On the Attribution of Black and Brown Carbon Light Absorption using the Ångström Exponent

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We would like to thank the reviewers for highlighting some issues with our manuscript, which obviously fell short in its ability to share what we believe to be important messages.

Prior to addressing each of the reviewer's concerns we would like to highlight a couple of important points:

1) The Angstrom method for attribution of various absorbers is a theoretical method that utilizes some assumptions regarding the magnitude of Angstrom exponents for given aerosol components. These assumptions are based on theoretically-calculated and measured Angstrom exponents for BC, and/or internally mixed BC. Section 2 provides a summary of the Angstrom method and an uncertainty analysis for its application to systems that do not include dust. We recognize that these sections require improved writing and discussion.

2) The exclusion of dust in this discussion was done for a number of reasons:
   a) Measurements included in our case study did not include dust and thus we have no experimental data with which to evaluate errors associated with the attribution of dust absorption using the AAE-method. This study is the first of its kind and uses what is, to our knowledge, the first aerosol absorption dataset that is comprehensive enough in nature to enable it. That our measurements do not include dust is unfortunate, but this does not detract from the important message that we are able to present.
   b) BC, BrC and other non-absorbing particulates are more commonly co-emitted (fossil fuel combustion, biomass combustion), and so limiting the scope to this type of system is deemed an appropriate step.
   c) The theoretical discussion of the AAE method would be complicated by inclusion of dust. Given that our analysis does not include dust, this would have over complicated this introductory section.

3) The final section of the paper attempts to provide a case study to compare the theoretical attribution method to a system where the absorption by BC, internal mixing and BrC was quantified independently of the Angstrom attribution method. We did a poor job of highlighting the fact that there are extremely limited data sets where the contribution of absorption by BC and all other absorbers are known. The reviewers have

asked us to include other case studies, however this is simply not possible as these data sets do not exist.
To elaborate, the criteria required to perform this analysis are:

- Unambiguous attribution of component absorption without using the Angstrom attribution method. To our knowledge the dataset in this paper is amongst the first fulfilling this criteria.
- Sufficiently accurate and bias free instrumentation to provide 'ground truth' data
- Sufficiently high signal to noise so that uncertainties are limited by instrument accuracy and not sensitivity.
- Appropriate combination of absorbers,

The data set we used in this case study is new and unique and is included because it achieves most of the above criteria. To report on case studies where a system has just BC and internal mixing absorption, or just BC and BrC absorption, or just BC and dust would require datasets that do not currently exist.

For these reasons, we cannot expand the manuscript as the reviewers suggest. The current manuscript is unique, and worthy of publication, in our view because the case study we present is in fact available to be presented. This combined with the theoretical discussion makes for the most detail we can provide at this stage. If the reviewers disagree then we would appreciate more detail on how the requested case studies that match the required criteria could be found elsewhere.

Reviewer 1:

The paper really does not treat dust, and that is acceptable to limit the scope.

We have added text at the end of section 1 to explain further why we have limited the analysis to dust.

In this paper we provide a theoretical discussion on the method of using the AAE to separate absorption of BC and BrC (section 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 (section 3). Dust is excluded from the following discussions for two reasons. The first is to provide clarity in the theoretical description of the method. Second it that common physical and optical in-situ particle measurements, such as size distributions, angstrom exponent of

scattering, > 1um particle mass, or modeled back trajectories are often used to exclude the presence of dust which is the case for the study presented.

"Given that the primary interest is in determining the MAE of BrC..." which does not agree with my understanding of the goal.
We have reworded this section to be explicit that it is the absorption by BrC that is desired over absorption by BrC and internal mixing combined.

"Given that the primary interest is in determining the absorption contribution of just BrC. …"

We have also reworded the text to explain why the focus is on the absorption by BrC.

A useful contribution would be providing an understanding of the magnitude of the attribution uncertainty.
Figure 2a provides the theoretical uncertainty in the method when attributing BC absorption.
We have added a figure (Figure 2b) that shows the uncertainty in BrC attributed absorption depending on the contribution on of BrC to total absorption.

