Toward Improved Understanding of Black and Brown Carbon Radiative Impacts over South Asia

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Toward Improved Understanding of Black and Brown Carbon Radiative Impacts over South Asia by
Apoorva Pandey

A dissertation presented to
The Graduate School
of Washington University in
partial fulfillment of the requirements for the degree of Doctor of Philosophy

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ABSTRACT OF THE DISSERTATION

Toward improved understanding of Black and Brown Carbon radiative impacts over South Asia

by

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Atmospheric aerosols directly affect the Earth’s radiative budget by absorbing and scattering solar radiation. Carbonaceous aerosols constitute 20-90% of the global aerosol mass burden and are recognized by the Intergovernmental Panel on Climate Change as important drivers of direct radiative forcing (DRF). Aerosol radiative impacts have been implicated in regional atmospheric warming in South Asia: changing Indian monsoon patterns, and accelerating melting of the Himalayan glaciers. There are systematic global discrepancies between estimates of aerosol absorption optical depths derived from observations and those from climate models. Over South Asia, models predict six times lower aerosol absorption than ground-based observations, leading to a low bias in modeled DRF. To resolve this bias, there is a need to (1) account for relevant emission source types, and associated emission rates, and (2) constrain aerosol optical properties: mass absorption cross-sections (MAC), single scattering albedo (SSA) and scattering directionality parameters (asymmetry parameter or upscatter fraction). To that end, two broad classes of light absorbing carbonaceous aerosols need to be separately dealt with: black carbon (BC) and brown carbon (BrC).
BC is known to strongly absorb visible solar radiation and its optical properties have been characterized using both direct measurements and optical models. BC aerosols exhibit aggregate morphologies, with fractal dimensions of 1.8 and 2.6 for fresh and aged particles, respectively. As a simplification, current climate models usually approximate BC aerosols as volume-equivalent spheres and use analytical solutions (known as the Lorenz-Mie theory) of Maxwell’s equations for estimating their optical properties. Recent modeling studies employed the numerically-exact superposition transition-matrix method to compute optical cross-sections of fractal aggregates of varying sizes and fractal dimensions. These studies highlight the effect of morphology on BC optical behavior soot but their findings (expressed in terms of fractal properties) cannot be used directly by aerosol experimentalists and climate modelers. Exploiting the theoretical bases of aerosol sizing techniques, I determined empirical relationships between numerically-exact optical properties of fractal BC particles and their equivalent diameters, that can be measured by common aerosol instrumentation. In a related study, I reported improved relationships between scattering directionality parameters of BC aggregates, and compared them with the canonical equations which did not allow for treatment of particle morphology.

The second branch of my thesis is concerned with light absorbing organic carbon (OC). OC is conventionally modeled as purely light scattering in radiative transfer calculations. However, this approach has been challenged by mounting observational evidence of a class of OC aerosols exhibiting strong absorption in the near ultra-violet wavelengths and little to no absorption in the near-infrared region. This wavelength dependence of absorption leads to a brownish appearance, hence the name brown carbon. Absorption properties of BrC depend on fuel properties and combustion phase (flaming/smoldering): their observed values are source-specific, spanning an order of magnitude in literature. The focus of this part of my research is on the largest source of
OC emissions in South Asia: household biomass cookstoves. I conducted a field study in a household in central India in December 2015 and developed a dataset of emission rates for commonly used biomass fuels from various regions of India, which showed that (1) laboratory cookstove tests underestimated particulate mass emission factors by 2-4 times and (2) cookstove aerosol emissions were dominated by thermally stable OC, which is linked with stronger light absorption than volatile OC.

To constrain the MAC values for cookstove OC emissions, I performed optical (transmission and reflection) measurements on filter samples of aerosols collected during the field study. Filter optical measurements are associated with artifacts arising from the interaction of the filter medium with light. Through a laboratory study of a wide variety of combustion aerosols, I developed correction schemes for estimating aerosol-phase light absorption from filter-based measurements. This aided the estimation of absorption characteristics of cookstove particulate emissions and their OC components. We found that light absorbing OC contributes roughly as much as BC to total absorption cross-sections of cookstove emissions at 550 nm wavelength, enhancing their direct forcing efficiency. We proposed values for key absorption characteristics of cookstove OC emissions for use within climate impact assessment and mitigation efforts.
Chapter 1: Background and motivation

Atmospheric aerosols—liquid and/or solid particles suspended in air—originate from various natural and anthropogenic processes. They may be emitted directly to the atmosphere (primary) or formed from precursor gases through atmospheric reactions (secondary). The composition of atmospheric aerosols is source-dependent and varies across the globe and in time (Myhre et al., 2013). There are regional patterns in aerosol composition because of their short lifetime and seasonal patterns due to the facts that atmospheric conditions govern the evolution of their properties. Many physical processes that affect atmospheric aerosol are a function of particle size; broadly, aerosols are classified as coarse or fine mode.

The scientific interest in aerosols (Pöschl, 2005) and their complexity is in large part attributable to their range of climate (Stocker et al., 2013), health (Davidson et al., 2005) and visibility impacts. Aerosols affect the climate through several mechanisms—the direct effects involve a change in the atmospheric radiative budget from scattering and absorption by aerosols, while the indirect effects include their influence on cloud and ice formation and modification of the reflectance of snow and ice deposits (Pöschl, 2005; Bond et al., 2013; Stocker et al., 2013). Figure 1.1 shows a schematic of these direct and indirect mechanisms of aerosol climate effects and associate feedback loops that demonstrate the response of the climate system.
The direct effects of aerosols are quantified as *radiative forcing* which is defined as the change in the net (downwelling – upwelling) solar and terrestrial energy flux (in Wm$^{-2}$) induced by a change in atmospheric composition relative to a baseline. In this definition, stratospheric temperatures are allowed to adjust to radiative equilibrium while surface and tropospheric temperatures are held fixed (implying that rapid adjustments in the troposphere are not included). Aerosol effects on clouds and snow, albeit involve more complicated physics, are also expressed as net changes in radiative flux or forcings. Aerosol radiative forcings for various aerosol types relative to a pre-industrial era (1750) are shown in Figure 1.2. These are in the context of all climate-relevant pollutants, such as greenhouse gases and short-lived gaseousforcers, included in the Intergovernmental Panel of Climate Change (IPCC) 2013 assessment of climate change (Stocker et al., 2013).
Figure 1.2: Radiative forcing relative to 1750, categorized by pollutant type. Source: Stocker et al. (2013).

Two of the emitted aerosol components in the figure above are particularly linked with the combustion of fossil and biomass fuels: organic carbon (OC) and black carbon (BC). These carbonaceous aerosol components, which are products of incomplete combustion of carbon fuels, are significant because of their ability to absorb solar radiation from ultraviolet to near-infrared wavelengths. My thesis focuses on contributing towards improving their representation in radiative models. Particularly, I will largely deal with mass emissions of BC and OC and their absorption and scattering efficiencies normalized to mass (mass absorption/scattering cross-sections: MAC/MSC in m²g⁻¹). In Chapter 1.1, the state of knowledge regarding BC and OC optical and chemical characteristics is reviewed. This is followed by a discussion of measurement and modeling techniques for estimating the optical properties of aerosols (Chapter 1.2). Finally,
Chapter 1.3 examines aerosol emissions and their radiative effects over South Asia, to motivate the focus of my thesis research toward better characterizing an important aerosol emission source in that region.

1.1. **Black and organic carbon (BC and OC) aerosols: optical and chemical properties**

Black carbon is an optical definition of a form of carbonaceous aerosol—primarily emitted from flaming combustion—that strongly absorbs visible light. It is associated with the typical black appearance of smoke and is generally assumed to be equivalent to soot. Soot carbon is incepted in high-temperature flames as small spherules (monomers) from the condensation of large polyaromatic hydrocarbons; these monomers form aggregates whose morphologies and compositions are a function of flame properties (Sorensen et al., 1992). Most soot carbon is predominantly (85-95%) composed of elemental carbon (EC), is refractory and is insoluble in water and organic solvents. (Andreae and Gelencsér, 2006) BC and EC are widely considered synonymous to each other and to soot. In practice, they are both proxies for soot and both their measurements can be biased by the presence of other compounds as well as inherent analytical limitations (Andreae and Gelencsér, 2006; Bond and Bergstrom, 2006; Bond et al., 2013). With these caveats in mind, Bond and Bergstrom (2006) carefully reviewed BC MAC measurements in literature and constrained its value as 7.5±1.2 m²g⁻¹ at 550 nm, with an inverse wavelength dependence. This dependence is parametrized by the absorption Ångström exponent or AAE (MAC~λ⁻AAE); for BC aerosols AAE=1 throughout the visible spectrum. This wavelength dependence is consistent with the optical band-gap theory, a model for BC light absorption at the molecular level (Sun et al., 2007). In the atmosphere, BC might be internally-mixed (coated) with
non-absorbing inorganic/organic compounds which could enhance its MAC value by approximately 50% (Bond and Bergstrom, 2006; Cappa et al., 2012; Bond et al., 2013).

OC is an umbrella term for the carbon mass that is a part of aerosol phase organic compounds. Given the large chemical diversity in organic aerosols, OC physical and optical properties like refractoriness, polarity and crucially, absorption efficiency span a large inter-linked range (Figure 1.3). Generally, volatile, low molecular-weight organic compounds do not absorb light. While most climate models, and the IPCC climate assessment discussed above, treat all OC as purely light scattering, there is a large body of observations of weakly to moderately light-absorbing organic aerosols (Andreae and Gelencsér, 2006; Chakrabarty et al., 2010; Chen and Bond, 2010; Chakrabarty et al., 2013; Saleh et al., 2013; Saleh et al., 2014; Washenfelder et al., 2015; Saleh et al., 2018). These light-absorbing aerosols are typically organic compounds with large molecular weights, with low volatility and high thermal stability (Sun et al., 2007; Saleh et al., 2018). Chemical speciation analyses have identified several such classes of compounds like nitroaromatic compounds, derivatives of polyaromatic hydrocarbons like quinones and charge transfer complexes of unsaturated organic compounds with transition metals (Phillips and Smith, 2014; Laskin et al., 2015; Lin et al., 2016; Bluvshtein et al., 2017).
The range of experimentally observed OC absorption characteristics—derived for primary OC emissions from a variety of biomass burning sources—span over an order of magnitude. In Figure 1.4, this variability is represented as the range of the imaginary parts ($k$) of OC refractive indices (which are determinants of MAC values) derived from observations of biomass combustion emissions. Cluster A in this figure shows $k$ values for OC released from low-temperature (smoldering/pyrolysis) combustion of biomass (Chakrabarty et al., 2010; Chen and Bond, 2010; Saleh et al., 2013; Li et al., 2016) while cluster B shows those from flaming combustion (Kirchstetter et al., 2004; Saleh et al., 2013; Saleh et al., 2014), that produces BC along with OC. The difference between these clusters shows the dependence between OC absorption efficiency and combustion conditions, specifically the extent to which they favor BC formation (Saleh et al., 2014; Saleh et al., 2018; Cheng et al., 2019). In addition to observations linking combustion-related parameters to OC optical properties, these findings also necessitate the development of a source-linked database of OC MAC (or $k$) under realistic burn conditions. Despite the noted variability, a common feature of OC light absorption is a strong wavelength dependence with preferential absorption in near-UV wavelengths or AAE>2 (Andreae and Gelencsér, 2006; Sun et

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**Figure 1.3:** Continuum of carbonaceous aerosol properties. Source: Pöschl (2003).

<table>
<thead>
<tr>
<th>Thermochemical Classification</th>
<th>Molecular Structure</th>
<th>Optical Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental Carbon (EC)</td>
<td>Graphene Layers (graphitic or turbostratic)</td>
<td>Black Carbon (BC)</td>
</tr>
<tr>
<td>Refractory Organics</td>
<td>Polycyclic Aromatics, Humic-Like Substances, Biopolymers, etc.</td>
<td>Colored Organics</td>
</tr>
<tr>
<td>Non-Refractory Organics (OC)</td>
<td>Low-MW Hydrocarbons and Derivatives (carboxylic acids, etc.)</td>
<td>Colorless Organics (OC)</td>
</tr>
</tbody>
</table>

[Image of the table and diagram]
al., 2007; Laskin et al., 2015). This gives rise to a yellowish-brown appearance (when sampled on a filter medium, shown in Figure 6.3), therefore, light absorbing OC is also termed brown carbon (BrC).

![Figure 1.4: Imaginary part of OC refractive index, at 550 nm wavelength observed from biomass combustion and controlled benzene/toluene combustion. Adapted from Saleh et al. (2018).](image)

1.2. Aerosol light absorption: measurement techniques and models

Aerosol light absorption measurement techniques (detailed review in Moosmüller et al. (2009)) can be broadly classified as \textit{in-situ} (on particles in their native, suspended state) or filter-based (on deposits of particles on a filter substrate). A first-principle method of measuring \textit{in-situ} aerosol light absorption is photoacoustic spectroscopy (PAS), which employs lasers at selected wavelengths to heat the aerosols, in turn heating the surrounding air and causing it to expand, thereby producing a detectable pressure (or acoustic) signal (Arnott et al., 1999). The photoacoustic principle is illustrated in Figure 1.5. The microphone signal can be calibrated against a reference material or a laser power extinction signal to provide an absorption coefficient (m\(^{-1}\)) value. Absorption can also be estimated as the difference between \textit{in-situ} measurements of
extinction and scattering (Schnaiter et al., 2005; Sheridan et al., 2005). Properties of strongly light-absorbing, refractory materials like BC can be measured based on their incandescence under a high power laser beam; this forms the principle of the single particle soot photometer or the SP2 instrument (Stephens et al., 2003; Schwarz et al., 2006).

![Photoacoustic effect diagram](image)

Figure 1.5: The photoacoustic effect showing that the (A) incident radiation absorbed by the particle (B) causes the particle to heat up, in turn (C) heating the surrounding air and generating a (D) pressure disturbance that is detected as a sound wave. Source: Moosmüller et al. (2009).

Alternatively, a commonly adopted technique for estimating light absorption uses measurements of transmittance and/or reflectance for aerosol particles collected on a filter substrate. Instruments based on this technique, including the aethalometer (Hansen et al., 1984) and the Particle Soot Absorption Photometer or PSAP (Virkkula et al., 2005), facilitate semi-continuous sampling of particles and produce time-averaged bulk absorption measurements. Particles may also be collected on a filter substrate and analyzed for their absorption using standalone spectrophotometers (Martins et al., 2009; Zhong and Jang, 2011; Pandey et al., 2016; White et al., 2016). The change in filter transmittance or reflectance due to the deposited particles is a measure of their light absorption. If this change could indeed be entirely attributed to aerosol light
absorption, attenuation of light through the filter medium would be exactly equal to the absorption optical depth of the aerosol deposits.

Filter-based measurements are attractive because of their ease of deployment in field settings and low cost, but they suffer from several artifacts. Particles embedded in a multiple-scattering medium experience a larger optical path length than in their native suspended state, leading to the appearance of enhanced light absorption (Clarke, 1982; Bond et al., 1999; Gorbunov et al., 2002). This is referred to as the multiple scattering artifact and depends on the choice of filter medium. A higher loading of absorbing aerosols can diminish the effect of multiple scattering, inducing an aerosol dependent loading artifact (Weingartner et al., 2003; Arnott et al., 2005). Highly scattering aerosols could enhance multiple scattering and lead to increased backscatter, which leads to an overestimation of absorption (Weingartner et al., 2003; Lack et al., 2008). These artifacts have been evaluated for several commonly used filter-based instruments, such as those aforementioned, by comparing their measurements with contact-free aerosol light absorption measurements or using reference materials with known optical properties. Typically, correction algorithms (detailed in Chapter 5.1) for these artifacts are formulated as functions of some combination of filter and aerosol properties (Weingartner et al., 2003; Arnott et al., 2005; Collaud Coen et al., 2010; Virkkula, 2010) and are specific to a given measurement system.

For homogenous, spherical particles, Maxwell’s equations for scattering and absorption of electromagnetic radiation have been analytically solved, in terms of the vector spherical harmonics of the incident plane wave (Mie, 1908; Bohren and Huffman, 2008). These solutions, known as the Lorenz-Mie theory, enable calculation of absorption and scattering cross-sections as functions of particle size, refractive index and wavelength of incident radiation. The availability of efficient Mie computational codes (Mishchenko and Travis, 2008) and the widespread characterization of
aerosol size in terms of equivalent diameters (based on, for example, electrical mobility and
eaerodynamic behavior) make them easy to implement in radiative transfer codes (Bond et al.,
2013). Therefore, assumptions of spherical morphology are commonly made for BC particles.
Homogenous particles of irregular shapes can be treated by the transition matrix (T-matrix) method
(Mishchenko et al., 2004) in which the relationship between incident and scattered fields is
described by a 2x2 matrix whose elements are computed by numerical integration over the surface
of a particle. The discrete dipole approximation (DDA) involves modeling a particle as a collection
of dipoles that interact with the incident radiation and with each other, making it suitable for even
inhomogeneous particle with irregular morphologies (Purcell and Pennypacker, 1973). One
approach to improving the parameterization of BC in climate models is to connect accurate
modeling of BC in optical calculations with the requirements of the broader aerosol experimental
and modeling research.

1.3. Aerosol emissions in South Asia

Aerosol burden over much of the Indian subcontinent is five times higher than that over developed
countries like the United States, largely because of larger emissions of primary particles and
aerosol-precursors (David et al., 2018). The Indian subcontinent has been termed a spot for
anthropogenic emissions (Ramanathan and Carmichael, 2008). Carbonaceous aerosol burden over
India is linked to surface dimming (Kambezidis et al., 2012), solar warming of the lower
atmosphere (Ramanathan et al., 2001; 2007), changing regional monsoon patterns (Menon et al.,
2002; Chung and Seinfeld, 2005; Ramanathan et al., 2005), and accelerated melting of Himalayan
glaciers (Ramanathan et al., 2007). Particulate matter (PM) emissions—particularly particles with
aerodynamic diameters less than 2.5 µm (PM$_{2.5}$)—are also associated with numerous adverse
consequences for human health (Pope and Dockery, 2006; Pope et al., 2009). The Global Burden
of Disease study has identified indoor air pollution as the largest risk factor and outdoor air pollution as the seventh largest risk factor for disability-adjusted life years in India (Murray et al., 2013). The knowledge of aerosol emissions characteristics like mass emission rates and optical properties for regionally significant sources is crucial for assessing source-specific aerosol radiative (and health) impacts.

The most recent emissions inventory for India indicated that residential biomass cookstoves are the largest contributors to total annual $\text{PM}_{2.5}$, EC and OC emissions (Pandey et al., 2014; Sadavarte and Venkataraman, 2014). In 2010, 67% of Indian households, more than 160 million total, relied primarily on solid fuels for cooking (Census, 2011). The solid fuels included fuel-wood, agricultural residues (like straws and stalks) and dried cattle dung. The above fraction does not capture household in a ‘transition income band’ that use biomass as a secondary fuel (in addition to LPG/kerosene) as a cost-saving measure (Venkataraman et al., 2010). Therefore, the emissions impact of biomass cookstoves is likely larger than current estimates.

Despite several national initiatives to promote the use of improved biomass stoves (Venkataraman et al., 2010), traditional mud stoves (or chulha) and three-stone type brick and metal stoves are commonly used (Kar et al., 2012). Operational challenges and the lack of adequate repair and maintenance services contributed to low user adoption rates of the stoves disseminated under the National Program on Improved Cookstoves (Kishore and Ramana, 2002). Moreover, the in-field emissions performance of the improved cooking devices was found to be similar to that of the traditional stoves (Ramakrishna et al., 1989). Stove performance is characterized by two efficiencies: (1) the combustion efficiency captures how much of the energy content of the fuel is converted to heat and carbon dioxide, and (2) the heat transfer efficiency relates to how much of the heat generated is absorbed by the pot. A third measure, the overall thermal efficiency, is the
fraction of the fuel energy absorbed by the pot: it can be obtained as the product of the first two efficiencies. Traditional cookstoves have low combustion efficiencies, resulting in incomplete combustion and high PM emissions (Smith et al., 2000). The early generation of improved cookstoves distributed in India provided fuel savings by increasing the heat transfer efficiency, through improved insulation of the combustion chamber, but largely failed to deliver emissions reductions. Although a new program, the National Cookstove Initiative was announced to develop and disseminate low-emissions cookstoves (Venkataraman et al., 2010), biomass cooking technology in India can still considered to be predominantly inefficient (Pandey et al., 2014).

Evaluating the contribution of biomass cookstoves to regional pollutant burdens requires the knowledge of their emissions performance, expressed as mass emission factors (g-pollutant kg\(^{-1}\)-fuel). Most of the emission factors used in inventory calculations were from laboratory cookstove tests (Bond et al., 2013; Pandey et al., 2014). These studies largely rely on a water-boiling test (WBT) with high and low power phases for simultaneous measurement of thermal and emissions performance, even if not all cooking actually involves the boiling of water in this manner (Johnson et al., 2009; Chen et al., 2012). There is study-to-study variation in test conditions such as amounts of water boiled, the length and definition of low and high power phases, the moisture content of the fuel, the use of a lid on the pot, the method of measuring emissions and other parameters, yet represent currently best available numbers. Field-based measurements, made during actual cooking processes, indicate significantly worse emissions performance of traditional stoves, than what was previously established through lab testing because of differences in burn rate and firing practice between laboratory and field settings, even for similar fuel characteristics (Roden et al., 2009; Chen et al., 2012; Jayarathne et al., 2018; Weyant et al., 2019). More evaluations of in-use
emissions performance of traditional cookstoves using common South Asian biomass fuels are needed, in addition to inputs for designing realistic laboratory burn cycles.

Discussions of the climate impacts of aerosol emissions from residential biomass use (Venkataraman et al., 2005; Grieshop et al., 2011) largely include only BC as a light absorbing component. Experimental observations (Kirchstetter et al., 2004; Andreae and Gelencsér, 2006; Kirchstetter and Thatcher, 2012; Saleh et al., 2014; Saleh et al., 2018) and recent modeling studies (Chung et al., 2012; Feng et al., 2013; Wang et al., 2014) indicate the potential significance of light absorbing OC to radiative forcing estimation. Accounting for light absorbing OC in radiative models may be a step towards resolving the factor of ~6 underestimation (Bond et al., 2013; Gustafsson and Ramanathan, 2016) of aerosol absorption optical depth over South Asia by climate models, in comparison with ground-based observation of the same. Estimating representative OC MAC values for cookstove emissions, to serve as inputs to climate models, is crucial for addressing the model bias.
References


Kishore, V. and Ramana, P.: Improved cookstoves in rural India: how improved are they?: A critique of the perceived benefits from the National Programme on Improved Chulhas (NPIC), Energy, 27, 47-63, 2002.


Chapter 2: Research objectives

My first research objective was to aid accurate morphological representation of black carbon in optical parameterizations, bridging the gap between optical models that explicitly handle the fractal morphology of BC aggregates and radiative transfer models that assume spherical morphology for all aerosols. Optical models that account for BC morphology are (1) able to predict BC MAC values very close to the average of those experimentally observed and (2) demonstrate that an equivalent sphere of the same mass or a group of non-interacting individual spherules show very large deviations from these ideal predictions (Liu and Mishchenko, 2007; Liu et al., 2008; Sorensen et al., 2018). However, radiative modules within global climate models do not include computationally-expensive, detailed morphological representations and may opt to scale optical calculations to match observations (Bond et al., 2013). Further, observations of BC size distribution are based on common aerosol sizing instruments; descriptors of fractal size and shape can only be measured using more sophisticated techniques, like small-angle light scattering (Heinson et al., 2016). To surmount these obstacles, I developed empirical relationships between BC optical cross-sections and widely used equivalent diameters. These results, discussed in Chapter 3.1, have been reported in Pandey et al. (2015). A second goal was to test the validity of the prevalent relationships between scattering directionality parameters of BC (Moosmüller and Ogren, 2017). These relationships are based on an analytical approximation of the angular distribution of radiations scattered by (any type of) particles: the Henyey-Greenstein phase function (Henyey and Greenstein, 1941). In Pandey and Chakrabarty (2016), I examined the errors
associated with using the above relationships for estimating scattering directionality of BC aggregates (Chapter 3.2).

Given the magnitude of particulate pollution in India and the bias in the modeled values of aerosol light absorption in this region (modeled values are much smaller than observations), it is crucial to assess which model inputs can be improved. I focused on the largest source of primary particle emissions in India: residential biomass cookstoves. My second research objective was to estimate aerosol emission factors from field study of cookstove emissions in India. Mass-based emission factors are critical inputs to inventory models which are then used to calculate pollutant burdens. A small number of field observations showed that laboratory cookstove studies (which formed the bulk of the observations included in inventory models) significantly underestimate particle emission rates. In Chapter 4, I report PM$_{2.5}$, EC and OC emission factors from a field study of common biomass fuels in India (Pandey et al., 2017). One goal was to determine the emissions performance of a traditional stove, using fuels locally scavenged from regions that have large biomass user populations, during real-world operation that involved preparing common meal items. Another was to examine the relationship between emission factors and (1) fuel-type and (2) the stage of combustion (ignition or fueling, flaming, smoldering). This can inform future studies by identifying factors that control emissions behavior: for example, whether it is necessary to speciate emissions by (and therefore perform measurements on) a large variety of fuel types.

