated aerosol size distribution, rather than for individual sizes, so information regarding mixing and “more” and “less” hygroscopic modes is not available.

Both of the above mentioned techniques to measure growth curves rely on measurements of particle size in a changing relative humidity environment. Another method for estimating particle growth is to condition the aerosol sample in a nephelometry system. Day et al. (2000) describes an experimental technique used to measure dry and humidified light scattering coefficients from which light scattering growth curves ( $f(RH) = b_{sp}(RH)/b_{sp}(dry)$ ) have been derived for several special studies in national parks (e.g., Day and Malm, 2001; Malm et al.,

2003; Malm et al., 2005b). Several investigators have used a variation on this technique of measuring a dry and humidified  $b_{sp}$  to compute  $f(RH)$  (e.g., Sheridan et al., 2001; Eldering et al., 2002; Carrico et al., 2003). Growth curves derived from nephelometry systems ( $f(RH)$ ) and from TDMA systems ( $D/D_o$ ) are not directly comparable because, besides being a function of aerosol composition and mixing characteristics (similar to  $D/D_o$ ),  $f(RH)$  curves are also a function of aerosol size distributions which could be changing independently of RH effects during a measurement cycle, and correspond to an average of scattering due to aerosol types growing at different rates.

Laboratory studies suggest that mixed salt particles have a complicated growth behavior with multiple deliquescence points (Tang, 1997), but the behavior is fairly well understood and can be predicted by several equilibrium models (Kim et al., 1993; Clegg et al., 1998a,b; Nenes et al., 1998). Less is understood about the hygroscopic properties of organic aerosols or inorganic/organic aerosol mixtures. Laboratory and some field studies have investigated the role that organic species have in the hygroscopic growth of inorganic salts or minerals and indicate that organics can change the deliquescent point of the pure inorganic species (e.g., Andrews and Larson, 1993; Lightstone et al., 2000), and depending on the properties and mass fractions of the organic compounds, can enhance, reduce, or not effect the rate of growth of the inorganic species (Andrews and Larson, 1993; Saxena et al., 1995; Hansson, et al., 1998; Lightstone et al., 2000; Chan and Chan, 2003; Prenni et al., 2003; Brooks et al., 2004; Gysel et al., 2004; Mikhilov et al., 2004; Carrico et al., 2005; Malm et al., 2005b). Many organic compounds have been shown to have no deliquescent or efflorescent behavior at all (e.g., Peng et al., 2001). Virkkula et al. (1999) found during a field study in Spain that internally mixed particles of ammonium sulfate and organic compounds take up water independently of one another.

In the atmosphere the aerosols are a complicated mixture of inorganic and organic species with complex growth behaviors that may not be well represented by laboratory studies. It is likely that a large fraction of hygroscopic particles exist in supersaturated equilibrium as aqueous droplets below their deliquescence RH, based on the numerous studies that report a smooth function of particle growth with relative humidity rather than step-wise growth behavior. This behavior has been observed for  $D/D_o$  growth curves in southeast Texas (Santarpia et al., 2004, 2005), Great Smoky Mountains National Park (Hand et al., 2000), and Yosemite National Park (Carrico et al., 2005). Smooth  $f(RH)$  curves have also been observed in the Netherlands (ten Brink et al., 1996), Great Smoky Mountains, Grand Canyon, Big Bend, and Yosemite national parks (e.g., Malm and Day, 2001; Malm et al., 2003; 2005b), Portugal (Carrico et al., 2000), China (Xu et al., 2002), North Carolina (Im et al., 2001), the Maldives (Eldering et al., 2002), and during the Aerosol Characterization Experiment in Asia (ACE-Asia) (Carrico et al., 2003). Although a variety of aerosol types likely exist at these locations, their smooth growth curves suggest these particles exist either in a equilibrium state, lacking growth characteristics like deliquescence points due to their non-soluble/soluble mixture, or in a supersaturated equilibrium state with a very low efflorescence RH (i.e., acidic aerosols). In either case, water appears to be associated with these aerosols at low values of RH.

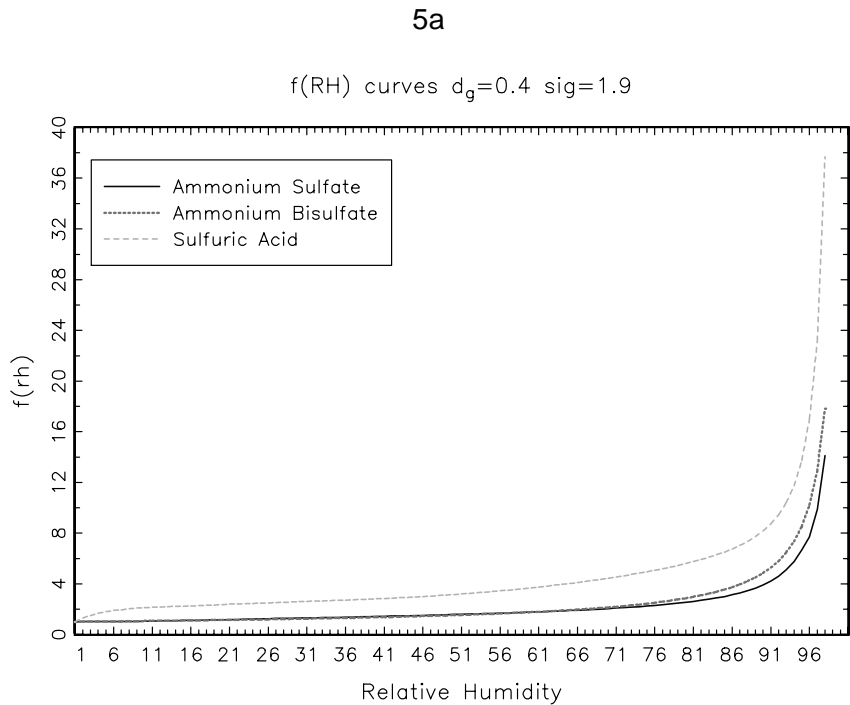
The difference between  $f(RH)$  for ammoniated sulfate states between fully neutralized ammonium sulfate and more acidic sulfate is summarized in Figures 5a, 5b, and 5c. Figure 5a shows the  $f(RH)$  “no solids” curves (Clegg et al., 1998b) for ammonium sulfate, bisulfate, and sulfuric acid for a mass size distribution with  $D_g=0.4 \mu\text{m}$  and  $\sigma_g=1.9$ . Notice there is little difference between the ammonium sulfate and bisulfate  $f(RH)$  curves up to  $\sim 70\%$  RH, while for  $\text{RH} > 70\%$  the bisulfate  $f(RH)$  curve is about 1.2 times the ammonium sulfate curve. The

sulfuric acid  $f(RH)$  curve is about twice the ammonium sulfate curve for most RH values. However, the dry mass scattering efficiencies for ammonium sulfate, bisulfate, and sulfuric acid are 3.72, 3.35, and 2.66  $\text{m}^2 \text{g}^{-1}$ , respectively, offsetting the differences in  $f(RH)$  curves at high humidity. The mass scattering efficiencies for ammonium sulfate, bisulfate, and sulfuric acid are plotted as a function of RH in Figure 5b to assess the effective scattering of a fixed amount of sulfate ion interpreted as any of these three forms of sulfate. Notice that at low RH the mass scattering efficiency for bisulfate is lower than ammonium sulfate mass scattering efficiency and about equal at higher RH. Sulfuric acid mass scattering efficiency is about the same as ammonium sulfate mass scattering efficiency at low RH but greater at high RH. Figure 5c summarizes these differences. The ratio of the sulfate ion mass scattering efficiency interpreted as ammonium bisulfate and as sulfuric acid to the ammonium sulfate efficiency curve is shown as a function of RH. Notice that at low RH (10–70%) the bisulfate efficiency is about 20% lower than the ammonium sulfate mass scattering efficiency, and at high RH they are about equal. Sulfuric acid mass scattering efficiencies are 10–20% greater than ammonium sulfate efficiencies over most of the RH range and 40% greater at very high RH values (95–98%).

In the IMPROVE formulation, the form of sulfate is assumed to be ammonium sulfate. From Figure 5c it is evident that this choice of ammonium sulfate can either be an over- or underestimate of true sulfate scattering, depending on the ratio of the ammonium to sulfate ion. However, the current  $f(RH)$  growth curve used in the IMPROVE equation is based on an interpolated  $D/D_0$  curve between the ascending and descending branches of growth for ammonium sulfate and reaches a value 1 at 40% RH (no water is associated with the particles below 40% RH) (Sisler and Malm, 1994). This curve was derived to approximate smooth growth curves observed in field studies. We propose applying an  $f(RH)$  growth curve corresponding to

equilibrium calculations for ammonium sulfate below the deliquescence point to 0% RH using the AIM model with the “no solids” option (Clegg et al., 1998b). This smooth curve also approximates the behavior observed for mixtures of aerosols as those observed in the studies cited above; however, it differs from the current curve in that it allows water to be associated with the aerosol for RH values below 40%. Organics are assumed to be non-hygroscopic because laboratory and field results suggest they are weakly to non-hygroscopic (Malm et al., 2003, Carrico et al., 2005; Malm et al. 2005b).

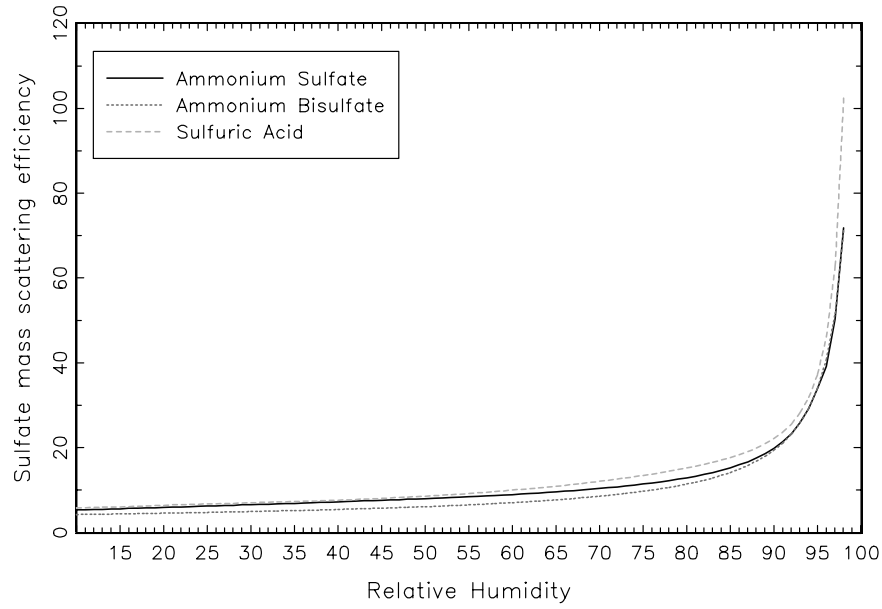
**Figure 5. (a)  $f(RH)$  curves using the “no solids” method for ammonium sulfate, ammonium bisulfate, and sulfuric acid (assuming a size distribution with  $D_g = 0.4 \mu\text{m}$  and  $\sigma_g = 1.9$ ). (b) Sulfate mass scattering efficiencies for ammonium sulfate, ammonium bisulfate, and sulfuric acid using the curves in part (a). (c) Ratios of ammonium bisulfate and sulfuric acid mass scattering efficiencies to the ammonium sulfate mass scattering efficiency shown in (b).**





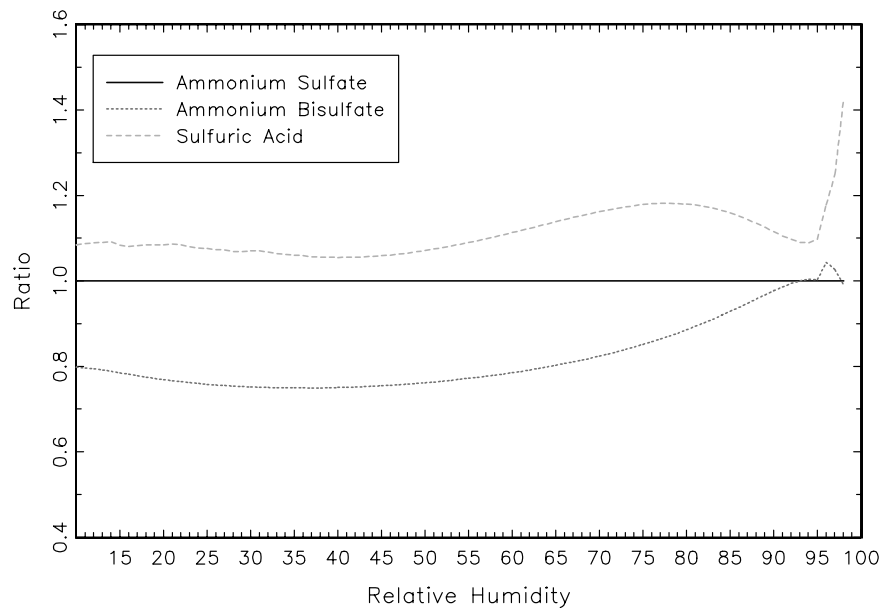
5b

Sulfate mass scattering efficiency



5c

Normalized to Ammonium Sulfate



## 5. Mass Scattering Efficiencies

In order to review mass scattering efficiencies, it is important to understand the terminology used and the impact of assumed aerosol models upon the resulting estimates. We motivate this section by a theoretical discussion of mass scattering efficiencies, including derivations and effects of the assumed model on derived estimates. Later we review other empirical methods used for estimating mass scattering efficiencies from measurements and how the assumptions applied in these methods may result in estimates that, although they may be referred to as mass scattering efficiencies, in fact may actually differ in their physical meaning. The final sub-sections provide a survey of reported measured mass scattering efficiencies using different methods and estimates derived from IMPROVE data.

### 5.1. *Theoretical Discussion*

The role of aerosols in visibility degradation or climate forcing has motivated efforts to quantify the optical properties of specific aerosol species. The terminology used and the impact of assumed models on the amount of extinction change apportioned to individual aerosol species have been the subject of debate. For example, ranges in estimates of mass scattering efficiency of sulfate aerosol applied in climate forcing models (Penner et al., 1993) arose due to different assumptions regarding the presence of other chemical species (e.g., ammonium and/or water) or assumptions concerning how size distributions shift with changes in aerosol mass in the calculation of mass scattering efficiency (Zhang et al., 1993; Anderson et al., 1994; McMurry et al., 1996). White (1986) presents a thorough discussion of the definitions of extinction efficiency and the consequences of various assumptions of the assumed aerosol microstructure upon the apportionment of extinction to its chemical components.

Mass extinction (or scattering) efficiencies are defined as the total aerosol extinction (or scattering) divided by the total aerosol mass and can be calculated theoretically for spherical

particles of known composition and size using Mie theory (van de Hulst, 1981). Aerosol models typically assume that 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”. However, 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.

For the following discussion, the aerosol size distribution refers to an externally mixed aerosol of a single chemical component,  $j$ . For a corresponding 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 with equation 7 and has units of inverse length.

$$b_{ext,j} = \int_0^{\infty} \frac{\pi}{4} D_p^2 Q_{ext}(n_j, D_p, \lambda) f_{N,j}(D_p) dD_p \quad (7)$$

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 ( $\lambda$ ). Equation 7 can be reformulated in terms of aerosol mass size distribution  $f_{M,j}(D_p)$  by making the following substitution for the number distribution (equation 8), with species particle density given by  $\rho_j$ :

$$f_{N,j}(D_p) = \frac{6}{\rho_j \pi D_p^3} f_{M,j}(D_p) \quad (8)$$

Substituting equation 8 into equation 7 gives

$$b_{ext,j} = \int_0^{\infty} \alpha_{ext,j}(n_j, D_p, \lambda) f_{M,j}(D_p) dD_p \quad (9)$$

where the single particle mass extinction efficiency ( $\alpha_{ext,j}$ ) has units of  $\text{m}^2 \text{g}^{-1}$  and is given by

$$\alpha_{ext,j} = \frac{3}{2} \frac{Q_{ext}(n_j, D_p, \lambda)}{\rho_j D_p} \quad (10)$$

Normalizing equation 9 by the total mass concentration of species  $j$  ( $M_j$ ) allows the extinction efficiency to be written as

$$\alpha_{M_j} = \int_0^{\infty} \alpha_{ext,j} f'_{M,j}(D_p) d(D_p) \quad (11)$$

where  $f'_{M_j}(D_p)$  is the normalized mass distribution. If  $f'_{M_j}(D_p)$  does not vary with total mass concentration, then the average mass scattering efficiency for species  $j$  can be considered a constant and the light extinction coefficient corresponding to species  $j$  can be written as

$$b_{ext,j} = \alpha_{M_j} M_j \quad (12)$$

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

$$b_{ext} = \sum \alpha_{M_j} M_j \quad (13)$$

Equation 13 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.

