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On the attribution of black and brown carbon light absorption using the Ångström exponent

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Abstract. The absorption Ångström exponent (AAE) of externally mixed black carbon (BC_{Ext}), or BC internally mixed with non-absorbing material (BC_{Int}), is often used to determine the contribution of brown carbon (BrC) light absorption at short visible wavelengths. This attribution method contains assumptions with uncertainties that have not been formally assessed. We show that the potential range of AAE for BC_{Ext} (or BC_{Int}) in the atmosphere can reasonably lead to +7 % to −22 % uncertainty in BC_{Ext} (or BC_{Int}) absorption at short wavelengths derived from measurements made at longer wavelengths, where BrC is assumed not to absorb light. These uncertainties propagate to errors in the attributed absorption of BrC. For uncertainty in attributed BrC absorption to be $\leq \pm 33$ %, 23 % to 41 % of total absorption must be sourced from BrC. These uncertainties would be larger if absorption by dust were also to be considered due to additional AAE assumptions. For data collected during a biomass-burning event, the mean difference between measured and AAE attributed BrC absorption was found to be 34 % – an additional uncertainty in addition to the theoretical uncertainties presented. In light of the potential for introducing significant and poorly constrained errors, we caution against the universal application of the AAE method for attributing BrC absorption.

1 Introduction

The Ångström exponent was originally developed to describe the wavelength dependence of visible light extinction by atmospheric particles (Ångström, 1929). The Ångström exponent for extinction is mostly influenced by particle size and is often used to differentiate large particles (e.g. desert dust, sea salt) from fine-mode particles (e.g. anthropogenic organics, sulfates and nitrates) in atmospheric samples (Bergstrom et al., 2007; Meloni et al., 2006). Equation (1) shows the calculation of the Ångström exponent using a pair of observations at two different wavelengths:

$$AE(\lambda_1\lambda_2) = \frac{\ln\left(\frac{b_{Optical}(\lambda_1)}{b_{Optical}(\lambda_2)}\right)}{\ln\left(\frac{\lambda_1}{\lambda_2}\right)}, \quad (1)$$

where $b_{Optical}$ is the optical coefficient of interest, such as particle light extinction, absorption, single scattering albedo (SSA) or optical depth, at wavelength λ, where $\lambda_2 > \lambda_1$.

Black carbon is the primary absorbing aerosol component in the atmosphere. The absorption Ångström exponent (AAE) for externally mixed black carbon (BC_{Ext}) is predicted to be wavelength-independent (AAE = 1) for particles < 50 nm diameter (Moosmüller et al., 2011; Moosmüller and Arnott, 2009; Bergstrom et al., 2002, and references therein). However, the AAE for ambient particles (measured between a short and long visible wavelength) has often been observed to be larger than 1. There are a number of factors that contribute to these observations including enhanced absorption by BC internally mixed with non-absorbing material, and/or absorption by non-BC absorbers such as brown carbon (BrC) or desert dust (Russell et al., 2010; Kirchstetter et al., 2004). These mechanisms are treated in turn below.

BC absorption under dry atmospheric conditions can in theory be enhanced at all wavelengths by the presence of transparent coatings (Bond et al., 2006; Jacobson, 2001;

Bohren and Huffman, 1983; Fuller et al., 1999). The mechanism for this enhancement is one in which the coating acts as a lens to focus radiation into the absorbing BC core. Absorption enhancements of this nature have been observed in some laboratory and field studies (e.g. Cappa et al., 2012; Cross et al., 2010; Schnaiter et al., 2005; Lack et al., 2009, 2012b). Theoretical calculations have bounded the likely range of AAE for internally mixed BC (BC_{Int}). They have shown that the AAE can vary from a baseline of 1 to an upper limit of ~ 1.7, depending on the size and optical properties of the core and non-absorbing coating and the wavelength pairs used to determine AAE (Gyawali et al., 2009; Lack and Cappa, 2010).

Non-BC absorbers could potentially enhance AAE more significantly, although it should be noted that the spectral variability of absorption by BrC or dust may not be captured well by the AAE model (e.g. Updyke et al., 2012). Values of AAE for BrC up to 9.5 have been observed (wavelength pairs: 400, 700 nm) (Andreae and Gelencser, 2006, and references therein; Rizzo et al., 2011; Flowers et al., 2010; Lewis et al., 2008; Corr et al., 2012) while AAEs for desert dust range from 2.5 to 6.0 (wavelength pairs: 467 nm, 660 nm) (e.g. Weinzierl et al., 2011).

