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Contribution of organic carbon to wood smoke particulate matter absorption of solar radiation

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Abstract

Spectroscopic analysis shows that 115 residential wood smoke-dominated particulate matter samples absorb light with strong spectral selectivity, consistent with prior work that has demonstrated that organic carbon (OC), in addition to black carbon (BC), appreciably absorbs solar radiation in the visible and ultraviolet spectral regions. Apportionment of light absorption yields the absorption Ångström exponent of the light absorbing OC in these samples, which ranges from 3.0 to 7.4 and averages 5.0, and indicates that OC and BC, respectively, would account for 14 % and 86 % of solar radiation absorbed by the wood smoke in the atmosphere (integrated over the solar spectrum from 300 to 2500 nm). OC would contribute 49 % of the wood smoke particulate matter absorption of ultraviolet solar radiation at wavelengths below 400 nm. These results illustrate that BC is the dominant light absorbing particulate matter species in atmospheres burdened with residential wood smoke and OC absorption is secondary but not insignificant. Further, since biomass combustion generates a major portion of atmospheric particulate matter globally, these results suggest that OC absorption should be included when particulate matter effects on the radiative forcing of climate are considered, and that OC absorption may affect the ultraviolet actinic flux and thus tropospheric photochemistry.

1 Introduction

This article is about the relative contributions of black and organic carbon (BC and OC) to the absorption of solar radiation by wood smoke particulate matter. BC, combustion-generated particulate matter that appears black in sunlight, is the primary light absorbing component atmospheric particulate matter (IPCC, 2007). The spectral absorption of BC is reasonably well approximated by a power law relationship from the near ultraviolet to the near infrared: absorption = $k\lambda^{-AAE}$, where k is a constant, λ is wavelength, and the exponent is referred to as the absorption Ångström exponent (AAE). (The

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interested reader can refer to Moosmuller et al. (2011) for a deeper theoretical discussion of AAE.) With an AAE of approximately 1, freshly emitted BC absorbs solar radiation without much wavelength selectivity (Kirchstetter et al., 2004). The observation that particulate matter, and especially biomass combustion-generated particulate matter, can exhibit AAEs much greater than 1 is the basis for concluding that species other than BC contribute to absorption of solar radiation, namely biomass smoke OC (Hoffer et al., 2006; Kirchstetter et al., 2004). Here, we consider that OC is the collection of hundreds or more particle-phase organic compounds, some of which absorb solar radiation. Biomass smoke particles often look brown rather than black because they absorb solar radiation with a stronger wavelength selectivity than BC, which has led to use of the term brown carbon to refer to biomass smoke particulate matter (Andreae and Gelenscer, 2006). AAE values for biomass smoke (or brown carbon) generally range from greater than 1 to about 3 (Kirchstetter et al., 2004; Bergstrom et al., 2007). The range reflects variation in combustion conditions and the chemical composition of the observed particles. A few studies have estimated the mass specific absorption of wood smoke OC (in units of $m^2\,g^{-1}$), which in the visible region of the spectrum tends to be at least an order of magnitude smaller that of BC (Sun et al., 2007; Kirchstetter et al., 2004; Barnard et al., 2008). The fact that OC is often much more abundant than BC in wood smoke suggests that the contribution of OC to wood smoke absorption of solar radiation can, however, be significant.

2 Methods

In this paper, we consider the spectral absorption selectivity of 115 particulate matter samples that were collected on quartz filters in the residential community of Cambria, California, where wood burning is prevalent and the only significant source of nighttime particulate matter generation (Thatcher et al., 2011). It is likely that many residents in Cambria burn Pinus radiate, also known as Monterey Pine, as it is the native species in region. Particulate matter samples were collected during evening and nighttime hours

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(from 18:00 h to 06:00 h) in the winter (of 2010) to maximize the collection of wood smoke particles and minimize the collection of particles from other anthropogenic or natural sources. Elevated chimney temperatures, measured using an infrared camera, verified that residents were operating their fireplaces. Little vehicle activity was observed in the area during the evening and nighttime.

Samples were analyzed using a spectrometer in transmission mode in a manner similar to that described by Kirchstetter et al. (2004). Light transmission through (dry) particulate matter on quartz filters is predominantly due to particle light absorption rather than particle light scattering when the particulate matter is even weakly absorbing (Arnott et al., 2005): absorption = k'ATN, where k' is nominally constant and ATN is the optical attenuation computed from measured transmission (T): ATN = 100 ln(1/T). Thus, we infer spectral absorption selectivity (i.e., AAE) of the particulate matter from these attenuation measurements.