To utilize the filter samples of cookstove emissions from the aforementioned field study for estimating the absorption characteristics of these emissions, I used filter-based ultraviolet-visible (UV-vis) spectroscopy. The artifacts involved in estimating aerosol phase light absorption from filter optical measurements are instrument specific: published correction schemes apply only to a limited number of instruments. Much of the artifact correction literature deals with the scattering
effects of inorganic aerosols (Bond et al., 1999; Weingartner et al., 2003; Arnott et al., 2005; Virkkula, 2010) and the validity of these schemes has not been tested for liquid-like organics (Subramanian et al., 2007) that spread on filter fibers. Finally, these correction methods require an independent measurement of aerosol light scattering concurrent with filter sampling. Therefore, my third objective involved estimating aerosol-phase light absorption from filter-based optics using a correction scheme applicable to biomass burning aerosols, potentially without the need for scattering observations (Chapter 5). The requisite experimental plan involved generating combustion aerosols with a wide range of intrinsic properties (therefore, representative of various types of biomass burning) and allowing for comparison between in-situ (PAS based) and filter optical properties. A radiative transfer model of the filter-particle system supplemented experimental findings and a measurement method capable of meeting the above requirements was identified (Pandey et al., 2019).

Few studies report MAC values of cookstove particulate emissions, fewer still attribute the total absorption to BC and OC. This poses a challenge in expanding the conventional discussion of aerosol climate impacts where OC light absorption is neglected. In Chapter 6, I describe my final objective: constraining the contribution of organic carbon to light absorption by cookstove emissions. First, I discuss initial estimates of OC absorption properties based on a preliminary round of sampling (prior to the more comprehensive field study) cookstove emissions in India, in the context of the challenges inherent to this analysis (Pandey et al., 2016). The methods used then were later updated to reflect the improvements in filter artifact correction and applied to the field study samples. Assumptions on the spectral behavior of BC (its AAE value) also required updating, based on observations and models of coated BC aggregates (Gyawali et al., 2013; Liu et al., 2018). With a range of probable values of $\text{AAE}_{\text{BC}}$, MAC and AAE for cookstove emitted OC
were constrained. Another goal of this research was to examine the contribution of OC to direct radiative forcing associated with cookstove emissions. Though the estimation of the magnitude forcing efficiency requires scattering cross-sections—not measured in my work—in addition to absorption, the portion of forcing efficiency attributable of OC light absorption can be well-constrained independent of any assumptions regarding scattering. These calculations indicate that OC light absorption could likely tip the net direct radiative impact of cookstove emissions from cooling to warming.
References


Pandey, A., Pervez, S., and Chakrabarty, R. K.: Filter-based measurements of UV–vis mass absorption cross sections of organic carbon aerosol from residential biomass combustion:


Chapter 3: Accurate morphological representation of BC in optical parameterizations

Black carbon, also known as soot, is formed from high-temperature, incomplete combustion of a variety of fuels. In a typical combustion system, BC particles are first formed as spherical monomers (30-50 nm diameter) from the condensation of polyaromatic hydrocarbon precursors, after which they undergo Brownian collisions in 3-dimensional (3-d) space to form clusters of monomers (hereafter referred to as “aggregates”) (Chakrabarty et al., 2014). This aggregate formation mechanism is now well studied as the Diffusion Limited Cluster Aggregation (DLCA) process (Sorensen, 2001; Chakrabarty et al., 2014). The resulting non-spherical morphology of the BC aggregates (interchangeably referred to as soot aggregates or SA) can be represented by the fractal scaling law for length-scales much greater than the monomer size (Sorensen et al., 1992; Liu et al., 2008; Chakrabarty et al., 2014):

\[
N = k_o \times \left( \frac{R_g}{r_o} \right)^{D_f}
\]

(3.1)

where \(N\) is the number of particles enclosed within a radius of gyration \(R_g\), \(r_o\) is the average monomer radius, \(D_f\) is the non-integral fractal dimension, and \(k_o\) is a constant prefactor. Thus, the structure of fractal aggregates can be completely defined using the parameters \(D_f\) and \(k_o\), which quantify the aggregate geometry and packing factor of monomers, respectively (Wu and Friedlander, 1993). Both parameters are governed by the aggregate formation mechanism and the
aging processes encountered in the atmosphere (Zhang et al., 2008). Fresh aggregates formed by
the DLCA mechanism have been universally observed to yield $D_f$ and $k_o$ values of $\approx 1.8$ and 1.2,
respectively (Sorensen et al., 1992; Chakrabarty et al., 2014). After release into the atmosphere,
BC could change their morphology owing to atmospheric processing to form more compact, near-
spherical structures with a $D_f \approx 2.6$ [1].

BC particles are important drivers of climate change: they are strong visible-light absorbers, affect
cloud formation and associated properties and alter the albedo of ice. Uncertainty in the radiative
forcing estimates due to these particles plagues current climate models (Liu et al., 2008; Bond et
al., 2013). Estimation of forcing from aerosols requires knowledge of their intrinsic optical
properties—single scattering albedo ($\omega$) and asymmetry parameter ($g$) or upscatter fraction ($\beta$) as a
function of wavelength (Chakrabarty et al., 2014). The value of $\omega$ is a measure of brightness; it is
0 for a perfectly absorbing particle and 1 for a perfectly scattering particle. At a given wavelength,
$\omega$ is defined as the ratio of the scattering cross-section ($C_{scat}$) to extinction cross-section, which is
the sum of scattering and absorption ($C_{abs}$) cross-sections. The directionality of aerosol light
scattering is represented in aerosol radiative transfer models using single-valued parameters—$\beta$ or
$g$ (Wiscombe and Grams, 1976; Chylek and Wong, 1995; Bond and Bergstrom, 2006).

The following analytical expression (Bond and Bergstrom, 2006) describes the direct radiative
forcing efficiency (termed simple forcing efficiency or SFE), per unit aerosol mass:

$$\frac{dSFE}{d\lambda} = - \frac{1}{4} \frac{dS(\lambda)}{d\lambda} \tau_{atm}(\lambda)(1 - F_c) \times [2(1 - a^2)\beta(\lambda)MSC(\lambda) - 4a_s MAC(\lambda)]$$  \hspace{1cm} (3.2)

where $dS(\lambda)/d\lambda$ is the spectral solar irradiance, $\tau_{atm}$ is the atmospheric transmissivity (typically
fixed at 0.79), $F_c$ is the cloud cover fraction (fixed at 0.6), $a_s$ is the surface albedo (0.19 earth
average), $\beta$ is the value of upscatter fraction, MSC is the mass scattering cross-section and MAC is
the mass absorption cross-section ($C_{scat}$ and $C_{abs}$, respectively, normalized to the mass of the
particle). Average values for MSC and MAC of freshly emitted BC particles are 2.5 and 7.5 m$^2$/g, respectively, at 550 nm wavelength (Bond and Bergstrom, 2006; Chen, 2011). This calculation (with the prescribed values of $\tau_{atm}$, $F_c$ and $a_s$ above) provides a reasonable approximation of top-of-the-atmosphere aerosol forcing under clear sky conditions (Moosmüller et al., 2009). The simplicity of this approximation lends itself to investigating the sensitivity of forcing to one or more of the aerosol properties.

Radiative transfer calculations made within climate models use more sophisticated forcing estimates than equation 3 but the same fundamental absorption and scattering (including directionality of scattering) properties are calculated in their aerosol optical models. Global models do not treat the morphological complexity of BC particles and employ a spherical approximation, despite significant discrepancies between MAC and MSC values predicted for spherical BC and those estimated from direct measurements (Bond et al., 2013).

### 3.1. BC optical properties as functions of measurable equivalent diameters

Current radiative transfer models usually approximate BC aggregates as equivalent spheres and use Lorenz-Mie analytical solutions for estimating their radiative properties. The aggregate structure of BC leads to interactions in the scattering and absorption behavior of neighboring monomers, which cannot be captured by the classical Lorenz-Mie theory (Liu et al., 2009; DeCarlo et al., 2004). Several studies conducted in recent years take into account the fractal nature of BC and calculate its numerically-exact optical properties (Liu et al., 2008; Moosmüller et al., 2009; Mishchenko et al., 2010). The absorption cross-section of a fractal soot aggregate (freshly emitted, $D_f=1.8$) is roughly 1.12-1.3 times that of a corresponding number of externally-mixed monomers but could be 0.85-1.5 times that of a volume equivalent sphere (Liu and Mishchenko, 2005b; Liu
et al., 2008). These discrepancies are much more exaggerated in the scattering cross-section and scattering directionality of aggregates. Without exception, the studies discussed above calculated the optical properties as a function of aggregate $D_f$ and $N$. Although these results highlight the stark differences in optical properties between spherical and fractal morphology, they are ultimately found to be unusable by aerosol experimentalists and climate modelers in their research. Common instruments used for measuring equivalent aerosol diameters include the Scanning Mobility Particle Sizer (SMPS), the Single Particle Soot Photometer (SP2), and the Soot Particle - Aerosol Mass Spectrometer (SP-AMS). The SMPS, which is the most widely used aerosol size characterization instrument, measures a number size distribution for aerosols based on their electrical motilities (DeCarlo et al., 2004). It measures the particle mobility diameter, $d_m$, which is the diameter of a sphere having the same electrical mobility as that of an unknown particle. The SP2, on the other hand, calculates a mass equivalent diameter, $d_{me}$, for BC aggregates by measuring the visible-range radiation emitted from the refractory fraction of carbon in a particle as it is heated to its boiling point (Laborde et al., 2012). The SP-AMS is a combination of time-of-flight aerosol mass spectrometer (ToF AMS) and the SP2, and measures the vacuum aerodynamic diameter $d_{va}$ of a particle (Onasch et al., 2012). This diameter is defined as the diameter of a sphere with a density of 1 kg/m$^3$ and has the same settling velocity as the investigated non-spherical particle in the free-molecular regime (DeCarlo et al., 2004; Lindskog and Nordin, 2009). The motivation behind this work was to provide simple mathematical formulations connecting numerically-exact optical properties of BC aggregates and their measurable equivalent diameters.

3.1.1. Relationships between fractal parameters and equivalent diameters of aggregates

Computer simulation of a statistically significant number of 3-d BC aggregates with $D_f=1.8$ and 2.6, mimicking freshly-emitted and atmospherically aged BC particles, respectively, were first
performed. The prefactor $k_o$ in our simulations was fixed at 1.19 per past recommendation (Sorensen and Roberts, 1997). For each $D_f$, at least one hundred aggregates were generated with $N$ chosen randomly between 10 and 300 for each aggregate. A soot monomer diameter of 50 nm, typically observed in real-world particles (Liu et al., 2008), was used in our calculations. Each 3-d aggregate was oriented in 25 random orientations, with ~15 orientations, on an average, identified to be stable. For every identified stable orientation, three aggregate equivalent diameters – $d_m$, $d_{me}$ and $d_{Va}$ – were calculated. The $d_m$ of an aggregate, in the transition flow regime, is equal to its stably-oriented projected area equivalent diameter as estimated from electron microscopy images (Park et al., 2004). Following this observation, $d_m$ size distributions for our simulated aggregates were calculated from their stably-oriented projected images. The $d_{me}$ of an aggregate was calculated as:

$$d_{me} = d_{mono} \times N^{1/3}$$  \hspace{1cm} (3.3)

where $d_{mono} (= 50 \text{ nm})$ is the diameter of monomers and $N$ is the number of primary particles of an aggregate. The aggregate vacuum aerodynamic diameter $d_{Va}$ was calculated using the established equation (DeCarlo et al., 2004):

$$d_{Va} = \frac{\rho_p}{\rho_o} \times \frac{d_{ve}}{\chi}$$  \hspace{1cm} (3.4)

where $\rho_p$ is the particle density (1.8 kg/m$^3$ for BC: (Bond et al., 2013)), $\rho_o$ is the standard density (1 kg/m$^3$), $d_{ve}$ is the volume equivalent diameter and $\chi$ is the dynamic shape factor in the free-molecular regime. In this work, $d_{ve}$ was assumed to be equal to $d_{me}$, implying that the aggregates do not have any internal voids (DeCarlo et al., 2004). This is a reasonable assumption for chain-like freshly-emitted BC, but aged BC may have up to 10% internal voids (Bond and Bergstrom, 2006). The dynamic shape factor $\chi$, in a given flow regime, is a measure of the increase in drag
force because of the non-spherical shape of the aggregate. The general expression for the shape factor for any flow regime is obtained as (DeCarlo et al., 2004):

\[ \chi = \frac{d_m}{d_{ve}} \times \frac{C(Kn_{ve})}{C(Kn_m)} \]  

(3.5)

Here \( C \) is the Cunningham slip correction factor and \( Kn_{ve} \) and \( Kn_m \) are the Knudsen numbers corresponding to \( d_{ve} \) and \( d_m \), respectively. A mean free path of 4 m, representative of the high vacuum (10\(^{-3}\) to 10\(^{-4}\) Pa) region at the end of the expansion zone in an AMS (DeCarlo et al., 2004), was used for calculating \( \chi \) using Equation (3.5).

The calculated mean values of the three aerosol equivalent diameters are presented in Table 3.1. While \( d_{me} \) of an aggregate is independent of its \( D_f \), the \( d_m \) values are observed to be decreasing with increasing \( D_f \). This decrease becomes significant (as much as 25%) with increasing \( N \). An explanation of this phenomenon is that \( D_f = 1.8 \) aggregates are open-ended fractals, which yield a larger 2-d projected area and \( d_m \) compared to the more collapsed and compact structured \( D_f = 2.6 \) aggregates. An alternate way of stating this is that \( D_f = 1.8 \) aggregates experience more drag force and therefore have lower mobility, which translates to a larger equivalent sphere diameter. From the perspective of drag force, \( D_f = 1.8 \) aggregates have smaller terminal velocities, which results in smaller \( d_{Va} \) than those of \( D_f = 2.6 \) aggregates for a fixed \( N \). This effect of drag force on an aggregate is captured by the shape factor \( \chi \) (Equation 3.5), which is a direct measure of the increase in drag force for a particle with its structural departure from spherical shape.
Table 3.1. Estimated equivalent aerosol diameters (nm) for fresh and aged soot aggregates as a function of monomer number (N)

<table>
<thead>
<tr>
<th>N</th>
<th>Mobility diameter(^1) (nm)</th>
<th>Mass equivalent diameter(^2) (nm)</th>
<th>Vacuum aerodynamic diameter(^1) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh soot ((D_f=1.8))</td>
<td>Aged soot ((D_f=2.6))</td>
<td>Fresh and aged soot</td>
</tr>
<tr>
<td>5</td>
<td>114±0.6</td>
<td>105±4.2</td>
<td>85</td>
</tr>
<tr>
<td>10</td>
<td>151±4.8</td>
<td>135±6.2</td>
<td>107</td>
</tr>
<tr>
<td>25</td>
<td>227±8.4</td>
<td>198±10</td>
<td>146</td>
</tr>
<tr>
<td>50</td>
<td>317±10.5</td>
<td>260±7.5</td>
<td>184</td>
</tr>
<tr>
<td>100</td>
<td>427±7.0</td>
<td>341±12</td>
<td>232</td>
</tr>
<tr>
<td>150</td>
<td>531±15</td>
<td>402±5.0</td>
<td>265</td>
</tr>
<tr>
<td>200</td>
<td>605±18.6</td>
<td>455±28</td>
<td>292</td>
</tr>
<tr>
<td>250</td>
<td>663±15.4</td>
<td>489±20</td>
<td>315</td>
</tr>
<tr>
<td>300</td>
<td>703±44</td>
<td>530±12</td>
<td>333</td>
</tr>
</tbody>
</table>

\(^1\) All values given as mean+95% confidence intervals
\(^2\) No standard deviation is associated with the mass equivalent diameter for a known \(N\) and \(D_f\)

3.1.2. Numerically estimated optical cross-sections and asymmetry parameter

The numerically-exact superposition transition matrix \((T\)-matrix\) method (Liu et al., 2008; Moosmüller et al., 2009) was used to determine the scattering and absorption cross-sections \((C_{scat}\) and \(C_{abs}\), respectively) and asymmetry parameter \((g)\), of the simulated aggregates as a function of \(N\) and \(D_f\). This method expresses the incident and transmitted fields as series of vector spherical functions. The relationship between the incident and transmitted electromagnetic field is captured by a 2 x 2 transition super matrix \((or the T\)-matrix\), which is a function of the intrinsic properties of the particle and the coordinate system (Mackowski and Mishchenko, 1996a; Mishchenko et al., 2002; Moosmüller et al., 2009). Each element of the matrices within this super matrix is calculated by numerically integrating the vector spherical functions of the incident and scattered fields over the particle surface. Past computational investigations conducted using this method have shown that \(D_f\) is an important parameter for accurately estimating the optical properties of an aggregate (Liu and Mishchenko, 2005a). Interactions between the monomers are significant for chain-like structures and become even more important as aggregates age and form closely packed compact
structures (Liu et al., 2008). A complex refractive index of 1.95–0.79i was chosen for the soot monomers in this work following the recommendation of Bond and Bergstrom for atmospherically relevant BC aggregates (Bond and Bergstrom, 2006).

Relationships between optical properties and equivalent aerosol diameters were determined using a non-linear least squares optimization technique known as the Trust-Region-Reflective Least Squares, implemented using the MATLAB Curve Fitting Toolbox. The goodness of fit for these equations is characterized by adjusted R-squared ($R^2$) and Root Mean Square Error (RMSE). Empirical equations correlating the numerically-exact aggregate optical properties $C_{\text{scat}}$, $C_{\text{abs}}$ and $g$ with the three aerosol diameters, $d_m$, $d_{Va}$, and $d_{me}$ are reported for fresh ($D_f$ = 1.8) and aged ($D_f$ = 2.6) BC (Tables 3.2-3.4). The aggregate optical cross-sections exhibit simple power-law dependencies on the equivalent aerosol diameters. For correlating $g$, simple polynomial functional forms were found give the best fits to the data. At minimum, all the equations fits satisfy adjusted $R^2 \geq 0.86$ and RMSE < 0.03.

Table 3.2. Best fit empirical equations connecting the mobility diameter, $d_m$ (in μm) and the optical properties of fresh and aged SA.

<table>
<thead>
<tr>
<th>Optical property</th>
<th>Fresh SA ($D_f$ =1.8)</th>
<th>Aged SA ($D_f$ =2.6)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Equation</td>
<td>Adjusted $R^2$</td>
</tr>
<tr>
<td>$C_{\text{scat}}$</td>
<td>$0.24 \times (d_m^{2.8})$</td>
<td>0.998</td>
</tr>
<tr>
<td>$C_{\text{abs}}$</td>
<td>$0.4 \times (d_m^{2.1})$</td>
<td>0.998</td>
</tr>
<tr>
<td>$g$</td>
<td>$-1.94 \times d_m^2 + 2.51 \times d_m - 0.13$</td>
<td>0.993</td>
</tr>
</tbody>
</table>
Table 3.3. Best fit empirical equations connecting the mass equivalent diameter, $d_{me}$ (in μm) and the optical properties of fresh and aged SA.

<table>
<thead>
<tr>
<th>Optical property</th>
<th>Fresh SA ($D_f$=1.8)</th>
<th>Aged SA ($D_f$ =2.6)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Equation</td>
<td>Adjusted $R^2$</td>
</tr>
<tr>
<td>$C_{scat}$</td>
<td>$5.83 \times (d_{me}^{3.76})$</td>
<td>0.999</td>
</tr>
<tr>
<td>$C_{abs}$</td>
<td>$5.83 \times (d_{me}^{3.76})$</td>
<td>1</td>
</tr>
<tr>
<td>$g$</td>
<td>$-9.77 \times d_{me}^2 + 6.32 \times d_{me} - 0.35$</td>
<td>0.995</td>
</tr>
</tbody>
</table>

Table 3.4. Best fit empirical equations connecting the vacuum aerodynamic diameter, $d_{va}$ (in μm) and the optical properties of fresh and aged SA.

<table>
<thead>
<tr>
<th>Optical property</th>
<th>Fresh SA ($D_f$=1.8)</th>
<th>Aged SA ($D_f$ =2.6)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Equation</td>
<td>Adjusted $R^2$</td>
</tr>
<tr>
<td>$C_{scat}$</td>
<td>$2.9 \times 10^6 \times (d_{va}^{8.61})$</td>
<td>0.863</td>
</tr>
<tr>
<td>$C_{abs}$</td>
<td>$4.43 \times 10^5 \times (d_{va}^{7.36})$</td>
<td>0.863</td>
</tr>
<tr>
<td>$g$</td>
<td>$-112.7 \times d_{va}^2 + 38.12 \times d_{va} - 2.38$</td>
<td>0.922</td>
</tr>
</tbody>
</table>

Figures 3.1-3.3 show the best fit curves for the relationship between aggregate optical properties and equivalent diameters. These plots are typically non-linear, owing to the complex electromagnetic interactions between the point-contacting monomers in an aggregate.

![Graphs](image_url)

Figure 3.1: Variation of (a) $C_{scat}$ (μm²), (b) $C_{abs}$ (μm²), and (c) $g$, with mobility diameter, $d_m$ (μm) of soot aggregates with $D_f$ equal to 1.8 (fresh) and 2.6 (aged).
Figure 3.2: Variation of (a) $C_{\text{scat}}$ ($\mu$m$^2$), (b) $C_{\text{abs}}$ ($\mu$m$^2$), and (c) $g$, with mass equivalent diameter, $d_{me}$ ($\mu$m) of soot aggregates with $D_f$ equal to 1.8 (fresh) and 2.6 (aged).

Figure 3.3: Variation of (a) $C_{\text{scat}}$ ($\mu$m$^2$), (b) $C_{\text{abs}}$ ($\mu$m$^2$), and (c) $g$, with vacuum aerodynamic diameter, $d_{va}$ ($\mu$m) of soot aggregates with $D_f$ equal to 1.8 (fresh) and 2.6 (aged).

From Figure 3.1, it can be seen that the aggregate optical cross-sections of aged BC aggregates have a steeper variation with mobility diameter compared to those of fresh BC. As aggregate $D_f$ changes from 1.8 to 2.6, the aggregate morphology becomes more compact giving rise to intensification of monomer-monomer electromagnetic wave interactions. This manifests as a non-linear change in the aggregate scattering cross-sections and directionality which in turn affects the $\omega$ and $g$ values. It must be noted that for a given value of $d_m$, an aged SA would contain a larger number of monomers (see Table 3.1), or a larger amount of material that can scatter and absorb light, than a fresh SA. This effect is partly responsible for the large gap between the fresh and aged SA curves in Figure 3.1. On the other hand, $d_{me}$ is only a function of $N$ and therefore the fresh and
aged SA curves in Figure 3.2 only reflect the increase in monomer-monomer interaction with aging. This significantly affects $C_{scat}$ and $g$, while the change in $C_{abs}$ due to aging is very small. The variation of optical properties with $d_{Va}$ is steeper for fresh SA than for aged SA (Figure 3.3), because a given value of $d_{Va}$ corresponds to a larger number of monomers for a fresh SA than for an aged SA (Table 3.1). We found that for fresh SA, optical properties are not as strongly correlated with $d_{Va}$ as they are with $d_m$ and $d_{me}$. For fresh SA, $d_{Va}$ shows a non-monotonic variation with $N$, wherein the same value of $d_{Va}$ could correspond to two different values of $N$. In contrast, the investigated optical properties monotonically increase with $N$. This leads to a many-to-one relationship between optical properties and $d_{Va}$, resulting in relatively lower $R^2$ values for fresh SA (Table 3.4).

It should be noted that variations in refractive index of BC could alter the reported empirical relationships, especially for mass-equivalent aerosol diameter. Also noteworthy to mention is that freshly-emitted BC may have variations in their fractal prefactors, while aged BC may be hydrophilic in nature thereby resulting in different composition and/or surface structures than those simulated in this study. The fractal generation methodology and $T$-matrix calculations used in this work do not account for this effect. A thorough sensitivity analysis of varying fractal parameters and refractive index on the equivalent diameter and optical properties of BC is needed. Future work is also needed to investigate the influence of monomer overlap and sintering in comparison to point-contacting (as done in this study) on the variation in optical properties.

3.2. Relationships between scattering directionality parameters for BC aggregates

Scattering directionality parameters are condensed representations of the scattering phase function $S_{11}$ of the aerosol system under study (illustrated in Figure 3.5). The Henyey-Greenstein (HG)
phase function (Henyey and Greenstein, 1941b; Marshall et al., 1995) is a simple, analytical function that is widely used for calculating and relating these parameters for atmospheric aerosols (Sagan and Pollack, 1967; Wiscombe and Grams, 1976; Sheridan and Ogren, 1999; Andrews et al., 2006). It does not explicitly take particle size and shape into consideration. Experimentally, the aerosol backscatter fraction \( b \) is measured using a nephelometer, and using the HG phase function relationships, approximate values of \( g \) and \( \beta \) are estimated. Alternatively, for spherical particles, \( g \) can be calculated using Mie theory for a known particle size (or size distribution) and refractive index. Improving the representation of radiative properties for BC particles in climate models and satellite retrieval algorithms has been an ongoing effort (Bond et al., 2013). Revising the approximate relationships between their \( g, \beta \) and \( b \) parameters with more accurate ones is a step towards that direction.