In this paper we provide a theoretical discussion on the method of using assumed AAEs to attribute total absorption to BC and BrC (Sect. 2). We then provide a case study for this method using measurements from a biomass burning plume, which contains absorption by BC, internal mixing and BrC (Sect. 3). Dust is excluded from the following discussions for two reasons. The first is to provide focus and clarity to the theoretical description of the method. The consideration of dust, while adding complexity, does not significantly change the approach to considering uncertainty propagation with the AAE method. Second, this study utilizes a unique experimental data set which does not include absorption by dust, limiting our ability to test dust absorption attribution methods at present.

2 Ångström attribution of absorption

2.1 Methods

The AAE has often been used in a simple method for attributing short visible wavelength absorption to BC and non-BC sources. The attribution method utilizes a pair of measurements usually spanning extremes of the visible wavelength spectrum (~ 400 nm to ~ 700 nm). Absorption at the longer wavelength is assumed to be due only to dry BC_{Ext}, or dry BC_{Int}. Unless the measurements exclude internally mixed material (e.g. by pre-conditioning aerosol to remove coatings), the measurement will represent absorption by BC_{Int}. This absorption measurement is extrapolated to the shorter wavelength using an assumed AAE, most commonly 1. The difference between the measured and attributed absorption at the short wavelength is then attributed to absorption by non-BC entities.

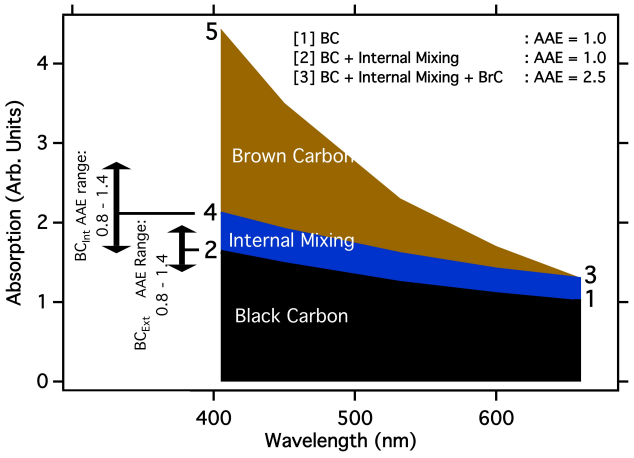

Fig. 1. Illustration of the attribution of absorption using the absorption Ångström exponent. We assume this system does not contain any dust. The absorption by BC_{Ext} is assumed to have an AAE = 1, line 1–2. Absorption by BC internally mixed with non-absorbing material (BC_{Int}) is often assumed to have an AAE = 1, line 3–4. In this example the AAE of all ambient particles, including brown carbon, is 2.5, line 3–5. The AAE for BC_{Ext} and BC_{Int} may range from 0.8 to 1.4, which is indicated by the uncertainty arrows on points 2 and 4.

Figure 1 shows an illustration of this method. The figure was constructed by arbitrarily setting the absorption level of BC_{Ext} to 1 at 658 nm and assuming an AAE of 1 for BC_{Ext} (line 1–2). Absorption enhancement by internal mixing of BC with non-absorbing material, with an AAE of 1 (see discussion below), was added to the BC_{Ext} absorption (line 3–4). Absorption due to BrC was represented using an AAE = 2.5 (line 3–5) assuming no BrC absorption at 658 nm. Studies that utilize this attribution method would commonly have absorption measurements at points 3 and 5, and extrapolate absorption to point 4.