While a small particle light scattering-induced error may be important for determining absolute values of particle light absorption, Bond (2001) reported that particle light scattering does not significantly affect spectral absorption selectivity. Gyawali et al. (2009) noted that coating of BC by light scattering (i.e., non-absorbing) OC, which may amplify the light absorbed by BC, also may increase spectral absorption selectivity if the coating collapses the fractal BC aggregate. Therefore, it is conceivable that filter-based analysis methods like the one we employ here may attribute some of the measured absorption selectivity to light-absorbing OC rather than non-absorbing OC that increases BC absorption selectivity.

The so-called filter-loading or shadowing artifact, which causes k' to increase as the collection filter becomes increasingly loaded with particles, may be important for determining spectral absorption selectivity. Some studies (e.g., Weingartner et al., 2003) have reported that the filter-based light transmission method accurately measures the spectral dependence of aerosol light absorption while others (e.g., Schmid et al., 2006) have shown that this artifact is wavelength dependent. Generally speaking, this artifact is most pronounced for highly absorbing particulate matter, such as black soot from

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diesel engines or kerosene flames (Kirchstetter, 2007; Arnott et al., 2005), which the particulate matter in this study is not. In the present study, there is no correlation between filter loading expressed in terms of ATN at 880 nm and AAE (linear correlation coefficient, $r^2 = 0.003$), thus, we don't expect this artifact to have a large influence on our results.

3 Results

Figure 1 shows the spectral attenuation of a representative particulate matter sample collected for this study. The AAE value for this sample is 2.36. Assuming that only BC absorbs at 880 nm, an assumption consistent with prior work (Kirchstetter et al., 2004; Sun et al., 2007), we estimate the contribution of BC to this sample's spectral attenuation assuming that the AAE of BC is 0.86. This is the minimum AAE value exhibited by the wood smoke particulate matter samples in this study (discussed below) and it is close to the nominal value of 1 that theory predicts for small BC particles (Bohren and Huffman, 1998). As shown, BC accounts for the overwhelming majority of this sample's attenuation at wavelengths above 700 nm. At shorter wavelengths, the sample absorbs more radiation than is attributed to BC. We attribute the additional attenuation to OC. The OC attenuation shown in Fig. 1 is determined by subtracting the BC attenuation from the total sample attenuation. OC attenuation rises sharply with decreasing wavelength and is well described by a power law over the wavelength region shown. In the current example, the AAE of OC is 4.89.

We performed this analysis for all samples and generated the AAE histograms shown in Fig. 2. The AAE of all wood smoke particulate matter samples ranged from 0.86 to 3.48 and averaged 1.89 ($n = 115$). These AAE values are consistent with the predominance of wood smoke during sample collection. The AAE of OC in the wood smoke samples ranged from 3.02 to 7.39 and averaged 5.00 ($n = 87$, AAE values could not be computed for a minority of samples because of some slightly negative values of OC attenuation). These values are consistent with those of Sun et al. (2007) who suggest

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a range of 4 to 6 for light-absorbing OC generated under a range of combustion conditions.

Based on the apportionment of spectral attenuation to BC and OC (as illustrated in Fig. 1), we computed for every wood smoke sample the fraction of radiation, at each wavelength in the solar spectrum, that would be absorbed by OC rather than BC, $f_{OC}(\lambda)$. The averages and standard deviations are shown in Fig. 3. The red line in Figure 3 is a model of $f_{OC}(\lambda)$ based on a 5th order polynomial fit of our measurements (our spectrometer operated between 350 and 990 nm), a prescribed value of zero above 880 nm (rather than unrealistic negative values that result from an imperfect extrapolation of BC attenuation), and a linear extrapolation of the data below 350 nm. On average, the fraction of light absorbed by the wood smoke particulate matter that we attributed to OC decreased approximately linearly from 0.43 at 400 nm to 0.26 at 500 nm to 0.11 at 600 nm.

Using the model for $f_{OC}(\lambda)$, we computed the fraction of solar radiation that OC rather than BC in the wood smoke would absorb in the atmosphere, F_{OC}:

$$F_{OC} = \frac{\int_{300\,nm}^{2500\,nm} f_{OC}(\lambda) i(\lambda) d\lambda}{\int_{300\,nm}^{2500\,nm} i(\lambda) d\lambda} \quad (1)$$

where $i(\lambda)$ is the solar spectral irradiance measured at the earth's surface. As shown in Fig. 3, about half of the sun's energy is in the infrared at $\lambda > 700$ nm, where $f_{OC}(\lambda)$ is mostly zero, and about 6% is in the ultraviolet at $\lambda < 400$ nm, where $f_{OC}(\lambda)$ is highest. Using Eq. (1) we find that 14 % of the solar radiation absorbed by the wood smoke particulate matter would be absorbed by OC rather than BC.