Instead the reader gets the impression that these values of aAbs are equally possible.
Section 2 reports the experimental and theoretical studies that are used to show the extremes in Angstrom and the more reasonable values. The more reasonable values for BC and BC_{Int} are provided in the text, and Figure 2a.

For example two theoretical studies are described with range of aAbs of 1-1.7. What conditions caused the range?
The following updated text is included.

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).

Can the value be constrained, especially for the experimental data reported in this paper?
A value of 1.2 is a constrained value and was calculated from the data presented in the Lack PNAS study. This AAE is used as a constrained value for BCInt for this case study. This is discussed at the end of section 4.

If the attribution can be improved with some additional measurements, what should they be?

We have added the following to the end of section 2:

For this theoretical method to be improved measurements of the AAE of just BC_{Ext}, via a coating denuding step, would help to reduce the uncertainty in applied AAE. However the attributed non-BC absorption would then include enhanced absorption by internal mixing. Careful estimation of the AAE of BC_{Int} is therefore needed, which can only be achieved by knowing the dimensions and optical properties of the BC core and coating.

Value of aAbs=0.55 from one study is also treated as equally possible under all conditions. Is it plausible?

This value is included because it is used in a peer-reviewed paper. We do not think it is likely but because it has been used in other studies we feel it should be included. The analysis in section 5 shows that the AAE of 0.55 does not produce reasonable results. We have added the following to section 2:

Analysis of a range of atmospheric measurements of AAE for aerosol sourced from fresh fossil fuel, and regional urban pollution (where the dominant absorber was BC) show an average AAE (467nm and 660nm) of 1.1 ± 0.3 (1σ) (Lack et al., 2008;Clarke et al., 2007;Virkkula et al., 2005;Rosen et al., 1978;Bergstrom et al., 2007;Bergstrom et al., 2002;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 as extreme boundaries only.

What is the calculation in Fig 3b? How is the "internal mixing lensing effect" removed?

We have added a description of this in section 4.

"The removal of the effects of internal mixing were performed in the study of Lack et al. (2012b). It was assumed that all particles, and the BC core were spherical. Studies of particles from inefficient combustion such as biomass burning (Alexander et al., 2008;Chakrabarty et al., 2010;Lewis et al., 2008a), comparisons of spherical and fractal optical modeling (Chakrabarty et al., 2007), and presence of large amounts of organic coating material in this case study suggest that this assumption is reasonable. Next, measured size distributions of the BC core, and the BC core and coating were modeled with Mie theory at a wavelength containing only absorption by BC and enhanced absorption by BC coatings, from which the mass of non-BC material internally mixed with BC was determined. This allowed for Mie modeling of the contribution of enhanced absorption by coatings at 404 nm, and the separation of absorption between BC, internally mixed BC and BrC. Uncertainties on the calculated $MAE_{BB\text{-}BrC}$ did not exceed 15%."

Is the internal mixing lensing effect included in Fig 3a?
Yes. The following text was included in section 5:
"The first MAE value (MAE_{Obs}) was calculated using Equation 2 and includes contributions from both internal mixing effects and BrC absorption. A histogram of MAE_{Obs} at 404nm is shown in Figure 3a"

The reasoning in the discussion of this figure is roundabout. Just say which values have greater physical evidence to support them and which theoretical models they agree with best. Perhaps a scatterplot would be better for comparing paired values and could replace Figs 3 and 4.
We have rewritten this section, deleted the last figure and included a table of the mass absorption efficiencies. We feel that this has simplified the discussion a lot.

Also, isn't there an estimate of MAE for BC– used in the calculation of observed values? How does this compare with inferred MAE for BC?
No. The observed values of MAE use non-BC mass particle mass derived from an aerosol mass spectrometer and absorption from the PAS. This was indicated in equation 2.

Authors imply that any two wavelengths will suffice for this method. Certainly one must make some choice of a wavelength where only BC absorbs.
We state in section 2:
"Absorption at the longer wavelength is assumed to be due only to dry BC_{Ext}, or dry BC_{Int}."

