Filter-based measurements of UV-Vis mass absorption cross sections of organic carbon aerosol from residential biomass combustion: Preliminary findings and sources of uncertainty

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Abstract

Combustion of solid biomass fuels is a major source of household energy in developing nations. Black (BC) and organic carbon (OC) aerosols are the major PM_{2.5} (particulate matter with aerodynamic diameter smaller than 2.5 μm) pollutants co-emitted during burning of these fuels. While the optical nature of BC is well characterized, very little is known about the properties of light absorbing OC (LAOC). Here, we report the mass-based optical properties of LAOC emitted from the combustion of four commonly-used solid biomass fuels, namely fuel-wood, agricultural residue, dung-cake, and mixed, in traditional Indian cookstoves. As part of a pilot field study conducted in central India, PM_{2.5} samples were collected on Teflon filters and analyzed for their absorbance spectra in the 300-900 nm wavelengths at 1 nm resolution using a UV-Visible spectrophotometer equipped with an integrating sphere. The mean mass absorption cross-sections (MAC) of the emitted PM_{2.5} and OC, at 550 nm, were 0.8 and 0.2 m^2g^{-1} , respectively, each with a factor of ~ 2.3

uncertainty. The mean absorption Ångström exponent (A_{AE}) values for $\text{PM}_{2.5}$ were 3 ± 1 between 350 and 550 nm, and 1.2 ± 0.1 between 550 and 880 nm. In the 350-550 nm range, OC had an A_{AE} of 6.3 ± 1.8 . The emitted OC mass, which was on average 25 times of the BC mass, contributed over 50% of the aerosol absorbance at wavelengths smaller than 450 nm. The overall OC contribution to visible solar light (300-900 nm) absorption by the emitted particles was 26-45%. Our results highlight the need to comprehensively and accurately address: (i) the climatic impacts of light absorption by OC from cookstove emissions, and (ii) the uncertainties and biases associated with variability in biomass fuel types and combustion conditions, and filter-based measurement artifacts during determination of MAC values.

Keywords: Light-absorbing organic carbon; residential biomass; cookstove; mass absorption cross section; filter correction; UV-Vis spectrophotometry

1. Introduction

Atmospheric aerosols directly alter the Earth's radiative budget by absorbing and scattering solar radiation. Carbonaceous aerosols constitute between 20-90% of the global aerosol mass [1], and have been recognized as important climate change drivers because of their light absorbing characteristics in the visible and ultraviolet (UV) wavelengths . Black (BC) and Organic carbon (OC) constitute the two broad categories of atmospheric carbonaceous aerosols. BC is known to strongly absorb visible solar radiation [2-4] and its optical properties have been well characterized using a variety of measurement and modeling techniques [2, 3, 5]. Light absorption by freshly-emitted BC is known to vary inversely with wavelength, which is parameterized by an absorption Ångström exponent (A_{AE}) value of 1 [3]. The mass absorption cross-section (MAC) value for fresh BC, at 550

nm, is $7.5 \pm 1.2 \text{ m}^2\text{g}^{-1}$ [3]. This value could be enhanced by a factor of 1.2-1.7 upon atmospheric processing [3, 6].

OC is conventionally modeled as purely light scattering in radiative transfer calculations [7, 8]. However, this approach has been recently challenged by mounting observational evidence of carbonaceous aerosol exhibiting a strong absorption in the near ultra-violet wavelengths of the shortwave spectrum with an $A_{\lambda}E > 1$ [2, 9-12]. This increased absorption at shorter visible wavelengths has been attributed to a class of near-UV light absorbing OC aerosols (hereafter referred to as light-absorbing OC or LAOC) [13]. Consequently, the newer generation climate models have started incorporating LAOC optical properties in their calculations [14]. Visually, LAOC aerosols deposited on filter media looks brown/yellowish in color, and therefore are also referred to as brown carbon [2, 9].