![Illustration of a scattered waveform and the scattering angle relative to the incident radiation.](image)

Figure 3.4: Illustration of a scattered waveform and the scattering angle relative to the incident radiation.

### 3.2.1. The scattering phase function and definitions of scattering directionality

The Stokes scattering matrix for a particle is a black representation of the relationship between the incident field and scattered field, as a function of the scattering angle (Mishchenko et al., 1996).
The first element of the matrix, that is $S_{11}$, satisfies the following normalization condition (Wiscombe and Grams, 1976):

$$\frac{1}{2} \int_{0}^{\pi} S_{11} (\theta) \sin \theta \, d\theta = 1$$

(3.6)

where $\theta$ is the scattering angle.

In this study, we examined the variations in $\beta$, $g$ and $b$ with BC aerosol morphology, for particle sizes and shapes typically found in the atmosphere. We used the numerically exact superposition $T$-matrix method to perform quantitative calculation of these parameters for simulated BC aggregates with varying mass fractal dimensions $D_f$ (Mackowski and Mishchenko, 1996b; Mishchenko et al., 1996; Liu and Mishchenko, 2005b, 2007). We performed several simulations for generating aggregates with varying $N$ and monomer diameter $d$. We assigned a range of values for the complex refractive index, $m$, of these aggregates based on past recommendations for atmospheric BC (Bond and Bergstrom, 2006). The choice of the wavelength of incident light was 550 nm, the peak of the visible solar spectrum.

Figure 3.6 shows the normalized $S_{11}$ for $D_f = 1.9$ aggregates with varying values of $d$, $N$, and $m$. Increasing $d$ or $N$, both of which correspond to an increase in the overall aggregate size, results in higher values of the $S_{11}$ peak, or the near-forward scattering intensity. The $S_{11}$ curves converge around scattering angle of 60°. By varying $m$, the normalized angular distribution of scattered radiation is unaltered. This behavior could be explained by the fact that scattering directionality is predominantly affected by variations in particle size and shape, and not $m$ (Marshall et al., 1995; Liu and Mishchenko, 2005b). A similar invariant behavior of $S_{11}$ was also observed for $D_f = 3.0$ aggregates (not shown here). Therefore, we excluded $m$ as a varying parameter and fixed its value at 1.95-0.79i for all future analyses (Bond and Bergstrom, 2006).
Figure 3.5: Normalized phase function $S_{11}$ at 550 nm wavelength for $D_t = 1.9$ black carbon aggregates with varying (A) monomer diameter, (B) number of monomers, and (C) refractive index. For (A) and (B), the refractive index was fixed at $1.95 - 0.79i$. For (B) and (C), the monomer diameter was fixed at 50 nm. For (A) and (C), the number of monomers was fixed at 32.

The $\beta$ values our simulated aggregates can be estimated from the following definition:

$$\beta = \int_0^\pi \beta_{\theta_0} \sin \theta_0 \, d\theta_0$$

where $\beta_{\theta_0}$ is the fraction of solar radiation scattered towards the upward hemisphere for a solar zenith angle of $\theta_0$ and is a function of $S_{11}$ as (Wiscombe and Grams, 1976; Schwartz, 1996):
\[
\beta_{\theta_0} = \frac{1}{2\pi} \int_{\frac{\pi}{2} - \theta_0}^{\frac{\pi}{2} + \theta_0} S_{11}(\theta) \sin \theta \cos^{-1}(\cot \theta_0 \cot \theta) \, d\theta + \frac{1}{2} \int_{\frac{\pi}{2} + \theta_0}^{\pi} S_{11}(\theta) \sin \theta \, d\theta
\]  
(3.8)

Note that \( b \) equals \( \beta \) for the case of zero solar zenith angle. The values of \( g \) and \( b \) were calculated using equations 3.9 and 3.10, respectively (Wiscombe and Grams, 1976; Andrews et al., 2006):

\[
g = \frac{1}{2} \int_0^{\pi} S_{11} \sin \theta \cos \theta \, d\theta
\]  
(3.9)

\[
b = \beta(\theta_0 = 0) = \frac{1}{2} \int_{\frac{\pi}{2}}^{\pi} S_{11} \sin \theta \, d\theta
\]  
(3.10)

### 3.2.2. The Henyey-Greenstein phase function

An approximate analytical expression for the angular distribution of light scattered by interstellar dust was developed by Henyey and Greenstein (1941b) and is widely used in atmospheric sciences for deriving the desired particle light-scattering directionality parameter from a measurement (\( b \)) or a modeled value (\( g \)). This phase function \( P_{HG}(\theta) \) describes the angular distribution of the scattered light with the asymmetry parameter, \( g \), as (Henyey and Greenstein, 1941a; Marshall et al., 1995; Boucher, 1998a)

\[
P_{HG}(\theta) = \frac{1-g^2}{(1+g^2-2g \cos \theta)^{3/2}}
\]  
(3.11)

From equation 3.10 (plugging in \( P_{HG} \) as \( S_{11} \)), \( b_{HG} \) can be calculated as a function of \( g \). However, this function cannot be inverted to yield an explicit function for calculating \( g \) as a function of \( b \) (as would be required in practice. Instead, a third-order polynomial approximation for the inverse relationship is typically used (Andrews et al., 2006):

\[
g_{HG} = 7.143889b^3 + 7.464439b^2 - 3.9635b + 0.9893
\]  
(3.12)
Similarly, Sheridan and Ogren (1999) have integrated the HG phase function to compute $\beta_{HG}$ and $b_{HG}$ (per equations 3.8 and 3.10, respectively) and provided a second-order polynomial to calculate the former in terms of the latter parameter:

$$\beta_{HG} = -2.9682b^2 + 1.8495b + 0.0817 \quad (3.13)$$

Finally, the following approximate relationship is available to calculate $\beta_{HG}$ as a function of $g_{HG}$ (Sagan and Pollack, 1967):

$$\beta_{HG} = \frac{(1-g_{HG})}{2} \quad (3.14)$$

Previous evaluations of the HG phase function (Marshall et al., 1995; Boucher, 1998b) for spherical particles have indicated discrepancies between asymmetry parameters derived using the phase function ($g_{HG}$ from measured $b$) and those calculated using Mie theory for a measured size distribution.
3.2.3. Empirical relationships between the scattering directionality parameters

Scatter plots of $g$ versus $b$, and $\beta$ versus $b$ are shown for varying values of $d$ (Figure 3.7) and $N$ (Figure 3.8). For values of $d$ between 40-70 nm, the relationships between $g$ and $b$, and $\beta$ and $b$ are nearly linear for both $D_f = 1.9$ and 3.0 aggregates. For $D_f = 3.0$ aggregates, with increasing $N$, $g$ increases; while $\beta$ decreases in an approximately linear fashion with increasing $b$. Contrarily, for $D_f = 1.9$ aggregates, the relationships of $g$ and $\beta$ with $b$, for different values of $N$, are non-linear, and not one-to-one. Consistent with our findings, previous $T$-matrix calculations for BC aggregates (Liu and Mishchenko, 2005b) have shown that $g$ increases with increasing $N$ for $N \leq 100$, beyond which the value of $g$ saturates. Expectedly, $\beta$ and $b$ also show a similar behavior.

![Figure 3.6: Scatter-plots of asymmetry parameter, g (panels A, C), and upscatter fraction, $\beta$ (panels B, D), versus hemispherical backscattering fraction, $b$, for $D_f = 1.9$ and $D_f = 3$ aggregates, with varying monomer diameters. The number of monomers, refractive index and wavelength were fixed at 32, 1.95-0.79i, and 550 nm, respectively.](image-url)
Figure 3.7: Scatter-plots of asymmetry parameter, $g$ (panels A, C), and upscatter fraction, $\beta$ (panels B, D), versus hemispherical backscattering fraction, $b$, for $D_f = 1.9$ and $D_f = 3$ aggregates, with varying number of monomers. The monomer diameter, refractive index and wavelength were fixed at 50 nm, 1.95-0.79i, and 550 nm, respectively.

In Figure 3.9, we show the relationships between $g$ and $b$ (panel A), $\beta$ and $b$ (panel B), and $\beta$ and $g$ (panel C) calculated using $T$-Matrix for all aggregates simulated in this study. The $g_{HG}$ and $\beta_{HG}$ values obtained using equations 3.12-3.14 are plotted for comparison purposes. Values of $g$ calculated using the HG phase function agree very well (within 5%) with those calculated using $T$-matrix for $0.4 > b > 0.2$. For $b < 0.2$, use of equation 3.12 over-predicts $g$ values by 5-10% for $D_f = 3.0$ aggregates, it under-predicts them for $D_f = 1.9$ aggregates. For $D_f = 3$ aggregates, we propose the following empirical expression for predicting the value of $g$ for $0 \leq b < 0.4$ (with an adjusted-$R^2$ of 0.9988):

$$g = 0.9686b^2 - 2.021b + 0.8055$$  \hspace{1cm} (3.15)$$

We find that equation 3.13 under-predicts $\beta$, by up to 25%, for $D_f = 3$ aggregates. A better relationship between $\beta$ and $b$ for these aggregates is (adjusted-$R^2$ of 0.9959):
\[ \beta = -0.5582b^2 + 0.8973b + 0.1723 \]  

(3.16)

For \( D_f = 1.9 \) aggregates, equation 7 under-predicts \( \beta \) values for \( 0.4 > b > 0.2 \). In this range of \( b \), we suggest the use of equation 3.16 instead of equation 3.13. For \( b < 0.2 \), use of equation 3.12 gives smaller error values (~5-8%) compared to equation 3.16. Finally, for both aggregate morphologies, the approximate equation 8 under-predicts the value of \( \beta \), for a given value of \( g \), by 10-35%. The following universal linear relationship between \( \beta \) and \( g \) was found to give significantly better predictions of \( \beta \) than equation 3.14, in the entire range of relevant \( g \) values (adjusted-\( R^2 \) of 0.9987):

\[ \beta = -0.3978g + 0.505 \]  

(3.17)

We further assessed the error that could be introduced in direct radiative forcing of BC from using the HG phase function approximation. The direct radiative forcing efficiency (W/g/nm) at 550 nm was calculated using equation 3.2: \[ \frac{dS(\lambda)}{d\lambda} = 1.755 \text{ W/m}^2/\text{nm} \] at 550 nm, MSC = 2. and MAC = 7.5 m²/g. The upscatter fractions based on the HG phase function were estimated using two approaches. First, for the range of \( b \) values in this study, which can be measured in practice, we calculated the values of \( \beta \) from equations 3.13 and 3.16. The x- and y-axes of Figure 3.10A show the estimated \( \frac{dSFE}{d\lambda} \) using \( \beta \) from equations 3.13 and 3.16, respectively. Second, mass equivalent diameters were calculated for aggregates of different sizes, as \((N \times d^{3})^{\frac{1}{3}}\). Values of \( g \) were calculated for these equivalent spheres using Mie theory (Mätzler, 2002) and corresponding \( \beta \) values were estimated using equation 3.14. To compare the deviation of these approximate \( \beta \) values from exact ones, we used equation 3.17 to estimate \( \beta \) based on the \( T \)-matrix method for the same set of aggregates (that is, same values of \( N, d \) and \( m \)). The values of \( \frac{dSFE}{d\lambda} \) from Mie theory and
equation 3.14 are plotted on the x-axis of Figure 3.10B; the y-axis shows the corresponding values from $T$-matrix and equation 3.17.

Figure 3.8: Relationships between (A) asymmetry parameter, $g$, and hemispherical backscattering fraction, $b$, (B) upscatter fraction, $\beta$, and $b$, and (C) $\beta$ and $g$, at 550 nm wavelength, for $D_f = 1.9$ and $D_f = 3$ aggregates. The fits $g(b)$, $\beta(b)$ and $\beta(g)$ are given in Equation 3.15-3.17.
Figure 3.9: Scatter plots of simple forcing efficiency (W/g/nm) at 550 nm for upscatter fraction, $\beta$, estimated from a range of (A) backscatter fraction, $b$, values, using the HG approximation (equation 3.13) and $T$-matrix based relationship (equation 3.16), and (B) asymmetry parameter, $g$, values, using the HG approximation (equation 3.14) and $T$-matrix based relationship (equation 3.17). In equation 3.17, $g$ was from $T$-matrix calculations for aggregates of different sizes, while Mie theory-based estimates of $g$, for equivalent spheres, were used in equation 3.14.

The simple forcing efficiencies estimated using the first method showed that the HG phase function based parameterization resulted in underestimation of $\beta$ by 2-25% and overestimation of the forcing by up to 5%. In the second method, using Mie theory expectedly resulted in underestimation of $g$ (Liu and Mishchenko, 2005b, 2007), which along with the use of the HG approximation, led to overestimation of $\beta$ by 5-35%. This corresponded to underestimation of the forcing efficiency by up to 8%. The strongly absorbing nature of BC (MAC ~ 3 times of MSC),
implies that the second term (in brackets) on the RHS of equation 3.17 dominates. Therefore, while
the use of the HG phase function approximation using equations 3.11-3.13 could cause significant
errors in estimates of \( g \) and \( \beta \), the resulting errors have relatively small contributions to forcing
efficiency.
References

Chapter 4: Aerosol emission factors from field study of cookstove emissions in India

Emissions performance of cookstoves is commonly expressed in terms of mass-based emission factors (EFs) or mass of pollutant emitted per unit mass of fuel burned. PM emission rates depend on fuel properties, combustion device, operator behavior and cooking patterns (Roden et al., 2009; Sahu et al., 2011; Leavey et al., 2015). Cookstove heating efficiencies and EFs are often measured in a laboratory setting using a water-boiling test (WBT) with high- (boiling) and low- (simmering) power phases (Smith et al., 2000; Habib et al., 2008; MacCarty et al., 2008). These standardized tests are useful for comparing different stove-fuel combinations, but they do not represent real-world stove behaviors found in the field (Roden et al., 2006; Smith, 2007; Roden et al., 2009). Habib et al. (2008) changed the amount of water boiled from 0.5 kg to 1.5 kg in the WBT test, thereby changing the fuel burn rate and burn cycle duration and observed a factor of ~2.7 increase in the PM$_{2.5}$ EF and a factor of ~2 increase in the OC fraction. A real-world study of Honduran wood-burning cookstoves (Roden et al., 2006) found higher PM$_{2.5}$ EFs and OC content than those from previous laboratory studies. Roden et al. (2006; 2009) found that real-world fire tending and cooking practices (and therefore burn conditions) were important factors determining PM EFs and compositions.

Real-world EFs for commonly used fuel types and cooking technologies in India are needed for accurate bottom-up emission estimates (Bond et al., 2004; Bond et al., 2013; Pandey et al., 2014). Inventoried emission rates serve as inputs to regional and global atmospheric transport models that predict spatiotemporal profiles of pollutant burdens and associated impacts on climate and human
health (Schulz et al., 2006; Bond et al., 2013; Guttikunda and Calori, 2013; Sadavarte et al., 2016). Alternatively, these inventories are used in conjunction with impact metrics such as intake fraction (Grieshop et al., 2011) and global warming potential (Shindell et al., 2012) to evaluate mitigation policies (MHFW, 2015; Sagar et al., 2016). Such measurements identify key parameters to be monitored during laboratory testing and appliance certification.

4.1. Experimental and data analysis techniques

With the above goals, we measured cookstove emission characteristics in a rural Indian household (Pandey et al., 2017). Local meals were prepared with a traditional mud stove or chulha (Figure 4.1) using biomass fuels collected from different regions of India. Real-time measurements of emitted gas concentrations were conducted, and PM$_{2.5}$ filter samples were collected at regular time intervals during each cooking cycle. PM$_{2.5}$, OC and EC EFs are reported here as a function of fuel-type and combustion phase. Thermal carbon fractions provided by the IMPROVE_A protocol are also examined.

![Figure 4.1: Traditional one-pot mud chulha used in this work.](image)

Thirty separate cooking tests were conducted between December 19 and 30$^{th}$ of 2015 in a rural household on the outskirts of Raipur, a city located in the central Indian state of Chhattisgarh (abbreviated as Chh.). ~77% of Chhattisgarh households are located in rural areas and rely almost
entirely on solid biomass fuels for cooking (Census, 2011). On a national level, fuel-wood, agricultural residue and dung are used as primary cooking fuels by 49%, 9% and 8% Indian households respectively (Census, 2011). Accounting for average combustion efficiencies and calorific values of these fuels, annual fuel usage estimates are 250 MT fuel-wood, 73 MT agricultural residue and 100 MT dung (Pandey et al., 2014). For this study, fuel-wood was obtained from Uttar Pradesh (U.P.), Rajasthan (Raj.), Andhra Pradesh (A.P.), Bihar, and Punjab which collectively account for 35% of the total fuel-wood user base in India. All wood fuels were in the form of chunks with typical dimensions of 5 – 15 cm. Cattle dung (in the form of dung cakes dried in the sun) was collected from U.P. and Bihar, which account for 60% of the dung use for cooking in India. Agricultural residues from tur crops (a type of woody stalk) and rice straw were procured from a village near the study location. Test fuels were collected and stored in sealed bags, and later analyzed for elemental (carbon, oxygen, hydrogen, nitrogen) composition and moisture content. Fuel compositions are compared in Table 4.1. Per real-world practice, fuel samples were naturally dried in the sun and stored indoors, bringing moisture contents to < 9%. These compositions are consistent with those reported in other tests (Smith et al., 2000; Habib et al., 2008).
Table 4.1: Elemental composition and moisture content of the biomass fuels in this study.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Elemental composition (%)</th>
<th>Moisture content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carbon</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>U.P. dung</td>
<td>33.1</td>
<td>4.0</td>
</tr>
<tr>
<td>Bihar dung</td>
<td>41.4</td>
<td>5.1</td>
</tr>
<tr>
<td>Chh. rice straw</td>
<td>40.7</td>
<td>5.5</td>
</tr>
<tr>
<td>Chh. tur stalk</td>
<td>48.4</td>
<td>6.5</td>
</tr>
<tr>
<td>Punjab wood</td>
<td>50.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Raj. Wood</td>
<td>49.7</td>
<td>5.6</td>
</tr>
<tr>
<td>U.P. wood</td>
<td>49.9</td>
<td>0.1</td>
</tr>
<tr>
<td>A.P. wood</td>
<td>48.3</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table 4.2 describes the fuels used and the foods cooked; replicate tests were made for some of these combinations with at least three for each fuel. Dung (20-50 g) was doused with approximately 10 ml kerosene for initial ignition and the test fuel was added after a steady flame was achieved. Additional fuel of the same type was added as needed to complete the recipe. A ten-minute period following lighting of the fire is designated as ignition phase. The remainder of the cooking cycle was designated as the flaming phase when a visible flame was present. Combustion entered the smoldering phase when the flame died down. The U.P. dung and Chh. rice straw could not sustain the flaming phase for more than a few minutes. Dung is typically smoldered for low-power cooking applications, and it is used as kindling material for igniting fuel-wood in a typical rural household. The low carbon content of U.P. dung (Table 4.1) possibly hinders its ability to sustain a flame, more so than Bihar dung. Rice straw has a low material density and high surface-to-volume ratio, and therefore tends to burn out very quickly. It also produces large amounts of smoke, making its use as a standalone fuel impractical and harmful for the cook’s health. To
circumvent these limitations, a few experiments established a steady flame using U.P. dung/Chh. rice straw mixed with U.P. wood (approximately 2.5:1 ratio of test fuel mass to wood mass).

Table 4.2: List of cooking experiments conducted during the 10-day intensive study period. Abbreviations for Indian states: U.P. = Uttar Pradesh, Raj. = Rajasthan, A.P. = Andhra Pradesh, Chh. = Chhattisgarh.

<table>
<thead>
<tr>
<th>Day</th>
<th>Primary fuel used</th>
<th>No. of replicate experiments</th>
<th>Food cooked</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bihar dung</td>
<td>1</td>
<td>lentil-rice</td>
</tr>
<tr>
<td>2</td>
<td>U.P wood</td>
<td>2</td>
<td>rice, vegetables</td>
</tr>
<tr>
<td>3</td>
<td>U.P wood</td>
<td>1</td>
<td>tea</td>
</tr>
<tr>
<td></td>
<td>Raj. wood</td>
<td>4</td>
<td>lentils, rice, vegetables</td>
</tr>
<tr>
<td>4</td>
<td>U.P. wood</td>
<td>2</td>
<td>lentils</td>
</tr>
<tr>
<td></td>
<td>A.P. wood</td>
<td>1</td>
<td>rice</td>
</tr>
<tr>
<td>5</td>
<td>A.P. wood</td>
<td>2</td>
<td>rice, vegetables</td>
</tr>
<tr>
<td></td>
<td>Bihar dung</td>
<td>1</td>
<td>tea</td>
</tr>
<tr>
<td>6</td>
<td>Chh. tur stalks</td>
<td>3</td>
<td>rice, vegetables, tea</td>
</tr>
<tr>
<td>7</td>
<td>U.P. dung</td>
<td>3</td>
<td>vegetables, rice</td>
</tr>
<tr>
<td></td>
<td>Bihar dung</td>
<td>1</td>
<td>tea</td>
</tr>
<tr>
<td>8</td>
<td>Chh. rice straw</td>
<td>3</td>
<td>rice, vegetables</td>
</tr>
<tr>
<td></td>
<td>Chh. wood</td>
<td>1</td>
<td>tea</td>
</tr>
<tr>
<td>9</td>
<td>Raj. wood</td>
<td>4</td>
<td>water heated, rice and curry</td>
</tr>
<tr>
<td>10</td>
<td>Punjab wood</td>
<td>1</td>
<td>milk porridge</td>
</tr>
</tbody>
</table>

Two experiments for each fuel conducted with fuel-wood mixed with the test fuel

The test kitchen (Figure 4.2) was on the first floor of house, separate from all other rooms. A permanently open door was the only entry from an open terrace. A partially covered window was a second ventilation source. The sampling and measurement systems are shown in Figure 4.3. The combustion device was a traditional mud *chulha*; such stoves have poor heat insulation, poor combustion efficiency and do not allow proper mixing of fuel and air (Smith et al., 2000;
An eight-armed stainless steel probe (based on Roden et al. (2006)) sampled naturally-diluted emissions at ~1.2 m above the top of the stove. Each arm of the probe was 0.5 m in length, with 4 uniformly placed holes facing the plume. This probe was connected to three real-time instruments—a Kanomax Portable Mobility Particle Sizer (PAMS) (Kulkarni et al., 2016), a TSI Sidepak (Zhu et al., 2007), and a Testo-350 gas analyser (Wang et al., 2012). The PAMS recorded particle size distributions from 10 – 400 nm mobility diameter. The Sidepak provides a light-scattering (670 nm) surrogate for measured PM$_{2.5}$ mass that is calibrated with Arizona Road Dust (O'Shaughnessy and Slagley, 2002). PM concentrations exceeded the upper measurement limits of these instruments during high emission episodes. The Testo-350 gas analyzer was factory-calibrated prior to the experiments for carbon monoxide (CO) and carbon dioxide (CO$_2$). Measured concentrations (acquired every second) were at least five times the detection limits of 1 ppm CO and 0.01 % CO$_2$ by volume. PM$_{2.5}$ was collected on 47 mm Teflon-membrane and pre-baked quartz-fiber filters several times during a cooking cycle using Minivol (5 L min$^{-1}$) samplers (AirMetrics Model 4.2) with greased impactor inlets located in the plume ~0.9m above the stove. Filter sample durations ranged from 0.5 to 4 minutes, based on the continuous SidePak reports, to prevent filter overloading. Field blanks were collected (minimum sampling duration of 15 minutes) each day before testing. The Teflon filters were weighed before and after sampling to obtain the net mass deposit which was divided by the sample volume (flow rate times duration) to obtain the concentration. The mass of Teflon filter deposits ranged 50 – 300 µg. Quartz filters were analyzed using the Interagency Monitoring of Protected Visual Environments – A (IMPROVE_A) thermal-optical reflectance (TOR) method (Chow et al., 2007b; 2011) to determine elemental and organic carbon fractions in the sampled particulates.
minimum detection limits of the TOR analysis are about 9 µg for OC and 1 µg for EC (Solomon et al., 2014).

Figure 4.2: Schematic layout (top-view) of the kitchen.
Using the carbon mass balance technique, fuel-based EFs were calculated for each filter:

$$EF_i = CMF_{fuel} \frac{C_i}{\Delta C_{CO2} \left( \frac{M_C}{M_{CO2}} \right) + \Delta C_{CO} \left( \frac{M_C}{M_{CO}} \right)}$$  \hspace{1cm} (4.1)$$

where $EF_i$ is the EF of species $i$ in grams emitted per gram of fuel consumed. $CMF_{fuel}$ is the carbon mass fraction of the fuel, which ranged from 33% to 50% for the tested fuels. $C_i$ is the concentration of emittant $i$, in this case PM$_{2.5}$, OC, or EC, in g m$^{-3}$, determined for each Teflon and quartz filter. $\Delta C_{CO2}$ and $\Delta C_{CO}$ are the concentrations above ambient levels of CO$_2$ and CO in g m$^{-3}$, respectively. $M_C$, $M_{CO2}$, and $M_{CO}$ are the atomic or molecular weights of C, CO$_2$, and CO in g mole$^{-1}$.

