INFERRING THE SPECIFIC ABSORPTION AND CONCENTRATION OF BLACK CARBON FROM AERONET AEROSOL RETRIEVALS

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by
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Abstract

Black carbon is ubiquitous in the atmosphere and the main anthropogenic absorbing particulate. Absorption by black carbon is thought to be comparable to the cooling associated with sulfate aerosols, although present day satellites are incapable of obtaining this measurement and model estimates are highly uncertain. More measurements of black carbon concentration are necessary for improving and validating transport and general circulation models. The aerosol robotics network (AERONET) of 180 worldwide radiometers offers an opportunity to obtain these measurements. We use the Maxwell Garnett effective medium approximation to infer the column-averaged black carbon concentration and specific absorption of AERONET retrievals at 46 locations. The yearly-averaged black carbon column concentrations exhibit the expected regional dependence, with remote island sites having values about an order of magnitude lower than the biomass burning locations. The yearly-averaged specific absorption cross section is consistent with other measured values, 9.9 m$^2$ g$^{-1}$ for 19591 retrievals, but varies from 7.7 to 12.5 m$^2$ g$^{-1}$. We also observe this variability in calculations associated with nine aerosol climatologies where specific absorption varies by a factor of 2 or more. We attribute this variability to the details of the size distributions and the fraction of black carbon contained in the aerosol mixture. Transport models generally use aerosol size distributions with externally-mixed black carbon and are unable to account for this variability of specific absorption associated with internal mixing. We also used the Maxwell Garnett equations to parameterize the imaginary refractive index with respect to the black carbon volume fraction, enabling simple but accurate absorption estimates for aerosol mixtures. The black carbon concentrations that we derive from AERONET measurements are validated with surface measurements and represent an alternative to absorption optical thickness in the link between models and AERONET measurements.
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The product of mental labor — science — always stands far below its value, because the labor-time necessary to reproduce it has no relation at all to the labor-time required for its original production.

KARL MARX, 1818-1883
Chapter 1

Introduction

It is often reported that aerosols have slowed global warming by scattering incident solar radiation back into space, and that the impact of anthropogenic aerosols is a global cooling comparable in magnitude (but opposite in sign) to the warming associated with anthropogenic infrared-active gases (Charlson et al., 1991; Charlson et al., 1992; Penner et al., 1992; Harshvardhan, 1993; Schwartz, 1996; Delene and Ogren, 2002). While scattering is the predominant radiative effect of aerosols at shortwave wavelengths (i.e., less than 4 μm), significant absorption by aerosols occurs at these wavelengths as well (Liousse et al., 1996; Haywood et al., 1997; Schult et al., 1997; Myhre et al., 1998; Penner et al., 1998). The most recent report from the Intergovernmental Panel on Climate Change (IPCC, 2001) estimates that absorption by black carbon aerosols can reduce the direct radiative impact of sulfate aerosols by 50–100 percent. Aerosol absorption is significant enough that the radiative impact of aerosols at the top of the atmosphere could change in sign from cooling to warming in regions of highly absorbing aerosols (Chylek and Coakley 1974; Charlock and Sellers, 1980; Haywood and Shine, 1995). This is especially important when aerosols are located over highly reflective surfaces such as snow or clouds (Haywood and Shine, 1997). Absorbing aerosols may also be responsible for a second indirect effect, whereby clouds evaporate more rapidly because of absorbing haze and cloud condensation nuclei (Ackerman et al., 2000). A recent study also indicates that such aerosols reduce the albedo of ice and snow and increase melt rates (Hansen and Nazarenko, 2004).

Absorption by nondust aerosols in the atmosphere at wavelengths less than 4 μm is mainly caused by the graphitic form of carbon (Rosen et al., 1978; 1982). This highly absorbing particulate is often called carbon black, soot, elemental carbon, or black carbon in the atmospheric literature. Differences between these species do exist, however. Carbon blacks refers to commercially available spherical particles created in a controlled environment. These particles are composed of concentric graphite platelets with diminishing graphitic order near the center (Hess and Herd, 1991). Their commercial availability simplifies the characterization of their physical and optical properties and these properties are often extrapolated to characterize particulate carbon found in atmospheric soot. Atmospheric soot is produced by the same mechanism as carbon blacks (incomplete combustion), but it also contains a variety of impurities (Novakov, 1982; Bansal and Donnet, 1993). For instance, diesel exhaust soot has a much lower carbon content than commercial carbon blacks (∼ 45 percent versus ∼ 95 percent) even though they both exhibit very similar primary particle sizes and graphitic internal structure (Clague et al., 1999). The term elemental carbon implies a purity of substance...
and is generally reserved for thermal analysis of light absorbing carbon, the philosophy being that the various impurities volatilize at a lower temperature than the graphitic component. The term black carbon is often reserved for optical measurements of light absorbing carbon (A.D.A. Hansen, 2003; www.mageesci.com), which can show excellent agreement with thermal elemental carbon measurements (Moosmuller et al., 1998). We adopt the term black carbon to refer to nonorganic particulate carbon in the atmosphere with the understanding that the optical and physical properties that we obtain from the literature may be associated with carbon blacks or soot.

Current satellite technology does not include aerosol absorption measurements, so global estimates must be obtained from transport models and general circulation models (GCMs). The models are typically initialized with gridded emission inventories of all known significant aerosol sources and assumed size distributions. The aerosols are then transported across the globe, changing in mass and optical properties as the modeled relative humidity changes. Removal occurs by wet and dry deposition. The carbon emissions inventories used to initialize the models are highly parameterized and created on the basis of multiple sparse datasets (such as fuel use inventories and emission factors). The resulting inventories are uncertain by at least a factor of 2 and this uncertainty is carried forward to the model output (Bond et al., 1998; Cooke et al., 1999; Streets et al., 2001).

Complicating matters further, aerosol models usually assume external mixtures so that the hygroscopic growth and radiative impact of each component may be considered separately. (The external mixture assumption presumes that each aerosol particle contains a single species, whereas multiple species are contained within each particle in an internal aerosol mixture). Measurements show that black carbon and sulfate concentrations are highly correlated, indicating that these two species are probably internally mixed (Pinnick et al., 1993; Krivacsy et al., 2001). This hypothesis is confirmed with high-resolution scanning electron microscopy images (Ebert et al., 2002) and is consistent with the deposition rates required by models to remove carbon from the atmosphere; dry deposition is too slow, so modelers regularly assume a hydrophobic to hydrophilic conversion for wet removal of carbon (Collins et al., 2001). Such a conversion would be unlikely in reality unless the carbon was already mixed with a hydrophilic substance. Sulfate is extremely hydrophilic and created in the same combustion processes as soot. Hence, sulfate aerosols provide a plausible physical substrate for this parameterization.

The external or internal mixing state of black carbon is important because it has a direct impact on the specific absorption (absorption per unit mass of black carbon aerosol particles). Internally mixed carbon has a higher specific absorption because of the increased absorption cross section associated with the larger sizes of the mixed aerosols. Values as high as 20 m² g⁻¹ have been observed in the atmosphere and are not possible with external aerosol mixtures, which produce values of only a few m² g⁻¹ (Fuller et al., 1999). Regions with some internally mixed aerosols
and some externally mixed aerosols will have intermediate values of specific absorption. Specific absorption is also sensitive to the fraction of black carbon within an internal mixture, although this has received less attention (Petzold et al., 1997; Neusub et al., 2002a).

Ultimately, the community desires models that accurately calculate atmospheric absorption, and black carbon specific absorption offers a possible parameterization for relating black carbon concentration to its predominant radiative effect. That is, one could use the specific absorption associated with real aerosol mixtures to convert modeled carbon concentrations to a map of aerosol absorption cross sections (Bond et al., 1998). Unfortunately, the black carbon specific absorption is dependent upon the details of the aerosol size distribution and measurements vary by a factor of 4, making the conversion from black carbon concentration to atmospheric absorption nebulous (Liousse et al., 1993).

The reality of this difficulty is demonstrated with two recent studies. Sato et al. (2003) used current aerosol emissions inventories and transport models to calculate absorption optical depths and compared their results to aerosol robotics network (AERONET) measurements at 322 locations worldwide. They found that increasing the black carbon emissions inventories by a factor of 2–4 provided the best match to the AERONET measurements. Park et al. (2003) did a similar study (but geographically limited to the United States) where they compared elemental carbon concentrations to measurements of the Interagency Monitoring of Protected Visual Environments (IMPROVE) network. The Park et al. (2003) study required a 15 percent increase in the black carbon emissions inventories. Both studies used current emissions inventories and external aerosol mixtures. While it is not prudent to draw conclusions based upon two individual studies, the differences in these studies demonstrate the need for both black carbon concentration and absorption measurements.

Worldwide black carbon concentration measurements are needed to assess the efficacy of the carbon emissions inventory and transport model output. This requires long-term measurements in many regions, as model success in one region or season does not apply to all regions and seasons (Cooke et al., 1999). AERONET is an automated network of more than 180 surface radiometers located throughout the world (Holben et al., 1998; 2001). The sky radiance measurements obtained by AERONET are inverted to provide column-averaged aerosol refractive indices and size distributions for the AERONET database (Dubovik and King, 2000). As we demonstrate in this thesis, the AERONET database provides enough information to derive column-averaged black carbon contents and specific absorptions that are radiatively correct, providing a link between AERONET and the transport models.

In this study, we infer the column averaged black carbon content and specific absorption at 46 AERONET locations, assuming that black carbon is internally mixed with the remaining aerosols. We begin by describing the AERONET aerosol retrieval products (Chapter 2) and how to incorporate them into a discrete ordinates radiative transfer model (Chapter 3). This is followed by forward
calculations of the specific absorption for nine climatological aerosol size distributions (Chapter 4), which illustrate that specific absorption is highly sensitive to the volume fraction of black carbon in the aerosol mixture. We describe our inverse calculation next, whereby black carbon concentration and specific absorption are inferred from the AERONET retrieval products at 46 locations in the years 2000 and 2001 (Chapter 5). We validate the black carbon retrieval technique with independent measurements of surface radiances and irradiances (Chapter 6). A number of assumptions are required for our black carbon retrieval, and these are highlighted with sensitivity studies and a literature review (Chapter 7). Moreover, we develop an empirical relationship between the volume fraction of black carbon in an aerosol mixture and the imaginary refractive index, enabling a simple parameterization of the Maxwell Garnett equations for increased computational speed. Finally, we conclude that the black carbon concentration and specific absorption can be inferred from the worldwide AERONET data products, and that this valuable tool can be instrumental in improving and validating transport models (Chapter 8).
Chapter 2

The AERONET product

The aerosol robotics network (AERONET) is described in detail in Holben et al. (1998). It consists of more than 180 sun- and sky-scanning radiometers located at surface sites throughout the world. The radiometers have a narrow field of view (1.2 degrees) and are mounted on programmable trackers, enabling direct sun measurements as well as sky radiance measurements. A filter wheel allows measurements in up to 8 spectral bands, typically centered at wavelengths of 0.34, 0.38, 0.44, 0.5, 0.67, 0.87, 0.94, and 1.02 µm. Each band has a full width at half maximum (FWHM) of approximately 0.010 µm. All of these spectral bands are utilized in the direct sun measurements, but only four of the wavelengths are used for the sky-radiance measurements (0.44, 0.67, 0.87, and 1.02 µm). Instruments are calibrated on a 6-month rotation and the optical filters are changed every 2 years.

2.1 Almucantar radiance-scan retrievals

One component of the sky-radiance measurements is the almucantar scan, which forms the basis of the size distribution and refractive index retrievals in the AERONET database (Dubovik and King, 2000). This scan provides radiances at the solar zenith angle and 76 relative azimuth angles, nearly covering the full azimuthal circle. An azimuthal symmetry requirement eliminates some measurements but at least 21 pairs of angles must survive for a quality retrieval. A homogeneous mixture of molecules and aerosols is assumed for the retrieval and the aerosol properties are adjusted until a forward radiation model matches the measurements in a “best fit” sense. The retrieval provides the columnar aerosol volume size distribution \((dV/d\ln r)\) for 22 radii between 0.05 and 15 µm and the refractive index at the scanning wavelengths.

The size distribution accuracy expected for fine-mode dominated aerosols is 15–25 percent for radii between 0.1 and 7 µm, 25–100 percent otherwise. The real refractive index is expected to be accurate to 0.04, while the imaginary refractive index estimated accuracy is 30–50 percent for optically-thick aerosols. The uncertainties are higher for coarse-mode dominated aerosols (such as dust) and optically-thin aerosols. An accuracy assessment of the AERONET retrievals can be found in Dubovik et al. (2000).

We emphasize that the AERONET size distributions and refractive indices are obtained from radiative transfer retrievals, and as such they are necessarily radiatively correct. Throughout this paper we consider only AERONET retrievals with averaged residual radiance errors less than 5
percent obtained over at least 21 azimuth angles. Solar zenith angles must be greater than 45 degrees but less than 77 degrees. The minimum solar zenith angle of 45 degrees assures a retrieval based upon scattering angles of at least 90 degrees (the maximum scattering angle in an almucantar measurement occurs at twice the solar zenith angle). The maximum scattering angle of 77 degrees assures validity of the plane parallel assumption (which is violated by curvature effects when the sun is near the horizon). We include no restriction on aerosol optical depth, as our testing indicates that accurate surface irradiances are obtained with these restrictions on the AERONET retrievals, even at low optical depths.

2.2 Cloud screening

The temporal and spatial variability of optical depth is generally greater for clouds than for aerosols, and this phenomenon is the basis of the AERONET cloud-screened optical depth product (Smirnov et al., 2000). Both short term (1-min) and long term (1-day) variations are screened as follows. Each AERONET direct sun measurement is actually a triplet of measurements obtained 30 seconds apart. The triplet variation in the cloud screened data set is required to be less than 0.02, or 3 percent of the optical depth (whichever is greater). All optical depths on days with standard deviations less than 0.015 after triplet screening are deemed good — otherwise, further diurnal tests are applied. Measurements with optical depths or Angstrom exponents outside of 3 standard deviations of the daily mean are removed from the data set. A smoothness criteria (based upon empirical results) is applied that limits the root mean square of the aerosol optical depth 2nd derivative with respect to time over the course of a day. Finally, the solar zenith angle is required to be less than 77 degrees for all cloud screened data because of the higher probability of cloud obstruction at low sun elevations.

The almucantar inversions are subject to a different sort of screening. All of the azimuth angles in the almucantar are redundant with at least one other value in the 360-degree scan, and the angles near the forward peak are multiply redundant. Of the 76 measurements, only 30 of them are unique. This allows a symmetry check — radiances of equal azimuth that do not match to within 15–20 percent are not used in the retrieval (O. Dubovik, personal communication). The remaining radiances are averaged with their equal-azimuth partner and incorporated into the retrieval. A quality-controlled retrieval requires that at least 21 radiances match the model-calculated radiances to within 5 percent when averaged over all angles and all four wavelengths. This effectively parses many measurements with clouds in almucantar field of view. The robustness of the almucantar cloud-screening was checked with the whole-sky imager that is co-located with the AERONET scanning sunphotometer at the Atmospheric Radiation Measurement program’s Clouds and Radiation Testbed site, or ARM CART site. The author inspected 34 whole-sky images obtained within 4 minutes of successful AERONET retrievals on 10 days in October 1999, and found no clouds throughout the entire hemispherical field of view (the aerosol optical depth at
the retrieval times varied from 0.05 to 0.32). Moreover, later in this thesis we show that we can use clear-sky radiative transfer calculations and the AERONET almucantar inversions to accurately calculate surface irradiance at the time of the inversion.

