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Light Absorption by Carbonaceous Particles: An Investigative Review

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Light Absorption by Carbonaceous Particles: An Investigative Review

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The optical properties of the light-absorbing, carbonaceous substance often called “soot,” “black carbon,” or “carbon black” have been the subject of some debate. These properties are necessary to model how aerosols affect climate, and our review is targeted specifically for that application. We recommend the term *light-absorbing carbon* to avoid conflict with operationally based definitions. Absorptive properties depend on molecular form, particularly the size of *sp*²-bonded clusters. Freshly-generated particles should be represented as aggregates, and their absorption is like that of particles small relative to the wavelength. Previous compendia have yielded a wide range of values for both refractive indices and absorption cross section. The absorptive properties of light-absorbing carbon are not as variable as is commonly believed. Our tabulation suggests a mass-normalized absorption cross section of 7.5 ± 1.2 m²/g at 550 nm for uncoated particles. We recommend a narrow range of refractive indices for strongly-absorbing carbon particles, of which the highest is 1.95–0.79i. Our refractive indices are consistent with most measurements reported in the literature, and values used in present-day climate modeling are in error. Realistic

refractive indices underpredict measured absorption by about 30% when used with common theories for spherical particles or aggregates. Field programs since about 1970 have measured quantities relevant to light absorption, but have only recently made enough measurements to isolate the light-absorbing carbonaceous component and determine its absorptive properties.

1. INTRODUCTION

Optical properties and radiative effects of atmospheric trace species may be predicted from their concentrations and chemical composition. This assumption is fundamental to modeling how anthropogenic activities affect climate. It was first used to model carbon dioxide (Hansen et al. 1981) and other greenhouse gases (Ramanathan et al. 1985). Later followed models of sulfate aerosols (Charlson et al. 1991; Kiehl and Briegleb 1993), mineral dust (Tegen et al. 1996), and carbonaceous aerosols (Penner et al. 1992; Chylek and Wong 1995; Haywood and Shine 1995).

It has long been believed that carbonaceous particles could affect climate. Light-absorbing particles warm the atmosphere, counteracting cooling caused by particles such as sulfates that predominantly scatter light. The role of carbonaceous particles in determining whether aerosols warm or cool has stimulated a large body of research. The choice of optical properties is critical in calculating the effects of aerosols on radiative transfer, but these calculations have frequently relied on values from compilations more than two decades old.

The present article was motivated by two deficiencies in the literature. First, tabulations of optical properties should be updated to include recent measurements. This paper tabulates information on light-absorbing carbon (LAC) particles, especially the extensive combustion literature. Second, measured absorptive properties demonstrate variability that has not been represented in climate models. This variability needs to be explained, or fundamental uncertainties will remain in simulations of radiative transfer.

Writing this paper has proven an exhausting and humbling experience. It is clear that we could have rewritten it indefinitely to accommodate new results. Although we have limited the topics included here, we have included some discussions that may

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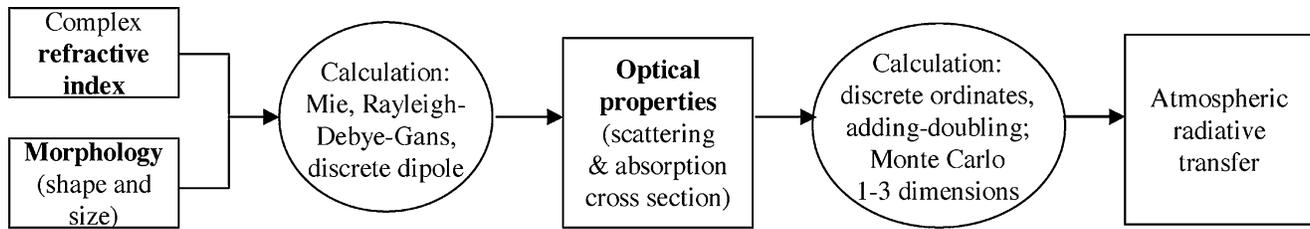


FIG. 1. Calculating radiative transfer

be somewhat foreign to atmospheric scientists. The remainder of this section discusses our approach to this review by identifying information required for climate research. Section 2 gives a history of examinations of light-absorbing carbon particles. Because this field has been fraught with inconsistencies in definition, we discuss nomenclature in Section 3. We review causes of variation in refractive indices of LAC (Section 4), methods of calculating mass absorption cross section (Section 5), measurement techniques (Section 6), measurements of absorption by freshly-generated particles (Section 7), and measurements of absorption in the atmosphere (Section 8). Finally, we recommend values for use in radiative-transfer modeling (Section 9).

1.1. Details: The Chemistry-Optics Paradigm

The use of transport models to calculate climatic effects of any species relies on two implicit assumptions:

1. *There is a predictable relationship between emission (generation of new particles) and spatially distributed atmospheric concentration.* This relationship is governed by advection, chemical transformation, and removal.
2. *There is a predictable relationship between atmospheric concentration and its effects on radiative transfer.* This relationship involves the optical properties of the species.

A model of radiative transfer requires knowledge of emissions and simulations of the two relationships above, all embedded in a characterization of the Earth system usually called a climate model. Emissions of carbonaceous particles are treated in other papers (Cooke et al. 1999; Liou et al. 1996; Bond et al. 2004). The transport models that perform calculation (1) above are numerous and are also described elsewhere (Penner et al. 1998; Haywood and Ramaswamy 1998; Myhre et al. 1998; Koch 2000; Jacobson 2001; Cooke et al. 2002; Chin et al. 2002; Chung and Seinfeld 2002).

The present paper focuses on the second assumption: the relationship between chemical constituents and radiative transfer. Predicting this relationship is a greater challenge for aerosols than for greenhouse gases, because scattering and absorption depend on the particles' physical form. For sulfate aerosols, size distribution and growth with relative humidity are important. Carbonaceous aerosols introduce new challenges. It is not clear how well the optics of these particles *can* be characterized by common measurements of their physical and chemical nature.

Climate forcing is most often defined as the change in net radiative flux at the tropopause attributable to a specific component. A positive forcing is an increase in flux, tending toward warming of the Earth-atmosphere system. Forcing is so called because it is an input to the system determined by factors outside it. Figure 1 shows how the change in radiative transfer is determined from atmospheric concentration of light-absorbing particles. Most climate modelers first assume physical properties (size, shape and state of mixing, categorized as *morphology*) and a refractive index, obtain scattering and absorption cross sections, and apply those properties to modeled concentrations. A few models of global climate have examined effects of differing morphology (Haywood and Shine 1998; Chung and Seinfeld 2002) by comparing climate forcing calculated with different assumptions. Only one global model (Jacobson 2001) has simulated changing particle morphology within the model to account for changing optical properties. All models have assumed that particles are spherical, and have chosen single values for the refractive index. If underlying model assumptions are inappropriate, then scattering, absorption, and radiative forcing estimates will be incorrect. While our discussion will end with calculating scattering and absorption, it provides suggestions for improvements in climate models and has repercussions for calculation of radiative forcing.

The global information provided by satellite remote sensing may soon allow observationally based estimates of climate forcing. Estimates of radiative flux can be correlated with observed aerosol properties at the Earth's surface, and used to estimate aerosol forcing without invoking the relationship between chemistry and optics (e.g., Christopher et al. 2000). However, interpretation of these results, as well as all historical or future projections of climate forcing by aerosols, will continue to rely on global simulations. Inversions used to infer aerosol optical depth from observed radiance also rely on assumptions about aerosol properties.

1.2. Why Another Review?

There is a need to understand optical properties of carbonaceous aerosols for both climate modeling and remote sensing applications. At a minimum, the following tasks are necessary: (1) Understand the variability in the refractive index of carbonaceous particles. (2) Identify critical aspects of morphology that affect absorption and scattering. (3) Reduce these aspects to

observable quantities that can be assessed with widespread atmospheric measurements. (4) Represent this information in climate models with efficient parameterizations.

The present article contributes to the first two tasks and provides information for the fourth. There are many tabulations of relevant properties for atmospheric particles (Horvath 1993a; Liou et al. 1996; Fuller 1999), or combustion-generated particles (Medalia and Richards 1972; Dobbins and Megaridis 1994; Smyth and Shaddix 1996). In the combustion literature, a typical tabulation presents a range of measured refractive indices and discusses the resulting uncertainty in absorption; the authors might then select one value after criticizing the methods of some previous investigators. In the literature on atmospheric aerosols, reviews often collect a range of mass absorption cross sections and seek an explanation for such variability, perhaps based on particle mixing state, but without considering all possible refractive indices.

Missing from previous investigations has been a resolution of the reported variability. If variation in the refractive index is fundamentally inexplicable, then climate forcing will remain similarly uncertain, despite the ability to compute optics of tortuous morphologies. If extremely complex morphologies are required to predict measured mass absorption cross sections, then the likelihood of representing these particles in global atmospheric models is questionable.

In this article, we provide a critical review of refractive indices and mass absorption cross sections of fresh LAC. We suggest explanations for the wide range of values that have appeared in the literature for pure, combustion-generated particles. We also discuss observed mass absorption cross sections and the prospects for predicting them in climate models. Most of the refractive indices used to model LAC have been appropriated from measurements made for other purposes, so we identify only those materials that are similar to atmospheric LAC. Finally, we make recommendations for the most appropriate values to use in climate studies.

1.3. Limits of this Review

Our discussion will not revisit some relevant presentations that appear elsewhere. First, we do not tabulate modeled estimates of total climate forcing. These are summarized by the Intergovernmental Panel on Climate Change (IPCC 2001), have recently been reviewed by Haywood and Boucher (2000), and will also be reviewed for the IPCC assessment due in 2005.

Second, we do not attempt a comprehensive tabulation of field measurements of light absorption, except to note the scope of the measurements that have been made. We also restrict most of our discussion to absorption in the mid-visible (550 nm), although we briefly discuss absorption at other visible wavelengths.

Finally, the task of measuring total aerosol carbon is a simple one, although not immune to sampling artifacts (e.g., Cadle et al. 1983; Huebert and Charlson 2000; Kirchstetter et al. 2001). The

strongly light-absorbing component forms just a few percent of the carbonaceous aerosol, and separating it from the remainder of the atmospheric aerosol is difficult. Methods for identifying this component include exposing the sample to high temperatures (e.g., Chow et al. 1993; Birch and Cary 1996), washing the sample with solvents such as benzene (Gundel et al. 1984) or hydrogen peroxide (Ogren et al. 1983), or interpreting Raman spectroscopy (Rosen et al. 1978; Dippel et al. 1999). The separation of light-absorbing carbon by heating the particles to different temperatures is an area of active research. We review neither this method nor its uncertainties. Without delving into the peculiarities and methods of thermally-measured elemental carbon, we point out that this quantity may have a poor relationship with light absorption (Huffman 1996; Reid et al. 1998; Martins et al. 1998), and that combined thermal and optical techniques may not perfectly separate the strongly absorbing component (Mayol-Bracero et al. 2002a; Yu et al. 2002).

Errors in measuring the quantity of light-absorbing carbon in a sample affect the estimate of light absorption per mass (e.g., Carrico et al. 2003) and could alter conclusions about whether absorption can be predicted from mass measurements. We will only compare absorption and mass of LAC when mass determination does not rely on thermal methods. This decision eliminates a large number of atmospheric measurements from consideration. While such comparisons can be important, they do not advance the purposes of this review.

2. HISTORY: HOW DID WE GET HERE?

Much is known about the optics of particles. The solution to Maxwell's equations for scattering and absorption by spherical particles was presented by Mie (1908), and treatments of the problem appeared decades earlier (Logan 1965). Mie theory has been corroborated by measurements in the intervening years. Books by Van de Hulst (1957), Kerker (1969), and Bohren and Huffman (1983) give extensive theoretical and practical discussions. A critical review by Sorensen (2001) covers optics of agglomerated spheres, commonly assumed as the structure of freshly generated LAC. The present article is not a substitute for such fundamental work. The reader is particularly referred to Section 14.2 in Bohren and Huffman (1983) for discussions and cautions regarding theories that have been applied to atmospheric aerosols.

Table 1 shows that the study of light absorption by carbonaceous particles is not a new field, either. (Here we provide only some of the earliest references in each field.) The 1940s brought the excitement of X-ray analysis and the ability to compare the structures of carbon black and graphite (Biscoe and Warren 1942). Atmospheric aerosols were observed with electron microscopes in the mid-1950s; heating was used to drive off volatile carbon compounds (Cartwright et al. 1955).

Changes in radiative transfer due to particulate light absorption were first estimated around 1970 (Charlson and Pilat 1969; Schneider 1972). During the 1970s, few researchers

TABLE 1
Discussions that contribute to understanding of absorption by LAC

General topic	Material	Objective of study	Sample references
Air quality	Atmospheric aerosol	Determine causes of visibility reduction and health impacts	Cartwright et al. 1955 Groblicki et al. 1981 Malm et al. 1994
Astrophysics	Soot, graphite, amorphous carbon	Identify composition of interstellar matter	Draine and Lee 1984 Sakata et al. 1995 Henning et al. 1999
Climate	Atmospheric aerosol	Estimate impact of anthropogenic activity on Earth's radiative balance	Charlson and Pilat 1969 Schneider 1972 Haywood and Shine 1995
Combustion diagnostics	Flame-generated carbon	Determine soot volume fraction with nonintrusive techniques	Santoro et al. 1983 Mountain and Mulholland 1988 Minutolo et al. 1994
Manufacturing	Carbon black	Predict paint color and rubber properties	Biscoe and Warren 1942 Heckman 1964 Medalia and Richards 1971 Mudgett and Richards 1973
Heat transfer	Flame-generated carbon	Calculate heat transfer out of flames	Dalzell and Sarofim 1969 Tien and Lee 1982 Köylü and Faeth 1994
Nuclear winter	Combustion products	Estimate climate of Earth after nuclear war	Turco et al. 1983 Penner and Molenkamp 1989 Nelson 1989
Petrology	Coal	Identify different coal types	Van Krevelen 1958 McCartney et al. 1958 Foster and Howarth 1968
Solid-state physics	Amorphous carbon	Generate thin films with precisely controlled optical properties	McKenzie et al. 1983 Smith 1984 Robertson 1987

believed there was much absorption in atmospheric aerosols. Most researchers believed that the light-absorbing material in urban atmospheres did not travel very far from their source. Models of the atmospheric aerosol either ignored absorbing particles (Toon and Pollack 1976) or assumed that they occurred only in urban aerosols (Shettle and Fenn 1979). There was simply not enough information to create a more detailed view of atmospheric aerosols.

There had been a long history of measurements of aerosol absorption, particularly those known as “soiling index” and

“British Smoke Shade” (e.g., Waldram 1945; Roach 1961). However, the first systematic measurements of aerosol absorption were made in the early 1970s at the University of Mainz (Fischer 1970) and at the University of Washington (Lin et al. 1973). Some of the first measurements of absorption due to mineral dust were made by groups at White Sands, New Mexico (Lindberg 1975) and Leningrad, Soviet Union (Kondratyev et al. 1973).

The energy crisis of the 1970s led to increasing use of diesel vehicles, and extensive work on soot formation and

measurement ensued. Soot formation in idealized flames and heat transfer by soot in boilers were also hot topics in combustion research (McLean et al. 1981; Seeker et al. 1981), resulting in many measurements of pure soot. Concurrently, a series of field experiments investigated the light-absorbing component of atmospheric aerosol in Denver, Colorado (Wolff et al. 1981). A 1980 conference at General Motors produced a pair of books on combustion soot and atmospheric elemental carbon, a partnership that was regrettably neglected for some years.

The 1980s saw the advent of real-time instruments for measuring light absorption, including photoacoustic (Japar and Szkarlat 1981) and filter-based (Hansen et al. 1982) methods. The comparative ease of measuring absorption led to a desire to understand the relationship between absorption and mass of light-absorbing carbon. If the relationship were simple, the more rapid optical methods could be used to measure both diesel emissions (regulated by mass) and atmospheric concentrations. At the same time, detailed aerosol-climate studies appeared under the guise of studies on nuclear winter (Turco et al. 1983; Nelson 1989; Penner and Molenkamp 1989). These investigations raised questions complementary to the information required by automobile manufacturers: given a mass emission rate of aerosol from conflagrations following nuclear war, how much light would be absorbed by that aerosol, and how would climate change?

Despite a long history of using absorption as a surrogate for mass, significant difficulties in establishing the relationship between the two still exist. Determining the relationship for atmospheric aerosol requires extracting the light-absorbing component from a complex mixture. Methods for accomplishing that task were not available much before 1980, and are open to question even today. Mueller and Appel had used thermal methods to extract light-absorbing material in the Los Angeles ACHEX study during the 1970s (Hidy 1980), but it wasn't until the 1978 Denver Brown Cloud study that a single atmospheric field program measured both absorption and thermally measured elemental carbon (Groblicki et al. 1981). Even the early Aerosol Characterization Experiments (Quinn et al. 1998; Raes et al. 2000) under the umbrella of the International Global Atmospheric Chemistry organization did not provide both absorption and mass measurements. Monitoring programs that did make such paired measurements, such as the Interagency Monitoring of Protected Visual Environments (Malm et al. 1994) gave useful information on air quality trends and the nature of pollutants, but did not explain the observed magnitude of absorption.

In the mid-1990s, simple estimates of forcing by light-absorbing carbonaceous particles were developed (Haywood and Shine 1995). These estimates were low ($+0.1 \text{ W m}^{-2}$ for fossil-fuel emissions) compared with those of greenhouse gases ($+2.45 \text{ W m}^{-2}$). Three-dimensional transport models of carbonaceous aerosols were developed a few years later, and gave somewhat higher estimates ($\sim +0.2 \text{ W m}^{-2}$ for fossil-fuel emissions; Haywood et al. 1997; Haywood and Ramaswamy 1998; Penner et al. 1998; Myhre et al. 1998; Cooke et al.