Wireless optical particle sensors (details available in Patel et al. (2017)) were attached to the Minivol sampler and the sampling probe during six experiments to check for any significant differences in the particle concentrations measured at the two locations. Measurements where
either sensor was saturated were discarded, and a linear regression analysis performed on the valid data points (Figure 4.4). The saturation voltage for the sensors is close to 750 mV, discarding all values higher than 750 mV, regression analysis of the remaining points yields a slope of 0.96. However, if the saturation threshold was set at 745 mV, the slope changed to 0.89. This is probably because saturation behavior for these sensors is a soft-limit saturation, such that the input-response relationship becomes non-linear at some voltage lower than the final limiting value of 750 mV. If measurements from this non-linear region are included, the linear regression analysis would give erroneous results. Therefore, we systematically reduced the threshold values until we observed negligible change in the regression slope. Finally, we discarded the data points where either of the sensors had readings above the linearity threshold (720 mV). About 60% of all data points were used, and a slope of 0.63 (R^2=0.65) was obtained. Therefore, the concentration measured by the Minivol sampler was adjusted upwards by a factor of 1.6 (=1/0.63). Equation 1 assumes that the carbon emitted in CH₄, NMHC, and PM is negligible compared to that in CO and CO₂, it was therefore corrected to account for the small fraction of fuel carbon that gets converted to gaseous volatile organic carbon, assumed as 2.4% (Roden et al., 2006; Habib et al., 2008).

![Figure 4.4: Raw signals from the PM sensors located at the sampling probe (Sensor1) and the Minivol PM_{2.5} sampler (Sensor2) during one cooking test.](image-url)
4.2. Emission factors by fuel and combustion phase

EFs for all the test fuels are represented as box-and-whisker plots in Figure 4.5. There were no statistically significant (unpaired, two-sided Student’s $t$-test at $p=0.05$) EF differences for wood fuels from different regions of India. This can be interpreted as the variability in emissions for a given fuel being comparable to the differences in average emission rates for different wood fuels. Note that all fuel-wood types had low moisture contents (naturally dried for ease of use) and were chopped in roughly the same manner even though individual wood pieces varied in size. Bihar dung EFs exceeded those for U.P. dung, possibly owing to the addition of wood to sustain flaming. On average, PM$_{2.5}$ and OC emission factors for dung were higher than those for fuel-wood. EFs for dung, rice straw and tur stalk show a larger spread than corresponding EFs for fuel-wood. A detailed list of all emission factors (speciated by fuel and combustion stage) is provided in Appendix A2.
Figure 4.5: Box plots of (a) PM$_{2.5}$ emission factors, (b) OC emission factors, and (c) EC emission factors. All emission factors are expressed in g-pollutant per kg of fuel burnt. Boxes denote lower and upper quartiles; whiskers are 1.5 times the interquartile ranges of the upper and lower quartiles. The numbers above the error bars in panel (c) indicate the number of samples for each fuel.
Figure 4.6 compares EFs for the different burning phases. PM$_{2.5}$ EFs are highest during the ignition phase for all fuels. The OC/EC ratio (Figure 4.6b) increases from ignition and flaming, to smoldering for all fuels. Similarly, emission factors of CO are shown in Figure 4.7. Expectedly, smoldering combustion is associated with the largest CO emissions. Both CO and PM$_{2.5}$ are products of incomplete combustion are their mass emission rates measured during lab cookstove tests are found to correlate (Roden et al., 2009). In this study, no correlation was observed between the estimated CO emission factors and corresponding PM$_{2.5}$ emission factors (Figure 4.8A), consistent with a similar analysis of field study results in Roden et al. (2009). Further, we plotted modified combustion efficiencies (MCE), calculated as the ratio of CO$_2$ concentration to CO+CO$_2$ concentration, against OC-to-EC ratios. MCE is typically treated as an identifier of combustion phase, with values greater than 0.9 associated with (Reid et al., 2005; Zhang et al., 2008). We found estimated MCE values above 0.9 for roughly 90% of all run time, even when no flaming phase was visibly observed. They showed no correlation with OC-to-EC ratios (Figure 4.8B).

![Figure 4.6](image)

Figure 4.6: Fuel-wise average values of (a) PM$_{2.5}$ emission factors, (b) OC/EC ratios, (c) OC emission factors, and (d) EC emission factors, categorized by observed combustion phases. All emission factors are expressed in g-pollutant per kg of fuel burnt. One-sided error bars
are shown to denote one standard deviation from the mean. The numbers above the error bars in panel (d) indicate the number of samples for each fuel and combustion phase.

Figure 4.7: Fuel-wise average values of CO emission factors categorized by observed combustion phases. Emission factors are expressed in g-pollutant per kg of fuel burnt. One-sided error bars are shown to denote one standard deviation from the mean.

Figure 4.8: Comparisons of (a) CO vs PM$_{2.5}$, EFs and (b) OC/EC ratios vs modified combustion efficiency (MCE) values.
4.3. **Average emission factors by fuel category; comparison with previous studies**

Average EFs for the entire burn cycle were calculated as a time-weighted sum of EFs for each phase of combustion. Fuel-wood and agricultural residue are used predominantly in flaming conditions to carry out the bulk of cooking operations, resulting in weights of 17% ignition, 66% steady flame and 17% smoldering. For dung, the weights are 17% ignition, 17% flaming and 66% smoldering because dung was used for longer low-power operations such as heating water/milk and roasting vegetables. These EFs are compared with other reported EFs in Figure 4.9. Average fuel-wood PM$_{2.5}$ EFs and OC/EC ratios in this study are 20% larger than those reported by (Roden et al., 2006) for Honduran cookstoves, but they are 2-8 times as large as those reported for laboratory studies (Habib et al., 2008; MacCarty et al., 2008; Saud et al., 2012). For agricultural residue and dung, the average EFs and OC/EC ratios are 1.8 – 4.2 times and 1.3 – 2.2 times higher, respectively, compared to those reported by Saud et al. (2012) and Habib et al. (2008).
Figure 4.9: Average PM$_{2.5}$ emission factors and OC/EC ratios for the three fuel categories in this study, compared with relevant studies. Error bars for values estimated in this study denote 95% confidence intervals based on standard errors of the means. Error bars for other studies are the bounds reported within those studies.

The emission factors shown in Figure 4.9 are averages from a selection of studies that used fuels and stoves comparable to those used in our field study. A detailed list of cookstove particulate emission factors measured in laboratory and field studies, including those shown in Figure 1.9, is provided in Table 4.3. Most studies included in the following table tested South Asian stoves and fuels, with two exceptions: Roden et al. (2009) studied traditional Honduran wood burning stoves and improved cookstoves, while Johnson et al. (2008) tested Mexican Patsari stoves and open cooking fires. These studies are included because they provide comparisons between the field and laboratory emission behavior for the same (or similar: see Table 4.4 for details) stove and fuel-
type. Only studies that reported PM emission factors along with their EC and OC components are reported here.

Emission factors of PM$_{2.5}$, OC and EC measured during in-field cooking were all larger (unpaired, two-sided Student’s t-test) than those from WBT based studies, at significance levels of $p=0.019$, 0.033 and 0.01, respectively. The corresponding effect sizes based on differences between the means, quantified by Cohen’s $d$, were 0.89, 0.82 and 1, respectively. As a rule of thumb, effect sizes>0.8 are considered large. (Sawilowsky, 2009). Note that these significant differences were found even though emission factors for various fuel and stove types were combined for this analysis. On average, real-world PM$_{2.5}$, OC and EC emission factors are larger than their counterparts from simulated cooking cycles by factors of 2.1, 1.5 and 3.1, respectively. The difference between EC/OC ratios for field and WBT studies was not significant because of the effect of fuel type: emissions from dung combustion consistently have a smaller EC fraction than those from fuel-wood burning. However, we previously demonstrated lower EC/OC (larger OC/EC in Figure 4.9) from field studies than fuel-matched laboratory observations.
Table 4.3: Summary of reported mass emission factors of PM$_{2.5}$, EC and OC emissions from biomass cookstoves. All emission factors are expressed as mean (standard deviation).

<table>
<thead>
<tr>
<th>Study</th>
<th>Test protocol</th>
<th>Stove</th>
<th>Fuel</th>
<th>Emission factors$^a$ (g kg$^{-1}$ fuel)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>PM$_{2.5}$</td>
<td>EC</td>
</tr>
<tr>
<td>Habib et al. (2008)</td>
<td>Laboratory WBT, low burn rate</td>
<td>Indian traditional mud</td>
<td>fuel-wood</td>
<td>1.9 (0.8)</td>
</tr>
<tr>
<td></td>
<td>Laboratory WBT, high burn rate</td>
<td></td>
<td>fuel-wood</td>
<td>5.1 (1.4)</td>
</tr>
<tr>
<td></td>
<td>Laboratory WBT</td>
<td></td>
<td>agricultural residue: woody stalks</td>
<td>7.5 (3.3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>agricultural residue: rice straw</td>
<td>9.3 (4.1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>dung</td>
<td>5.4 (2.4)</td>
</tr>
<tr>
<td>Johnson et al. (2008)</td>
<td>Laboratory WBT</td>
<td></td>
<td>fuel-wood</td>
<td>4.9 (0.8)</td>
</tr>
<tr>
<td></td>
<td>Field WBT</td>
<td>open fire</td>
<td></td>
<td>3.7 (2.2)</td>
</tr>
<tr>
<td></td>
<td>Field cooking</td>
<td></td>
<td></td>
<td>8.8 (3.1)</td>
</tr>
<tr>
<td></td>
<td>Laboratory WBT</td>
<td></td>
<td>fuel-wood</td>
<td>4.8 (1.9)</td>
</tr>
<tr>
<td></td>
<td>Field WBT</td>
<td>Mexican ‘Patsari’</td>
<td></td>
<td>2.8 (1.3)</td>
</tr>
<tr>
<td></td>
<td>Field cooking</td>
<td></td>
<td></td>
<td>5.4 (2.3)</td>
</tr>
<tr>
<td>Roden et al. (2009)</td>
<td>Field cooking</td>
<td>Honduran traditional</td>
<td>fuel-wood</td>
<td>8.5 (1.6)</td>
</tr>
<tr>
<td></td>
<td>Laboratory WBT</td>
<td>traditional three-stone</td>
<td></td>
<td>1.7 (0.1)</td>
</tr>
<tr>
<td></td>
<td>Field cooking</td>
<td>improved, no chimney (‘rocket’ stove)</td>
<td></td>
<td>5.6 (0.4)</td>
</tr>
<tr>
<td></td>
<td>Laboratory WBT</td>
<td></td>
<td></td>
<td>1.4 (0.1)</td>
</tr>
<tr>
<td>Saud et al. (2012)</td>
<td>Laboratory, test cycle not reported</td>
<td></td>
<td>fuel-wood</td>
<td>4.1 (1.2)</td>
</tr>
<tr>
<td></td>
<td>Laboratory, test cycle not reported</td>
<td>open fire</td>
<td>agricultural residue</td>
<td>6.8 (4.1)</td>
</tr>
<tr>
<td></td>
<td>Laboratory, test cycle not reported</td>
<td></td>
<td>dung</td>
<td>14.3 (5.3)</td>
</tr>
<tr>
<td>Study</td>
<td>Fuel Type</td>
<td>Indian Traditional Mud</td>
<td>Nepalese Traditional Mud</td>
<td>‘Terai’</td>
</tr>
<tr>
<td>------------------------------</td>
<td>------------------------------------</td>
<td>------------------------</td>
<td>--------------------------</td>
<td>---------</td>
</tr>
<tr>
<td>Pandey et al. (2017)</td>
<td>Field cooking</td>
<td>Fuel-wood</td>
<td>10.5 (1.4)</td>
<td>4.9 (0.8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Agricultural Residue</td>
<td>11.1 (2.1)</td>
<td>7 (1.6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dung</td>
<td>22.6 (5.0)</td>
<td>12.9 (4.0)</td>
</tr>
<tr>
<td>Jayarathne et al. (2018)</td>
<td>Laboratory WBT</td>
<td>Fuel-wood</td>
<td>4.9 (0.9)</td>
<td>2.5 (0.3)</td>
</tr>
<tr>
<td></td>
<td>Field cooking</td>
<td>Fuel-wood</td>
<td>10.7 (1.6)</td>
<td>5.9 (0.7)</td>
</tr>
<tr>
<td></td>
<td>Laboratory WBT</td>
<td>Dung</td>
<td>19.7 (3.0)</td>
<td>8.5 (1.0)</td>
</tr>
<tr>
<td></td>
<td>Field cooking</td>
<td>Dung</td>
<td>14.5 (2.2)</td>
<td>9.9 (1.2)</td>
</tr>
<tr>
<td>Weyant et al. (2019)</td>
<td>Field cooking</td>
<td>Fuel-wood, Dung</td>
<td>11.9 (7.6)</td>
<td>5.6 (5.2)</td>
</tr>
<tr>
<td></td>
<td>Indian Traditional Mud</td>
<td>Fuel-wood, Agricultural Residue, Dung</td>
<td>6.7 (2.6)</td>
<td>2.3 (1.8)</td>
</tr>
<tr>
<td></td>
<td>Nepalese Traditional Mud</td>
<td>Fuel-wood, Agricultural Residue, Dung</td>
<td>5.8 (2.6)</td>
<td>3.3 (1.7)</td>
</tr>
<tr>
<td></td>
<td>Nepalese ‘Terai’</td>
<td>Fuel-wood, Agricultural Residue, Dung</td>
<td>4.3 (0.8)</td>
<td>3.4 (2.1)</td>
</tr>
<tr>
<td></td>
<td>Nepalese Improved Stove, No Chimney</td>
<td>Fuel-wood, Agricultural Residue, Dung</td>
<td>42.7 (26.0)</td>
<td>31.6 (19.8)</td>
</tr>
<tr>
<td></td>
<td>Tibetan Open Stove</td>
<td>Dung</td>
<td>23.2 (12.6)</td>
<td>16.2 (10.2)</td>
</tr>
<tr>
<td></td>
<td>Tibetan Chimney Stove</td>
<td>Fuel-wood</td>
<td>12.7 (10.2)</td>
<td>8.5 (7.3)</td>
</tr>
</tbody>
</table>

A scatterplot of all OC and PM$_{2.5}$ emission factors from Table 4.3 is shown Figure 4.10. Over field and WBT studies, OC mass constituted approximately 60% of the total particle mass. Therefore, studies that underestimate PM emission factors likely use cooking cycles characterized by more frequent strong flaming conditions (with low OC emissions) than actual cooking. This hypothesis is supported by a detailed analysis of optical measurements from field and laboratory tests (Chen...
et al., 2012): lab tests predominantly skew towards events with low SSA particles (mostly EC). On the other hand, field tests contain events dominated by low, intermediate and high SSA particles.

![Graph](image)

Figure 4.10: The relationship between OC and PM$_{2.5}$ emission factors from all the studies listed in Table 4.3. All WBT based measurements (lab or field) are grouped. The dashed line represents an ordinary least-squares fit (R$^2$=0.92)

### 4.4. Thermal carbon fractions from TOR analysis

Thermal fractions of total carbon constituted by the IMPROVE_A protocol are shown in Figure 4.11. OC1, OC2, OC3 and OC4 refer to carbon that evolves at temperatures of 120 °C, 250 °C, 450 °C, and 550 °C respectively, in the inert helium atmosphere. OP denotes pyrolyzed carbon, OC charring in the inert helium carrier. EC1, EC2 and EC3 fractions evolve in a 2%O$_2$/98%He oxidizing atmosphere at 550 °C, 700 °C and 800 °C, respectively. Figure 4.11 compares fractions from this study with those reported for controlled biomass (hardwood and softwood) burning reported in Chow et al. (2007a). We also compare our results with a source profile developed for PM$_{2.5}$ emissions from wood chulhas, as part of source apportionment studies conducted by the
Central Pollution Control Board (CPCB) of India (CPCB (2011)). This profile was based on laboratory burns, but details of the test fuel and burn protocol are not known. OC3 was the most abundant fraction, ~50% of the total carbon mass, while the profiles in literature ranged 10%–34% in the OC3 fraction. The OC1 fraction for all fuels in this study was uniformly less than 3%, a finding comparable only to the 5% OC1 reported for softwood, but not for the other two profiles. Carbonaceous aerosol source profiles are useful for source apportionment, and they may also have implications for climate and health impact assessments. In an previous study (Pandey et al., 2016), we reported that light absorbing OC may play a larger role in light absorption by cookstove emissions than that from earlier work on biomass burning in the U.S.A. The difference in constituents of OC emissions from the two sources might contribute to the observed difference in their optical characteristics, since thermal stability is known to be inversely related to the light absorption efficiency of organic compounds (Andreae and Gelencsér, 2006; Saleh et al., 2013).

Figure 4.11: Fraction of total carbon emissions contributed by the IMPROVE_A thermal carbon fractions.

4.5. Insights from real-time measurements

A sample plot of real-time particle and gas concentration profiles from day 9 of the study is shown in Figure 4.12. It should be noted that the Sidepak instrument does not measure actual particle
mass concentration, but instead measures light scattering at 670 nm wavelength and provides an equivalent concentration of Arizona Test Dust that would produce the same magnitude of light scattering.

Over a period of two hours, Sidepak PM measurements and CO concentration (solid in panel B) fluctuated every few minutes. Sidepak was saturated at an equivalent concentration of 20 µg/m3, giving the appearance of a steady state. Re-fueling was typically followed by a sudden spike in particulate and CO emissions. Ignition with ‘dirty’ fuels like dung, straws and kerosene as well as re-fueling or rekindling (per the cook’s convenience) are critical features of a realistic cooking cycle. Carefully maintained steady burn conditions in laboratory tests reduce the emission variability and may be the major cause of the low bias in WBT emission factors (Roden et al., 2009).
4.6. Inventoried emissions for biomass cookstoves in India

The global harmonized emissions database EDGAR-HTAP (a globally consistent inventory that combines the Emissions Database for Global Atmospheric Research and Hemispheric Transport of Air Pollution inventories) provides model-ready emissions inputs (Janssens-Maenhout et al., 2012). Emissions for South Asia in this dataset were taken from the Regional Emission inventory in ASia (REAS), with annual estimates of PM$_{2.5}$, BC and OC emissions for the domestic sector
(base year 2008) = 2467, 371 and 1700 Tg y\(^{-1}\), respectively (Kurokawa et al., 2013). Top-down fuel consumption estimates based on an energy balances dataset from the International Energy Agency were used in that study. A detailed, bottom-up national inventory (Speciated Multi-pOllutant Generator or SMOG) estimated residential PM\(_{2.5}\), BC and OC emissions as 2803, 546 and 1035 Tg y\(^{-1}\), respectively, for the year 2015 (Pandey et al., 2014). This includes emissions from household cooking and kerosene-based lighting, with cookstoves contributing 92%, 60% and 100%, respectively, of the total residential PM\(_{2.5}\), BC and OC emissions. Ratios of fuel-wise cookstove PM emission factors from our field study to those in the SMOG inventory (an average of best available values published till date) ranged 2.2-2.5, those for OC emission factors ranged 2.5-4.2. Using our field-based emission factors with the fuel use estimates from Pandey et al., 2014, I calculated annual cookstove emitted PM\(_{2.5}\), BC and OC as 5694, 442 and 3023 Tg y\(^{-1}\), respectively.
References


Schulz, M., Textor, C., Kinne, S., Balkanski, Y., Bauer, S., Berntsen, T., Berglen, T., Boucher, O., Dentener, F., and Guibert, S.: Radiative forcing by aerosols as derived from the AeroCom present-day and pre-industrial simulations, Atmospheric Chemistry and Physics, 6, 5225-5246, 2006.


Chapter 5: Estimating aerosol-phase light absorption from filter-based optics

Common filter-based optical instruments like the Particle Soot Absorption Photometer (PSAP), the aethalometer or the Tricolor Absorption Photometer (TAP) estimate particle light absorption based on semi-continuous transmission measurements through a sample spot on the filter medium.

The measured optical coefficient ($\sigma_{\text{meas}}$) is given by:

$$\sigma_{\text{meas}} = \frac{A}{Q\Delta t} \times ATN_t = \frac{A}{Q\Delta t} \ln \left( \frac{T_{t-\Delta t}}{T_t} \right) \tag{5.1}$$

where $A$ is the area of the sample spot, $Q$ is the sample flow-rate through the filter during a time interval $\Delta t$, $ATN_t$ is the Beer-Lambert attenuation through the filter and $T_{t-\Delta t}$ and $T_t$ are the transmission ratios measured at the start and the end of the interval, respectively. Transmission ratios are measured by comparing transmitted intensity ($I(t)$) through the sample spot to that through a reference sport ($I_0(t)$), normalized to the same ratio calculated for an unloaded filter:

$$T_t = \frac{I(t)/I_0(t)}{I(0)/I_0(0)} \tag{5.2}$$

If the transmitted intensity depended only on particle light absorption and attenuation could be calculated using the Beer-Lambert law (as shown in equation 5.1), then $\sigma_{\text{meas}}$ would be equal to the particle absorption coefficient ($\sigma_{\text{ap}}$). In general, optical depth measures for a filter sample are correlated to particulate phase absorption optical depth $\tau_{a,p}$ of the sampled particles, but not equal to it. This absorption optical depth is related to $\sigma_{ap}$ as attenuation is related to the attenuation coefficient:
\[ \tau_{a,p} = \sigma_{ap} \times \frac{Q_{\Delta t}}{A} \neq ATN \] (5.3)

The inequality arises because filter media are multiple-scattering, leading to a larger optical path length than when particles are in their suspended, single-scattering state. This causes the appearance of enhanced light absorption (Clarke, 1982; Bond et al., 1999; Gorbunov et al., 2002), and is referred to as the multiple scattering artifact. While the multiple-scattering effect is typically treated as a function of only the filter medium, loading of absorbing aerosols can diminish its effect, inducing an aerosol dependent loading artifact (Weingartner et al., 2003; Arnott et al., 2005; Virkkula et al., 2005; Virkkula, 2010). Aerosol light scattering could enhance multiple scattering which leads to an overestimation of absorption (Weingartner et al., 2003; Lack et al., 2008), implying that filter-based measurements are also sensitive to the particle absorption coefficient \( (\sigma_{sp}) \). Further, the particle size distribution can affect the penetration of aerosols into the filter medium and their backscattering and therefore, the measured transmittance. Therefore, any filter optical measure is a function of the aerosol phase absorption \( (\tau_{a,p}) \) and scattering \( (\tau_{s,p} = \sigma_{sp} \times \frac{Q_{\Delta t}}{A}) \) optical depths and particle size distribution. A theoretical treatment of these artifacts using the two-stream approximation provides insight about the interaction of filter and particle optical characteristics, but several parameters required by the model are difficult to measure. Typically, filter artifacts have been evaluated for commonly used instruments, by comparing their measurements with contact-free aerosol light absorption measurements or using reference materials with known optical properties.

5.1. Filter artifact correction literature

Bond et al. (1999) formulated measured PSAP extinction coefficients as a combination of particle-phase absorption \( (\sigma_{ap}) \) and scattering \( (\sigma_{sp}) \) coefficients:
\[ \sigma_{PSAP} = K_1 \sigma_{sp} + K_2 \sigma_{ap} \]  \hspace{1cm} (5.4)

where \( \sigma_{PSAP} \) is the value reported by the instrument after applying an empirical correction (for loading-artifacts) determined by the manufacturer, further corrected by Bond et al. (1999) for flow-rate and spot size:

\[ \sigma_{PSAP} = \sigma_{meas} \times \frac{1}{1.2369 \times T_t + 0.8135} \]  \hspace{1cm} (5.5)

This study investigated the validity of the manufacturer’s correction by directly measuring \( \sigma_{PSAP} \) and \( \sigma_{sp} \) (via a nephelometer) and inferring \( \sigma_{ap} \) as the difference of in-situ extinction (via an optical extinction cell) and scattering for pure nigrosine and ammonium sulphate aerosols, as well as mixtures of the two aerosol types in varying proportions. Coefficients \( K_1 \) and \( K_2 \) were then estimated as 0.02 and 1.22, respectively, yielding:

\[ \sigma_{ap} = \frac{\sigma_{PSAP} - 0.02 \sigma_{sp}}{1.22} \]  \hspace{1cm} (5.6)

Virkkula (2010) and Virkkula et al. (2005) performed a similar empirical calibration for the PSAP, with the addition of a photoacoustic spectrometer to measure particle-phase light absorption, for diesel soot, kerosene soot, graphite, ammonium sulphate and polystyrene latex aerosols. The authors used the form of the correction equation proposed by (Bond et al., 1999):

\[ \sigma_{ap} = \frac{\sigma_{meas} \times g(T_t) - K_1 \sigma_{sp}}{K_2} = \sigma_{meas} \times f(T_t) - s \sigma_{sp} \]  \hspace{1cm} (5.7)

For the aerosol types investigated in this study, a good fit for \( f \) was found to be a logarithmic function of the loading \( T_t \), with an additional dependence on the particle-phase SSA (\( \omega_p \)):

\[ f(T_t, \omega_p) = k_0 + k_1 (h_0 + h_1 \omega_p) \ln(T_t) \]  \hspace{1cm} (5.8)

The constants \( k_0, k_1, h_0, h_1 \) and \( s \) were determined for three wavelengths.
Arnott et al. (2005) used the two-layer, two-stream radiative model of filter optics discussed above to derive an approximate function form of a loading correction function for the aethalometer:

\[
\sigma_{ap}(t + \Delta t) = \frac{\sigma_{meas} - \sigma_{sp}}{M} \sqrt{1 + \frac{Q \Delta t \sigma_{ap}(t)}{\chi \tau_{a,f}}} \tag{5.9}
\]

where \( \Delta t \) is the measurement interval. The quantities \( \alpha, M \) and \( \chi \tau_{a,f} \) were empirically determined using simultaneous aethalometer, photoacoustic spectrometer and nephelometer measurements on kerosene soot and ammonium sulphate aerosols. Equation 5.9 captures the incremental change in loading from measurement to measurement following each filter change (at the time of filter change, \( t=0 \)).