2.3 Climatologies

The AERONET database has been operational at some sites since 1993, resulting in a new climatological dataset that is summarized in Dubovik et al. (2002). Briefly, this climatology provides averaged aerosol size distributions, refractive indices, and optical depths at 12 regions worldwide. The size distributions are presented as bimodal lognormal distributions in their Equation (1):

\[
\frac{dV(r)}{d\ln r} = \sum_{i=1}^{2} C_{v,i} \sqrt{2\pi}\sigma_{i} \exp\left[-\frac{(\ln r - \ln r_{v,i})^2}{2\sigma_{i}^2}\right].
\]  

(2.1)

Here, \(C_{v,i}\) represents the particle volume concentration, \(r_{v,i}\) is the median radius, and \(\sigma_{i}\) is the standard deviation of each mode. These parameters and other aerosol optical properties are summarized for the 12 regions in their Table 1. Their parameterizations include four urban-industrial climatologies (GSFC at the Goddard Space Flight Center in Greenbelt, Maryland; Crete-Paris in Europe; Mexico City; and Maldives/INDOEX near India), four biomass burning climatologies (Amazonian Forest, Brazil; South American cerrado, Brazil; African savanna, Zambia; Boreal Forest, U.S.A. and Canada), three desert dust climatologies (Bahrain-Persian Gulf; Solar Village, Saudi Arabia; Cape Verde) and one oceanic climatology (Lanai, Hawaii). We often use these 12 AERONET climatologies to illustrate key points in this thesis, sometimes limiting our calculations to the 9 nondust climatologies when invoking the spherical particle assumption.
Chapter 3

Radiative transfer calculations using
AERONET aerosol retrievals

This chapter describes how we incorporate aerosol size distributions and refractive indices from the AERONET product into a public domain discrete ordinates radiative transfer code (DISORT; Stamnes and Dale, 1981; Stamnes et al., 1988). For our calculations we used 12 computational streams to model a 12-km troposphere. We represent aerosols by the AERONET size distributions and assume them to be homogeneously mixed with molecules in the atmospheric boundary layer. We assume a 2-km aerosol boundary layer height for broadband irradiance calculations at the ARM CART site and use the colocated microwave radiometer value added product (Han and Westwater, 1995) for vertical profiles of scattering molecules and absorbing gases. Vertical profiles of atmospheric thermodynamic properties are not available at other AERONET locations, so we assume a homogeneous mixture of aerosols and nonabsorbing molecules in the troposphere for narrowband irradiance calculations.

Complex refractive indices for aerosols throughout the shortwave spectral region are approximated by an internal mixture of sulfate, soot, and water that is determined by a minimum $\chi^2$ fit to the AERONET values (details may be found in Chapter 5). We calculated aerosol phase functions, optical depths, and single-scatter albedos for the AERONET size distributions using Mie theory (Wiscombe, 1980). We approximate gas absorption by water vapor, oxygen, and carbon dioxide with a correlated-k distribution throughout the shortwave spectral region (Kato et al., 1999) for broadband calculations at the CART site. We calculate molecular scattering from first principles (Bodhaine et al., 1999; Bucholz, 1995) while obtaining ozone amounts from the Total Ozone Mapping Spectrometer (TOMS). We assume that the ozone absorption takes place above the tropopause and adheres to the extinction law (also known as Beer’s Law, Bouguer’s Law, Lambert’s Law, and various combinations of these names). We chose surface albedo values representative of vegetation or water at all of the AERONET sites.

3.1 Aerosol optical properties from AERONET retrievals

The AERONET retrievals can not be directly incorporated into a radiative transfer model, as we must first generate suitable phase functions and single-scatter albedos at the desired wavelengths. Both of these optical properties are easily calculated from size distributions and refractive indices using Mie theory if we assume that the aerosols are spherical particles. Additionally, the DISORT
model requires that we approximate the phase function as a series of Legendre polynomials. We outline the methodology for these calculations in the following two subsections.

### 3.1.1 Phase function and single-scatter albedo

The scattering phase function for a single particle may be written as (Stephens, 1994; p224)

$$p_{sngl}(\Theta) = \frac{4\pi}{k^2} \frac{|S_{sngl}(\Theta)|^2}{C_{sca}},$$  

(3.1)

where $\Theta$ is the scattering angle, $S_{sngl}(\Theta)$ is the amplitude function (dependent upon the particle size, shape, and composition), $k = \frac{2\pi}{\lambda}$ is the wavenumber at wavelength $\lambda$, and $C_{sca}$ is the scattering cross-sectional area. The scattering amplitude function and cross section are computed exactly for homogeneous spheres (e.g., van de Hulst, 1957):

$$|S_{sngl}(\Theta)|^2 = \frac{|S_1(x, m, \Theta)|^2 + |S_2(x, m, \Theta)|^2}{2}$$  

(3.2)

and

$$C_{sca} = Q_{sca}\pi r^2,$$  

(3.3)

where $S_1$ and $S_2$ represent the complex amplitude functions of orthogonal polarizations, $x = kr$ is the size parameter for a particle of radius $r$, $m$ is the complex refractive index, and $Q_{sca}$ is the scattering efficiency.

For a distribution of spheres, computation of the phase function requires that both the complex square of the scattering pattern and the scattering cross section be weighted with the size distribution $dN/dr$ and integrated over all sizes:

$$|S(\Theta)|^2 = \int_0^\infty |S_{sngl}(\Theta)|^2 \frac{dN}{dr} \, dr,$$  

(3.4)

and

$$\sigma_{sca} = \int_0^\infty Q_{sca}\pi r^2 \frac{dN}{dr} \, dr,$$  

(3.5)

The scattering phase function for a polydisperse distribution of spheres follows as

$$p(\Theta) = \frac{4\pi|S(\Theta)|^2}{k^2\sigma}.$$  

(3.6)

Alternatively, this may be written in terms of the volume distribution

$$\frac{dV}{dlnr} = r \frac{dV}{dr} = r(\frac{4}{3}\pi r^3) \frac{dN}{dr},$$  

(3.7)

as

$$p(\Theta) = \frac{4}{k^2} \frac{\int_0^\infty |S_{sngl}(\Theta)|^2 \frac{dV}{dlnr} \, dlnr}{\int_0^\infty \frac{Q_{sca}}{r} \frac{dV}{dlnr} \, dlnr}.$$  

(3.8)
A small matter of nomenclature needs to be discussed here. Strictly speaking, the aerosol number distribution \( dN/dr \) represents the number of particles with radii between \( r \) and \( r + dr \) in a unit volume of the media (the atmosphere, in this case). Likewise, the volume distribution \( dV/dlnr \) represents the volume of aerosol particles with radii between \( lnr \) and \( lnr + dlnr \) in a unit volume of media. Retrievals based upon scanning radiometers, however, use radiance from the entire atmospheric column of uncertain thickness. It is therefore customary to retrieve atmospheric column distributions — that is, the particle number or volume per unit area in the atmospheric column. (This is equivalent to integrating the distributions per unit volume over the height of the atmospheric column.) While the distributions per unit volume were used to derive the scattering phase function for polydisperse spheres above, they fortuitously appear in both the numerator and the denominator of Equations (3.6) and (3.8). Since the other variables in Equations (3.6) and (3.8) are not dependent upon altitude, equivalent results may be achieved by using column distributions. Henceforth, columnar size distributions will be used for the remainder of this thesis.

The total column aerosol optical depth is calculated using Mie theory for a distribution of spheres as

\[
\tau_{ext} = \int_0^\infty Q_{ext} \pi r^2 \frac{dN}{dr} dr = \int_0^\infty \frac{3Q_{ext}}{4r} \frac{dV}{dlnr} dlnr,
\]

where \( Q_{ext} \) is the Mie extinction efficiency; \( dN/dr \) and \( dV/dlnr \) are the aerosol column number and volume distributions, respectively. The component of aerosol optical depth associated with scattering may also be calculated using Mie theory:

\[
\tau_{sca} = \int_0^\infty Q_{sca} \pi r^2 \frac{dN}{dr} dr = \int_0^\infty \frac{3Q_{sca}}{4r} \frac{dV}{dlnr} dlnr.
\]

Then the single-scatter albedo may be expressed as

\[
\omega_0 = \frac{\tau_{sca}}{\tau_{ext}}.
\]

3.1.2 Legendre polynomial expansion of phase functions

The phase function in the form provided by Equation (3.8) is not amenable as input to the DISORT model. Rather, the phase function must be expanded as a series of Legendre polynomials and the corresponding Legendre coefficients are input to the model. This section describes the expansion of AERONET-retrieved phase functions in terms of Legendre polynomials and provides an empirical recommendation for the number of Legendre coefficients necessary for the Nakajima-Tanaka radiance correction (Nakajima and Tanaka, 1988).
3.1.2.1 Technique

It is standard fare to expand the phase function in terms of Legendre polynomials (Chandrasekhar, 1950; see also Liou, 1992):

\[ p(\mu) = \sum_{n=0}^{N_{leg}} \omega_n P_n(\mu) \]  

(3.12)

where \( p(\mu) \) is the phase function, \( \mu \) is the cosine of the scattering angle, \( \omega_n \) are the Legendre coefficients and \( P_n \) are Legendre polynomials. Typically the Legendre polynomials are built from the first two polynomials and recurrence relations (e.g., Arfken, 1985; p. 646–647):

\[ P_0(\mu) = 1, \]  

(3.13)

\[ P_1(\mu) = \mu, \]  

(3.14)

\[ P_2(\mu) = \frac{1}{2}(3\mu^2 - 1), \]  

(3.15)

and

\[ P_{n+1}(\mu) = 2\mu P_n(\mu) - P_{n-1}(\mu) - \frac{\mu P_n(\mu) - P_{n-1}(\mu)}{(n+1)}. \]  

(3.16)

Note that \( n \) represents the polynomial order of \( P_n(\mu) \); hence, Equation (3.12) approximates the phase function as a polynomial of order \( N_{leg} \).

The Legendre coefficients are computed using the orthogonality of Legendre polynomials (Liou, 1992):

\[ \omega_n = \frac{(2n + 1)}{2} \int_{-1}^{1} p(\mu)P_n(\mu)d\mu, \]  

(3.17)

where the first term in the expansion gives the single-scattering albedo (Liou, 1992):

\[ \omega_0 = \frac{1}{4\pi} \int_{0}^{2\pi} \int_{-1}^{1} p(\mu)d\mu d\phi. \]  

(3.18)

For pure scattering \( (\omega_0 = 1) \) this satisfies the normalization condition (Chandrasekhar, 1950; Liou, 1992):

\[ \frac{1}{4\pi} \int_{0}^{2\pi} \int_{-1}^{1} p(\mu)d\mu d\phi = 1. \]  

(3.19)

This is all straightforward, except that the number of Legendre polynomials \( (N_{leg}) \) must be determined and the corresponding Legendre coefficients \( (\omega_n) \) need to be numerically evaluated. It is customary to limit the number of Legendre polynomials in radiative transfer calculations to the number of computational polar angles, or *streams*, with the rational being that little can be
gained from phase functions that are more precise than the model that employs them (Thomas and Stamnes, 1999; p.194). Since the computation time is proportional to the cube of the number of streams (Stamnes et al., 2000), it is important to limit the number of streams (and hence the number of Legendre moments). This poses a problem for calculations involving the highly anisotropic phase functions associated with aerosols, as low-order Legendre polynomials are not capable of capturing the strong forward scattering peak.

Modern radiative transfer codes (such as DISORT) account for strong forward scattering by approximating the forward peak as a Dirac \( \delta \)-function weighted according to the number of streams (Thomas and Stamnes, 1999, p 191; Wiscombe, 1977; Stamnes et al., 2000). The remainder of the phase function (i.e., polar angles outside of the forward peak) is scaled and the number of moments is limited to the number of streams. This scaled and truncated phase function oscillates about the original phase function \( p(\mu) \), so an additional correction is necessary for radiance calculations. The final correction is accomplished with the Nakajima-Tanaka procedure (Nakajima and Tanaka, 1988; Thomas and Stamnes, 1999; Stamnes et al., 2000) by differencing single-scattering radiance calculations with exact values obtained from the untruncated phase function and modifying the multiple scattering results accordingly.

All of the above steps are performed within the DISORT radiative transfer code, but an exact phase function in the form of Legendre polynomial coefficients with significantly more moments than the number of computational streams is required for the Nakajima-Tanaka procedure. The large number of terms necessary for this exact phase function calculation has a detrimental effect on computation time. Consequently, we concluded that determining the minimum acceptable value for \( N_{leg} \) up front was necessary for our calculations. This issue, as well as the numerical integration of \( \omega_n \) in Equation (3.17), are addressed in the next subsection.

### 3.1.2.2 Number of expansion coefficients

Accurate representation of the Legendre coefficients \( \omega_n \) is necessary to avoid a nonsensical phase function expansion. Unfortunately, documented techniques for integrating Equation (3.17) are rare in the literature. Using the trapezoid rule produces poor results when the \( \omega_n \) are inserted into Equation (3.12) and plotted alongside the original phase function, \( p(\mu) \). Chu and Churchill (1955) used up to 28 quadrature points to integrate Equation (3.17) and got poor results, so they derived a very complicated exact solution for \( \omega_n \). Wiscombe (1977) suggested a modification of the Lobatto quadrature proposed by Hunt (1970), which gives accuracies to three decimal places for 60 quadrature points with Henyey-Greenstein phase functions. We presently describe an accurate numerical method for integrating Equation (3.17) using Gaussian quadrature.

Chandrasekhar (1950) writes of the merits of Gaussian quadrature for accurate integration, and Arfken (1985) devotes an appendix to the topic. Given an arbitrary function \( f(\mu) \), we seek a
discrete form of the integral
\[ \int_{-1}^{1} f(\mu) d\mu. \] (3.20)

Chandrasekhar (1950) shows that if \( f(\mu) \) is an arbitrary polynomial of degree \( 2N_q - 1 \) or less, then
\[ \int_{-1}^{1} f(\mu) d\mu = \sum_{j=1}^{N_q} w_j f(\mu_j) \] (3.21)
is an exact solution. The \( \mu_j \) are the zeros of the Legendre polynomial \( P_{N_q}(\mu) \) and are obtained using Newton’s method; the Gaussian weights \( w_j \) are determined by (Press et al., 1986)
\[ w_j = \frac{1}{P'_{N_q}(\mu_j)} \int_{-1}^{1} \frac{P_{N_q}(\mu)}{(\mu - \mu_j)} d\mu = \frac{2}{(1 - \mu_j^2)(P'_{N_q})^2}. \] (3.22)

Hence, the orthogonality relation in Equation (3.17) can be evaluated with the Gaussian quadrature of Equation (3.21):
\[ \omega_n = \frac{(2n + 1)}{2} \sum_{j=1}^{N_q} w_j p(\mu_j) P_n(\mu_j). \] (3.23)

Analytically, aerosol phase functions are not polynomials so the problem becomes one of wisely choosing \( N_q \).

Our choice of \( N_q \) begins with numerical integration of the first Legendre polynomial coefficient \( (n = 0 \text{ in Equation 3.23}) \):
\[ \omega_0 = \frac{1}{2} \sum_{j=1}^{N_0} w_j p(\mu_j). \] (3.24)

Since \( \omega_0 = 1 \) for scattering phase functions, we can determine an adequate value for \( N_0 \) by incrementation until \( \omega_0 = 1 \). Since Gaussian quadrature is exact for polynomials of degree \( 2N_0 - 1 \), we can safely estimate that some polynomial of degree \( 2N_0 - 1 \) will accurately represent \( p(\mu) \) when \( N_0 \) is chosen in this manner. Recall that we have already implicitly assumed that \( p(\mu) \) is a polynomial of degree \( N_{leg} \) in Equation 3.12, so we set
\[ N_{leg} = 2N_0 - 1. \] (3.25)

This implies that the kernel of Equations (3.17) and (3.23) is a polynomial of degree \( N_{leg} + n \), or \( 2N_{leg} \) if we are considering the last term of the expansion. Chandrasekhar’s requirement for exact numerical integration of the last Legendre coefficient in Equation (3.23) becomes \( 2N_q - 1 \geq 2N_{leg} \), or
\[ N_q \geq N_{leg} + 1 \] (3.26)
if we consider only integers. Substituting Equation (3.25) into Equation (3.26) yields
\[ N_q \geq 2N_0. \] (3.27)
Equations (3.24), (3.25), and (3.27) provide the recipe for determining minimal values for \( N_{\text{leg}} \) and \( N_q \). That is, we increment \( N_0 \) in Equation (3.24) until \( \omega_0 \rightarrow 1 \) \((\omega_0 \approx 0.995 \) seems to be sufficient\) and use the other two equations to obtain \( N_{\text{leg}} \) and \( N_q \). In practice, we often include an additional Legendre polynomial so that

\[
N_{\text{leg}} = N_q = 2N_0. \tag{3.28}
\]

This produces no discernible change in the reconstructed phase function.