More complex multi-wavelength methods for absorption attribution have been reported and mostly use satellite, aircraft, or ground-based measurements of multi-spectral aerosol optical depth, actinic flux, scattering, or back scattering and extinction (Tesche et al., 2011; Arola et al., 2011; Kaufman et al., 2002; Schuster et al., 2005; Bergstrom et al., 2004; Corr et al., 2012). These methods use radiation models and complex Mie modelling retrievals to determine particle type (fine vs. coarse mode), and multi-spectral particle refractive index, SSA and absorption. Despite their greater complexity, some of these methods still rely on assumed values of the AAE for BC (Arola et al., 2011; Kaufman et al., 2002; Schuster et al., 2005). The advantages of these methods are their expansive coverage via satellite and aircraft platforms, and wide wavelength coverage. However retrievals and subsequent data products can be subject to significant

uncertainty that is difficult to quantify (Li et al., 2009). Here we focus on the simple AAE approach on account of its widespread use in peer-reviewed studies (Bahadur et al., 2012; Cazorla et al., 2013; Chung et al., 2012; Clarke et al., 2007; Esposito et al., 2012; Favez et al., 2009; Fialho et al., 2005; Gadhavi and Jayaraman, 2010; Herich et al., 2011; McNaughton et al., 2011; Sandradewi et al., 2008a, b; Wang et al., 2013; Yang et al., 2009).

2.2 Uncertainties in attribution of BC

Uncertainties in the AAE attribution method primarily arise from the choice of AAE used to characterize BC_{Ext} or BC_{Int}. As stated previously, the AAE for BC_{Ext} is approximately 1 for particles < 50 nm in diameter, but can range from 0.8 to 1.1 for diameters of 50–200 nm (Gyawali et al., 2009). These larger BC particle sizes can exist in the atmosphere due to coagulation and collapse of smaller BC_{Ext} spherules (e.g. Cross et al., 2010; Zhang et al., 2008), or from direct formation during inefficient combustion (Schwarz et al., 2008). A recent study also suggested a lower limit of AAE = 0.55 for atmospheric "elemental carbon" (a term functionally similar to BC) (Bahadur et al., 2012), which is included here for completeness. Despite this potential variability in the AAE for BC_{Ext}, an AAE = 1 is a commonly used community standard.

For BC_{Int} the situation is somewhat different. As described previously, the theoretical AAE for BC_{Int} can range from the uncoated baseline to ~ 1.7 (Gyawali et al., 2009; Lack and Cappa, 2010). In contrast, Bahadur et al. (2012) assumed that internal mixtures did not affect the AAE and used an AAE for BC_{Int} = 0.55. Analysis of a range of atmospheric measurements of the AAE for aerosol sourced from fresh fossil fuel burning and urban pollution (where the dominant absorber was BC) shows an average value for the AAE of 1.1 ± 0.3 (1σ) derived using the wavelength pair 467 nm and 660 nm (Lack et al., 2008; Clarke et al., 2007; Virkkula et al., 2005; Rosen et al., 1978; Bergstrom et al., 2002, 2007; Kirchstetter et al., 2004). This suggests that the AAE extremes presented (0.55 and 1.7) are likely not common in the atmosphere for BC_{Ext} and BC_{Int}, and serve here as extreme boundaries only. Although there is variability in the AAE, these studies have been used previously to support the use of an AAE = 1 for BC_{Ext} (Bond et al., 2013), and it is common to assume that the AAE for BC_{Int} is equal to that of BC_{Ext}. These studies provide evidence that although an AAE of 1 may be an accepted average for BC_{Ext} and BC_{Int}, an uncertainty range should be considered and propagated through any absorption attribution procedure performed (this range is represented in Fig. 1 by the vertical arrow on points 2 and 4).

Figure 2a (grey line) shows the uncertainty in attributed short wavelength BC_{Ext} and BC_{Int} absorption arising from use of an AAE of 1. It should be interpreted as follows: if an average AAE of 1 is used to attribute short wavelength BC_{Int} absorption from a long wavelength measurement, when in fact the AAE was 1.2, then the attributed absorption will be low by 10 %. In most circumstances practitioners of the AAE method do not know what the true AAE for BC_{Ext} or BC_{Int} is, and use of an AAE = 1 is the common default. Using the widest ranges of BC_{Ext} or BC_{Int} AAE reported in literature, attribution biases of +20 % to −40 % are possible. Using a more plausible experimentally based range derived from the studies referenced above of 1.1 ± 0.3 (Fig. 2a, red markers), a more likely uncertainty in attributed short wavelength BC_{Ext} or BC_{Int} absorption is +7 % to −22 %. This uncertainty will contribute to uncertainty in attributed BrC absorption, the magnitude of which will depend on the total level of absorption.