1999; Koch 2000; Chung and Seinfeld 2002). While these studies acknowledged uncertainties in the optical properties of the aerosols, only a few propagated these uncertainties into estimates of radiative forcing (Wang 2004).

Mixing between carbonaceous aerosols and other negligibly-absorbing substances (discussed in Section 5) might increase absorption by a factor of two, and this increase was not included in most estimates of radiative forcing (Ackerman and Toon 1981; Chylek et al. 1995; Haywood and Shine 1995). It was also known that open biomass burning emitted about the same quantity of LAC as fossil-fuel burning (Lioussé et al. 1996; Bond et al. 2004). However, Jacobson (2001) drew new attention to the particles' contribution to climate forcing when he combined both total global emission and considerations of mixing state to obtain a high radiative forcing estimate of $+0.54 \text{ W m}^{-2}$.

Around the same time, measurement campaigns identified large concentrations of both absorbing and negligibly-absorbing atmospheric aerosols (Novakov et al. 1997; Quinn and Bates 2003), and measured how they alter the Earth's radiative balance (Satheesh and Ramanathan 2000). Other simulations examined more complex changes caused by these particles, such as changes in cloud cover (Ackerman et al. 2000; Ramanathan et al. 2001; Menon et al. 2002).

Recent years have seen proposals by Hansen et al. (2000, 2001) and Jacobson (2002) that reducing emissions of black carbon might ameliorate global warming, and disagreements about whether carbonaceous aerosols cause warming at all (Penner et al. 2003). Uncertainties in optical properties of these particles prevent assessing some of these ideas.

3. NOMENCLATURE: WHAT SHALL WE CALL IT?

The strongly light-absorbing component known to climate modelers as "black carbon" has had a variety of different names, of which *soot* is probably the most common. The remaining less-absorbing carbonaceous aerosol is loosely called "organic carbon," a catchall term whose remedy is outside the scope of this review. We list some common terminology in this section, first discussing terms relevant to composition, and then nomenclature describing absorption and mixing state.

3.1. Strongly-Absorbing Carbon

According to chemists, truly elemental carbon has three forms: graphite, diamond, and C-60 (buckminsterfullerene or buckyballs). Although fullerenes may contribute to growth of LAC particles (Johnson et al. 2002), they are relatively rare compared to other forms and will not be discussed further in this review. Graphite consists of sp^2 -bonded carbon in planar layers, and diamond contains sp^3 -bonded carbon in crystalline form. Neither of these pure forms is found in the atmosphere (or aerosol scientists would be considerably wealthier). An array of names has represented the carbon that exhibits extensive arrays of sp^2 bonds.

Elemental carbon, as used in atmospheric chemistry, usually identifies carbon that does not volatilize below a certain temperature, usually about 550°C. This term is an operational definition based on the stability of carbon at elevated temperatures (Huntzicker et al. 1982; Chow et al. 1993; Birch and Cary 1996). A more precise name for this substance is *refractory carbon*. The fraction identified as elemental carbon under this method depends on the heating conditions (Schmid et al. 2001). The component that does not dissolve in hydrogen peroxide (Ogren et al. 1983) has also been called elemental carbon. For diesel exhaust, there is a strong correlation between light absorption and the refractory carbon content (Scherrer et al. 1981; Japar et al. 1981; Szkarlat et al. 1983), but this relationship has not been tested for all carbon particles. For example, the relationship between absorption and refractory carbon content for particles from benzene flames varies with pyrolysis temperature (Lee 1983).

Graphitic carbon refers to the molecular state of the carbon. This label is accurate to describe strongly absorbing carbon particles because the conjugation of unsaturated bonds results in light absorption (see Section 4); it is inaccurate because planes in light-absorbing carbonaceous particles are confined to spherical surfaces rather than infinite in extent as in graphite (see Sections 5 and 7). Carbonaceous material has also been called graphitic if its Raman spectrum is like that of graphite (Rosen et al. 1978). The response of Raman spectroscopy also depends on crystallite size and particle surface area (Dippel et al. 1999), and many complex aromatic molecules exhibit similar spectra.

The term *soot* is used by the Intergovernmental Panel on Climate Change to denote any light-absorbing, combustion-generated aerosols (IPCC 1996). Combustion researchers often classify all combustion-generated carbonaceous aerosol as soot. Because soot is a vague term that may include any dark-appearing, carbon-containing compound generated in combustion (Watson and Valberg 2001), Cachier (1998) recommends the term *black carbon*. The term *smoke*, an early name for the same aerosols, abounds in literature of the early 20th century (e.g., Popplewell 1901).

Black carbon is probably the most widely used term for light-absorbing carbonaceous aerosols among climate modelers. The term implies carbonaceous aerosols that have strong absorption across a wide spectrum of visible wavelengths. Some instruments such as the aethalometer (Hansen et al. 1984) report concentrations of black carbon based on light attenuation. The reported value is the mass of strongly light-absorbing carbon that would absorb as much light as the sample.

Because the present article examines the nature and causes of light absorption, we will use the term “light-absorbing carbon,” abbreviated *LAC*, which has been suggested by Malm et al. (1994). We deliberately avoid names that have been used for some other purpose; such a choice might perpetuate conflicts in an already splintered field. The words “graphitic” and “elemental” imply identification of the molecular carbon structure that is

inappropriate. The word “black” has come to be associated with measurements by filter-based optical methods, which frequently assume a particular wavelength dependence and absorption per unit mass. Thus, we decline to use any of these terms.

Other work has identified forms of carbon that have weak light absorption with strong wavelength dependence (Millikan 1961; Bond 2001; Sato et al. 2003; Kirchstetter et al. 2004). Although this type of carbon may affect climate, we deliberately do not address it here, so that we can focus on the strongly-absorbing carbonaceous particles. We also recognize that “strongly light-absorbing carbon” is a more descriptive term for the material we examine here, but the resulting acronym is not as tasteful. (We apologize to the Stanford Linear Accelerator Center for this admittedly arbitrary judgment.)

3.2. Other Forms of Light-Absorbing Carbon

Some substances are not associated with atmospheric research, but their study has contributed to the understanding of atmospheric carbon.

Carbon black is used to make pigments and ink and to reinforce automobile tires. Its properties, including optical properties, depend on the manufacturing process, which involves burning either natural gas or oil under very controlled conditions. Early work on scattering and absorption by black particles examined this substance.

Amorphous carbon is a solid that has no long-range crystalline order, composed of a mixture of sp^2 and sp^3 bonds. The International Union of Pure and Applied Chemistry excludes material with sp^2 -bonded clusters greater than 1 nm in extent (approximately seven aromatic rings). It is usually generated by vapor deposition and may contain hydrogen and nitrogen.

Coal is geologically processed vegetable matter. Its ranks or grades range from lignite to anthracite. Exposure to high pressures and elevated temperatures on geologic time scales results in increased aromatic content. As this change occurs, the material appears more black (van Krevelen 1981).

Graphite is one of the pure forms of elemental carbon. As we discuss in Section 7.1.3, both the macroscopic shape and the crystalline structure of graphite differ from that of LAC. The carbon particles of interest to this review may differ from graphite in their optical properties and density.

Tar has a wide variety of meanings; the term often indicates non-black viscid combustion residue of high molecular weight. However, in research on solid-fuel combustion, tar can mean any condensable product ejected from solid matter.

There is also a rich literature on the topic of black carbon in sediments (e.g., Kuhlbusch 1995; Clark 1997; Masiello and Druffel 1998; Schmidt and Noack 2000; Nguyen et al. 2003). It is comforting, but not reassuring, to note that the atmospheric community’s difficulties in separating LAC from other types of carbon are repeated in sediment research (and probably elsewhere), although with different analytical techniques.

3.3. Scattering and Absorption

The term *absorption coefficient* is commonly used to describe the absolute magnitude of atmospheric absorption. This quantity has units of inverse length, or cross section per volume of air. It is often given the symbol b in atmospheric literature, with subscripts indicating the nature and source of the extinction, e.g., b_{ap} is the absorption coefficient due to particles. The symbol σ has also been suggested. In the radiative transfer literature, the coefficients are given Greek symbols such as β (extinction), κ (absorption), or σ (scattering).

It is often desirable to normalize scattering and absorption cross sections to the mass of particles, and the terminology describing this normalized value is not consistent. The units are often cross section of absorption or scattering per mass of material (m^2/g), and α , σ , k , B , E , “mass absorption coefficient,” and “mass absorption efficiency” have all appeared as nomenclature. The term “*efficiency*” is more appropriate to identify the ratio between optical and geometric cross sections, when the result is properly dimensionless. We suggest the more descriptive term “*mass absorption cross section*” (MAC), which does not conflict with other definitions. This term may be criticized as a new entry into an already crowded field; we choose it because it is unambiguous, not because it is satisfying. The modifier “mass” indicates that the absorption cross section is referenced or normalized to the mass of the particle.

Another quantity of interest is the *single-scattering albedo*, or scattering divided by extinction (absorption plus scattering). If single-scattering albedo is close to one, extinction results primarily from scattering. Lower values—even as high as 0.85—indicate that the aerosol has significant absorption and may result in positive forcing (Haywood and Shine 1995).

3.4. Morphology

Several terms have been used to describe the distribution of absorbing and negligibly-absorbing material within particles, as illustrated in Figure 2. In each of these models, the properties of the particle ensemble are obtained by summing the properties of each type of particle separately.

The term *external mixture* implies a heterogeneous population of homogeneous particles (Figure 2(a)), none of which has acquired other material since its formation. The term *internal mixture* is used inconsistently. It can be used to describe any

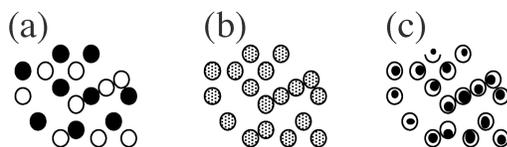


FIG. 2. Idealized relationships between absorbing and nonabsorbing material. (a) External mixture: a heterogeneous population of internally homogeneous particles. (b) volume averaged mixture: a homogeneous population of internally homogeneous particles. (c) Heterogeneous particle composition and population. Both (b) and (c) have been called “internal mixtures”.

occurrence of multiple species in the same particle, but it is an incomplete description of the mixing that may affect absorption, as we will discuss in Section 5. Internal mixtures may describe a homogeneous population of homogeneous particles, where the strongly absorbing material is perfectly mixed with other material at the molecular level (Figure 2(b)); we suggest that the term “*volume mixture*” is more descriptive.

An internal mixture may also refer to a particle that is internally heterogeneous (Figure 2(c)), with absorbing and negligibly absorbing material distributed unevenly throughout each individual particle. An absorbing core surrounded by a shell of negligibly-absorbing material is one way, but not the only way, to visualize particles that are internally heterogeneous. Descriptions such as “shell-and-core” imply a concentricity that may not exist; we favor the term “*encapsulated*,” initiated by Fuller et al. (1999), as most descriptive of the likely mixing state of these particles.

4. Refractive Index: From Molecular Structure to Bulk Optics

In this section, we review research on the relationship between molecular form and complex refractive index of light-absorbing carbon, discussing the material properties that govern light absorption. Measurements leading to inferred (and prevalent) values of the refractive index are discussed in Section 7.

The interaction between a material and incident radiation can be expressed as a function of either the material’s complex refractive index ($m = n - ik$) or its square, the complex dielectric function (ϵ), as long as the material is not magnetic. In this review, we have adopted the convention of writing the imaginary part of the refractive index as a negative number, implying that time dependence is expressed as $\exp(i\omega t)$. Equations to calculate scattering and absorption by particles are often presented as functions of refractive index. While light absorption is closely related to the imaginary part of refractive index (k), it is also affected by the real part (n). Use of either m or ϵ assumes that a single average property represents the material’s nanoscale electronic and molecular variations.

4.1. Carbon Bonding

Chemical and optical properties of carbonaceous material are governed by the molecular form. In diamond, the s -orbital and the three p -orbitals are hybridized into a symmetric set of four tetrahedrally directed bonds known as sp^3 bonds. In graphite, three of the valence electrons are found in hybrid sp^2 orbitals that combine the s -orbital and two p -orbitals; these lie in a plane with an angle of 120° between them. The fourth valence electron is in a π -orbital normal to the plane and, not participating in bonds, is loosely held.

Carbonaceous particles with a high fraction of graphitic bonds are different from other atmospheric aerosols. The stability engendered by the aromatic bonds makes the material nearly inert in the atmosphere; it resists oxidation at atmospheric

temperatures, and it is insoluble in water and many other solvents. The free movement of π -electrons makes this substance one of the only non-metallic compounds with high electrical and thermal conductivity. The energy levels of these loosely-held electrons are closely spaced, so the material absorbs electromagnetic radiation across a broad spectrum. Unlike pure graphite, flame-generated carbon contains sp^3 bonds in addition to sp^2 bonds, and it also includes hydrogen and oxygen (Akhter et al. 1985a). In this respect, flame-generated carbon and atmospheric LAC are similar to amorphous carbon and coal, which also contain both sp^3 and sp^2 bonds.

4.2. Explaining the Refractive Index

Some studies have used physical principles, such as the predicted density of electronic states, to link refractive index with the molecular structure of carbon (Xanthakis 2000; Fanchini and Tagliaferro 2001). More common than this computationally-intensive process is a hybrid of theory and empirical data. A model for the expected interaction with light (reflectance or absorption) is chosen based on physical principles. Then, model parameters (including the refractive index) are adjusted until predictions match measurements.

4.2.1. Elemental Composition

Attempts to explain the absorptive properties of carbon by using elemental composition, mainly H/C (hydrogen-to-carbon) ratio, span several decades. Millikan (1961) reported changes in the wavelength dependence of flame-generated carbon with H/C ratio. Medalia and Richards (1972) suggested that values of k exhibit a linear relationship with H/C ratio for carbon black. Dalzell and Sarofim (1969) found that the refractive index of soot has no relationship with fuel H/C ratio, but did not investigate the H/C ratio of the soot. Habib and Vervisch (1988) found that k did decrease with H/C ratio. Vaglieco et al. (1990) provided a physical explanation for variations with H/C ratio: hydrogen atoms “act as traps for the electrons, removing them from the π valence band.” The H/C ratio of flame-generated particles tends to be higher than that of carbon black (Medalia and Rivin 1982). Cachier et al. (1989) measured the H/C ratio of soot as 0.15 ± 0.05 , and of ambient aerosol as 0.20–1.50.

This explanation is simplistic; the H/C ratio is only the beginning of a predictive relationship. Felske et al. (1984) dismiss such approaches as being “without theoretical basis.” Changes in this ratio may be informative, but they do not uniquely identify the molecular form of the carbon. Other theories account for molecular form more directly.

4.2.2. Linear Oscillators

The dispersion equations¹ (e.g., Ditchburn 1976; Born and Wolf 1981) represent the classical Lorentz-Drude approach to

¹So called because they represent the variation of refractive index with wavelength, the reason for “dispersion” of white light passing through a prism.

electromagnetic radiation. Electrons are treated as linear oscillators that interact with radiation, and optical properties of a material are obtained by summing the interactions of the electrons it contains. The complex refractive index (m) as a function of frequency is related to properties of the j electrons:

$$m(\omega)^2 = 1 + \frac{e^2}{m_e \epsilon_0} \sum_{j=1}^{nc} \left[\frac{n_j (\omega_{res,j}^2 - \omega^2 + i\omega g_{d,j})}{(\omega_{res,j}^2 - \omega^2)^2 + \omega^2 g_{d,j}^2} \right] \quad [1]$$

where ω is the frequency of the incident radiation ($2\pi c/\lambda$), e is the electronic charge, m_e is the effective electron mass, ϵ_0 is the electric permittivity of free space, nc is the number of electron types or oscillators, and n_j , $\omega_{res,j}$ and $g_{d,j}$ are the number density, resonant frequency, and damping frequency of the j th type of electron, respectively. (The lengthier form of the dispersion equations can be simplified to the equation above.)

Stull and Plass (1960) introduced the dispersion equations to model the refractive index of carbon, estimating parameters from the data of Senftleben and Benedict (1918). Boynton et al. (1968) and Dalzell and Sarofim (1969) were among the first to apply the theory to carbon in flames. Subsequent studies provided different measurements and interpretations (Lee and Tien 1981; Ben Hamadi et al. 1987; Habib and Vervisch 1988; Chang and Charalampopoulos 1990). Most commonly, three types of electrons are considered: (1) sp^2 -bonded electrons, (2) π electrons, and (3) free conduction electrons, which have a resonant frequency of zero. Electrons in the σ shell absorb at ultraviolet wavelengths and do not affect visible absorption (Lee and Tien 1981).

The dispersion equations predict the wavelength dependence of the refractive index, as shown in Figure 3 using parameters from two studies. This model predicts a minimum in k at 450 nm.

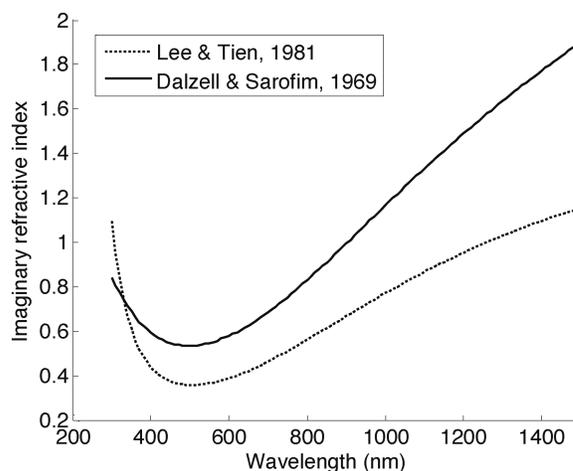


FIG. 3. Imaginary refractive index predicted by the dispersion model with the parameters of Lee and Tien (1981) and Dalzell and Sarofim (1969). The figure differs from that of Lee and Tien because it is evaluated at 300 K instead of flame temperature. See the text (Section 4.2.2, 7.2.2, and 7.6) for caveats on the use of the dispersion model to represent flame generated carbon.