Müller et al. (2014) used previous empirical corrections for the PSAP (equations 5.6-5.8) to initialize a two-stream filter radiative model (detailed model description in Chapter 5.2 and Appendix A1) to develop an experimentally constrained description of filter optical behavior (henceforth, the CTS method). Instead of the flow-rate and sampling time dependent optical coefficients, they employ ‘relative optical depths’ or attenuation (ATN) optical depth measurements:

\[
ATN_{meas} = \ln \left( \frac{T_{t-\Delta t}}{T_t} \right) \tag{5.10}
\]

Attenuation optical depths were also derived from the model (\( \tau^{mod} \)) (see equations 5.14A and 5.14B in Chapter 5.2). With reasonable assumptions for parameters that cannot be directly observed for each sample, \( \tau^{mod} \) can be computed for any input values of \( \tau_{a,p}, \tau_{s,p} \) and \( g_p \).

Sensitivity of the relative optical depths to pure black and white particles were defined as:

\[
F_{a}^{meas/mod}(\tau_{a,p}) = \frac{ATN^{meas/mod}(\tau_{a,p}, \tau_{s,p}=0)}{\tau_{a,p}} \tag{5.11A}
\]
These sensitivities can be readily calculated from the model, but they need to be constrained by experimental observations. $F_a^{\text{meas}}$ was calculated by reformulating the correction equations (expressing them in terms of $\tau_{a,p}$ and $\tau_{s,p}^{\text{meas}}$) reported by Virkkula (2010) and Bond et al. (1999) for black soot particles. $F_s^{\text{meas}}$ was derived by measuring the response of the PSAP to white NaCl particles generated in the laboratory and fitting a curve to the observed relationship. Then the attenuation optical depth was constrained by matching measured and modeled depths for black and white particles:

$$ATN_{\text{meas}}^{\text{meas}}(\tau_{a,p}, \tau_{s,p}, g_p) = \frac{F_a^{\text{meas}} \tau_{a,p} + F_s^{\text{meas}} \tau_{s,p}}{F_a^{\text{mod}} \tau_{a,p} + F_s^{\text{mod}} \tau_{s,p}} \times ATN_{\text{mod}}(\tau_{a,p}, \tau_{s,p}, g_p)$$

Equation 5.10 can be iteratively solved to find a value of $\tau_{a,p}$ that minimizes the difference between the measured relative optical depth and the right hand side of the equation.

The studies discussed here relied on empirical scattering response functions determined from measurements on inorganic white aerosols. The validity of these schemes for organic aerosols (pure scattering as well as light absorbing) has not been evaluated. Scanning electron microscopy images of filters loaded with particles emitted smoldering biomass have shown that liquid-like organic aerosols can coat filter fibers (Subramanian et al., 2007). This creates biases in filter measurements that are not accounted for by existing correction schemes (Weingartner et al., 2003; Cappa et al., 2008; Lack et al., 2008). These biases were proportional to organic mass loading for laboratory-generated (Cappa et al., 2008) and ambient urban aerosols (Lack et al., 2008); in both cases, the organic aerosols were non light absorbing. Davies et al. (2019) evaluated the ratio of TAP absorption coefficients to in-situ photoacoustic spectrometer (PAS) absorption coefficients for different ambient aerosol. TAP measurements corrected using the Bond et al. (1999) scheme
showed large deviations from the PAS data for all aerosol types (urban, fresh biomass burning and aged biomass burning) examined. The application of the CTS correction technique (Müller et al., 2014) lowered the bias in TAP measurements on urban and fresh biomass burning aerosols but resulted in increased variability in the measurements on aged biomass burning aerosols. This analysis underscored that filter-based absorption estimates are strongly influenced by aerosol type. Given that (1) organic aerosols exhibit diverse physical and optical properties and (2) these properties are correlated with combustion phase (Subramanian et al., 2007; Chakrabarty et al., 2010; Chen and Bond, 2010; Saleh et al., 2013; Saleh et al., 2014), experimental evaluations of systematic errors in filter-based absorption estimation are needed for aerosols generated from a representative range of combustion conditions.

5.2. Significance of Teflon filter samples

The instruments discussed above measure transmittance semi-continuously through a filter sample. Standalone ultraviolet-visible (UV-vis) spectrophotometers allow both transmittance and reflectance measurements as post sampling analysis of filters. These measurements can be taken with the front (sample side) or the back (clean side) of the filter facing the incident radiation. Measures of filter optical depth can then be defined using these discrete measurements.

In many field settings, aerosol samples are collected on polytetrafluoroethylene (PTFE) membrane filters (commonly known as Teflon filters) for inferring ambient or near-source particulate mass concentrations using gravimetric analysis (Koistinen et al., 1999). Major aerosol monitoring networks, such as the Interagency Monitoring of PROtected Visual Environments (IMPROVE) network (Chow et al., 2010; Solomon et al., 2014), the Chemical Speciation Network (CSN) (Solomon et al., 2014) and the Surface PARTiculate mAtter Network (SPARTAN) (Snider et al.,
collect particle samples on Teflon filters for gravimetric and elemental measurements. PTFE filters are chemically inert and unlike quartz fiber filters, present a very low surface area for organic vapor adsorption (Kirchstetter et al., 2001; Vecchi et al., 2014). Correction schemes developed for instruments that use fiber filters (like the PSAP and aethalometer) cannot be applied to transmittance and/or reflectance measurements on PTFE filters. A previous study on the artifacts associated with this filter type used a reference material and provided a constant multiple scattering correction factor for optical loadings smaller than a certain threshold (Zhong and Jang, 2011). Another recent study (White et al., 2016) proposed a theory-based model to calibrate attenuation measurements for Teflon filter samples and applied this new model to a historical dataset from IMPROVE network. They found that the reevaluated absorption values for the PTFE samples were well-correlated with thermo-optical elemental carbon (EC) measurements for co-located quartz fiber filters.

In this work, we generated carbonaceous aerosols with varying physicochemical properties from the combustion of biomass fuels and kerosene. Kerosene combustion was used as a surrogate for fossil fuel burning, which is linked with soot or EC emissions (Andreae and Gelencsér, 2006; Bond et al., 2013). The combustion of wildland- and fuel-biomass is implicated in emissions of EC as well as light absorbing organic carbon (LAOC) (Andreae and Gelencsér, 2006; Chakrabarty et al., 2010; Chen and Bond, 2010). EC is known to absorb light throughout the visible and ultraviolet (UV) wavelengths, while LAOC absorbs preferentially in the near-UV and UV regions (Kirchstetter et al., 2004; Andreae and Gelencsér, 2006; Bond and Bergstrom, 2006; Sun et al., 2007). Therefore, we measured in-situ and contact-free aerosol light absorption and scattering coefficients using integrated photoacoustic-nephelometer (IPN) spectrometers operated at three wavelengths - 375, 405 and 532 nm. Co-located with these measurements was a sampling system
to collect particles onto Teflon membrane filters. Subsequent filter optical measurements, using a Lambda-35 UV-vis spectrophotometer, were performed. Observed empirical relationships between particle light absorption and filter optical depth measures were established in conjunction with predictions from a one-dimensional (1-D) two-stream radiation transfer model.

5.3. Two-stream radiative transfer model of a filter-particle system

A 1-D two-stream radiative transfer framework for multiple scattering in absorbing media was developed in Bohren (1987)–widely known as the Kubelka-Munk theory (Kubelka, 1948)–and subsequently discussed in relation to aerosol-filter systems in several studies (Clarke, 1982; Gorbunov et al., 2002; Petzold and Schönlinner, 2004; Arnott et al., 2005).

Consider the layer of filter in which sampled particles are embedded to be a one-dimensional uniform medium with an optical thickness $\tau_0$, a single scattering albedo $\omega<1$ and a scattering asymmetry parameter $g$ (Figure 5.1). Now, consider a ‘forward’ direction: at any point in the medium the energy intensity propagating in this direction is given by $I_f$. Conversely, the backward propagation intensity is $I_b$.

Figure 5.1: Transmission and reflection of radiation through a one-dimensional, uniformly multiple-scattering medium.
Energy conservation in the medium can be written as (Bohren, 1987):

\[
\frac{d(l_f - l_b)}{d\tau} = -(1 - \omega_b)(l_f + l_b)
\]  

(5.13A)

\[
\frac{d(l_f + l_b)}{d\tau} = -(1 - \omega_b g)(l_f - l_b)
\]  

(5.13B)

The solution of these radiation balance equations for an aerosol-laden filter medium yields the following expressions for transmittance \(T_l\) and reflectance \(R_l\), respectively (see Appendix A1 for details):

\[
T_l = \frac{2}{[2K-\omega_l(1-g_l)\sinh(K\tau_{e,l})+2K\cosh(K\tau_{e,l})]}
\]  

(5.14A)

\[
R_l = \frac{\omega_l(1-g_l)\sinh(K\tau_{e,l})}{[2K-\omega_l(1-g_l)\sinh(K\tau_{e,l})+2K\cosh(K\tau_{e,l})]}
\]  

(5.15B)

Here, \(\omega_l\), \(g_l\) and \(\tau_{e,l}\) denote the SSA, asymmetry parameter and extinction optical depth, respectively, of the composite layer. A schematic representation of the two-layer system—the aerosol laden layer with properties \(T_l\) and \(R_l\) and a clean filter layer with properties \(T_f\) and \(R_f\)—is shown in Figure 5.2. The parameter \(K\) is defined as:

\[
K = \sqrt{(1 - \omega_l)(1 - g_l\omega_l)}
\]  

(5.16)
Figure 5.2: Two-layer model of a filter sample consisting of an aerosol laden layer ‘l’ and a clean layer ‘f’.

Arnott et al. (2005) used the above model to derive the form for an approximate correction factor for the aethalometer. The aethalometer uses optically-thick quartz fiber filters, which are strongly multiple scattering, transmitting only ~10% of light in the visible wavelengths. A mathematical consequence of strong multiple scattering is that the term $K_{e,l}$ is much greater than unity and equations 5.14A and 5.14B can be replaced by simplified approximations. In contrast, the Teflon filters used in this study are optically thin and constitute a weak multiple scattering medium: they transmit 70-80% of incident visible light. Therefore, the full equations for $T_l$ and $R_l$ were solved for the filter-particle system, using a range of plausible values of dimensionless aerosol optical properties: absorption optical depth ($\tau_{a,s}$) and SSA. Two other required inputs could not be measured: the penetration depth of aerosols into the filter was assumed to be 10% of the total filter thickness, and the asymmetry parameter of the aerosols was fixed at 0.6, based on the typical values reported for biomass burning emissions (Martins et al., 1998; Reid et al., 2005).
Transmittance and reflectance ($T_s$ and $R_s$, respectively) through the filter, when light is first incident on the aerosol-laden layer (or ‘sample-side’) is given by (Gorbunov et al., 2002):

$$T_s = \frac{T_l T_f}{1 - R_l R_f} \quad (5.17A)$$

$$R_s = R_l + \frac{T_l^2 R_f}{1 - R_l R_f} \quad (5.17B)$$

If the light first passes through the clean filter layer, the model predicts that transmittance, $T_c$, is still given by equation 5.17A. However, filter substrates are not uniform over their depths and have visually distinguishable front and back surfaces. Therefore, measurements of $T_s$ and $T_c$ are expected to differ. For the model substrate, reflectance $R_c$ is given by:

$$R_c = R_f + \frac{T_f^2 R_l}{1 - R_l R_f} \quad (5.18)$$

Attenuation ($ATN$) due to the aerosol deposit is calculated by applying Beer-Lambert’s law relating to the reduction in transmittance of an exposed filter ($T_s$) relative to a blank ($T_b$) (Campbell et al., 1995; Bond et al., 1999). For a non-absorbing filter substrate, all attenuation of incident light must be caused by aerosol light absorption. Therefore, $ATN$ is a measure of $\tau_{a,s}$.

$$ATN = \ln \left( \frac{T_b}{T_s} \right) = \ln \left( \frac{1 - R_b}{T_s} \right) \quad (5.19)$$

Here, $R_b$ is the reflectance of the blank. An alternate measure of filter-aerosol optical depth utilizes transmittance and reflectance of the clean face of the filter (Campbell et al., 1995; White et al., 2016). This reflectance measurement $R_c$ can be assumed to be approximately equal to $R_b$. PTFE blanks are non-absorbing, therefore the numerator in equation 5.19 can be replaced by $T_b = 1 - R_b \approx 1 - R_c$. It should be noted that for translucent Teflon filters, $R_b$ and $R_c$ cannot be assumed to be exactly equal (Clarke, 1982; Campbell et al., 1995). Therefore, we represent this measure of
optical depth by a separate variable, $OD_c$, where the subscript denotes that the transmittance and reflectance values used corresponds to the clean side of the filter:

$$OD_c = \ln\left(\frac{1-R_c}{T_c}\right)$$  \hspace{1cm} (5.20)

Finally, we define an optical depth measure using sample-side transmittance and reflectance, which can be interpreted as a measure of transmission of the fraction of incident radiation that is not backscattered by the filter-aerosol system:

$$OD_s = \ln\left(\frac{1-R_s}{T_s}\right)$$  \hspace{1cm} (5.21)

Values of $ATN$, $OD_c$ and $OD_s$ for a range of $\tau_{a,s}$ values (0-1) are shown in Figure 5.3 for two cases: (1) highly absorbing aerosols (SSA=0.3) and (2) highly scattering aerosols (SSA=0.95). We illustrate that $OD_c$ is nearly equal to $ATN$ for the absorbing aerosol case, but there are significant differences between the two optical measures when the filter is loaded with highly scattering aerosols. This is because a translucent substrate with a reflective coating on its back behaves like a mirror: reflectance of the substrate increases when such a coating is applied. We also find that $ATN$ shows the largest variation with SSA for a given value of $\tau_{a,s}$ while $OD_s$ exhibits the smallest variation. This can be attributed to the changing relationships between $R_s$ and filter loading for different SSA values. Figure 5.4 shows the change in $R_s$ with respect to $R_b$ plotted against the associated change in $T_s$, with increasing filter loading, for two discrete SSA values. For large SSA, $R_s > R_b$ and therefore, from equations 5.19 and 5.20, $OD_s < ATN$. The converse is true for small SSA values. It should be noted that fixed blank optics–based on the mean of transmittance and reflectance measurements (measurement techniques are described in the following section) on 20 blank filters–were used to model $ATN$, $OD_c$ and $OD_s$. The purpose of this exercise was to illustrate the sensitivity of the above optical depth measures to SSA values of aerosols deposited on identical
media. A sensitivity analysis (Figure 5.5) showed that these findings hold for a large range (1-30%) values of the fractional penetration depth ($\chi$).

![Graph showing modeled values of filter optical depth measures ($OD_c$, $ATN$ and $OD_s$) with increasing aerosol optical depth ($\tau_{a,s}$) of deposited highly absorbing (SSA=0.3) or highly scattering (SSA=0.95) aerosols. Fixed blank optics were assumed.](image)

Figure 5.3: Modeled values of filter optical depth measures ($OD_c$, $ATN$ and $OD_s$) with increasing aerosol optical depth ($\tau_{a,s}$) of deposited highly absorbing (SSA=0.3) or highly scattering (SSA=0.95) aerosols. Fixed blank optics were assumed.

The variation in filter optical measures with SSA was quantified by calculating the means and standard deviations of $ATN$, $OD_c$ and $OD_s$ over SSA values ranging 0.2-0.99 for each input value of $\tau_{a,s}$. A total of 500 linearly spaced points along the SSA range were used. Blank filter properties were also varied within the model in accordance with the range observed over the 20 lab blanks. For every model sample, defined by a given SSA and $\tau_{a,s}$ combination, a model blank was generated assuming a normal distribution of blank transmittance values (mean=0.7, standard deviation = 0.02). Figure 5.4 shows the ratio of standard deviation to the corresponding average values of each filter optical depth measure. The relatively low standard deviation in $OD_s$ (for most loading values) implies that this variable is a good candidate for estimating aerosol light absorption from filter optical measurements, for a wide range of aerosol types. The increase in standard
deviation with increasing loading is mainly contributed by very high SSA points which are typically associated with lower absorption per unit mass; therefore very high mass loadings of such aerosols would be required to yield the upper range of the $\tau_{a,s}$. For SSA<0.9, modeled attenuation values show little spread (<15% variability around the mean) with changing SSA. A surface plot of $OD_s$ for all model data points (0.2<SSA<0.99 and 0<$\tau_{a,s}$<1) is shown in Appendix A1.

Figure 5.4: Change in sample-side reflectance as a function of the corresponding change in transmittance for predominantly absorbing (SSA=0.3) and scattering (SSA=0.95) aerosol types when blank optics are fixed.
Figure 5.5: Same as Figure 5.4 but for different assumed values of aerosol fractional penetration depth $\chi$.

5.4. Experimental methods

Diverse biomass fuels including wood and needles from pine, fir and sage trees, grass, peat and cattle dung were burned in a 21 m$^3$ stainless steel combustion chamber located at Washington University (Sumlin et al. (2017); Sumlin et al. (2018)). Flaming, smoldering and mixed combustion phases were employed to generate a range of intrinsic aerosol properties: SSA values at 375, 405 and 532 nm ranged 0.4-0.99 and Absorption Ångström Exponents (AÅE) for 375-532 nm ranged 1.2-6.8. A kerosene lamp was used to generate soot particles, with an SSA of ~0.3 and AAE within 0.70-1.1. A schematic of the experimental setup is shown in Figure 5.6. Experimental conditions and intrinsic aerosol optical properties for each fuel-combustion phase combination are listed in Table 5.1. Burn protocols for the three combustion phases were as follows:

1. Peat was smoldered using a heating plate at a temperature of 200$^\circ$ C. Other biomass types were smoldered by first establishing flaming (for 1-2 min) by igniting the fuel with a lighter and then starving the flame by covering the fuel container. While the biomass was flaming, the chamber exhaust was left open; the exhaust was closed once the flames were extinguished. The sample line between the chamber and mixing volume was connected 5 min after closing the exhaust.

2. To isolate the flaming phase, the biomass was ignited with a lighter and the chamber exhaust was closed. We monitored the flame visually from outside the combustion chamber, closing off the sample line between the chamber and the mixing volume once the flames were out.
3. For mixed phase sampling, flaming was established following the procedure above and emissions were continuously pulled into the mixing volume even after the flames were extinguished.

4. Some biomass types like Ponderosa pine and Douglas fir did not sustain smoldering combustion and were only sampled in flaming and mixed conditions. Other types like dung and Lodgepole pine were found to not sustain a flame. Kerosene was burned using a wick lamp. Intrinsic optical properties from the combustion of certain biomass types varied from burn to burn for the same combustion protocol. For such cases, the ranges of observed properties are given in the table below. During each burn, a steady state (10-40 min long) was established within which the absorption and scattering coefficients were nearly constant.

Approximately 10-50 g of a given type of woody biomass/grass/dung was placed in a stainless-steel pan and ignited using a flame. It was either allowed to continue flaming or brought to a smoldering phase by starving the flame with a lid. In the same type of pan, 5-15 g of peat was smoldered by using a ring heater to raise its temperature to 200 °C. In one set of experiments, smoke from the chamber was directly sampled, while in another set, a hood placed over the pan was used for sampling the aerosols. The chamber exhaust was closed during the burns. The outlet from the hood or chamber was passed through a diffusion dryer and a semi-volatile organic compound (SVOC) denuder into a mixing volume, from which aerosols were continuously sampled by the four IPNs.
Figure 5.6: Schematic representation of the experimental setup. Inlet to the semi-volatile organic compound denuder was taken from either the chamber sampling port or the hood. IPN stands for integrated photoacoustic-nephelometer spectrometers.
Table 5.1: Number of burns conducted, and filter samples collected for each fuel type and combustion phase in this study. Intrinsic optical properties of emissions from each study condition are also given.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Combustion phase</th>
<th>SSA 375 nm</th>
<th>SSA 405 nm</th>
<th>SSA 532 nm</th>
<th>AAE 375-532 nm</th>
<th># of burns</th>
<th># of filter samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dung</td>
<td>smoldering</td>
<td>0.86</td>
<td>0.95</td>
<td>0.98</td>
<td>6.1-6.6</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>Peat</td>
<td>smoldering</td>
<td>0.92</td>
<td>0.97</td>
<td>0.99</td>
<td>4.8-6.8</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Sage</td>
<td>mixed</td>
<td>0.75-0.87</td>
<td>0.86-0.93</td>
<td>0.93-0.97</td>
<td>2.8-5.3</td>
<td>4</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>flaming</td>
<td>0.56-0.77</td>
<td>0.69-0.84</td>
<td>0.71-0.87</td>
<td>1.5-2.3</td>
<td>3</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.43-0.65</td>
<td>0.62-0.69</td>
<td>0.69-0.77</td>
<td>0.9-1.4</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>Grass</td>
<td>smoldering</td>
<td>0.74</td>
<td>0.87</td>
<td>0.94</td>
<td>3.2-4.7</td>
<td>3</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>flaming</td>
<td>0.76</td>
<td>0.81</td>
<td>0.85</td>
<td>1.7</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Lodgepole pine</td>
<td>smoldering</td>
<td>0.84</td>
<td>0.93</td>
<td>0.97</td>
<td>4.2</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Ponderosa pine</td>
<td>mixed</td>
<td>0.61-0.84</td>
<td>0.74-0.91</td>
<td>0.76-0.95</td>
<td>1.2-3.0</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>flaming</td>
<td>0.56</td>
<td>0.65</td>
<td>0.65</td>
<td>0.7</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Douglas fir</td>
<td>mixed</td>
<td>0.82</td>
<td>0.89</td>
<td>0.93</td>
<td>2.7</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>flaming</td>
<td>0.60</td>
<td>0.70</td>
<td>0.71</td>
<td>0.9</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Hardwood pellets</td>
<td>mixed</td>
<td>0.80-0.87</td>
<td>0.92-0.95</td>
<td>0.95-0.98</td>
<td>4.1-6.1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Kerosene</td>
<td>flaming</td>
<td>0.27</td>
<td>0.30</td>
<td>0.31</td>
<td>0.7-1.1</td>
<td>3</td>
<td>7</td>
</tr>
</tbody>
</table>

During each burn, optical (absorption and scattering coefficients) signals were monitored using IPNs until a steady state was reached. During the steady state, particle samples were collected on 47 mm PTFE membrane (Pall) filters. The filter sampling flow rate was set to 5 liters per minute and the sampling durations were between 2 and 20 minutes. For each filter sample, $\tau_{a,s}$ of the deposited aerosols was calculated from the absorption coefficients measured using the IPNs:

$$\tau_{a,s} = \frac{b_{abs,av} \times Q \times t_s}{10^9 A_s}$$ (5.22)
where $b_{abs,av}$ is the average absorption coefficient (in Mm$^{-1}$) during the sampling duration $t_s$ (in min), $Q$ is the flow rate (in liters per minute or lpm) through the filter and $A_s$ is the filter sample area (in m$^2$). Optical depth $\tau_{a,s}$ for the samples in this study ranged between 0.01 and 0.68. The uncertainty in these estimates was predominantly from the standard deviation in $b_{abs,av}$ over the averaging interval, and was within 10% for all samples. Values of $b_{abs,av}$ at 532 nm ranged from ~300 Mm$^{-1}$ for smoldering samples to ~20000 Mm$^{-1}$ for flaming phase samples; the corresponding range at 375 nm was ~3000-30000 Mm$^{-1}$.

Sample-side transmittance ($T_s$) and reflectance ($R_s$) for the filter samples were measured using a Perkin-Elmer LAMBDA 35 UV-vis spectrophotometer (described in Zhong and Jang (2011)). This instrument contains an integrating sphere and two sample holders. Transmittance was measured by placing the sample in the first holder ahead of the sphere, in the direction of the sample beam, while a white standard was placed in the second holder (behind the sphere). Reflectance was measured by keeping the first holder empty and placing the sample in the second holder. Both measurements were performed on the sample face of the filter: light was incident on the side that was exposed to the sample air. Each measurement was normalized to the baseline transmittance/reflectance value of the measurement system: between every 10 sample scans, transmittance/reflectance were measured with no sample placed in the first holder and a white standard was placed in the second holder. Sample transmittance/reflectance values were then divided by the corresponding baseline. Only $T_s$ and $R_s$ were measured for all samples in this study as model results indicated that $OD_s$ is better suited than $OD_c$ for estimating $\tau_{a,s}$. To test the validity of this assumption, transmittance and reflectance were also measured on the clean side of the filter ($T_c$ and $R_c$, respectively) for a subset of the samples (n=54). This subset corresponded to samples

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collected during 17 biomass burning experiments which yielded aerosols with SSA (375, 405 and 532 nm) ranging 0.54-0.99. For all samples, we found $T_s > T_c$.