Page 15496. Line 19. "Additional absorption. . . was added. . . also assuming aAbs=1". Doesn't this contradict authors' earlier statements that coating could change aAbs– perhaps they should use Mie theory to predict this? Then "additional absorption due to BrC was represented..." It seems that authors are describing the construction of an absorption spectrum– NOT illustrating absorption decomposition. Later they go to the decomposition, but this is less clearly explained.

We have substantially re-written this section, and re-configured the figure to make this clearer.
"Figure 1 shows an illustration of this method from 658nm to 404nm (to simulate the wavelengths used in sections 4 and 5). The figure was constructed by arbitrarily setting the absorption level of BC_{Ext} to 1 at 658nm and assuming an AAE of 1 for BC_{Ext} (line 1-2). Absorption 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 absorption at 658nm. Studies that utilize this attribution method would commonly have absorption measurements at points 3 and 5, and extrapolate absorption to point 4."

Page 15496. Line 22. "Other more complex multi-wavelength methods..." Please describe some of them briefly. A reader might wonder if the method described here (whose uncertainties are pointed out) is sufficient, and might benefit from learning about the other tricks.

We have expanded this discussion to indicate the required measurements for the more complex methods, in addition to the advantages and disadvantages:

Other 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 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 integrate spherical particle, and various mixing rule assumptions, radiation models and complex Mie modeling retrieval models to produce separation of particle types (fine vs coarse mode), multi-spectral particle refractive index (RI), SSA and absorption. Despite the complexities of these methods some of them (Arola et al., 2011;Kaufman et al., 2002;Schuster et al., 2005) still utilize assumptions of AAE for BC to achieve the results. The advantages of these methods are their expansive satellite coverage, diverse sample regions via aircraft sampling and wide wavelength coverage. However the associated measurements and assumptions used in the retrievals can still lead to significant uncertainty in derived products (Li et al., 2009).

Page 15499. Line 10. "to achieve an uncertainty..." Most analyses are not trying to achieve large values of uncertainty. Why not say what the uncertainty is for different relative values of BrC. This could be a useful figure.

We have taken the reviewers suggestion and produced a figure (Figure 2b) that shows the uncertainty in attributed absorption as a function of the relative contribution of BrC to total absorption. We have also re-worded parts of this section to remove the inappropriate language.

Page 15500. Line 4. "The actual MAE..." A calculation is not an actual MAE, but an inferred or calculated one. Are particles assumed to be spherical? How does that assumption affect the calculations?

We have removed 'actual' from the text. Particles were assumed to be spherical, and the discussion in Lack etal. 2012b discuss the uncertainty associated with this assumption. We have added text to section 4 to describe in a little more detail how the MAE of BrC was calculated.

The removal of the effects of internal mixing were performed in the study of Lack et al. (2012b). It was assumed that all particles, and the BC core were spherical. Studies of particles from inefficient combustion such as biomass burning (Alexander et al.,

2008;Chakrabarty et al., 2010;Lewis et al., 2008a), comparisons of spherical and fractal optical modeling (Chakrabarty et al., 2007), and presence of large amounts of organic coating material in this case study suggest that this assumption is reasonable. Next, measured size distributions of the BC core, and the BC core and coating were modeled with Mie theory at a wavelength containing only absorption by BC and enhanced absorption by BC coatings, from which the mass of non-BC material internally mixed with BC was determined. This allowed for Mie modeling of the contribution of enhanced absorption by coatings at 404 nm, and the separation of absorption between BC, internally mixed BC and BrC. Uncertainties on the calculated $MAE_{BB\text{-}BrC}$ did not exceed 15%.

Page 15501. Line 16. "...is likely an indication of a fundamental methodological problem with the aABS approach." Overstated. It probably just means that aAbs isn't that high (>1).

Agreed. We have changed that text:

"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 for some parts of the time series studied."

Terminology:

- We have chosen to use AAE instead of the symbol we first used.
- MAE: "MAE" is used exclusively to refer to the MAE of brown carbon, except for one use of MAE for brown carbon plus absorption by internal mixing (which we have clarified in the text). We do not understand how confusion with MAE of BC could arise. The use of "MAE" without a subscript is done when talking generally about the MAE of BrC, while subscripted MAE terms are used when they refer to specific MAEs measured or calculated using different methods. We now use $MAE_{BCInt+BrC}$ instead of MAE_{Obs} and MAE_{BrC} instead of $MAE_{BB\text{-}BrC}$
- We have chosen to describe externally mixed BC absorption at BC_{Ext}.
- We have changed $m_{nr\text{-}pm}$ to $m_{non\text{-}BC}$.

