Impact of brown and clear carbon on light absorption enhancement, single scatter albedo and absorption wavelength dependence of black carbon

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Abstract. The presence of clear coatings on atmospheric black carbon (BC) particles is known to enhance the magnitude of light absorption by the BC cores. Based on calculations using core/shell Mie theory, we demonstrate that the enhancement of light absorption (E_ABS) by atmospheric black carbon (BC) when it is coated in mildly absorbing material (C_Brown) is reduced relative to the enhancement induced by non-absorbing coatings (C_Clear). This reduction, sensitive to both the C_Brown coating thickness and imaginary refractive index (RI), can be up to 50% for 400 nm radiation and 25% averaged across the visible radiation spectrum for reasonable core/shell diameters. The enhanced direct radiative forcing possible due to the enhancement effect of C_Clear is therefore reduced if the coating is absorbing. Additionally, the need to explicitly treat BC as an internal, as opposed to external, mixture with C_Brown is shown to be important to the calculated single scatter albedo only when models treat BC as large spherical cores (> 50 nm). For smaller BC cores (or fractal agglomerates) consideration of the BC and C_Brown as an external mixture leads to relatively small errors in the particle single scatter albedo only when models treat BC as large spherical cores (> 50 nm). For smaller BC cores (or fractal agglomerates) consideration of the BC and C_Brown as an external mixture leads to relatively small errors in the particle single scatter albedo only when models treat BC as large spherical cores (> 50 nm). For smaller BC cores (or fractal agglomerates) consideration of the BC and C_Brown as an external mixture leads to relatively small errors in the particle single scatter albedo only when models treat BC as large spherical cores (> 50 nm). For smaller BC cores (or fractal agglomerates) consideration of the BC and C_Brown as an external mixture leads to relatively small errors in the particle single scatter albedo only when models

1 Introduction

1.1 Black carbon and clear coatings

The absorption of solar radiation by atmospheric black carbon (BC) is thought to lead to positive top-of-atmosphere radiative forcing (i.e. atmospheric warming) about 1/4 of the magnitude of anthropogenic CO₂ (IPCC, 2007). Accordingly, the sources, emission strengths and climate impact of BC are a topic of significant research.

The impact of other atmospheric particulate components on BC absorption, in the form of internal mixtures of BC with primary and secondary organic aerosol (POA, SOA) and inorganic salts such as sulfate, has also drawn significant attention (e.g. Bond et al., 2006; Jacobson, 2001; Zhang et al., 2008). This is because the light absorption by an absorbing core can be enhanced when coated with a purely scattering shell (Fuller et al., 1999). The shell acts as a lens and focuses more photons onto the core than would reach it otherwise. This lensing effect has been shown theoretically to increase the absorption by an individual BC particle by 50–100% for core and shell sizes typical of the atmosphere (Bond et al., 2006) and is thought to have an important influence on the radiative forcing by BC (Jacobson,
Absorption enhancement due to lensing has been observed for BC particles coated with SOA (Schnaiter et al., 2005) or sulfuric acid (Zhang et al., 2008), for absorbing polystyrene spheres coated with organic material (Lack et al., 2009a), graphite coated with oleic acid or glycerol (Shiraiwa et al., 2009) and for absorbing mineral dust coated in aqueous inorganic material (Lack et al., 2009b). The absorption enhancement, $E_{\text{Abs}}$, is defined as the ratio of the absorption cross section, $\sigma_{\text{Abs}}$, of a coated absorbing particle (usually BC) to an equivalent uncoated particle (see Eq. 1 below).

$$E_{\text{Abs}} = \frac{\sigma_{\text{Abs-Core-Shell}}}{\sigma_{\text{Abs-Core}}}$$ (1)

Evaluation of recent field data of particulate organic matter (OM, including both primary and secondary aerosol) concentrations show that particulate OM is often present with abundances similar to or larger than that of inorganic particulate matter, such as sulfate and nitrate salts (e.g. Zhang et al., 2007). In particular, a large amount of directly emitted OM is internally mixed with BC from sources such as biomass and biofuel combustion (Alexander et al., 2008; Gustafsson et al., 2009; Roden et al., 2006), and BC from internal combustion engines can become thickly coated in condensable material within hours to days of emission (e.g. Quinn et al., 2004). It is therefore reasonable to expect that a significant amount of ABC is internally mixed with OM, which therefore provides a significant opportunity for absorption enhancement and is thus the focus of current research on the evolution of mixing state of BC (e.g. Moteki et al., 2007; Schwarz et al., 2008).

### 1.2 Black carbon and brown coatings

Emerging research suggests that a variety of particulate OM can absorb radiation, particularly at the shorter visible and UV wavelengths (Adler et al., 2009; Barnard et al., 2008; Dinlal et al., 2008; Hoffer et al., 2006; Kirchstetter et al., 2004; Rincon et al., 2009; Roden et al., 2006; Schnaiter et al., 2006; Schwier et al., 2009; Shapiro et al., 2009; Sun et al., 2007; Yang et al., 2009). In fact the mass absorption cross-section (MAC) of this so-called “brown carbon” ($C_{\text{Brown}}$) (Andreae and Gelencser, 2006) has been estimated to be of the same order as BC at 400 nm (Barnard et al., 2008; Clarke et al., 2007). Given the large abundance of particulate OM relative to BC in the atmosphere, this suggests that absorption by $C_{\text{Brown}}$ may be a significant fraction of total atmospheric light absorption (Clarke et al., 2007). Despite the potential contributions of $C_{\text{Brown}}$ to absorption of solar radiation, all theoretical studies to date of the lensing-induced $E_{\text{Abs}}$ have focused solely on the role of non-absorbing coatings. In the present study, we directly address how the presence of $C_{\text{Brown}}$ coatings (i.e. coatings that are not purely scattering) on BC cores influence the magnitude of $E_{\text{Abs}}$.