When computing total extinction using Mie theory, the microscopic structure of the aerosol (that is, the extent of internal or external mixing) is found to be relatively unimportant, so that the assumption of internally vs. externally mixed particles does not have much impact on the predicted results. This insensitivity of total scattering or extinction to the aerosol mixture has

been demonstrated by a number of authors, including Hasan and Dzubay (1983), Sloane (1983), Pilinis et al. (1995) and McMurry et al. (1996).

The mass extinction (or scattering) efficiency is a stronger function of density and size than optical properties such as refractive index (see equation 10). Several investigators have reported on the size dependence of mass scattering efficiencies (Malm and Pitchford, 1997; Li et al, 2000; Hand, 2001; Malm et al, 2003). Other authors report the dependence of mass scattering on mass concentrations (Malm et al., 2003) or on light scattering coefficients (Lowenthal and Kumar, 2004); however, these relationships arise due to the dependence of  $b_{sp}$  and mass on particle size.

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” ( $\alpha_{ext,part}$ ):






$$\alpha_{ext,part} = \left( \frac{\partial b_{ext}}{\partial M_j} \right) \quad (14)$$

The partial extinction efficiency is dependent on change in composition as well as change in aerosol size as species are added or removed. For example, McMurry et al. (1996) examined  $\alpha_{ext,part}$  as a function of formation mechanisms for sulfate. If sulfates were formed by gas phase reactions, lower humidity conditions led to smaller particles sizes, whereas when sulfates were formed in aqueous processes, the higher relative humidity conditions led to larger particle sizes.

A simple example illustrating some of these concepts is shown in Figure 6 (Malm and Kreidenweis, 1997). The insensitivity of the total computed scattering to the mixing assumption is presented in Figure 6a. Two aerosol species with the same total volume, size distribution, and index of refraction, but with densities differing by a factor of 2, are externally mixed. They have

mass scattering efficiencies of  $3 \text{ m}^2 \text{ g}^{-1}$  and  $6 \text{ m}^2 \text{ g}^{-1}$ , respectively. The externally mixed aerosol contains  $10 \text{ } \mu\text{g m}^{-3}$  of species 1 and  $5 \text{ } \mu\text{g m}^{-3}$  of species 2, with each species contributing  $30 \text{ Mm}^{-1}$  to the total aerosol scattering of  $60 \text{ Mm}^{-1}$ .

**Figure 6. (a) Diagram contrasting mass scattering efficiencies for internally versus externally mixed particles. (b) Partial scattering efficiencies for internally and externally mixed particles.**

		Figure 6A		Figure 6B	
		species 1	species 2	species 1	species 2
mass	external case	$10 \text{ } \mu\text{g/m}^3$	$5 \text{ } \mu\text{g/m}^3$	$10 \text{ } \mu\text{g/m}^3$	species 2 removed
aerosol type					
species density		$2 \text{ g/cm}^3$	$1 \text{ g/cm}^3$	$2 \text{ g/cm}^3$	
specific mass scattering efficiency		$3 \text{ m}^2/\text{g}$	$6 \text{ m}^2/\text{g}$	$3 \text{ m}^2/\text{g}$	
particle scattering		$30 \text{ Mm}^{-1}$	$30 \text{ Mm}^{-1}$	$30 \text{ Mm}^{-1}$	
total scattering		$60 \text{ Mm}^{-1}$		$30 \text{ Mm}^{-1}$	
mass	internal case	$15 \text{ } \mu\text{g/m}^3$		$10 \text{ } \mu\text{g/m}^3$	
aerosol type					
species density		$1.5 \text{ g/cm}^3$		$2 \text{ g/cm}^3$	
specific mass scattering efficiency		$4 \text{ m}^2/\text{g}$		$2 \text{ m}^2/\text{g}$	
total scattering		$60 \text{ Mm}^{-1}$		$20 \text{ Mm}^{-1}$	

If species 1 and species 2 are now assumed to be internally mixed (see lower part of Figure 6a), the specific mass scattering efficiency for the mixed particle is now required for calculation of the total aerosol scattering. The specific mass scattering efficiency can be computed as the mass-weighted average of the efficiencies of the individual species ( $4 \text{ m}^2 \text{ g}^{-1}$ ), assuming several conditions are met. The optical properties of the mixture must be similar to those for the individual species (which must also be similar; this condition is met, for example, by a mixture of ammonium sulfate and organics, with real refractive indices of 1.53 and 1.5,

respectively). Volume conservation must be invoked, and the size distribution of the internal mixture must be similar to the size distributions of the external mixtures. By applying the specific mass scattering efficiency, a total aerosol  $b_{sp}$  for the sample is again computed as  $60 \text{ Mm}^{-1}$  (see Figure 6a).

However, the apportionment of scattering to species 1 and 2 is different under these two models. Using the externally mixed model, species 1 and 2 each contribute 50% of the total scattering. In the internally mixed case, species 1 contributes 66% of the scattering budget (since it makes up 66% of the total mass), while species 2 contributes 33%. This discrepancy arises because when the species are internally mixed, the same scattering efficiency is assigned to both species, although independently they have different efficiencies. *This discrepancy can only be resolved if the specific mass scattering efficiency of the mixed aerosol is prorated to its chemical constituents, based on their relative densities. The apportionment of scattering to specific species thereby becomes independent of whether an externally or internally mixed model is assumed.*

This simple example demonstrates that the contribution of each species to total extinction is sensitive to the assumed microscopic structure of the aerosol. White (1986) refers to this as the apportionment problem, distinct from the problem of computing total extinction from estimates of size-dependent chemical composition that we just demonstrated to be similar for the two cases in Figure 6a. For the externally mixed case, the total extinction for the mixture is calculated by computing the contribution of each species separately, and the species contribution to the total is well-defined if we know the size distribution of each species. For the internally mixed case, it may be misleading to assign a percentage of the total extinction to each species on a mass-weighted basis, as demonstrated in Figure 6a.

The previous discussion concerns itself with apportioning extinction to a species as it resides in the ambient atmosphere. From a regulatory standpoint, the change in total scattering as a function of removal of a species may be of interest. Total scattering can be computed for the mixture and for the case when one species has been removed from the mixture; the difference between these values provides the contribution of the species to total scattering. As an example, we compute the partial scattering efficiency for species 2 under the assumptions of externally mixed particles. The partial scattering efficiency is obtained by computing the total aerosol scattering assuming only species 1 is present ( $30 \text{ Mm}^{-1}$ , see Figure 6b). Subtracting this value from the total scattering obtained for the mixture ( $60 \text{ Mm}^{-1}$ , see Figure 6a), we deduce that species 2 contributed  $30 \text{ Mm}^{-1}$  (half) to the mixed aerosol scattering. The derived partial scattering efficiency of  $6 \text{ m}^2 \text{ g}^{-1}$  for species 2 [ $\Delta b_{sp}/\Delta mass = (60-30 \text{ Mm}^{-1})/(5 \mu\text{g m}^{-3})$ ] is the same as its mass scattering efficiency from Figure 6a.

Investigating the same scenario but for the internally mixed case (see the lower part Figure 6b), we assume that the removal of one species from the internal mixture would conserve particle number concentrations but reduce particle size. This size reduction alters the specific scattering efficiency of the mixture, which is now assumed to be  $2 \text{ m}^2 \text{ g}^{-1}$ . The total aerosol scattering is thus  $20 \text{ Mm}^{-1}$ , which leads to the conclusion that the partial scattering efficiency of species 2 is  $8 \text{ m}^2 \text{ g}^{-1}$  [ $\Delta b_{sp}/\Delta mass = (60-20 \text{ Mm}^{-1})/(5 \mu\text{g m}^{-3})$ ]. White (1986) presents a thorough discussion of the definitions of specific extinction and mass extinction efficiency and of the consequences of various assumptions of aerosol microstructure upon the apportionment of extinction to its chemical components.

Issues also arise when apportioning scattering to species that have different hygroscopic properties. Consider an external mixture of hygroscopic and non-hygroscopic aerosols species



with similar masses. The mass scattering efficiencies of the dry non-hygroscopic and hygroscopic species are each  $3 \text{ m}^2 \text{ g}^{-1}$ , respectively, while that of the wet hygroscopic species is, because of associated water,  $8 \text{ m}^2 \text{ g}^{-1}$ . When internally mixed, the wet specific mass scattering efficiency will be between  $3$  and  $8 \text{ m}^2 \text{ g}^{-1}$ , depending on the hygroscopic properties of the mixed aerosol. Several authors discuss aerosol growth characteristics as a function of RH and have successfully predicted the scattering characteristics of the mixed particles (Anderson et al., 1994; Sloane, 1983, 1986; Malm and Pitchford, 1997; Malm et al., 2000, 2003, 2005b). However, the apportionment of scattering to a particular species is still problematic. Typically, one growth curve is developed for the mixed species, and scattering due to water is apportioned proportionally among all aerosol components, even though only one of the species may be hygroscopic. An example would be a mixture of ammonium sulfate and a weakly hygroscopic organic species.

## **5.2. *Methods for Deriving Mass Scattering Efficiencies***

The methods typically used to estimate mass scattering efficiencies depend on the type of measurements and data available. In this section we will discuss the most common methods used. We use the term “mass scattering efficiency” to refer to estimates that correspond to a single aerosol component such as dry ammonium sulfate, and although one could argue that species such as POM and soil correspond to a combination of chemical components, we will use this term to correspond to those efficiencies as well. We use the term “specific mass scattering efficiency” to refer to aerosols composed of more than one species, for example, a “fine mode specific mass scattering efficiency”. We will also use this term to refer to aerosols that include water mass. For example, if an efficiency for an inorganic salt particle with associated water mass is reported, we refer to it as a “specific mass scattering efficiency”.

The simplest method for computing efficiencies is with measured mass concentrations from filter samples and measured light scattering coefficients from nephelometry. For an aerosol population, a specific mass scattering efficiency  $\alpha_{sp\_spec}$  can be defined as the ratio of a light scattering coefficient corresponding to the mass concentration ( $M$ ) of that population:

$$\alpha_{sp\_spec} = \frac{b_{sp}}{M} \quad (15)$$

The average specific mass scattering efficiency can be estimated by dividing the average scattering coefficient by the average mass concentration for a given set of measurements, or a linear regression can be performed on the data and the slope of the linear fit can be interpreted as the specific mass scattering efficiency. Specific mass efficiencies derived in this manner represent an average aerosol that could be changing due to variations in relative humidity, size distribution, and composition during the sampling period. Mass concentrations used in this method could be either gravimetric mass or the sum of chemically analyzed masses, or be computed from integrated volume distributions using an assumed density.

A number of investigators have taken advantage of the form of equation 13 ( $b_{ext} = \sum \alpha_{M_j} M_j$ ) to construct a multi-linear regression (MLR) model with  $b_{ext}$  as the independent variable, and the measured aerosol mass concentrations for each species  $j$  ( $M_j$ ) as the dependent variables. The regression coefficients are then interpreted as mass extinction (or scattering or absorption) efficiencies. The assumptions required in this formulation are that all the components contributing to extinction are included, that equation 13 is a reasonable approximation to the relationship between extinction and the various aerosol species, the number of samples is large enough to give stable results, and the concentrations of the species are uncorrelated.

However, as stated by White (1991), “Model simulations show the procedure to yield usefully accurate results under favorable conditions. An important liability is that the availability

of standard software makes it easy to perform regression under unfavorable conditions.” Regression-derived efficiencies are vulnerable to a variety of systematic and random errors. At the most basic level, there is the issue that meteorologically driven fluctuations of the existing aerosol concentrations may cause aerosol mass concentrations of different species to be collinear. The high degree of collinearity commonly found among aerosol species can make regression results very sensitive to the choice of species to be included in the analysis. A more practical difficulty is that regression results can be biased by random uncertainties in the measurements. Standard regression models tend to overpredict the coefficients of species that have lower uncertainties (e.g., sulfates) and underpredict the coefficients of species with larger measurement uncertainties (e.g., organics), similar to the discussion in section 3.1.

The theoretical approach described at the beginning of this section (see equations 7–10) is often used to compute mass scattering efficiencies from mass (or number) distributions of aerosol species from impactor measurements or mobility or optical measurements. However, this method requires assumptions of the measured species chemical form and mixing properties of the aerosols, as well as their optical properties. Estimates from this method often assume an externally mixed aerosol, but if the size distribution measurement is obtained by mobility or optical measurements (number size distribution), an internally mixed aerosol is assumed, but perhaps for separate size modes. This method has been shown to accurately reconstruct light scattering. For example, measurements of size distributions have been incorporated with estimates of aerosol optical properties to reconstruct measured scattering (and estimate specific mass scattering efficiencies) on fine time scales (Hand et al., 2002; Malm et al., 2005a; McMeeking et al., 2005). These estimates have the added advantage of allowing for the investigation of the functional dependence of efficiencies on particle size, composition, and

humidity. The theoretical method provides the most accurate estimate of efficiencies out of those discussed in this section. A disadvantage to this method is that size distribution measurements are more analytically intensive and not often available for routine monitoring, so computing mass scattering efficiencies by this method is not routinely possible.

Estimating mass scattering efficiencies as the change in  $b_{ext}$  resulting from the removal (or addition) of a single species is different from assigning a fraction of measured extinction to a chemical species or a mixture of species. The change in extinction resulting from a change in aerosol species concentration was described previously (equation 14). As species are added or removed from an aerosol, the efficiency is dependent on change in composition as well as on change in aerosol size. Computing partial mass scattering efficiencies in this context requires a model to account for the effects of removal of mass on light scattering coefficients, such as the ELSIE (Elastic Light Scattering Interactive Efficiencies) model (Sloane, 1983; Sloane et al., 1991; Lowenthal et al., 1995; Omar et al., 1999). Among the assumptions in the ELSIE model are those associated with removing aerosol mass. Mass can be removed or added by assuming that the particle size changes but not the particle number, or that the particle number changes but not the particle size (Lowenthal et al., 1995). Unless the option is chosen to keep the size constant, the efficiencies derived from this method cannot be compared to efficiencies from other methods. Also, assumptions must be made regarding how to treat water mass associated with a removed species. Although this technique is useful in a regulatory context, in practice it is not possible to measure the change in light scattering due to a change in mass concentration, so more empirical approaches were adopted to estimate mass scattering efficiencies.

### **5.3. *Survey of Mass Scattering Efficiencies***

A survey of ground-based measured mass scattering efficiencies from peer-reviewed literature since 1990 includes values derived from the four different methods described above

(theoretical, measurement, multi-linear regression, and partial scattering approach) and are summarized by several tables (Tables 2–5 in Appendix 2). The tables can be understood in the following way: the mass scattering efficiencies are listed by species (e.g., sulfate, POM) or as specific mass scattering efficiencies for mixtures of aerosols by size mode (i.e., fine, coarse, or total). The tables also list the study location, study name, aerosol characteristics (e.g., smoke) if noted, and the study time period. Each method table has a corresponding notes table that provides details of the measurements, size ranges, the relative humidity of the measurements, assumptions, and the wavelength at which the measurements were made if it was different than 550 nm; these can be found in Appendix 2. Occasionally this information may also be found in a footnote in the mass scattering efficiency method table for quick reference. Citations are numbered consecutively in alphabetical order (a full citation list can also be found in Appendix 2). The “note” column in the table refers to the citation number as well as the entry in the notes table. When appropriate, we compute the average (and one standard deviation) for values in the cited literature and noted in the footnotes. Except for averages, values are listed as found in the literature, and furthermore, sulfate mass scattering efficiencies have been normalized to dry ammonium sulfate when possible. This normalization is performed because sulfate efficiencies are reported under a variety of conditions. For example, they may be reported in terms such as sulfate ion, ammonium sulfate mass, or ammoniated sulfate mass (depending on the acidity), and they may be reported for a range of relative humidity values corresponding to associated water mass. Sulfate mass scattering efficiencies reported for  $RH > 45\%$  were converted to dry ammonium sulfate mass scattering efficiencies based on reported ammonium to sulfate molar ratios and  $f(RH)$  curves corresponding to ammonium sulfate. For all the entries, the original sulfate mass scattering efficiencies are reported, along with corrected dry ammonium sulfate

mass scattering efficiencies in italicized font (if already reported in the cited manuscript), or noted with a (†) symbol if we performed the correction to a dry ammonium sulfate basis. Occasionally there was not enough information available to do this correction. Other corrections in the table include normalizing the POM efficiencies to a multiplier of 1.8. Most of the estimates were reported corresponding to POM computed with multipliers of 1.2, 1.4, 1.6, or 2.1 (see notes table for each method). We normalized the efficiencies to  $R_{oc} = 1.8$  so that estimates derived in the next section can be directly compared. Both efficiencies are listed in the tables but the normalized value is italicized. Table 6 provides a summary of average estimates from the methods and will be discussed after each method is presented.