We tested this technique by comparing phase functions calculated using Mie theory (Equation 3.8) to their reconstructed counterparts (Equation 3.12). We calculated the Legendre coefficients with Gaussian quadrature (Equation 3.23), varying the number of integration terms \( N_q \) and maintaining the number of Legendre polynomials at \( N_{\text{leg}} = N_q \), per Equation (3.28). Results for phase functions calculated from the climatological aerosols at the GSFC site of Dubovik et al. (2002), using 50, 100, and 500 integration terms are shown in Figure 3.1. The corresponding \( \omega_0 \) obtained from Equation (3.23) are shown in Table 3.1.

As expected, the accuracy of the phase function improves as more terms are included in the numerical integration of the Legendre coefficients. Using 500 terms produces a reconstructed phase function that is essentially identical to the original phase function but is computationally expensive (green line in Figure 3.1). Limiting the Legendre coefficient quadrature to 50 terms produces a reconstructed phase function that differs from the original by less than 4 percent at most scattering angles but can produce errors as high as 19 percent at forward scattering angles (blue line in Figure 3.1; Table 3.1). Note that 50 quadratures produces a value of \( \omega_0 = 0.995 \), so doubling the number of quadratures to 100 will produce the phase function we recommend for radiative transfer models utilizing the Nakajima-Tanaka correction. In this case, the reconstructed phase function reproduces the original phase function to within 1 percent, except at the extreme scattering angles. We repeated this test for all 12 AERONET climatological aerosols of Dubovik et al. (2002), including the dust climatologies, and found that 100 quadratures produced reconstructed phase functions within 7 percent of the original phase functions (for scattering angles between 3 and 179 degrees).

One might conclude from Equation (3.26) that setting \( N_q \) to an arbitrary value greater than \( N_{\text{leg}} \) can do no harm, but this can produce inferior results in practice. This is illustrated in Figure 3.2, where we show the exact aerosol phase function for the GSFC climatological aerosols calculated using Mie theory, and Legendre polynomial approximations with \( N_q = 10, 50, \) and 1000 to calculate \( \omega_n \) in Equation (3.23). The number of Legendre polynomials was held fixed at \( N_{\text{leg}} = 10 \) in all polynomial approximations. The calculations for all phase functions were performed at 1800 scattering angles, but we highlight the Gaussian abscissas with green squares for the \( N_q = N_{\text{leg}} = 10 \) case. Figure 3.2 illustrates that the quality of the reconstructed phase function becomes worse for increasing \( N_q \) and fixed \( N_{\text{leg}} \). In fact, \( N_q = 10 \) produces the best results at all scattering angles.
Fig. 3.1. Ratio of phase function created from Legendre polynomial expansion to the phase function calculated from Mie theory using 50, 100, and 500 terms for numerical integration of the Legendre coefficients.
Table 3.1. Zero-th Legendre coefficient ($\omega_0$) and the maximum phase function error calculated with various orders of Gaussian quadrature for climatological aerosols at GSFC.

<table>
<thead>
<tr>
<th>$N_q$</th>
<th>$\omega_0$</th>
<th>$N_{leg}$</th>
<th>Max error for $3 \leq \Theta \leq 179$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.960971</td>
<td>10</td>
<td>38. %</td>
</tr>
<tr>
<td>50</td>
<td>0.994850</td>
<td>50</td>
<td>19.</td>
</tr>
<tr>
<td>100</td>
<td>0.999287</td>
<td>100</td>
<td>4.</td>
</tr>
<tr>
<td>150</td>
<td>0.999954</td>
<td>150</td>
<td>1.6</td>
</tr>
<tr>
<td>200</td>
<td>1.0 (9D)</td>
<td>200</td>
<td>0.7</td>
</tr>
<tr>
<td>250</td>
<td>1.0 (11D)</td>
<td>250</td>
<td>0.3</td>
</tr>
<tr>
<td>500</td>
<td>1.0 (11D)</td>
<td>500</td>
<td>Exact at all angles</td>
</tr>
<tr>
<td>500</td>
<td>1.0 (11D)</td>
<td>200</td>
<td>4.</td>
</tr>
<tr>
<td>500</td>
<td>1.0 (11D)</td>
<td>100</td>
<td>28.</td>
</tr>
<tr>
<td>500</td>
<td>1.0 (11D)</td>
<td>10</td>
<td>178.</td>
</tr>
<tr>
<td>100</td>
<td>0.999287</td>
<td>10</td>
<td>175.</td>
</tr>
<tr>
<td>100</td>
<td>0.999287</td>
<td>500</td>
<td>408.</td>
</tr>
</tbody>
</table>
Fig. 3.2. Mie scattering phase function (solid red line) and 10-term Legendre polynomial approximation of the same using 10, 50, and 1000 quadratures to integrate the Legendre coefficients. Ten quadratures (dashed green line) produces the best results and 1000 quadratures produces the worst results (orange line). The squares indicate the location of the Gaussian abscissas for the 10-term integration.
The reason for the degradation of the reconstructed phase function with increasing \( N_q \) is as follows. Chandrasekhar (1950) reports that Gaussian quadrature is exact for polynomials of degree \( 2N_q - 1 \) or less (Equation 3.21). It is implicit in this statement that polynomials satisfying the or less criteria have \( \omega_n = 0 \) for a certain number of high order coefficients. Aerosol phase functions are not polynomials, however, and increasing \( N_q \) effectively increases the degree of polynomial approximation for \( p(\mu) \) in Equation (3.23). The phase function expansion in Equation (3.12) is also a polynomial approximation of the phase function, but of a degree \( N_{\text{leg}} \). If \( N_{\text{leg}} < N_q \) and not sufficiently large to resolve the phase function exactly, then nonzero \( \omega_n \) terms exist (for \( n > N_{\text{leg}} \)) that are not considered in the phase function expansion. Hence, the phase function is effectively truncated and oscillations similar to those in Figure 3.2 appear in the polynomial approximation of the phase function. Reducing the number of quadratures \( (N_q) \) provides a set of \( \omega_n \) that are the exact solution to some polynomial of correspondingly reduced order, and limiting \( N_q \) to the equality in Equation (3.26) ensures that the quadrature in Equation (3.23) does not approximate a polynomial of order greater than \( N_{\text{leg}} \).

We found the requirement that \( N_q \approx N_{\text{leg}} + 1 \) to be true even when using a large number of Legendre polynomials to expand the phase function. For instance, the phase function in Figure 3.2 can be accurately reproduced with a Legendre polynomial expansion using \( N_q = N_{\text{leg}} = 100 \) at most scattering angles, but setting \( N_q = 500 \) with \( N_{\text{leg}} = 100 \) produces high frequency oscillations about the exact phase function. This is dramatically illustrated in Figure 3.3, which shows phase function ratios similar to Figure 3.1 but with a larger scale for the y-axis. The red line in this figure is identical to the red line in Figure 3.1, with \( N_q = 100 \). The blue line is the result of using \( N_q = 500 \) to integrate the Legendre coefficients \( \omega_n \) but retaining only \( N_{\text{leg}} = 100 \) terms in the reconstructed phase function. While using \( N_q = 100 \) produces a phase function with errors less than one percent at most angles (Figures 3.1 and 3.3), increasing \( N_q \) to 500 results in significant errors at all scattering angles in this case. This problem does not occur for sufficiently large \( N_{\text{leg}} \) such that the phase function is resolved exactly. That is, choosing \( (N_q, N_{\text{leg}}) = (1000, 500) \) will produce the exact phase function in Figure 3.2, as does \( (1000, 1000) \) and \( (500, 500) \). For completeness, we note that using \( N_{\text{leg}} \gg N_q \) (in violation of Equation 3.26) produces even worse results, as noted by the huge error associated with \( (N_q, N_{\text{leg}}) = (100, 500) \) shown in Table 3.1.

What about other quadrature schemes? Some authors prefer to use Lobatto quadrature for integration of the Legendre coefficients on the grounds that less terms are required to obtain the orthogonal solutions of Equation (3.17); (Wiscombe, 1977). We have not tested Lobatto quadrature, but merely remark that using more precise Legendre expansion coefficients does not result in more accurate phase function expansions. For instance, we see in Figure 3.1 that the exact GSFC phase function can be reconstructed at all scattering angles using \( N_q = N_{\text{leg}} = 500 \). We have also verified that using \( N_q = 500 \) in Equation (3.23) produces \( \omega_0 = 1 \) with accuracy to 11 decimal places, indicating a highly orthogonal set of Legendre coefficients. To the extent that Lobatto
Fig. 3.3. Ratio of phase function created from Legendre polynomial expansion to the phase function calculated from Mie theory using 100 polynomials ($N_{\text{leg}} = 100$). Increasing the number of quadratures used to determine $\omega_n$ can degrade the accuracy of the resulting phase function.
quadrature is able to reproduce these coefficients it will also reproduce the large oscillations in Figure 3.3 when only 100 terms are retained in the phase function expansion. In fact, we see in Table 3.1 that using $N_q = N_{leg}$ produces better results than the highly orthogonal coefficients calculated using $N_q = 500$ for any given value of $N_{leg}$. Hence, increasingly precise integration of Equation (3.17) does not translate into increasingly accurate reconstructed phase functions. Hu et al. (2000) arrived at a similar conclusion and developed a “δ-fit” procedure. The “δ-fit” procedure also provides an alternate to the orthogonal Legendre coefficients that results in improved reconstructed phase functions for a limited number of polynomials. Users need to be aware of these issues if they are to input the correct Legendre coefficients for the exact phase function required by the Nakajima-Tanaka correction. We note that the Nakajima-Tanaka correction is not used for irradiance calculations, so any quadrature that produces a normalized phase function ($\omega_0 = 1$) is adequate. The resulting irregularities associated with truncating the phase function tend to be smoothed over by multiple-scattering processes (Thomas and Stamnes, 1999).

3.2 Radiative transfer in the troposphere and stratosphere

Aerosols and molecules co-exist in the troposphere, so their phase functions must be weighted appropriately and combined for radiative transfer computations. In this section we describe our procedure for combining aerosol and gas properties. First, the molecular extinction and phase function are computed, and the molecular phase function is expressed as a combination of two Legendre polynomials. Then the aerosol phase function is computed from the retrieved aerosol size distribution and expanded into a series of Legendre polynomials. The combined aerosol-molecular phase function is constructed by weighting each phase function with the relative scattering contributed by the scattering components. We next calculate the gas absorption at appropriate wavelengths using the correlated-k distribution of Kato et al. (1999). The aerosol-molecular single-scatter albedo follows as the ratio of the scattering sum to the extinction sum for all components.

The radiative impact of aerosols in the stratosphere is negligible at wavelengths less than 4 $\mu$m during the period of our study. Ozone absorption is significant, however. We use satellite measurements to determine the total column ozone concentration and we locate all of the retrieved ozone in the stratosphere. This enables us to use the extinction law with ozone as the sole attenuator to determine the incoming solar irradiance at the tropopause.

3.2.1 Molecular extinction

We calculate the molecular optical depth from first principles using the method of Bodhaine et al. (1999). We chose this approach because fast computer run times make tables and empirical functions obsolete, especially at lower wavelengths where other methods are generally inadequate (Teillet, 1990). Briefly, the molecular scattering cross section $\sigma$ is computed from the refractive
index and depolarization factor for dry air (assuming the gaseous composition documented in Seinfeld and Pandis, 1998). Then the total column molecular scattering optical depth is computed as

\[ \delta(\lambda) = \frac{PN_A}{m_a g} \sigma(\lambda), \]  

(3.29)

where \( P \) is the atmospheric pressure measured at the surface, \( N_A \) is Avogadro’s number, \( m_a \) is the mean molecular weight of dry air, \( g \) is the acceleration due to gravity (corrected for altitude and latitude), and \( \lambda \) represents the wavelength of interest.

At this time the surface pressure is not available at most AERONET sites, but the altitude is available at each location. Hence, we assume a pressure of 1013 mb at sea level and an exponential atmosphere with a scale height of 8 km to approximate the surface pressure at the appropriate altitude. Surface pressure is available for at least two AERONET sites, the CART and COVE sites, which we utilize when available. We use standard sea level pressure (1013 mb) at these locations during downtime periods.

### 3.2.2 Molecular scattering phase function

The molecular scattering phase function is generally written as (e.g., Thomas and Stamnes, 1999):

\[ p^R(\mu) = \frac{3}{4}(1 + \mu^2), \]  

(3.30)

where \( \mu \) represents the cosine of the scattering angle. Accounting for molecular anisotropy results in a slightly modified phase function (Chandrasekhar, p49):

\[ p^R(\mu) = \frac{3}{4} \left[ \frac{(1 + 3\gamma)}{(1 + 2\gamma)} + \frac{(1 - \gamma)}{(1 + 2\gamma)} \mu^2 \right], \]  

(3.31)

where \( \gamma \) is related to the depolarization factor \( \rho \) by

\[ \gamma = \frac{\rho}{2 - \rho}. \]  

(3.32)

Typical values of \( \gamma \) for wavelengths between 0.2 to 1.0 \( \mu \) range from 0.023 to 0.014. The phase function in Equation (3.31) can differ from the one one in Equation (3.30) by as much as 1.5 percent (Bucholtz, 1995). The molecular scattering phase function can be expressed as a linear combination of the Legendre polynomials \( P_0 \) and \( P_2 \) by equating coefficients in like powers of \( \mu \) in Equations (3.13) and (3.15) to the same in Equation (3.31). This results in a normalized Legendre polynomial expansion of the molecular scattering phase function:

\[ p^R(\mu) = P_0 + \frac{(1 - \gamma)}{2(1 + 2\gamma)} P_2(\mu) = P_0 + \frac{(1 - \rho)}{2(1 + \rho)} P_2(\mu). \]  

(3.33)
The scattering phase function for atmospheric layers containing both aerosols and molecules is obtained by weighting the individual phase functions with their respective scattering optical depths:

\[ p^{AM}(\mu) = \frac{\tau_{sca}}{\tau_{sca} + \delta} p(\mu) + \frac{\delta}{\tau_{sca} + \delta} p^{R}(\mu). \]  \hspace{1cm} (3.34)

Inserting the Legendre polynomial expansions of the aerosol and molecular phase functions from Equations (3.12) and (3.33) yields the normalized aerosol-molecular phase function:

\[ p^{AM}(\mu) = 1 + \frac{\delta}{\tau_{sca} + \delta} \left[ \frac{1 - \rho}{2(1 + \rho)} \right] P_2(\mu) + \frac{\tau_{sca}}{(\tau_{sca} + \delta)} \sum_{n=1}^{N_{leg}} \omega_n P_n(\mu). \]  \hspace{1cm} (3.35)

In practice, the aerosol scattering optical thickness of each aerosol-containing layer is calculated by dividing the total columnar value by the number of computational layers the boundary layer. Likewise, the molecular scattering optical thickness of each layer in the troposphere is calculated by dividing the columnar value obtained from Equation (3.29) by the number of computational layers in the troposphere. Hence, scattering in the atmosphere is modeled with a uniform distribution of molecules throughout the troposphere and a uniform distribution of aerosols and molecules in the boundary layer.