A wide range of MAC and imaginary RI values for $C_{\text{Brown}}$ ($k_{\text{Brown}}$) have been reported in the literature. Reported $k_{\text{Brown}}$ values (at ~550nm) range from 0.002 to 0.27 (Alexander et al., 2008; Hoffer et al., 2006), which compare to a value of ca. 0.71 for pure BC (Bond and Bergstrom, 2006). MACs vary from 0.02 to 2 m² g⁻¹ at mid visible wavelengths and from 1–10 m² g⁻¹ at 350 nm. These values were derived from field measurements of particulate OM observed from Asian pollution outflow (Yang et al., 2009), African biomass combustion (Kirchstetter et al., 2004), Mexico City pollution (Barnard et al., 2008) and humic-like substances ($HULIS$) extracted from Amazonian biomass combustion particles (Hoffer et al., 2006). These $C_{\text{Brown}}$ MACs compare to a BC MAC of ca. 7.5 m² g⁻¹ at 550 nm or ca. 12–13 m² g⁻¹ at ~350 nm (from Adler et al., 2009) and calculated assuming an absorption Angstrom exponent = 1 and extrapolating from Bond and Bergstrom (2006); see Eq. 2). The large variability in MAC for particulate OM is likely related to the variability in the composition of the OM fraction, which can include $HULIS$, lignin and polycyclic aromatic compounds (Andreae and Gelencser, 2006).

Attribution of observed atmospheric light absorption to $C_{\text{Brown}}$ is an important step in understanding the overall climate effects of aerosol. Some studies have attempted this attribution based on assumptions as to the wavelength dependence of absorption (e.g. Favez et al., 2009; Yang et al., 2009). It is often assumed that the imaginary RI for BC is wavelength ($\lambda$) independent and that the absorption cross-section for BC varies as $\lambda^{-1}$ (Bond and Bergstrom, 2006) (discussed further below). The variation of absorption with wavelength is characterized by the absorption Angstrom exponent ($AAE$), defined as

$$AAE = -\left(\frac{\ln(\sigma_{\text{Abs-\lambda_1}}/\sigma_{\text{Abs-\lambda_2}})}{\ln(\lambda_1/\lambda_2)}\right)$$ (2)

where $\sigma_{\text{Abs}}$ is the absorption cross-section (or observed absorption). An $AAE = 1$ corresponds to a $\lambda^{-1}$ dependence of absorption. It is thought that $C_{\text{Brown}}$ shows strong deviations from the $\lambda^{-1}$ relationship and it has therefore been assumed that the observation of an $AAE$ larger than 1 is an indication of absorption by $C_{\text{Brown}}$ (or dust if present). However, as mentioned by Gyawali et al. (2009), the $AAE$ of BC cores with >10nm diameter and of BC cores that are coated in scattering shells may deviate from the typically assumed $AAE = 1$ relationship. For example, the $AAE$ for BC alone can be greater or less than 1, depending on the modeled core size. This must be explicitly kept in mind when assigning contributions to light absorption to $C_{\text{Brown}}$.

As research into the absorption properties and ubiquity of $C_{\text{Brown}}$ progresses, it is prudent to consider what the impact of $C_{\text{Brown}}$ is on the lensing-induced absorption enhancement for BC. Consider that whereas absorption by a BC core with a purely scattering shell will have contributions to absorption by the core and $E_{\text{Abs}}$ by the lensing effect, a BC core coated in $C_{\text{Brown}}$ will have absorption contributions from the core, the absorbing shell and the $E_{\text{Abs}}$ from the lensing effect.
FIG. 1. Schematic of the effect of $C_{\text{clear}}$ and $C_{\text{brown}}$ shells on BC absorption.

(see Fig. 1 for a schematic of this effect). Given the different optical properties of $C_{\text{brown}}$ compared to a purely scattering shell, the $E_{\text{abs}}$ is very likely to be dependent on the wavelength of light, the absorption properties of the $C_{\text{brown}}$ and shell thickness. In an effort to address the above issue, we present here a series of calculations performed using core-shell Mie theory (Bohren and Huffman, 1983) wherein we investigate the impact of a slightly absorbing, rather than purely scattering, shell on the absorption enhancement factor, $E_{\text{abs}}$ and aerosol single scatter albedo (SSA). This modeling study builds on the work of Bond et al. (2006) and we remain consistent with that study by using many of the same terms, modeling parameters and discussion points. We also investigate the impact of BC cores coated in purely scattering shells on the AAE to provide further insight and recommendations for future studies attempting to elucidate the contribution of BC, $C_{\text{brown}}$, and purely scattering shells.

2 Modeling

To model the absorption enhancement impact of $C_{\text{brown}}$ we remain consistent with the study of Bond et al. (2006) and use a RI for BC of 1.85–0.71i and a real RI of 1.55 for the non-absorbing shell (defined here as a clear coating, $C_{\text{clear}}$). The BC core is modeled as a lognormal (LN) distribution of cores having a geometric standard deviation (GSD) of 1.1 (unless otherwise stated). The “core” and “shell” diameters, $d_{p,\text{core}}$ and $d_{p,\text{shell}}$, refer to the central sizes in the LN particle distribution. The core diameter refers to the diameter of the core alone, while the shell diameter is the diameter of the entire particle, i.e. core + shell ($d_{p,\text{shell}} = d_{p,\text{particle}}$). The LN distribution is coated by applying the central shell-to-core diameter ratio to each core of the LN distribution (i.e. the ratio $d_{p,\text{shell}}/d_{p,\text{core}}$ is conserved).