Depending on the parameters chosen, π electrons affect predicted absorption most; the number of free conduction electrons is much lower and they have little effect. Absorption increases and its spectral dependence decreases when the density of π -electrons increases, or when their damping constant decreases.

An advantage of the dispersion model is its plausible physical explanation for how materials interact with light. A disadvantage is a lack of predictive capability. For non-crystalline substances, the dispersion model is considered empirical, not exact (Stagg and Charalampopoulos 1993). Disagreement about values of n , ω_{res} , and g_d for each type of electron results in discrepancies in predicted refractive index (Fletcher et al. 1997), as shown in Figure 3. The parameters are estimated for carbon particles by fitting the model to measurements of extinction or scattering at several wavelengths. Observations are often insufficient to constrain the parameters, and the fitted values do not agree between studies. A second disadvantage is the possible inadequacy of the dispersion equations to represent LAC. Graphite may contain only the three electron types listed above, but LAC has a more complex structure. Finally, the model predicts features that are not observed in atmospheric LAC, such as the 450-nm minimum in k and the large magnitude of n .

4.2.3. Medium-Range Order and the Optical Gap

Band-gap theory was first used by Tauc et al. (1966) to explain the absorption behavior of germanium. Formally, the theory follows from the oscillator theory of interaction between a material and radiation. The optical gap is the energy required for an electron to reach the first excited state: the difference between the highest-energy occupied molecular orbital and the lowest-energy unoccupied molecular orbital. Photons of higher energy may cause electronic transitions; photons with lower energy cannot cause transitions and are not absorbed. The optical-gap concept has been used to explain the electronic behavior of carbon containing many different types of electrons. The theory has been applied to flame-generated carbon (Minutolo et al. 1996), amorphous carbon (McKenzie et al. 1983; Robertson 1991), and emissions from burning of solid fuel (Bond 2001).

The absorption coefficient α follows the relationship

$$\sqrt{\alpha E} = B(E - E_g),$$

where E is the energy of the incident radiation, B is a constant, and E_g is the optical gap. (Here, absorption coefficient is the chemists' definition of $4\pi k/\lambda$, not the atmospheric scientists' definition discussed previously.) In practice, E_g is determined by plotting αE as a function of E and extrapolating to zero absorption. The band-gap model has complications not discussed here; these include disagreements about whether the model is appropriate for amorphous carbon (e.g., Fanchini and Tagliaferro 2001), or the exact form of the tail which deviates from the model's predictions (Theye and Paret 2002).

The structure of amorphous carbon on the scale of several atoms is known as medium-range order (as opposed to order in an entire crystal or on an atomic scale). Both theory and re-

search indicate that electronic properties are controlled by this medium-range order—specifically, the number of sp^2 -bonded rings (Robertson 1991) that are adjacent or clustered together. The optical gap for benzene, with one ring, corresponds to a wavelength of about 200 nm. As adjacent rings are added, the optical gap decreases and photons of lower energy or longer wavelength can be absorbed. For material with many adjacent aromatic rings, the optical gap approaches zero. Platt (1949) explained this shift theoretically by postulating a classical wavefunction directed around the perimeter of adjacent rings. As the perimeter's length increased, the energies of this wavefunction would become more closely spaced. Coulson et al. (1959) also demonstrated this concept with a computational method.

The finding that the extent of sp^2 -islands governs the optical or electronic properties is an important one, and has been confirmed in several clever and detailed experiments (Chhowalla et al. 2000; Chen and Zhao 2000; Choi et al. 2001). Increasing island size decreases the optical gap and increases absorption. The optical gap affects the real part of the refractive index as well (Bouzerar et al. 2001).

The sp^2 -bonded clusters are surrounded by sp^3 -bonded carbon. Unlike optical properties, structural properties of amorphous carbon are controlled by these sp^3 -containing boundaries. Manufacture of amorphous carbon has capitalized on the ability to control optical and physical properties separately by manipulating the molecular form. For example, a decrease in sp^2 bonding and an increase in optical gap can be obtained by adding hydrogen to the formation environment (Jäger et al. 1999).

The transformation between carbon with primarily sp^3 bonds and that with sp^2 bonds is often called *graphitization*, and is promoted by elevated temperatures. This transition has been studied to understand how coal changes when it is heated (e.g., Oberlin 1984) and to transform amorphous carbon (e.g., Sattel et al. 1997). It is also important in determining the optical properties of flame-generated carbon particles.

A variant of graphitization occurs as particles pass through flames, with non-graphitic particles observed low in the flames (Wersborg 1975; Saito et al. 1991; d'Alessio et al. 1992; Dobbins et al. 1994). These particles may appear yellow to brown. *Sooting*, when these tarry precursor particles transform to a more graphitic substance, appears to occur rapidly (van der Wal 1996). The particles become even more like graphite as they remain in the flame longer (Muñoz and Charalampopoulos 1998). The dominant mechanism of soot formation might affect the molecular form of the material, and hence its optical properties. For discussions of soot formation mechanisms, we suggest the standard work of Glassman (1988); reviews by Haynes and Wagner (1981) and Kennedy (1997) on formation kinetics; Smith (1981) on formation in diesel engines, or Lahaye and Ehrburger-Dolle (1994) on carbon black formation.

4.2.4. Final Comments on Structure

The role of sp^2 bonds and cluster size explains why H/C ratio is a reasonable but imperfect predictor of absorption. Hydrogen

is a likely partner for carbon with sp^3 bonds, but sp^2 -bonded carbon has no such partners. LAC, however, is chemically complex, and hydrogen content is not a perfect proxy for the number of non-carbon constituents or sp^2 bonds. Even if the fraction of sp^2 bonds were known, chemical composition is not uniquely correlated with cluster size.

Only processes that affect sp^2 cluster size or other absorbing structures can change the absorptive properties. At atmospheric temperatures, addition to or destruction of these stable clusters proceeds slowly, although changes in optical properties may occur (Gelencser et al. 2003). Cluster size can change at elevated temperatures even if overall chemical composition does not (Chhowalla et al. 2000). The refractive index is most likely to be established or altered in two environments: formation during combustion, and measurement of elemental carbon by thermal analysis techniques.

5. MORPHOLOGY: FROM BULK OPTICS TO ABSORPTION BY PARTICLES

Absorption and scattering cross sections are common measures of particles' interaction with light. While mass absorption cross section, or MAC, is not the only measure of interest, it serves as one convenient proxy for the relationship between radiative transfer and the aerosol mass represented in models. In this section, we discuss the relationship between absorption and scattering cross sections and a particle's chemical composition (represented by refractive index), shape, and size.

Mie theory predicts absorption and scattering by spherical particles (van de Hulst 1957; Kerker 1969; Bohren and Huffman 1983). Other theories have been discussed for non-spherical particles (e.g., Jones 1979; Berry and Percival 1986; Nelson 1989; Mountain and Mulholland 1988; Chen et al. 1991; Dobbins and Megaridis 1991; Köylü and Faeth 1994; Fuller 1994; Mackowski et al. 1994; Farias et al. 1995; Mishchenko et al. 1996; Sorensen 2001; to name just a few). We do not review these theories, except to determine the knowledge of the refractive index, size and shape, and single-particle homogeneity required to model absorption and scattering.

For this section only, we will present results as *volume absorption cross sections*—that is, cross section per particle volume, rather than per particle mass. Density does not enter into calculations of absorption and scattering cross sections, and is determined with unrelated measurements. When normalized to volume instead of mass, absorption cross section depends only on size and refractive index. For volumetric absorption cross section, we adopt the somewhat awkward units of m^2/cm^3 . MAC is easily obtained by dividing by an appropriate density.

5.1. Spherical, Homogeneous Particles

The equations presented by Gustav Mie predict absorption and scattering from the complex refractive index and size of the particles and the wavelength of incident light. The solutions to the electromagnetic equations in spherical coordinates are for-

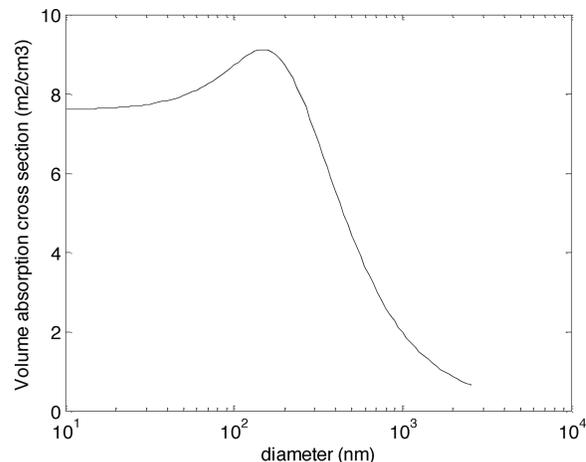


FIG. 4. Volume absorption cross section versus diameter. Refractive index is $1.56-0.47i$ from Dalzell and Sarofim (1969), wavelength is 550 nm. These results are often divided by the particles' material density and presented as mass absorption cross section. (We favor other refractive indices to represent pure LAC; see Section 7.)

mulated in terms of the non-dimensional parameter $x = \pi d/\lambda$, where d is the particle diameter.² They contain series expansions and are usually calculated with computer codes provided by Dave (1970) or Bohren and Huffman (1983, BHMie). A listing of the available codes, including those by Warren Wiscombe, is presently at <http://atol.ucsd.edu/~pflatau/scatlib/scatterlib.htm>

Figure 4 shows the type of calculation results provided in several papers (Bergstrom 1973; Roessler 1982; Horvath 1993a; Martins et al. 1998; Fuller et al. 1999). Cross section is plotted versus particle diameter for one complex refractive index and wavelength; sometimes results for a few different refractive indices are presented. Common features include constant MAC for very small particles (diameters below about 100 nm), uniformly-decreasing MAC for larger particles (diameters above about 300 nm), and a higher peak in between. The small-particle and large-particle behavior can be understood geometrically; if light can penetrate to the center of the particle, the entire particle mass participates in absorption. If it cannot, then only the particle's skin contributes to absorption, and MAC decreases roughly as d^{-1} . The peak between the two has no such geometric interpretation, but follows from the Mie solutions.

For particles small relative to the wavelength, an approximation provides simple equations for the scattering and absorption cross sections (C) per particle volume (v) in units of inverse length (van de Hulst 1957; Kerker 1969; Bohren and Huffman 1983):

$$C_{abs}/v = 6\pi/\lambda \text{Im}[(m^2 - 1)/(m^2 + 2)] \quad [2]$$

$$C_{sca}/v = 4\pi^4 d^3/\lambda^4 |(m^2 - 1)/(m^2 + 2)|^2 \quad [3]$$

²The parameter $k = 2\pi/\lambda$ is also frequently used in these equations. We do not use it in this review in order to avoid confusion with the imaginary refractive index.

atmosphere. The particles collapse from lacy structures to more compact ones when they are wetted (Hallett et al. 1989; Colbeck et al. 1990; Ramachandran and Reist 1995; Nyeki and Colbeck 1995) or after aging (Schnaiter et al. 2003), a change that corresponds to an increase in fractal dimension. Collapse affects both absorption and scattering, and is one explanation for a decrease in absorption with atmospheric lifetime (Liousse et al. 1993).

The primary spherule size, d , also depends on particle generation: it lies between 20–50 nm for many soots (e.g., Köylü and Faeth 1992; Clague et al. 1999; Lee et al. 2002a; Hu and Koylu 2004) but is just a few nanometers for spark-generated soot (Wentzel et al. 2003). Some particle diameters assumed in climate models (e.g., d’Almeida et al. 1991) are similar to those of primary spherules, not entire particles.

The simplest method of predicting absorption and scattering for aggregates is the Rayleigh-Debye-Gans (RDG) theory, which assumes that multiple scattering and interactions between particles are negligible. For an aggregate of N component spherules, the theory can be summarized as follows: (1) Scattering and absorption by aggregates can be represented as functions of scattering and absorption of a single spherule; (2) Aggregate absorption is N times the sum of absorption by a spherule; (3) Aggregate scattering scales approximately as N^2 times the sum of scattering by spherules. Further details can be found elsewhere (Dobbins and Megaridis 1991; Köylü and Faeth 1994; Sorensen 2001); the paper by Sorensen (2001) provides an admirable review of the state of knowledge. RDG theory predicts that particles with $D_f < 2$ (such as freshly-generated combustion soot) absorb about the same as and scatter more than spheres of equivalent mass, particularly when aggregates contain a large number of spherules.

Another method, more accurate but computationally intensive, involves calculating the electromagnetic field considering the spherule interactions, and integrating around the aggregate to determine scattering (e.g., Jones 1979; Fuller 1994, and references therein). By comparing RDG theory with more exact calculations, several authors (Drolen and Tien 1987; Nelson 1989; Fuller 1994; Farias et al. 1995; Mackowski 1995; Farias et al. 1996; Sorensen 2001) suggest that it reasonably approximates scattering and absorption of combustion-generated particles at visible wavelengths. Farias et al. (1996) found that errors in scattering predicted by RDG are lower than 30% for common values of refractive index and size.

Other reports disagree with the finding that RDG estimates absorption well. Mackowski (1995) showed that the RDG simplification could underpredict absorption at infrared wavelengths. Fuller et al. (1995) calculated that the interaction between neighboring spherules could increase absorption by about 30% above the sum-of-spheres approximation for a small, compact group of spherules. Iskander et al. (1991) showed that this increase could range from zero to 50%, depending on the number and size of primary spherules.

Figure 6 shows the ratio between RDG and Mie theory for particles of equivalent solid volume or equivalent mass. (This ra-

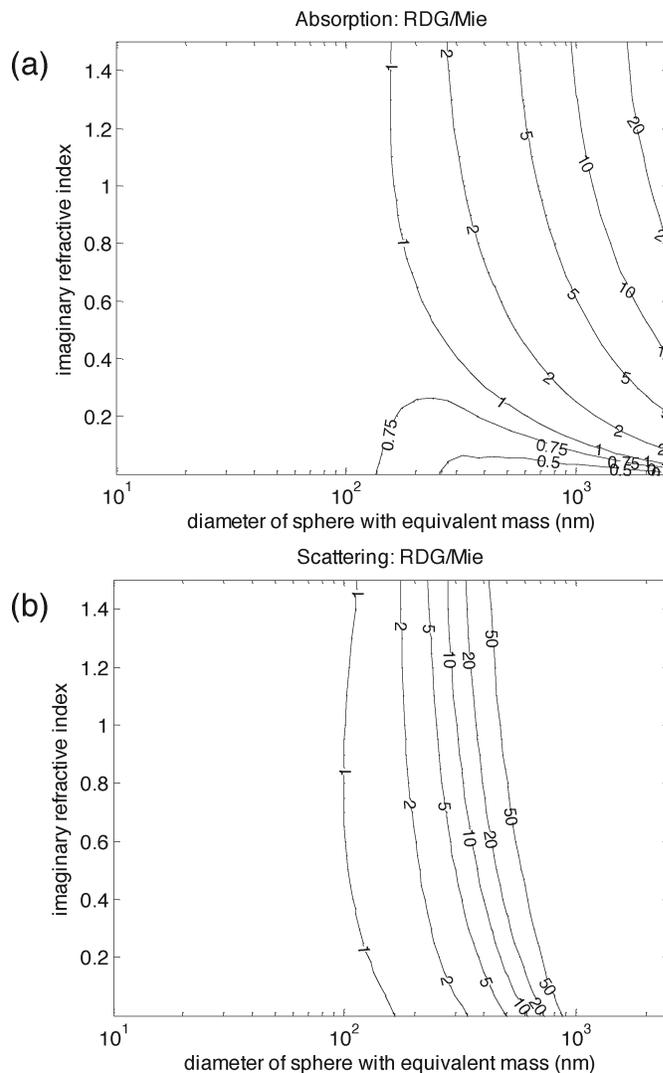


FIG. 6. Ratio between predictions of Rayleigh-Debye-Gans aggregate theory and Mie theory for two particles of equivalent mass. Where no contours appear, ratio is constant. Assumptions: real refractive index 1.55, primary spherule diameter 25 nm, wavelength 550 nm.

tio is useful for relating scattering and absorption cross sections to particle mass, but a different relationship is needed when particle size is measured by mobility methods.) If a particle’s solid volume is lower than that of a 100-nm sphere, then calculations assuming spherical particles give reasonable estimates of scattering and absorption. For larger particles, the spherical-particle assumption can greatly underpredict both absorption and scattering. Because aggregate absorption is the sum of absorption by small particles, the small-particle limit for light absorption applies even to large particles, and the lower MAC observed in Figure 5 for large particles no longer applies. As an aggregate collapses and becomes more like a sphere, the absorption decreases.

The RDG formalism may not be appropriate for collapsed atmospheric particles with $D_f > 2$, but it should be used to interpret

measurements on suspended particles in flames, whence many inferences of refractive index originate. In particular, the wavelength dependence of scattering may be affected by the particles' form.

5.3. Addition of Negligibly Absorbing Material

A particle that absorbs light strongly at the beginning of its atmospheric lifetime may acquire negligibly absorbing compounds when vapors condense on it or when it coagulates with other particles. Absorption is predicted to increase as a result of this mixing (Kattawar and Hood 1976; Ackerman and Toon 1981; Chylek and Hallett 1992; Chylek et al. 1995; Haywood and Ramaswamy 1998; Jacobson 2000). Our investigation of this issue, originally intended for inclusion here, evolved to extend beyond the review nature of this paper and will be provided elsewhere (Bond et al. 2005). Here, we review only the basic ideas and some cautions. The terminology used in this section is defined in Section 3.