We begin our review with the theoretical method efficiencies so that later discussions of efficiencies derived by more simple methods can be understood in the context of theoretical predictions. Theoretical mass scattering efficiencies are reported in Table 2. These efficiencies are the most representative estimates because the effects of particle size and composition can be included in the calculation for a single time period, and as previously mentioned, derived efficiencies accurately reconstruct scattering over very fine time resolutions. The theoretical method relies on computed scattering that is dependent on Mie theory and corresponding assumptions of spherical particles and optical properties.

### **5.3.1. Theoretical Method**

The average fine mode dry ammonium sulfate mass scattering efficiency from the theoretical method is  $2.45 \pm 1.14 \text{ m}^2 \text{ g}^{-1}$ . Most of the values reported correspond to the fine mode, although coarse and total sulfate are reported and noted in Table 2 (see Appendix 2). The highest value in this table ( $6.0 \text{ m}^2 \text{ g}^{-1}$ ) was reported for China by Li et al. (2000) and we have corrected it from ammonium bisulfate to ammonium sulfate but performed no humidity correction. It is unclear at what relative humidity this value is reported, although Li et al. (2000)

state that particle growth based on Tang (1997) has been assumed. Having some water mass associated with this estimate would be consistent with its higher value compared to the other estimates. For example, wet specific mass scattering efficiencies reported for Hopi Point AZ, Meadview AZ, Shenandoah VA, and Great Smoky Mountains TN correspond to different RH values (see notes table) and demonstrate the large effect water mass has on efficiencies, especially at Shenandoah where the ambient humidity is high in summer. Removing the highest value ( $6.0 \text{ m}^2 \text{ g}^{-1}$ , reported by Li et al., 2000) from the calculated average results in a mean dry ammonium sulfate mass scattering efficiency of  $2.2 \pm 0.6 \text{ m}^2 \text{ g}^{-1}$ . The lowest value in the table ( $1.12 \text{ m}^2 \text{ g}^{-1}$ ) was observed in the Southern Ocean region south of Australia during the ACE-1 study (Quinn et al., 1998), corresponding to smaller average surface mean diameter of  $0.20 \pm 0.04 \text{ }\mu\text{m}$ . It is interesting that given the global distribution in the measurements, a fairly low variability in dry ammonium sulfate efficiencies is observed, perhaps a reflection on the robustness of this method for computing efficiencies, especially when the optical and hygroscopic properties are well understood.

The average POM mass scattering efficiency without corrections for  $R_{oc}$  differences was  $5.9 \pm 1.0 \text{ m}^2 \text{ g}^{-1}$ , and was most likely affected by the assumptions in computing POM from measured organic carbon and the range of types of organics measured. To correct for the different multipliers used to compute POM, we normalized these values to an  $R_{oc}$  of 1.8, and the resulting normalized average POM mass scattering efficiency was  $5.5 \pm 1.6 \text{ m}^2 \text{ g}^{-1}$ . The normalization did not significantly change most of the estimates (see italicized values in the table) because most of the studies use  $R_{oc}$  values ranging from 1.4 to 2.1. This normalization did change the estimate by Li et al. (2000) in China because no  $R_{oc}$  was reported in that study, so we assumed they used a value of 1. Most of the authors in these studies applied  $R_{oc}$  values consistent

with Turpin and Lim's (2001) suggested values that vary according to aerosol type. For example, during the Aerosols99 study, Quinn et al. (2001) reported values for locations ranging from the Atlantic Ocean off the coast of Virginia to Cape Town, South Africa, with aerosol origins ranging from remote marine to African dust and biomass burning. They applied a POM multiplier of 1.6 for North American air masses (more urban aerosols), and 2.1 for all other air masses. With the exception of Li et al. (2001), these studies did not assume organics were hygroscopic; however, the RH corresponding to the value by Li et al. (2001) is unspecified.

Average fine, coarse, and total (fine + coarse) dust mass scattering efficiencies were  $3.4 \pm 0.5$ ,  $0.7 \pm 0.2$ , and  $1.2 \pm 0.3 \text{ m}^2 \text{ g}^{-1}$ , respectively. It is probable that fine dust corresponds to the tail of the coarse mode dust distribution; however, the higher fine mode efficiencies are a result of these sizes interacting more efficiently with light, compared to the coarse mode. Mid-range values corresponding to the total aerosol mode reflect the integration over all sizes. The variability for each of these estimates is fairly low, considering differences in dust composition and size distributions, the study locations, and dust origins, which include Asia, the Indian Ocean, and off the coast of North Africa (Chiapello et al., 1999; Li et al., 2000; Quinn et al., 2001, 2002b, 2004).

The average fine and coarse mode specific mass scattering efficiencies were  $4.3 \pm 0.7 \text{ m}^2 \text{ g}^{-1}$  and  $1.62 \pm 1.03 \text{ m}^2 \text{ g}^{-1}$ , respectively. The fine mode values could include ammoniated salts, carbonaceous aerosols, and mineral aerosols. These efficiencies were reported for a range of humidities and no corrections to a dry aerosol were performed because of the lack of information on the fine mode composition. The cut-off diameter for these modes may also vary from study to study (1–2.5  $\mu\text{m}$ ). Given these differences, there is still a fairly narrow range of values reported for fine mode specific efficiencies. A much larger variation in the coarse mode efficiencies was



observed. The composition, size distribution, and optical properties of the coarse mode may vary considerably given the studies reported here. For example, the lowest value of  $0.6 \text{ m}^2 \text{ g}^{-1}$  at Big Bend National Park (Hand, 2001) reflects the fact that soil dominated the coarse composition (~40% on average). In contrast, the values derived from the many cruise-based measurements (Quinn et al., 2001, 2002b, 2004) may be influenced by sea salt or other species.

Average fine, coarse, and total sea salt specific mass scattering efficiencies were  $5.3 \pm 0.8$ ,  $1.2 \pm 0.3$ , and  $2.3 \pm 0.9 \text{ m}^2 \text{ g}^{-1}$ , respectively. Sea salt specific mass scattering efficiencies are not corrected for relative humidity and include the effects of aerosol water mass. Similar to dust mass scattering efficiencies, the fine mode sea salt specific mass scattering efficiencies are larger than the coarse mode, with the total aerosol (fine + coarse) in the middle of the range.

### **5.3.2. Measurement Method**

Estimates of mass scattering efficiencies for the measurement method are reported in Table 3 (see Appendix 2). Most of these values correspond to specific mass scattering efficiencies for the fine or coarse mode because the measurements were performed for fine (or coarse) mass and measured light scattering. These values are not averaged together because they vary based on the relative humidity at which the measurements are made, the types of mass data (gravimetric or sum of chemically analyzed), and the composition and size ranges corresponding to each mode; therefore normalizing these data to a common RH or composition is not possible. Some studies have several values reported (such as in the Maldives during the INDOEX (Indian Ocean Experiment) study) because they are reported for ranges of light scattering coefficients and for different measurement methods (land- and cruise-based) by different investigators and averaging them together would be inappropriate. Even with these differences, some possible spatial patterns are noticeable. The highest fine mode specific mass scattering efficiencies ( $> 5 \text{ m}^2 \text{ g}^{-1}$ ) are reported in urban locations, such as Mexico City, Mexico (Chow et al., 2002), Fort

Meade MD (Chen et al., 2003), and the New England–mid-Atlantic region (Poirot and Husar, 2004). These values could be high due to relative humidity effects (especially in the eastern United States), or due to the aerosol composition. For example, the efficiency of  $6 \text{ m}^2 \text{ g}^{-1}$  reported by Poirot and Husar (2004) corresponds to smoke aerosol that may have higher efficiencies (Malm et al., 2005a; McMeeking et al., 2005). With the exception of sites in Phoenix AZ and sites near Denver CO the urban (e.g., Beijing, China, Atlanta GA, Dallas TX) fine mode specific mass scattering efficiencies are greater than  $3 \text{ m}^2 \text{ g}^{-1}$ . Most of the rural sites in the southwestern United States correspond to lower specific efficiencies (less than  $\sim 2.5 \text{ m}^2 \text{ g}^{-1}$ ) in Meadview AZ, Mount Zirkel in Colorado, and Spirit Mountain NV, which are close to the theoretical mass scattering efficiencies computed for dry ammonium sulfate. The exceptions to these low values are those reported for the northwestern United States (Mount Rainier WA and North Cascades WA) and in Bondville IL with efficiencies greater than  $4 \text{ m}^2 \text{ g}^{-1}$ . Higher specific mass scattering efficiencies (usually greater than  $3 \text{ m}^2 \text{ g}^{-1}$ ) were observed during the INDOEX experiment in the Maldives. Specific mass scattering efficiencies for this study are ordered as a function of light scattering coefficients and no significant difference was observed for low scattering ( $b_{sp} < 25 \text{ Mm}^{-1}$ ) compared to high scattering periods ( $b_{sp} > 55 \text{ Mm}^{-1}$ ), in contrast to the relationship Lowenthal and Kumar (2004) observed for data from the IMPROVE network. The specific efficiencies reported for the Maldives are for an RH of 33%, so the effects of aerosol water mass are probably not significant for these data. Specific efficiencies corresponding to the total aerosol mode were reported for Yulin, China (Alfaro et al., 2003), during the ACE-Asia study. Values were higher during polluted periods compared to periods dominated by dust aerosols, probably because of the change in aerosol size distributions.

### 5.3.3. MLR Method

Estimates of mass scattering efficiencies obtained using the MLR method are summarized in Table 4 (see Appendix 2). These values are subject to variability based on how the regressions were performed (with or without intercepts, or accounting for measurement uncertainties) and the types of data used. Average fine mode specific mass scattering efficiencies were  $3.1 \pm 1.5 \text{ m}^2 \text{ g}^{-1}$ , which were somewhat lower than the average estimate derived from the theoretical method, although with much larger variability. The highest values ( $> 5 \text{ m}^2 \text{ g}^{-1}$ ) were reported in Israel, and the lowest values ( $2\text{--}3 \text{ m}^2 \text{ g}^{-1}$ ) were reported in the southwestern United States (Nevada, Arizona, and Colorado), which is similar to the spatial distribution seen with the results from the measurement method. Average coarse mode specific mass scattering efficiencies are  $0.7 \pm 0.6 \text{ m}^2 \text{ g}^{-1}$ , ranging from values greater than  $1 \text{ m}^2 \text{ g}^{-1}$  in Nevada and Arizona to values less than  $0.5 \text{ m}^2 \text{ g}^{-1}$  in Colorado, Arizona, and Israel. The variability of coarse mode composition and size distributions could result in large variability in derived efficiencies.

The average fine mode dry ammonium sulfate mass scattering efficiency was  $4 \pm 3 \text{ m}^2 \text{ g}^{-1}$ , higher than theoretically predicted for fine mode dry ammonium sulfate and with a large variability due to outliers. Removing the outliers (i.e.,  $10.9$  and  $8 \pm 3 \text{ m}^2 \text{ g}^{-1}$ ) results in an average dry ammonium sulfate efficiency of  $3.2 \pm 1.2 \text{ m}^2 \text{ g}^{-1}$ , much closer to what has been theoretically derived. It is possible that these high values are due to water associated with the nephelometer data, or due to uncertainties in the nephelometer data. Many of the sulfate mass scattering efficiencies reported in the MLR table were corrected to a dry ammonium sulfate basis, which could also contribute to uncertainties in these values. Variations in relative humidity or aerosol acidity could result in uncertainties in the corrections as these were applied in an average sense. The lowest value reported in the table ( $0.83 \text{ m}^2 \text{ g}^{-1}$ ) corresponds to the total ( $D_p < 10 \text{ }\mu\text{m}$ ) size distribution, demonstrating the effects of averaging over larger particles (higher

mass) that have less efficient light scattering properties. Also, it is probable that the chemical form of sulfate in the coarse mode was different from ammonium sulfate.

The un-normalized average value of POM mass scattering efficiency was  $3 \pm 4 \text{ m}^2 \text{ g}^{-1}$ , with large variability reflecting the range in values reported. The average POM mass scattering efficiency normalized to an  $R_{oc}$  of 1.8 is  $2 \pm 3 \text{ m}^2 \text{ g}^{-1}$ . Outliers in these values are reported for Uniontown PA ( $12 \pm 8 \text{ m}^2 \text{ g}^{-1}$ , Lowenthal et al., 1995), and removing that outlier from the normalized efficiencies results in an average value of  $1.6 \pm 0.6 \text{ m}^2 \text{ g}^{-1}$ , which is considerably lower than the average value of  $5.5 \pm 1.6 \text{ m}^2 \text{ g}^{-1}$  derived with the theoretical method. Besides the outlier, the highest value reported is for Bondville IL ( $4.11 \text{ m}^2 \text{ g}^{-1}$ ) (Koloutsou-Vakakis et al., 2001) and has not been normalized because it corresponds to a carbonaceous aerosol that includes both organic and light-absorbing carbon. The low values of POM mass scattering efficiency derived by this method provide a good example of how uncertainties associated with organics may result in an underprediction of derived mass scattering efficiencies.

The average ammonium nitrate mass scattering efficiency was  $4 \pm 2 \text{ m}^2 \text{ g}^{-1}$ . The highest values are reported for Meadview AZ and Mount Zirkel CO. However, no spatial dependence is seen as the lowest values reported are also in the southwestern United States (Grand Canyon AZ, Canyonlands UT, and Phoenix AZ). The average fine, coarse, and total dust mass scattering efficiencies are  $3 \pm 2$ ,  $0.40 \pm 0.08$ , and  $0.7 \pm 0.2 \text{ m}^2 \text{ g}^{-1}$ , respectively. Fine mode dust mass scattering efficiencies are quite similar to those derived using the theoretical method ( $3.4 \pm 0.5 \text{ m}^2 \text{ g}^{-1}$ ); however, coarse mode and total dust efficiencies are somewhat lower for the MLR method. Given the range of assumptions and different measurements that are incorporated into these estimates, the convergence of fine dust efficiencies towards  $3 \text{ m}^2 \text{ g}^{-1}$  is notable.

The average sea salt specific mass scattering efficiencies for the fine, coarse, and total modes are  $4.0 \pm 1.6$ ,  $1.57 \pm 1.16$ , and 2.2 (one number reported)  $\text{m}^2 \text{g}^{-1}$ , respectively. These values are also quite similar to those reported in the theoretical table. Sea salt is hygroscopic; therefore any water associated with measured scattering could be attributed to sea salt in the regression.

#### **5.3.4. Partial Scattering Method**

Values of mass scattering efficiency derived from the partial scattering approach are reported in Table 5 (see Appendix 2). Most of these studies employed the ELSIE model, as described previously. Species included in the model are sulfate, POM, nitrate, dust, elemental carbon, and fine mode aerosols. The two entries listed in the table per site for the first eight entries correspond to model results using two scenarios: (1) assuming a homogeneous composition with constant particle size, and (2) a core/shell scenario with constant particle number. All estimates reported in the table using the constant size assumption are in bold font. It is not appropriate to average efficiencies computed with both scenarios because the second scenario corresponds to changing size distributions that would also change the efficiency. The entries listed for Hopi Point toward the end of the table all correspond to estimates made at different relative humidities.

The average dry ammonium sulfate partial scattering efficiency for the first scenario (including those we corrected) in Table 5 is  $2.7 \pm 0.4 \text{ m}^2 \text{g}^{-1}$ , similar to the results from the theoretical method, as would be expected because the theoretical basis is the same. Most of the studies included in this table occurred in the western or southwestern United States with the exception of the rural sites of Bondville IL and Uniontown PA. The sites in the Southwest are mostly rural with the exception of Phoenix AZ. No strong spatial variation is noticeable. Values derived in Meadview AZ are somewhat higher than those derived in Hopi Point. Both locations

are near the Grand Canyon, with Hopi Point on the southern rim of the canyon and Meadview on the western edge of the canyon. Observations from Meadview have been used to characterize sub-regional aerosol and visibility in the Southwest (MOHAVE study) (Turpin et al., 1997; Lowenthal et al., 2000). It is possible that the aerosols measured in Meadview were influenced by long-range transport and therefore probably aged, resulting in somewhat higher efficiencies. The average normalized POM mass scattering efficiency is  $3.0 \pm 1.4 \text{ m}^2 \text{ g}^{-1}$ . High values were measured in Uniontown PA, Denver CO, and the Grand Canyon (Hopi Point), a mix of rural and urban locations. The ELSIE model treats POM mass as partly soluble (values for these studies range from 25 to 60% solubility, and that fraction is as soluble as ammonium sulfate), so a direct comparison of POM partial scattering efficiency from this method to the other methods is not appropriate. The average ammonium nitrate partial scattering efficiency is  $3.8 \pm 1.5 \text{ m}^2 \text{ g}^{-1}$ , with an outlier value in Denver CO. The average fine dust mass scattering efficiency is  $3 \pm 1 \text{ m}^2 \text{ g}^{-1}$ . Especially high dust efficiencies were reported for Uniontown PA.