From normalized $T_s$ and $R_s$ measurements, $OD_s$ was calculated using equations 5.21. When this equation is applied to blank filters, it results in $OD_s$ values between 0.01-0.03. A wavelength dependent “blank optical depth” was subtracted from the sample data. Triplicate transmission and reflection measurements were used to estimate measurement uncertainty, which is attributable to random fluctuations in the measurements. Means and standard deviations of the $OD_s$ values calculated from the replicate measurements yielded an uncertainty (ratio of standard deviation to mean) of 5% in $OD_s$. Similarly, $OD_c$ was calculated for the 54-sample subset.

A correction factor ($C$) that captures the net effect of multiple scattering and aerosol loading can be defined as:

$$\tau_{a,s} = C \times OD_s \implies C = \frac{\tau_{a,s}}{OD_s}$$  \hspace{1cm} (5.23)

A list of relevant parameters (measured or assumed from previous studies) described in Chapters 5.3 and 5.4 is shown in Table 5.2.
Table 5.2: Particle and filter properties for artifact correction.

<table>
<thead>
<tr>
<th>Filter-aerosol system</th>
<th>absorption and scattering optical depths ( \tau_{a,s} )</th>
<th>derived from transmittance and reflectance measurements on pristine filters ( (T_b, R_b) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerosol</td>
<td>absorption and scattering optical depths ( \tau_{a,p}, \tau_{s,p} )</td>
<td>calculated from \textit{in-situ} absorption and scattering coefficient measurements</td>
</tr>
<tr>
<td></td>
<td>asymmetry parameter ( (g_p) )</td>
<td>fixed value assumed in the model ( (0.6) )</td>
</tr>
<tr>
<td>Filter-aerosol system</td>
<td>relative particle penetration depth ( (\chi) )</td>
<td>fixed value assumed in the model ( (10%) )</td>
</tr>
<tr>
<td></td>
<td>transmittance and reflectance of the particle laden layer ( (T_i, R_i) )</td>
<td>modeled as a function of ( \tau_{a,f}, \tau_{s,f}, g_f, \tau_{a,p}, \tau_{s,p}, g_p, \chi )</td>
</tr>
<tr>
<td></td>
<td>transmittance and reflectance of the two-layer system ( (T_s, R_s, R_c) )</td>
<td>modeled as a function of ( \tau_{a,f}, \tau_{s,f}, g_f, \tau_{a,p}, \tau_{s,p}, g_p, \chi )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>measured through spectrophotometry</td>
</tr>
</tbody>
</table>

### 5.5. Empirical correction scheme for filter artifacts

The model described in Chapter 5.3 was used to calculate filter optical depths for each experimental sample (using measured \( \tau_{a,s} \) and SSA values as inputs). Modeled and experimental values of \( OD_s \) for the samples are shown in Figure 5.7. The two datasets are highly correlated (Pearson \( R = 0.92 \)), but the model predicted larger values of \( OD_s \) than those experimentally determined. This disagreement may partially be due to differences between assumed parameters in our model and their real-world values. It is also likely that assuming an average propagation direction of diffuse radiation within the two-stream approximation (Sagan and Pollack, 1967; Arnott et al., 2005) causes this systematic difference.
Figure 5.7: Modeled filter optical depth ($OD_s$) for absorption optical depth and single scattering albedo values of the aerosols sampled in this study compared with the corresponding filter measurements. A 1:1 line is shown in red. The average ratio of modeled to measured $OD_s$ is 0.79.

In Figure 5.8, we combined all experimental ($\tau_{a,s}$ versus $OD_s$) data corresponding to the three wavelengths since our measurements showed no clear stratification with varying wavelength. The relationships between $\tau_{a,s}$ and modeled values of $OD_s$, $OD_c$ and $ATN$ are presented in Figure 5.9; modeling predicts the lowest scatter in the $\tau_{a,s}$-$OD_s$ curve. Further, Figure 5.10 shows $\tau_{a,s}$ plotted against measured $OD_s$ and $OD_c$ (at all three wavelengths) for the aforementioned 54 filter sample subset, demonstrating that $\tau_{a,s}$ is better correlated with $OD_s$ than with $OD_c$. Ordinary least-squares regression was applied to obtain power-law fits included in the plot legend. The corresponding relationship for all points in Figure 5.8 is given by ($R^2 = 0.87$):

$$\tau_{a,s} = 0.48 \left(OD_s\right)^{1.32} \quad (5.24)$$
Figure 5.8: Relationship between *in-situ* aerosol optical depth ($\tau_{a,s}$) and filter optical depth $OD_s$ for all (n=75) samples, measured at 375, 405 and 532 nm (N=225 data points). The best fit curve is given by equation 5.24, with $R^2 = 0.87$. The black perforated line has a fixed slope of 0.67 per Zhong and Jang (2011)). Uncertainties (1 standard deviation) in $OD_s$ ranged 2-5%, while those in $\tau_{a,s}$ were 5-10%.

Figure 5.9: The relationship between experimentally measured *in-situ* aerosol optical depth ($\tau_{a,s}$) and modeled values of filter optical depth measures ($OD_c$, ATN and $OD_s$). Blank optics were randomly generated for each sample point from a normal distribution with mean=0.7 and standard deviation=0.02.
Figure 5.10: Relationship between *in-situ* aerosol optical depth ($\tau_{a,s}$) and measured values of filter optical depth measures $OD_c$ and $OD_s$ for a subset of 54 filter samples, measured at 375, 405 and 532 nm (N=162 data points). Uncertainties were as in Figure 5.8.

Also shown in Figure 5.8 are estimated values estimated using a constant correction factor $C$ of 0.67 proposed by Zhong and Jang (2011) (black perforated line); this correction factor clearly overestimates $\tau_{a,s}$ for most $OD_s$ values investigated in this study. We find our data to be better represented by an approximate $C = 0.46$ based on a linear least-squares fit ($R^2 = 0.79$). However, any constant $C$ value does not capture the non-linearity of the interaction between aerosol properties and the multiple-scattering within the filter medium. It should be noted that $C$ in equation 5.23 represents the net effects of all filter artifacts. There are measurement errors associated with both $OD_s$ and $\tau_{a,s}$, and therefore, $C$ contains propagation of uncertainties from both parameters. No correlation was observed between $C$ and $OD_s$. We observed an inverse relationship between $C$ and SSA (Figure 5.11), consistent with results the from the two-stream radiative transfer model. For a given value of $\tau_{a,s}$, $OD_s$ will always be higher for aerosols with higher SSA.
values. Consequently, we should expect $C$ to decrease with increasing SSA; this decreasing relationship in our data is given by:

$$C = -0.76 \times SSA + 1.02$$  \hspace{1cm} (5.25)

Values of $C$ and SSA for individual samples were aggregated into five SSA bins to demonstrate the inapplicability of an empirical correction factor formulation to low SSA data points in this study. The large spread in $C$ values for low SSA is likely due to noise amplification from dividing two small ($\tau_{a,s}$ and $OD_s < 0.2$) numbers. For SSA>0.6, the above linear fit holds.

Figure 5.11: Correction factor $C$ for filter artifacts as a function of single scattering albedo of the deposited aerosols. Error bars show one standard deviation around the mean. The numbers in parentheses denote the number of data points in each bin.

In summary, the relationship between in-situ aerosol light absorption and attenuation of aerosol deposits on Teflon filters was evaluated for combustion aerosols (encompassing $0.25 \leq SSA \leq 0.99$), at 375, 405 and 532 nm wavelengths. An empirical non-linear relationship was found between the absorption optical depth of sampled aerosols and attenuation through filter samples; the nature of this function was consistent with predictions from a two-stream radiative transfer
model of the filter-aerosol system. Following equation 5.24, we propose the estimation of aerosol MAC (m²g⁻¹) values from filter $OD_s$ measurements using:

$$MAC = [0.48 \ (OD_s)^{1.32}] \ \frac{A_s}{m} \ \ \ \ \ \ \ (5.26)$$

where $A_s$ is the filter sample area (in m²) and $m$ is the mass on deposited particles (in g). Additionally, aerosol absorption coefficients ($b_{abs}$; in Mm⁻¹) can also be calculated using:

$$b_{abs} = [0.48 \ (OD_s)^{1.32}] \ \frac{10^9 A_s}{Q \times t_s} \ \ \ \ \ \ \ (5.27)$$

The quantities $Q$ and $t_s$ are as used in equation 5.22. Caution must be taken, as suggested by the two-stream model results, on the limits of applicability of the empirical relationships—significant errors could result from application of the relationships if the aerosol SSA>0.9 and $OD_s$ values are beyond the range of this work.

Teflon filters are routinely used for gravimetric and elemental analysis across monitoring networks (Chow et al., 2010; Solomon et al., 2014; Snider et al., 2015), as well as field and laboratory source characterization studies. In many measurement systems, such as the Hybrid Integrating Plate and Sphere (HIPS) method (Bond et al., 1999) used by the IMPROVE network, transmittance and reflectance are measured on the clean side of the filter and the optical depth $OD_c$ is calculated (Campbell et al., 1995; White et al., 2016). The relationship between aerosol optical depth, $\tau_{a,s}$, and $OD_s$ showed a larger variability across varying SSA than that between $\tau_{a,s}$ and $OD_c$. Therefore, we suggest further evaluation of $OD_s$ as an optical depth measure that can be empirically connected to particulate phase light absorption for a range of aerosol types.
References


Chapter 6: Constraining OC contribution
to light absorption by cookstove emissions

As discussed in Chapter 4.2, cookstove emissions performance has been characterized by mass emission factors of aerosol (and gaseous) pollutants through laboratory WBT studies and more recently, field measurements on in-use cookstoves. A few of the studies (Roden et al., 2006; Habib et al., 2008; Stockwell et al., 2016; Weyant et al., 2019) summarized in Table 4.4 also reported the light absorption properties of cookstove aerosol emissions. Roden et al. (2006) reported MAC and MSC values determined from real-time PSAP and nephelometer measurements, respectively, made during their Honduran field study. Habib et al. (2008) calculated MAC and AAE from transmittance measurements on Nucleopore filters (sampled in their detailed laboratory study of Indian biomass fuels) made using an integrating plate nephelometer. In Weyant et al. (2019), PSAP and narrow-angle red-wavelength light sensor measurements were used to estimate MAC and MSC, respectively, for Indian, Nepalese and Tibetan stoves. All of these studies applied the Bond et al. (1999) correction scheme to their multi-wavelength filter-based absorption measurements, which might lead to a ~20-45% overestimation of the MAC values (Davies et al., 2019). Stockwell et al. (2016) used photoacoustic spectroscopy to measure in-situ absorption, at 405 and 870 nm, for Nepalese biomass cookstoves. The more recent studies (Stockwell et al., 2016; Weyant et al., 2019) provide an estimate of light absorption attributable to OC emissions but neither reported spectral MAC values for cookstove OC emissions. This poses a challenge in expanding the conventional discussion of aerosol climate impact which considers BC emitted as the only significant form of light-absorbing carbonaceous aerosol (Ramanathan et al., 2001; Venkataraman et al., 2005; Ramanathan and Carmichael, 2008; Carmichael et al., 2009; Bond et al., 2013). In
this section, I first discuss the difficulties in apportioning light absorption to BC and OC and the sources of uncertainties in such an analysis. Initial estimates of OC absorption properties based on a preliminary round of sampling cookstove emissions in India are presented in Chapter 6.2. This study had a small sample size and was conducted following approaches and assumptions typically used in literature. A larger number of aerosol samples, from the field study described in Chapter 4, were later analyzed with crucial improvements made to filter optical analysis (Chapter 6.3). These updated findings are compared with the studies discussed above in Chapter 6.4.

### 6.1. Attributing aerosol light absorption to OC and EC

Conventionally, all light absorption by combustion generated aerosols was attributed to BC particles but newer generations of climate models include brown carbon as a light-absorbing form of OC in addition to the strongly absorbing BC (Chung et al., 2012; Feng et al., 2013; Wang et al., 2014). The light-absorbing efficiency of OC aerosols is connected with their physical and chemical properties, a function of fuel properties and combustion conditions (Chen and Bond, 2010). Optical properties and refractiveness of OC particles lie on interlinked continua: absorption efficiency and thermal-stability are linked with high molecular weight organic compounds formed under flaming conditions (Andreae and Gelencsér, 2006; Sun et al., 2007; Saleh et al., 2014; Laskin et al., 2015; Saleh et al., 2018). Higher relative abundances of BC are correlated with higher light absorbing efficiency of the co-emitted OC (Saleh et al., 2014). Cookstove emissions in this study are characterized by fuel-wise average BC/OC ratios of 0.08-0.15, which is on the lower end of the range (0.04-1.67) from laboratory cookstove tests of similar fuel types (Habib et al., 2008) but larger than field measurement of BC/OC ratios (0.02-0.08) for open biomass burning (Aurell et al., 2015; Strand et al., 2016; Holder et al., 2017). Thermal carbon profiles of the emissions in this study show that thermally stable OC, that evolves at 450 °C in an inert atmosphere, is the largest
particulate fraction (~50% of total carbon mass, on average) (Pandey et al., 2017). Therefore, OC is expected to be important contributor to light absorption by cookstove emissions. However, there are fundamental challenges in separately measuring the properties of co-emitted BC and OC in addition to specific limitations pertaining to cookstove studies.

In a real-time measurement system, a thermodenuder can be used to vaporize organic aerosols and absorption measurements taken before and after denuding (Cappa et al., 2012; Lack et al., 2012; Lack and Langridge, 2013; Saleh et al., 2013; Saleh et al., 2014). The optical measurements are typically supplemented with size or mass observations of the total aerosol and its BC/OC components in order to perform optical closure, yielding absorption cross-section or refractive index of OC. There are two sources of bias in such an analysis: (1) thermodenuding does not remove non-refractory OC which likely contributes to light absorption (Cappa et al., 2013) and (2) BC particles coated with non-absorbing organics show an absorption enhancement (Cappa et al., 2008; Lack et al., 2008; Lack et al., 2012; Saleh et al., 2013), referred to as the “lensing effect”, which needs to be treated separately from absorption due to externally-mixed OC. Further, thermodenuder measurements are performed sequentially which can lead to confounding observations (like enhanced absorption after denuding) about the optical behavior of emissions that fluctuate over time (Cappa et al., 2013). Finally, the power requirement for a thermodenuder, and associated pumps, may be prohibitive for field studies of cookstoves in rural areas of the developing world.

A prevalent method for estimating OC light absorption is the extraction of organic material into a suitable organic solvent or water from a filter sample of emissions (Chen and Bond, 2010; Liu et al., 2013) followed by optical analysis with a UV-vis spectrometer. This approach allows for physical isolation of OC aerosols but studies report that 2-15% of all OC mass is not soluble in
even non-polar solvents (Chen and Bond, 2010; Cheng et al., 2016; Xie et al., 2017). The magnitude of this insoluble fraction and its (unmeasured) absorption efficiency depends on OC composition which is known to widely vary with fuel and combustion characteristics (Andreae and Gelencsér, 2006; Laskin et al., 2015). The extraction efficiency of OC in water is significantly lower (Chen and Bond, 2010) but several studies consider water-soluble organics as a proxy for all OC.

Particle light absorption ($\text{ABS}$) estimated from filter-based optical analyses (detailed in Chapter 5) can be attributed to BC and OC using a two-component model (Kirchstetter et al., 2004; Kirchstetter and Thatcher, 2012). This technique exploits the difference in the spectral absorption dependences of these components (Figure 1). It is assumed that absorption at wavelengths greater than a certain threshold ($\lambda_t$) is due to BC alone. Values of $\lambda_t$ in literature range 660-880nm (Kirchstetter et al., 2004; Kirchstetter and Thatcher, 2012; Pokhrel et al., 2017). A fixed spectral dependence of light absorption by BC is assumed, consistent with a body of experimental observations and theoretical analyses for freshly emitted small BC particles (Kirchstetter et al., 2004; Andreae and Gelencsér, 2006; Bond et al., 2013). This dependence is parameterized by BC absorption Angstrom exponent ($\text{AAE}_{BC}$). OC contribution to wavelengths smaller than $\lambda_t$ is estimated as:

$$ABS_{OC}(\lambda) = ABS_{PM} - ABS_{BC} = ABS_{PM} - ABS_{PM,700} \left( \frac{\lambda}{700} \right)^{-\text{AAE}_{BC}}$$

(6.1)
Kirchstetter et al. (2004) found that the values of OC absorption estimated using AAE$_{BC}$ of 1 compared well with those calculated from acetone extracts of the aerosol samples. However, the validity of this assumption requires further testing against first principle measurements (Andreae and Gelencsér, 2006; Lack and Langridge, 2013; Laskin et al., 2015).

### 6.2. Preliminary study of light absorption by cookstove OC emissions

#### 6.2.1. Sampling and analysis

Between October and December 2014, we conducted sampling of particulate matter emissions from traditional “three-stone” cookstoves in rural households in Chhattisgarh, a state in central India. This region has witnessed accelerated warming and anomalous rainfall patterns (Jain and Kumar, 2012; Khavse et al., 2014), which in turn have impacted the agricultural yield, food security, and livelihood (Sastri, 2009; Murali and Afifi, 2014). Over 97% of the households in rural Chhattisgarh use solid biomass fuels for cooking purposes (Census, 2011). On a national
level, 62%, 12% and 11% of rural households rely primarily on fuel-wood, agricultural residue and dung cake, respectively, to meet their cooking energy needs. Mud *chulhas* and three-stone *On* an average, they have similar particulate emissions characteristics (Habib et al., 2008; MacCarty et al., 2008), and are often treated as a single ‘baseline biomass stove’ (Pandey et al., 2014) technology category.

Three households that primarily used one of the three primary solid fuel types (one each for users of fuel-wood, agricultural residue, dung cake) were selected in rural Chhattisgarh, India. Additionally, based on the typical practice in the region, a fourth fuel category was identified – mixed fuel (a combination of roughly 25% dung cake, 60% fuel-wood, 10% agricultural residue and 5% coal cake), which was used in each of these households. The fuels were locally purchased or scavenged by the households, which did not facilitate the quantitative determination of their moisture content. Sampling was conducted during one of the two typical cooking times: morning (around 6:30AM to 9:00AM) and evening (around 5:30 PM to 7:30PM). The households prepared their regular meals consisting of rice, vegetables, and/or *chapatis* (wheat-flour breads).

The sampler inlets were placed at ~ 1 m from the emission point to allow for cooling and dilution with ambient air. Emissions of particulate matter with aerodynamic diameter smaller than 2.5 µm (or PM$_{2.5}$) were drawn from the plume of each source through Harvard sharp impactors using MiniVol portable air samplers (AirMetrics Model 4.2). Pre-fired 47 mm quartz-fiber filters and Teflon membrane filters were mounted to the air samplers. Flow rates through the filters were programmed at 5 LPM. Sampling duration was varied between 15 and 65 min, depending on the cooking operation at hand. Five quartz-fiber and five Teflon filters were used to collect aerosol samples emitted from each of the four fuel types. The aerosol deposit yields ranged 0.5–1.8 mg/filter. Field blank collection was carried out before each of the morning and evening cooking
activities. Aerosols were also deposited on Transmission Electron Microscopy (TEM) grids (Ted Pella, Inc.) to characterize their morphology.

Relative abundances of Elemental Carbon (EC) and OC in the aerosol samples were estimated using the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal/optical reflectance (TOR) method (Watson and Valberg, 2001; Chow et al., 2007). In this study, the estimated EC mass in aerosol samples has been approximated to be the BC mass (Venkataraman et al., 2005; Chakrabarty et al., 2014). This approximation, while having found wide usage in the aerosol community, has its limitations. EC is operationally defined as the fraction of carbon that is oxidized above a set temperature during thermal or thermal-optical analysis (Andreae and Gelencsér, 2006). Corresponding to a particular temperature threshold and the protocol used, corrections are applied to best estimate the mass of pure carbon in its refractory (or graphitic) form (Andreae and Gelencsér, 2006; Chow et al., 2007). In theory, BC and EC are equivalent proxies for combustion generated refractory carbon (Andreae and Gelencsér, 2006; Bond et al., 2013). Experimentally, their measurements have potential sources of bias, especially in the presence of OC (including light absorbing OC or LAOC) in the sample. Past studies have estimated these biases to result in at least a factor of 2 uncertainty in BC and EC masses (Andreae and Gelencsér, 2006; Bond et al., 2013; Petzold et al., 2013). Therefore, we qualify our approximation with the caveat that BC in this manuscript refers to the apparent refractory carbon.

The absorption coefficients of sampled aerosols in Teflon media were measured using a PerkinElmer LAMBDA 35 ultraviolet-visible spectrophotometer (Zhong and Jang, 2011). In this instrument, a double integrating sphere system detects the intensity of radiation, with a wavelength between 200-1100 nm, transmitted or reflected through a sample deposited on a filter medium. The spectral resolution of this instrument is 1 nm. For wavelengths ranging 300-900 nm, we
measured the transmittances through field-blank and loaded filters. The relative lowering of transmission through a loaded filter, compared to a blank filter, could be attributed primarily to light absorption by the deposited aerosols. From this, the Beer-Lambert Law (Kirchstetter et al., 2004; Zhong and Jang, 2011) is used to relate aerosol absorbance \((ABS)\) to light attenuation \((ATN)\) through the filter as:

\[
ATN(\lambda) = \ln \left( \frac{I_0(\lambda)}{I(\lambda)} \right)
\]  

(1A)

\[
ABS(\lambda) \approx \frac{ATN(\lambda)}{C}
\]

(1B)

where \(C\) is a correction factor \((=1.5\pm0.15)\), that accounts for increased path length due to multiple scattering in Teflon filters (Zhong and Jang, 2011; Drinovec et al., 2014), and \(I_0\) and \(I\) are the radiation intensity transmittance (\%) values through blank and loaded filters. A normally distributed instrument uncertainty was applied to the measured transmittance values based on the observed random error, which was within 5% of the average measurement values. The resulting uncertainty in \(ATN (= \ln(I_0/I))\) was estimated by analytically propagating the instrument error. The output uncertainties also followed a normal distribution. The confidence intervals for \(ABS\) were calculated by combining in quadrature the relative uncertainties in \(C\) and \(ATN\) (equation 1B).

Another artifact pertinent to filter based measurements is the loading effect of absorbing aerosols, which serves to lower the apparent attenuation with increasing aerosol loading. Empirical calibration factors for filter measurements of BC absorption (Weingartner et al., 2003; Arnott et al., 2005; Drinovec et al., 2014) typically correct for this artifact, but similar corrections are not available for LAOC loading artifact. We evaluated this effect for the present samples by plotting the filter mass loading values against \(ATN\) at 350 nm (Figure S2). A weak linear relationship
(R²=0.35) was found to best fit the data. Similar results were obtained for ATN values at 550 and 880 nm as functions of the mass loading. This does not provide any conclusive evidence on the effects of filter mass loading on the ATN values in this study. Based on previous studies, the absorption related loading artifact for aerosols emitted from biomass burning is expected to be weak (Kirchstetter and Thatcher, 2012). Additionally, high loading of scattering aerosols (like OC) results in an increase in optical path (Subramanian et al., 2007; Cappa et al., 2008; Lack et al., 2008), leading to the overestimation of ABS. The net effect of high loadings of (absorbing and scattering) aerosols depends on the optical nature and relative abundances of BC, LAOC and non-absorbing OC. We noted here that the development of filter artifact correction factors for biomass cookstove (or other OC dominated) emissions was needed to improve the accuracy of filter-based analyses. To that end, we conducted the study discussed in Chapter 5 and the results of that study were applied to future analysis.

We attributed the entire attenuation at λₜ = 880 nm to BC (Chakrabarty et al., 2010; Kirchstetter and Thatcher, 2012) and estimated ABS_OC using equation 6.1 a mean AAE_BC value of 1. In order to account for the variability in the wavelength dependence of light absorption by BC externally mixed with non-absorbing OC, we assumed a range of 0.7-1.3 for AAE_BC (Schnaiter et al., 2006; Gyawali et al., 2009; Chung et al., 2011; Lack and Langridge, 2013). For the above range of AAE_BC values, the variation in ABS_OC at 350 nm, with respect to its mean value at AAE_BC =1, was 6-14% (Figure 6.2). Therefore, one standard deviation uncertainties (±6-14%) were assigned to the deconvolution method and combined analytically with the other uncertainties in equation 1.
Figure 6.2: Average LAOC ABS values at 350 nm wavelength as functions of BC AAE for fuel-wood, agricultural residue, dung cake and mixed fuel.