The results of this study depend on the value of the AAE of BC assumed in the apportionment of light attenuation (Fig. 1). To illustrate this sensitivity, we recalculated most results assuming values for BC AAE of 1.00 and 1.15 rather than 0.86 (Table 1). The larger the value of BC AAE, the smaller is the contribution of OC to wood smoke absorption: for BC AAE values of 1.00 and 1.15, OC accounts for 10 % and 7 %, respectively, of the solar radiation absorbed by the wood smoke particulate matter.

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4 Significance

The AAE of OC in wood smoke has potential application for apportionment of solar radiation absorption to different particulate matter species and apportionment of atmospheric particulate matter to different sources (e.g., Russell et al., 2010; Praveen et al., 2012). The AAE values we report for a large number of wood smoke particulate matter samples (AAE = 1.9, $n = 115$) and especially for the light-absorbing OC fraction (AAE = 5.0, $n = 87$) may be useful in this regard.

The significant fraction of solar radiation that would be absorbed by OC rather than BC in wood smoke particulate matter (14 %) indicates that BC is the dominant light absorbing species in atmospheres burdened with residential wood smoke and OC absorption is secondary but not insignificant. While the results of this study apply strictly to the residential wood smoke samples collected in Cambria, we note that the fraction of light absorbed by OC rather than BC in the wood smoke particulate matter in this study is similar to that which we previously reported for samples collected over southern Africa during the dry biomass burning season (Kirchstetter et al., 2004). Our results are also consistent with those of Hoffer et al. (2006), who found that OC in Amazonian biomass smoke particles contributed up to 50 % of light absorption at 300 nm and significantly to absorption of broadband solar radiation, and those of Flowers et al. (2010), who found that OC accounted for up to 50 % of the 400 nm light absorption of particulate matter transported over mainland Asia. The similarity across studies despite different analytical methods and differences in location, fuels, and combustion processes suggests that light-absorbing OC is ubiquitous in atmospheres influenced by biomass burning. Since biomass combustion generates a major portion of atmospheric carbonaceous particulate matter globally (Bond et al., 2004), and since carbonaceous particulate matter affects climate (Ramanathan and Carmichael, 2008), these observations support the notion that light-absorbing OC should be considered when particulate matter effects on the radiative forcing of climate are evaluated (Chakrabarty et al., 2010). It is likely that some but not all climate models in the next assessment of the

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Intergovernmental Panel on Climate Change will include light-absorbing OC.

Last we note that our results show that wood smoke OC and BC absorb a comparable amount of solar radiation at wavelengths below 400 nm (Table 1). OC absorption may significantly affect the ultraviolet actinic flux and, thus, may appreciably influence tropospheric photochemistry (Li et al., 2011; Vuilleumier et al., 2001).

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Table 1. As they depend on the value chosen for the AAE of BC, shown are the OC AAE and the fractional contributions of OC to wood smoke absorption of solar radiation.

		fraction of solar radiation absorbed by OC rather than BC in wood smoke at the wavelength or spectral region indicated				
BC AAE	OC AAE	400 nm	500 nm	600 nm	full solar spectrum[a]	UV[b]
0.86	5.00	0.43	0.26	0.11	0.14	0.49
1.00	5.48	0.36	0.20	0.06	0.10	0.42
1.15	6.19	0.28	0.13	0.00	0.07	0.34

[a]integrated over the solar spectrum, $300 < \lambda < 2500$ nm

[b]integrated over the ultraviolet region of the solar spectrum, $300 < \lambda < 400$ nm

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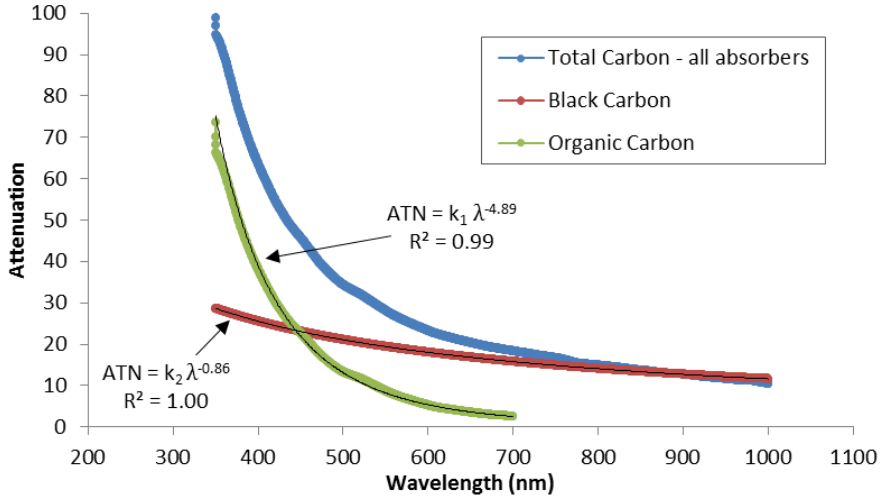

Fig. 1. Estimated contributions of black and organic carbon to the spectral attenuation of a residential wood smoke particulate matter sample. The exponents of the power law trend lines, 0.86 and 4.89, are the absorption Ångström exponents of the black and organic carbon, respectively, for this sample.