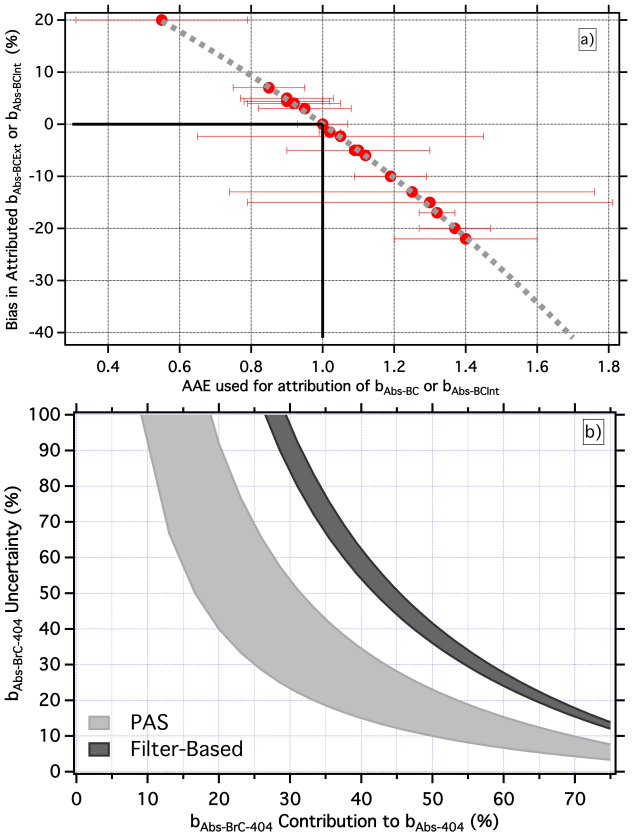

Fig. 2. (a) Theoretical uncertainties in attributed BC_{Ext} (or BC_{Int}) 404 nm absorption when AAE = 1, rather than another value within the possible range suggested for BC_{Ext} or BC_{Int}. Red data show average AAE measured for particles assumed to be mostly BC (y axis for red data forced to match black line for clarity). **(b)** Uncertainty in attributed BrC absorption (at 404 nm) based on the uncertainties in AAE used for the absorption attribution process and the uncertainties in the absorption measurement method.

2.3 Uncertainties in attribution of BrC

Following determination of the short wavelength BC_{Int} absorption using the Ångström attribution method, BrC absorption can be attributed. The uncertainty associated with

derived BrC absorption can be assessed by combining uncertainty in the AAE attribution method with the uncertainty in the absorption measurements themselves. This resulting total uncertainty depends on the fractional contribution of BrC to the total aerosol absorption.

First we consider uncertainties in the AAE attribution method. In Sect. 2 we showed that the uncertainty in short-wavelength absorption by BC_{Int} determined by extrapolation using an AAE = 1 ranged from +7 % to −22 %. To simplify the following analysis, rather than report asymmetric uncertainties, we report uncertainty in the format high (low). For example, the uncertainty in attributed BC_{Int} absorption is represented as ±22 % (±7 %).

Second we consider experimental uncertainties. For this analysis we assume absorption measurements were made using the photoacoustic aerosol absorption spectrometer (PAS) technique, with an uncertainty of ±5 % (Lack et al., 2009, 2012a). We investigate a system where we assume that the PAS was used to measure BC_{Int} absorption at 658 nm (±5 %), which was then used to attribute BC_{Int} absorption at 404 nm. The AAE and PAS measurement uncertainties are treated independently and propagated in quadrature yielding an uncertainty range in attributed BC_{Int} absorption at 404 nm of ±22.6 % (±8.6 %). To this estimate, we add the uncertainty in PAS-measured total absorption (BC_{Int} + BrC absorption) at 404 nm (±5 %), which yields a total uncertainty range for attributed BrC absorption at 404 nm of ±23 % (±10 %). It is clear that the most significant contributor to the total uncertainty arises from the choice of AAE used.

This analysis indicates that in order for the uncertainty in attributed BrC absorption at 404 nm to be less than ±100 %, the absolute contribution from BrC absorption must be at least 23 % (10 %) of that from BC_{Int}, or 19 % of the total absorption. Figure 2b shows the relationship between the uncertainty in attributed BrC absorption and the contribution of BrC to total absorption when using the PAS technique. We note that if filter-based methods for measuring absorption are used (e.g. Aethelometer® or particle soot absorption photometer), which have estimated uncertainties of the order of 25 % (Bond et al., 2013), the minimum contribution of BrC to total absorption must be larger to provide similar uncertainties (these results are also shown in Fig. 2b). This estimate neglects the influence of additional suspected biases that may add further uncertainty to filter-based methods (Lack et al., 2008; Subramanian et al., 2007).