Absorption calculated for a particle ensemble depends on how the mixing between strongly-absorbing and negligibly absorbing material is represented (Ackerman and Toon 1981; Chylek and Hallett 1992; Chylek et al. 1995; Haywood and Ramaswamy 1998; Jacobson 2000). For example, Jacobson (2000) calculated that radiative forcing by LAC was lowest in an external mixture (+0.27 W/m²), twice as high in a more realistic shell-and-core model (+0.54 W/m²), and highest in a volume mixture (+0.78 W/m²).

The volume-mixture idealization is one of the most common methods of representing mixing, but it is one of the poorest. Indices of refraction are produced by weighting the real and imaginary parts of each component's refractive index by the volume fraction, and Mie calculations are performed using these calculated refractive indices. This method is presently used in most, but not all, climate models that report forcing by internally-mixed particles (e.g., Haywood and Shine 1995; Haywood and Ramaswamy 1998; Myhre et al. 1998; Chung and Seinfeld 2002). Jacobson (2000) pointed out that the volume-mixture model is physically inconsistent for small absorbing carbon particles, which do not dissolve. Section 4 suggests another inconsistency: distributing absorbing material evenly throughout a particle would disrupt the medium-range order that governs absorption. A more detailed treatment (Bond et al. 2005) suggests that much of the enhanced absorption due to volume mixing is artificial and would not be replicated by real particles.

Other mixing rules have been suggested to provide effective refractive indices of mixed material (Heller 1965; Graham 1974; Bohren and Huffman 1983). The Bruggeman approximation may be best for void-containing soot pellets (Felske et al. 1984), while the Maxwell Garnett approximation might be used for small black particles suspended in water (Lesins et al. 2002).

Although perfect mixing of LAC and negligibly absorbing material within a particle is implausible, heterogeneously-mixed particles are likely. Ackerman and Toon (1981) described a likely situation: absorbing carbonaceous particles, often called cores

or inclusions, surrounded by shells or coatings of negligibly absorbing material. Natural mechanisms that cause coatings include ionic compounds condensing on LAC particles and promoting water uptake (Redemann et al. 2001), and organic compounds with low vapor pressures condensing on these particles. Model results predict that most LAC is mixed with other substances within 5 days of emission (Jacobson 2001). Detailed examinations of ambient particles demonstrate that such mixed particles are common (e.g., Okada 1983; Liou et al. 1993; Pósfai et al. 1999; Naoe and Okada 2001; Heintzenberg et al. 2002; Whiteaker et al. 2002).

Laboratory studies have shown that absorption can be enhanced by 35% when particles are coated (Schnaiter et al. 2003). Very high enhancements require particular conditions, such as a very small inclusion located exactly at the center of a large particle (Fuller 1995; Fuller et al.; 1999). Some enhancement of absorption is likely, but extreme enhancement is unlikely. More specific guidelines regarding absorption enhancement are presented elsewhere (Bond et al. 2005).

5.4. Summary and Cautions

Particle size and not imaginary refractive index primarily determines MAC for spherical LAC particles with diameters greater than about 100–150 nm. Particle size is always important in determining scattering. If large particles behave optically as spheres, then accurate size measurements may be sufficient to represent their scattering and absorption. For smaller spherical particles, and for aggregates of such smaller particles, both real and imaginary parts of the refractive index must be known.

For aggregates, the particle size and fractal dimension D_f govern whether particle diameter or refractive index dominates absorption. However, the quantities of large (>150 nm), spherical LAC particles in the atmosphere are not usually measured. Exceptions include size-resolved measurements of elemental carbon (Kleeman et al. 1999; Dillner et al. 2001) and density measurements that may indicate the number of fluffy particles (McMurry et al. 2002).

Finally, we suggest caution in using the concept of the effective refractive index for atmospheric aerosol. The effective refractive index is a value that causes a particular theory to agree with measured scattering, absorption, or other observations. Many combinations of morphology and refractive index can lead to the same MAC, as noted over 20 years ago (Ackerman and Toon 1981). Scattering and absorption are affected by mass fraction of LAC, particle size or fractal dimension, and coating. Any of these may change while the particles reside in the atmosphere, resulting in different effective values at different locations. Mixing models (Mallet et al. 2004), or black carbon fractions (Fiebig et al. 2002) that agree with optical properties of the aerosol at one location may not be valid at other locations, and the resulting predictions of scattering and absorption may be in error. Investigators in astrophysics, attempting the inverse task of identifying interstellar matter from its extinction, have concluded that the range of possible solutions precludes

identifying the form or content of the material (Michel et al. 1999). Fortunately, atmospheric researchers have the option of capturing the material and measuring its properties with other methods.

6. TOOLBOX: MEASUREMENT METHODS

Instruments used to measure light absorption by particles in the atmosphere are discussed elsewhere (Bohren and Huffman 1983; Horvath 1993a; Heintzenberg et al. 1997). These descriptions are not repeated here. We limit our discussion to two topics: first, developments that occurred after earlier reviews, and second, assumptions in each measurement method that affect interpretation of the results.

For atmospheric aerosol, light absorption is a small fraction of the total extinction. Measuring absorption has proven more difficult than measuring scattering, because unlike scattered light the absorbed photons have disappeared and cannot be sensed. We separate the discussion of measurements into those that are *direct* and those that are *remote*. The meaning of these terms varies among scientific fields. We define direct methods as those that measure changes in transmission or temperature due to absorption, and remote methods as those that measure backscattering or forward scattering and use theories to infer the aerosol properties.

No method of measuring absorption is specific to LAC particles. In contrast to gas measurements, which can select a particular absorption feature or line unique to a particular gas,³ these measurements are sensitive to any particle that absorbs. Many measurements are made at a single wavelength, frequently 550 nm, while others cover just a few wavelengths. Extrapolation beyond the measured wavelengths requires assumptions about the refractive index and particle nature. Instruments are developing to cover a wider range of wavelengths.

It is also important to remember that absorption is not a proxy for light-absorbing carbon mass. Many investigators assume a constant ratio between absorption and LAC mass. That practice is only valid when the particles to be measured always have the same absorptive properties as the particles originally used to determine the ratio. The present review, and the field studies summarized in Section 8, suggest that the mass absorption cross section is not constant.

6.1. Direct Measurement Methods

Direct measurement methods can measure either radiation transmitted through a layer of particles, or the change in temperature caused by absorption. Table 2 summarizes the most common direct techniques, including filter-based measurement

³Aerosol absorption can even affect gas measurements. In fact, the TOMS technique discussed below was developed because aerosol absorption interfered with ozone measurements. The aerosol from the eruption of Pinatubo was detected because it interfered with stratospheric gas measurements.

TABLE 2
Direct methods of measuring absorption by particles

Method	References
Particles collected on filter	
Most operate on similar principle	
Integrating plate	Lin et al. 1973; Horvath 1997
Integrating sandwich	Clarke et al. 1987
Laser transmission	Rosen and Novakov 1983; Gundel et al. 1984
Aethalometer	Hansen et al. 1984; Weingartner et al. 2003
Particle soot absorption photometer (PSAP)	Weiss and Waggoner 1984; Bond et al. 1999
Multi-angle absorption photometry (MAAP)	Petzold et al. 2005
Integrating sphere	Fischer 1970; Heintzenberg and Meszaros 1985; Hitzenberger 1996
Particles suspended in air	
Photoacoustic	Terhune and Anderson 1977; Japar and Killinger 1979; Foot 1979; Roessler and Faxvog 1979; Arnott et al. 1997
Difference (extinction minus scattering)	Lewis and Dzubay 1986; Horvath 1993b
Flux divergence	Pilewskie et al. 2003

methods that are equivalent in principle but yield somewhat different responses to absorption.

6.1.1. Filter-Based Measurements

The integrating plate, sphere, and sandwich as well as the laser transmission method are laboratory instruments that determine absorption by aerosols collected on filters. The term *integrating* refers to the fact that these methods collect or integrate the scattered light, so that absorption alone should reduce transmitted light. The aethalometer and particle soot absorption photometer continuously measure absorption using the same principle as the integrating plate; because of their rapid time response, they have been used at ground sites or on aircraft. Some models measure at multiple wavelengths (seven for the aethalometer, three for the particle soot absorption photometer).

Except for carefully designed integrating spheres, most of these techniques suffer from errors, because aerosol scattering does affect transmitted light despite the instrumental design (Hitzenberger 1993; Horvath 1993b; Petzold et al. 1997; Bond et al. 1999). Also, absorption by particles collected on a filter is increased above that of the same particles in suspension,

TABLE 3
Correction factors for absorbing particles collected on filter

Filter type	Absorption correction	Scattering correction	Particle orientation	Notes/Citation
Zefluor	2.43 ± 0.13	—	Toward detector	No loading correction apparent. Szkarlát and Japar 1981
Zefluor	1.3 ± 0.14	—	Toward lamp	Szkarlát and Japar 1981
Pallflex E70-2075W (PSAP)	2.2 ± 0.2^a	0.04 ± 0.04	Toward detector	Value given is for lightly loaded filter; loading correction is supplied by manufacturer. Bond et al. 1999
Nuclepore (Integrating Plate)	1.23 ± 0.13	0.09 ± 0.02	Toward detector	No filter orientation effect observed. ^b No loading correction determined. Bond et al. 1999
Quartz 2500 Q20F (Aethalometer AE-30)	2.14 ± 0.6	0.007 ± 0.004	Toward lamp	Averaged data for 450 and 660 nm; higher correction for coated aerosol. Weingartner et al. 2003
Quartz and Millipore (Laser transmission)	3.5	—	Toward detector	Combined Sadler et al. 1981 comparison of laser transmission and IP with Bond et al. 1999 calibration of IP

^aIncorporates both manufacturer's correction and additional calibration.

^bUnpublished data taken during calibration study described in Bond et al. 1999.

because multiple scattering by the filter allows more than one chance for a photon to be absorbed. The enhancement depends on the filter type because of differences in filter scattering and particle embedding (Bond *et al.* 1999; Arnott *et al.* 2005). Table 3 summarizes some of these enhancement factors for different filters.

Finally, a new development measures both reflectance at multiple angles and transmittance for particles on a filter. The technique, known as multi-angle absorption photometry, may correct for some of the artifacts associated with other filter-based measurements (Petzold *et al.* 2005).

6.1.2. Flux Divergence

Transmitted and scattered radiation can also be measured for an aerosol layer in the atmosphere. A layer's absorption is determined by measuring the net solar flux above and below a layer (Pilewskie *et al.* 2003). The method is actually quite old, dating to the 1940s. Both broad-band (Bush and Valero 2002) and discrete-band (Hignett *et al.* 1999; Pilewskie *et al.* 2003; Wendling *et al.* 2002) instruments have been used. Total absorption can be obtained by measurements alone, but calculation of the atmospheric absorption coefficient, or absorption per atmospheric volume, requires a radiative transfer model (Bergstrom *et al.* 2003). This method requires clear skies, aerosol layers that

are stable with respect to time and space, large aerosol depths, and an underlying surface of uniform albedo (Pilewskie *et al.* 2003).

6.3.1. Photoacoustic and Calorimetry

Two instruments measure a change in temperature resulting from absorption of light and redistribution of energy. These are the photoacoustic method (Terhune and Anderson 1977; Foot 1979; Adams *et al.* 1988; Arnott *et al.* 1997) and the calorimeter (Hänel and Hildebrandt 1989). The photoacoustic technique reacts to the amount of light actually absorbed, but relies on converting that absorption to a change in pressure.

In the past, these instruments have not been used widely, in part because they are more complex than filter-based measurements (Moosmuller *et al.* 1998), and in part because of their high detection limits. Recent advances have allowed these instruments to measure absorption at atmospheric concentrations, and they are presently very promising because they disturb the aerosol less than filter-based measurements. These instruments also respond to gaseous absorption; in fact, the ability to calibrate with absorbing gases is one of their advantages.

6.1.4. Difference (Extinction Minus Scattering)

Subtracting scattering from total extinction (e.g., Lewis and Dzuby 1986) to obtain absorption has a long history as well.

Compared to other techniques, such as filter-based collection and photoacoustic, this method requires the least perturbation of the aerosol, and thus has been used as a reference method in calibration (Horvath 1993b; Bond et al. 1999; Sheridan et al. 2005). However, the method uses a small difference of two large numbers; even corrections for angular truncation required to adjust scattering measurements by nephelometers (Anderson and Ogren 1998) might be of the same magnitude as the absorption. Further, at atmospheric concentrations, a long extinction path is required to obtain sufficient sensitivity, and the sample volume needed is much greater than that needed for scattering measurements. Thus, extinction and scattering may be measured on air volumes containing different aerosol.

The cavity-ring-down instrument has recently been applied to extinction by atmospheric aerosol (Strawa et al. 2002). This instrument uses a pulsed laser beam that travels a number of times between two mirrors on both sides of a sensing volume. The path length can be made large enough to accurately determine extinction, and scattering is determined simultaneously. This instrument eliminates some of the sensitivity issues of the difference method, and can be mounted in an airplane.

6.1.5. Instrument Comparisons

Measurement techniques have been assessed by comparing the instruments' response to the same aerosol. The first study took place over 20 years ago (Gerber and Hindmann 1982), and there has been a series of comparisons since that time (Edwards et al. 1983; Clarke et al. 1987; Foot and Kilby 1988; Hansen and McMurry 1990; Campbell et al. 1995; Bond et al. 1999; Hitzenberger et al. 1999; Weingartner et al. 2003; Sheridan et al. 2005.) Other evaluations have occurred in connection with specific field programs (e.g., Reid et al. 1998; Lavanchy et al. 1999). The studies generally show some degree of scatter between the methods, never demonstrating perfect correlation. Each method has advantages, and the question of which measurement should be considered the reference invariably arises.

6.2. Remote Measurements

Remote measurements infer absorption from scattered atmospheric radiation⁴, and both space and surface observations have been used for this purpose (Kaufman et al. 2001; Kaufman et al. 2002a). Satellite instruments measure reflection from the atmosphere and surface, while transmitted and downward-scattered radiation are measured at surface sites. Neither measurement can determine the MAC or refractive index of light-absorbing particles without additional measurements of chemical composition.

Remote methods invert the equation of radiative transfer to determine aerosol optical depth and, sometimes, aerosol size;

they are known as *inversion techniques* for that reason. The procedure cannot retrieve a full description of the aerosol, including quantity, size distribution and refractive index. Instead, the assumption is made that a fixed set of properties is associated with each type of aerosol, such as urban pollution or desert dust. This assumed description is termed an *aerosol model*, and is implicit even when the inversion accounts for mixed or regionally specific aerosol types. Inversion accuracy is limited by variation in aerosol properties; a constant set of aerosol properties cannot represent any location.

As long as the aerosol model defines the complex refractive index, the technique does not measure absorption, but identifies a hypothetical aerosol consistent with the measured radiance. The earliest aerosol models used in satellite retrievals assumed spherical particles with no absorption (Gordon et al. 1983; Gordon et al. 1997). Other models assigned distinct properties to aerosol with different origins (Shettle and Fenn 1976). Current inversions of satellite data use an approach in which results of radiative transfer calculations with specific aerosol models are performed for various optical depths, solar angles and satellite observing angles, and saved in a look-up table. The table is then used to infer the aerosol present by obtaining the best fit of the observed satellite radiances to combinations of values in the table (Kaufman and Tanré 1998).

6.2.1. Satellite Measurements

Early satellite instruments measured radiance at only one wavelength band, and thus retrieved only one unknown variable: optical depth (Husar et al. 1997). More recently, multi-wavelength satellite measurements have identified the location and amount of absorbing particles using a method known as the TOMS technique (Gordon et al. 1997; Torres et al. 1998). TOMS (Total Ozone Mapping Spectrometer) was designed to measure ozone at ultraviolet wavelengths, but a feature that could not be explained by ozone absorption was found to indicate the presence of absorbing aerosols. Several research groups have applied the TOMS technique to data from other satellites to identify the location of absorbing particles. Quantifying the amount of aerosol absorption by this technique has proven difficult (Quijano et al. 2000; Mahowald and Dufresne 2004), and its accuracy has not been established (Torres et al. 2005).

The wavelength dependence of the optical depth can assist in determining whether the aerosol is composed of absorbing small particles (assumed to contain LAC), absorbing large particles (assumed to contain dust), negligibly absorbing small particles (sulfates) and negligibly absorbing large particles (sea salt) (Higurashi and Nakijima 2002; Hsu et al. 2004). Recently, Hsu et al. (2004) combined the TOMS technique with detailed information about surface reflectance and were able to infer different absorptive properties for dust from different deserts. Similar studies may examine sources of LAC in the near future. Other techniques envisioned to measure absorption directly have been proposed (Kaufman et al. 2002b) but are not yet realized.

⁴We refer to measurements in the solar spectrum. LAC does not dominate absorption at infrared wavelengths, although other particles do contribute to it.

6.2.2. Surface-Based Measurements

The most extensive remote surface measurements come from the AERONET network (e.g., Holben et al. 2000). Directly-transmitted beam and skylight radiance at specific wavelengths are used to estimate the optical depth and single-scattering albedo. Again, the technique involves a suite of aerosol models combined with radiative-transfer calculations. While comparison with other measurements is difficult because the single-scattering albedo is derived for the entire atmospheric layer, the results have been shown to be consistent with likely spectrally dependent properties of LAC and dust (Dubovik et al. 2002). There are hundreds of operating sites around the world (see the AERONET web site <http://aeronet.gsfc.nasa.gov/> for details).

7. MEASURED OPTICAL PROPERTIES OF FLAME-GENERATED CARBON

In this section, we discuss the measurements that have provided the optical properties and inferred refractive indices of flame-generated carbon. This section most directly addresses the tasks outlined in the introduction, although the material presented in earlier sections was required in order to conduct the following discussion. We tabulate LAC refractive indices and absorption cross sections, seeking explanations for variations in these properties. Our goal is to determine the appropriate optical properties for atmospheric LAC.