### **5.3.5. Apportionment Method**

As part of the National Acid Precipitation Assessment Program (NAPAP) Report 24 on visibility (1991), mass scattering efficiencies were computed from light scattering coefficients and mass data based on several studies around the United States. Scattering was apportioned to major species such as ammonium sulfate and organics (White, 1991). The intention of the apportionment scheme was to provide the range of efficiencies based on extreme assumptions. Low estimates of sulfate mass scattering efficiencies were derived assuming that sulfates, nitrates, and POM scatter twice as efficiently as the remaining aerosol. The high estimates for sulfates were derived assuming that sulfates alone scatter twice as efficiently as all other fine aerosol. Low estimates of POM mass scattering efficiency were derived assuming that POM and non-sulfate species scatter half as efficiently as sulfates. High POM mass scattering efficiencies

were derived assuming that POM is three times as efficient, and sulfate is twice as efficient, as the remaining aerosol in the fine mode. The range of these values is reported in Table 6, along with a summary of efficiencies for all the methods. Values for POM mass scattering efficiencies are normalized to an  $R_{oc}$  multiplier of 1.8. The values reported in Table 6 for the apportionment method are from studies that occurred around urban and rural U.S. locations. The average specific mass scattering efficiency for the fine mode was  $2.6 \pm 0.9 \text{ m}^2 \text{ g}^{-1}$ , with higher values in the rural and urban eastern United States ( $4.5 \pm 0.8$  and  $3.5 \pm 0.4 \text{ m}^2 \text{ g}^{-1}$ , respectively). The lowest values were computed for the rural and urban western United States, especially San Jose CA ( $1.83 \text{ m}^2 \text{ g}^{-1}$ ). The apportionment method fine mode specific mass scattering efficiency was the lowest of all the methods; however, it was closest to the MLR method. Although these values are reported as dry, it is possible that the RH environment where the measurements were made has an effect on the values derived, perhaps through associated water on the filter or aerosol processing effects.

**Table 6. Summary of mass scattering efficiencies reported in Tables 2 through 5 (Appendix 2). The “Apportionment” column refers to results from White (1991). The “IMPROVE” column lists values used in the current IMPROVE formulation. Entries correspond to the fine mode unless otherwise stated in the row header.**

<b>Summary of Mass Scattering Efficiencies from All Methods*</b>					
<b>Species/ Mode</b>	<b>Theoretical (m<sup>2</sup> g<sup>-1</sup>)</b>	<b>MLR (m<sup>2</sup> g<sup>-1</sup>)</b>	<b>Partial (m<sup>2</sup> g<sup>-1</sup>)</b>	<b>Apportionment** (m<sup>2</sup> g<sup>-1</sup>)</b>	<b>IMPROVE</b>
<b>Fine</b>	4.3 ± 0.7 (26)	3.1 ± 1.5 (17)		2.7 ± 0.8 (30)	
<b>Coarse</b>	1.62 ± 1.03 (21)	0.7 ± 0.6 (13)			0.6
<b>Total</b>	2.15 ± 1.01 (9)				
<b>Sulfate</b>	2.45 ± 1.14 (16)	3.2 ± 1.2 (24)	2.8 ± 0.7 (24)	3.0 ± 0.9 – 3.9 ± 0.9 (30)	3.0
<b>Nitrate</b>		4 ± 2 (16)	3.8 ± 1.6 (11)		3.0
<b>POM</b>	5.86 ± 1.01 (20)	2.29 ± 1.02 (23)	5.4 ± 1.8 (26)	1.5 ± 0.3 – 3.2 ± 0.9 (30)	4.0
<b>Fine Dust</b>	3.4 ± 0.5 (19)	3 ± 2 (19)	3 ± 1 (9)		
<b>Coarse Dust</b>	0.7 ± 0.2 (21)	0.40 ± 0.08 (2)			1.0
<b>Total Dust</b>	1.2 ± 0.3 (9)	0.7 ± 0.2 (3)			
<b>Fine Sea Salt</b>	5.3 ± 0.8 (22)	4.0 ± 1.6 (3)			
<b>Coarse Sea Salt</b>	1.2 ± 0.3 (20)	1.57 ± 1.16 (3)			
<b>Total Sea Salt</b>	2.3 ± 0.9 (9)	2.2 ± 0 (1)			

\* Number of observations in parentheses

\*\* Apportionment values from Table H-1 in Appendix H in White, 1991, and references therein.

Dry ammonium sulfate mass scattering efficiencies derived from the apportionment method ranged from  $3.0 \pm 0.9$  to  $3.9 \pm 0.9 \text{ m}^2 \text{ g}^{-1}$  for the low and high apportionment strategies, respectively. These estimates are similar to the values derived from the other methods but still larger than what is derived from the theoretical method. The POM mass scattering efficiencies are lower than other estimates reported in Table 6, although the MLR method estimates fall within the range of low and high values from the apportionment schemes. It is interesting that derived sulfate mass scattering efficiencies are fairly insensitive to the low and high apportionment scheme, while the POM efficiencies are approximately double, based on the apportionment scheme, probably due to uncertainties associated with organic carbon



measurements. The spatial variability in both sulfate and POM mass scattering efficiencies are similar to the fine mode specific efficiency. The highest values are derived in the eastern United States (both rural and urban) and the lowest values in the urban West.

### **5.3.6. Mass Absorption Efficiencies**

Reported estimates of mass scattering and absorption efficiencies of LAC, as well as for other species, are reported in Table 7 (see Appendix 2). Efficiencies listed in this table have been derived using all the methods described above, which is noted in the first column of the table. Typically, mass absorption efficiencies are computed by the measurement method, by dividing a light absorption coefficient measured by transmittance, (measured with an aethalometer or particle soot absorption photometer (PSAP)), by the mass of LAC from thermal analyses. Light absorption coefficients measured with a photoacoustic technique also are used to derive mass absorption efficiencies (e.g., Arnott et al., 2003). The theoretical method can be used if the size distribution of LAC is measured, or by applying a complex refractive index to number or volume size distributions in the Mie calculation. In Table 7 the values reported for a wavelength other than 550 nm have been corrected to 550 nm assuming a  $\lambda^{-1}$  relationship (Bohren and Huffman, 1983). It is well known that large uncertainties surround the values of mass absorption efficiencies by LAC, as is evidenced by the range of values reported in the table. Much of the uncertainty stems from the fact that estimates of LAC mass concentrations are method-dependent (as described in section 2.3), as are light absorption efficiencies, on the wavelength at which the measurements are performed, due to the spectral dependence of light absorption.. Uncertainties also arise due to the wide range in optical properties (i.e., complex refractive index) of LAC applied in theoretical methods.

Reconstructed extinction equations typically treat LAC as externally mixed (see equations 4 and 5), as well as assume that it is the only component of the aerosol that is absorbing solar radiation in the visible wavelengths. This formulation is based on the assumption that LAC refers only to “soot” particles; however, there is substantial evidence that some of the carbonaceous aerosol, especially biomass smoke, being characterized as LAC by thermal methods, is not soot and in fact is probably refractory organic carbon. Others have reported that light-absorbing carbon and a significant fraction of organic carbon from biomass smoke have similar volatility and combustion temperatures, causing the split between LAC and OC to be poorly defined (and method-dependent) and leading to an overestimation of LAC and an underestimation of OC for biomass smoke [Novakov and Corrigan, 1995; Gelencsér et al., 2000; Mayol-Bracero et al., 2002; Formenti et al., 2003; Guyon et al., 2003]. A previous study by Malm et al. (1994b) in the northwestern United States showed that light absorption coefficients (as measured independently) correlated well with higher temperature fractions of OC as well as LAC. Analyses of single particle data from Yosemite National Park (Hand et al., 2005) showed that both the measured LAC and OC from TOR analysis corresponded to a type of non-graphitic refractory carbonaceous particle called tar balls, which are efficient at both scattering and absorbing light. Caution should be taken in always interpreting data from TOR analyses only as externally mixed OC and LAC particles, because TOR analyses are based on the refractory properties of carbon particles, and not necessarily on their light absorbing characteristics.

Theoretical calculations have been performed (Fuller et al., 1999) that suggest a reasonable LAC mass absorption efficiency of  $6.5 \text{ m}^2 \text{ g}^{-1}$ ; however, the average value of the empirical values listed in Table 7 is  $13 \pm 6 \text{ m}^2 \text{ g}^{-1}$ . The IMPROVE equation applies a value of  $10 \text{ m}^2 \text{ g}^{-1}$ ; the scattering due to LAC is not considered in the IMPROVE equation. Estimates

reported in Table 7 suggest an average fine mode LAC mass scattering efficiency of  $3.6 \pm 1.3 \text{ m}^2 \text{ g}^{-1}$ . Clearly, more work is needed to understand the absorption characteristics of carbonaceous aerosols.

The summary of the survey results for all methods, including values currently used in the IMPROVE formulation, is reported in Table 6. The results suggest that POM mass scattering efficiencies are higher than what is applied in the IMPROVE reconstruction equation, even though the current IMPROVE formulation assumes an  $R_{oc}$  multiplier of 1.4. However, in general the IMPROVE efficiencies fall within the range of the variability seen in the survey results. Fine soil in the IMPROVE formulation is assumed to correspond to the tail of the coarse dust size distribution; therefore the mass scattering efficiency associated with dust in a reconstructed  $\text{PM}_{2.5} b_{ext}$  calculation corresponds to a coarse dust mass scattering efficiency. If the fine dust concentration actually corresponds to a size distribution that peaks in the fine mode, the corresponding mass scattering efficiency would actually be quite higher ( $\sim 3 \text{ m}^2 \text{ g}^{-1}$ ). Size distribution measurements at IMPROVE sites suggest this is not typically the case (e.g., Hand et al., 2002; Lee et al., 2004a, 2004b).

Lowenthal and Kumar (2004) suggest that the mass scattering efficiencies applied in the IMPROVE formulation should be reevaluated based on a comparison of measured and reconstructed scattering that implies that scattering is overestimated 66% of the time on average at 20 IMPROVE sites. Dry ammonium sulfate mass scattering efficiencies from the survey are somewhat lower and ammonium nitrate efficiencies are somewhat higher than the IMPROVE values, but the IMPROVE mass scattering efficiencies fall within the variability seen in the survey results. Coarse mass (CM) efficiency is assumed to be  $0.6 \text{ m}^2 \text{ g}^{-1}$ , and the absorption efficiency for light-absorbing carbon (LAC) is  $10 \text{ m}^2 \text{ g}^{-1}$ , both falling within the range of

variability reported in the survey. In general the values of dry mass scattering efficiency applied in the IMPROVE equation are reasonable, given the range of ground-based values reported in the literature since 1990.

#### 5.4. *Estimates of Dry Mass Scattering Efficiencies from IMPROVE Data*

The form of the equation for reconstructing extinction in the tracking progress guidance is

$$b_{ext} = (3.0)f(RH)\{[(NH_4)_2SO_4] + [NH_4NO_3]\} + (4.0)[POM] + 1.0[Soil] + (0.6)[CM] + (10.0)[LAC] \quad (16)$$

where  $b_{ext}$  is the extinction coefficient and enclosed in the brackets is the aerosol species mass concentration. The parenthetically enclosed numerals in front of POM, soil, and coarse mass (CM) are the optimal dry mass scattering efficiencies as reviewed by White (1990) and Malm et al. (1994a). A nominal mass scattering efficiency value of  $3.0 \text{ m}^2 \text{ g}^{-1}$  is applied for dry ammonium sulfate and dry ammonium nitrate. The ratio of wet and dry scattering as a function of RH is the relative humidity scattering enhancement factor  $f(RH)$ .

In the IMPROVE monitoring program, nephelometers collocated with particle mass samplers have been operated at 22 sites, in some cases for more than 10 years. Therefore the validity of the assumptions associated with equation 16 can be explored and possibly refined by comparing measured and reconstructed scattering. Three methods will be used as part of this strategy to estimate mass scattering efficiencies. We describe each method below, followed by a comparison of results from each method for one site (Acadia) and later for all sites. In addition to the uncertainties described above, the results from these methods are subject to uncertainties in the  $b_{sp}$  values measured by Optec NGN nephelometers at a wavelength of 550 nm.

The first method uses a simple linear regression technique that assumes the relationship between scattering and species mass concentrations can be represented by equation 17. POM is assumed to be 1.8·OC, sea salt is estimated as 1.6·Cl<sup>-</sup>, and soil and CM are grouped together.

$$b_{sp} = a_o + a_1 f(RH)[(NH_4)_2SO_4] + a_2 f(RH)[NH_4NO_3] + a_3[POM] + a_4[soil + CM] + a_5[sea\ salt] \quad (17)$$

The regression coefficients are interpreted as the mass scattering efficiencies and the  $f(RH)$  curves are those associated with ammonium sulfate assuming a mass mean diameter of  $D_g = 0.2$   $\mu\text{m}$  and geometric standard deviation of 2, and an ammonium sulfate  $D/D_o$  curve estimated using the AIM (Asian-Pacific Integrated Model) “no solids” model (assumes equilibrium below the crystallization point). The  $f(RH)$  was calculated on one-hour intervals and averaged to 24 hours to be commensurate with the one-day sampling duration of the aerosol samples.

The second approach for deriving mass scattering efficiencies assumes an aerosol model of a fine mode internal mixture of inorganic ammonium salts (sulfate and nitrate) and POM that is externally mixed from soil, coarse mass, and sea salt. The measured fine mode mixture scattering ( $b_{mix}$ ) is approximated by:

$$b_{mix} = b_{open} - b_{CM} - b_{soil} - b_{SS} \quad (18)$$

where  $b_{open}$  is measured with the PM<sub>10</sub> open air nephelometer, and  $b_{CM}$ ,  $b_{soil}$ , and  $b_{SS}$  (scattering due to sea salt) are estimated using coarse mass, fine soil, and sea salt mass (1.6·Cl). Sea salt scattering is estimated by multiplying the sea salt mass by a mass scattering efficiency of  $1 \text{ m}^2 \text{ g}^{-1}$  and the  $f(RH)$  value defined above. If the assumptions are met that allow scattering associated with an internal and external mixture to be approximately equal, then

$$\alpha_{mix} M_{mix} = [(NH_4)_2SO_4 + NH_4NO_3] \alpha_{inorg} + 1.21[POM] \alpha_{inorg} \quad (19)$$

where the specific mass scattering efficiency  $\alpha_{mix}$  of the mixed aerosol mass ( $M_{mix} = [(NH_4)_2SO_4 + NH_4NO_3 + POM]$ ) is prorated to its chemical constituents based on their relative densities (1.21 = 1.7/1.4). The specific mass scattering efficiency of ammonium sulfate and ammonium nitrate is  $\alpha_{inorg}$ , and  $\alpha_{POM}$  corresponds to the mass scattering efficiency of POM. Implicit assumptions in equation 19 are that the refractive indices of all the species are similar, and the

mixing ratios of the species are independent of the size distribution of the mixed aerosols.

Therefore the estimated scattering of the mixture ( $b_{mix\_est}$ ) is written as

$$b_{mix\_est} = (3.0)f(RH)[(NH_4)_2SO_4 + NH_4NO_3] + 3.63[POM] \quad (20)$$

where  $3 \text{ m}^2 \text{ g}^{-1}$  is the nominal mass scattering efficiency assigned to ammonium sulfate and ammonium nitrate, and  $3.63 \text{ m}^2 \text{ g}^{-1}$  is the density-weighted mass scattering efficiency of POM (1.21·3). A regression is performed for  $b_{mix}$  and  $b_{mix\_est}$  and the regression coefficient is  $a_1$ . The inorganic and organic specific efficiencies can therefore be written as  $\alpha_{inorg} = a_1 \cdot 3.0$  and  $\alpha_{org} = a_1 \cdot 3.63$ , respectively.