3 A case study for BrC attribution

3.1 Methods

This section provides experimental details of a case study in which detailed optical property measurements are used, for the first time, to compare BrC absorption attributed using the AAE method to that derived using a fully independent method. Data were collected during a dense biomass burning event, where emissions were sampled 24 h after the start of a ponderosa pine forest fire near Boulder, Colorado, during September 2010. Details of this data set can be found in Lack et al. (2012b) and are only briefly summarized here.

Particle emissions were dominated by BC (measured using a soot particle photometer, Schwarz et al., 2008) and organics (measured using an aerosol mass spectrometer, AMS, Bahreini et al., 2009). Organic compounds consistently accounted for > 90 % of non-BC particle mass (m_{non-BC}). A PAS measured dry total absorption at 658 nm and 404 nm ($b_{Abs-658}$, $b_{Abs-404}$) and thermal-denuded absorption at 404 nm ($b_{Abs-404-BC}$) (Lack et al., 2012a). The thermal denuder heated the sample flow to 200 °C and removed the majority of semi-volatile coatings. Following Lack et al. (2012b), non-BC absorption is reported here in the form of a mass absorption efficiency (MAE). We stress that all MAE values presented refer to non-BC absorption at 404 nm wavelength. The experimentally observed total non-BC MAE was determined using Eq. (2), and includes contributions from both BC_{Int} and BrC ($MAE_{BCInt+BrC}$).

$$MAE_{BCInt+BrC} = \frac{b_{Abs\text{-}404} - b_{Abs\text{-}404\text{-}BC}}{m_{non\text{-}BC}} = \frac{b_{Abs\text{-}404\text{-}non\text{-}BC}}{m_{non\text{-}BC}} \quad (2)$$

The MAE of the non-BC mass with the effects of BC internal mixing removed (MAE_{BrC}) was calculated independently of the AAE method. Briefly, measured size distributions of the BC core and coatings were used with Mie theory to calculate absorption at a wavelength where only absorption from BC contributed. Comparison of model and PAS-measured absorption at this wavelength enabled the fraction of non-BC material internally mixed with BC to be determined. This information was used in subsequent Mie calculations to determine the contribution of coating enhancements to absorption at 404 nm (BC_{Int}). This procedure enabled the complete attribution of absorption between BC, BC_{Int} and BrC at this wavelength. All calculations assumed that particles and BC cores were spherical. There is evidence supporting this assumption from previous studies of particles from inefficient combustion such as biomass burning (Alexander et al., 2008; Chakrabarty et al., 2010; Lewis et al., 2008) and from comparisons of spherical and fractal particle optical modelling (e.g. Chakrabarty et al., 2007). Uncertainties in the calculated MAE_{BrC} were estimated to not exceed 20 %. Further details can be found in Lack et al. (2012b).

The contribution of dust to total absorption in the biomass plume was assumed minimal due to observations of low background levels of aerosol extinction and absorption measured under conditions not strongly influenced by the biomass plume, and sample mass size distributions that peaked in the accumulation mode at approximately 300 nm.

The AAE attribution method was applied to the same data set to determine the MAE using four different AAE values for BC_{Int}: 0.55 (extreme lower limit; Bahadur et al., 2012), 1.0 (community standard), 1.7 (upper limit; Gyawali

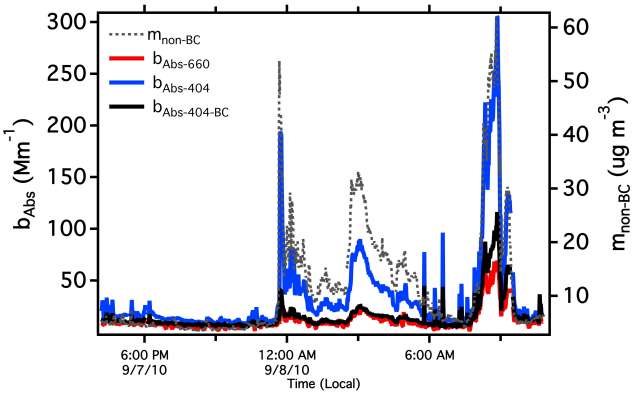

Fig. 3. Time series of measured 404 nm and 658 nm absorption of ambient particles (blue and red lines), 404 nm thermo-denuded absorption (black) and non-refractory aerosol mass (dashed grey line).