The RI of $C_{\text{brown}}$ is expected to vary with wavelength and so we model across the visible radiation spectrum (380–750 nm). We have also performed some calculations at a specific wavelength of 400 nm to illustrate a single wavelength impact. Wavelengths around 400 nm are commonly used in in-situ aerosol optical property measurements. In general, the solar spectrum averaged results are more relevant for the overall climate impacts whereas the single wavelength results will assist in assessing in-situ measurements. Wavelength-dependent $k_{\text{brown}}$ values have been estimated from literature observations. The SSA of particulate OM was measured by Barnard et al. (2008) to be 0.75 (at 380 nm) and is used to calculate $k_{\text{brown}}$ at 380 nm. To do this we assume a particle diameter of 200 nm, a real RI of 1.55 and calculate the $k_{\text{brown}}$ (using Mie theory) required to achieve an SSA of 0.75 at 380 nm: the calculated $k_{\text{brown}}$ is 0.06 at 380 nm. We then apply the form of the MAC vs. wavelength curve modeled by Sun et al. (2007) (and similar to that measured by Kirchstetter et al., 2004) to produce a wavelength dependent $k_{\text{brown}}$ (Fig. 2). The actual $k_{\text{brown}}$ remains somewhat uncertain and may vary with location and source. To approximately account for this, we have also investigated the sensitivity of the results to the chosen $k_{\text{brown}}$ by a) increasing the original $k_{\text{brown}}$ by 50% and b) subtracting 0.03 from the original $k_{\text{brown}}$. These changes simulate more and less absorbing OM as measured in some studies (Adler et al., 2009; Dinar et al., 2008; Hoffer et al., 2006; Schnaiter et al., 2006) (Fig. 2).
We also note here that the use of Mie theory assumes spherical particles. There is sufficient evidence that BC, usually fractal when emitted from efficient combustion, can become more compact and the overall particle spherical when coated in other inorganic and organic material (Alexander et al., 2008; Lewis et al., 2009; Zhang et al., 2008). Our modeling mostly deals with coated BC cores. In the limit of thinly coated cores, where fractal BC is more likely, the work of Liu et al. (2008) provides guidance on the differences in absorption for fractal vs. spherical BC. For smaller (15 nm) and larger (25 nm) BC spherule sizes, absorption will likely be overestimated by up to 10% and underestimated by up to 20% if represented as spherical. Recent laboratory studies of spherical particles using absorbing cores with non-absorbing coatings showed generally good agreement with predictions from Mie theory for absorption (Shiraiva et al., 2009; Lack et al., 2009a) and extinction (Abo-Riziq et al., 2008; Lang-Yona et al., 2010). However, when non-absorbing cores with slightly absorbing coatings were considered the model/measurement agreement for extinction measurements was found to be worse (Lang-Yona et al., 2010). Given the challenges with dealing even with spherical particles, this suggests that the computational results presented here should be considered as a guide to understanding the general influence of CBrown on aerosol absorption, but that experimental verification will ultimately be needed.

3 Defining absorption enhancement - \( E_{\text{Abs}} \)

The \( E_{\text{Abs}} \) of a core-shell system is defined as the ratio of absorption cross-sections (\( \sigma_{\text{Abs}} \)) of the coated and uncoated particles (Eq. 1) and here is calculated for all visible wavelengths. The physical interpretation of \( E_{\text{Abs}} \) for a BC core with a Clear shell is relatively straightforward compared to systems with absorbing shells because the addition of a Clear shell leads to an increase in absorption by lensing only. However, when the shell also has an absorbing component, absorption from both the shell material and the lensing effect created by the shell contribute and must be accounted for. Here we distinguish between the contributions from the two CBrown absorption effects. First, the \( \sigma_{\text{Abs}} \) of a homogenous particle (with diameter \( d_{\text{p, shell}} \)) of CBrown (e.g. using \( k_{\text{Brown}} \) from Fig. 2) system is calculated across all visible wavelengths. This is repeated for a CBrown particle with diameter \( d_{\text{p, core}} \). The difference between these two \( \sigma_{\text{Abs}} \) provides a measure of the absorption by the CBrown coating after accounting for the size dependence of absorption and scattering. This absorption by CBrown is then subtracted from \( \sigma_{\text{Abs}} \) calculated as for step 1 except using a BC core with the same CBrown coating (and where the core diameter = non-absorbing core diameter as above, see Table 1). The resultant quantity is the absorption by the BC core including lensing (but not absorption) by CBrown, and the calculated \( E_{\text{Abs}} \) provides an estimate of the lensing effect of the CBrown. Figure 3 shows the calculated \( E_{\text{Abs}} \) (across all visible wavelengths) for 3 systems; 1) \( E_{\text{Abs} - \text{CL}} \): the “standard” \( E_{\text{Abs}} \) for a CBrown core and Clear shell 2) \( E_{\text{Abs} - \text{BR}} \): the \( E_{\text{Abs}} \) for a BC core and CBrown shell including both the absorption and lensing components of the CBrown and 3) \( E_{\text{Abs} - \text{BR} - X} \): the \( E_{\text{Abs}} \) for a BC core and shell with the absorption contribution of the CBrown removed as described above.

Based on these definitions (given explicitly in Table 1), \( E_{\text{Abs} - \text{BR} - X} \) provides information on the magnitude of the lensing effect of CBrown only. \( E_{\text{Abs} - \text{BR} - X} \) may differ from \( E_{\text{Abs} - \text{CL}} \) due to either (i) modification of the photon path through the particle due to the absorbing coating, thus causing fewer (or more) photons to be focused towards the core, or (ii) absorption of photons by the coating material, thus causing fewer photons to reach the core. In this second case, the total absorption by the coated particle will be conserved (i.e. it does not matter whether a photon is absorbed within the shell or the core), but the magnitude of \( E_{\text{Abs}} \) has been decreased. When \( E_{\text{Abs} - \text{BR} - X} > 1 \), this indicates that photons at that wavelength are still being focused onto the core due to the lensing effect. However, when \( E_{\text{Abs} - \text{BR} - X} < 1 \), this is an indication that the enhancement due to the lensing effect is overwhelmed by absorption by the coating material. In the limit of a strongly absorbing, thick coating no photons will make it to the core and \( E_{\text{Abs} - \text{BR} - X} \rightarrow 0 \).