### 3.2.3 Gas absorption in the troposphere

Tropospheric gas absorption is not considered for calculations at the AERONET scanning wavelengths of 440, 670, 870, and 1020 nm because these wavelengths correspond to spectral regions where absorption is small. We use broadband irradiance calculations later in this thesis to assess the efficacy of the aerosol retrievals and our calculations, and proper characterization of gas absorption is required for these radiative transfer calculations.

We approximate the gas absorption cross sections for water vapor, oxygen, and carbon dioxide with a correlated-k distribution throughout the shortwave spectral region (Kato et al., 1999). The layer absorption optical depth \( \alpha_i(\lambda) \) associated with any of these gases is computed as

\[ \alpha_i(\lambda) = \sigma_i(\lambda) N \Delta t, \]  \hspace{1cm} (3.36)

where \( \sigma_i \) is the absorption cross section for the corresponding gas in the correlated-k band centered at wavelength \( \lambda \), \( N \) is the number density of oxygen molecules, and \( \Delta t \) is the thickness of the computational layer. The absorption cross sections are sensitive to the temperature and pressure of the molecules. We obtain vertical profiles of these thermodynamic properties from a suite of instruments included in the microwave radiometer value added product (Han and Westwater, 1995). Once the gas absorption is known for each layer the single-scatter albedo of the aerosol-molecular layers may be expressed as

\[ \omega^{AM}_0 = \frac{(\tau_{sca} + \delta)}{(\tau_{ext} + \delta + \alpha)}. \]  \hspace{1cm} (3.37)
where \( \alpha \) represents the gas absorption optical thickness. Ozone is modeled above the tropopause, which we discuss in the next section.

### 3.2.4 Ozone absorption in the stratosphere

Approximately 90 percent of the Earth’s atmospheric ozone is located in the stratosphere (Seinfeld and Pandis, 1998; Fishman et al., 1990). Hence, we assume that all ozone is located above the troposphere in our calculations and attenuate the incoming solar radiation according to the extinction law:

\[
I = I_0 e^{-\tau_{oz}/\mu_0},
\]

(3.38)

where \( I_0 \) and \( I \) represent the solar constant above and below the ozone layer, \( \tau_{oz} \) is the ozone optical depth, and \( \mu_0 \) is the cosine of the solar zenith angle. The amount of ozone is obtained from the Total Ozone Mapping Spectrometer (TOMS) dataset, which reports daily total column ozone amount over the globe with 1.0 degree resolution in latitude and 1.25 degree resolution in longitude (http://toms.gsfc.nasa.gov).

TOMS provides ozone measurements in dobson units, which must be converted to optical depth for attenuation calculations. A dobson unit (DU) is related to the thickness that a layer of ozone would have at standard temperature and pressure (STP; 0 degrees Centigrade and 1 Atmosphere pressure), with 1000 DU corresponding to an ozone layer 1 cm thick. Since the density of ozone is \( 2.69 \times 10^{19} \text{ cm}^{-3} \) at STP and there are 0.001 cm per dobson unit, the ozone extinction may be expressed as

\[
\tau_{oz} = (2.69 \times 10^{19} \text{ cm}^{-3})(0.001 \text{ cm DU})/(N_{DU})\sigma_{oz}(\lambda),
\]

(3.39)

where \( \sigma_{oz} \) is the ozone absorption cross section (cm\(^2\)) and \( N_{DU} \) is the number of Dobson units. The ozone absorption cross sections are obtained from subroutines in the Santa Barbara DISORT atmospheric radiative transfer model (SBDART) for the 185–365 nm spectral range (Ricchiazzi et al., 1998). The moderate resolution transmittance (MODTRAN) database is used for the Chappuis band in the 407–1090 nm spectral range (http://www.vs.afrl.mil/Division/VSBYB).
Chapter 4

Effect of aerosol morphology on black carbon specific absorption

Consider the impact of aerosol morphology on the specific absorption of black carbon. Surface measurements of specific absorption indicate a large range of values, and this is often attributed to the degree of internal or external mixing of an aerosol size distribution (Liousse et al., 1993). Indeed, Ackerman and Toon (1981) found black carbon spheres coated with uniform sulfate shells to be more absorbing than external mixtures with equivalent volume mixing ratios. This is caused by two effects: 1.) the sulfate coating increases the effective absorption cross sectional area of the carbon particles (radiation that would otherwise miss the black carbon particle is refracted into it by the sulfate coating) and 2.) varying the volume mixing ratio of black carbon while maintaining the same total size distribution necessarily varies the size of the soot particles in the concentric sphere model. The specific absorption decreases with respect to particle size because black carbon is extremely absorbing, with an e-folding distance of the order of 0.05 $\mu$m at a wavelength of 0.55 $\mu$m. Hence, molecules at the center of soot particles with radii much larger than 0.05 $\mu$m contribute to the mass but not the absorption because they are shielded from incident radiation by the perimeter molecules.

We discuss some possible internal mixture scenarios in the next section and methods for calculating the associated aerosol optical properties. Then we use nine AERONET climatological size distributions to show that the measured specific absorption variability can be explained with aerosols that are exclusively internally mixed.

4.1 Effective medium approximations for internal aerosol mixtures

Chain aggregates of soot containing soluble compounds collapse to form sphere-like structures when subjected to increasing relative humidity (Hallet et al., 1989) and are often encapsulated in sulfate (Ebert et al., 2002). This type of aerosol lends itself to a concentric sphere model of a carbon core within a sulfate shell. Alternatively, very small carbon particles may be spread throughout a sulfate host aerosol. (Here, small means that the electric field is uniform throughout the particle). We can calculate an effective refractive index for such a mixture and use Mie theory to determine the optical properties. There are a variety of effective medium approximations available for this purpose, with the Maxwell Garnett effective medium approximation being appropriate for mixtures of small insoluble particles suspended in a solution (Lesins et al., 2002). The Maxwell Garnett and
concentric sphere models render different optical properties for equivalent volume fractions of black carbon and neither of them can be expected to accurately describe all aerosol mixtures in the atmosphere.

An ensemble average of black carbon inclusions at all positions within a nonabsorbing host aerosol is probably a more realistic way to compute aerosol optical properties. Unfortunately, calculations of this type are computationally expensive and not amenable to routine processing of a variety of size distributions (Chylek et al., 1995; Fuller et al., 1999). However, the position-averaged model is useful for assessing the accuracy of the Maxwell Garnett and concentric sphere models in select cases, as was done by Fuller et al. (1999). They compared the specific absorption ($\lambda = 0.55 \mu m$) calculated with all three models for mass fractions of carbon from 0.01 to 0.2 and composite particle radii up to 1 $\mu m$. (Atmospheric aerosols typically have mass fractions of elemental carbon less than 0.2; Malm et al., 1994.) Fuller et al. (1999) found that the position-averaged specific absorption equals or exceeds the Maxwell Garnett values for host radii less than about 0.2 $\mu m$ but is less than the concentric sphere specific absorption in this size range. At larger radii, the position-averaged and concentric sphere specific absorption converges to a value below the Maxwell Garnett values. Hence, we can use the concentric sphere and Maxwell Garnett models to estimate the range of specific absorptions for internally mixed atmospheric aerosols.

4.2 Specific absorption of the AERONET climatologies

We used the concentric sphere, Maxwell Garnett, and an external mixture model to calculate the range of specific absorptions (at $\lambda = 0.55 \mu m$) of the nine AERONET nondust climatological size distributions in Dubovik et al. (2002). We used the average optical depths listed in Table 1 of Dubovik et al., (2002) for the volume concentrations, mean radii, and standard deviations necessary to describe the bimodal lognormal size distributions of Equation 2.1 (i.e., their Equation 1). We assumed a mixture of black carbon with ammonium sulfate to approximate a dry aerosol mixture, allowing the volume fraction of black carbon to vary from 0 to 1 (which necessarily adjusted the composite refractive index for the Maxwell Garnett model). We then used standard algorithms to calculate the absorption optical thickness (Wiscombe, 1980; Toon and Ackerman, 1981) and divided by the black carbon concentration to obtain the black carbon specific absorption in units of $m^2 g^{-1}$. For the external mixture, we assume that all of the black carbon is confined to the fine mode (radii less than 0.6 $\mu m$) in equal fractions at each radius and we perform the calculations for a 3-mode distribution (consisting of fine mode black carbon, fine and coarse mode sulfate). However, at black carbon fractions greater than the fine mode fraction we allow black carbon in the coarse mode in equal fractions at each coarse mode radius. (That is, we allow the coarse mode to fill after the fine mode has been completely occupied with black carbon). We use a black carbon refractive index of $2 - 1i$ (Janzen, 1979) and a ammonium sulfate refractive index of $1.53 - 10^{-7}i$ (Toon et al., 1976).
The range of specific absorptions calculated using the concentric sphere and Maxwell Garnett models for all nine nondust climatologies is indicated by the shaded area in Figure 4.1; the bar in Figure 4.1 indicates the range of values calculated with fine mode black carbon in the external mixture model. The lines in Figure 4.1 correspond to the GSFC climatology with the three different mixing scenarios and are qualitatively similar to the other climatologies. Scaling the various size distributions to a single optical depth had no effect on the results because the specific absorption is sensitive to the shape of the size distribution (i.e., modal effective radii and standard deviations) and not the magnitude.

As expected, the concentric sphere specific absorption (dashed line) is greater than the Maxwell Garnett specific absorption (solid line) at the low black carbon fractions common for atmospheric aerosols. This is because low black carbon fractions correspond to small cores that are efficient absorbers in the concentric sphere model, and concentric black carbon cores are more efficient absorbers than eccentric black carbon cores (Fuller et al., 1999). Small, efficient absorbers are assumed to be located throughout the host for the Maxwell Garnett effective medium approximation, but some of the absorbers are in eccentric positions (and hence less efficient). At larger volume fractions of black carbon the concentric sphere model uses larger core particle sizes that are less efficient absorbers than their smaller counterparts. No such size increase is incurred for the Maxwell Garnett effective medium approximation, so this model becomes the more efficient absorbing scenario.

The external mixture specific absorption (long dashes) remains constant at 4.3 m² g⁻¹ when the black carbon is confined to the fine mode because the shape of the black carbon size distribution is assumed constant in this case. It decreases when the volume fraction of black carbon for the external mixture exceeds the fine mode volume fraction, indicative of the changing shape of the now bimodal black carbon distribution (Figure 4.1). This is because small black carbon particles are more efficient absorbers than large black carbon particles. All three mixtures (Maxwell Garnett, concentric sphere, and external) converge to the same specific absorption of 2.8 m² g⁻¹ when the volume fraction of black carbon approaches unity. (Incidentally, this is the same specific absorption that is obtained for any volume fraction of black carbon when it is externally mixed with equal fractions at all radii in the GSFC climatology.) There is a region where the external mixture is more absorbing than the internal mixtures because particle absorption efficiency is greater in the fine mode. Recall that the fine mode is completely occupied before any black carbon is added to the coarse mode in the external mixing scheme, whereas the two modes are occupied at the same fraction in the internal mixing scheme. The internal mixture is always more absorbing than an external mixture with equivalent volume fractions of black carbon at each radii.

The specific absorptions for both internal mixtures are a factor of 1.9–2.8 greater than the external mixture for black carbon fractions less than 5 percent. This enhanced absorption is caused by the increased number of absorbers associated with the internal mixtures (i.e., a system with
Fig. 4.1. Black carbon specific absorption ($l = 0.55 \mu m$) inferred from size distribution climatologies in Dubovik et al. (2002) and black carbon mixed with ammonium sulfate. The shaded area indicates the range of results for internal mixtures of all nine nondust size distributions. Lines represent calculations using the GSFC distribution, including the Maxwell Garnett (solid line), concentric sphere (dashed line), and external mixture morphologies (long dashes). The bar indicates the range of specific absorptions calculated for all nine distributions with external mixtures of black carbon in the fine mode.
many slightly absorbing particles is more absorbing than a system with a few highly absorbing particles). As the volume fraction of black carbon increases the effect becomes less obvious because the number of absorbers of the external mixture approaches the number of absorbers of the internal mixture. Likewise, the effective refractive index of the internal mixture approaches the refractive index of the external mixture.

Recognizing that the specific absorption is sensitive to the chosen size distributions, we also calculated (but do not show) the specific absorption for external mixtures utilizing black carbon particle size distributions identical to the black carbon core sizes of our concentric sphere models. The specific absorption varies with the volume fraction of black carbon for this type of external mixture, but the maximum specific absorption for the GSFC climatology is still only 4.5 m$^2$ g$^{-1}$ and the maximum for all of the AERONET climatologies is 4.9 m$^2$ g$^{-1}$ (occurring at a black carbon volume fraction of about 5 percent). This indicates that the enhanced absorption of the concentric sphere model shown in Figure 4.1 is not caused by the variable black carbon core sizes in that model.

The results in Figure 4.1 are consistent with measurements of ambient aerosols at visible wavelengths by other authors. The inverse relationship between specific absorption and the fraction of black carbon aerosol has been observed with in situ measurements (Petzold et al., 1997; Neusub et al., 2002). Moosmuller et al. (1998) observed 10 m$^2$ g$^{-1}$ (at a wavelength $\lambda$ of 0.532 $\mu$m) using photoacoustic and filter-based measurements during the winter in Brighton, Colorado. Arnott et al. (2003) measured 8.1 m$^2$ g$^{-1}$ during the summer and Fall at the Big Bend National Park in Texas using the same technique. Hartley et al. (2000) found that 14 m$^2$ g$^{-1}$ ($\lambda = 0.535$ $\mu$m) was the best fit to all of their flight data in the summer over the Atlantic Ocean. Indeed, Liouesse et al. (1993) measured specific absorptions from 5 to 20 m$^2$ g$^{-1}$ (wavelength unspecified) for ambient aerosols depending upon the location, and speculated that the differences are caused by variability in the aerosol mixing state (internal or external).

Laboratory-generated aerosols seem to produce lower values. Colbeck et al. (1997) measured 3 to 8.1 m$^2$ g$^{-1}$ ($\lambda = 0.632$ $\mu$m) for various smokes, depending upon the type of fuel chosen for the experiment. Bruce et al. (1991) measured 4.55 m$^2$ g$^{-1}$ ($\lambda = 0.488$ $\mu$m) for diesel fuel burned on a wick. Since laboratory measurements are obtained for fresh aerosols close to the source they probably represent external mixtures or internal mixtures with black carbon fractions greater than commonly found in atmospheric aerosols (i.e., regions to the right in Figure 4.1).

Figure 4.1 illustrates that the range of black carbon specific absorption measurements found in the literature can be explained with the details of the size distribution and the volume fraction of black carbon. This result is independent of the combustion process, as we used the same refractive indices in all tests. We used nine plausible size distributions to define the shaded area in Figure 4.1, which indicates a large variability associated with internal aerosol mixtures. We discuss the implications of aerosol morphology on black carbon specific absorption further in the next chapter.
when we show similar results for real AERONET retrievals using wet aerosols (i.e., 3-component mixtures).
Black carbon content and specific absorption at AERONET sites

Black carbon concentration is correlated with the submicron aerosol concentration, suggesting that it is internally mixed (Pinnick et al., 1993; Krivacsy et al., 2001). The degree of internal mixing is unknown, but specific absorption measurements consistently indicate values of $10 \text{ m}^2 \text{ g}^{-1}$ and higher that can not be achieved with realistic external mixtures (Fuller et al., 1999; see also Figure 4.1). An internal mixture is also inherently assumed in the AERONET almucantar-scan retrievals, as particles of all sizes are assumed to have the same refractive index (Dubovik and King, 2000). This enables us to use the Maxwell Garnett effective medium approximation to deduce a radiatively correct black carbon concentration associated with the AERONET refractive index retrievals. Choosing a different mixing scenario (such as the concentric sphere model) will require adjustments in other aerosol properties to accurately describe the almucantar-scan radiances, effectively undoing the original retrieval.