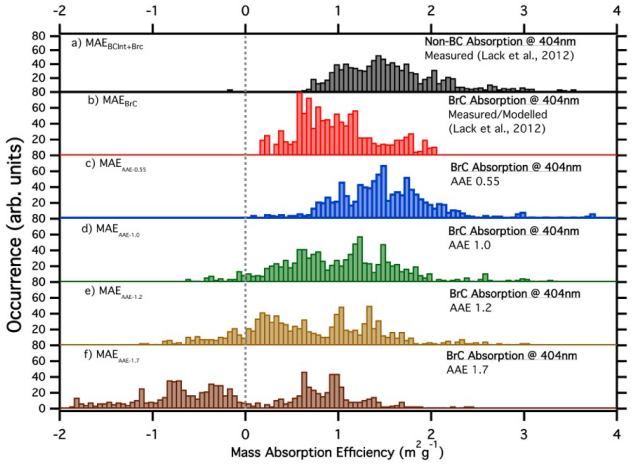

Fig. 4. Histograms of measured and calculated mass absorption efficiency of NR-PM. **(a)** $MAE_{BCInt+BrC}$: measured MAE including internal mixing and BrC, **(b)** MAE_{BrC}: MAE of just BrC from Lack et al. (2012), and the MAE of BrC using the AAE attribution method using **(c)** AAE = 0.55, **(d)** AAE = 1.0, **(e)** AAE = 1.2, and **(f)** AAE = 1.7.

et al. (2009) and Lack and Cappa, 2010), and 1.2. This last value represents a Mie modelled average AAE for BC coated in non-absorbing material derived from the same modelling work that removed absorption by internal mixing. All AAEs used were for the wavelength pair 404 nm and 658 nm.

3.2 Results

In this section we compare BrC absorption values derived from both direct attribution and AAE methods. All absorption values are presented using the MAE.

Absorption measurements for this forest fire revealed significant contributions from both internal mixing of BC and absorption by BrC to total absorption (Fig. 3 and Lack et al., 2012b). The two AAE-independent MAE values ($MAE_{BCInt+BrC}$ and MAE_{BrC}) are compared to those calculated using the AAE attribution method. Histograms of all MAEs are shown in Fig. 4, and the mean and standard deviations shown in Table 1.

In order to make a quantitative assessment of the differences between these methods, we calculated a point-by-point percentage difference between the MAE_{BrC} time series and those for $MAE_{AAE-0.55}$, $MAE_{AAE-1.0}$, $MAE_{AAE-1.2}$ and $MAE_{AAE-1.7}$. Using this information the mean difference was calculated (ΔMAE% shown in Table 1). A negative ΔMAE% indicates that, on average, the attributed MAE was less than MAE_{BrC}. We recognize that the ΔMAE% distributions for each MAE AAE trial had different characteristic shapes, and therefore the mean does not provide a truly representative statistic for comparing trials. However, despite this limitation it still serves as a useful general metric.

The attributed $MAE_{AAE-1.0}$, $MAE_{AAE-1.2}$, and $MAE_{AAE-1.7}$ all show values below zero, with the fraction of MAE values <0 increasing with the assumed AAE used. Uncertainty in the absorption measurements ($\pm 5\,\%$) used to derive these quantities suggests that some negative MAE values may be expected. However, observation of a progressively larger number of negative MAE values as the assumed AAE increases is likely an indication that the chosen AAE is less reasonable.

The MAE derived using AAE of 0.55, which has been assessed as an extreme lower limit, is similar to $MAE_{BCInt+BrC}$. However, it is important to recognize that that the $MAE_{BCInt+BrC}$ includes absorption by internal mixing, whereas the attributed $MAE_{AAE-0.55}$ does not. Given that the primary objective of this case study is to compare the absorption contribution of just BrC, it is more appropriate to compare AAE-attributed values to MAE_{BrC}, rather than $MAE_{BCInt+BrC}$. $MAE_{AAE-0.55}$ shows an average overestimation compared to MAE_{BrC} of 56 %. At the other end of the spectrum, using the AAE of 1.7 produces a difference of $-104\,\%$ in addition to yielding a much wider distribution and a substantially larger number of negative values. Both of these AAEs do not attribute absorption correctly.