Both of the above-described approaches assume that the discrepancy between measured and estimated scattering can be accounted for by a single multiplicative constant, either for each species or for the mixed aerosol. These approaches do not account for the possibility that mass scattering efficiencies vary as a function of mass concentration (due to its functional dependence on particle size, as described in the section 5.1). Therefore the third approach was used to investigate how mass scattering efficiencies may vary with mass concentrations. A scattering correction factor ( $SCF$ ) is defined as the ratio of measured scattering of the mixture ( $b_{mix}$ ) from equation 18 to the estimated scattering for the mixture ( $b_{mix\_est}$ ):

$$SCF = \frac{b_{mix}}{b_{mix\_est}} = \frac{b_{open} - b_{CM} - b_{soil} - b_{SS}}{3.0f(RH)[(NH_4)_2SO_4 + NH_4NO_3] + 3.63[POM]} \quad (21)$$

The  $SCF$  should equal 1 for all mass values if the assumptions used in computing  $b_{mix}$  and  $b_{mix\_est}$  are appropriate and if there is not a functional dependence between mass scattering efficiency and  $M_{mix}$ . The functional relationship of  $SCF$  with the mixture mass ( $M_{mix}$ ) was explored using equation 22:

$$SCF = a_o + a_1[M_{mix}] \quad (22)$$

where  $a_0$  and  $a_1$  are the regression coefficients determined using a Theil regression analysis, and  $SCF$  is the scattering correction factor computed from equation 21. In this case a linear relationship is hypothesized; however, any functional relationship could be assumed. A new estimate of  $b'_{mix}$  can be calculated using

$$b'_{mix\_est} = SCF'\{3f(RH)[(NH_4)_2SO_4 + NH_4NO_3] + 3.63[POM]\} \quad (23)$$

where  $SCF'$  is the estimated scaling factor derived from equation 22. New inorganic and organic specific mass scattering efficiencies are then calculated as  $\alpha'_{norg} = 3.0 \cdot SCF'$  and  $\alpha'_{org} = 3.63 \cdot SCF'$ .

### ***Comparison of Methods for Acadia National Park***

To demonstrate the differences in these three methods and their effect on subsequent reconstructed scattering, results from Acadia National Park (ACAD) will be presented for each method. Reconstructed total scattering ( $b_{sp\_tot}$ ) was computed using

$$b_{sp\_tot} = (3.0)f(RH)[(NH_4)_2SO_4 + NH_4NO_3] + 3.63[POM] + (1.0)[Soil] + (0.3)[CM] + (1.0)[Sea\ salt] \quad (24)$$

We applied ammonium sulfate and ammonium nitrate mass scattering efficiencies of  $3.0 \text{ m}^2 \text{ g}^{-1}$ , a POM mass scattering efficiency of  $3.63 \text{ m}^2 \text{ g}^{-1}$  (assuming a POM multiplier of 1.8), and a CM specific efficiency of  $0.3 \text{ m}^2 \text{ g}^{-1}$  to account for coarse particle truncation issues in the nephelometer. A statistical summary of the mass concentrations, RH, average number of hours in each 24-hour period of useable nephelometer data, average  $f(RH)$  using ambient RH and RH inside the nephelometer chamber, and new and presently used  $f(RH)$  curves for ACAD are provided in Table 8. A summary of measured and reconstructed total ambient scattering, absorption, and contributions to scattering from each species is found in Table 9. Also listed in Table 9 is estimated scattering due to absorbed water on the ammoniated salts. Reconstructed total ambient scattering associated with dry mass is overestimated by about 15% on average, and

scattering due to absorbed water is about half of the scattering due to inorganic mass, emphasizing the importance of selecting an appropriate  $f(RH)$  curve (see Appendix 3 for similar tables for all sites).

**Table 8.** A statistical summary of mass concentrations ( $\mu\text{g m}^{-3}$ ) at Acadia National Park (ACAD). CM and FM refer to coarse mass and fine ( $\text{PM}_{2.5}$ ) mass, respectively. AS and AN refer to ammonium sulfate and ammonium nitrate, respectively. POM is particulate organic matter using a  $R_{oc}$  factor of 1.8. RH refers to ambient relative humidity. The number of nephelometer data points in a 24-hr average is given by  $N(b_{sp})$ . The values of the revised  $f(RH)$  curves for the ambient RH ( $f(RH)_{amb,new}$ ) and the nephelometer chamber RH ( $f(RH)_{chamb,new}$ ) are also listed. Similar values are reported for the current  $f(RH)$  curves ( $f(RH)_{amb,old}$  and  $f(RH)_{chamb,old}$ ).

Variable	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
$b_{sp}$ ( $\text{Mm}^{-1}$ )	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
$f(RH)_{chamb,old}$	1.66	0.41	1.00	3.29	637	0



**Table 9. A summary of  $b_{sp}$  ( $Mm^{-1}$ ) for Acadia National Park (ACAD). Values correspond to measured total ambient scattering ( $b_{sp}$ ), reconstructed total ambient scattering ( $b_{sp\_recon}$ ), measured scattering associated with inorganics and organics ( $b_{mix}$ ), estimated scattering associated with inorganics and organics ( $b_{mix\_est}$ ), scattering due to ammonium sulfate ( $b_{sp}(AS)$ ), ammonium nitrate ( $b_{sp}(AN)$ ), particulate organic material ( $b_{sp}(POM)$ ), soil and coarse mass ( $b_{sp}(soil+CM)$ ), sea salt ( $b_{sp}(SS)$ ), and water ( $b_{sp}(H_2O)$ ). Light absorption ( $b_{ap}$ ) was computed assuming a mass absorption efficiency of  $10 m^2 g^{-1}$ . New  $f(RH)$  curves were used to estimate wet scattering. POM was computed assuming an  $R_{oc}$  factor of 1.8 and mass scattering efficiency of  $3.63 m^2 g^{-1}$ .**

Variable	Mean	Std Dev	Minimum	Maximum	Valid	Missing
$b_{sp}$	21.36	25.46	2.38	235.13	267	370
$b_{sp\_recon}$	24.32	24.34	3.74	217.90	267	370
$b_{mix}$	20.17	25.26	0.74	234.37	267	370
$b_{mix\_est}$	23.13	24.07	3.30	217.14	267	370
$b_{sp}(AS)$	14.14	19.55	1.75	184.85	267	370
$b_{sp}(AN)$	2.45	3.18	0.19	27.76	267	370
$b_{sp}(POM)$	6.54	4.69	0.79	29.95	267	370
$b_{sp}(Soil)$	0.29	0.24	0.01	2.27	267	370
$b_{sp}(CM)$	1.72	1.94	-0.21	25.19	267	370
$b_{sp}(SS)$	0.05	0.23	0.00	2.80	267	370
$b_{sp}(soil+CM)$	2.01	2.04	-0.02	25.80	267	370
$b_{ap}$	2.30	1.56	0.43	11.27	267	370
$b_{sp}(H_2O)$	8.51	11.76	0.85	112.63	267	370

The fractional contribution of each species to total scattering using equation 24 is presented in Table 10. The results from the OLS regression in method 1 are reported in Table 11. A comparison of measured total ambient scattering and reconstructed total scattering using equation 24 and method 1 is shown in Figure 7 (similar tables and figures corresponding to method 1 for all sites can be found in Appendix 4). Notice that reconstructed scattering from equation 24 is underestimated for low values of  $b_{sp}$  and overestimated at high values of  $b_{sp}$ , suggesting that mass scattering efficiencies vary with mass concentration. Reconstructed  $b_{sp}$  derived from method 1 removes the biases observed at low and high  $b_{sp}$  but at the expense of having what appears to be unrealistic mass scattering efficiencies. The CM + soil specific scattering efficiency is negative, which is unphysical, and the sea salt efficiency is  $5.32 m^2 g^{-1}$  (see Table 11), similar to values reported by Quinn et al. (2001, 2002b, 2004) for higher RH values. The average ammonium sulfate and POM mass scattering efficiencies of  $3.38 m^2 g^{-1}$ , and  $2.17 m^2 g^{-1}$ , respectively, are physically reasonable. However, sulfate mass scattering efficiencies

may be overestimated and POM mass scattering efficiencies may be underestimated due to the relative uncertainties in each of those measurements.

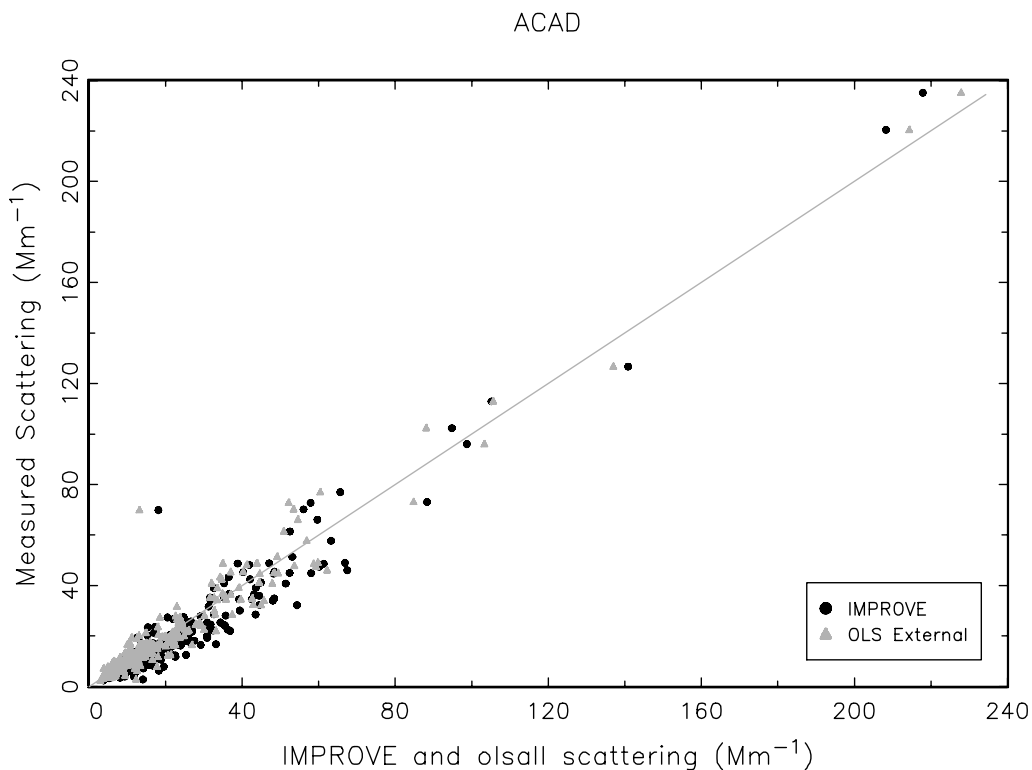
**Table 10. Fractional contribution to total ambient scattering at Acadia National Park using equation 24 in the text. AS corresponds to ammonium sulfate and AN corresponds to ammonium nitrate. Particulate organic matter (POM) fraction was computed assuming an Roc factor of 1.8. The coarse mode fraction is given by CM.**

Species	Fraction of $b_{sp}$
AS	0.701
AN	0.121
POM	0.324
Soil	0.014
CM	0.085
Sea salt	0.002
$\frac{(b_{mix} - b_{mix\_est})}{b_{mix}}$	-0.147

**Table 11. The results from the ordinary least squares regression of method 1 for Acadia National Park (see equation 17). The regression coefficients ( $a_i$ ) are listed, along with the standard error. Derived mass scattering efficiencies are also listed for ammonium sulfate (AS), ammonium nitrate (AN), particulate organic matter (POM = 1.8\*OC), coarse mass combined with soil (CM+soil) and sea salt. The number of valid cases was 267 and there were 370 missing data points. The  $r^2$  coefficient was 0.95.**

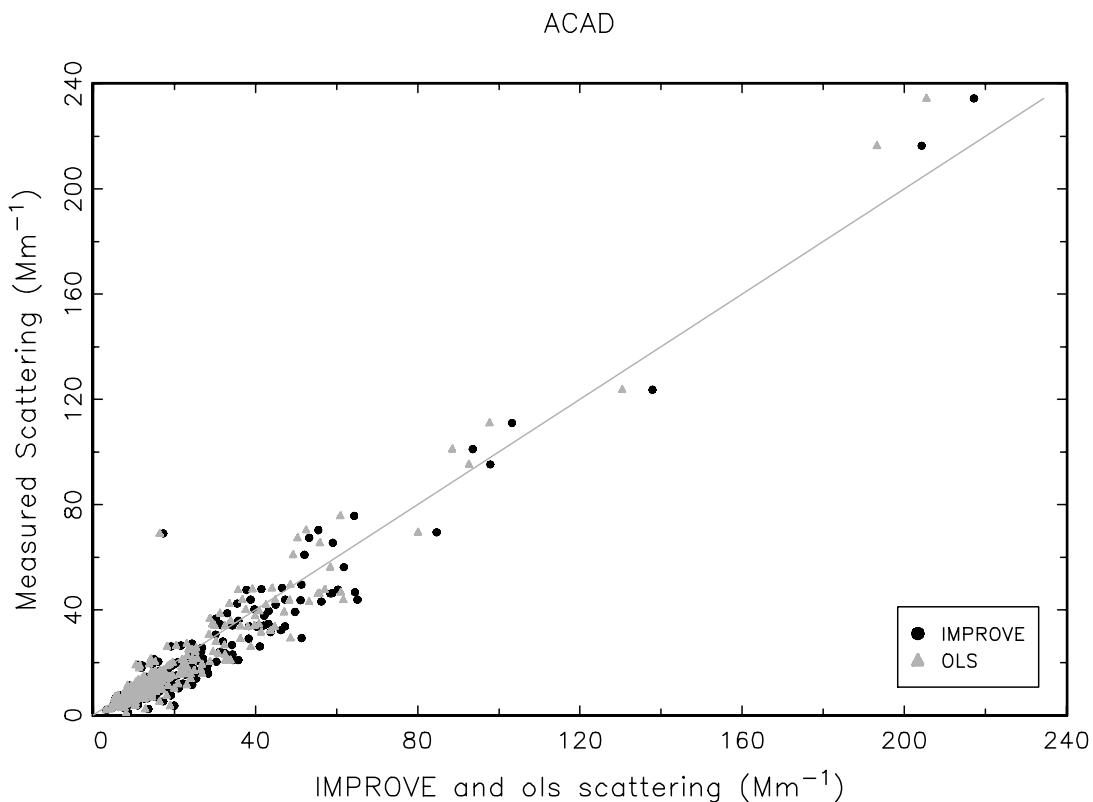
Acadia NP			
Variable	Coefficient ( $a_i$ )	Standard Error	Derived Mass Scattering Efficiency ( $m^2 g^{-1}$ )
AS	1.13	0.03	3.38
AN	0.88	0.12	2.65
POM	0.60	0.09	2.17
CM+Soil	-0.39	0.17	-0.23
Sea salt	5.32	1.56	5.32

**Figure 7. Measured total ambient scattering and reconstructed total scattering using equation 24 and method 1 for Acadia National Park.**



Estimates of specific scattering efficiencies for ammoniated salts (sulfates and nitrates) and POM mass scattering efficiency derived from method 2 are reported in Table 12. The derived sulfate and nitrate specific efficiency was  $2.84 \text{ m}^2 \text{ g}^{-1}$  and the POM mass scattering efficiency was  $3.43 \text{ m}^2 \text{ g}^{-1}$ . Comparisons of measured mixed  $b_{mix}$  to reconstructed mixed  $b_{mix,est}$  using method 2 and equation 20 are shown in Figure 8 (similar tables and figures corresponding to all sites for method 2 are found in Appendix 5). The single multiplication factor derived from the regression between  $b_{mix}$  and  $b_{mix,est}$  that was used to correct the inorganic and organic mass scattering efficiencies does not remove the biases observed at low and high scattering values. It only serves to make the average method 2 OLS reconstructed scattering equal that which is measured.