As an illustrative example, we consider a system with a BC core diameter of 300 nm and a shell diameter of 500 nm. For these conditions, it is found that \( E_{\text{Abs} - \text{CL}} \) is essentially wavelength independent with a value of ca. 1.8 (Fig. 3). In contrast, the \( E_{\text{Abs} - \text{BR}} \) varies between 1.7 and 2.4 across
Table 1. Parameter descriptions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Symbol</th>
<th>Calculation Method/Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption Cross Section</td>
<td>BC Core</td>
<td>$\sigma_{\text{AbsCore}}$</td>
<td>Mie Theory ($RI_{\text{core}} = 1.85 + 0.7i$)</td>
</tr>
<tr>
<td></td>
<td>BC Core $&amp;$ C Clear Shell</td>
<td>$\sigma_{\text{AbsCoreCClear}}$</td>
<td>Core Shell Mie Theory ($RI_{\text{core}} = 1.85 + 0.7i, RI_{\text{clear}} = 1.55 + 0.0i$)</td>
</tr>
<tr>
<td></td>
<td>BC Core $&amp;$ C Brown Shell</td>
<td>$\sigma_{\text{AbsCoreCBrown}}$</td>
<td>Core Shell Mie Theory + Brown Carbon Imaginary RI ($k_{\text{Brown}}$) from Fig. 2. ($RI_{\text{core}} = 1.85 + 0.7i, RI_{\text{clear}} = 1.55 + k_{\text{Brown}}$)</td>
</tr>
<tr>
<td></td>
<td>C Brown Particle of $d_{p, \text{shell}} - C_{\text{Brown}}$</td>
<td>$\sigma_{\text{AbsBrown}}$</td>
<td>Core Shell Mie Theory + Brown Carbon Imaginary RI ($k_{\text{Brown}}$) from Fig. 2. ($RI_{\text{core}} = 1.55 + k_{\text{Brown}}$)</td>
</tr>
<tr>
<td>Absorption Enhancement</td>
<td>BC Core $&amp;$ C Clear Shell</td>
<td>$E_{\text{Abs-CL}}$</td>
<td>$E_{\text{Abs-CL}} = \frac{\sigma_{\text{AbsCoreCClear}}}{\sigma_{\text{AbsCore}}} - 1$</td>
</tr>
<tr>
<td></td>
<td>BC Core $&amp;$ C Brown Shell</td>
<td>$E_{\text{Abs-BR}}$</td>
<td>$E_{\text{Abs-BR}} = \frac{\sigma_{\text{AbsBrown}}}{\sigma_{\text{AbsCore}}} - 1$</td>
</tr>
<tr>
<td></td>
<td>BC Core $&amp;$ C Brown Shell $- C_{\text{Brown}}$</td>
<td>$E_{\text{Abs-BR-X}}$</td>
<td>$E_{\text{Abs-BR-X}} = \frac{\sigma_{\text{AbsBrown}}}{\sigma_{\text{AbsCore}}} + \frac{\sigma_{\text{AbsBrown}}}{\sigma_{\text{AbsCoreCClear}}} - 1$</td>
</tr>
<tr>
<td>Absorption Enhancement Loss</td>
<td>Difference between enhancement with C Clear and C Brown shell.</td>
<td>$E_{\text{Abs-Remaining}}$</td>
<td>$E_{\text{Abs-Remaining}} = \frac{\sigma_{\text{AbsRemaining}}}{\sigma_{\text{AbsCoreCClear}}} - 1$</td>
</tr>
</tbody>
</table>

Table 2. Central core and shell diameters from the five $E_{\text{Abs}}$ regimes of Bond et al. (2006)

<table>
<thead>
<tr>
<th>Bond et al. (2006) Regime #</th>
<th>Central Core Diameter (nm)</th>
<th>Central Shell Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>1500</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>1500</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>330</td>
</tr>
<tr>
<td>4</td>
<td>300</td>
<td>400</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>1500</td>
</tr>
</tbody>
</table>

the visible spectrum. This larger $E_{\text{Abs-BR}}$ results from absorption by $C_{\text{Brown}}$. When the absorption of the $C_{\text{Brown}}$ shell is accounted for we see that the adjusted enhancement, $E_{\text{Abs-BR-X}}$, is reduced below the $E_{\text{Abs-CL}}$ at all wavelengths. The wavelength dependence of $E_{\text{Abs-BR}}$ derives from the wavelength dependence of the $C_{\text{Brown}}$ absorption, described above. The reduction in $E_{\text{Abs}}$, for any conditions is characterized by calculating the remaining enhancement, $E_{\text{AbsRemaining}}$, as defined in Table 1.

4 Results

In this section we use the definitions of the five core/shell diameter regimes given by Bond et al. (2006) to provide insights into the ‘$E_{\text{Abs}}$ lost’ (presented as $E_{\text{AbsRemaining}}$) that results from the coating being $C_{\text{Brown}}$ rather than $C_{\text{Clear}}$. Of these Bond regimes the most common expected in the atmosphere are regimes 3 and 4 (see Fig. 4). Regime 3 corresponds to particles with core diameters <175 nm and thick shells (relative to the core size, with $d_{\text{core}}/d_{\text{shell}} > 0.55$ but $d_{\text{shell}} > 500\text{nm}$) while regime 4 corresponds to thin shells.