7.1. Structure and Morphology of Absorbing Materials

To the best of current knowledge, strongly absorbing carbon particles in the atmosphere are produced exclusively by combustion of carbon-based fuels. Major sources include diesel engines, accidental and intentional burning of biomass, and coal combustion in industrial and domestic applications (Bond et al. 2004). Ideally, optical properties used for atmospheric LAC would be determined from particles emitted from these types of burning. In fact, refractive indices have been derived from measurements of coal, graphite, carbon black, and particulate carbon from spark discharge and laboratory flames. Which of these materials are most like atmospheric LAC? We should choose their optical properties for use in climate models.

Indicators that can suggest whether two materials are similar include elemental content, molecular structure, size, and shape. As discussed in Section 3, elemental content does not uniquely indicate the medium-range order that governs absorption. However, differences in elemental content might suggest that molecular structures, and hence absorptive properties, are *not* the same.

7.1.1. Carbon Black and Other Controlled Flame Generation

Nearly three decades of research on the microstructure of carbon black (neatly reviewed by Heckman 1964) resulted in enough confidence in its form that it was selected as a standard for electron microscopy (Heidenreich et al. 1968). The form is an onion-like structure with an outside armor of layered graphitic

platelets and an inner core of amorphous material. The platelet layers are not parallel as they are in graphite, but disordered and wrinkled, a condition termed *turbostratic* (Biscoe and Warren 1942).

Both carbon black and LAC are formed when carbon-containing fuels decompose at high temperatures, and both are aggregates. For that reason, carbon black is probably similar to LAC, although material vaguely called “soot” may also contain both negligibly-absorbing carbon and ash (Watson and Valberg 2001). There is a wide variety of carbon black formation processes (Marsh et al. 1971), used to manufacture material with specific physical and optical properties (Donoian and Medalia 1967; Medalia and Heckman 1969). Investigators who use carbon black as a surrogate for LAC would do well to identify the type examined. However, Palotás et al. (1996b) reported that at least one type of carbon black is structurally similar to diesel soot. Medalia and Richards (1972) found that particle size could account for most of the variability in absorption.

The nature of a carbon particle depends on the pathway it has followed through the flame region and the exhaust. For example, temperatures as low as 500°C can affect the structure of partially aromatized amorphous carbon (Jäger et al. 1998; Celzard et al. 2000; Chhowalla et al. 2000). Higher temperatures affect both structural and optical properties. These changes may be kinetically limited, and the final molecular form depends not only on maximum temperature but also on the residence time at each temperature.

Quenching, or cooling from flame temperature, stops the reactions that affect composition and optical properties. LAC from common combustion is quenched more slowly than carbon black (Clague et al. 1999). Spark-discharge soot is quenched even more rapidly than carbon black; it is disordered (Wentzel et al. 2003) and differs from diesel soot (Kirchner et al. 2003), probably because ordered graphitic layers did not have time to form. More orderly carbon black (Palotás et al. 1996a) or diesel soot (Ishiguro et al. 1991) results from either oxidation or elevated temperatures (Smith 1984; Buseck et al. 1987; Jäger et al. 1998).

Other reactive compounds may be incorporated into the particles. Even different lubricating oils may affect the structure of LAC in a diesel engine (Donnet et al. 1997). Inorganic materials may be present as well (Watson and Valberg 2001; Lee et al. 2002b). The impurities may adsorb to the particle surface, possibly affecting the refractive index (Chang and Charalampopoulos 1990). They may also be incorporated in the molecular structure of LAC itself (Akhter et al. 1985a, 1985b; Jäger et al. 1999). Commercial carbon blacks are formed in controlled environments, and contain less hydrogen and oxygen than soot from oil furnaces (Medalia and Rivin 1982) or diesel soot (Clague et al. 1999). However, Clague et al. (1999) found little difference between diesel soot and carbon black using several advanced techniques.

Because many aspects of the formation environment affect material properties, carbon black and flame-generated particles should be most like atmospheric LAC when the formation

conditions are similar to those in widely practiced combustion. Much of the literature on optical properties of soot (e.g., Dalzell and Sarofim 1969; Lee and Tien 1981; Chang and Charalampopoulos 1990; Köylü and Faeth 1994; Wu et al. 1997; Mulholland and Choi 1998) has examined particles formed in flames with simple structures, such as diffusion flames. The fuels used are more pure, and the combustion is more controlled, than those in widespread sources such as diesel engines and burning of solid-fuels. Carbon black and laboratory soot may differ from LAC formed in a less pure environment with a different time-temperature history.

Both combustion soot and carbon black might contain material that would not be classified as LAC. Refractive indices of this mixed material would be lower than those of pure LAC. However, reported hydrogen contents are usually low, suggesting a high LAC content (Dalzell and Sarofim 1969; Wu et al. 1997). At least one type of carbon black is nearly 100% elemental carbon, as measured by thermal-optical methods (Schauer et al. 2003). Some of the soot and carbon black measured in studies of optical properties is probably similar to pure, flame-generated LAC. However, these substances may differ from the impure, less-carefully generated LAC in the atmosphere.

7.1.2. Amorphous Carbon

As discussed previously, amorphous carbon covers a wide range of materials, with varying optical gaps controlled by sp^2 -cluster size (e.g., Smith 1984; Robertson 1991). The formation of this material is tightly controlled, and it is created in thin films rather than in aggregates of particles. Research on amorphous carbon helps to understand flame-generated carbonaceous material, but it is not like atmospheric LAC.

7.1.3. Graphite and Coal

Coal contains a high fraction of sp^3 bonds as well as nitrogen and oxygen bridges between carbon atoms (e.g., Smith et al. 1993). Like amorphous carbon films that become progressively graphitized as temperature rises, coals exhibit a continuum. If they have been exposed to higher temperatures and pressures, they have more graphitic bonds. These coals also have higher heating values, and are called "high-rank" in coal-science terms. Some optical properties depend linearly on H/C ratio (Ergun and McCartney 1960) or aromatic fraction (White et al. 1987). Graphite and coal are both planar; graphite, containing exclusively sp^2 bonds, lies at the most aromatized end of the coal continuum.

The electronic properties of particles emitted from diesel soot, which comprises a large fraction of atmospheric LAC, may lie along the continuum between high-rank coal and graphite. Jiang et al. (2002) reported that the conductivity of diesel soot was greater than that of high-rank coal, and that ^{13}C -NMR results positioned it between coal and graphite.

There are at least two differences between graphite and carbon black. First, the interplanar distance in graphite is smaller than that in carbon black, a difference that disappears with in-

creasing temperature (Franklin 1951). Second, the platelets surrounding a particle have finite extent, and their optical properties may differ from those of planes with nearly infinite extent. Heckman (1964) summarized literature indicating that these platelets become more like graphite, as particles increased in size. Such a change would affect optical properties, as discussed in Section 4. In support of this hypothesis, the much smaller spherules formed by spark-discharge appear less absorbing than diesel-generated particles (Schnaiter et al. 2003).

Examining graphite and coal may be instructive in terms of understanding the optical properties of light-absorbing carbon. However, these materials differ too greatly even from carbon black to be taken as representative of atmospheric LAC. The difference appears in molecular structure, electronic properties, and form.

7.2. Inferred Refractive Indices

We now revisit the literature on inferred refractive indices, with the aim of determining which are most representative of atmospheric LAC. We emphasize that refractive indices are *always* inferred by assuming a theory and applying it to optical measurements. Table 4 tabulates inferred values of refractive index, showing a bewildering range. For comparability, the real part n appears to vary from that of water to that of diamond; the imaginary part k varies from that of negligibly absorbing material to that of graphite.

Although previous reviews on atmospheric aerosol have reported a wide range of refractive indices available for LAC, most of these tabulated values are traceable to only a few original studies. Table 4 contains *all* the primary references incorporated into other frequently cited tabulations (Twitty and Weinman 1971; Medalia and Richards 1972; Dobbins and Megaridis 1991; Horvath 1993a; Fuller et al. 1999), as well as the secondary references cited by these authors. Table 4 also contains some values, mostly from combustion-oriented journals, that are not frequently cited in atmospheric literature.

Inferences that appear to generate new refractive index values are separated in Table 4. For example, Medalia and Richards (1972) extrapolated data given by Ergun and McCartney (1960) to a different H/C ratio, and Horvath (1993a) postulated data for particles containing 50% and 75% air based on measurements given by Janzen (1979), but these values do not constitute new information. We have deliberately excluded values inferred from mass cross sections of absorption and scattering (e.g., Schnaiter et al. 2003) because we use those values later in a closure comparison. We have eliminated inferences (e.g., Vaglieco et al. 1990; Köylü and Faeth 1994) that rely on values drawn from earlier publications (Lee and Tien 1981; Dalzell and Sarofim 1969, respectively).

Before discussing the data in the table, we will review some cautions on the two most common methods of measuring optical properties of LAC. While many other methods can measure optical properties (e.g., Palik 1991), the two we discuss are the most

TABLE 4
Published values of LAC refractive index

Reference	Cited by	Real (n)	Imag. (k)	Material
Measurements				
Coal				
McCartney et al. 1965	TW	1.7–2.0	0.25–0.5	Coal of various ranks
Gilbert 1962		1.8–2.05	0–0.8	Coal from specific mines
Carbon particles				
1 Batten 1985	H	1.20–1.35	0.1–0.22	Kerosene soot
2 Chang and Charalampopoulos 1990		1.77	0.63	Premixed propane-oxygen, $\phi = 1.8$
3 Chippett and Gray 1978		1.9	0.35	Smoke generator
4 Dalzell and Sarofim 1969	H	1.56	0.47	Average of coal and propane soots
5 Erickson et al. 1964		1.4	1.0	Benzene-air flame
6 Habib and Vervisch 1988		1.3	0.3	Premixed flames, various fuels
7 Janzen 1979	FMK	2.0	1.0	Carbon black
8 Lee and Tien 1981	CHH	1.95	0.48	Polystyrene and plexiglas flames
9 Mullins and Williams 1987		1.88–1.93	0.39–0.45	Toluene, propane, n-heptane
10 Marley et al. 2001		1.87	0.56	Soot from candle flame
11 Marley et al. 2001		1.68	0.56	Diesel soot
12 Pluchino et al. 1980	H, CHH	1.7–1.8	0.6–0.8	Carbon black, single particle
13 Powell and Zinn 1983	CHH	1.108	0.075	Flaming polymeric materials
14 Senftleben and Benedict 1918	TW	1.9	0.65	Arc-lamp soot
15 Stagg and Charalampopoulos 1993		1.52	0.36	Propane flame
16 Wu et al. 1997		1.58	0.51	Turbulent diffusion flames
Graphite				
Egan 1982	CHH	1.67–2.05	0.01–0.7	1st Intercomparison work
Taft and Phillip 1965		2.58	1.44	Graphite (normal incidence)
Tsu et al. 1978	CHH	2.05–2.75	0.66–1.46	3 grades of graphite
17 Greenaway et al. 1969	MR	2.72/1.46	1.34/0.0	Graphite (normal/parallel incidence)
Stagg and Charalampopoulos 1993		2.65	1.39	Pyrolytic graphite
Derived Values				
Original source	Cited by	Real (n)	Imag. (k)	Notes
Dalzell and Sarofim 1969	MR	1.84	0.46	Adjusted for void fraction
Janzen 1979	H, FMK	1.25	0.25	Hypothesized for 75% air, 25% soot
Janzen 1979	H, FMK	1.5	0.5	Hypothesized for 50% air, 50% soot
Ergun and McCartney 1960 ^a	MR	2.02	0.56	Interpolated to H/C ratio of carbon black
Secondary References				
Citing reference	Cited by	Real (n)	Imag. (k)	Original source
Ackermann and Toon 1981	H	1.94	0.66	Senftleben and Benedict 1918
Bergstrom 1972	FMK, CHH	1.95	0.66	Senftleben and Benedict 1918
Bergstrom 1973	H	2.0	0.66	Senftleben and Benedict 1918
Twitty and Weinman 1971	FMK	1.80	0.8	See this tabulation
Hess and Herd 1993	FMK	2.0	1.0	Janzen 1979
Hänel 1987	H	1.9	1.0	Value not found in Hänel paper
Janzen 1979	CHH	1.4–2.35	0.46–1.42	Values not found in this paper
Jaenicke 1988	H, CHH	1.75	0.44	Twitty and Weinman
Kattawar and Heard 1976	H	1.95	0.66	Senftleben and Benedict 1918
Ouimette and Flagan 1982	H	1.56	0.47	Dalzell and Sarofim 1969
Roessler and Faxvog 1980	H	1.96	0.66	Senftleben and Benedict 1918
Roessler and Faxvog 1980	CHH	1.75	0.5	Value not found in cited paper
Roessler and Faxvog 1980	H	2.0	0.66	Value not found in cited paper
Shettle and Fenn 1979	H	1.76	0.45	Average of Twitty and Weinman 1971
“various textbooks”	H	2.0	1.0	Probably from Janzen 1979

^aPaper assumed to contain data from conference proceedings paper by Horvath (1993) citation.

common for highly-absorbing material that cannot be deposited from the gas phase.

7.2.1. Cautions: Measuring Optical Properties of Compressed Solids

Optical properties of a bulk solid may be determined from reflectance at different angles or from ellipsometry, using the phase difference between the incident and reflected light. Accurate determination of the refractive index requires a specular⁵ surface, and for that reason coal is polished before measurement. Flame-generated carbon is compressed into pellets to obtain such a surface. This procedure leads to two major uncertainties in the inferred refractive indices.

First, the refractive index that should be used in Mie or RDG theory is that of void-free LAC. Felske et al. (1984) reported that pellets contain about 18% void, even after they were compressed at 280 MPa. They emphasized that the void fraction affecting optical measurements is near the pellet's surface. They pointed out that the Bruggeman approximation is more appropriate for compressed soot pellets than Maxwell Garnett approximation, but they also found that the inferred refractive index did not depend greatly on the chosen mixing rule.

The second problem is less tractable. Voids in the surface of a compressed solid are about as large as the wavelength of visible light. The surface is specular for infrared light but not for visible light (Janzen 1979; Felske et al. 1984). Stagg and Charalampopoulos (1991) found that inverting polarization measurements can correct for this problem, but that both real and refractive indices can be underestimated without correction. Mullins and Williams (1987) also estimated that accounting for surface roughness would increase the inferred value of k .

In summary, refractive indices inferred from reflectance should be considered suspect at visible wavelengths unless great care is taken. Both real and imaginary parts appear to be *biased low* if not corrected for void fraction or surface roughness.

7.2.2. Cautions: Measuring Optical Properties of Suspended Particles

Scattering and absorption by suspended particles has also been used to infer the refractive index. Studies have measured extinction alone or angular scattering of polarized light (e.g., Dobbins et al. 1983). The particles may be suspended within a flame (e.g., Chippett and Gray 1978), above a flame (Köylü and Faeth 1994), or in a medium after collection (Janzen 1979; Mullins and Williams 1987). The refractive index is inferred by obtaining a best fit to either Mie or RDG theory. Particle size distributions affect this determination and are usually estimated from microscopy (e.g., Chang and Charalampopoulos 1990) or changes in transmitted light with wavelength (e.g., Lee and Tien

1981). Charalampopoulos and Shu (2002) showed that ignoring polydispersity of the primary spherules could lead to slight underestimates and overestimates of the real and imaginary refractive indices, respectively.

As discussed in Section 5, the scattering behavior of aggregates differs from that of spheres, and inferences based on assuming spherical particles may be incorrect. If the particles are actually agglomerates, the effective refractive index obtained from scattering measurements is probably that of a void-containing particle (Dobbins et al. 1983). Particles early in the flame are thought to consist of polyaromatic hydrocarbons (Wersborg 1975; Vaglieco et al. 1990; Minutolo et al. 1994), and the assumption of spherical particles may be justified. These young particles differ from the chain agglomerates that leave the flame. They may form part of the atmospheric aerosol, but their optical properties are not like those of the material currently classified as LAC.

Figure 5 shows that absorption cross section alone is insufficient to constrain refractive index. The same is true of extinction cross section; for example, 75-nm particles in air with $m = 1.5 - 0.6i$ and $m = 1.86 - 0.75i$ have similar cross sections. Obtaining enough data to fit theory to measurements requires either multiple wavelengths or multiple angles. One must be particularly cautious when inferences have assumed spherical particles. Mie theory represents neither the angular nor the spectral dependence of scattering by aggregates.

Inverting multi-wavelength measurements requires further constraints on the spectral dependence of the refractive index. Assumed relationships have included a constant refractive index (Janzen 1979; Chippett and Gray 1978), dispersion equations (Lee and Tien 1981; Habib and Vervisch 1988; discussed in Chapter 3), or Kramers-Kronig relations (Chang and Charalampopoulos 1990). The Kramers-Kronig relations are exact, but measurements over a wavelength range broad enough to support the calculation are frequently not made. Results constrained by the dispersion equations should be interpreted with caution for refractive indices at visible wavelengths. Data points at infrared wavelengths may strongly influence the fitted parameters, while a minimum in k at visible wavelengths is predetermined by the electron resonant frequencies, which are not treated as adjustable. Boynton et al. (1968) reported difficulty matching dispersion theory to measured data across the entire visible and infrared range. Adjustments to dispersion constants proposed by Habib and Vervisch (1988) are also based on infrared data.

7.2.3. Analysis of Refractive Indices

We now return to Table 4 with the intent of constraining values to use for atmospheric LAC. We examine the variation further by plotting the real part n against the imaginary part k in Figure 7. In the following discussion, the year associated with each reference will be followed by the number used to mark the relevant point in Figure 7. The refractive indices of graphite are unlike those of the other materials, and we use only one point to represent the two values in Table 4.

⁵“Specular” means that the parallel component of the reflectivity equals the square of the perpendicular component of the reflectivity for light incident at 45°. When this condition is violated, the material does not obey Fresnel theory used to infer the refractive index.