Using the ratio of OC and EC content from IMPROVE-TOR analysis, and assuming a mean value of 1.9 (with a standard deviation of 0.15) for organic matter (OM) to OC ratio (Turpin and Lim, 2001; Pitchford et al., 2007; Chen, 2011), the total PM$_{2.5}$ mass was apportioned to BC and OC mass as:

$$m_{BC} = \frac{m_{PM_{2.5}}}{1+1.9 \frac{OC}{EC}}$$  

(6.2)

$$m_{OC} = m_{BC} \frac{OC}{EC}$$  

(6.3)

where $m_{BC}$ and $m_{OC}$ are the respective values of BC and OC masses, and OC/EC is the mean ratio of OC to EC mass for each fuel type. The MAC values for the bulk aerosol deposits, BC and OC mass were calculated as:

$$MAC(\lambda) = A \frac{ABS(\lambda)}{m}$$  

(6.4)
where $A$ is the area of the filter and $m$ is the mass of aerosol deposited. Confidence intervals around the mean MAC values were estimated from analytical propagation of the underlying uncertainties. A lognormal distribution was used to calculate asymmetric 95% confidence intervals when the resulting uncertainty (ratio of standard deviation to mean) was greater than 30%. Since $ATN$ is the only directly measured quantity which captures the wavelength dependence of light absorption, we calculated AAEs by fitting power law curves to the $ATN$ datasets in the wavelength range of 350-550 nm. Values of $ABS$ and MAC were calculated by multiplying the measured $ATN$ values with wavelength independent quantities. Therefore, the uncertainties in AAE arise only from the uncertainties in $ATN$.

The total PM$_{2.5}$ $ATN$ and its LAOC attributable fraction were integrated over spectral solar irradiance between $\lambda = 300$ and 900 nm to estimate the fraction of light absorbed by LAOC (instead of BC):

$$F_{LAOC} = \frac{\int_{300 \, nm}^{900 \, nm} ATN_{LAOC}(\lambda) i(\lambda) d\lambda}{\int_{300 \, nm}^{900 \, nm} ATN_{PM_{2.5}}(\lambda) i(\lambda) d\lambda}$$

(6.7)

where $F_{LAOC}$ is the fraction of the visible solar radiation absorption attributable to LAOC (W/g PM$_{2.5}$), and $i$ is the solar insolation as a function of wavelength $\lambda$ (W/m$^2$ nm).
6.2.2. Appearance of filter samples and deposited particles

The color of the particulate matter collected on quartz and Teflon filters was yellow-brown to brown (Figure 6.3), consistent with previous observations of LAOC-dominated filter samples from biomass burning (Andreae and Gelencsér, 2006; Chakrabarty et al., 2010). Figure 6.4A shows typical TEM images of an amorphous OC particle (Chakrabarty et al., 2010). Such particles, with sizes ranging 100-300 nm, were found in abundance in the samples collected from different fuel emissions in this study. These particles were co-emitted with BC aggregates (Figure 6.4B), composed of 40-70 nm diameter monomers.

Figure 6.3: Images of Teflon filter samples of aerosols from the combustion of (A) fuel-wood, (B) agricultural residue, (C) dung-cake and (D) mixed fuel in traditional cookstoves.
Figure 6.4: TEM images of (A) an amorphous OC particle typically emitted from fuels in this study and (B) OC particle with co-emitted BC aggregate.

6.2.3. Absorbance and MAC values of PM, BC and OC

Average aerosol $\text{ABS}$ for PM$_{2.5}$ emissions from the four fuel types are shown in Figure 6.5A. The de-convoluted spectra for BC and LAOC (per equation 6.1) show that the majority of the aerosol $\text{ABS}$ in the 300-500 nm wavelength range could be attributed to LAOC. Consistent with previous studies, absorption by biomass-emitted LAOC nearly drops to zero around 600 nm (Kirchstetter et al., 2004; Kirchstetter and Thatcher, 2012).

![Graph](image)

Figure 6.5: Average biomass $\text{ABS}$ values for (A) PM$_{2.5}$ emissions, and their (B) BC and (C) LAOC components. Error bars represent 95% CI around the means, based on the standard errors of the means.

Estimated OC/EC ratios for each biomass fuel sample are presented in Table 6.1. A mean ratio of 12 was measured for fuel-wood, which is within the range of values reported from past field
measurements (0.5-13.5) by Roden et al. (2006). However, this ratio is 3-30 times higher than those typically reported from laboratory-based experiments (Habib et al., 2008; MacCarty et al., 2008). Differences in testing procedure, fuel characteristics, and operating conditions make direct comparisons between field and laboratory measurements difficult, but there is evidence that real-world cooking conditions result in a higher number of smoldering events and higher particulate organic content than standard laboratory testing protocols (Roden et al., 2009). The mean OC/EC ratios for agricultural residue and dung cakes were a factor of 8-20 and 1.5-5 higher, respectively, than previous laboratory measurements (Parashar et al., 2005; Habib et al., 2008; Saud et al., 2012). Habib et al. (2008) suggested that the low density and high surface-to-volume ratios of rice straw and other crop residues could lead to large amounts of emissions of OM. This may explain why this study found the OC/EC ratios for agricultural residue to be 4-5 times higher than those for other biomass fuels.
Table 6.1: Ratio of OC to BC mass and optical properties (MAC and AAE) for aerosol samples by biomass fuel type.

<table>
<thead>
<tr>
<th>Fuel type</th>
<th>OC/EC$^{1,2}$</th>
<th>PM$_{2.5}$ MAC at 550 nm$^1$ (m$^2$/g)</th>
<th>BC MAC at 550 nm$^1$ (m$^2$/g)</th>
<th>OC MAC at 350 nm$^{1,3}$ (m$^2$/g)</th>
<th>PM$_{2.5}$ AAE$^{1,4}$</th>
<th>OC AAE$^{1,4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel-wood</td>
<td>12.1 (3.2-31.0)</td>
<td>1.3 (0.67-2.5)</td>
<td>12.2</td>
<td>4.4</td>
<td>2.4 (2.2-2.7)</td>
<td>5.8 (5.6-5.9)</td>
</tr>
<tr>
<td>Agricultural residue</td>
<td>60 (24-133)</td>
<td>0.6 (0.2-1.5)</td>
<td>32.2</td>
<td>3.6</td>
<td>3.3 (3.0-3.7)</td>
<td>5.8 (5.5-6.0)</td>
</tr>
<tr>
<td>Dung cake</td>
<td>15.4 (11-22)</td>
<td>0.5 (0.29-0.86)</td>
<td>15.1</td>
<td>3.4</td>
<td>3.6 (3.3-3.6)</td>
<td>7.7 (7.5-7.9)</td>
</tr>
<tr>
<td>Mixed fuel</td>
<td>14.5 (11-20)</td>
<td>0.9 (0.61-1.15)</td>
<td>17.9</td>
<td>4.1</td>
<td>3.0 (2.8-3.1)</td>
<td>6.0 (5.8-6.1)</td>
</tr>
</tbody>
</table>

$^1$ All values expressed as means (95 % confidence intervals)
$^2$ OC/EC values listed here are from the IMPROVE-TOR method
$^3$ OC MAC ~ 0.001-2 at 550 nm
$^4$ AAE is between 550 nm and 350 nm

We find that the values of PM$_{2.5}$ MAC (Table 6.1, see Figure 6.6 for detailed plots) for fuel-wood and agricultural residue in this study are slightly lower than those reported in Habib et al. (2008) and Roden et al. (2006), while our AAE values are higher. This is consistent with the substantially larger OC content measured in emissions from those fuel types in this study, compared to Habib et al. (2008). Our estimates of BC MAC (Table 6.1) fall within the broad range of values reported in literature (collated in Chen (2011)). The only exception being the BC MAC value estimated for agricultural residue emissions, which are significantly higher compared to those for other fuels. Samples from this particular fuel showed very low EC content and a large uncertainty in the OC/EC ratios (Table 6.1).
Figure 6.6: Fuel-wise PM$_{2.5}$ MAC values (m$^2$/g) as a function of the wavelength of incident radiation. The error bars represent 95% CI around the means, based on the standard errors of the means.

The average MAC values for OC emissions from the four fuel types are shown in Figure 6.7. We estimate average MAC values of 0.1 and 3.1 m$^2$g$^{-1}$ at 550 and 350 nm, respectively, with a mean AAE of 6.3 (±1.8) in this wavelength range. We found that the OC MAC values for different fuel types showed little variability: ~ 10% variation from the overall mean, while the uncertainty in each fuel ranged between 20-50%. Previous estimates of OC MAC for woody-biomass burning in the United States (Kirchstetter et al., 2004; Lack et al., 2012; Washenfelder et al., 2015) are also shown for comparison. While the methodology for apportioning the OC component of aerosol absorption varies between the studies, there is good agreement between the resulting MAC values.
Figure 6.7: Fuel-wise OC MAC values (m²/g) as a function of the wavelength of incident radiation. The error bars represent 95% CI around the mean. Symbols represent the mean OC MAC values reported from wood burning in literature [circle = Kirchstetter et al. (2004) square = Washenfelder et al. (2015); triangle = Lack et al. (2012); star = Chen (2011)].

As 70% of the incoming solar radiation energy is distributed in the 300-900 nm range, the integration of total PM$_{2.5}$ ABS and its LAOC component over solar insolation (in Wm$^{-2}$nm$^{-1}$) in this range gives a measure of their overall absorption behavior. Figure 6.8A shows the fraction of the total ABS attributed to LAOC in a typical aerosol sample from each fuel type, as a function of wavelength. Figure 6.8B shows the overall fraction of solar radiation in the 300-900 nm wavelength range that would be absorbed by LAOC rather than BC. Since aerosol scattering measurements were not conducted as part of this study, we could not compute the overall direct forcing efficiency, which could have provided a more quantitative estimate of the net climate impacts of LAOC. Nevertheless, our results indicate that LAOC contributes significantly (26-45%) to light absorption by real-world cookstove emissions. Agricultural residue emissions have the
highest OC/EC ratio (Table 6.1) and therefore the highest contribution to light absorption by LAOC. Compared to Kirchstetter and Thatcher (2012), we attribute a larger portion of the total absorption by biomass burning aerosol to LAOC, highlighting regional differences in the fuel properties and combustion technologies.

Figure 6.8. (A) Fraction of the total aerosol absorbance attributed to light absorbing OC as a function of wavelength. (B) Fraction of solar radiation (in the 300-900 nm range) absorption (Wm$^{-2}$ aerosol) attributed to LAOC, per biomass fuel type. Error bars represent 1 standard error about the mean.

### 6.3. Analysis of comprehensive field study samples with updated filter correction

**6.3.1. Sampling and analysis**

Experimental methods for the field study conducted between December 19 and 30th of 2015 in Chhattisgarh, India have been detailed in Chapter 4. Briefly, thirty cooking tests with three fuel types (fuelwood, agricultural residue and cattle dung) were performed on a traditional mud *chulha*. Fuels were sourced from different regions that have a biomass user population. Each cooking test involved the preparation of a local meal item. A Testo-350 gas analyser continuously measured carbon monoxide (CO) and carbon dioxide (CO$_2$) during the cooking tests. PM$_{2.5}$ samples were collected on 47 mm Teflon membrane and quartz fiber filters using Minivol (5 L min$^{-1}$) samplers (AirMetrics Model 4.2), during different times in each cooking cycle. Teflon filters were weighed
before and after sampling using a microbalance at Pt. Harishankar Shukla University, Raipur, India to obtain the net mass deposited. Both sets of filters were stored in a freezer (-20 °C) after each day of sampling. At the end of the study, the quartz filters were transported to Desert Research Institute, Nevada, where they were analyzed using the Interagency Monitoring of Protected Visual Environments – A (IMPROVE_A) thermal-optical reflectance (TOR) method (Chow et al., 2007; 2011) to determine elemental and organic carbon fractions in the sampled particulates. The Teflon filters were brought to Washington University in St Louis for optical analysis. For each filter, sample-side transmittance ($T_s$) and reflectance ($R_s$) were measured for wavelengths 350-900 nm (Pandey et al., 2019b) using a Perkin-Elmer LAMBDA 35 UV-vis spectrophotometer. The relevant optical depth ($OD_s$) of the filter-particle system was calculated as:

$$OD_s(\lambda) = \ln\left(\frac{1-R_s(\lambda)}{T_s(\lambda)}\right)$$

(6.8)

This optical depth was converted to particle-phase light absorption optical depth ($ABS_{PM}$) using the empirical correction scheme developed for carbonaceous aerosols in Chapter 5:

$$ABS_{PM}(\lambda) = 0.48 \ (OD_s(\lambda))^{1.32}$$

(6.9)

The assumptions in the apportionment analysis were updated to reflect recent findings: BC particles emitted from biomass burning are likely to be coated with organic material that enhances light absorption with respect to pure BC. While the wavelength dependence of BC light absorption is described by an AAE of 1, modeling (Liu et al., 2018) and experimental (Gyawali et al., 2013) studies show that coated fractal-like BC aggregates have AAE ranging 0.9-1.5. A central BC AAE value of 1.2 (with 0.9 and 1.5 as lower and upper extremes, respectively) was used to describe BC spectral behavior here. All light absorption for wavelengths larger than $\lambda_t = 700$ nm was attributed to coated BC, and BC light absorption at smaller wavelengths was estimated from BC absorption
at 700 nm using the above AAE value. A lower value of \( \lambda_t \) was used here than in Pandey et al. (2016) because most samples in this study had negligible absorption at wavelengths greater than 700 nm. This was because care was taken to avoid overloading the filter samples so as not to exceed the limits of validity of our artifact correction scheme. OC light absorption was estimated as the difference between the total and coated BC absorption values. While the true value of BC AAE for each sample is uncertain, the use of a reasonable range of BC AAE values allows us to constrain OC contribution to light absorption.

Particulate absorption cross-sections were normalized by fuel consumption to estimate absorption emission factors (AEFs). The carbon mass balance technique was used to estimate the amount of fuel consumed during each sample collection interval, \( \Delta t_s \). Absorption emission factors were calculated as:

\[
\text{AEF}_{PM} = \text{ABS}_{PM} \times A_s \times \frac{\text{CMF}_{\text{fuel}} \times Q \times \Delta t_s}{\Delta C_{CO_2} \left( \frac{M_C}{M_{CO_2}} \right) + \Delta C_{CO} \left( \frac{M_C}{M_{CO}} \right)}
\]

where \( A_s \) is the sample area (in m\(^2\)) on the filter and the last term on the right-hand side is the inverse of the mass of fuel consumed (g\(^{-1}\)). \( \Delta C_{CO_2} \) and \( \Delta C_{CO} \) are the concentrations above ambient levels (background measured before each cooking test) of CO\(_2\) and CO in g m\(^{-3}\), respectively. \( M_C, M_{CO_2}, \) and \( M_{CO} \) are the atomic or molecular weights of C, CO\(_2\), and CO in g mole\(^{-1}\). CMF\(_{\text{fuel}}\) is the carbon mass fraction of the fuel, which ranged from 33% to 50% for the tested fuels. \( Q \) is the volumetric flow rate through the filter, in m\(^3\) s\(^{-1}\). Absorbances of the OC and BC components were used to calculated absorption emission factors (AEF\(_{OC}\) and AEF\(_{BC}\), respectively), in a similar manner to the AEF\(_{PM}\) calculation above.
Dimensionless absorption or \(ABS\) for PM\(_{2.5}\), BC and OC was also normalized by their respective mass loadings (in g/m\(^2\)) to calculate the corresponding mass absorption cross-sections (MAC\(_{PM/BC/OC}\)):

\[
MAC_{PM/OC/BC} = ABS_{PM/OC/BC} \times \frac{1}{L_{PM/OC/BC}} \tag{6.11}
\]

OC contribution to forcing by cookstove emissions was isolated by calculating a MAC value for PM\(_{2.5}\) emissions with only BC-attributed light absorption:

\[
MAC_{PM,\text{noOC}} = \frac{ABS_{BC}}{L_{PM}} = (ABS_{PM} - ABS_{OC}) \times \frac{1}{L_{PM}} = ABS_{PM}(1 - f_{OC}) \times \frac{1}{L_{PM}} \tag{6.12}
\]

6.3.2. Absorption emission factors and light absorption emissions of BC and OC

Real-world cookstove operation can be treated as a series of combustion events situated between strongly flaming and pure smoldering conditions (Chen et al., 2012). Intrinsic optical properties of emitted particles are largely a function of burn conditions: previous cookstove studies observed strongly absorbing (BC like) emissions during strong flaming and a range of weakly absorbing emissions during other phases (Roden et al., 2006; Chen et al., 2012). Expectedly, AEFs in this study varied by the observed combustion conditions, with smoldering phase AEF values lower than AEFs for steady flaming conditions (Figure 6.9A). The unsteady flame conditions during the ignition phase are reflected in the large variability in ignition AEFs. Variability in burn conditions drives optical characteristics more than fuel type (Weyant et al., 2019): the differences between AEFs for the three fuel categories were statistically insignificant (unpaired Student’s \(t\)-test, differences between groups not significant at \(p=0.05\)). Pooled AEF data for all samples show an approximately lognormal distribution factor with a large spread. We report a combined geometric mean of 3.7 m\(^2\)kg\(^{-1}\) fuel and 95% confidence intervals (CI) of 0.6-23.3 m\(^2\)kg\(^{-1}\) fuel.
Figure 6.9: PM$_{2.5}$ absorption emission factors, or AEF$_{PM}$ in m$^2$kg$^{-1}$ fuel consumed, (A) grouped by observed combustion phase: boxes denote the upper and lower quartiles and whiskers denote 1.5 times the interquartile range, outliers are shown as red + symbols, number of samples for each category are specified above the whiskers and (B) shown as a histogram of all samples, overlaid by a fitted lognormal distribution.

Distributions of OC and BC AEF values are shown in Figure 6.10. For BC AAE of 1.2, we determined the ratio of geometric mean values of OC AEF to PM absorption at 550 nm as 0.37; this ratio for different BC AAE values ranged 0.30-0.43. Previous apportionment analyses of savanna wildfire smoke (Kirchstetter et al., 2004) and residential fireplace emissions (Kirchstetter and Thatcher, 2012) showed lower OC contributions to light absorption (13-32% at 500 nm). These absorption emission factors were combined with fuel use data to estimate annual light absorbing emissions, in Gm$^2$y$^{-1}$ (Figure 6.11). Bottom-up biomass fuel use estimates disaggregated at the district level (Pandey et al., 2014) and multiplied by biomass-average AEFs. These emissions were gridded to a 0.1 by 0.1º spatial resolution. Mean value and 95% CI for absorption cross-section emissions from OC were 577 (64-2266) Gm$^2$ y$^{-1}$, while those from BC were 988 (110-3897) Gg y$^{-1}$. Such optical inventories can be used to compare sectoral contributions to light absorption by BC and OC and discern patterns in the spatial distributions of these contributions. Figure 6.11 demonstrates absorption emissions hotspots over the Indo-Gangetic Plain, which is
associated with a higher than average aerosol burden (David et al., 2018) with a large contribution from the residential sector (Chowdhury et al., 2019).

Figure 6.10: Absorption emission factors in m²kg⁻¹ fuel consumed: (A) AEF_{OC} grouped by observed combustion phase: boxes denote the upper and lower quartiles and whiskers denote 1.5 times the interquartile range, outliers are shown as red + symbols, number of samples
6.3.3. **Intensive optical properties of OC and their radiative impact**

Estimating radiative impact of emissions requires optical cross-sections normalized to pollutant mass. Average MAC values for OC emissions and the contribution of OC to total light absorption, integrated over solar irradiance in 350-900 nm wavelength range, are reported in Table 6.3. We further calculated PM MAC values with and without OC absorption (distribution plots are in Appendix A3) to evaluate the contribution of OC to direct radiative forcing by cookstove emissions. $\text{MAC}_{\text{PM}}$ values have an approximately lognormal distribution with average and 95% confidence intervals of 0.54 (0.10-1.46) m$^2$g$^{-1}$. When OC light absorption is set to zero, $\text{MAC}_{\text{PM, no-OC}}$ can be calculated by normalizing the remaining (BC only) absorption to PM mass. This quantity depends on the assumed values of BC AAE and also exhibits a lognormal distribution with a large spread. Mean values of $\text{MAC}_{\text{PM, no-OC}}$ ranged 0.39-0.45 m$^2$g$^{-1}$. The large, overlapping ranges of $\text{MAC}_{\text{PM}}$ and $\text{MAC}_{\text{PM, no-OC}}$ pose a challenge in constraining OC contribution to direct forcing. However, these parameters do not vary independently of each other: at 550 nm wavelength, higher

---

Figure 6.11: Spatial distribution of annual emissions expressed as light absorption cross-section (AE: Gm$^2$y$^{-1}$) at 550 nm attributed to (A) OC and (B) BC components of cookstoves emissions in India. BC AAE = 1.2 was used.
absorption efficiencies of cookstove emissions are associated with a larger contribution from BC (Figure 6.13A). In other words, MAC\textsubscript{PM} and MAC\textsubscript{PM,\text{no-OC}} are positively correlated and their dependence can be captured by a linear relationship (Figure 6.13B).

Figure 6.12: (A) The contribution of OC light absorption to MAC\textsubscript{PM} at 550 nm, f\textsubscript{OC}, decreases with increasing values of MAC\textsubscript{PM}. This implies that (B) MAC\textsubscript{PM,\text{no-OC}} is positively correlated with MAC\textsubscript{PM}. Linear fits between the two parameters are in Table 6.2.

Table 6.2: Slope (m), intercept (c) and adjusted R\textsuperscript{2} for the linear fits: MAC\textsubscript{PM,\text{no-OC}} = m*MAC\textsubscript{PM} + c.

<table>
<thead>
<tr>
<th>BC AAE</th>
<th>m</th>
<th>c</th>
<th>Adjusted R\textsuperscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>0.82</td>
<td>-0.09</td>
<td>0.97</td>
</tr>
<tr>
<td>1.2</td>
<td>0.88</td>
<td>-0.09</td>
<td>0.97</td>
</tr>
<tr>
<td>1.5</td>
<td>0.94</td>
<td>-0.1</td>
<td>0.97</td>
</tr>
</tbody>
</table>

This correlation (Table 6.2) was exploited for forcing calculations. MAC\textsubscript{PM} was sampled from the distribution observed (Appendix A3), then MAC\textsubscript{PM,\text{no-OC}} was calculated from the linear fit above. Bounds for cookstove emissions mass scattering cross-section (MSC) values were taken from measurements on traditional south Asian chulhas (Weyant et al., 2019) as 1.5-2.5 m\textsuperscript{2}g\textsuperscript{-1}. Simple forcing efficiency (SFE) was calculated as a function of MAC and MSC (Bond and Bergstrom,
While the magnitude of SFE is dependent on the choice of MSC, for a fixed MSC, change in SFE due to OC light absorption ($SFE_{PM} - SFE_{PM, no-OC}$) only depends on the respective MAC values. OC contributions to SFE are reported as a function of the BC AAE used for absorption apportionment in Table 6.3. OC absorption added 8.6-12.1 Wg$^{-1}$ to forcing over ground and 36.3-51.5 Wg$^{-1}$ to forcing over snow by fresh cookstove emissions. For MSC = 1.5 m$^2$g$^{-1}$, SFE for cookstoves PM$_{2.5}$ emissions over ground was estimated as 11±23 Wg$^{-1}$. Using the mean value of this estimate, we observe that if all cookstove OC was non-absorbing, it would purely offset BC forcing, leading to a mean net forcing efficiency of -1.1-2.4 Wg$^{-1}$. Distributions of SFE estimates with and without OC absorption and those of SFE attributed to OC are in Appendix A3.

Table 6.3: Simple forcing efficiency of cookstove emissions attributed to OC light absorption (in Wg$^{-1}$ PM$_{2.5}$), MAC$_{OC}$ (in Wg$^{-1}$ PM), AAE$_{OC}$, and contribution of OC to PM$_{2.5}$ light absorption (percentage of total absorption). These estimates depend on the value of BC AAE used in absorption apportionment. All values are reported as mean±1 standard deviation.

<table>
<thead>
<tr>
<th></th>
<th>BC AAE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.9</td>
</tr>
<tr>
<td>SFE attributed to OC (Wg$^{-1}$)</td>
<td>ground</td>
</tr>
<tr>
<td>MAC$_{OC}$ (m$^2$g$^{-1}$)</td>
<td>550 nm</td>
</tr>
<tr>
<td></td>
<td>350 nm</td>
</tr>
<tr>
<td>AAE$_{OC}$ (350-700 nm)</td>
<td>5.8±1.3</td>
</tr>
<tr>
<td>Integrated (350-900 nm) OC contribution to light absorption (%)</td>
<td>56 ±26</td>
</tr>
</tbody>
</table>

6.4. Comparison with findings in literature

Absorption and scattering cross-sections of PM$_{2.5}$ emitted from cookstoves are compared in Table 6.4. The measurement wavelengths differed in these studies, but the reported AAE values can be used to compare the findings. With the improved filter artifact correction method, we find lower average MAC values than our results in Pandey et al. (2016). Our estimates are also significantly
lower than those reported from filter-based measurements in other studies but close to those from the PAS measurements (Stockwell et al., 2016; Jayarathne et al., 2018), which range 0.1-0.6 at 550 nm (extrapolated from observations at 405 nm using reported AAE values). In to the findings included in the table below, Stockwell et al. (2016) also measured absorption at 870 nm. This measurement was used to apportion total absorption to BC and OC, using a BC AAE of 1, yielding an estimate of 80-93% OC contribution to particle light absorption at 405 nm. Our estimates of the corresponding OC contribution range 50-70%. Weyant et al., (2019) used a linear regression model with an interaction term to express the total AEF as a function of the mass emission factors of OC and EC:

\[ AEF_{PM} = a_1 EF_{EC} + a_2 EF_{OC} + a_3 EF_{EC} \times EF_{OC} \]  \hspace{1cm} (6.13)

The coefficients of regressions a1 and a2 may be taken to represent MAC values of EC and OC, respectively but the presence of the interaction term complicates this interpretation. Given the complex interplay between combustion conditions, EC and OC abundance in the resulting emissions and their associated absorption efficiencies, the explanatory power of such an analysis is uncertain. With that caveat, we note the estimated ~10% OC contribution to light absorption at 530 nm in the above study, compared to an estimate of ~40% in our work.
Table 6.4: Summary of optical cross-sections of particulate emissions from biomass cookstoves.