The absorption properties of LAOC emissions are dependent on their physical and chemical nature, which is typically a function of fuel properties and combustion phase (flaming/smoldering) [9, 10]. Recent studies have attributed emission of LAOC to the smoldering phase of biomass combustion [9, 13, 15-17]. Studies have also indicated that the integrated light absorption over the visible spectra by a unit mass of LAOC is significantly lower than that by BC [10, 12, 18]. However, LAOC could be an equally important light absorbing source in regions where biomass combustion dominates, because the amount of OC mass emitted from biomass burning could be over 10 times of the BC mass [17, 19].

Biomass fuels (fuelwood, charcoal, dung and agricultural residues) are a primary source of energy for more than 2 billion people in developing countries [20]. Residential

71 cooking consumes the major fraction of energy from burning of these fuels (IEA, 2013;
72 Daioglou et al., 2012). In the Indian subcontinent approximately 70% of the residents are
73 reliant on solid biomass fuels for meeting their household cooking needs [21]. These
74 households, mostly located in rural areas, use energy-inefficient, traditional cookstoves for
75 biomass combustion, which release large amounts of OC [22]. A recent comprehensive
76 emissions inventory estimated that solid biomass cookstoves contribute around 62% of the
77 OC and 31% of the BC emissions in India [22, 23]. In the past decade, the atmospheric
78 warming effects of BC emitted from cookstoves in India have received significant attention
79 [3, 4, 24, 25]. However, there is yet to be a study conducted on the optical properties of co-
80 emitted OC from cookstoves and their potential role in light absorption and consequent
81 radiative forcing.

82 In this article, we present the results of a pilot study conducted in a rural region of
83 central India to investigate the potential radiative impacts of OC emitted from residential
84 combustion of four commonly used solid biomass fuels. We measured the spectrally
85 varying MAC values, and $\Delta A E$, of emitted OC using a combination of optical and
86 gravimetric techniques. Finally, estimates of the relative contribution of OC to visible light
87 absorption by total particulate matter emissions are provided. The uncertainties associated
88 with filter-based sampling and analysis of field emissions are assessed, and implications of
89 our findings are briefly discussed.

90 **2. Aerosol Sampling**

91 Between October and December 2014, we conducted sampling of particulate matter
92 emissions from traditional “three-stone” cookstoves in rural households in Chhattisgarh, a
93 state in central India. This region has witnessed accelerated warming and anomalous

rainfall patterns [26, 27], which in turn have impacted the agricultural yield, food security, and livelihood [28, 29]. Over 97% of the households in rural Chhattisgarh use solid biomass fuels for cooking purposes [21]. 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 fires are the most common traditional biomass cookstoves in India [30-32]. On an average, they have similar particulate emissions characteristics [32-35], and are often treated as a single ‘baseline biomass stove’ [22, 36] 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 $\text{PM}_{2.5}$) 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.

3. Analysis Methods and Associated Uncertainties

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 [37, 38]. In this study, the estimated EC mass in aerosol samples has been approximated to be the BC mass [39, 40]. 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 [2]. 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 [2, 37]. In theory, BC and EC are equivalent proxies for combustion generated refractory carbon [2, 3]. Experimentally, their measurements have potential sources of bias, especially in the presence of OC (including 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 [2, 3, 41]. 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 [42]. 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 [12, 42] is used to relate aerosol absorbance (*ABS*) to light attenuation (*ATN*) through the filter as:

$$ATN(\lambda) = \ln \left(\frac{I_0(\lambda)}{I(\lambda)} \right) \quad (1A)$$

$$ABS(\lambda) \approx \frac{ATN(\lambda)}{C} \quad (1B)$$

where *C* is a correction factor ($=1.5 \pm 0.15$), that accounts for increased path length due to multiple scattering in Teflon filters [42, 43], 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 (see *Supplementary Information* section 1 for a typical *ATN* dataset and uncertainties therein). 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 [43-45] 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 ($R^2=0.35$) 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 [11]. Additionally, high loading of scattering aerosols (like OC) results in an increase in optical path [46-48], 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 note that development of filter artifact correction factors for biomass cookstove (or other OC dominated) emissions is needed to improve the accuracy of filter-based analyses.