Fig. 4. (a) Calculated $E_{\text{Abs-Remaining}}$ for different BC core and $C_{\text{Brown}}$ shell diameters at 400 nm wavelength. Regime numbers from Bond et al. (2006) and position of central values used for these regimes also shown. (b) Same as (a) but integrated over all visible light wavelengths.
4.1 Impact of \( C_{\text{Brown}} \) shell thickness and \( BC \) core size

For a given wavelength and \( k_{\text{Brown}} \), as the thickness of the \( C_{\text{Brown}} \) shell increases \( E_{\text{Abs}} \) decreases. For example, for 400 nm wavelength radiation in regimes 3 and 4 (Fig. 4a), \( E_{\text{Abs}} \) loss can be up to 50%. For very thin shells (regime 4) the \( E_{\text{Abs}} \) loss can be up to 10% and as shell thickness decreases, the \( C_{\text{Brown}} \) coating behaves more like \( C_{\text{Clear}} \). For much thicker shells \( E_{\text{Abs}} \) can be reduced by 80% or more (i.e. in regimes 1, 2 or 5). When averaged across all visible wavelengths (from 380–750 nm, Fig. 4b) the \( E_{\text{Abs}} \) loss is 15–20% in regimes 3 and 4 and \( \sim30\text{-}50\% \) in regimes 1, 2 and 5. The difference between 400nm \( E_{\text{Abs}} \) and the wavelength averaged \( E_{\text{Abs}} \) results from the assumed wavelength dependence of absorption by \( C_{\text{Brown}} \). The \( E_{\text{Abs}} \) loss depends only weakly on \( BC \) core size (Fig. 4), indicating that for a given wavelength (i.e. \( k_{\text{Brown}} \)), the \( E_{\text{Abs}} \) loss is predominantly a function of the amount of \( C_{\text{Brown}} \).

4.2 Core shell regimes from Bond et al. (2006)

Here we use core and shell diameters that form the central value of each of the five Bond et al. (2006) regimes (Fig. 4a and Table 1) and the central values for \( k_{\text{Brown}} \) from Fig. 2 to gain further insight into the effect of \( C_{\text{Brown}} \) on \( E_{\text{Abs}} \). Figure 5 presents these results with regime numbers given in the top left of each plot. As discussed above it is clear that \( E_{\text{Abs}} \) is reduced for very thick \( C_{\text{Brown}} \) shells (Fig. 5a, b and e). It is also evident that not only does the \( C_{\text{Brown}} \) shell reduce the number of additional photons being directed to the core (i.e. reduction in lensing), but sufficiently thick \( C_{\text{Brown}} \)
we consider the lensing effect due to clear coatings (i.e. treatment of the aerosol population as an external rather than an internal mixture) may lead to an underestimation of the radiative forcing of BC by a factor of 2–3. However, if the lensing effect is reduced due to absorption by C\textsubscript{Brown} then this underestimation of radiative forcing will be similarly reduced, with the actual reduction dependent on the assumed wavelength dependence of the C\textsubscript{Brown}.

### 4.4 Consideration of mixing state

Even though $E_{\text{Abs}}$ can be large under some conditions (e.g. when C\textsubscript{Brown} coatings are thick), our focus has been on the influence of C\textsubscript{Brown} on the lensing effect. It has tacitly been assumed that absorption by C\textsubscript{Brown}, whether considered as an internal or external mixture with BC, would be accounted for and quantified (for example in models) by the mass and MAC of the C\textsubscript{Brown}. We now consider how a reduction in the lensing effect (due to C\textsubscript{Brown}) for an internal mixture will influence the SSA and how this compares to an external mixture of BC and C\textsubscript{Brown}. A reduction in lensing means that the fraction of absorption due to the BC core will be reduced and, depending on how the contribution from C\textsubscript{Brown} is considered in a model, this may lead to uncertainty in the calculated SSA, which is the primary parameter that determines the sign of the radiative forcing by particles. For example, Jacobson (2000, 2001) showed that failure to consider the lensing effect due to clear coatings (i.e. treatment of the aerosol population as an external rather than an internal mixture) may lead to an underestimation of the radiative forcing of BC by a factor of 2–3. However, if the lensing effect is reduced due to absorption by C\textsubscript{Brown} then this underestimation of radiative forcing will be similarly reduced, with the actual reduction dependent on the assumed wavelength dependence of the C\textsubscript{Brown}.

#### 4.4.1 Mixing state assumptions and Single Scatter Albedo (SSA)

One way to interpret the lensing effect is to recognize that it corresponds to a decrease in the SSA when compared to an equivalent mass external mixture. We have calculated the difference in SSA values between an external and an internal mixture of BC and C\textsubscript{Brown} (at 400 nm assuming a k\textsubscript{Brown} of 0.05 and GSD = 1.1) and similarly for BC and C\textsubscript{Clear} (ΔSSA\textsubscript{ext–int} = SSA\textsubscript{ext} − SSA\textsubscript{int}, where the ext and int indicate external and internal mixtures, respectively; Fig. 7). For the C\textsubscript{Brown} case (Fig. 7a), at small core sizes (<50 nm) the difference between the internal and external mixture SSA values is small (<0.03). For the C\textsubscript{Clear} case, for small core sizes certain coating thicknesses will give somewhat larger ΔSSA (see Fig. 7b), but for most core/shell combinations ΔSSA\textsubscript{ext–int} is small. Additionally, ΔSSA\textsubscript{ext–int} is small when the coating is very thick (i.e. within regimes 1 and 2). However, for larger assumed BC core sizes the difference can become large, especially for intermediate coating thicknesses. This indicates that even though the $E_{\text{Abs}}$ is generally largest for small BC cores and/or very thick coatings (c.f. Fig. 5 in Bond et al., 2006), in these regimes accurate specification of the mixing state will not strongly influence the radiative properties of BC and C\textsubscript{Brown}. We have also considered the mixing state of C\textsubscript{Brown} and BC and the role of lensing in determining the sign of the radiative forcing by particles.
repeated these calculations at longer wavelengths (532 nm and 700 nm) and find that the general discussion given above remains valid even though the imaginary refractive index for \( C_{\text{Brown}} \) is smaller than at 400 nm. The main influence of mixing state in these regimes is to increase the overall particle size (i.e. cross section), which will tend to increase the total light extinction, but this will have minimal influence on the balance between absorption and scattering. However, when larger \( BC \) core sizes are used within a model, mixing state is seen to be an important factor. This is generally true whether \( C_{\text{Brown}} \) or \( C_{\text{Clear}} \) coatings are considered, although for \( C_{\text{Brown}} \) coatings the importance of mixing state is lessened (consistent with the reduction in the lensing effect identified above).