<table>
<thead>
<tr>
<th>Study</th>
<th>Absorption measurement method</th>
<th>MAC (m²g⁻¹)ᵃ</th>
<th>AAE</th>
<th>MSC (m²g⁻¹)ᵃ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roden et al. (2006)</td>
<td>PSAP, Bond et al. (1999) correction</td>
<td>2.8ᵇ 530 nm</td>
<td>1.8ᶜ</td>
<td>2.2ᵇ 530 nm</td>
</tr>
<tr>
<td>Habib et al. (2008)</td>
<td>Integrating plate, Bond et al. (1999) correction</td>
<td>0.5-2.7ᵈ 525 nm</td>
<td>0-3.4ᵈ</td>
<td>-</td>
</tr>
<tr>
<td>Pandey et al. (2016)</td>
<td>UV-vis spectrometer, Zhong and Jang (2011) constant correction</td>
<td>0.5-1.3ᵈ 550 nm</td>
<td>2.4-3.6ᵈ</td>
<td>-</td>
</tr>
<tr>
<td>Stockwell et al. (2016)</td>
<td>PAS</td>
<td>0.4ᵉ⁻ᵍ, 1.5ᶠᵍ 405 nm</td>
<td>3.0ᵉ, 4.6ᶠ</td>
<td>3.7ᵉ⁻ᵍ, 3.4ᶠᵍ</td>
</tr>
<tr>
<td>Weyant et al. (2019)</td>
<td>PSAP, Bond et al. (1999) correction</td>
<td>1.6-6.6ʰⁱ 530 nm</td>
<td>1.6-2.3ʰ</td>
<td>1.7-3.0ʰ 530 nm</td>
</tr>
<tr>
<td>Pandey et al. (2019a)</td>
<td>UV-vis spectrometer, Pandey et al. (2019a) correction</td>
<td>0.36-0.7ˡ 550 nm</td>
<td>2.7-3.0ˡ</td>
<td>-</td>
</tr>
</tbody>
</table>

ᵃWavelength for each measurement is specified
ᵇMean values for wood burning Honduran cookstoves. Standard deviations are ~0.6
ᶜAAE reported by Chen et al., 2011 (an extended analysis of observations from Roden et al., 2006)
ᵈRange of values reported from field cookstove tests involving various common biomass fuels (wood, agricultural residues and dung)
ᵉMAC, AAE and MSC for dung cooking fires
ᶠMAC, AAE and MSC for wood cooking fires
ᵍMAC and MSC were estimated by combining absorption and scattering emission factors, respectively, with corresponding PM emission factors reported in Jayaratne et al., 2018 (based on the same field study)
ʰRange of values reported from field tests of South Asian chulhas, not speciated by fuel type
¹MAC<sub>PM</sub> estimated from reported values of MAC<sub>EC</sub> using the EC and PM emission factors provided
.major| Range of values reported from field cookstove tests involving various common biomass fuels. MAC values showed the trend: dung<wood<agricultural residue

We suggest the use of MAC<sub>OC</sub> = 0.3-0.5 m²g⁻¹ at 550 nm and AAE<sub>OC</sub> = 6 for emissions from traditional Indian cookstoves. Given the link between combustion conditions and OC light absorption (Saleh et al., 2014; Saleh et al., 2018), these values could also represent other biomass combustion sources with BC/OC ratios ~0.1-0.2. Recent global radiative models that evaluated the
enhancement in aerosol light absorption due to OC (Feng et al., 2013; Wang et al., 2014) assumed that a fraction (50-66%) of the OC is light-absorbing and derived the index of refraction of this component using reported absorption efficiencies of solvent extracted OC particles. When normalized to the mass of all OC (as in this work), the absorption cross-sections employed in these studies ranged 0.05-0.47 m²g⁻¹ at 550 nm and 1.50-2.27 m²g⁻¹ at 350 nm. Cookstove emitted OC has an absorption efficiency comparable to that of “strongly absorbing” type of OC modeled in (Feng et al., 2013), which was linked with shifting the net global radiative forcing of organic aerosols from cooling to warming. Likewise, our simple forcing calculations suggest that OC light absorption could tip the net impact of carbonaceous cookstove emissions to positive direct forcing.
References


dependence of light absorption by organic carbon particles formed by propane combustion,

Stockwell, C. E., Christian, T. J., Goetz, J. D., Jayaratne, T., Bhave, P. V., Praveen, P. S.,
Adhikari, S., Maharjan, R., DeCarlo, P. F., and Stone, E. A.: Nepal Ambient Monitoring and
Source Testing Experiment (NAMaSTE): emissions of trace gases and light-absorbing carbon
from wood and dung cooking fires, garbage and crop residue burning, brick kilns, and other

Moore, M., and Rorig, M.: Grassland and forest understorey biomass emissions from
prescribed fires in the south-eastern United States–RxCADRE 2012, International Journal of

Subramanian, R., Roden, C. A., Boparai, P., and Bond, T. C.: Yellow beads and missing particles:
Trouble ahead for filter-based absorption measurements, Aerosol Sci. Technol., 41, 630-637,
2007.

Sun, H., Biedermann, L., and Bond, T. C.: Color of brown carbon: A model for ultraviolet and

Turpin, B. J. and Lim, H.-J.: Species contributions to PM2.5 mass concentrations: Revisiting

biofuels in South Asia: carbonaceous aerosol emissions and climate impacts, Science, 307,
1454-1456, 2005.

Wang, X., Heald, C., Ridley, D., Schwarz, J., Spackman, J., Perring, A., Coe, H., Liu, D., and
Clarke, A.: Exploiting simultaneous observational constraints on mass and absorption to
estimate the global direct radiative forcing of black carbon and brown carbon, Atmos. Chem.

Washenfelder, R., Attwood, A., Brock, C., Guo, H., Xu, L., Weber, R., Ng, N., Allen, H., Ayres,
B., and Baumann, K.: Biomass burning dominates brown carbon absorption in the rural

Watson, A. Y. and Valberg, P. A.: Carbon black and soot: two different substances, AIHAJ-

Weingartner, E., Saathoff, H., Schnaiter, M., Streit, N., Bitnar, B., and Baltensperger, U.: Absorption
of light by soot particles: determination of the absorption coefficient by means of

Weyant, C. L., Chen, P., Vaidya, A., Li, C., Zhang, Q., Thompson, R., Ellis, J., Chen, Y., Kang,
S., and Shrestha, G. R.: Emission measurements from traditional biomass cookstoves in South

Xie, M., Hays, M. D., and Holder, A. L.: Light-absorbing organic carbon from prescribed and
laboratory biomass burning and gasoline vehicle emissions, Scientific reports, 7, 7318, 2017.

spectrometer connected with an integrating sphere, Atmos. Environ., 45, 4263-4271, 2011.
Chapter 7: Conclusions

7.1. BC optical parameterization

To bridge the gap between optical models that explicitly handle the fractal morphology of BC aggregates and radiative models that assume spherical morphology for all aerosols, I have developed relationships between numerically-exact calculations of BC optical properties and equivalent aerosol (mobility, mass equivalent and vacuum aerodynamic) diameters, for freshly emitted and aged aggregates. The above descriptors of particle size are measured by widely used aerosol instrumentation such as SMPS, SP2, and the SP-AMS. A major finding was that a larger fractal dimension (representing atmospherically aged BC) corresponds to more intense interactions between monomers, from a more compact structure, and usually serves to intensify the variation of radiative properties with aggregate size. One critical area for future research is to assess the range in BC refractive index upon coating of BC particles with organic and inorganic aerosols.

Radiative transfer models typically use the upscatter fraction to represent scattering directionality: $\beta$ is estimated from asymmetry parameter calculated from Mie theory or the backscatter ratio measured using a nephelometer. An approximate analytical expression (the HG phase function) for the angular distribution of light scattered by small particles is commonly used to aid the above computations. I examined the applicability of relationships based on the HG phase function to fractal BC aggregates:

- Upscatter fractions derived using these approximate relationships are lower than its actual values.

- Improved parameterizations from my study can be used to connect the three directionality parameters for collapsed aggregates
• For open aggregates, analytical expressions cannot accurately describe the parameter relationships for large particles (mass equivalent diameter > 200 nm) because one-to-one relationships do not exist.

The error in $\beta$ from use of approximate HG-based relationships could be up to 35%, the corresponding error in simple forcing efficiency is within 8%. Further evaluation is needed on the suitability of HG-based relationships for coated fractal aggregates and nonideally shaped particles like mineral dust.

7.2. Aerosol emissions from biomass cookstoves

My field study of traditional cookstove (chulha) performance in India, using a variety of regionally significant fuels showed that cookstoves are a larger culprit in particulate pollution in India than previously estimated (Pandey et al., 2014). The major findings from this study are:

• Emission factor differences for four types wood fuels from different regions of India were statistically insignificant because the variability in emissions for a given fuel type was comparable to the differences in average emission rates for different wood fuels. Agricultural residues and dung are associated with larger emissions than fuel-wood.

• Ignition and rekindling consistently produce much more emissions than steady flaming conditions. Real-time particle concentrations (based on light scattering) and CO concentration measurements fluctuate over a cooking cycle, in contrast with findings from laboratory studies.

• Ratios of fuel-wise cookstove PM emission factors from our field study to those in the SMOG inventory (an average of best available values published till date) ranged 2.2-2.5, while those for OC emission factors ranged 2.5-4.2. Other recent field evaluations of cookstove performance support these findings: on average, real-world PM$_{2.5}$, OC
and EC emission factors are larger than their counterparts from simulated cooking cycles (water boiling test) by factors of 2.1, 1.5 and 3.1, respectively

- Over field and WBT studies, OC mass constituted approximately 60% of the total particle mass. This indicates that studies that underestimate PM emission factors likely use cooking cycles characterized by more frequent strong flaming conditions than actual cooking.

### 7.3. Filter artifact correction for UV-vis spectroscopy on Teflon membrane filters

Teflon filters are routinely used for gravimetric and elemental analysis across monitoring networks and field and laboratory source characterization studies. UV-vis spectrophotometers are used to measure transmittance and reflectance measurements for these filters, in order to estimate the absorption properties of deposited particles. Artifacts associated with this estimation are not well-characterized. I compared in-situ aerosol light-absorption observations with optical measurements made on concurrently collected filter samples, Through radiative transfer modeling, I assessed the suitability of three measures of filter-based optical depth for robustly describing particulate-phase light absorption over a range of single scattering albedo (SSA) values: (1) $OD_s$—a measure of transmission of the fraction of incident radiation that is not backscattered by the filter system—utilizes transmittance and reflectance of the sample side of the filter, (2) the commonly-used $OD_c$ uses transmittance and reflectance of the clean side of the filter, and (3) $ATN$ or the Beer-Lambert attenuation. The key findings were:

- $OD_s$ showed the least sensitivity to SSA, for fixed filter loading. Therefore, this measure is the best choice for estimating aerosol light absorption from filter optical measurements for a wide range of aerosol types.
• A simple, wavelength-independent formulation can be used for calculating aerosol MAC and absorption coefficients from measurements of \( OD_s \).

• The ratio between in-situ particulate absorption optical depth and \( OD_s \) is inversely proportional to aerosol SSA.

In many measurement systems, such as the Hybrid Integrating Plate and Sphere method (Bond et al., 1999) used by the IMPROVE network, transmittance and reflectance are measured on the clean side of the filter and the optical depth \( OD_c \) is calculated (Campbell et al., 1995; White et al., 2016). The relationship between aerosol optical depth, \( \tau_{a,s} \), and \( OD_c \) showed a larger variability across varying SSA than that between \( \tau_{a,s} \) and \( OD_s \). Therefore, we suggest further evaluation of \( OD_s \) as an optical depth measure that can be empirically connected to particulate phase light absorption for a range of aerosol types.

7.4. Light absorption by cookstove OC emissions
Climate models have conventionally neglected atmospheric light absorption by OC. Among the key inputs needed for in expanding the conventional discussion of aerosol climate impacts are MAC and AAE values for OC aerosols. OC physical and optical properties like refractoriness, polarity and crucially, absorption efficiency span a large inter-linked range, and show a dependence on combustion conditions. My analysis of in-use cookstove performance showed that cookstove PM emissions are dominated by thermally-stable OC indicating a potential for significant light absorption. I applied my recently-developed artifact correction scheme to optical measurements on the Teflon filter samples collected during the cookstove field study. I used a two-component model to apportion total particle light absorption to BC and OC, exploiting the difference in their spectral absorption dependences. I concluded that:
• OC contributes nearly as much as BC to light absorption by cookstove emissions at mid-visible wavelengths. This estimate is well-constrained with respect to the potential variability in BC AAE.

• Estimated MAC and AAE values of OC emissions are in agreement with those used for a “strongly absorbing” type of OC included in recent climate modeling exercises.

• OC light absorption has a significant positive contribution to the direct forcing efficiency of carbonaceous cookstove emissions.

Taken as a whole, my findings indicate that replacement of traditional cookstoves with clean technologies could mitigate aerosol related warming in addition to reducing particulate exposure and the associated disease burden (Chowdhury et al., 2019) in South Asia. However, if these clean technologies include advanced biomass stoves, improved laboratory testing (Chen et al., 2012) and field validation are crucial for evaluating the extent, if any, of the health and climate benefits of technology replacement. Light-absorbing OC should be addressed as a distinct short-lived-climate-forcing agent in discussions of cookstove impacts in India. These findings may also be applicable to other regions of Asia, as well as Africa and South America, where cooking with solid biomass fuels is prevalent.
References


Appendix

A1. Two-stream radiative transfer model

Consider the layer of filter in which sampled particles are embedded to be a one-dimensional uniform medium with an optical thickness $\tau_0$, a single scattering albedo $\omega<1$ and a scattering asymmetry parameter $g$. Now, consider a ‘forward’ direction: at any point in the medium the energy intensity propagating in this direction is given by $I_f$. Conversely, the backward propagation intensity is $I_b$.

Energy conservation in the medium can be written as (Bohren, 1987):

\[
\frac{d(I_f-I_b)}{d\tau} = -(1 - \omega_0)(I_f + I_b) \tag{A1.1a}
\]

\[
\frac{d(I_f+I_b)}{d\tau} = -(1 - \omega_0 g)(I_f - I_b) \tag{A1.1b}
\]

The general solution of the above equations has the following form:

\[
(I_f - I_b) = p_1 \exp(-K\tau) + p_2 \exp(K\tau) \tag{A1.2a}
\]
\[(I_f + I_b) = q_1 \exp(-K\tau) + q_2 \exp(K\tau)\]  \hspace{1cm} \text{(A1.2b)}

where \(K = \sqrt{(1 - \omega_0)(1 - \omega_0g)}\)

Assume that the medium is (1) illuminated from the top: \(I_f(\tau = 0) = I_0\) and (2) does not reflect at the opposite edge: \(I_b(\tau = \tau_0) = 0\). Reflectance \(R_l\) and transmittance \(T_l\) of the medium are respectively defined as: \(I_b(\tau = 0) = R_l\) and \(I_f(\tau = \tau_0) = T_l\). With these boundary conditions, the constants \(p_1, p_2, q_1\) and \(q_2\) can be estimated. Then the quantities of interest, \(R_l\) and \(T_l\), are given by (Arnott et al., 2005):

\[R_l = \frac{\omega_0(1-g)\sinh(K\tau_0)}{[2K-\omega_0(1-g)\sinh(K\tau_0)+2K\cosh(K\tau_0)]} \hspace{1cm} \text{(A1.3a)}\]

\[T_l = \frac{2}{[2K-\omega_0(1-g)\sinh(K\tau_0)+2K\cosh(K\tau_0)]} \hspace{1cm} \text{(A1.3b)}\]

The subscript \(l\) is used in the equations above to denote the properties of a composite aerosol-filter layer. \(\tau_0\) denotes the total optical depth of the layer:

\[\tau_0 = \tau_{e,l} = \tau_{e,f} + \tau_{a,s} + \tau_{sc,s} \hspace{1cm} \text{(A1.4)}\]

Subscripts \(e, a\) and \(sc\) denote extinction, absorption and scattering optical depths. The second subscript \(f\) corresponds to the portion of the filter that was penetrated by the aerosol, while \(s\) represents the aerosol sample. Equation (A1.4) can be rewritten as:

\[\tau_{e,l} = \chi\tau_{e,f} + \tau_{a,s} \frac{(1+SSA)}{(1-SSA)} \hspace{1cm} \text{(A1.5)}\]

where \(\chi\) is the penetration depth of the aerosols in the filter (assumed 0.1 in this study). The optical depth of the filter in the first layer is proportional to the penetration depth and the optical depth of
a blank filter, $\tau_{e,F}$. In equation A1.5, SSA is the single scattering albedo of the deposited aerosols.

The single scattering albedo and asymmetry parameter of this composite layer are given by:

$$\omega_0 = \frac{\tau_{a.s}(\frac{SSA}{1-SSA}) + \chi \tau_{e,F}}{\tau_{a.s}(\frac{1+SSA}{1-SSA}) + \chi \tau_{e,F}}$$  \hspace{1cm} (A1.6)

$$g = \frac{g_s \times \tau_{a.s}(\frac{SSA}{1-SSA}) + g_F \times \chi \tau_{e,F}}{\tau_{a.s}(\frac{SSA}{1-SSA}) + \chi \tau_{e,F}}$$  \hspace{1cm} (A1.7)

The respective asymmetry parameters of the particles and filter are denoted by $g_s$ and $g_F$. In this study, was $g_s$ fixed at 0.6 (based on Martins et al. (1998); Reid et al. (2005)).

For the pristine portion of the filter (no aerosol embedded, therefore single scattering albedo is unity), the solution to Equations (A1.1a) and (A1.1b) is greatly simplified. The reflectance ($R_f$) and transmittance ($T_f$) of this layer is given by:

$$R_f = \frac{(1-\chi)\tau_F^*}{1+(1-\chi)\tau_F^*}$$  \hspace{1cm} (A1.8a)

$$T_f = \frac{1}{1+(1-\chi)\tau_F^*}$$  \hspace{1cm} (A1.8b)

where $\tau_F^* = \left(1 - g_F\right)\tau_F$ is estimated from the measurements of transmittance and reflectance through blank filters. Since a blank filter is non-absorbing, equations (A1.8a) and (A1.8b) can be applied to it, setting $\chi$ as zero (i.e. no loading). Measured transmittance through 20 lab blank PTFE membrane filters for wavelengths ranging 350-550 nm was 0.7±0.02. This range (2 standard deviations are ~6% around the mean) is slightly narrower than that (~10%) observed by White et al., 2016 for 534 passively exposed field blanks from the IMPROVE network. It is comparable to the variability in transmittance (~7%) of 150 clean blanks reported by Presler-Jur, 2017.

For $T_{blank}$=0.7, $\tau_F^*$ is calculated as:
\[
\tau_F^* = \frac{1}{\tau_{\text{blank}}} - 1 = 0.43 \tag{A1.9}
\]

This value of \( \tau_F^* \) was used in the fixed blank optics assumption (as discussed in Chapter 1.5) when examining the sensitivity to filter optical measures to a given model input. Some calculations were also performed assuming a realistic range of randomly-varying blank filter properties.

It can be shown that all calculations in equations A1.3a through A1.8b require only \( \tau_F^* \) and not \( \tau_F \) and \( g_F \). Therefore, any non-zero value can be assumed for \( \tau_F \) and \( g_F \) can be calculated such that the value of \( \tau_F^* \) is satisfied. With these filter properties (\( \tau_F \) and \( g_F \)), and assumed aerosol penetration depth \( \chi \) (see Figure 5.5 for sensitivity of model outputs to this parameter) and asymmetry parameter \( g_s \), \( R_l \), \( R_f \), \( T_l \) and \( T_f \) were calculated for a range of aerosol properties (\( \tau_{a,s} \) and SSA). Then, overall filter transmittance and reflectance, with light incident on the sample side of the filter, were estimated by performing an energy balance (Gorbunov et al., 2002):

\[
T_s = \frac{T_l T_f}{1 - R_l R_f} \tag{A1.10a}
\]

\[
R_s = R_l + \frac{\tau_F^2 R_f}{1 - R_l R_f} \tag{A1.10b}
\]

The optical behavior of PTFE filters was modeled for SSA varied between 0.2 and 0.99, and \( \tau_{a,s} \) between 0 and 1. A surface plot of \( OD_s \) as a function of SSA and \( \tau_{a,s} \) over the above input range is shown in Figure A1.2.
Figure A1.2: Modeled filter optical depth ($OD_s$) as a function of single scattering albedo (SSA) and aerosol optical depth ($\tau_{a,s}$) of deposited aerosols.
A2. List of aerosol emission factors by fuel and burn phase.

Table A2.1: Emission factors of PM$_{2.5}$, CO, OC and EC (in g pollutant kg$^{-1}$ fuel) for each test fuel and combustion phase.

<table>
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<th>Burn phase</th>
<th>Emission factor (g/kg fuel)</th>
<th></th>
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</thead>
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<td>PM$_{2.5}$</td>
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<tr>
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<tr>
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<td>Steady flame</td>
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<td>39</td>
</tr>
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<td>51</td>
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<tr>
<td></td>
<td>Smoldering</td>
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<td></td>
<td>Ignition</td>
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<tr>
<td>Chh. tur stalk</td>
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A3. Radiative forcing efficiency of cookstove emissions: probability distributions

Probability density distributions of the MAC values for cookstove emissions, with and without OC absorption (respectively, MAC$_{PM}$ and MAC$_{PM,\text{no-OC}}$) are shown in Figure A3.1. The distribution in panel A was combined with the empirical linear fits described in Chapter 6.3.3 to estimate MAC$_{PM,\text{no-OC}}$ as a function of MAC$_{PM}$ for different assumptions of BC AAE.

![Figure A3.1: Probability distributions of (A) MAC$_{PM}$ and (B) MAC$_{PM,\text{no-OC}}$ for all samples in this study.](image)

Simple forcing efficiency ($Wg^{-1}$ aerosol) is given by:

$$SFE = -\frac{1}{4} S(\lambda) \tau_{atm}^2 (1 - Fc) \times [2(1 - \alpha_s)^2 \beta \cdot MSC(\lambda) - 4\alpha_s \cdot MAC(\lambda)]$$  \hspace{1cm} (A3.1)

SFE calculations were performed for 550 nm wavelength ($\lambda$). The following atmospheric parameters were fixed: solar irradiance ($S=1370$ Wm$^{-2}$) atmospheric transmissivity ($\tau_{atm} = 0.79$), cloud fraction ($F_c=0.6$) and surface albedo ($\alpha_c=0.19$ for ground and 0.8 for snow). Particle upscatter fraction ($\beta$) was fixed at 0.15. With the above parameters fixed, SFE is a function of MAC and MSC values. MSC was not measured in this study but the relationship between OC light absorption
and SFE can be demonstrated by calculating SFE with $\text{MAC}_{PM}$ and $\text{MAC}_{PM,\text{no-OC}}$, in turn. In Figure A3.2 S3, the distribution of SFE values over ground and snow for $\text{MSC}=1.5 \text{ m}^2\text{g}^{-1}$ is shown.

![Diagram](https://via.placeholder.com/150)

**Figure A3.2**: Probability distributions of simple forcing efficiency of cookstove particulate emissions over (A) ground and (B) snow. Forcing was calculated with and without OC light absorption, with a fixed MSC = $1.5 \text{ m}^2\text{g}^{-1}$.

The difference between $SFE_{PM}$ and $SFE_{PM,\text{no-OC}}$ depends only the difference in the respective MAC values:

$$SFE_{PM} - SFE_{PM,\text{noOC}} = S(\lambda) \tau_{atm}^2 (1 - F_c) \alpha_S \times [\text{MAC}_{PM}(\lambda) - \text{MAC}_{PM,\text{noOC}}(\lambda)]$$  \hspace{1cm} (A3.2)

This difference can be interpreted as the contribution of OC light absorption to forcing by cookstove emissions. Estimated probability distributions of SFE attributed to OC light absorption are shown in Figure A3.3.
Figure A3.3: Probability distributions of simple forcing efficiency of cookstove particulate emissions attributed to OC light absorption over (A) ground and (B) snow.

References