Kirchstetter, Novakov [12] proposed that light absorption by carbonaceous aerosol could be treated as the sum of independent absorption by two distinct components discussed above. Thus, the total absorption can be de-convoluted on the basis of the difference in the spectral absorption dependences of BC and OC. Accordingly, we assumed a fixed spectral dependence of light absorption by BC, consistent with a body of experimental observations and theoretical analyses for freshly emitted small BC particles

[2, 3, 12]. We attributed the entire attenuation at $\lambda = 880$ nm to BC [9, 11] and extrapolated the BC component of ATN over the wavelength range using a mean $\mathring{A}E$ value of 1:

$$ATN_{BC}(\lambda) = ATN_{PM_{2.5}}(880) \times \left\{ \frac{\lambda}{880} \right\}^{-\mathring{A}E_{BC}} \quad (2)$$

The LAOC component of aerosol ATN was obtained by subtracting the contribution of BC from estimated total ATN :

$$ATN_{LAOC}(\lambda) = ATN_{PM_{2.5}}(\lambda) - ATN_{BC}(\lambda) \quad (3)$$

Kirchstetter, Novakov [12] found that the values of LAOC attenuation estimated using BC $\mathring{A}E$ 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 [2, 13, 49]. Here, 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 BC $\mathring{A}E$ [49-52]. For the above range of BC $\mathring{A}E$ values, the variation in ABS_{LAOC} at 350 nm, with respect to its mean value at $\mathring{A}E=1$, was 6-14% (Figure 1). Therefore, one standard deviation uncertainties ($\pm 6-14\%$) were assigned to the deconvolution method, and combined analytically with the other uncertainties in equation 3.

Figure 1. Average OC MAC values (m^2/g) 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 [53-55], the total $\text{PM}_{2.5}$ mass was apportioned to BC and OC mass as:

$$m_{BC} = \frac{m_{PM_{2.5}}}{1 + 1.9 \frac{OC}{EC}} \quad (4)$$

$$m_{OC} = m_{BC} \frac{OC}{EC} \quad (5)$$

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:

$$MAC(\lambda) = \frac{A}{m} ABS(\lambda) \quad (6)$$

$$MAC_{BC}(\lambda) = \frac{A}{m_{BC}} \frac{ATN_{BC}(\lambda)}{C} \quad (7)$$

$$MAC_{OC}(\lambda) = \frac{A}{m_{OC}} \frac{ATN_{LAOC}(\lambda)}{C} \quad (8)$$

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 $\hat{A}\hat{A}Es$ 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 $\hat{A}\hat{A}E$ 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):

$$F_{LAOC} = \frac{\int_{300nm}^{900nm} ATN_{LAOC}(\lambda) i(\lambda) d\lambda}{\int_{300nm}^{900nm} ATN_{PM_{2.5}}(\lambda) i(\lambda) d\lambda} \quad (9)$$

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 λ (W/m².nm).

4. Results and Discussion

The color of the particulate matter collected on quartz and Teflon filters was yellow-brown to brown (Figure 2), consistent with previous observations of LAOC-dominated filter samples from biomass burning [2, 9]. Figure 3A shows typical TEM images of an amorphous OC “tar ball” [9]. Such amorphous OC 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 3B), composed of 40-70 nm diameter monomers.

Figure 2. 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 3. TEM images of (A) an amorphous OC tar ball typically emitted from fuels in this study and (B) OC tar ball with co-emitted BC aggregate.

Average aerosol *ABS* for $PM_{2.5}$ emissions from the four fuel types are shown in Figure 4A. The de-convoluted spectra for BC and LAOC (per equations 2 and 3) show that the majority of the aerosol *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 [11, 12].