### 4.4.2 Mixing state and micro-physical model assumptions

To our knowledge, no atmospheric models explicitly account the fact that \( BC \) is actually a fractal agglomerate composed of many small (10’s of nm in diameter) spherules (van Poppel et al., 2005). \( BC \) is instead represented as spherical particles of some size (or with some size distribution), and the optical properties are calculated based on the spherical particle size. Rayleigh-Debye-Gans (RDG) theory posits that for a fractal particle such as \( BC \) the absorption behavior is instead dictated by the size of the individual (small) spherules, and not by the agglomerated particle as a whole, i.e. that absorption is additive (Sorensen, 2000). If coated \( BC \) particles should be treated in accordance with RDG theory (i.e. as aggregates of 20–30 nm spheres), rather than as larger spherical particles, then the above discussion suggests that the importance of treating \( BC \) as an internal mixture may be limited in terms of the direct radiative effects even though \( E_{\text{Abs}} \) may be relatively large. However, the fact that models tend to use \( BC \) particles with relatively large diameters (i.e. >80 nm) (e.g. Kinne et al., 2003) means that the calculated radiative properties may be particularly sensitive to the choice and representation of \( BC \) mixing state.

In part, it is for the above reasons that we believe it remains a useful exercise to consider core-shell Mie theory results using \( BC \) core diameters that go beyond the typical spherule size range when calculating \( E_{\text{Abs}} \), SSA and AAE values for coated \( BC \) particles. Furthermore, what few experimental measurements that exist of \( E_{\text{Abs}} \) for coated soot appear more consistent with the soot particles being single large spheres rather than small spherules (Schnaiter et al., 2003; Zhang et al., 2008). Additionally, AAE values <1 are routinely observed in ambient measurements (Bergstrom et al., 2007; Lack et al., 2008), a result that is theoretically predicted for \( BC \) spheres that are larger than \( \sim 150 \) nm. Certainly more work is necessary to establish what the appropriate core size is for use in \( E_{\text{Abs}} \) and AAE calculations in order to facilitate both interpretation of ambient measurements and accurate calculation of the radiative effects of \( BC \) (and \( C_{\text{Brown}} \)) in models.

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**Fig. 7.** Contour plots of the calculated difference in the SSA between an external mixture and an internal mixture for a coated \( BC \) particle with a \( C_{\text{Clear}} \) coating (a) and a \( C_{\text{Brown}} \) coating (b) are shown as a function of core and shell diameter. Contours are shown only when \(|\text{SSA}_{\text{ext-int}}| > 0.03\). The color scale shown applies to both graphs. The actual SSA for the \( BC/C_{\text{Clear}} \) (c) and \( BC/C_{\text{Brown}} \) (d) internal mixtures are shown for reference. Note that absorption by the \( C_{\text{Brown}} \) shell narrows the size region over which large differences between the internal and external mixture are found.
4.5 Absorption wavelength dependence

The wavelength dependence of absorption is typically characterized by the absorption Angstrom exponent ($AAE$, Eq. 2). For “pure” $BC$ in the atmosphere the $AAE$ is assumed to be 1 (Bond and Bergstrom, 2006) and observations of $AAE>1$ are often taken as evidence of $C_{Brown}$ (or dust). In actuality, for $AAE=1$ the $BC$ must be of sufficiently small diameter (e.g. 10 nm) or, following from $RDG$ theory, a $BC$ core must be a fractal agglomerate composed of many sufficiently small individual spherules. As discussed above, some ambient data provides evidence of large $BC$ cores (i.e. with $AAE$ of <1). In addition, $AAE$ values>1 are theoretically possible for $BC$ coated in $C_{Clear}$ (not $C_{Brown}$) as discussed in Gyawali et al. (2009). Therefore, an assumed $AAE=1$ to anchor $BC$ absorption, and attribute $C_{Brown}$ absorption contains significant potential errors.

4.5.1 $AAE$ variability of $BC$ with $C_{Clear}$

Here we extend the calculations of Gyawali et al. (2009) in order to make clearer the need for caution in the use of the $AAE$ when attributing light absorption to $C_{Brown}$. Figure 8a shows the $AAE_{380nm−750nm}$ calculated for spherical $BC$ cores coated in various thicknesses of $C_{Clear}$. The $RI$ used are the same as presented in the sections above, while a larger GSD of 1.7 is assumed for the $LN$ distribution, which represents a particle size distribution from biofuel or biomass combustion (Bond et al., 2006). Figure 8a shows that the $AAE_{380nm−750nm}$ for $BC$ cores coated in $C_{Clear}$ is reasonably constant within 4 of the 5 core-shell regimes (regimes 1–3 and 5). Regime 4 (thin coatings on all core sizes) shows a large variability in $AAE_{380nm−750nm}$, ranging from 0.2 to 1.7, similar to the $AAE$ behavior of uncoated $BC$. For the other “realistic” regime (regime 3), the $AAE_{380nm−750nm}$ is generally in the range 1.4–1.6. Therefore one can only attribute absorption to $C_{Brown}$ with confidence if the $AAE_{380nm−750nm}$ is greater than 1.4–1.6; consistent with the findings of Gyawali et al. (2009).

