Inferring the Specific Absorption and Concentration of
Black Carbon from AERONET Aerosol Retrievals

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ABSTRACT:
Longterm black carbon measurements are needed throughout the world to assess the efficacy of general circulation model output. We use the Maxwell Garnett effective medium approximation with the aerosol refractive indices and size distributions in the AERONET database to retrieve black carbon concentration and specific absorption.

Key words: soot, black carbon, absorption efficiency, absorption coefficient

REFERENCES
1.- Introduction

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.

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 (Liouesse et al., 1993).

The reality of this difficulty is demonstrated with two recent studies, which is illustrated schematically in Figure 1. 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 (Dubovik and King, 2000). This is enough information to derive column-averaged black carbon concentrations and specific absorptions that correctly describe the radiation field.

2.- Description of black carbon retrieval

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). We use the Maxwell Garnett equations to calculate the amount of internally mixed black carbon that would be necessary to obtain the refractive index provided by the AERONET retrievals. Our technique is described in detail in Schuster et al. (2004); we provide a schematic of the procedure in Figure 2. Briefly, the volume fraction of black carbon inclusions embedded in a water host 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 $[BC]$ through multiplication by the black carbon density ($\rho_{bc}$) and the size integrated aerosol volume distribution:

$$[BC] = f_{bc} \rho_{bc} \int \frac{dV}{d\ln r} d\ln r,$$

where $V$ is particle volume and $r$ is particle radius. The units in Equation (1) 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 $\tau_{abs}$ to obtain the specific absorption cross section for black carbon in units of m$^2$ g$^{-1}$:

$$\alpha = \frac{\tau_{abs}}{[BC]}.$$  

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

3.- Black carbon retrieval at 46 AERONET locations

We used the refractive index and size distributions at 46 AERONET sites with Maxwell Garnett $\chi^2$-iteration (Figure 2) to calculate the black carbon fractions and specific absorptions, 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 3.

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. Rather, the data in Figure 3 indicates that the large variability in specific absorption found in the literature could be caused by different internally mixed size distributions with different black carbon fractions.

3.a.- Inferred concentration of black carbon at selected AERONET locations for 1993–2002
The column-averaged black carbon concentration was calculated using Equation (1) 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 4. 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 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 as 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.

The yearly-averaged black carbon specific absorption for the 46 AERONET sites is shown in Figure 5. The whiskers in Figure 5 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 m² g⁻¹ at Tahiti to 12.6 m² 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 m² g⁻¹ at Boulder to 11.4 m² g⁻¹ at the CART site. The biomass burning sites in South America and South Africa have the lowest specific absorptions: 7.15 m² g⁻¹ at Cuiaba-Miranda to 10.6 m² g⁻¹ at Alta Floresta.

These yearly-averaged results are consistent with the instantaneous data of Figure 3, 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.


The corresponding column-averaged black carbon concentrations at these sites is shown in Figure 6. 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 µg m⁻³ at urban locations and less than 0.3 µg 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 6.

4.- 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. Nonetheless, 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. Still, radiatively correct black carbon concentrations
represent an improvement over current climatologies and emission inventories.

4.a.- 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. 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 discrete ordinates radiative transfer model calculations to test the efficacy of the retrieval (Stamnes and Dale, 1981; Stamnes et al., 1988). 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 5292 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 7.

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 radiance errors of less than 10 percent and 99 percent of them have average radiance errors of less than 20 percent. Unfortunately, this AOT constraint severely limits the amount of available data, as only 862 of the 5292 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 7) we obtain another 3842 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 7), yet 83 percent of the retrievals still produce principal plane radiance errors of less than 10 percent and 91 percent of the retrievals have radiance errors of less than 20 percent. Of the 5292 retrievals at these 46 AERONET sites in 2001, 588 had optical depths less than 0.05, or 12 percent.

Comparisons of the almucantar radiance 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.

Since the real and imaginary refractive indices of black carbon, water, and ammonium sulfate are spectrally flat throughout the visible and
near-infrared wavelengths, the $\chi^2$-iterated black carbon concentration is essentially constrained to the wavelength-averaged refractive index of the AERONET retrieval. Hence, one can use wavelength-averaged refractive indices from the AERONET database and expect to achieve histograms similar to Figure 7.

Figure 7 – Principle plane radiance errors (averaged over all angles and the four scanning wavelengths) at 46 AERONET sites for the year 2001.

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.

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. Regional 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. 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.

The retrieval technique presented here enables a comparison between model estimates of black carbon concentrations and worldwide AERONET measurements. We emphasize that this is an optical retrieval based upon surface radiance measurements, and as such we can only provide “optically equivalent” results; we have not validated our results with elemental carbon measurements throughout the atmospheric column. Nonetheless, the black carbon concentrations and specific absorptions that we deduce from AERONET measurements correctly describe the surface radiance field.

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