Reviewer 2:

The weaknesses however are that this paper does not consider dust as a significant absorbing quantity,

In addition to the comments in the introduction of this reply, we have added text at the end of section 1 to explain further why we have limited the analysis to dust.

"In this paper we provide a theoretical discussion on the method of using the $å_{Abs}$ to separate absorption by different particle absorbers (section 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 (section 3). Dust is excluded from the following discussions for two reasons. The first is to provide clarity in the theoretical description of the method. This is supported by the fact that common physical and optical in-situ particle measurements, such as size distributions, angstrom exponent of scattering, >1um particle mass, or modeled back trajectories can usually provide an indicator of the presence of dust and can therefore exclude dust events if necessary. Second, there is minimal (if any) contribution of dust to the case study."

and considers absorption at only two wavelengths – thereby ignoring the wavelength dependence of the Absorption exponent itself.

We agree with the reviewer that the AAE is not a likely accurate model for BrC or dust, however, the Angstrom exponent model has been shown to be acceptable for BC (as a broadband absorber. If more complicated attributions were to be performed, say by assuming AAEs for BrC or Dust then the errors the reviewer refers to would be of concern. In addition, we are presenting a method that has been, and continues to be used by many others, not us. The purpose of the paper is to highlight the uncertainties in that method.

I also find the use of a single forest-fire type event to be insufficient here – at the very least the authors need to also consider the converse case – an event without significant brown carbon absorption.

See out discussion in the introduction of this response.

In my opinion to merit publication, the Authors need to expand the scope of their paper significantly – perhaps either by performing a comparative analysis of brown and black carbon attribution obtained by using already published methodologies,
We have expanded our discussion on the more complex methods for attribution. Some of these methods, although more complex, use the same AAE assumptions as the simple methods discussed in the paper. We must point out that we were able to find 17 studies that used the basic concepts of the method we describe and as such this paper provides a focused discussion for this body of work to be evaluated. While we have added an expanded review of the more complex methods, we are unable to provide any comparative analysis to these methods because of the complex measurements needed

for those methods. We do no measure multi-spectral optical depth, actinic flux or backscattering.

We do not mean to sound dismissive of the reviewer comments on this point however we just do not see any way that we can expand the manuscript as suggested. We simply do not have the datasets to do so. Given that these datasets are not prevalent, we feel it is important to publish the first attempt at such comparisons and warn the community of the uncertainties associated with these methods.

or by including a few other case studies pertaining to scenarios not considered here.
See response above.

The paper suffers from containing a large number of acronyms and values in the text and thus is not reader-friendly. The authors may want to consider moving this information and presenting it in tabular format – for example the information on pages 15501 and 15502.

We have moved a lot of the quantitative information to a table, and deleted one figure. We have also attempted to clarify and simplify the acronyms. Unfortunately in some manuscripts it is necessary to simplify the text using acronyms.

As far as I could tell, the authors acknowledge that particle size does influence optical extinction but do not examine the effect on attribution, relying solely on absorption. As recent papers (Russell et al 2010, Bahadur et al 2012, and Cazorla et al 2013) utilize both the absorption and scattering components of extinction, the authors could perhaps examine that element in their included case study.

Although the combination of AAE and SAE can separate out the likely occurrence of different absorbers, the attribution of absorption itself still requires assumption of an AAE for each absorbing quantity. The study of Bahadur is unique in that they extract AAEs for various absorbers from their measurements, however they still must assume that these AAEs are correct and they still require propagation of the uncertainty of those AAEs through to achieve appropriate uncertainties. The methods employed by these studies, still contain the associated uncertainty described in this paper. We have data for the extinction Angstrom exponent however there is no value to applying it here because our dataset does not have periods where BC or BrC is the only absorber. Therefore extraction of AAEs specific to each absorber is not possible, as in the study of bahadur.