**Figure 8. Comparisons of measured mixed scattering ( $b_{mix}$   $Mm^{-1}$ ) to reconstructed mixed scattering ( $b_{mix,est}$   $Mm^{-1}$ ) using method 2 and equation 24 (fine mode contributions) for Acadia National Park.**



**Table 12. Results for method 2 regression for estimating specific mass scattering efficiencies for inorganics ( $\alpha_{inorg}$ ) and organics ( $\alpha_{org}$ ) for Acadia National Park. See text for full description.**

<b>Results for Method 2 Regression (Acadia NP)</b>	
<i>a1</i> coefficient	0.95
Standard error in <i>a1</i>	0.01
$\alpha_{inorg}$ ( $m^2 g^{-1}$ )	2.84
$\alpha_{org}$ ( $m^2 g^{-1}$ )	3.43

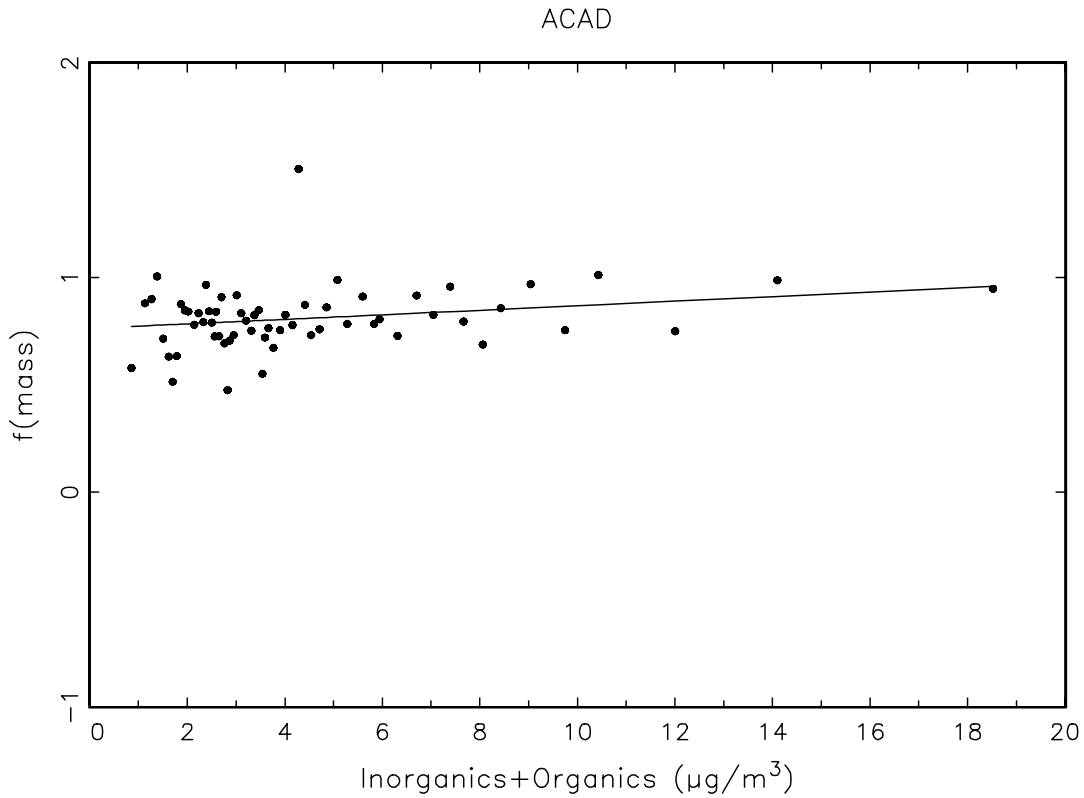
Statistical summaries of method 3 for Acadia are reported in Tables 13–15. The intercept and slope from the Thiel regression of  $SCF$  versus mass ( $M_{mix}$ ) are presented in Table 13. A slope of 0 corresponds to a constant mass scattering efficiency over the entire mass range while the intercept is proportional to the over- or underestimation of the assumed mass scattering

efficiencies for sulfates and POM (3 and 3.63 m<sup>2</sup> g<sup>-1</sup>, respectively). An intercept of one and slope of zero would imply that the assumed values provided good agreement between measured and reconstructed mixed (inorganic and POM) scattering. The comparison of fine mode inorganic and organic mass concentrations and *SCF* is shown in Figure 9 (similar figures and tables for all sites corresponding to method 3 can be found in Appendix 6). The Thiel regression line is also shown, demonstrating a fairly flat slope as reported in Table 13. Upper and lower mass scattering efficiencies for ammoniated salts and POM that are associated with the 15% upper and lower mass concentrations are reported in Table 14. Finally, the comparison of reconstructed and estimated mixed scattering using efficiencies derived from method 3 is shown in Figure 10. The summary of derived efficiencies from method 3 and the *SCF* factor is reported in Table 15. Accounting for the dependence of mass scattering efficiency on mass with method 3 removes these biases observed at low and high scattering by increasing the value of the efficiencies for low mass concentrations, and decreasing efficiencies that correspond to high mass concentrations (see Figure 10). As shown in Table 15, the average inorganic specific mass scattering efficiency using method 3 at Acadia NP is 2.44 m<sup>2</sup> g<sup>-1</sup> (ranging from 2.31 to 3.40 m<sup>2</sup> g<sup>-1</sup>). The mean POM mass scattering efficiency was 2.95 m<sup>2</sup> g<sup>-1</sup>, ranging from 2.79 to 4.12 m<sup>2</sup> g<sup>-1</sup>.

**Table 13. Results of the method 3 Thiel regression of *SCF* versus mass ( $M_{mix}$ ) for Acadia National Park.**

<b>Method 3 Thiel Regression results (Acadia NP)</b>	
<b>Intercept</b>	0.763
<b>Slope</b>	0.011
<b>Significance</b>	0.078

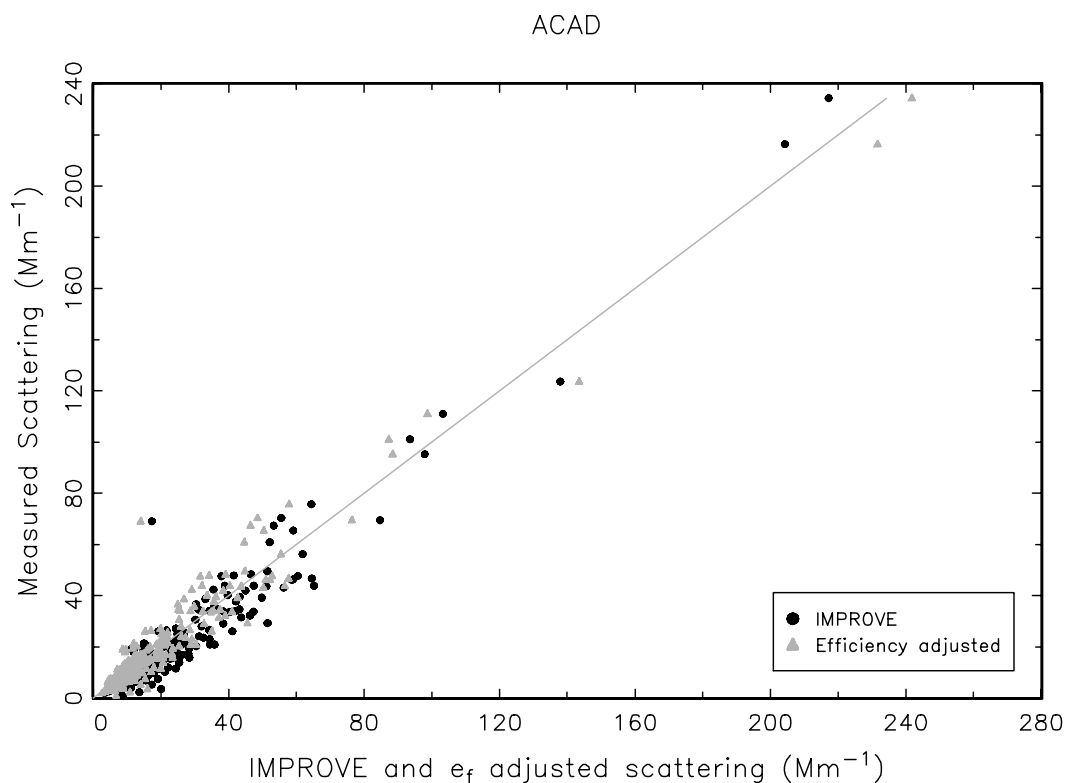
**Figure 9.** The comparison of fine mode mixed inorganic and organic mass concentrations ( $M_{mix}$   $\mu\text{g m}^{-3}$ ) and the scattering correction factor (SCF) for Acadia National Park. The Thiel regression line is shown.



**Table 14.** Estimates of the upper and lower specific scattering efficiencies associated with the 15% upper and lower mass concentrations of mixed inorganic and organic mass. These estimates were derived with method 3 for Acadia National Park.

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

**Figure 10. Comparisons of measured mixed scattering ( $b_{mix}$   $Mm^{-1}$ ) to reconstructed mixed scattering with the SCF correction ( $b_{mix,est}$   $Mm^{-1}$ ) using method 3 for Acadia National Park.**



**Table 15. Summary of the scattering correction factor (SCF) and specific mass scattering efficiencies for inorganics ( $\alpha_{inorg}$ ) and organics ( $\alpha_{org}$ ) using method 3 for Acadia National Park.**

ACADIA NP						
Variable	Mean	Std Dev	Minimum	Maximum	Valid data	Missing data
SCF	0.81	0.29	0.08	3.98	267	370
$\alpha_{inorg}$ ( $m^2 g^{-1}$ )	2.44	0.13	2.31	3.40	617	20
$\alpha_{org}$ ( $m^2 g^{-1}$ )	2.95	0.16	2.79	4.12	617	20

From the discussion of these methods for Acadia, it is clear that incorporating the dependence of mass scattering efficiencies on mass concentrations does remove the biases observed between measured and reconstructed extinction, and improved the comparison of reconstructed and measured scattering. For most sites a linear relationship between mass and

*SCF* appeared to be a reasonable assumption, except at Great Smoky National Park (GRSM) where there seems to be a distinct nonlinearity. At GRSM the *SCF* is about 0.5 at lower mass concentrations ( $< 5.0 \mu\text{g m}^{-3}$ ) and rapidly approaches one for higher mass concentrations.

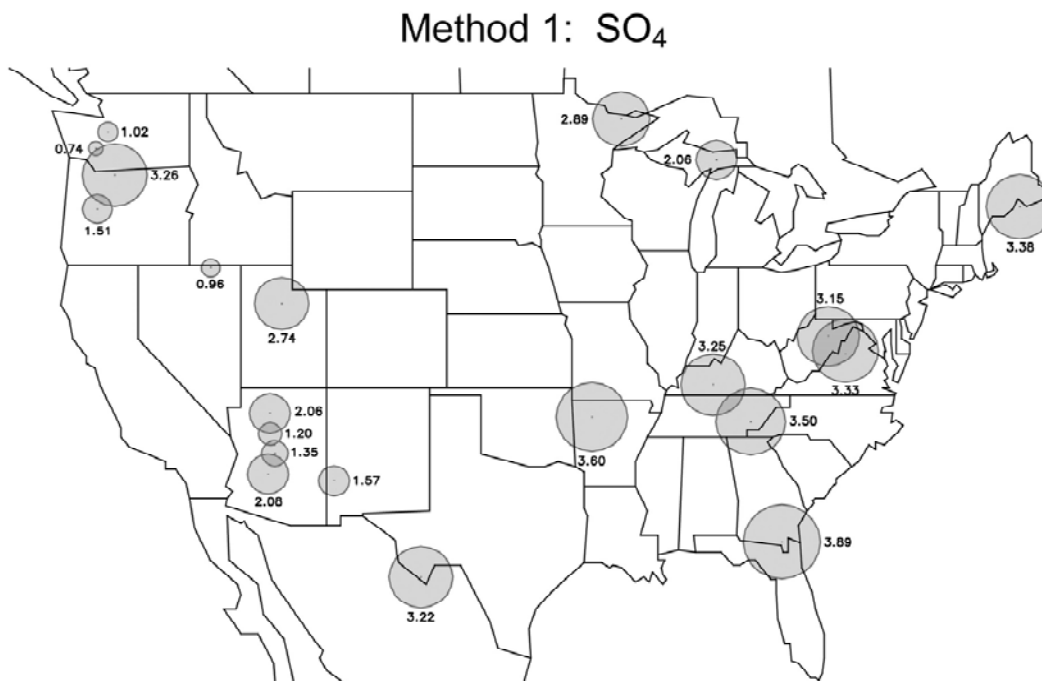
We will now summarize and discuss these methods for all of the sites where the analyses were performed. The mass scattering efficiencies derived from the OLS regression in method 1 are summarized in Table 16, along with the standard error associated with each estimate. For ammonium sulfate the regression coefficients are all statistically significant, except for Mount Rainier National Park (MORA) and Snoqualamie WA (SNPA), both of which are in or near the Cascade Mountain Range in the northwestern United States. The values are summarized for all sites in Figure 11, where the size of the circle corresponds to the magnitude of the mass scattering efficiency. The site in the Columbia River Gorge WA (CORI) is influenced by air masses from Portland, is in a high RH environment, and has a dry ammonium sulfate mass scattering efficiency that is greater than  $3.0 \text{ m}^2 \text{ g}^{-1}$ . However, typically the highest ammonium sulfate mass scattering efficiencies are found in the eastern United States, as well as Big Bend National Park TX (BIBE) where they are typically greater than  $3.0 \text{ m}^2 \text{ g}^{-1}$ . In the southwestern United States, the values are about  $2.0 \text{ m}^2 \text{ g}^{-1}$  with the site in Ikes Backbone AZ (IKBA) having the lowest value at  $1.35 \text{ m}^2 \text{ g}^{-1}$ . The average implied dry ammonium sulfate mass scattering efficiency for all sites is  $2.49 \pm 1.05 \text{ m}^2 \text{ g}^{-1}$ . This value is similar to the average values reported in the literature review of the theoretical method.



**Table 16. Summary of mass scattering efficiencies ( $m^2 g^{-1}$ ) and standard errors for all sites using the ordinary least squares multi-linear regression analysis of method 1. Mass scattering efficiencies are listed for ammonium sulfate (AS), ammonium nitrate (AN), particulate organic matter (POM = 1.8\*OC), soil and coarse mass (soil + CM), and sea salt.**

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
<b>Average</b>	2.49	0.50	4.45	1.62	3.27	0.76	0.05	0.27	-54.98	184.39
<b>Std Dev</b>	1.05		4.26		2.17		0.66		174.24	

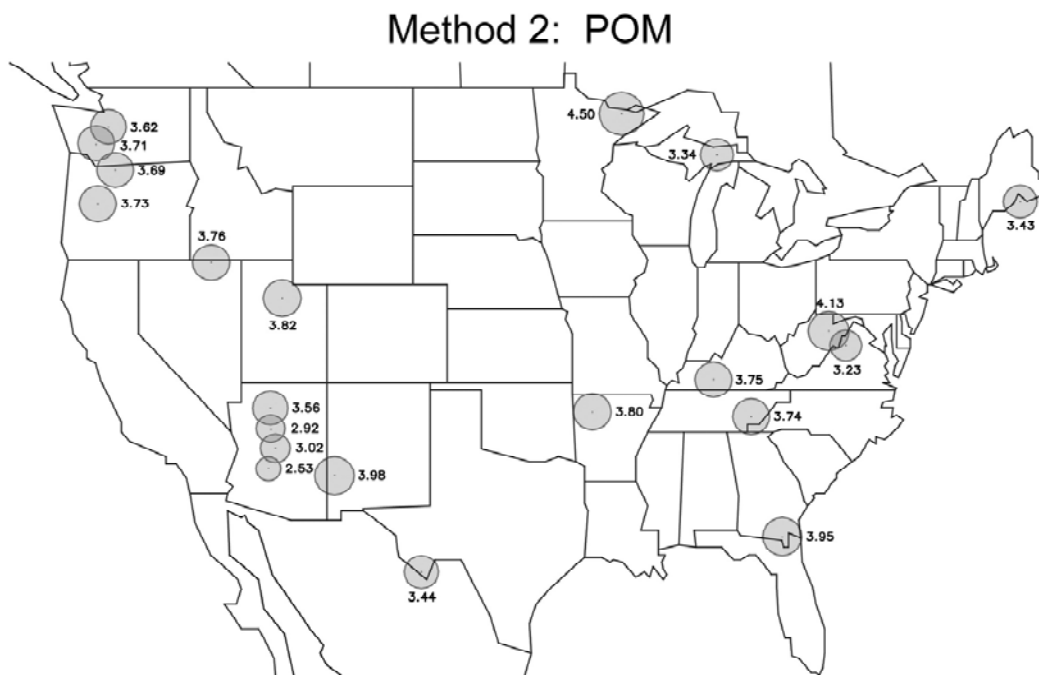
**Figure 11. Map of the mean ammonium sulfate mass scattering efficiencies for the United States derived using method 1. The size of the circle reflects the magnitude of the efficiency.**



The derived mass scattering efficiencies for POM are statistically significant at all sites except at Shenandoah VA (SHEN). The values are summarized in Figure 12. A negative value was derived at the Virgin Islands (VIIS) (not shown), which is unphysical. In the East, as with sulfates, the implied mass scattering efficiencies are near  $3.0 \text{ m}^2 \text{ g}^{-1}$  or greater; at Dolly Sods WV (DOSO) the coefficient is  $7.0 \text{ m}^2 \text{ g}^{-1}$ . In the West, the coefficients are higher and variable but all within ranges that would be considered physically reasonable. Those sites typically influenced by wild fires tend to have higher POM mass scattering efficiencies, consistent with recent analysis by Malm et al. (2005a) and Pirot and Husar (2004). The average POM mass scattering efficiency is  $3.27 \pm 2.17 \text{ m}^2 \text{ g}^{-1}$  and is within range of the values reported in Table 5, although

closest to the MLR average value. The ratio of ammonium sulfate to POM mass scattering efficiencies on average is 1.31, which is similar to the ratio of POM to ammonium sulfate density of 1.21.