4.5.2 $AAE$ Variability of $BC$ with $C_{Brown}$

If $AAE_{380nm−750nm}$ is measured to be less than ~1.6 this does not necessarily rule out $C_{Brown}$ as a significant contributor to the observed absorption. For certain core/shell size pairings, the $AAE_{380nm−750nm}$ for $BC$ cores with $C_{Brown}$ coatings can actually be close to (or even less than) unity, dependent upon the assumed $k_{Brown}$. We consider this in more detail by determining how the $AAE_{380nm−750nm}$ depends on the assumed $k_{Brown}$ for $C_{Brown}$ coatings on $BC$ cores. This is important to consider because, even if $k_{Brown}$ is large, only in certain regions (e.g. downwind of a forest fire) will the ambient aerosol be predominately composed of $BC$ and OC. More common will be situations where inorganic ions (or non-absorbing OC) also contribute to the aerosol burden, thus decreasing the effective imaginary $RI$ of the coating. As expected, the relationship between $AAE_{380nm−750nm}$ and $k_{Brown}$ depends explicitly on the core and shell diameters (Fig. 9). We have investigated three specific cases where the shell/core ratio has been varied; case 1: $d_{p,core}/d_{p,particle}=2$; case 2: $d_{p,particle}/d_{p,core}=3$; case 3: $d_{p,particle}/d_{p,core}=4$. This equates to shell/core volume ratios of 7, 26 and 63, respectively. For comparison, $BC$ has often been found in ambient samples to be ca. 5-10% of the total particle mass (Quinn et al., 2002; Quinn et al., 2004), corresponding approximately to cases 1 and 2, although $BC$ mass fraction can vary greatly depending on proximity to sources.

Considering Case 1 (Fig. 9a), it is apparent that for many core sizes the $AAE_{380nm−750nm}$ does not rise above 1.6 until the $k_{Brown}$ is at least > 0.03 and for $d_{p,core}$≥125 nm the $AAE_{380nm−750nm}$ is not > 1.6 even when $k_{Brown}$ = 0.06. However, for particles with 50 nm ≤ $d_{p,core}$≤100 nm the $AAE$ is noticeably greater than 1.6 after $k_{Brown}$ > 0.02. Thus, in a region where the coatings on $BC$ particles are relatively thin it is necessary to have relatively large $k_{Brown}$ in order to confidently distinguish contributions of $C_{Brown}$ from the generic
influence of $C_{\text{clear}}$ coatings on the AAE. As the shell/core volume ratio is increased the minimum $k_{\text{brown}}$ needed to give $AAE_{380\text{nm}-750\text{nm}} > 1.6$ is reduced. For example, for Case 3 the minimum $k_{\text{brown}}$ is $\sim 0.01$ for all core diameter sizes considered. This is because as the coating amount is increased the absorption due to the coating (as opposed to the core) is increased in proportion. Thus, for regions where the coatings on BC particles are thick it may be possible to readily identify $C_{\text{brown}}$ through the AAE.

The above discussion focuses on what conditions will allow for attribution of $C_{\text{brown}}$ to observed absorption. However, Fig. 9 also indicates that observation of AAE values around 1 does not definitively indicate that absorption is due to BC only. Instead, it is found that relatively significant absorption by $C_{\text{brown}}$ can still result in AAE values around 1. (Note that “significant” does not have a precise definition. Here we arbitrarily interpret significant to mean the minimum $k_{\text{brown}}$ needed to give a calculated SSA$_{380\text{nm}} > 0.95$ for a 200 nm $d_p$ $C_{\text{brown}}$ particle. Thus, with this definition we see that significant absorption by $C_{\text{brown}}$ occurs when $k_{\text{brown}} \geq 0.01$. This value can be compared to the $k_{\text{brown}}$ that would give a “noticeable” deviation in the SSA from unity (i.e. SSA $< 0.98$), which occurs for $k_{\text{brown}} > 0.003$. For reference, the SSA values corresponding to a particular $k_{\text{brown}}$ for these 200 nm particles are shown in Fig. 9.) Consistent with the above discussion, significant contributions of $C_{\text{brown}}$ to absorption that still result in $AAE_{380\text{nm}-750\text{nm}} \sim 1$ are most common for thinner coatings but still have a reasonable probability of occurring for thicker coatings. And in the absence of specific knowledge about the actual BC core diameter and coating thickness from measurements it is really more appropriate to consider the $AAE_{380\text{nm}-750\text{nm}}$ limit of 1.6 (instead of 1), in which case it is difficult to rule out contributions of $C_{\text{brown}}$ to observed absorption for nearly any reasonable core/shell combination. However, if simultaneous measurements of the total particle size distribution, BC size distribution and/or the BC mass fraction are made the above-identified limitations on $C_{\text{brown}}$ identification may be relaxed somewhat. This is because then one would know where on the $d_p,\text{coat}$ vs. $d_p,\text{core}$ AAE contour the measurements should be compared.