In this chapter, we use the Maxwell Garnett effective medium approximation and a 3-component mixture of water, ammonium sulfate, and black carbon to deduce the black carbon concentration and specific absorption for the AERONET size distribution and refractive index retrievals. We apply the method at five locations where longterm retrievals are available and show a seasonal variability in black carbon concentration. We use the same method at 46 AERONET sites for the years 2000 and 2001 and show that black carbon specific absorption is highly variable but consistent with the surface measurements of other authors. Regional concentrations of black carbon behave as expected, with the lowest values at remote island sites, higher values at continental sites, and the highest values at biomass burning sites.

5.1 Applying Maxwell Garnett equations to real-time AERONET retrievals

The complex refractive index for an aerosol mixture may be used to determine the volume fraction of three known components in an internally mixed distribution. Ideally, the three aerosol components are obtained from compositional analysis but the deduced volume fraction of black carbon is independent of the other constituents if it is the only absorber at the observed wavelengths. The technique is demonstrated here using a water aerosol with black carbon and ammonium sulfate inclusions, but other components will work as well. These components were chosen because they were frequently found during the tropospheric aerosol radiative forcing experiment (TARFOX, Hegg...
et al., 1997) and the Lindenberg aerosol characterization experiment (LACE 98; Ebert et al., 2002), indicating that this composition of aerosols is usually present in hazy urban regions.

The Maxwell Garnett effective medium approximation allows the computation of the average dielectric function based upon the average electric fields and polarizations of a host matrix and its constituents, and is the appropriate effective medium approximation for mixtures of insoluble particles suspended in solution (Bohren and Huffman, 1983; Lesins et al., 2002). The dielectric functions of atmospheric aerosols are not typically tabulated in the literature, so they must be computed from the square of the refractive index. Once the dielectric functions are known for the host and its constituents, the Maxwell Garnett dielectric function may be calculated for a homogeneous material containing two spherical inclusions (Bohren and Huffman, 1983):

$$\varepsilon_{MG} = \varepsilon_m \left[ 1 + \frac{3 \left( f_1 \frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m} + f_2 \frac{\varepsilon_2 - \varepsilon_m}{\varepsilon_2 + 2\varepsilon_m} \right)}{1 - f_1 \frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m} - f_2 \frac{\varepsilon_2 - \varepsilon_m}{\varepsilon_2 + 2\varepsilon_m}} \right],$$

where $\varepsilon_m$, $\varepsilon_1$, and $\varepsilon_2$ are the complex dielectric functions of the host matrix and the two inclusions; $f_1$, $f_2$ are the volume fractions of the two inclusions. Then the following relations are used to obtain the corresponding refractive index of the mixture:

$$m_r = \sqrt{\frac{\sqrt{\varepsilon_r^2 + \varepsilon_i^2} + \varepsilon_r}{2}},$$

and

$$m_i = \sqrt{\frac{\sqrt{\varepsilon_r^2 + \varepsilon_i^2} - \varepsilon_r}{2}},$$

where $\varepsilon_r$ and $\varepsilon_i$ represent the real and imaginary components of the mixture dielectric function, $\varepsilon_{MG}$.

In our procedure we adjust the volume fraction of the inclusions until the $\chi^2$-fit of the complex refractive index for the mixture to the retrieved values in the AERONET database is minimized:

$$\chi^2 = \sum_{l=1}^{4} \frac{(m_l^{trv} - m_l^{mix})^2}{m_l^{trv}},$$

where $m_l^{trv}$ are the retrieved refractive indices, $m_l^{mix}$ are the calculated refractive indices for the mixture, and $l$ is the summation index over the four retrieval wavelengths. The extremely small imaginary refractive index of most noncarbon aerosols in the visible range ($\lesssim 10^{-7}$) allows the $\chi^2$-fit for the imaginary and real components to be computed separately. First, the volume fraction of black carbon in a black carbon and water mixture is adjusted until a minimum $\chi^2$-fit to the imaginary refractive index is obtained. Then the volume fraction of black carbon is held constant, and the volume fraction of ammonium sulfate in a mixture of ammonium sulfate, black
carbon, and water is adjusted until a minimum $\chi^2$-fit to the real refractive index is obtained. Since the imaginary refractive index of ammonium sulfate is extremely small it does not perturb the imaginary refractive index of the mixture and no further adjustment is necessary.

The black carbon volume fraction ($f_{bc}$) thus obtained can be converted to column-integrated black carbon concentration through multiplication by the black carbon density ($\rho_{bc}$) and the size-integrated aerosol volume distribution:

$$[BC] = f_{bc}\rho_{bc} \int \frac{dV}{dlnr} dlnr,$$

where $V$ is particle volume and $r$ is particle radius. The units in Equation (5.5) are mass per unit area because $[BC]$ represents a column-integrated concentration. The black carbon concentration obtained in this manner can be used in conjunction with the column absorption optical depth $\tau_a$ to obtain the specific absorption cross section for black carbon in units of $m^2$ g$^{-1}$:

$$\alpha = \frac{\tau_a}{[BC]}.$$

Alternatively, one could choose a single value for $\alpha$ (such as 10 m$^2$ g$^{-1}$) and deduce a black carbon concentration from $\tau_a$ and Equation (5.6), but this does not properly account for the variable specific absorption associated with the particle size distribution and black carbon fraction (Figure 4.1).

## 5.2 Inferred concentration of black carbon at selected AERONET locations for 1993–2002

The column-averaged black carbon concentration was calculated using Equation (5.5) and the almucantar retrievals at five AERONET sites for all available data in the period from 1993 through 2002; the results are shown in Figure 5.1. The Mongu and Alta Floresta sites are at biomass burning locations in Africa and South America; the Goddard Space Flight Center (GSFC) site is at an urban location (Washington DC metropolitan area) subject mainly to automobile exhaust; the Clouds and Radiation Testbed site (CART) is in central Oklahoma (USA) at a rural location; the Mauna Loa site is located on a mountaintop in Hawaii and is often representative of background aerosols.

The deduced black carbon concentration at these locations behaves as expected. The Mauna Loa site is characterized by background levels of black carbon throughout the year (less than 0.5 mg m$^{-2}$) with slightly higher values in the spring and summer months. It is probable that these slight perturbations are caused by dust transported from Asia. The rural aerosols at the CART site are also characterized by low black carbon concentrations (less than 1.0 mg m$^{-2}$) but the frequency and the magnitude of the anomalies are much greater than for Mauna Loa, indicative of a location closer to combustion sources. The urban aerosols at GSFC have much higher black
Fig. 5.1. Black carbon concentrations calculated from the AERONET retrievals at 5 locations from 1993 through 2002 (note the difference in scales). Seasonal variations at the biomass burning sites (Mongu and Alta Floresta) and the urban site (GSFC) are obvious.
carbon loading throughout the year than either Mauna Loa or the CART site. Additionally, a seasonal variation is apparent at GSFC during the 10 years of this data set. Black carbon loading is always lower at the beginning and end of the year than it is during the spring and summer months, possibly a result of increased automobile traffic during these time periods. The seasonal variability at GSFC is not correlated with either aerosol optical depth or column-integrated water vapor. Seasonal variation is even more obvious at the two biomass burning sites.

5.3 Black carbon retrievals at 46 AERONET locations for 2000–2001

We used the refractive index and size distributions at the 46 AERONET sites listed in Table 5.1 with Maxwell Garnett $\chi^2$-iteration (Equation 5.4) to calculate the black carbon fractions and specific absorptions using Equation (5.6), focusing on nondust regions where 50 or more retrievals are available in the years 2000 and 2001. Descriptions of many of the sites may be found in Holben et al., (2001). The range of values at all of these sites is shown in Figure 5.2. Note that they are similar to the shaded area for the nine climatologies shown in Figure 4.1.

The GSFC site is highlighted to show the variability exhibited at an individual site. Note the highly variable specific absorption at this site for black carbon fractions less than 0.02 (about 6 to 14 m$^2$ g$^{-1}$). Variable black carbon specific absorptions are common to all 46 AERONET sites. This variability is not caused by different combustion processes affecting the optical properties of soot, as we used the same refractive index for black carbon in all cases. Likewise, we consistently assumed that all particle size distributions are composed of spherical aerosols with internal black carbon inclusions, so aerosol morphology is not the culprit.

The variability in black carbon specific absorption at the sites is more easily explained with the shaded area of Figure 4.1. Vertical displacements in this area represent a single aerosol black carbon fraction but a variety of particle size distributions. Hence, the corresponding changes in specific absorption are caused by the varying absorption efficiencies associated with the sizes of the particles. Likewise, changing the amount of black carbon in a given particle size distribution changes the optical properties of the internally mixed aerosol. An example of this effect on specific absorption is shown by the solid line in Figure 4.1 for the GSFC climatology. Both of these effects occur because absorption efficiency is a function of particle radius and refractive index.

Figures 4.1 and 5.2 indicate that the large variation in specific absorption of 5–20 m$^2$ g$^{-1}$ found by Lioussse et al. (1993) could be caused in part by different internally mixed size distributions and black carbon fractions. Although we observe low end of this range near 5 m$^2$ g$^{-1}$ (and even lower), we never observe the opposite extreme values of 20 m$^2$ g$^{-1}$. As stated earlier, however, the Maxwell Garnett mixing rule tends to underestimate the specific absorption with respect to position-averaging of single inclusions for the black carbon fractions typically found in the atmosphere (Fuller et al., 1999). The specific absorption at any given location is highly sporadic on a
Table 5.1. Yearly averaged black carbon specific absorption ($\alpha; m^2 g^{-1}$), standard deviations, and number of retrievals at 46 AERONET sites for the years 2000 and 2001.

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<th>s.d.</th>
<th>Num</th>
<th>2000</th>
<th>$\alpha$</th>
<th>s.d.</th>
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<td>11.0</td>
<td>1.3</td>
<td>437</td>
<td>10.9</td>
<td>1.0</td>
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<td>0.8</td>
<td>305</td>
<td>9.3</td>
<td>1.4</td>
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<td>Toulouse</td>
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<td>Rome Tor Vergata</td>
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<td>.</td>
<td>.</td>
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<td>9.9</td>
<td>1.1</td>
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<td>IMC Oristano</td>
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<td>.</td>
<td>9.7</td>
<td>1.6</td>
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<td>Nes Ziona</td>
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<td>.</td>
<td>.</td>
<td>11.4</td>
<td>1.2</td>
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Table 5.1. *(Continued)* Yearly averaged black carbon specific absorption ($\alpha$; m$^2$g$^{-1}$), standard deviations, and number of retrievals at 46 AERONET sites for the years 2000 and 2001.

<table>
<thead>
<tr>
<th>SITE</th>
<th>Lat</th>
<th>$\alpha$</th>
<th>s.d.</th>
<th>Num</th>
<th>2000</th>
<th>$\alpha$</th>
<th>s.d.</th>
<th>Num</th>
<th>2001</th>
<th>$\alpha$</th>
<th>s.d.</th>
<th>Num</th>
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<td></td>
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<td>Mongu</td>
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<td>1.0</td>
<td>532</td>
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<td>1.0</td>
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<td>Shirahama</td>
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<td>Kanpur</td>
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<td>1.6</td>
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<td>MALE</td>
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<td>1.1</td>
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<tr>
<td><strong>Atlantic Islands &amp; Gulf of Mexico</strong></td>
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<td></td>
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<td>Azores</td>
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<td>0.9</td>
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<td>10.6</td>
<td>1.5</td>
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<td>Dry Tortugas</td>
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<td>12.0</td>
<td>0.7</td>
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<td>12.6</td>
<td>0.8</td>
<td>315</td>
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<td>1.1</td>
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<td>11.0</td>
<td>1.2</td>
<td>62</td>
<td></td>
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</tr>
<tr>
<td><strong>Pacific Islands</strong></td>
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<td></td>
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<tr>
<td>Midway Island</td>
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<td></td>
<td>11.8</td>
<td>1.0</td>
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<td>Coconut Island</td>
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<td>11.2</td>
<td>2.3</td>
<td>51</td>
<td>11.7</td>
<td>0.9</td>
<td>49</td>
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<td>Lanai</td>
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<td>0.5</td>
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<td>11.6</td>
<td>1.7</td>
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<tr>
<td>Mauna Loa</td>
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<td>9.9</td>
<td>0.7</td>
<td>461</td>
<td>10.0</td>
<td>0.8</td>
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<tr>
<td>Tahiti</td>
<td>-17.577</td>
<td>8.8</td>
<td>2.3</td>
<td>78</td>
<td>.</td>
<td>.</td>
<td>.</td>
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</tbody>
</table>
Fig. 5.2. Black carbon specific absorption at a wavelength of 0.55 µm versus black carbon fraction obtained from 46 AERONET sites for all successful retrievals in the years 2000 and 2001. The GSFC site is highlighted with circles. A refractive index of $m = 2 - 1i$ and a density of 2 g cm$^{-3}$ was used for black carbon.
daily basis, as shown for the year 2000 at the GSFC site in Figure 5.3. Therefore, short-term in situ measurements may not necessarily represent climatological values.

The yearly-averaged black carbon specific absorption for the 46 AERONET sites is shown in Table 5.1. The results are also shown in Figure 5.4 with latitude as the abscissa (to aid in comparisons with the table). The whiskers in Figure 5.4 represent one standard deviation in the yearly data set, indicating the large variability found at any AERONET site. The island sites tend to have the highest values, ranging from 8.8 m$^2$ g$^{-1}$ at Tahiti to 12.6 m$^2$ g$^{-1}$ at the Dry Tortugas. Values at the continental sites (e.g., North and Central America, Europe, and Asia) are slightly lower, ranging from 8.1 m$^2$ g$^{-1}$ at Boulder to 11.4 m$^2$ g$^{-1}$ at the CART site. The biomass burning sites in South America and South Africa have the lowest specific absorptions: 7.15 m$^2$ g$^{-1}$ at Cuiaba-Miranda to 10.6 m$^2$ g$^{-1}$ at Alta Floresta.

These yearly-averaged results are consistent with the instantaneous data of Figure 5.2, which indicate that the highest black carbon specific absorptions correspond to the lowest fractions of black carbon. Hence, the clean island sites have a higher specific absorption than the continental sites, which are typically located closer to sources of black carbon. The biomass burning sites are located near very strong sources of black carbon emissions, resulting in even higher fractions of black carbon and the lowest specific absorption. This effect is enhanced at sites where the data are acquired only during the burning season. These regional averages are summarized in Table 5.2.

Table 5.2. Yearly regional averages of black carbon concentration ([BC]; mg m$^{-2}$) and specific absorption (α; m$^2$ g$^{-1}$) for the years 2000 and 2001.