Figure 4. Average biomass 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 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, Bond [17]. However, this ratio is 3-30 times higher than those typically reported from laboratory-based experiments [33, 35]. 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 [56]. 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 [19, 33, 57]. 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 1. Ratio of OC to BC mass and optical properties (MAC and AÅE) for aerosol samples by biomass fuel type.

Fuel type	OC/EC ^{1,2}	PM _{2.5} MAC at 550 nm ¹ (m ² /g)	BC MAC at 550 nm ¹ (m ² /g)	OC MAC at 350 nm ^{1,3} (m ² /g)	PM _{2.5} AÅE ^{1,4}	OC AÅE ^{1,4}
Fuel-wood	12.1 (3.2-31.0)	1.3 (0.67-2.5)	12.2 (6.1-32.4)	4.4 (1.3-12)	2.4 (2.2-2.7)	5.8 (5.6-5.9)
Agricultural residue	60 (24-133)	0.6 (0.2-1.5)	32.2 (10.6-80.8)	3.6 (1.1-9.4)	3.3 (3.0-3.7)	5.8 (5.5-6.0)
Dung cake	15.4 (11-22)	0.5 (0.29-0.86)	15.1 (3.4-34.3)	3.4 (2-5.4)	3.6 (3.3-3.6)	7.7 (7.5-7.9)
Mixed fuel	14.5 (11-20)	0.9 (0.61-1.15)	17.9 (7.6-37.4)	4.1 (2.5-6.4)	3.0 (2.8-3.1)	6.0 (5.8-6.1)

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 AÅE is between 550 nm and 350 nm

We find that the values of PM_{2.5} MAC (Table 1, see Figure 5 for detailed plots) for fuel-wood and agricultural residue in this study are slightly lower than those reported in Habib, Venkataraman [33] and Roden, Bond [17], while our AÅE 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, Venkataraman [33]. Our estimates of BC MAC (Table 1) fall within the broad range of values reported in literature (collated in Chen [53]). 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 1).

Figure 5. Fuel-wise $\text{PM}_{2.5}$ 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. We estimate average MAC values of 0.1 and 3.1 m^2g^{-1} at 550 and 350 nm, respectively, with a mean AAE of 6.3 (± 1.8) in this wavelength range. We found that the LAOC MAC values for different fuel types showed little variability: $\sim 10\%$ 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 [6, 12, 58] are also shown for comparison. While the methodology for apportioning the LAOC component of aerosol absorption varies between the studies, there is good agreement between the resulting MAC values.

Figure 6. Fuel-wise OC MAC values (m^2/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, Novakov [12] square = Washenfelder, Attwood [58]; triangle = Lack, Langridge [6]; star = Chen [53]].

As 70% of the incoming solar radiation energy is distributed in the 300-900 nm range, the integration of total $\text{PM}_{2.5}$ ABS and its LAOC component over solar insolation (in $\text{W}/\text{m}^2/\text{nm}$) in this range gives a measure of their overall absorption behavior. Figure 7A 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 7B 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 1) and therefore the highest contribution to light absorption by LAOC. Compared to Kirchstetter and Thatcher [11], 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 7. (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 (W/m² aerosol) attributed to LAOC, per biomass fuel type. Error bars represent 1 standard error about the mean.

Our results underscore the need for further investigating the role of LAOC in aerosol radiative forcing over south Asia. Integration of LAOC in regional climate models and satellite retrieval algorithms requires the evaluation of its emission rates and microphysical properties. Comprehensive field studies in different regions (for e.g. – Bikkina, Rastogi [59]) should be combined with controlled laboratory experiments [10], for characterizing region-specific source emissions, as well as understanding the effect of atmospheric processing on LAOC optical properties. Field deployment of contact-free aerosol measurement instruments, as well as estimates of filter artifacts relevant to biomass cookstove emissions sampling, are needed to accurately characterize the microphysical properties of these aerosols.

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