4.5.3 Comparing modeled AAE with ambient measurements

Although an AAE of 1.6 is not an absolute reference point, especially given the results from 4.5.2, at the wavelengths considered here it does serve as a general first approximation and lower limit to AAE for absolute attribution of $C_{\text{brown}}$. With this in mind, it is interesting to consider that almost 90% of AAE measurements over 2 months of ambient sampling during the GoMACCS field campaign (SE USA, Bates et al., 2008) were less than 1.6 (Bergstrom et al., 2007). Additionally, our own analysis indicates that AAE values during the 2002 and 2004 NEAQS campaigns (NE USA, Bates et al., 2008) were less than 1.6 (Bergstrom et al., 2007).
et al., 2005; Sierau et al., 2006) were less than 1.6 ∼75% and 100% of the time, respectively. The campaign average $AAE_{370\text{nm}}-950\text{nm}$ from Yang et al. (2009) (East Asia) was 1.46(±0.27) and was only 1.49(±0.08) during periods identified as being influenced by biomass burning, where $C_{\text{Brown}}$ is expected. Favez et al. (2009) sampled agricultural biomass combustion and rarely saw $AAE>1.5$ in over a week of sampling. Again, these are combustion conditions where contributions from $C_{\text{Brown}}$ are somewhat expected. Gyawali et al. (2009) found that the $AAE_{405\text{nm}}-870\text{nm}$ during a month very strongly impacted by biomass burning fires was above the 1.6 limit ∼75% of the time (60% after accounting for the uncertainty in the measurements). Although differences in particle morphology may contribute to the observed variability in these ambient $AAE$ observations, taken all together this indicates that very few ambient $AAE$ measurements (in the diverse regions studied) are above the 1.6 limit and therefore cannot provide certain $C_{\text{Brown}}$ attribution (at least in the absence of more specific knowledge of the core and shell sizes during the measurement periods). However, at the same time none of these observations can rule out the possibility that $C_{\text{Brown}}$ is a pervasive contributor to sub-micron aerosol light absorption.

Therefore, when attempting to investigate the impact of $C_{\text{Brown}}$ on $AAE$ it is important to consider to some degree the underlying core shape, spherule density, shell diameter, mixing state and SSA before any reliable quantification can be undertaken. The difficulty in simultaneously quantifying these parameters in ambient experiments, particularly core shapes, spherule densities and coating thickness will be a challenging task. Related to this is whether in-situ filter-based methods of measuring absorption appropriately represent $AAE$. Given that $AAE$ is sensitive to both $C_{\text{Clear}}$ and $C_{\text{Brown}}$ coating thickness and that there is some evidence that filter based methods suffer from biases under elevated OC content (Cappa et al., 2008; Kondo et al., 2009; Lack et al., 2008), caution must be applied to these measurement methods and the derived parameters such as $AAE$. It must also be noted here that that the $AAE$ is dependent on the choice of wavelengths (as shown in Fig. 8b). Our discussion above is based on 380 nm and 750 nm radiation, the extreme wavelengths of the visible light spectrum.

4.5.4 Measurement and analysis of ambient $AAE$

As a final consideration, we mention that care must be taken in extracting $AAE$ values from measurements when absorption is measured at more than two wavelengths. In addition to Eq. (2), $AAE$ values have been determined from the linear-fit slope of a log-log plot of absorption vs. wavelength (e.g. Bergstrom et al., 2007). When there are many wavelengths considered (such as from sun photometer measurements), it is likely that the fitting method will give “good” results. However, if absorption is measured at only three wavelengths (as is commonly done from in-situ measurements) the fit results can give both qualitative and quantitatively different results than if wavelength pairs are used (Eq. 2). Take as an example the laboratory measurements of Schnaiter et al. (2005) where the influence of coatings of $\alpha$-pinene + ozone SOA on BC absorption was investigated. Based on the fitting method, they reported that the addition of the SOA coatings led to a decrease in the $AAE$, from 1.13 for uncoated BC to 0.8 for thickly coated BC. In contrast, we estimate (from their Fig. 9) that if the $AAE$ had instead been determined using Eq. (2), it would have been found to increase with the addition of SOA coatings, from ∼0.8 to 1.5 (for 450 nm–550 nm) and from ∼0.9 to 1.2 (for 450 nm – 700 nm). Thus, any discussion of $AAE$’s deduced from measurement must always be considered in the context of the analysis methodology.

5 Summary, conclusions and recommendations

Purely scattering shells on black carbon (BC) cores can significantly enhance the absorption by that core as a result of focusing of light towards the BC core by the shell material (Bond et al., 2006). However, if those shells are mildly absorbing ($C_{\text{Brown}}$) this enhancement ($E_{\text{Abs}}$) can be reduced, with the specific extent of reduction dependent upon the radiation wavelength, imaginary RI ($k_{\text{Brown}}$) and thickness of the shell. Estimates of the absorption strength of $C_{\text{Brown}}$ from the literature are highly variable, likely depending on the $C_{\text{Brown}}$ source and composition; certainly further research is required to fully understand this variability as the overall climate impacts of $C_{\text{Brown}}$ will depend importantly on the exact wavelength dependence of the absorption (e.g. Flores et al., 2009). Nonetheless, using a mid-range estimate for $k_{\text{Brown}}$ we have shown, using core/shell Mie theory calculations, that $E_{\text{Abs}}$ can be reasonably reduced from the clear coating case by up to 50% at 400nm radiation and up to 25–30% averaged across the visible radiation spectrum. This could be a significant reduction of predicted $E_{\text{Abs}}$ depending on the ubiquity of $C_{\text{Brown}}$. The $E_{\text{Abs}}$ reduction is sensitive to both the thickness of the $C_{\text{Brown}}$ shell and the $k_{\text{Brown}}$ but is relatively insensitive to BC core size for a given coating thickness. At the extreme limit of thick $C_{\text{Brown}}$ shells and shorter visible wavelengths, the $C_{\text{Brown}}$ can eliminate $E_{\text{Abs}}$ entirely by completely shielding the BC core from photons.

We have also assessed the importance of considering $C_{\text{Brown}}$ as an internal mixture with BC, as opposed to an external mixture, in terms of the effect on the particle single scatter albedo (SSA), and ultimately the direct radiative forcing. Large differences in the calculated SSA between the internal and external mixtures are only found when large BC cores are used. When small BC cores are used (or if it is assumed that the larger particles are actually aggregates of small individual spherules) the SSA differences are found to be minor (∆SSA<0.03). However, compared to the clear coating case, the potential mis-representation of the radiative forcing by not including the absorption enhancement effect

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