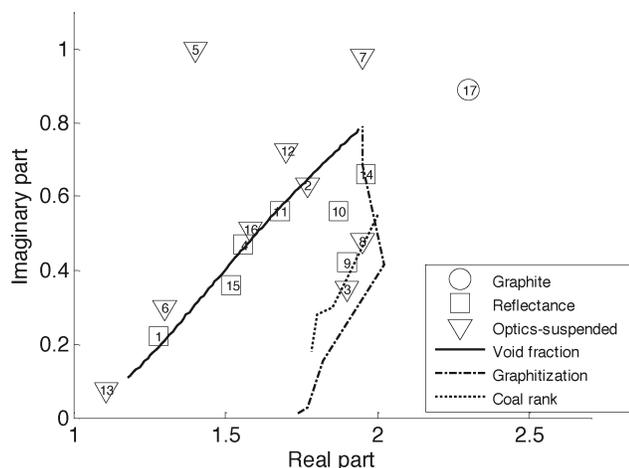


FIG. 7. Refractive indices from Table 4. Numbers on each data point refer to reference numbers in the table. Curve marked “void fraction” assumes that LAC has a single refractive index and that variation can be expressed by the Bruggeman effective-medium theory. Curve marked “graphitization” shows variation in refractive index of carbon containing different sp^2 -bond content. See text in Section 7.2.3 for further explanation.

We now hypothesize that strongly absorbing carbon with a single refractive index exists, and that some of the variation in reported refractive indices results from void fractions in the material. If our hypothesis is correct, n and k should vary together. Void fractions affect both compressed solids (Graham 1974; Felske et al. 1984) and suspended particles (Dobbins et al. 1983) that are erroneously assumed to be spherical. We assume that the voids are air ($n = 1.0$, $k = 0.0$), and that the refractive index of LAC with little to no void is $1.95 - 0.79i$. This refractive index corresponds to the properties of amorphous carbon heated to 750°C ; at this temperature, the band gap has decreased to zero (Smith et al. 1984). We chose this value instead of the refractive index of graphite, in which plane layers are more closely spaced. We solve the Bruggeman relationship at different void fractions to obtain the effective refractive index of LAC mixed with voids. The calculated relationship between n and k is marked “void fraction,” and corresponds to most of the data.

We do not assert that $1.95 - 0.79i$ is the refractive index of void-free carbon at 550 nm . It could represent carbon with voids, since it is very difficult to obtain void-free material. Alternatively, these values of n and k could both be too high; Figure 7 shows that most of the inferred refractive indices are lower. The value $1.95 - 0.79i$ merely provides agreement with many of the measurements. Other values that lie along the upper portion of the line could also be consistent with these measurements and are listed in Table 5. We consider this the likely range of refractive indices for LAC.

According to the discussion in Section 4, increasing sp^2 cluster size also affects the imaginary refractive index strongly and the real refractive index slightly. Characteristics of this process are a rapid, steady increase in k , and a slight increase in n . As mentioned previously, some studies of in-flame soot measure

TABLE 5
Refractive indices that lie along the upper void-fraction line in Figure 7, for $550\ \mu\text{m}$

n	k
1.75	0.63
1.80	0.67
1.85	0.71
1.90	0.75
1.95	0.79

particles before they aggregate. If graphitization and aggregation occur simultaneously, lower values of k may be expected for the particles that are early in the flame (Saito et al. 1991). Among others, Smith et al. (1984) and Sattel (1997) have verified this continuum of optics and structure.

The curved line in Figure 7, marked “graphitization,” represents the changes in refractive index as sp^2 -clusters grow. This curve shows the measured change in n and k for a film of amorphous carbon heated from 250° to 750°C (Smith 1984). Ergun and McCartney (1960) report values for coals of increasing rank that fall on a nearly identical line, labeled “coal rank.” Values that lie closer to the graphitization curve than to the void-fraction line are those of Chippett and Gray (1978, #3), Lee and Tien (1981, #8), Mullins and Williams (1987, #9), Marley et al. (2001, #10) and Senftleben and Benedict (1918, #14). Of these, #8 and #14 might be expected to be partially graphitized—#8 because it is taken low in an unusual flame, that of a burning solid, and #14 because the rapid quenching during arc-discharge does not result in fully graphitized carbon. The material studied in #3 and #9 should represent graphitized, aggregate carbon. Mysteriously, we were unable to reproduce the inferred refractive indices in these two studies given the data presented in the papers. Partially-graphitized carbon cannot represent these two data points, but they are not consistent with the data presented in the papers, either. The material in #10 (candle soot) may also differ from atmospheric LAC, particularly since quenching during collection may stop the reaction, but we do not have evidence to support that hypothesis.

One extreme outlier in Figure 7 ($1.3 - 1i$) is that of Erickson et al. (1964, #5). These authors admitted that their value was only consistent with the results of their angular-scattering technique. Other values closer to the void-fraction line can be derived from their data, including $1.8 - 0.8i$ and $1.9 - 0.75i$. In the interest of fairness, we also re-analyzed the results of Janzen (1979, #7), whose results lie much closer to our void-fraction line. These data are consistent with a range from $1.5 - 0.91i$ to $2 - 1i$, so this author could have just as easily produced a value that did not agree with the void-fraction line. It is interesting that the Janzen (1979) paper criticizes earlier work, particularly that of Dalzell and Sarofim (1969), and is frequently used as support for disregarding reflectance-based measurements. Yet the extinction measurements of Janzen (1979) are taken at a narrow range of

wavelengths, and can no more constrain the real and imaginary refractive indices than do other studies.

Two points lie just above the void-fraction line, suggesting that a higher value for solid LAC might be appropriate. These data are those of Pluchino et al. (1980, #12) and Janzen (1979, #7), and they correspond to measurements on fairly large carbon-black spheres ($8\ \mu\text{m}$ and $75\ \text{nm}$, respectively). These spheres are much larger than the spherules that make up flame-generated carbon; as spherule size increases, the platelets forming the outer shell become more perfect and graphitized (Heckman 1964). These large particles might have a higher imaginary refractive index than normal component spherules. While we appreciate the elegance of the approach in #12, these particles may overestimate the value of k for atmospheric LAC.

To summarize, some of the reported variation in refractive index is consistent with partial graphitization. Most of the variation is consistent with the idea that some of the material has voids, suggesting that a constant refractive index could represent solid carbon emitted from flames. We have not yet identified the point corresponding to void-free LAC, nor matched it with a density. Both of these tasks will be necessary in order to obtain a relationship between scattering and absorption and material mass.

7.3. Ensemble Properties: Absorption

In this section, we discuss the mass absorption cross section for freshly generated LAC. We assume that the ability to predict scattering and absorption by fresh combustion aerosol is a prerequisite to calculating optics of more complex, mixed aerosol. We wish to exclude the effects of atmospheric processing and mixing with negligibly absorbing substances, as well as possible problems in interpreting thermal-optical measurements intended to isolate LAC. We exclude ambient aerosol other than that sampled from traffic tunnels, because it could contain a large fraction of non-combustion aerosol.

Table 6 summarizes absorption cross sections of LAC measured at or near combustion sources. Measured material includes laboratory aerosol, diesel engines (including traffic tunnels), and carbon black. The latter part of the table includes values cited in other reviews (Horvath 1993a; Liousse et al. 1996) that are not measurements. These include values calculated from Mie theory, secondary references and ambient aerosol. Reports that provide extinction (absorption plus scattering) rather than absorption alone are excluded. The values tabulated in these two reviews average about $9.5\ \text{m}^2/\text{g}$. As shown in Figure 8(a), there is no clear mode, but most of the values lie between 5 and $13\ \text{m}^2/\text{g}$.

We make two corrections: (1) We adjust all measurements to a wavelength of $550\ \text{nm}$, assuming that cross section varies inversely with wavelength; this assumes that all particles examined are small relative to the wavelength. (2) We adjust absorption measured on filters according to Table 3 for the specific filter medium. Concurrent measurements of scattering are not usually available, and the correction for scattering is not applied. As we discuss below, the scattering cross section is about 25% of the

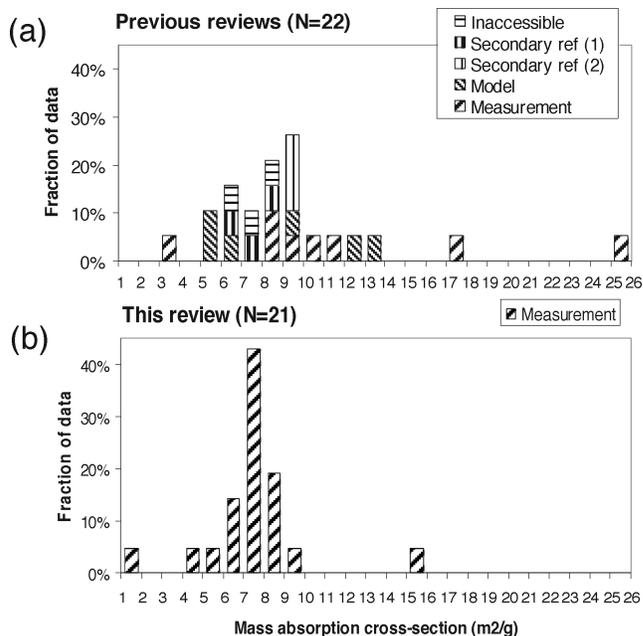


FIG. 8. Comparison of mass absorption cross sections tabulated (a) in previous reviews, showing large variability, and (b) in this review for near-source measurements, with much smaller variability. Legend in Figure 8a: (1) Traceable to value reported. (2) Not traceable to value reported.

absorption cross section, so that the overestimate of absorption due to scattering artifacts should be less than 10%.

Figure 8(b) summarizes data on MAC taken at and near sources, including aerosol from diesel engines and in traffic tunnels. Data for this figure exclude values of MAC that rely on normalization by thermal-optical methods, as well as ambient measurements that may represent substantially changed aerosol. In many cases, the two constraints are similar, because ambient measurements contain other material and require some kind of estimate of LAC fraction.

Given the previously reported wide range of MAC, the data are surprisingly consistent. Of 21 measurements, 16 lie between $6.3\text{--}8.6\ \text{m}^2/\text{g}$. The lowest value (Japar and Killinger 1979) was an early effort by a group that went on to produce much higher values, some of which are listed in this tabulation. While we have no reason to doubt their measurement, it is interesting that their later papers never cite it. The highest outlier (Truex and Anderson 1979) also results from the earliest days of work with photoacoustic measurements.

We suggest that there is a consistent value of MAC: about $7.5 \pm 1.2\ \text{m}^2/\text{g}$. The average is that of 17 measurements that exclude the lowest and highest values, and the two measurements that reported absorption cross section of particles in liquid. The uncertainty range is one standard deviation of those measurements. (The average including the liquid-suspended particles is $7.3\ \text{m}^2/\text{g}$.) Our statement contrasts with other reports that suggest a bewildering and inexplicable array of mass absorption cross sections, but it applies only to freshly generated LAC.

TABLE 6
Published values of LAC refractive index: original inferences, derived values and secondary references

Citation	Value (m ² /g)	Wave-length (nm)	Adjust-ments	Adjusted to 550 nm	Measurement	Normalization/ Comments on fuel
Measurements						
Diesel engines—direct						
Trux and Anderson, 1979	17	514	1	15.9	Photoacoustic	None
Japar and Szkarlat, 1981	8.9	514.5	1	8.3	Photoacoustic	Mass after extraction
Schnaiter et al. 2003	6.6 ± 0.4	550	—	6.6	Difference (ext-scat)	None
Scherrer et al. 1980	9.0	550	2	7.4	IP/Nuclepore	Non-volatile mass
Szkarlat and Japar, 1981	8.28 ± 0.23	514	1	7.7	Photoacoustic	Soxhlet extraction
Diesel engines—traffic tunnels						
Japar et al. 1981	8.0 ± 0.4	500	1	7.3	Calibrated IP	Extractable in organic solvent
Szkarlat and Japar, 1983	10.9	500	1,3	8.3	Calibrated IP	Mass after extraction
Other combustion aerosol						
Bruce et al. 1991	4.55	488	1	4.0	Photoacoustic	None
Colbeck et al. 1989	8.1	632	1	9.3	Ext minus scat	95% “elemental carbon”
Colbeck et al. 1997	7.5	632	1	8.6	Ext minus scat	None; C/H ratio 5 molar
Gundel et al. 1984	25.4	633	1, 4	8.4	Laser transmission	Solvent extraction
Japar & Killinger, 1979	1.5	600	1	1.6	Photoacoustic	Mass after extraction
Mullins & Williams, 1984	4.1 ± 0.1	450	1, 5, 6	5.8	Not identified	None; C/H ratio 6–9 molar
Marley et al. 2001	10.5	550	7	See note	Integrating sphere	None
Mulholland & Choi, 1998	6.4 ± 0.5	633	1	7.4	Difference (ext-scat)	None
Patterson et al. 1991	5.3 ± 0.7	633	1	6.1	Difference (ext-scat)	None
Roessler & Faxvog, 1979	8.3 ± 0.9	514.5	1	7.8	Photoacoustic	None
Röhl et al. 1982	11.9	600	1, 8	7.9	Photoac. on filter	None
Sheridan et al. 2005	7.5 ± 1.2	550	1	7.5	Difference (ext-scat)	Thermal; should be mostly EC
Carbon black						
Ballach et al. 2001	6.5	550	—	6.5	Integrating sphere	None
Donoian & Medalia, 1967 ^a	9.62	550	5	6.9	Difference (ext-scat)	None
Clarke and Noone, 1985	6.6–8	550	8	7.3	IP calibration curve	None
Spark discharge						
Ballach et al. 2001	2.9 ± 0.1	550	a	2.9	Integrating sphere	None
Schnaiter et al. 2003	2.9 ± 0.5	550	—	2.9	Ext minus scat	None
Ambient—fine						
Adams et al. 1990	10	514	1	9.3	Photoacoustic	Thermal-optical after extraction
Edwards et al. 1983	7–12	550	L		IP/Nuclepore	Thermal EC
Groblicki et al. 1981 ^b	11.8	550	L, H		IP/Nuclepore	Slope vs EC, SSA ~0.67
Japar et al. 1986	11–12	650	L		IP/Nuclepore	Thermal-optical
Liousse et al. 1993	5	Broadband			Aged	Thermal (presumably
”	20	Broadband			Fresh	Cachier method)

(Continued on next page)

TABLE 6
Published values of LAC refractive index: original inferences, derived values and secondary references (*Continued*)

Citation	Value (m ² /g)	Wave-length (nm)	Adjust-ments	Adjusted to 550 nm	Measurement	Normalization/ Comments on fuel
Ambient—coarse						
Groblicki et al. 1981 ^b	H 3.8	550				
Calculations						
Chylek et al. 1981	H 5	514				Comments
Chylek et al. 1981	L 12.5	514				No voids
Jennings and Pinnick, 1980	L 3.5–8.6					Value of 12.5 does not appear in this paper
Nelson, 1989	L 8–10	550				Mie, 2.0–1.0 i, particles 0.35–1.06 μm
Roessler, 1984	H 5.0	570				Fractal, m = 1.75–0.5 i and 2.0–1.0 i
Rosen and Hansen, 1984	L 8.3–18.1	500				Small-sphere limit, m = 2-li, density 2 g/cm ³
						Spherical, externally mixed, or internally mixed with organic and/or sulfate in observed ratios
Secondary references						
Clarke, 1989	H 9.68					Original source
Heintzenberg, 1982	L 9.68					Donoian and Medalia, 1967
Clarke et al. 1987	L 9.68					Donoian and Medalia, 1967
Japar et al. 1984	9.8 ^c					Donoian and Medalia, 1967
Patterson et al. 1986	L 6.75					Szkarlat and Japar, 1981; Szkarlat and Japar, 1983
Waggoner et al. 1981	L 5–11					Szkarlat and Japar, 1981
References not available to us						Denver Brown Cloud (perhaps Groblicki et al. 1981)
Marshall et al. 1986	H 6.7					Reference not given by Horvath
Hitzenberg, 1990	L 2–12					Conference proceedings
Kreiner, 1985	H 6.6					Ph.D. thesis

Adjustments: (1) Adjusted to 550 nm, assuming that absorption is inversely proportional to wavelength. (2) Corrected for enhancement by Nuclepore filter according to Table 3. (3) Used 9.1 m²/g (authors' regression of absorption on elemental carbon content) instead of authors' value, which was designed to estimate optical properties of diesel particulate emissions alone and contained higher uncertainty. (4) Corrected for enhancement by quartz filter according to Table 3. (5) Corrected for suspension in liquid medium, which increases absorption cross section relative to suspension in air. (6) Adjusted to log-base-e from log-base-10. (7) Integrating sphere used without calibration; correction factor unknown. (8) Authors used model to correct for filter effects, and we use the corrected value.

Notes: (a) Used values of five carbon blacks corresponding to smallest particles. Value often cited (9.68 m²/g) is for one carbon black, Monarch 71. (b) Horvath (1993) cites Wolff, 1980, which is not given in the reference list. We assume that this was a conference proceeding or personal communication regarding the Denver Brown Cloud study, for which MAC measurements are given by Groblicki et al (1981). We also assume that Horvath's citation of 12.7 m²/g was a preliminary value produced in this study. (c) See note for Adjustment 3.