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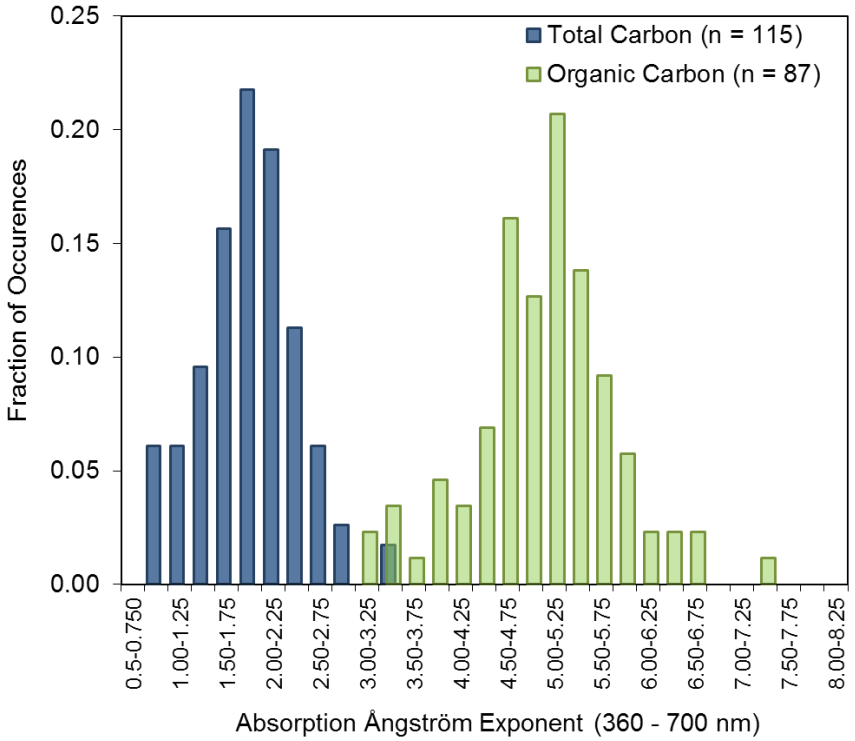

Fig. 2. Histograms of absorption Ångström exponents computed over the 360 to 700 nm spectral range: (blue bars) 115 residential wood smoke samples considered in this study and (green bars) the light-absorbing organic carbon portion in 87 of the wood smoke samples.

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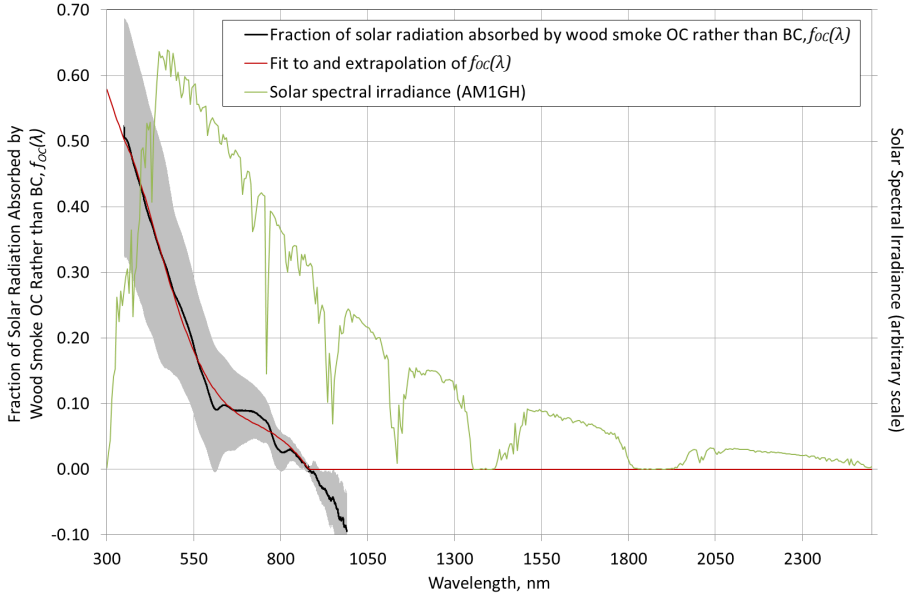

Fig. 3. Fraction of solar radiation absorbed by organic carbon rather than black carbon in residential wood smoke particulate matter, $f_{OC}(\lambda)$: (black line and gray region) average values for 115 samples ±1 standard deviation and (red line) a model fit to and extrapolation of the data. Also shown (green line) is the clear sky air mass one global horizontal (AM1GH) solar spectrum at the earth's surface (Levinson et al., 2010).

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