<table>
<thead>
<tr>
<th>SITE</th>
<th>2000</th>
<th>2001</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[BC]</td>
<td>Number</td>
</tr>
<tr>
<td><strong>Continental</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>North and Central America</td>
<td>0.957 10.2</td>
<td>3352</td>
</tr>
<tr>
<td>Europe</td>
<td>1.384 10.4</td>
<td>1462</td>
</tr>
<tr>
<td>Asia</td>
<td>1.648 10.5</td>
<td>395</td>
</tr>
<tr>
<td><strong>Biomass Burning</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>South America</td>
<td>2.668 8.4</td>
<td>750</td>
</tr>
<tr>
<td>South Africa</td>
<td>2.972 9.3</td>
<td>844</td>
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<tr>
<td><strong>Remote</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atlantic Islands</td>
<td>0.263 11.9</td>
<td>364</td>
</tr>
<tr>
<td>Pacific Islands</td>
<td>0.227 10.4</td>
<td>727</td>
</tr>
</tbody>
</table>
Fig. 5.3. Daily variability of black carbon specific absorption for the year 2000 at the GSFC AERONET site. Results are shown for three different soots (described in Section 7.1.3), but only Soot G produces values near 10 m$^2$ g$^{-1}$.
Fig. 5.4. Yearly-averaged black carbon specific absorption for the 46 AERONET sites in Table 5.1. Circles represent the year 2000, squares the year 2001; whiskers indicate the standard deviations. Colors represent various regions, including North America (red), Europe (grey), Asia (purple), South America (green), Africa (orange), Atlantic Islands (light blue), and Pacific Islands (dark blue).
The corresponding column-averaged black carbon concentrations at these sites is shown in Figure 5.5. The greatest black carbon concentrations are found at the biomass burning sites and the lowest concentrations at the remote island sites (consistent with comments in the previous paragraph). Comparisons with in situ measurements of black carbon concentration are difficult because of different sampling volumes, but in situ techniques typically produce values of less than 13.3 $\mu$g m$^{-3}$ at urban locations and less than 0.3 $\mu$g m$^{-3}$ in remote areas (Allen et al., 1999; Pinnick et al., 1993; Seinfeld and Pandis, 1998). If these concentrations were well-mixed in a 1-km boundary layer the corresponding column-averaged concentrations would be 13.3 mg m$^{-2}$ and 0.3 mg m$^{-2}$. All of the continental and biomass burning sites fall within this range of values, as do most of the island sites in Figure 5.5.
Fig. 5.5. Yearly-averaged black carbon concentrations corresponding to the 46 AERONET sites in Table 5.1. Circles represent the year 2000 and squares represent the year 2001. Colors represent various regions, including North America (red), Europe (grey), Asia (purple), South America (green), Africa (orange), Atlantic Islands (light blue), and Pacific Islands (dark blue).
Chapter 6

Validation of black carbon retrievals with shortwave radiation measurements

Atmospheric column measurements are difficult to verify with in situ techniques. Ideally, this would require a network of invisible non-polluting aircraft simultaneously measuring elemental carbon concentrations at all altitudes. This type of intensive operational period has not yet occurred over any of the AERONET sites at the time of this study. However, daily surface radiation measurements at all of the AERONET sites afford one method of assessing the fidelity of the inferred aerosol properties, which we utilize here. Retrievals that lead to correct radiation calculations when compared to measurements can be said to be radiatively correct. However, it is well recognized that radiative retrievals represent an ill-posed problem with multiple solutions, and the validation that we provide here is necessary but not sufficient proof that our inferred black carbon content and the AERONET size distributions are physically correct. Nonetheless, radiatively correct black carbon concentrations represent an improvement over current climatologies and emission inventories. We use the modeling techniques described in Chapter 3 and Section 5.1 to calculate shortwave radiation and compare the results to surface measurements in the following sections.

6.1 Narrowband radiance comparisons at 46 AERONET sites

Descriptions of the principal-plane and almucantar sky-radiance scans can be found in Holben et al. (1998). Briefly, the principal plane scan provides radiances at a single azimuth angle but multiple viewing zenith angles, while the almucantar scan provides radiances at the solar zenith angle and multiple azimuth angles. Some redundancy exists in the measurements. For instance, the principal plane measurements are obtained at 40 viewing zenith angles but represent only 32 unique scattering angles because of the angular symmetry above and below the sun. Likewise, azimuthal symmetry dictates that the 76 measurements in the almucantar scan correspond to 30 unique angles in a homogeneous atmosphere. When the two scans are simultaneously available they can provide up to 62 unique measurements for comparison to radiative transfer calculations.

We used the principal plane and almucantar radiance measurements and DISORT model calculations to test the efficacy of the retrieval. Vertical profiles of the aerosol and molecular densities are unavailable at most AERONET sites, so we assumed a homogeneous mixture of the two in an unstratified atmosphere for the calculations. Measurements at redundant angles were averaged with their symmetric counterparts before comparison. The errors in the calculated radiances are
determined at each unique angle with respect to the measured radiances for each of the scanning wavelengths of 0.44, 0.67, 0.87, and 1.02 µm. The resulting errors are averaged once more to obtain an average error over all angles and all wavelengths. Scattering angles less than 2.8 degrees are considered unreliable from both a measurement and a modeling perspective and are not included in the analysis. Viewing zenith angles greater than 74 degrees are not considered in the principal plane comparisons.

The principal plane radiances are not used for the AERONET retrievals at the time of this study; hence, they represent measurements that are independent of the retrievals. These measurements are limited to solar zenith angles less than 60 degrees and not necessarily available near the time of the almucantar scans. Since we consider only AERONET retrievals with solar zenith angles greater than 45 degrees, the overlap of the datasets is somewhat limited. Nonetheless, we calculated principal plane radiances corresponding to 5291 measurements obtained within nine minutes of an almucantar retrieval at 46 AERONET sites in the years 2001. Histograms of the results for three ranges of aerosol optical thickness (AOT) are shown in Figure 6.1.

The upper panel corresponds to retrievals with aerosol optical thickness greater than 0.4 as currently recommended by AERONET. For this case, 94 percent of the comparisons have average radianc errors of less than 10 percent and 99 percent of them have average radianc errors of less than 20 percent. Unfortunately, this AOT constraint severely limits the amount of available data, as only 862 of the 5291 retrievals (i.e., 16 percent) have AOTs greater than 0.4. Since globally-averaged aerosol optical depth is about 0.15 (Kiehl and Rodhe, 1995), these optically thick aerosols do not represent typical climatologies. If we consider the optical depths between 0.05 and 0.4 in this dataset (middle panel Figure 6.1) we obtain another 3841 retrievals. The quality of the retrievals degrades little from the high AOT retrievals recommended by AERONET, with 90 percent of the average radiances differing from the principal plane measurements by less than 10 percent and 98 percent of them differing by less than 20 percent. Aerosol optical thickness below 0.05 is the most problematic (lower panel in Figure 6.1), yet 83 percent of the retrievals still produce principal plane radianc errors of less than 10 percent and 91 percent of the retrievals have radianc errors of less than 20 percent. Of the 5291 retrievals at these 46 AERONET sites in 2001, 588 had optical depths less than 0.05, or 12 percent. These results are summarized in Table 6.1.

Comparisons of the almucantar radianc calculations with measurements are usually better than the principal plane comparisons. This is necessarily true because the retrievals are constrained to the almucantar measurements and are forced to agree with radiative transfer calculations to within a residual of 5 percent at 21 azimuth angles. However, these errors are sometimes greater than 5 percent when all angles are considered because of atmospheric inhomogeneity. Histograms of the difference between the computed and measured almucantar scan radiances (not shown) usually have narrower distributions of errors than the principal plane radiances, as indicated in Table 6.1.
Fig. 6.1. Comparison of calculated and measured principal plane radiances obtained within nine minutes of AERONET retrievals for three ranges of aerosol optical thickness. The efficacy of the calculations decreases only slightly for AOTs as low as 0.05 (middle panel) and results are usually better than five percent even at lower AOTs (bottom panel). A total of 5291 retrievals at 46 sites for the year 2001 are included in this dataset.
Table 6.1. Assessment of average radiance errors for three ranges of aerosol optical depth calculated at 46 AERONET sites in 2001.

<table>
<thead>
<tr>
<th>AOT</th>
<th>no. of rtrvlspctage of rtrvlspctage of avg errors</th>
<th>At 46 AERONET locations</th>
<th>At ARM during RSS periods</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Principal plane radiance</td>
<td>Almucantar radiance</td>
</tr>
<tr>
<td>less than 0.05</td>
<td>588</td>
<td>11</td>
<td>63</td>
</tr>
<tr>
<td>0.05 to 0.4</td>
<td>3841</td>
<td>73</td>
<td>68</td>
</tr>
<tr>
<td>greater than 0.4</td>
<td>862</td>
<td>16</td>
<td>73</td>
</tr>
<tr>
<td>less than 0.05</td>
<td>61</td>
<td>22</td>
<td>75</td>
</tr>
<tr>
<td>0.05 to 0.4</td>
<td>209</td>
<td>75</td>
<td>76</td>
</tr>
<tr>
<td>greater than 0.4</td>
<td>7</td>
<td>3</td>
<td>57</td>
</tr>
<tr>
<td>less than 0.05</td>
<td>75</td>
<td>16</td>
<td>83</td>
</tr>
<tr>
<td>0.05 to 0.4</td>
<td>373</td>
<td>78</td>
<td>91</td>
</tr>
<tr>
<td>greater than 0.4</td>
<td>27</td>
<td>6</td>
<td>63</td>
</tr>
</tbody>
</table>
6.2 Broadband irradiance comparisons at the CART site

While the radiance errors discussed above are encouraging it is ultimately desirable to determine the accuracy of irradiance calculations using these retrievals. We desire a very accurate measurement for this comparison but instantaneous measurement of irradiance is not a trivial matter. Measurements with shortwave pyranometers adhering to the strict Baseline Surface Radiation Network (BSRN) protocol are plagued by large negative nighttime offsets. The atmospheric science radiation community has characterized and solved this problem by using nighttime longwave radiometer data (3.5–50 µm) to correct the offset or by fielding black-and-white pyranometers that are less susceptible to this effect, but worldwide implementation has not yet occurred (Dutton et al., 2001; Haeffelin et al., 2001; Michalsky et al., 2003). Alternatively, the rotating shadowband spectroradiometer (RSS) provides accurate irradiance measurements in the 0.36–1.1 µm spectral range at the CART site (Harrison et al., 1999). In the following paragraphs we demonstrate that broadband calculations using our black carbon retrievals compare well to the RSS measurements. We will also demonstrate that most of the aerosol shortwave radiative forcing occurs within the spectral range of the RSS, making it a suitable instrument for validation of aerosol retrievals.

The narrowband calculations described in Section 6.1 correspond to “window” wavelengths with little gas absorption other than ozone. Broadband calculations in the 0.3–1.1 µm spectral range are more complicated because of water vapor and O\textsubscript{2} absorption. Complicating matters even further, the absorption coefficients for these gases are dependent upon their thermodynamic properties. Fortunately, vertical profiles of temperature, pressure, and water vapor density are available as retrieval products from a suite of ground-based instruments at the CART site (Han and Westwater, 1995). We use these hourly profiles for the temperature and pressure of both gases. We also use the hourly water vapor density profiles but scale the total column amount to the 5-minute averaged microwave radiometer column-integrated water vapor product. The O\textsubscript{2} density profile is computed as 21 percent of the hourly air density profile. The correlated-k distributions of Kato et al. (1999) are used to convert these vertical thermodynamic profiles into vertical absorption coefficient profiles in the 0.363–1.046 µm spectral range. Our testing indicated that aerosol forcing is not sensitive to boundary layer thickness in clear skies, so we assumed that all aerosols are confined to a 2 km boundary layer. Further details about how we calculate gas absorption in the troposphere and ozone absorption in the stratosphere may be found in Sections 3.2.3 and 3.2.4.

Results are shown for 193 retrievals from 2000 through 2002 in Figure 6.2. More than 93 percent of the irradiance calculations agree with measurements to within 5 percent and all of them agree to within 11 percent. We emphasize that the broadband computational inaccuracies are not caused by aerosols alone — correlated-k distribution errors, ozone absorption, and uncertainty in the water vapor retrieval and solar constant also play a role. Nonetheless, the computed irradiances based upon the black carbon and AERONET retrievals generally agree with measurements to within the instrument accuracy of about 5 percent. Also note that the discrepancies between the calculations
Fig. 6.2. Comparison of calculated and measured broadband irradiance (0.363–1.046 µm) at the CART site for 2000–2002 using 193 black carbon and AERONET retrievals. Results are generally better than five percent, even at low aerosol optical thickness. Measurements were obtained with the rotating shadowband spectroradiometer.
and measurements are not dependent upon aerosol optical thickness, further strengthening our contention that the black carbon and AERONET retrievals are radiatively correct at low optical depths. This level of computational accuracy is not unique to the CART site, as principal plane radiance difference histograms at this site for the periods in 2000–2002 when RSS data were available are similar to the global results (Table 6.1).

The RSS only covers a limited spectral region from 0.36 to 1.1 \(\mu\)m, so the question arises as to the validity of this instrument as a tool for validating retrieved aerosol properties. We calculated the aerosol radiative forcing at wavelengths less than 1.046 \(\mu\)m, as well as throughout the entire shortwave region (SW; 0.240 to 4.606 \(\mu\)m) using the same methods as the previous section. The results are shown as a spectral forcing ratio in Figure 6.3. The figure indicates that 96 percent of the aerosol radiative forcing at the surface occurs at wavelengths less than 1.046 \(\mu\)m, which we have labeled VNIR. Indeed, 99 percent of the forcing at TOA and 80–90 percent of the column absorption occurs within the RSS spectral region. Hence, inaccuracies associated with aerosol shortwave forcing outside of this spectral region can be expected to have a small effect on the broadband shortwave radiation, and the RSS is an appropriate validation tool for assessing the shortwave radiative effects of aerosols.

There are is another interesting feature in Figure 6.3. Sometimes the TOA spectral forcing ratio is greater than one, oddly indicating that more than 100 percent of the forcing occurs at the VNIR wavelengths. This occurs mathematically when the near infrared (NIR) aerosol radiative forcing has a sign opposite to the VNIR forcing; physically, it means that the cooling associated with the VNIR wavelengths (negative forcing) is offset slightly by warming associated with the NIR wavelengths (positive forcing) in these cases.
Fig. 6.3. Fraction of aerosol radiative forcing and column absorption at wavelengths less than 1.046 µm at the CART site for the year 2000.
Chapter 7

Discussion

We have shown that the techniques described in this study produce results that are radiatively correct at the surface. However, our implementation of the Maxwell Garnett effective medium approximation requires assumptions about the refractive indices, sizes, and shapes of the component aerosols in our black carbon specific absorption and concentration retrievals. We now discuss the impact of these assumptions on our retrievals, both through sensitivity studies and a discussion of the results found by others. The uncertainty in our retrievals associated with using a three-component mixture (i.e., water, ammonium sulfate, and black carbon) for all aerosols is quantified with a sensitivity study in Section 7.1.1. We expand this sensitivity study with an empirical relationship between the volume fraction of black carbon, the host real refractive index, and the mixture imaginary refractive index in Section 7.1.2. The refractive index of particulate soot is notoriously difficult to measure, so we include another sensitivity study to assess the impact of using various measured values on our retrievals in Section 7.1.3. Assumptions regarding aerosol particle sizes and shapes are not easily amenable to sensitivity analyses, so we rely on the work of others to guide us in this area (Section 7.2).

7.1 Sensitivity of black carbon fraction and specific absorption to aerosol optical properties

Although the AERONET database provides the refractive index associated with internal aerosol mixtures, it does not provide information about the aerosol components within the mixture. We assumed that the aerosol components were water, ammonium sulfate, and black carbon when we outlined our procedure in Section 5.1. Undoubtedly, a large fraction of aerosol mixtures do not fit this description, so we test our retrieval by applying the procedure to other aerosol mixtures. Comparison of the inferred black carbon using other mixtures to the inferred black carbon using our original mixture of water, ammonium sulfate, and black carbon forms the basis of our first sensitivity study. We found that the results are sensitive to the real refractive index of the host but not the 2nd inclusion, a result that we exploit in Section 7.1.2.