**Figure 12. Map of the mean POM mass scattering efficiencies ( $\text{m}^2 \text{g}^{-1}$ ) for the United States derived using method 1. The size of the circle reflects the magnitude of the efficiency.**



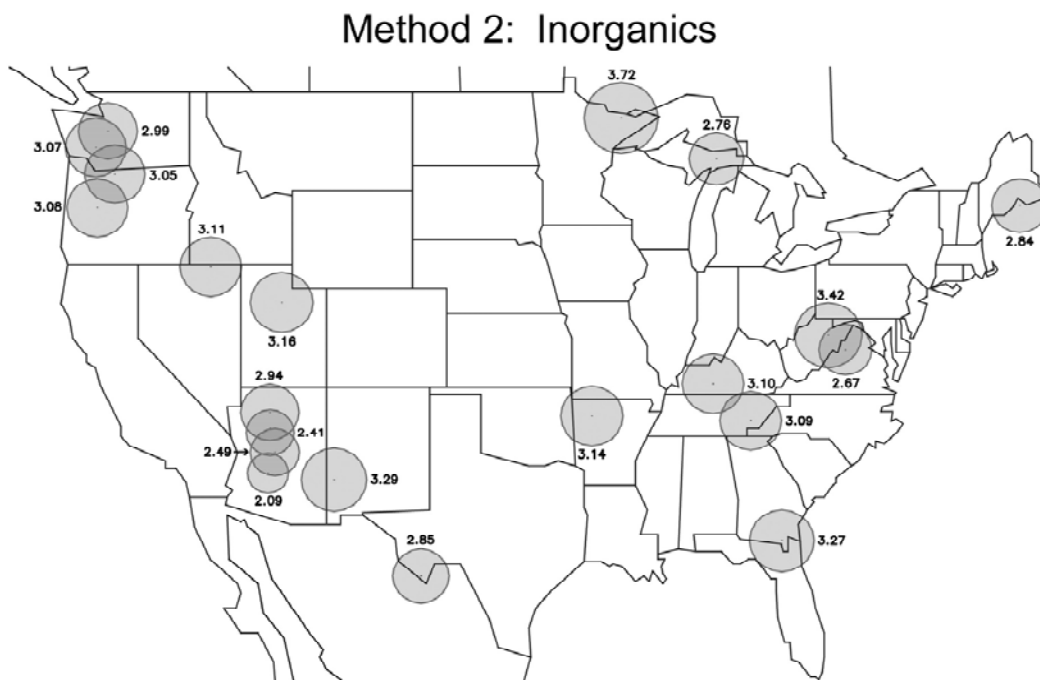
Many of the ammonium nitrate mass scattering efficiencies are higher than could be reasonably expected, possibly because fine nitrate may be a surrogate for coarse particle nitrate (see section 3.2). Coarse mass specific mass scattering efficiencies that are statistically significant vary from a low of  $1.54 \text{ m}^2 \text{g}^{-1}$  at Gila NM (GICL) to a high of  $6.24 \text{ m}^2 \text{g}^{-1}$  in the Virgin Islands (VIIS). Sea salt specific mass scattering efficiencies are only statistically significant at two locations, Acadia (ACAD) and the Virgin Islands.

The specific mass scattering efficiencies for ammoniated salts (sulfate and nitrate) and POM mass scattering efficiencies derived from method 2 are summarized for all of the sites in Table 17. The values of  $\alpha_{inorg}$  range from 2.09 to 5.82  $\text{m}^2 \text{g}^{-1}$ , with an average of  $2.98 \pm 0.70 \text{ m}^2 \text{g}^{-1}$ . A summary of the values is shown in Figure 13. The high value is in the Virgin Islands (not shown) where there is known to be large contributions to aerosol mass from sea salt and dust, so the inorganic salts could be influenced by those contributions. The low value occurred at Phoenix AZ (PHOE). The low and high values of efficiencies for POM also occurred at PHOE and VIIS, with 2.53 and 7.04  $\text{m}^2 \text{g}^{-1}$ , respectively. These estimates are summarized in Figure 14. Throughout most of the United States, POM mass scattering efficiencies vary between about 3.5 and 4.0  $\text{m}^2 \text{g}^{-1}$ , with the Arizona sites having the lowest values (Figure 14). POM mass scattering efficiencies are higher than those for inorganics; however, there is less spatial variability in POM mass scattering efficiencies compared to method 1 because of the internal mixing assumptions inherent in method 2. Because only one multiplicative factor is used to scale both the inorganics and the organics, the bias between measured and reconstructed scattering for low and high mass concentrations remains.

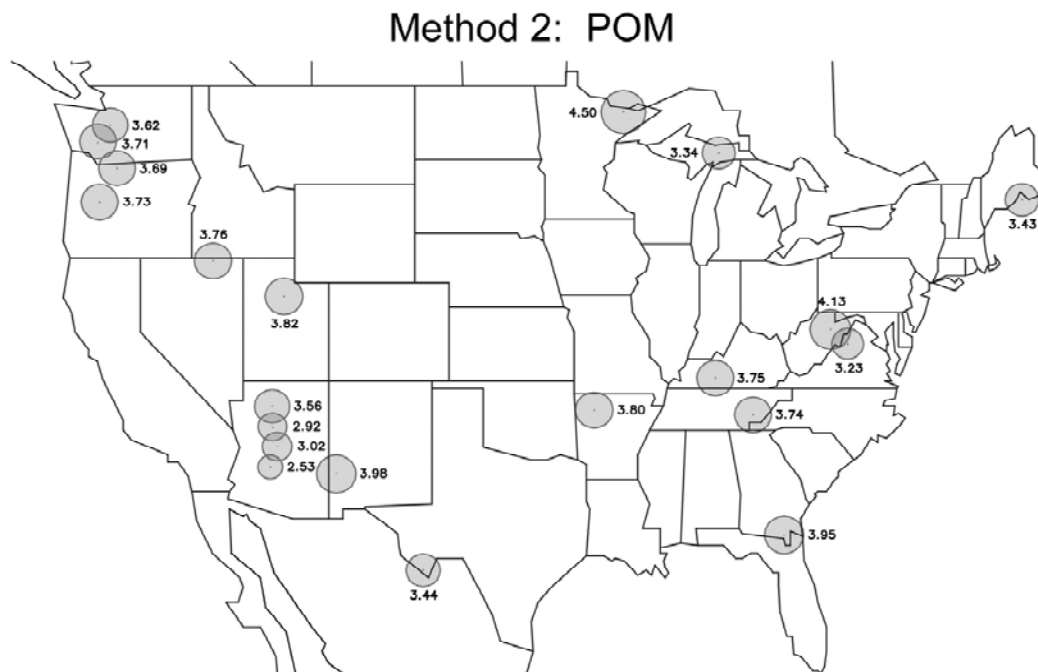
**Table 17. Summary of specific mass scattering efficiencies for inorganics ( $\alpha_{inorg}$ ) and organics ( $\alpha_{org}$ ) for all sites using method 2.**

Site	$\alpha_{inorg}$ ( $m^2 g^{-1}$ )	$\alpha_{org}$ ( $m^2 g^{-1}$ )
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
<b>Average</b>	2.98	3.60
<b>Std Dev</b>	0.70	0.85

Figure 13. Map of inorganic specific mass scattering efficiencies ( $\alpha_{inorg}$ ,  $\text{m}^2 \text{g}^{-1}$ ) for the United States using method 2. The size of the circle reflects the magnitude of the efficiency.



**Figure 14. Map of organic (POM) mass scattering efficiencies ( $\alpha_{org}$ ,  $m^2 g^{-1}$ ) for the United States using method 2. The size of the circle reflects the magnitude of the efficiency.**



The results from the Thiel regression of  $SCF$  and  $M_{mix}$  (intercept, slope, and t-values) from method 3 are listed in Table 18 for each site. As previously mentioned, a slope of zero corresponds to a constant mass scattering efficiency over the entire mass range, while the intercept is proportional to the underestimation of the assumed mass scattering efficiencies for sulfates and POM ( $3$  and  $3.63 m^2 g^{-1}$ , respectively). An intercept of one and slope of zero would imply that the assumed values provided good agreement between measured and reconstructed mixed (inorganic and POM) scattering. The average intercept for all 22 sites is  $0.69 \pm 0.04$  while the average slope is  $0.04 \pm 0.09$ .

**Table 18. Summary of the results from the Thiel regression of  $SCF$  and mass ( $M_{mix}$ ) from method 3 for each site. The fourth column corresponds to the percent change in specific mass scattering efficiency (either for inorganic or organics) from a doubling of the mixed inorganic and organic mass concentration ( $M_{mix}$ ).**

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
<b>Average</b>	0.686	0.036		10.39
<b>Std Dev</b>	0.52	0.09		14.71

The fourth column in Table 18 corresponds to the percent change in mass scattering efficiency (either for inorganic or organics) resulting from a doubling of the mixed inorganic and organic mass concentration ( $M_{mix}$ ). The results for are shown in graphical form in Figure 15. Notice that the percent change in mass scattering efficiency resulting from a doubling of mass concentration is lowest in the eastern United States, with only a few percent change along the Ohio River Valley. Great Smoky Mountains National Park has a 6% change in mass scattering efficiency for a doubling of mass, while OKEF (Okefenokee GA) has a 14% change. Sites in the western United States exhibit the largest change in mass scattering efficiency as a function of mass. Sites in the Northwest and Great Basin region all have percent changes between about 10



and 15%, while sites in Arizona vary from about a 1% change to as high as 50% at IKBE (Ikes Backbone). The intercept data is shown in Figure 16. Sites along the Ohio River Valley have intercepts between 0.9 and 1.0, implying  $3.0 \text{ m}^2 \text{ g}^{-1}$  and  $3.63 \text{ m}^2 \text{ g}^{-1}$  are reasonable choices for dry mass scattering efficiencies. In the western United States, the intercepts range between 0.5 and 0.7, with a low value of 0.27 at PHOE, implying a lower mass scattering efficiency would be more appropriate there. This result is consistent with what is observed at PHOE using the other methods.

**Figure 15. Map of percent change in specific mass scattering efficiency (for either  $\alpha_{inorg}$  or  $\alpha_{org}$ ) due to a doubling of mixture mass ( $M_{mix}$ ) using method 3. The size of the circle reflects the magnitude of the change.**

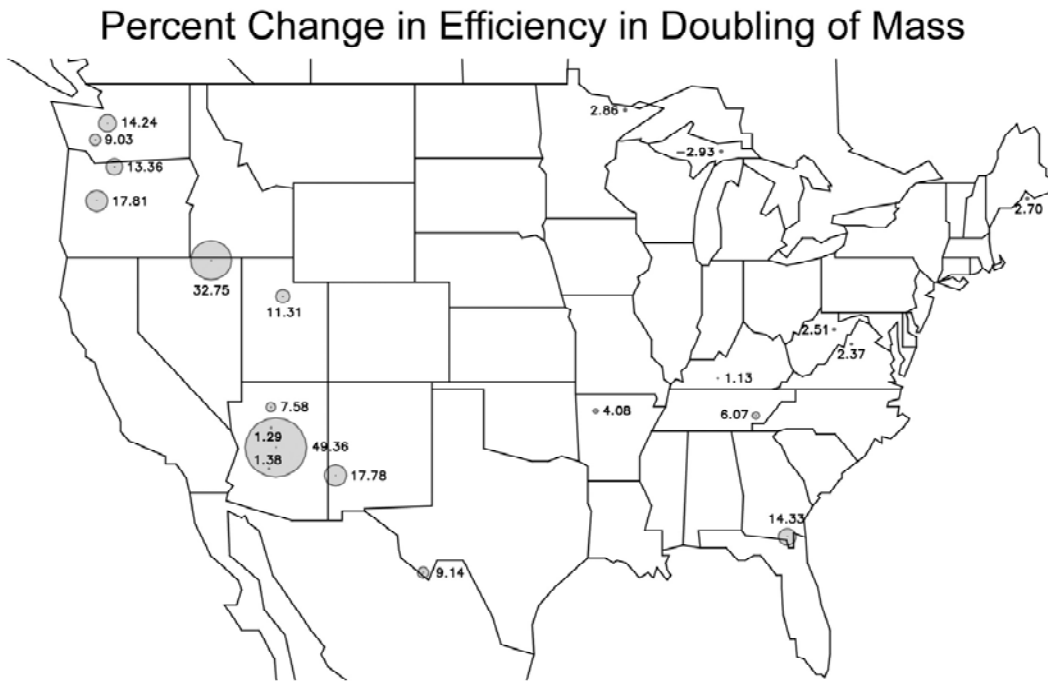
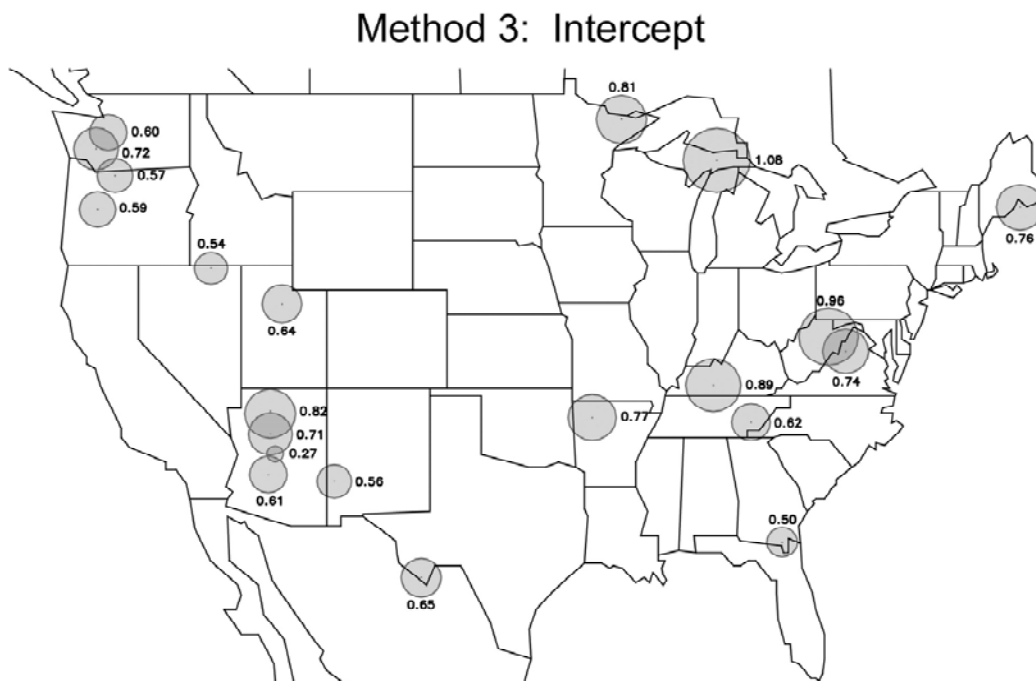


Figure 16. Map of the intercept from the Theil regression in method 3. The size of the circle reflects the magnitude of the intercept.