TABLE 7
Measured values of single-scattering albedo from fresh combustion aerosol

Reference	Wavelength (nm)	ω_0	Source
Roessler and Faxvog, 1980	514.5	0.15 ± 0.05	Acetylene smoke
Scherrer, 1981	535–550	0.17 ± 0.05	Diesel engine at several speeds
Colbeck et al. 1989	632	0.28–0.25	LPG combustion
Koylu, 1994	514.5	0.18–0.29	Turbulent diffusion flames: acetylene, propylene, ethylene, propane
Mulholland, 1998	633	0.19–0.25	Laminar & turbulent acetylene & ethylene flames
Schnaiter et al. 2003	550	0.20 ± 0.01	diesel engine

A commonly cited value for MAC is $10 \text{ m}^2/\text{g}$. That value is more than two standard deviations away from our central estimate and does not appear in our corrected tabulation. Many reports of $10 \text{ m}^2/\text{g}$ were secondary references traceable to the paper by Donoian and Medalia (1967). That paper reported measurements of carbon black suspended in water, where the absorption cross section would be much greater than in air (30–60% for reasonable refractive indices of LAC). Measurements uncorrected for enhancement by filter media also provide values of $10 \text{ m}^2/\text{g}$ (Horvath et al. 1993b; Petzold et al. 1997; Bond et al. 1999; Fuller et al. 1999). A large body of literature suggests that some ambient aerosol has mass absorption cross sections greater than $7.5 \text{ m}^2/\text{g}$. Table 6 contains some of these values. We do not refute these measurements, but we do emphasize that available measurements on fresh combustion aerosol do *not* exhibit MAC of that magnitude.

A full exploration of the higher values of MAC for atmospheric aerosol is beyond the scope of this review. We suggest at least two plausible explanations, and both probably contribute. First, there may be anomalies in the thermal-optical measurements used to normalize absorption to elemental carbon mass. Uncertainties in thermal-optical measurements are widely acknowledged, and have been identified as a reason for apparently high absorption (Martins et al. 1998). Second, particle coatings may increase the absorption cross section, as discussed in Section 4. When LAC and negligibly-absorbing material are emitted from the same combustion process, the form is probably that of an absorbing core surrounded by a negligibly absorbing (or less absorbing) shell. LAC is formed in high-temperature regions of the flame, where semi-volatile organic material can neither persist nor condense. As the exhaust gas cools, semi-volatile material condenses on available surfaces, including LAC. Further mixing occurs in the atmosphere: coagulation with other particles, coating by condensation, or coating after evaporation of a water droplet that contains LAC and other substances.

7.4. Ensemble Properties: Single-Scattering Albedo

While absorption cross section per unit mass is almost constant for the particle sizes emitted from combustion, scattering per mass depends more on particle size. Therefore, a consistent

value of mass scattering cross section for LAC particles is not expected. Because MAC is relatively constant, single-scattering albedo (scattering divided by absorption plus scattering) might also change. For combustion aerosol, total scattering is not frequently measured, but Table 7 lists a few values. They are surprisingly consistent, suggesting a single-scattering albedo of about 0.2–0.3.

These values of single-scattering albedo are higher than those predicted by Mie theory. Even 100-nm particles should have a single-scattering albedo of about 0.1, and ω_0 would be much lower for smaller particles. The spherical-particle assumption is unable to match scattering by these particles because they are aggregates. Sorensen (2001) points out that the single-scattering albedo is quite sensitive to the radius of the primary spherules, and reaches an asymptote with regard to the number of spherules in the aggregate. This asymptote matches measured ω_0 for primary particle diameters of 20–30 nm, in good agreement with observations.

7.5. Closure

Section 4 discussed theories—both Mie and aggregate—that predict scattering and absorption from the refractive index when particle size is known. We have estimated refractive index (Section 7.2.3) and should be able to combine it with an appropriate theory to match the separately-constrained absorption cross section (Section 7.3).

We assume that LAC does not lie along the graphitization line; rather, it consists of flame-generated particles that have become as graphitic as the flame can make them. We surmise that the refractive index must lie along the void-fraction line in Figure 7, although we admit that we do not know precisely where. It is possible to imagine conditions under which partially graphitized material would be emitted, but we investigate the more strongly absorbing carbon here. We also assume that Rayleigh-Debye-Gans (RDG) theory represents fresh LAC better than Mie theory. As long as the primary spherules are small (relative to the wavelength of light below about 80 nm), spherule size does not affect absorption. Observed spherule sizes are below that size. Thus, the MAC of any aggregate particle can be represented with that of some small particle, say 50 nm. Finally, we assume that

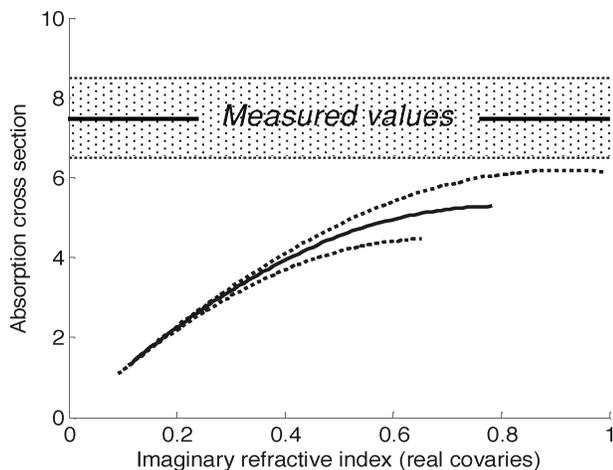


FIG. 9. Mass absorption cross sections m^2/g for fresh LAC: measured values from Figure 8(b) (shaded region, with central estimate marked by a thick line), and calculated values using the best guess of refractive index for fully-graphitized carbon; see Figure 7. Central curve shows “void-fraction” line in Figure 7 (approximately $1.8-0.74i$); higher and lower curves are similar “void-fraction” lines assuming that pure LAC has refractive indices of $2-i$ and $1.96-0.66i$. The latter two values are not expected to represent atmospheric LAC, as discussed in text. Assumed density is 1.8 g/cm^3 .

the density of the spherules is 1.8 g/cm^3 (Mullins and Williams 1987; Wu et al. 1997; Park et al. 2004).

Figure 9 examines whether any plausible void-free refractive indices are consistent with measured MAC. The figure shows the mass absorption cross section of spherical 50-nm particles (or aggregates of such spherules). While only the imaginary refractive index (k) is shown on the x -axis, the real refractive index also varies according to the void-fraction line in Figure 7. We do not know exactly which point along this line corresponds to void-free LAC, so we examine all of them as candidates. The figure also shows MAC along two additional lines based on the higher and lower values of refractive index in Figure 7. A constant density of 1.8 g/cm^3 is used in the calculations; the figure would look different if we were examining how MAC depended on voids in the material.

The band representing measured MAC is also shown in Figure 9. The prediction and the measurements do not overlap. The discrepancy is about 30%, with measured MAC greater than calculated. A discrepancy of 30% in absorption cross section may not be important in some disciplines, but would be significant in determining climate forcing. Figure 9 also demonstrates why attempts to calculate high MAC using realistic refractive indices have been unsuccessful. None of the predictions using plausible refractive indices overlap the measurements. One might try to increase calculated MAC by choosing higher values of k , but the corresponding increase in n (demonstrated in Figure 5) has an offsetting effect. The result is an asymptote at high n and k .

What are possible reasons for this discrepancy? There could be some uncertainty in the refractive index, which might allow the upper bound of the uncertain predictions to overlap the lower

bound of the uncertain measurements. However, the refractive index would have to be far outside the range of any of the values tabulated here.

Perhaps Mie theory is better than RDG for this type of particle, but it results in a smaller MAC for combustion-sized particles ($\sim 100 \text{ nm}$), not a greater one. Or perhaps the primary spherules lie in the region of peak absorption cross section, but primary spherules of this size (100–200 nm diameter) are not observed in combustion particles. Finally, our density of 1.8 g/cm^3 could be too high, particularly if gaseous adsorption does not measure the same volume that interacts with light. A density of about 1.35 g/cm^3 would be required to bring the high end of the calculated curves into agreement with the measurements. Such a major discrepancy does not seem realistic.

Despite our attempts to choose only freshly generated LAC, our collection of MAC could be drawn from coated particles for which absorption is enhanced. An enhancement of 30% would require either very thick coatings compared to those expected from fresh LAC or very large cores, as shown in a more detailed investigation (Bond et al. 2005). The particles could contain material other than carbon because they form in impure environments. Surface impurities could change the chemical nature and reduce the imaginary refractive index as discussed in Section 3. In that case, predictions would exhibit an even greater discrepancy with measurement. Oxygenation of the surface could reduce the real refractive index, as shown by Stagg and Charalampopoulos (1993) for amorphous carbon. A decrease of about 25%—less than that observed by Stagg and Charalampopoulos (1993)—would increase MAC by 30%. But such a change is less likely for turbostratic particles than for a glassy, shiny carbon.

As discussed in Section 5, Iskander et al. (1991) showed that interactions between spherules increase the MAC above that of RDG theory by factors up to 1.5; Fuller et al. (1999) estimated that this increase would be limited to about 30%. Although we consider this interactional enhancement a likely explanation for the 30% discrepancy (as did Iskander et al.), this result has yet to be demonstrated with measurements.

Our purpose here is to identify, as completely as possible, the parameters required to represent climate forcing of LAC. We have identified a range of possible refractive indices consistent with the varied measurements; this range provides an upper limit for calculated MAC. We have bounded the mass absorption cross section of fresh LAC. Finally, we have confirmed that measured MAC is greater by about 30% than prediction by simple theories (either Mie or RDG), and that variability in either refractive index or MAC is unlikely to account for the discrepancy.

Fuller et al. (1999) also identified several possible reasons for this discrepancy. Our work differs from theirs because we focus less on detailed calculations and more on systematically identifying the properties of pure, void-free LAC. The most plausible explanations for this discrepancy, about 30%, are (1) interactions between particles or (2) density estimates that are too high. These possibilities should be confirmed with measurements. There might be other explanations for the 30% discrepancy

between predicted and measured MAC. Clearly, the nature of these interesting little particles is not fully understood.

7.6. Beyond 550 nm

Our review, including the synthesis in Figures 7, 8, and 9, concentrated on identifying optical properties at the mid-visible wavelength of 550 nm. This limitation provided focus needed to conduct the review, but properties at a single wavelength are insufficient for climate modeling. Here, we address the possibility of extending these results to visible wavelengths (400–700 nm) for fully graphitized carbon that lies along the void-fraction line in Figure 7.

We propose that a *constant* refractive index for LAC at visible wavelengths is consistent with available data. This notion requires some support, which we will discuss below. We emphasize that this assumption is valid at visible wavelengths, and not ultraviolet or infrared wavelengths. Electronic transitions at ultraviolet wavelengths result in narrow peaks in absorption (e.g., Sakata et al. 1995). Both real and imaginary refractive indices are greater and non-constant at infrared wavelengths (e.g., Dalzell and Sarofim 1969; Foster and Howarth 1968; Jäger et al. 1998).

Refractive index estimates based on reflectance measurements (e.g., Senftleben and Benedict 1918) often show little spectral dependence. (Here, we express the relationship with wavelength as λ^n ; for example, λ^{-1} is an inverse dependence on wavelength). Stagg and Charalampopoulos (1993) provided data for wavelengths from 400–700 nm; the wavelength dependence of n and k are approximately $\lambda^{0.2}$ and $\lambda^{-0.1}$, respectively. The data of Marley et al. (2001) suggest $\lambda^{0.05}$ and $\lambda^{0.1}$ for n and k respectively. These are essentially constant within measurement error. Band-gap theory suggests a constant imaginary refractive index as an asymptote for large sp^2 clusters. Refractive indices of carbonaceous material exhibit large and sometimes rapid variations from ultraviolet to infrared; if n and k for LAC are constant across visible wavelengths, it is a fortuitous consequence of the narrow wavelength range.

The frequent observation of λ^{-1} dependence for aerosol absorption (e.g., Bergstrom et al. 2002; Schnaiter et al. 2003; Kirchstetter et al. 2004) also supports the notion of a constant refractive index, assuming that the particles observed were small relative to the wavelength. If the real refractive index had a wavelength dependence of even $\lambda^{-0.1}$, absorption would vary as $\lambda^{-0.84}$. The same wavelength dependence for imaginary refractive index would result in absorption varying as $\lambda^{-1.1}$. Perhaps these deviations from λ^{-1} do exist, but they are buried in the measurement uncertainties. There are limited data on the wavelength dependence of either refractive index or absorption; we can say only that they appear consistent with a constant refractive index at visible wavelengths.

Some measurements do suggest that LAC has a varying imaginary refractive index. These are scattering measurements in flames (e.g., Chang and Charalampopoulos 1990) and inferences from the dispersion model (e.g., Dalzell and Sarofim 1969; Lee

and Tien 1981; Habib and Vervisch 1988; Figure 3 of this review). The spectral dependence inferred from scattering measurements is greatly affected by the assumption of spherical particles. As discussed previously, the visible spectral dependence predicted by the dispersion model is questionable. In fact, measured data in the references cited are equally consistent with a constant refractive index throughout visible wavelengths.

Our statements about wavelength dependence apply only to LAC, not graphite or amorphous carbon. Some measurements of combustion-generated aerosol (Bond 2001; Kirchstetter et al. 2004), and spark-generated carbon (Schnaiter et al. 2003) have demonstrated that the imaginary refractive index may also depend on wavelength. This material also exhibits weak light absorption (Bond 2001), and is not the material we are calling LAC. We predict that it lies along the graphitization line in Figure 7.

7.7. A Return to History

The history of refractive index values tabulated by Shettle and Fenn (1976, 1979) is worth special mention. These are by far the most prevalent values for use in climate modeling, and have been incorporated into widely-cited literature, including a book by d'Almeida et al. (1991), and the Optical Properties of Aerosols and Clouds (OPAC) program (Hess et al. 1998). The original work by Shettle and Fenn (1976) averaged values from an earlier review by Twitty and Weinman (1971). In turn, the averaged data are taken from McCartney et al. (1965), who measured three coals, and Senftleben and Benedict (1918), who reported soot generated from an arc lamp. The review does not incorporate most of the findings on soot in the combustion literature, and indeed was written before most of that work was available. The precision of both n and k provided in OPAC values (three decimal places) is unwarranted, given this history. The OPAC value of $1.74-0.44i$ is drawn from incompletely graphitized carbon and has a lower value of k than most soot.

The value of Senftleben and Benedict (1918, $1.96-0.66i$) is also used to model LAC. Again, their material lies along the graphitization line in Figure 7 and is not LAC. Of the data used in climate models of previous years, only the data tabulated by Nilsson (1979) result from combustion soot, citing the data of Dalzell and Sarofim (1969) without correction for void fraction.

The optical and physical data for LAC propagated by d'Almeida et al. (1991) have some interesting properties. Along with an imaginary refractive index that is too low, these authors recommend: (1) a particle size that is far too small (23 nm is the approximate size of primary spherules, not aggregates); (2) a geometric standard deviation that is somewhat too large (2.0); and (3) a density that is far too low (a density of 1.0 is never observed; Fuller et al. (1999) tabulate measurements indicating densities of about 1.8 g/cm^3). Despite returning to the string of citations that led to d'Almeida et al. (1991), we have been unable to unearth the sources of these values. When compared with measured values, each of the individual assumptions above may

lead to an error of 50–75% in calculated properties that affect climate forcing.

Somewhat surprisingly, this combination of parameters yields a mass absorption cross section and single-scattering albedo that is close to the values we recommend. We speculate that, lacking recommendations from the measurement community, modelers simply selected values that match the absorptive properties of LAC, as suggested by Penner et al. (1998). Because aggregate particles have less absorption per mass than large spherical particles, models had to use very small sizes in order to represent strong absorption. (Assuming such a large number of particles per mass probably has implications for modeling how particles affect clouds.) These very small particles do not scatter much light, so a long lognormal tail provided a few large, scattering particles. The low value of imaginary refractive index yielded too little absorption per mass, and there was no method of accounting for the discrepancy between prediction and measured values. Those omissions were offset by very low particle densities. The parameters chosen for LAC were reasonable as long as they were treated in isolation. However, better estimates of radiative forcing require representing interactions with other particles. In such endeavors, reliance on offsetting errors is unwise.

Climate models must predict absorption and scattering by particles based on the mass of substance present, unless there is a change in the paradigm of representing optics as a function of chemistry. The refractive index is, at best, a convenience (although the discussion here may call that into question!). It should not be selected in isolation from other parameters, and modeled scattering and absorption should be compared with measurements.

7.8. What's Missing?

We began this section by asking which materials were representative of the LAC found in the atmosphere. In seeking closure between measured absorption cross section and theory based on particle characteristics, we used the most-graphitized material in Figure 7. Comparing light-absorbing properties and single-scattering albedos, particles emitted from diesel engines do appear similar to materials from controlled combustion, which tend to lie along the void-fraction line.

A similar confirmation has not been made for the remaining major sources of atmospheric LAC. Does carbon from all sources have identical optical properties? Less-graphitized carbon occurs within flames (e.g., Saito et al. 1991; d'Alessio et al. 1992; van der Wal 1996), and could have a lower absorption cross section than LAC. Optical properties of carbon particles from many combustion sources have not been investigated.

Although we have scarcely discussed wavelength dependence of absorption, limiting our focus to interactions with 550-nm light, absorption by incompletely graphitized carbon would have stronger wavelength dependence, as discussed by Bond (2001). Such material may be present in the atmosphere (e.g., Kirchstetter et al. 2004) and should be investigated.

It would be an unsatisfying review that reached so near to a conclusion and failed to give values and procedures to replace those we have criticized. Recommendations for representing LAC particles in climate models are contained in Section 9. We have separated these recommendations from the lengthier discussion here, for the convenience of those who are concerned about model inputs and not all that enthralled with the details.

8. MEASURED LIGHT ABSORPTION OF ATMOSPHERIC LAC

Relating the properties of freshly emitted LAC particles to the properties of the particles in the atmosphere is critical to determining their climatic effects. If particles change immediately or shortly after emission, fresh-particle properties cannot be used to represent all LAC particles. Plausible physical changes that affect scattering and absorption were discussed in Section 5.2.

An obvious procedure for investigating whether such changes occur is to examine important properties in ambient aerosol, compare them with those of fresh aerosol, and assess any differences in the shape, mixing or other properties. Such a comparison should indicate whether physical properties change in the atmosphere, and how those changes affect absorption and scattering. We had hoped to undertake such an evaluation with the tabulation given in this section, but as we will discuss, this task is not yet possible with the present body of measurements.