In Section 7.1.3 we consider the refractive index of black carbon, which exhibits a considerable range of measured values in the literature. We discuss some of the available measurements and our rationale for choosing \( m = 2 - 1i \) for our retrievals. Finally, we discuss the sensitivity of our retrieval to the density of black carbon and possible organic carbon absorption.
7.1.1 Choice of host aerosol

Black carbon is ubiquitous in the atmosphere and is found in the most remote locations, including background aerosols in the Arctic (Rosen et al., 1982). It is undoubtedly the dominant absorber in the AERONET retrievals when significant dust concentrations are not present. However, the other two components of our model aerosol mixture (i.e., water and ammonium sulfate) might not be present in some of the aerosols associated with our AERONET retrievals. Therefore, we investigated the impact of using various common aerosols as hosts and inclusions in our three-component mixture, always including black carbon inclusions. The aerosols we chose for this sensitivity study are water, sea salt, ammonium sulfate, and ammonium nitrate. We tested the black carbon retrieval with these various components at the CART, COVE, GSFC, and Lanai sites for the years 2000 and 2001 (2982 retrievals) and compared the deduced black carbon fractions with the baseline case of a water host with ammonium sulfate and black carbon inclusions.

We found that the results are sensitive to the real refractive index of the host but not the 2nd inclusion. The real refractive index of both the host aerosol and the black carbon inclusions has a significant effect on our retrieval because the imaginary and real refractive indices of the mixture are interdependent (Equations 5.1-5.3). However, the imaginary refractive indices of the nonabsorbing aerosols that we chose is very small ($m_i \lesssim 10^{-7}$) and do not affect our retrieval of black carbon. The refractive index of the 2nd inclusion does not affect our retrieval because the fraction of black carbon has already been determined when the 2nd inclusion is added (Section 5.1).

The retrieved black carbon fractions deduced with the nonwater hosts are 13–17 percent lower relative to the retrieved black carbon fractions for water hosts: 13 percent for sea salt, 15 percent for ammonium sulfate, and 17 percent for ammonium nitrate. The discrepancy increases as the host real refractive index increases, ($m_r$ equals 1.49 for sea salt, 1.53 for ammonium sulfate, and 1.56 for ammonium nitrate at the 0.55 $\mu$m wavelength). Black carbon concentration is directly proportional to black carbon fraction and the black carbon specific absorption is inversely proportional to black carbon fraction (Equations 5.5 and 5.6). Hence, the corresponding black carbon concentrations inferred from nonwater hosts are 13–17 percent higher and the specific absorptions are 13–17 percent lower than for water hosts.

It is interesting to note that the small range of differences in refractive indices between the nonwater hosts results in only a 4 percent discrepancy amongst that subset, much smaller than their discrepancy with the water host ($m_r = 1.33$ at 0.55 $\mu$m for water). We chose water as the host for our retrieval because it is ubiquitous in the atmosphere and expected to be a component of hygroscopic tropospheric aerosols, but the choice of another host aerosol may be more appropriate in dry regions. The potentially high bias in our black carbon fraction associated with inappropriate use of a water host may be offset somewhat by the Maxwell Garnett effective medium approximation, which produces lower absorptions than position averaging for particle radii less than 0.3 $\mu$m (Fuller
et al., 1999). The sensitivity of our retrieval to the real refractive index of the host aerosol is further illustrated in Section 7.1.2.

7.1.2 Parameterization of aerosol internal mixture components

Although the Maxwell Garnett effective medium approximation is accurate for inclusion size parameters as large as 0.5 (Chylek et al., 2000), many authors still use a volume averaged refractive index for aerosol mixtures. The volume averaged refractive index of an aerosol mixture is calculated by weighting the refractive index of the component aerosols with their corresponding volume fractions in the mixture. While the simplicity of this approach is attractive for computer algorithms, optical constants are not additive in general (Bohren, 1983; p.444). We offer a simple alternative here.

The refractive index is an intrinsic property; therefore, it is independent of the particle size distribution. We use Equations (5.1)-(5.3) to estimate the imaginary refractive index of three mixtures of nonabsorbing aerosols with black carbon and plot the results in Figure 7.1. In Figure 7.1, the symbols represent the Maxwell Garnett calculations and the line represents the results of volume averaged calculations. Two of the mixtures consist of nonabsorbing host aerosols with black carbon inclusions, while the third mixture consists of a black carbon host with nonabsorbing inclusions. Note that the volume average refractive index is independent of the real refractive index, so a single line suffices for all three mixtures. The real refractive index of $m_r = 1.33$ was chosen to represent water at wavelength of 0.55 $\mu$m; likewise, $m_r = 1.5$ was chosen to approximate other common atmospheric aerosols such as ammonium sulfate ($m_r = 1.53$), ammonium nitrate ($m_r = 1.56$), and sea salt ($m_r = 1.49$). In humid environments a real refractive index between 1.33 and 1.5 can be expected for the host aerosol composite, which is represented by the shaded region in Figure 7.1. A black carbon refractive index of $m = 2 - 1i$ was used for all three mixtures.

The imaginary refractive index is a smooth function of the black carbon volume fraction in the Maxwell Garnett calculations for all three mixtures (symbols in Figure 7.1). We limit the figure to black carbon fractions less than 0.2, but the smooth relationship for the Maxwell Garnett calculations is exhibited for all black carbon fractions. For the two mixtures with nonabsorbing hosts, a 2nd-order polynomial is required to accurately describe the imaginary refractive index at all black carbon fractions:

$$m_i(\lambda) = C_0(m_r, \lambda) + C_1(m_r, \lambda)f_s + C_2(m_r, \lambda)f_s^2,$$  \hspace{1cm} (7.1)

where $f_s$ is the volume fraction of black carbon. The coefficients $C_i$ are dependent upon the real refractive index and the wavelength. The imaginary refractive index of the mixture with a black carbon host can be described with a linear relationship (i.e., $C_2 = 0$ in Equation 7.1). The coefficients $C_i$ are given for a wavelength of 0.55 $\mu$m and several real refractive indices in Table 7.1.
Fig. 7.1. Imaginary refractive index of composite aerosols calculated using the Maxwell Garnett equations for various mixtures of black carbon and nonabsorbing aerosols. Circles represent a host real refractive index of 1.33 with black carbon inclusions, diamonds represent a host real refractive index of 1.5, and squares represent a black carbon host with inclusions having a real refractive index of 1.5. The line represents volume averaging and very closely approximates the black carbon host case. A black carbon refractive index of $m = 2 - 1i$ was used in all cases.
Table 7.1. Empirical parameters for approximating the Maxwelle Garnett imaginary refractive index of a mixture of inclusions in a host aerosol using Equation (7.1).
Wavelength = 0.55 µm.

<table>
<thead>
<tr>
<th>Host $m_r$</th>
<th>Inclusion $m_r$</th>
<th>$C_0$</th>
<th>$C_1$</th>
<th>$C_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.33</td>
<td>2.0</td>
<td>0.0043</td>
<td>0.6600</td>
<td>0.3348</td>
</tr>
<tr>
<td>1.35</td>
<td>2.0</td>
<td>0.0036</td>
<td>0.6838</td>
<td>0.3122</td>
</tr>
<tr>
<td>1.4</td>
<td>2.0</td>
<td>0.0021</td>
<td>0.7398</td>
<td>0.2590</td>
</tr>
<tr>
<td>1.45</td>
<td>2.0</td>
<td>0.0008</td>
<td>0.7906</td>
<td>0.2103</td>
</tr>
<tr>
<td>1.5</td>
<td>2.0</td>
<td>-0.0002</td>
<td>0.8366</td>
<td>0.1659</td>
</tr>
<tr>
<td>1.55</td>
<td>2.0</td>
<td>-0.0010</td>
<td>0.8780</td>
<td>0.1257</td>
</tr>
<tr>
<td>1.6</td>
<td>2.0</td>
<td>-0.0017</td>
<td>0.9152</td>
<td>0.0894</td>
</tr>
<tr>
<td>2.0</td>
<td>1.5</td>
<td>-0.0027</td>
<td>0.9970</td>
<td></td>
</tr>
<tr>
<td>volume avg</td>
<td>2.0</td>
<td>0.0</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>

Calculations for aerosol mixtures with a black carbon host and nonabsorbing inclusions are often called “inverted Maxwell Garnett” mixtures because these aerosols are not observed in the atmosphere, but we have included them in Figure 7.1 for completeness. These inverted Maxwell Garnett mixtures are more absorbing than their sulfate host counterparts because photons are absorbed in the black carbon matrix before arriving at the sulfate inclusions. (Interestingly, our results indicate that the inverted Maxwell Garnett aerosols are closely approximated by volume averaging.) If we take the other two Maxwell Garnett calculations as the “truth,” then volume averaging produces imaginary refractive index errors of 13–30 percent at black carbon fractions of 0.2. Similarly, using volume-averaged refractive indices to infer the black carbon fraction from the imaginary refractive index would produce errors of 13–23 percent for the same mixture. There is a maximum 13-percent variation in the Maxwell Garnett imaginary refractive index calculations for the two real refractive indices shown in Figure 7.1, which is the minimal volume-averaged error. Typical aerosol hosts such as hydrated sea salt and ammonium sulfate will have a real refractive index between 1.33 and 1.5 and a composite refractive index in the shaded area of Figure 7.1. Hence, Table 7.1 can be used with any estimate of the real refractive index between 1.33 and 1.5 and Equation 7.1 to produce a value for the imaginary refractive index somewhere in the shaded region, which is a better estimate of $m_i$ than obtained from volume averaging.

We can also use Figure 7.1 to expand the sensitivity study of Section 7.1.1 In that section, we used real AERONET data with our retrieval to assess the range of black carbon fractions obtained when assuming different host aerosols. Similarly, one could use Figure 7.1 to infer a black carbon fraction associated with an AERONET imaginary refractive index (for the mixture) and a host
real refractive index. This is demonstrated with the dashed lines in the figure. For instance, a retrieved imaginary refractive index of 0.05 implies a black carbon volume fraction of 0.059 for a host refractive index of 1.5. The same retrieved refractive index (0.05) implies a black carbon volume fraction of 0.068 for a host refractive index of 1.33. This represents a discrepancy of about 15 percent, or midrange of the values found in Section 7.1.1.

7.1.3 Refractive index and density of particulate carbon

There is considerable uncertainty in the refractive index of atmospheric soot (Horvath 1993; Chylek et al., 1995; Fuller et al., 1999; Bergstrom et al., 2002). The absorbing component of atmospheric soot is graphitic carbon (Rosen et al., 1978; 1982) which has a refractive index of $m = 2.67 - 1.34i$ at a wavelength of 0.54 $\mu$m (Borghesi and Guizzetti, 1991) and a density of 2.26 g cm$^{-3}$ (Hess and Herd, 1993). Vitreous carbon, on the other hand, has a refractive index of $m = 1.75 - 0.75i$ and a density of 1.5 g cm$^{-3}$ (Janzen, 1979). Refractive indices of soot in the atmospheric literature span this range and beyond (Marley et al., 2001).

Early measurements on carbon blacks by Senftlebent and Benedict (1918) indicated a refractive index of $m = 1.95 - 0.66i$ between 0.45 and 0.65 $\mu$m, according to Twitty and Weinman (1971) and Janzen (1979). Twitty and Weinman (1971) compiled a list of refractive index measurements on soots that were available at the time and chose $m = 1.80 - 0.5i$ as representative of the 0.25 to 15 $\mu$m wavelength range. This value has been widely adopted by the atmospheric research community. Indeed, the value of $m = 1.75 - 0.44i$ at a wavelength of 0.55 $\mu$m given in the Optical Properties of Aerosols and Clouds (OPAC) database is based upon the Twitty and Weinman survey (d’Almeida et al., 1991; Hess et al., 1998). Janzen (1979) argues that these earlier measurements are not applicable at particulate scales because of optical inhomogeneities and used Mie theory to measure the refractive index of 0.375-$\mu$m radii carbon blacks suspended in solution. By assuming a constant refractive index throughout the 0.3 - 1 $\mu$m wavelength range they inferred a value of $m = 2 - 1i$. These various refractive index measurements mentioned above were labeled Soot A ($m = 1.95 - 0.66i$), Soot B ($m = 1.80 - 0.5i$), and Soot G ($m = 2 - 1i$) by Fuller et al. (1999); we use the same nomenclature here.

The range of black carbon specific absorption obtained at the GSFC site (year 2000) using three black carbon refractive indices (Soot G, graphite, and OPAC) is shown in Figure 5.3. We also tested Soot A and Soot B but do not show their results because they fall within the range of values shown in Figure 5.3; Soot A produces results very close to graphite, Soot B produces results slightly greater than OPAC soot. Overall, there is a factor of 2 variation in the results of 5.3, with the highest specific absorption obtained for Soot G. We chose the optical properties of the commercial carbon black Soot G for our retrievals and outline the reasons in the following paragraphs.

The optical and physical properties of commercial carbon blacks are often used as a surrogate for atmospheric soot because carbon blacks are manufactured using the same physical process.
as in the creation of soot (i.e., incomplete combustion). Individual carbon blacks are composed of spherical arrangements of concentric graphite platelets with decreasing graphitization near the center (Hess and Herd, 1991), which is a similar morphology to diesel soot (Clague et al., 1999; Wentzel et al., 2003). The carbon contents of the two particulates differ significantly, however; diesel soot is approximately 47 percent carbon while carbon blacks are typically 95–98 percent carbon (Clague et al., 1999), indicating a high degree of impurity in the diesel soot.

The impurities affect both the refractive index and the density of the particulates, but this will not drastically alter our retrievals if the impurities are not too absorbing. We consider the nonabsorbing impurities to be either part of the host or part of the 2nd aerosol inclusion in the model that we outlined in Section 5.1. These impurities can be considered as part of the 2nd inclusion in our model if the fraction of impurities is small enough. Since our retrieval of black carbon is dependent only upon the host aerosol refractive index (and not the 2nd inclusion), small fractions of impurities will not affect our black carbon retrieval. However, if the concentration of impurities is large enough the impurities will effectively become the host aerosol. In this case, we can expect black carbon retrieval errors similar to those outlined in Section 7.1.1 (if we erroneously assumed a water host), or 13–17 percent for impurities with real refractive indices of 1.49-1.56.

Absorbing aerosols such as dust and organic carbon will induce errors in the retrieved values for black carbon. We have avoided using our black carbon retrieval in regions dominated by dust, but organic carbon is produced by the same incomplete combustion processes as black carbon (Seinfeld and Pandis, 1998). Organic aerosols have spectrally dependent absorption coefficients in general, typically with peak values at ultraviolet wavelengths (Jacobson, 1999). Ultraviolet wavelength absorption will not affect our visible wavelength radiometric retrieval, but the absorption tail may reach visible wavelengths for some organic carbon species. (Organic carbon aerosols with significant absorption at the AERONET retrieval wavelengths of 0.44, 0.67, 0.87, and 1.02 µm will contaminate the black carbon retrieval.) Complicating matters further, hundreds of aerosol species form the mixtures of organic carbon found in urban and remote regions, each with its own spectral absorption signature (Seinfeld and Pandis, 1998). Sato et al. (2003) used a specific absorption of 0.95 m² g⁻¹ and an imaginary refractive index of 0.013 (λ = 0.5 µm) as generic values for all organic carbon species in their study (based upon unpublished measurements). This imaginary refractive index is quite small compared with all accepted values for soot (about 0.44 to 1). Measured organic carbon concentrations vary significantly within about a factor of 7 of black carbon concentrations (Seinfeld and Pandis, 1998; Allen et al., 1999), so we conservatively estimate a positive bias of less than about 9 percent in our retrieval of black carbon when organic carbon aerosols are present (7 × 0.013/1.0).

Small hollow carbon spheres can be described using the Maxwell Garnett effective medium approximation (Bohren, 1986), and if this result holds true for complex porous soot then our model requires that we use the optical and physical properties of the dense material surrounding the pores.
We chose the optical properties of the carbon black Soot G instead of pure graphite for our retrieval because it represents nearly pure carbon (97 percent), has a similar morphology to atmospheric aerosols, and produces yearly-averaged specific absorption close to the commonly accepted value of 10 m$^2$ g$^{-1}$ (Huffman, 1996) inferred from in situ measurements (see Table 5.1).