The best agreement between the AAE attribution method and MAE_{BrC} is obtained using AAE = 1 (average $MAE_{AAE-1.0}$ is 1 % lower than MAE_{BrC}). This result would appear to support the use of the AAE absorption attribution method with AAE = 1. However, as stated previously, based upon the observations the most likely AAE for BC_{Int} in this fire was ~ 1.2. As such, it appears that the good agreement between $MAE_{AAE-1.0}$ and MAE_{BrC} was fortuitous. Using the constrained BC_{Int} AAE of 1.2, the MAE was $-34\,\%$ lower than MAE_{BrC}. Using the most probable range of AAE values for BC_{Int} found in literature (1.1 ± 0.3), the potential differences between the AAE modelled MAE and MAE_{BrC} were $+20\,\%$ to $-60\,\%$ (interpolated from ΔMAE% in Table 1).

Table 1. Measured and modelled mass absorption efficiencies (404 nm), and calculated differences.

	BC_{Int} + BrC	BrC	AAE = 0.55	AAE = 1	AAE = 1.2	AAE = 1.7
MAE ($m^2\,g^{-1}$)	1.58 ± 0.60	0.98 ± 0.45	1.54 ± 0.63	0.99 ± 0.75	0.66 ± 0.83	-0.05 ± 1.04
ΔMAE%		0%	56%	−1%	−34%	−104%

These results provide some indication of the range of uncertainty that arises from the choice of AAE used for BrC absorption attribution. At worst, differences of 50 % to 100 % in attributed MAE were observed in this case study. Even when using our best estimate of the true BC_{Int} AAE for this case study, an average disagreement of 34 % between cases was found.

4 Summary

The attribution of short-wavelength light absorption to black and brown carbon has commonly been achieved using the absorption Ångström exponent (AAE) relationship, assuming an AAE for externally mixed black carbon (BC_{Ext}) of unity, and assuming that internal mixing of BC (BC_{Int}) does not alter AAE. Theoretical investigations and literature values for BC_{Ext} and BC_{Int} (Fig. 2a) suggest that this assumption can lead to modest uncertainty in attributed short wavelength BC_{Ext} or BC_{Int} absorption of +7 % to −22 %. This uncertainty will contribute to uncertainties in attributed BrC absorption, which is dependent on the absolute amount of BrC present. For example, uncertainties in attributed BrC absorption will be $\leq \pm 33$ %, only when BrC comprises 23 % to 41 % of total absorption, assuming an absorption measurement uncertainty of ±5 %. For the biomass-burning case study presented, which is the most likely environment for the occurrence of strongly absorbing BrC, 60 % to 80 % of absorption was due to BrC, making the AAE attribution method viable.

For the same case study, we found that the AAE attribution method produced differences in attributed BrC absorption compared to direct analyses that did not use the AAE approach. When using an AAE of 1, as is often done, the average difference between the BrC mass absorption efficiency (MAE) calculated using the AAE and AAE-independent method was close to zero. However, the use of AAE = 1 for this system was likely not justified, given that the system contained BC coated in significant amounts of organic matter, which would have yielded an AAE (without the inclusion of brown carbon absorption) of at least 1.2. When this AAE was used to attribute absorption, an underestimation in BrC MAE of −34 % was found. This underestimation compounds the overall uncertainty of the attributed absorption by BrC.

Absorbing particles emitted from the same source will likely display a range of AAE based upon size, coatings and composition, which is very likely to change as atmospheric transport and processing occurs. Evolution of these AAE distributions will lead to evolving uncertainties in attributed BrC absorption when using the AAE method. Although not considered here, the attribution of absorption to dust (in addition to absorption due to BC_{Int}) will add further uncertainty to the attribution of BrC.

We therefore caution against the general application of the AAE method for absorption attribution without careful consideration of uncertainty propagation. In order to minimize uncertainties, the technique should only be applied when a significant fraction of the total absorption is sourced from BrC, and when the AAE of BC_{Ext} or BC_{Int} is constrained.

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