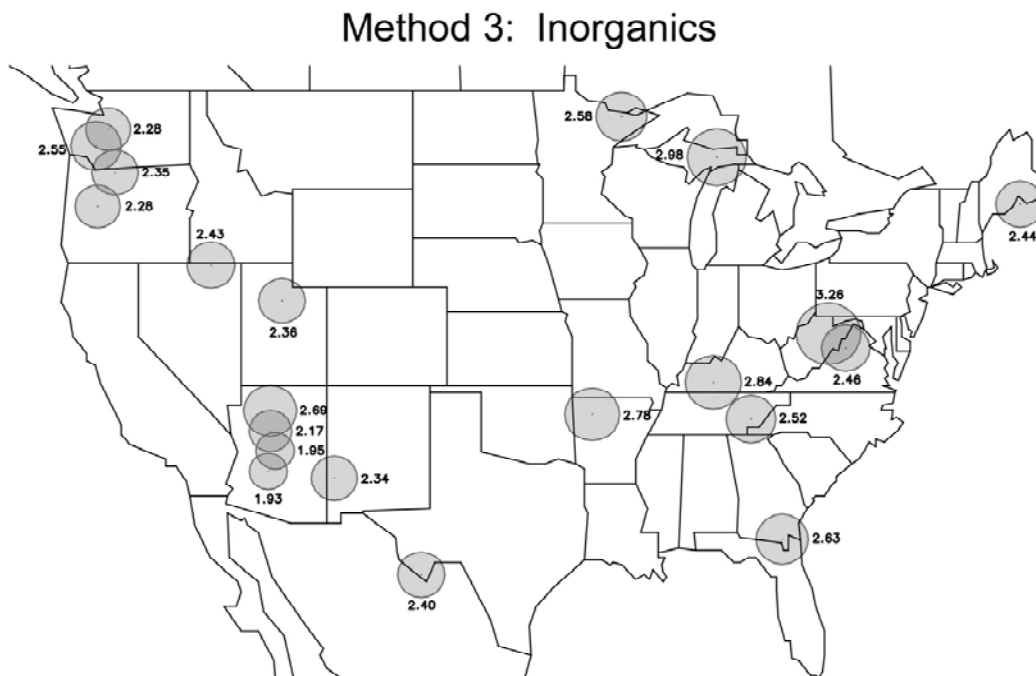
The mean, upper, and lower specific mass scattering efficiencies for the mixed ammonium salts and POM mass scattering efficiencies are reported in Table 19. The upper and lower mass scattering efficiencies are calculated by averaging the mass scattering efficiencies associated with the upper and lower 15% mixed mass concentrations ( $M_{mix}$ ). The percent change between the upper and lower mass scattering efficiencies (either inorganics or organics) is reported in the last column. The highest average inorganic specific mass scattering efficiencies are found along the Ohio River Valley where they are about  $3 \text{ m}^2 \text{ g}^{-1}$  or greater (see Figure 17 for spatial distribution). The inorganic specific scattering efficiencies decrease towards the central eastern United States. The lowest specific mass scattering efficiencies ( $< 2.5 \text{ m}^2 \text{ g}^{-1}$ ) are found in

the eastern United States. (Acadia ME, ACAD; Seney National Wildlife Refuge VA, SENY; and Boundary Waters MN, BOWA). All sites in the western United States with statistically significant results have inorganic specific mass scattering efficiencies that are less than  $2.4 \text{ m}^2 \text{ g}^{-1}$ , with two sites in Arizona (PHOE, IKBA) having specific mass scattering efficiencies less than  $2.0 \text{ m}^2 \text{ g}^{-1}$ . The inorganic specific mass scattering efficiency is  $2.49 \pm 0.98 \text{ m}^2 \text{ g}^{-1}$ .

**Table 19. The mean, upper, and lower specific scattering efficiencies for inorganics ( $\alpha_{inorg}$ ) and organics ( $\alpha_{org}$ ) computed with method 3. The upper and lower estimates are calculated by averaging the specific scattering efficiencies associated with the upper and lower 15% mixed mass concentrations ( $M_{mix}$ ). The percent change between the upper and lower mass scattering efficiencies (final column) corresponds to both ( $\alpha_{inorg}$ ) and ( $\alpha_{org}$ ).**

	$\alpha_{inorg}$ ( $\text{m}^2 \text{ g}^{-1}$ )	$\alpha_{inorg}$ ( $\text{m}^2 \text{ g}^{-1}$ )	$\alpha_{inorg}$ ( $\text{m}^2 \text{ g}^{-1}$ )	$\alpha_{org}$ ( $\text{m}^2 \text{ g}^{-1}$ )	$\alpha_{org}$ ( $\text{m}^2 \text{ g}^{-1}$ )	$\alpha_{org}$ ( $\text{m}^2 \text{ g}^{-1}$ )	PERCENT CHANGE $\alpha_{inorg}$ & $\alpha_{org}$
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

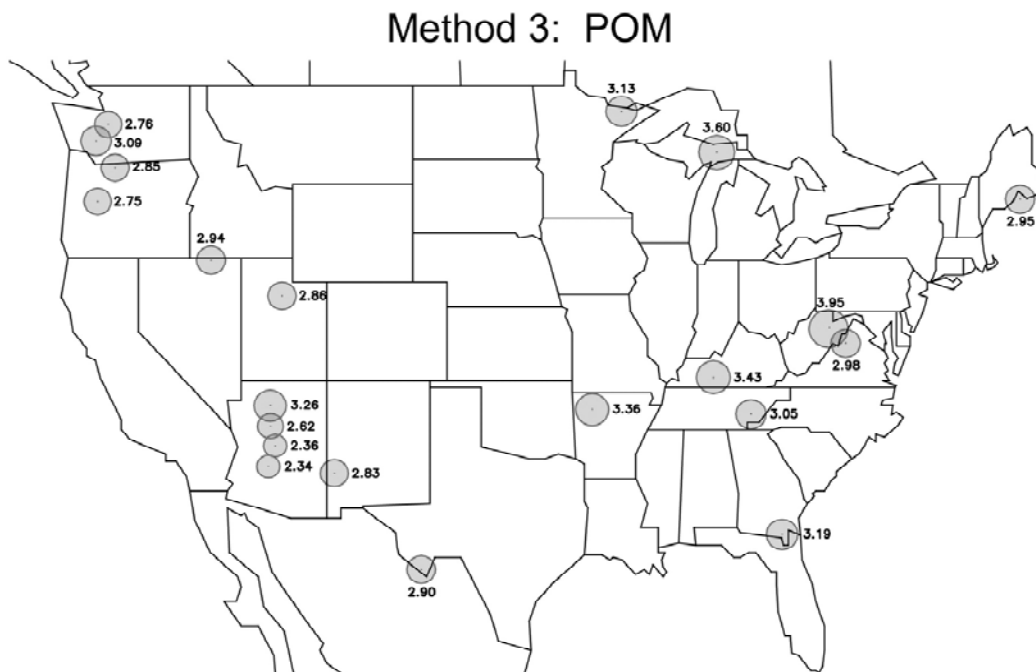
Figure 17. Map of inorganic specific mass scattering efficiencies ( $\alpha_{inorg}$ ,  $\text{m}^2 \text{g}^{-1}$ ) from method 3. The size of the circle reflects the magnitude of the efficiency.



The spatial distribution of POM mass scattering efficiencies from method 3 is shown in Figure 18. Inorganic and organic aerosols were assumed to be internally mixed; therefore the POM scattering efficiencies are scaled to inorganic efficiencies by the ratio of their densities (1.31) and the spatial variability across the United States is the same for both. Notice, however, that in the central eastern United States the POM scattering efficiencies are near the  $4.0 \text{ m}^2 \text{g}^{-1}$  currently assumed in the Regional Haze Rule guidance. Also note that at Great Smoky Mountains National Park there is less than a 6% change in mass scattering efficiency for a doubling of mass concentration, but that the actual variability in observed mass results in a 35% change in mass scattering efficiency between the upper and lower estimates when the functional

dependence on mass is accounted for by this method. The average POM mass scattering efficiency is  $3.01 \pm 1.28 \text{ m}^2 \text{ g}^{-1}$ , similar to that derived for inorganics.

**Figure 18.** Map of organic mass scattering efficiencies ( $\alpha_{org}$   $\text{m}^2 \text{ g}^{-1}$ ) from method 3. The size of the circle reflects the magnitude of the efficiency.



In the eastern United States the results for method 3 are similar to method 1. However, method 3 results are quite different from method 1 in western part of the country where the efficiencies were near  $2.0 \text{ m}^2 \text{ g}^{-1}$  or lower. One interesting feature showing up in both analyses is lower mass scattering efficiencies in Arizona than at adjacent monitoring sites.

## 6. Summary of Suggested Refinements to the IMPROVE Equation

The current equation used to estimate the extinction associated with measured aerosol species is

$$b_{ext} = \alpha_{AS}f(RH)_{AS}[AS] + \alpha_{AN}f(RH)_{AN}[AN] + \alpha_{POM}[POM] + \alpha_{soil}[Soil] + \alpha_{CM}[CM] + \alpha_{LAC}[LAC] \quad (25)$$

where it is assumed that the dry mass scattering and absorption efficiencies  $\alpha_{AS}$ ,  $\alpha_{AN}$ ,  $\alpha_{POM}$ ,  $\alpha_{soil}$ ,  $\alpha_{CM}$ , and  $\alpha_{LAC}$  are 3.0, 3.0, 4.0, 1.0, 0.6, and 10.0 m<sup>2</sup> g<sup>-1</sup>, respectively, and the  $f(RH)$  curve is calculated on an hourly basis and averaged to 24 hours to be commensurate with the 24-hour average aerosol mass measurements. The  $f(RH)$  curve is a “smoothed” ammonium sulfate curve that reflects continuous particle growth starting at 40% RH. The forms assumed for each of the aerosol species are ammonium sulfate and ammonium nitrate, 1.4\*OC, soil, and gravimetric coarse mass (PM<sub>10</sub>–PM<sub>2.5</sub>).

Uncertainty in estimated extinction is dependent on not only the assumed forms of each of the aerosol species and their respective mass scattering efficiencies and growth factors, but also on measurement and analytic accuracy and precision. One uncertainty of special concern is the variation in flow rate associated with the IMPROVE monitoring system, because uncertainties in the flow rate affect the cutpoint of the inlet. The IMPROVE 2.5 μm inlet intersects the size range corresponding to the coarse mode; therefore any changes in the cutpoint of the inlet (due to variations in the flow rate) cause significant and varying amounts of coarse material to be characterized as fine mass. The fine mode mass scattering efficiency associated with the fine tail of the coarse mode can vary significantly. This issue is especially important for sites where soil mass contributes significantly to estimated extinction (e.g., most sites in the West during spring months) and for sites where coarse particle nitrate concentrations are high. Some of the issues associated with measurement uncertainty have been discussed, but this report does not make any recommendations on changes in measurement methodology or analytic procedures.

Another significant uncertainty in reconstructed  $b_{ext}$  is the chemical form of each of the aerosol species. Again, this issue is discussed in some detail in this report, but because the ammonium ion is not measured, the current assumption of interpreting sulfate and nitrate in the fine mode as ammonium sulfate and ammonium nitrate is not changed. However, the multiplication factor ( $R_{oc} = 1.4$ ) used to estimate particulate organic material from measured organic carbon mass in the current equation is undoubtedly low. Based on recent literature review and an analysis of IMPROVE data, we recommend a value ranging between 1.7 to 1.8, although a value of 1.8 has been used in this report to develop new estimates for mass scattering efficiencies. We also recommend the inclusion of fine sea salt in the IMPROVE equation as  $1.8 \cdot Cl$  per the above discussion. Recognizing that fine sea salt is probably the fine tail of coarse mode sea salt, a new  $f(RH)$  function and dry mass scattering efficiency for sea salt should be developed. For purposes of the analysis presented in this report, we used the  $f(RH)$  curve that corresponds to ammonium sulfate and ammonium nitrate and a mass scattering efficiency of one ( $1 \text{ m}^2 \text{ g}^{-1}$ ) to estimate sea salt scattering. No new recommendation of fine mass absorption efficiency is made.

Because coarse mass is not speciated, we cannot recommend a change in coarse mass scattering efficiency. Coarse mass is not composed only of crustal material but also contains significant fractions of organic and inorganic species, some of which are hygroscopic and light-absorbing and therefore have mass scattering efficiencies that differ significantly from the currently assumed value of  $0.6 \text{ m}^2 \text{ g}^{-1}$ . Thus it should be recognized that coarse mass extinction is only a very rough estimate.. Coarse mass concentrations are also only approximate because the  $PM_{2.5}$  cutpoint intersects the size range that corresponds to the peak of the coarse mode mass size distribution and flow rate variability can cause the cutpoint to vary substantially.

The current form of the  $f(RH)$  curve does not account for aerosol growth below RH ~ 40%; however, a substantial number of measurements of  $D/D_o$  and  $f(RH)$  curves indicate that aerosol growth occurs at low RH values. A new  $f(RH)$  curve is recommended that is based on an ammonium sulfate  $D/D_o$  “no solids” growth curve with a mass size distribution of  $D_g = 0.2 \mu\text{m}$  and  $\sigma_g = 1.9$ , corresponding to a dry mass scattering efficiency of about  $3.0 \text{ m}^2 \text{ g}^{-1}$ . This assumed size distribution may change, depending on the new recommendations for dry mass scattering efficiencies of inorganic salts. The “no solids” curve extends the  $D/D_o$  curve to relative humidities below the ammonium sulfate crystallization point. Currently, organic mass is assumed to not be hygroscopic and no change is recommended in this assumption, although there is some evidence that ambient organics may be very weakly hygroscopic at high RH values (RH > 85%).

Recommendations for changes in the dry mass scattering efficiencies are more difficult. It is clear from the analysis of the IMPROVE data and the literature review that mass scattering efficiencies for inorganic salts should be decreased, while, under assumptions of a mixed aerosol, POM mass scattering efficiencies should also be decreased. However, at least under some circumstances, the POM efficiency is most likely higher than what is currently assumed. It also appears that as mass concentrations increase, mass scattering efficiencies also tend to increase; in most cases in an approximately linear fashion. However, this relationship is variable at the sites examined, with only a weak spatial pattern noticeable. The relationship appears to be stronger in the West than East; however, because of large fluctuations in mass loadings in the East, the consequence of any relationship between mass scattering efficiency and mass, although small, results in a large change in mass scattering efficiency between the clearest and haziest days.



Because there is no recognizable spatial pattern in the change in mass scattering efficiency as a function of mass, it is recommended that constant values of 2.5 and 3.0 m<sup>2</sup> g<sup>-1</sup> for inorganic salts and organic mass be assumed; these estimates are consistent with the literature review and analysis of IMPROVE data. It is further recommended that the other mass scattering efficiencies in the current IMPROVE equation remain the same and that a dry mass scattering efficiency of sea salt of 1.0 m<sup>2</sup> g<sup>-1</sup> be assumed. The following equation reflects these recommendations:

$$b_{ext} = (2.5)f(RH)[(NH_4)_2SO_4] + (2.5)f(RH)[NH_4NO_3] + (3.0)(1.8)[OC] + (1.0)[Soil] + (0.6)[CM] + 10[LAC] + (1.0)f(RH)(1.8*Cl) \quad (26)$$

### **Discussion of Biases between Reconstructed and Measured Scattering**

In this section we present a brief summary of the skill with which each method reconstructs total scattering as measured by the Optec ambient open air nephelometer. Table 20 presents the average bias ( $b_{sp\_meas} - b_{sp\_recon}$ ) for each method (1, 2, and 3) and for the current and recommended IMPROVE equations. The method 1 analysis yields results which, on average, have the smallest biases, while method 2 produces results that are only in slightly better agreement with  $b_{sp\_meas}$  than those derived from the current IMPROVE equation. Method 3, which incorporates the relationship between mass and mass scattering efficiency, produces the smallest average biases. Both the current and recommended IMPROVE equations have larger average biases than method 3, and the recommended IMPROVE equation has a slightly greater average bias than the current IMPROVE equation. Because the mass scattering efficiencies for both the current and recommended IMPROVE equation are not adjusted as a function of mass loadings, they both will be biased low under higher extinction days and high under lower extinction days.

**Table 20. Average biases between measured scattering ( $b_{sp\_meas}$ ) and reconstructed scattering ( $b_{sp\_recon}$ ) derived from methods (1-3), the current IMPROVE equation, and the recommended IMPROVE equation.**

Site	Method 1 ( $b_{sp\_meas} - b_{sp\_recon}$ )	Method 2 ( $b_{sp\_meas} - b_{sp\_recon}$ )	Method 3 ( $b_{sp\_meas} - b_{sp\_recon}$ )	Current IMPROVE ( $b_{sp\_meas} - b_{sp\_recon}$ )	Recommended IMPROVE ( $b_{sp\_meas} - b_{sp\_recon}$ )
ACAD	-0.08	-2.00	0.42	-0.29	0.94
BIBE	-0.81	-2.79	0.72	1.07	1.26
BOWA	-0.07	-4.18	3.66	3.30	4.71
CORI	-1.26	-3.15	1.27	0.60	1.26
DOSO	-1.20	-2.65	-1.10	10.49	12.64
GICL	-0.53	-3.17	0.33	0.58	0.91
HANC	-0.29	-1.18	0.08	0.69	0.85
GRSM	-1.98	-4.83	0.40	4.12	8.49
IKBA	-0.63	-2.71	0.20	-0.97	-0.72
JARB	-0.18	-2.01	-1.04	0.65	0.93
LOPE	-0.64	-3.37	1.08	0.92	1.43
MACA	-0.29	-1.17	3.57	6.96	9.69
MORA	0.26	-0.39	1.62	2.98	3.88
OKEF	-1.91	-3.95	3.24	5.54	8.32
PHOE	0.15	-3.96	0.58	-6.30	-4.70
SHEN	1.55	1.48	0.74	1.98	3.90
SENY	0.10	-1.44	0.74	-0.57	1.31
SNPA	-0.92	-2.15	0.75	1.15	2.04
SYCA	0.05	-4.66	0.58	-1.08	-0.74
THIS	-0.40	-1.84	-0.35	1.86	2.53
UPBU	-0.98	-3.61	-0.56	4.43	6.77
VIIS	0.71	0.59	0.60	18.39	16.94
<b>Avg</b>	-0.43	-2.42	0.80	2.57	3.75