8.1. Measurement Tabulation

There have been hundreds of reported measurements of absorption by carbonaceous particles in the atmosphere. Waggoner et al. (1981) discuss the measurements made up to that time, with emphasis on those made by a group at the University of Washington. Horvath (1993a) provides a general discussion of absorption measurements and methods, including many European measurements. Penner and Novakov (1998) discuss some early LAC measurements in the context of the series of conferences entitled Carbonaceous Particles in the Atmosphere, which began in 1978. Reid et al. (2004) recently reviewed the absorptive properties of biomass burning emissions.

Table 8 lists field programs that contain information about absorption by atmospheric aerosols. Until about 1978, aerosol measurements were limited to broad-band solar absorption by a column of aerosols. There were very few absorption measurements in field programs during the 1980s. Intensive aerosol characterization experiments began in about 1990. The variety of instruments used during each program increased, as researchers came to appreciate the need for coordinated measurements of many aerosol properties. For example, the intensive field campaign known as ACE-Asia (Huebert et al. 2003) consisted of measurements made on two ships, four aircraft, several satellites, and ground stations in three different countries.

8.2. Limitations of Atmospheric Measurements

The measurements listed in Table 8 have produced valuable data and have established light absorption by carbonaceous

TABLE 8
Atmospheric field programs that have measured quantities relevant to LAC or absorption

Date	Program	Location	Measurement		Reference	Notes
			Method			
Early Radiation Measurements— 1946, 1960's	British Met Office	London, UK	[1]		Waldram, 1945; Roach, 1961; Robinson, 1970	Divergence technique—found large heating rates $\sim 20^\circ/\text{day}$ presumably due to LAC
1970	CAENEX	Russian Desert	[1]	spectral	Kondratyev et al. 1973; 1979	First spectral flux divergence to estimate aerosol absorption; showed hematite absorption
1972	GAARS	Southwest US	[1]		Grams et al. 1972	Flux divergence technique to estimate absorption; (SSA = 0.9) over the S.W. US desert
1976	Sutro Tower	San Francisco, CA	[1]		Russell et al. 1979; 1984	Flux divergence from tower measurements; (SSA = 0.9) near SF
1983	AGASP-1	Arctic	[7], [1]		Hansen and Rosen, 1984; Bodhaine et al. 1984; Ackerman and Valero, 1984	measured absorption by LAC in Arctic Haze
Early LAC Measurements—no absorption						
1970	ACHEX	Los Angeles, CA	[3]		Hidy et al. 1980	First use of thermal method
1978	Denver Brown Cloud	Denver, CO	[3, 6]		Groblicki et al. 1981 Wolff et al. 1981	Established LAC as cause of the Denver Brown Cloud
1990–2002: Climate-Related Aerosol Field Programs						
1991	Kuwait Oil Fires	Kuwait	[1]		Pilewskie and Valero, 1992; Weiss and Hobbs, 1992	Measured large optical depths with high heating rates
1995	ACE-I	Tasmania	[6]		Quinn et al. 1998 ACE I special issue	Very little absorption
1996	NFRAQS	Colorado	–[9]		Moosmuller et al. 1998	Photoacoustic technique
1996	TARFOX	North Atlantic	[1]		Novakov et al. 1997; Hignett et al. 1999 Russell et al. 1999; Bergstrom et al. 2002	Measured absorption from NE US (SSA ~ 0.85)
1996	ARACHNE-96	Eastern Mediterranean	[6]		Formenti et al. 2001	Measured absorption above Negev Desert (SSA $\sim 0.89-0.94$)
1997	ACE II	Azores	[6]		Russell and Heintzenberg, 2000 Tellus special issue	Measured absorption from Southwest Europe
1998	LACE-98	Germany	[1]		Ansmann et al. 2002 Special reprint issue JGR	Reported mean refractive index
1998	MINT	Germany	[several]		Wex et al. 2002	
1998	STAAARTE-MED	Mediterranean	[6]		Formenti et al. 2002	SSA est 0.89
1999	INDOEX	Indian Ocean	[6, 2]		Mayol-Bracero et al. 2002b Quinn et al. 2002	SSA est 0.9; MAC 8.1

(Continued on next page)

TABLE 8
Atmospheric field programs that have measured quantities relevant to LAC or absorption (*Continued*)

Date	Program	Location	Measurement Method	Reference	Notes
2001	MINOS	Crete	[6]	Sciare et al. 2003	SSA est 0.87, MAC ~7
2001	ACE Asia	East Asia	[several]	Huebert et al. 2003 Bergstrom et al. 2004 JGR special issue	SSA range 0.88 for bc, 0.95 for dust Wide range of MAC's reported
2000–2003	APEX	Japan, Korea, China	[6]	Nakajima et al. 2003	SSA varies from 0.8 to 0.98
2002	CLAMS	North Atlantic	[6]	Magi et al. in press	Preliminary results SSA = 0.9
2002	NEAQS	North Atlantic	[6]	Quinn and Bates, 2003	SSA est 0.95
2003	ARM Aerosol IOP	Oklahoma	[several]	Ferrare <i>et al.</i> in preparation	
1990–2002:	Biomass burning				
1992	SAFARI 92	South Africa		Andreae et al. 1996	
1993	SCAR-A	US	[2]	Soulen et al. 2000	
1994	SCAR-C	US?	[2]	Martins <i>et al.</i> 1996	
1995	SCAR-B	Brazil	[several]	Kaufman et al. 1998 Reid et al. 1998 Martins et al. 1998	Compared several methods
1997	ZIBBEE-97	Africa	[2]	Eck et al. 2001	
1998	LBA	Brazil	[7]	Artaxo et al. 2002	Found SSA = 0.83–0.92
1999	BIBLE-B	East Asia		Liley et al. 2002	
2000	SAFARI 2000	South Africa	[1, 6]	Swap et al. 2003; Pilewskie et al. 2003 Bergstrom et al. 2003; Eck et al. 2004	Several methods used for absorption, no mass measurements
Continuous measurements					
	UK Smoke Network	184 sites in UK	Filter reflectance	Edwards et al. 1983	
	CMDL	5 baseline; 4 regional	[6]	Sheridan and Ogren, 1999	Remote locations
	IMPROVE	Continental US	[6]	Malm et al. 1994	Provides maps of BC
	GAW	22 sites worldwide		Lavanchy et al. 1999 GAW home page http://rea.ei.jrc.it/netsshare/wilson/WDCA/	Jungfraujoch
	AERONET	~ 200 worldwide	[2]	Holben et al. 1998 Dubovik et al. 2002	Routinely publishes SSA results
	TOMS (satellite)	Global coverage	[2]	Torres et al. 1998	Used extensively to show existence of absorbing particles
	MODIS (satellite)	Global coverage	[2]	Kaufman et al. 2002 Hsu et al. 2004	Publishes optical depth and size information Multi-component methods
	AVHRR (satellite)	Global coverage	[2]	Husar et al. 1997 Christopher et al. 1996	Broad band measurement
	SeaWiFS	Global coverage	[2]	Higurashi and Nakajima, 2002 Kahn et al. 2001	Multi-component methods
	MISR	Global coverage	[2]		Multi-Angle retrieval

Measurement methods: [1] Flux divergence from radiometer measurements at two levels in the atmosphere; [2] Inversion of sky or satellite radiance; [3] Thermal technique; [4] Integrating sphere; [5] Integrating plate; [6] PSAP; [7] Aethalometer; [8] Laser integrating plate, [9] photoacoustic

particles as an important factor in radiative transfer. Yet despite the large number of field programs, information needed to assess possible changes in MAC is lacking. Often LAC mass is not determined at the same time as the absorption, a situation that has only recently begun to improve. Remote measurements cannot estimate the mass of LAC particles in the column or determine MAC. These measurements establish the existence of atmospheric aerosol absorption, and sometimes its magnitude, but not the radiative properties of LAC alone. Meticulous inversions of remote data have estimated concentrations and MAC that are consistent with measured radiance (Schuster et al. 2005), but even these rely on assumptions about the refractive index and particle mixing.

Much effort has been spent on establishing the absorption properties of the *aerosols* in the atmosphere. However, the distinction between the effective optical properties of the atmospheric aerosol, and the optical properties of the LAC itself, is an important one. Knowledge about radiative properties of LAC itself is quite limited, and this quantity is needed to determine how changes in emissions will affect climate. This critique also applies to measurements of the single-scattering albedo, which is strongly affected by LAC. While crucial for determining the sign of radiative forcing by aerosols (Haywood and Shine 1995; Hansen et al. 1997) and useful in determining causes of absorption (Bergstrom et al. 2002; Dubovik et al. 2002), measuring the single-scattering albedo does not foster a link between emissions of LAC and its effect on radiation.

Some programs have provided the measurements needed to estimate atmospheric MAC by measuring both absorption and LAC. However, there have been difficulties in interpreting the results as representative of particular regions, source categories, or particle transformation. The variability observed in atmospheric MAC is greater than that of freshly emitted LAC particles. For example, the Aerosol Characterization Experiment conducted near the coast of Asia (ACE-Asia) reported MAC for carbonaceous particles varying from 5 to 25 m²/g (Huebert et al. 2003; Quinn et al. 2004). This range is not much different from that given by Liou et al. (1993): 6 to 20 m²/g. This variability could be caused by different sources, atmospheric transformation or measurement uncertainties. For example, dust absorption may have affected determinations of LAC absorption during ACE Asia (Bergstrom et al. 2004).

Throughout this section, we have raised concerns regarding the inability to assess absorption by LAC using atmospheric measurements. Following are some limitations of past measurement campaigns that should be addressed in the future:

1. All techniques, including remote sensing, measure absorption due to all particles, not just LAC particles.
2. If absorption is normalized to LAC mass, the absorption and mass measurements may be made on different samples.
3. When absorption is normalized to LAC mass, there is considerable uncertainty in the thermal-optical methods that are commonly used. This is a major uncertainty, one that

prevents understanding whether the range in atmospheric MAC values is real or an artifact of the measurements.

4. Even if the absorption and mass determinations are perfect, the morphology of the particles is usually unknown and often unknowable. Even detailed electron microscopy focuses on a small fraction of the particles. This lack of information prevents correlations between observed MAC and particle shape should form.

8.3. Outlook

Modeling scattering and absorption by LAC will improve if significant differences in important properties can be attributed to specific conditions, such as different combustion sources or atmospheric processing. In our view, it is not possible to assess the accuracy of the present tabulation of MAC in the atmosphere. To be sure, we can estimate a range for MAC, which varies by about a factor of four (5–20 m²/g). However, lack of a reliable method for measuring LAC mass prevents firm conclusions about whether this variability is real. For example, Carrico et al. (2003) calculated MAC using the same absorption measurement and three different methods of measuring LAC mass, resulting in values of 5.3, 9.5, and 18 m²/g. Martins et al. (1998) pointed out that extremely high values of MAC were associated with potassium, which affects the thermal-optical method. While ours may seem to be an overly negative outlook, we believe that the current focus on resolving some of these issues will rapidly counter the present uncertainty. Current research addresses the accuracy of thermal measurements and improved methods of measuring absorption.

Despite our extensive caveats, the available data do allow a few inferences. First, a lower bound of about 5 m²/g for submicron MAC particles is observed. The particle collapse observed by Schnaiter et al. (2003), even after just two hours, reduced absorption by just over 20%, corresponding to a change from our fresh value of 7.5 m²/g to about 5.8 m²/g. Clarke et al. (2004) reported values of 6–8 m²/g by normalizing absorption to the non-volatile fraction of the aerosol. We suggest that the lowest values of 5 m²/g are collapsed but uncoated. They may also represent large agglomerates formed in the thick plumes of open biomass burning, as suggested by Liou et al. (1993). These low values are less commonly observed than other values, and we suggest that the uncoated aerosol does not remain in that state for very long.

Observations of absorption above the fresh value of 7.5 m²/g are far more common than low values (e.g., Quinn et al. 2004). Ambient values of MAC in polluted regions tend to exhibit a mode around 9–12 m²/g. Perhaps not coincidentally, a spherical particle with our suggested refractive indices, with an absorption enhancement of about 80% due to coating (Bond et al. 2005), results in MAC of about 11 m²/g—in the range of the most prevalent observed atmospheric MAC.

What of the additional 30%, postulated due to spherule interaction, that we had to invoke to match the fresh MAC?

Fuller et al. (1999) showed that this interactional enhancement does not occur when the LAC particle is encapsulated. Absorption by aggregates without coatings is about 30% higher than that of uncoated spherical particles; absorption by coated particles is about 80% higher than that of uncoated particles. The coated particles that exist after some atmospheric lifetime have absorption about 50% higher than the particles emitted as aggregates.

9. RECOMMENDATIONS

We summarize here our recommended approach to representing LAC in climate models. As in the review, our approach is skewed toward representing freshly generated LAC, but we also suggest some methods of representing the material later in its lifetime. In providing these recommendations, we maintain the caveats that have been sprinkled liberally throughout this document. This is particularly true of our concerns about whether the material that has been studied is similar to that in the atmosphere.

9.1. Choice 1: Absorption and Scattering

Mass absorption cross section. As outlined in Section 7.3, we suggest a value of $7.5 \pm 1.2 \text{ m}^2/\text{g}$ for the MAC of fresh light-absorbing carbon. During a particle's lifetime, this value may increase due to coating and decrease due to particle coagulation and aggregate collapse, as discussed next.

Mixing/coating. A preliminary estimate of the enhancement due to coating by negligibly absorbing aerosol is a factor of 1.5. This value is supported by some observational evidence and by some theoretical investigations.

Single-scattering albedo. Values of 0.20–0.30, with a central value of about 0.25, appear supportable for fresh aerosol, as shown in Table 7. These values will increase after emission.

Backscattering fraction. We did not discuss this value previously, but the only published values we know of are those of Schnaiter et al. (2003): 0.16 to 0.18.

Wavelength dependence. Absorption cross section may be assumed to depend inversely on wavelength throughout the visible spectrum. We make no statements about the nature of absorption at ultraviolet and infrared wavelengths.

The values given here are sufficient to calculate one-dimensional climate forcing by fresh aerosol, as discussed in Section 9.4.

9.2. Choice 2: Optical Model

For those who wish to calculate scattering and absorption of fresh LAC, this section suggests a simple approach. These particles are not spherical, and it is possible to implement Rayleigh-Debye-Gans theory in a modeling framework or lookup table. We recommend the review by Sorensen (2001) as a primer; he tabulates the equations neatly. However, even though RDG theory is better than Mie theory, it underpredicts absorption by about 30%. More precise calculations would not be computationally

efficient enough for climate models. It is probably better to use a constant absorption cross section and single-scatter albedo for unmixed particles, and apply the parameters described below after the particles have mixed. This recommendation should be revisited as more measured absorptive properties of combustion aerosol become available.

Refractive index. The value commonly used by climate modelers ($m = 1.74 - 0.44i$ at 550 nm) represents *none* of the possible refractive indices and should be retired. It should be assumed that most LAC lies on the void-fraction line in Figure 7 and Table 5. Our best guess is that the high values in the table are most promising, but Figure 9 shows that the values are not distinguishable in terms of absorptive properties.

Density. The density of LAC has been measured as 1.7–1.9 g/cm^3 and the use of 1.0 g/cm^3 should be abandoned.

Aging. While Mie theory should be not used for fresh aerosol, Mie-based equations that represent encapsulated, concentric (shell-and-core) particles may be used for aged, coated aerosol along with the higher refractive indices in Table 5. These will yield MAC values similar to those observed in the atmosphere. Other guiding relationships on coating versus enhancement will be forthcoming (Bond et al. 2005).

Wavelength dependence. Refractive index may be assumed to be constant throughout the visible spectrum. We make no statements about its nature at ultraviolet and infrared wavelengths, but we emphasize that it is likely to be much different.

9.3. Cautions

All modelers should beware of blindly choosing particle sizes and applying Mie theory. The same is true of volume-mixing of refractive indices. This procedure is not physical and is discouraged.

Sensitivity studies on the optical models can be performed more rapidly than sensitivity studies on the global models of radiative transfer. These may suffice to inform modelers when results are very sensitive to the chosen input parameters. At the very least, values of mass absorption cross section and single-scattering albedo should be given for each modeling study that estimates climate forcing.

9.4. Simple Climate Forcing

The much-quoted forcing equation of Chylek and Wong (1995) can be modified to provide a direct forcing in watts per gram, if the mass absorption cross section, single-scattering albedo, and backscatter fraction are known. We term this modified equation the “simple forcing efficiency” (SFE):

$$\text{SFE} = \frac{S_0}{4} \tau_{am}^2 (1 - F_c) [2(1 - a_s)^2 \beta \cdot \text{MSC} - 4a_s \cdot \text{MAC}]$$

where SFE is in units of watts per gram, S_0 is the solar irradiance (1370 W/m^2), τ_{atm} is the atmospheric transmission (0.79), F_c is the cloud fraction (approximately 0.6), a is the surface albedo (average 0.19), β is the backscatter fraction, and MSC and MAC are the mass scattering and absorption cross sections per gram, respectively. The resulting value is lower than that calculated by climate models, but it provides a way to estimate the sensitivity of different model inputs. The SFE represents a one-dimensional, two-flux method, which is reasonably accurate for low optical depths. It represents the energy added to the Earth-atmosphere system by a given mass of particles in the atmosphere.

9.5. Suggested Reading

Although we have examined several references in preparing this review, some have been particularly instructive. The review of aggregates by Sorensen (2001), mentioned previously, is both readable and comprehensive. Heckman's 1964 review of carbon black microstructure is highly recommended as a reminder of what has been known and apparently forgotten. The paper by Fuller et al. (1999) is a good overview of absorption that can and cannot be explained with calculation. And of course, the delightful book by Bohren and Huffman (1983) should be consulted regularly.

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