For consistency with the optical properties above we use the density of carbon blacks in our retrieval. We chose a density of 2 g cm$^{-3}$ because this value is midrange of the available pycnometer and X-ray diffraction measurements. The lowest pycnometer measurements on carbon blacks indicate densities of 1.85 g cm$^{-3}$ and the highest X-ray diffraction measurements indicate densities of 2.11 g cm$^{-3}$ (Hess and Herd, 1991). Concentrations and specific absorptions of black carbon are directly and inversely proportional to the black carbon density (see Equations 5.5 and 5.6) so these extremes represent deviations of 7.5 and 5.5 percent in the black carbon retrievals.

7.2 Comments on mixture assumptions

There is considerable evidence that a significant fraction of black carbon is internally mixed with sulfate and water, which we review here. Both soot and sulfate are produced by incomplete combustion processes which renders their concentrations highly correlated and provides an opportunity for internal mixing (Pinnick et al., 1993; Krivacsy et al., 2001). Indeed, analysis of electron microscope photographs over Europe during LACE98 indicate that more than 50 percent of the soot is internally mixed with sulfate aerosols (Ebert et al., 2002). Transport models require wet deposition of black carbon in order to obtain reasonable residence times in the atmosphere, indicating that this hydrophobic aerosol is somehow drawn into the hydrological cycle. Sulfate aerosols are highly hygroscopic and provide a mechanism for the embedment of soot into fine mode particulate matter (i.e., radii less than about 0.6 µm) and the hydrological cycle that is consistent with observations and models. Finally, specific absorptions of 10 m$^2$ g$^{-1}$ or more that are commonly observed in the atmosphere can not be achieved with external mixtures of observed aerosol size distributions (Fuller et al., 1999).

At this time, the refractive index retrievals in the AERONET database provide a single value for all aerosol particle sizes. Hence, we chose to model a mixture of aerosols that approximates the AERONET method for our black carbon retrieval, or equal fractions of black carbon in the fine and coarse modes with an effective refractive index for the mixture. However, fine and coarse mode aerosols are created by different mechanisms and can not be expected to share the same fraction of black carbon. We discuss possible repercussions of using a uniform mixture of aerosols for all particle sizes in Section 7.2.1.

Additionally, the Maxwell Garnett effective medium approximation that we use in our retrieval is rigorously valid only when the inclusions in the aerosol mixture are small with respect to the radiative wavelength. Numerous studies have shown, however, that this assumption may be relaxed to include inclusion size parameters ($2\pi r/\lambda$) of at least 0.5. We discuss the morphology of
atmospheric soot in Section 7.2.2 and the sensitivity of absorption to the size of the inclusions in Section 7.2.3.

### 7.2.1 Inclusion of black carbon in the coarse mode

Soot particles near sources are small and unimodal with radii of about 0.05 \( \mu m \) (Steiner et al., 1992; Venkataraman and Friedlander, 1994; Kleeman et al., 2000; Bond et al., 2002). Like all submicron aerosols, however, the small soot particles near sources are not expected to aggregate into the coarse aerosol mode (radii greater than about 0.6 \( \mu m \)). This is because the coarse mode aerosols are not created by the same condensation and growth process typical of fine mode aerosols; rather, they are generated by mechanical processes like surface winds, sea spray, and volcanic emissions. Nonetheless, up to 25 percent of the elemental carbon mass is contained in the coarse mode of urban and biomass burning aerosols (Maenhaut et al., 1996; Virkkula et al., 1999; Neusub et al., 2002); the fine mode particulate mass fraction of elemental carbon varies from 10–22 percent and the coarse mode particulate mass fraction of elemental carbon varies from 2–12 percent. This indicates that the small carbon particles are attached to larger particles, either on the surface or internally. The carbon contained in the coarse mode aerosols is probably a resuspension of particles previously deposited on the surface.

We have included equal fractions of black carbon in the fine and coarse modes because it is inherently assumed in the AERONET retrievals that all particles have the same refractive index (Dubovik and King, 2000). The AERONET retrievals of refractive index are constrained to match measured radiances and can be expected to be radiatively correct; including black carbon in the fine mode without including it the coarse mode could alter the optical properties and nullify the radiative constraints that are the foundation of the original retrieval. The specific absorptions and concentrations of black carbon discussed here are constrained by the absorption optical depth inferred from the AERONET retrievals. Hence, large errors in the retrieved black carbon concentration will produce unreasonable values for the corresponding specific absorption (see Equation 5.6). The retrieved black carbon concentrations are accurate to the extent that the specific absorptions are correct, even when the physical representation is not quite correct. The most reliable results will occur when either the actual black carbon volume fractions are the same in both fine and coarse modes or when the aerosol size distribution is nearly monomodal.

### 7.2.2 Soot aggregates

Atmospheric soot is often observed as aggregates of primary black carbon spheres (or monomers) in transmission electron microscopy images (Martins et al., 1998; Ebert et al., 2002; Li et al., 2003a, 2003b; Wentzel et al., 2003). Aggregate clusters with linear branches of monomers are said to be “open,” whereas nonbranched clumps of monomers are said to be “closed.” Both open and closed
soot clusters have been observed in the atmosphere. Primary particle radii for diesel soot aggregates are about 0.003-0.011 \( \mu m \), corresponding to size parameters of 0.05-0.14 at a wavelength of 0.5 \( \mu m \) (Wentzel et al., 2003). However, motor vehicle emission measurements typically show radii of 0.05 \( \mu m \) (size parameter of 0.63 at a wavelength of 0.5 \( \mu m \)), indicating some aggregation at the source (Steiner et al., 1992; Venkataraman and Friedlander, 1994; Kleeman et al., 2000). The small primary particles that aggregate into clusters are often surrounded by highly hygroscopic ammonium sulfate (Ebert et al., 2002), and aging in conditions of high relative humidity breaks the aggregate chains into smaller clusters again (Hallet et al., 1989).

The aggregate soot can be adequately modeled with Mie theory if the primary particles are not too large. Mulholland et al. (1994) used the coupled electric and magnetic dipole method to show that open aggregates of 17, 52, and 165 spheres with monomer size parameters of less than 0.5 have the same specific absorption as single spheres to within 10 percent. Fuller (1995) obtained a maximum 14 percent difference for similar calculations using 5-carbon aggregates (closed-packed and linear chains) with monomer size parameters less than 0.57.

### 7.2.3 Soot monomer size

Rigorous application of the Maxwell Garnett mixing rule requires a uniform electric field throughout the inclusions, or equivalently, monomer size parameters much less than 1 (Bohren, 1986; Chylek et al., 2000). However, testing of specific cases by some authors has shown that this restriction may be relaxed for monomer size parameters as large as 0.5. We highlight several of these cases in the following paragraphs.

One method of testing an effective medium approximation is by comparison to “position averaging.” With position averaging, the absorption of a single eccentric inclusion is averaged over all possible positions within a nonabsorbing host aerosol. The single-position calculations can be done very accurately, and position averaging is often the basis for comparisons to effective medium approximations. Fuller et al. (1999) used position averaging and a multiple-reflection model to calculate the specific absorption of black carbon inclusions in a sulfate host (0.55 \( \mu m \) wavelength). They assumed a polydisperse size distribution for this internal mixture with a mass median radius of 0.21 \( \mu m \) and a geometric standard deviation of 2.0. They varied the mass fraction of black carbon from 0.01 to 0.2. They found the Maxwell Garnett specific absorption calculations to be 6 percent less than the position-averaged calculations.

Another method for testing effective medium approximations is the discrete dipole method, which provides an exact solution for multiple absorbing inclusions in a host aerosol. Chylek et al. (2000) used this method to model multiple carbon inclusions in water droplets as a basis for comparison to the Maxwell Garnett effective medium approximation. The black carbon volume fraction was held constant at 10 percent in their study, but the size parameter of the inclusions was varied from 0.33 to 1.44. They found the extinction and scattering efficiencies of the two methods
to differ by less than 4 percent for inclusion size parameters below 0.55. Absorption efficiencies differed by about twice that much, or 8 percent.

Martins et al. (1998) also used the discrete dipole approximation to assess the efficacy of Maxwell Garnett theory. They modeled closed soot clusters with nonabsorbing coatings; the mixture size parameters ranged from 0.57 to 4.7. The soot cluster was maintained at 52 percent of the volume of the mixture, and monomer soot size parameters of 0.65 were used in the largest mixtures. We emphasize that the size of their soot cluster was seven times larger than the monomers and essentially the same size as the mixture. Nonetheless, the specific absorptions that they calculated (0.55 \( \mu \)m wavelength) using the Maxwell Garnett effective medium approximation were within 10 percent of the exact values. This is particularly significant because of the large soot fraction used for this test.

The bias of the errors in this section may be negative or positive, depending upon the volumes of the particles and the sizes and fractions of the soot inclusions (Videen et al., 1994; Martins et al., 1998; Fuller et al., 1999; Chylek et al., 2000). Generally, theoretical studies indicate that the Maxwell Garnett effective medium approximation underestimates the absorption (i.e., a negative bias) for small particles and small fractions of black carbon, but the bias changes sign for large particles. Hence, we conclude that the Maxwell Garnett mixing rule is accurate to approximately \( \pm 10 \) percent for aerosol mixtures with randomly located black carbon inclusions, as long as the size parameters of the monomers are no greater than 0.5–0.6.
Chapter 8

Conclusions

Continuous worldwide measurements of black carbon concentrations are required to improve the current gridded carbon emissions inventories and transport models. Black carbon specific absorption measurements are also desirable for relating the modeled microphysics to aerosol optical properties. We have developed a technique for retrieving both the black carbon column concentration and specific absorption from the worldwide AERONET database.

We first demonstrated a method for incorporating aerosol microphysical and optical properties into a radiative transfer model. Of particular importance, we demonstrated a technique for minimizing the number of terms necessary to accurately expand the aerosol phase function as a series of Legendre polynomials. Our results indicate that it is necessary to limit the number of terms used for Gaussian integration of the Legendre orthogonality relations to approximately the number of terms used in the phase function expansion.

Particulate carbon absorbs visible radiation more efficiently when it is contained within a host aerosol (i.e., internal versus external mixing) but the increase in efficiency is not uniform for all internal mixtures of aerosols. We calculated the range of possible specific absorptions for internal mixtures of black carbon using nine climatological size distributions, and found a factor of 2 or more variability for black carbon fractions typical of atmospheric aerosols. The results are highly dependent upon the volume fraction of black carbon but independent of specific combustion processes, as we used a single refractive index for black carbon in this study. This indicates that a single number cannot be used to accurately convert thermal black carbon concentration measurements to absorption (and vice versa) without knowledge of the aerosol size distribution and fraction of black carbon.

We also used the Maxwell Garnett effective medium approximation to infer the column-averaged concentration and specific absorption of black carbon associated with the AERONET retrievals at 46 locations. The yearly-averaged black carbon column concentrations that we found are comparable to typical measured concentrations if a 1 km boundary layer is assumed: 0.22–0.28 µg m\(^{-3}\) at remote island locations, 0.96–3.47 µg m\(^{-3}\) in continental regions, and 2.7–3.7 µg m\(^{-3}\) in biomass burning locations (see Table 5.2). Likewise, the specific absorptions we infer at these locations are consistent with other reported values. The ocean sites have a higher specific absorption (averaging 11.3 m\(^2\) g\(^{-1}\) for 2200 retrievals) and the biomass burning sites have a lower specific absorption (8.9 m\(^2\) g\(^{-1}\) for 3942 retrievals) than the continental sites (9.9 m\(^2\) g\(^{-1}\) for 13,449 retrievals) because of the inverse relationship of specific absorption to black carbon concentration.
We also used the Maxwell Garnett effective medium approximation to parameterize the imaginary refractive index with respect to the black carbon volume fraction, enabling simple but accurate absorption estimates for aerosol mixtures when the black carbon fraction is known. The parameterization indicates that the mixture imaginary refractive index is sensitive to the real refractive index of the host aerosol. Additional aerosol inclusions have no effect on the imaginary refractive index of the mixture when using Maxwell Garnett mixing rules. We compared our parameterization to the volume averaging mixing rule and found an imaginary refractive index difference of 13–30 percent for the range of host aerosols tested. This corresponds to a 13–23 percent difference in the inferred black carbon if volume averaging is substituted for the Maxwell Garnett equations in our retrieval. We found the volume mixing approximation for the imaginary refractive index to be very similar to an “inverted Maxwell Garnett” mixture consisting of a black carbon host aerosol with nonabsorbing inclusions.

Our approach probably represents an upper limit to the black carbon concentration and a lower limit to the specific absorption (if all of the black carbon is internally mixed with equal fractions in the fine and coarse modes). We assumed a water aerosol host, and this will result in black carbon concentrations that are 13–17 percent too high in regions where other common aerosols are a more appropriate host. The presence of organic carbon will induce a retrieved black carbon bias of about 10 percent or less for organic to elemental carbon mass ratios of 7 or less. Absorbing dust will also produce a high bias in our black carbon retrieval, but we have not quantified this effect. The Maxwell Garnett effective medium approximation and uncertainty in the density of black carbon adds uncertainties of $\pm 15$ and $\pm 5$ percent to the retrieved black carbon. A simple sum of all these uncertainties indicates a possible bias of $-15$ to $+40$ percent in our black carbon concentration retrieval. Our results are effectively constrained by the absorption optical depth in the AERONET database, so the corresponding uncertainty in the black carbon specific absorption is $+15$ to $-40$ percent (e.g., Equation 5.6). The black carbon concentrations derived here represent an improvement over the factor of 2 uncertainty in the black carbon emissions inventories. The specific absorptions represent an improvement over using a single value for a parameter that varies by a factor of 4.

Uncertainty in published values of the black carbon refractive index could potentially alter our results by a factor of 2, but we require the retrieval to produce reasonable values for the black carbon specific absorption. We used a refractive index corresponding to a highly graphitized carbon, or $m = 2 - 1i$, which results in an average specific absorption of $10 \text{ m}^2 \text{ g}^{-1}$ for 19,391 retrievals; this is the commonly accepted value. We validated the retrieval with 5291 worldwide radiance measurements and 193 irradiance measurements at the ARM CART site. The results indicate that the retrieval is radiatively correct, even at low aerosol optical depths.
The retrieval technique presented here enables a comparison between model estimates of black carbon concentrations and worldwide AERONET measurements. General circulation models and transport models ordinarily use external mixtures to simulate black carbon aerosol concentrations. As such, direct calculation of aerosol absorption optical depths are a factor of 2–3 too low in regions dominated by internal mixtures of soot, even if the models correctly report the black carbon concentration. Hence, enhanced absorption associated with internal mixing of black carbon is often captured in models by parameterization of the black carbon specific absorption. Measurements of black carbon specific absorption vary by a factor of 4, however, indicating that using a single value for this parameter is inadequate. The black carbon concentrations and specific absorptions that we deduce from AERONET measurements are radiatively correct, and the plethora of longterm AERONET sites makes this retrieval a valuable tool for improving and validating general circulation and transport models.
Bibliography


Vita

Gregory L. Schuster was born in Michigan in 1961. In 1979 he enrolled at Michigan State University and concentrated on pre-engineering coursework. He transferred to the Aerospace Engineering program at the University of Michigan in 1981 and enrolled in the co-operative education program at NASA Langley Research Center in 1983. He received a Bachelor of Science degree (cum laude) from the University of Michigan in 1984 and was hired as a research engineer at NASA Langley shortly thereafter. He enrolled at the University of Colorado at Boulder in 1985 and received a Master's degree in Physics in 1987. He applied his engineering and physics training to solar powered laser research and coherent beam combining experiments from 1984 to 1993. In 1993 he transferred to the Atmospheric Sciences section of Langley Research Center and has subsequently focused his work on atmospheric measurements.