We thank the reviewers for their constructive comments and have made changes, where deemed appropriate. Specific responses to each of the comments are provided below (reviewers' comments in black and our responses in red).

Anonymous Reviewer #2:

General comments:

Liu et al. (2015) present aircraft measurements of light-absorbing carbonaceous aerosols, specifically black carbon (BC) and brown carbon (BrC). Through a combination of online optical and speciation measurements and offline spectrophotometric absorption measurements of extracts, they attempt to deduce the relative contribution of BC and BrC to atmospheric light absorption. They then use the results in a radiative transfer model to calculate the radiative effect. The measurements are interesting and timely, and seem to be of high quality. However, there are a few major issues that need to be addressed before the paper is suitable for publication in ACP.

Major comment 1:

The conversion of spectrophotometric absorbance measurements to aerosol "absorption coefficients" needs to be done more rigorously. Also, the method and terminology are poorly described.

1.1. It is not clear in the paper how the authors convert the bulk absorbance measurements to aerosol absorption coefficients. I had to go to their previous work (Liu et al., 2013) to get an idea. This needs to be described again, maybe in the SI, or at least a direct reference should be provided. Since they use data from both bulk and aerosol measurements, the authors need to be very clear on what they mean by "absorption coefficient" because in the former it's an intensive property related to the imaginary part of the refractive index and in the latter it's an extensive property (the total aerosol absorption cross-section per unit volume of air) – both having dimension L-1. Without referring to the earlier work (Liu et al., 2013), one could get the impression that the authors confuse the two "absorption coefficient" definitions in their analysis. Incidentally, in their nomenclature (Table 1) they express the units as (M/m), which I assume should be 1/Mm (1/mega-meters).

We agree with the reviewer that consistent and clear nomenclature is important to avoid confusion on this point. Hence, we use "absorption coefficient" only to describe the light absorption by BC and ambient aerosol throughout the paper. For BrC, we've used "solution absorption", "soluble absorption", "extracted absorption", or "absorption from extracts" to describe the light absorption determined from the bulk solution measurements, and "BrC aerosol light absorption" to describe the light absorption by ambient BrC aerosols, for clarification. Table 1 summarizes the nomenclature used throughout the paper, which is also consistent with previous publications using liquid-based methods.

Note that the conversion from solution bulk absorbance measurements to aerosol light absorption coefficients have been described in section 3.6.1 (Pg 5975), and the Liu et al. (2013) paper is also referred. This section also includes a discussion on the similarity of OA size distributions from the two studies. Furthermore, we discussed the similar conversion factors (~2) obtained by a different study and cite the paper (Washenfelder et al., 2015).

The expression of unit (M/m) has been changed to Mm^{-1} in the text.

References:

Washenfelder, R. A., et al. (2015). "Biomass burning dominates brown carbon absorption in the rural southeastern United States." Geophysical Research Letters 42(2): 2014GL062444.

1.2. How are the aerosol mass concentrations obtained for calculation of H2O_Abs and TOT_Abs?

The H2O_Abs and TOT_Abs were not calculated based on aerosol mass concentrations. As described in the method part (section 2.2), the solution absorption was measured from aerosol filter extracts, using a UV-Vis spectrophotometer, following the method in Hecobian et al. (2010). The equation from Hecobian et al. (2010) is:

$$Abs_{\lambda} = (A_{\lambda} - A_{700}) \frac{V_l \cdot l}{V_a} \cdot \ln(10)$$

Where V_l is the volume of solution the filter was extracted into (15 mL in this study, either water or methanol), V_a is the volume of sample air that passed through the filter, l is the absorbing path length, and A_{λ} the absorbance from UV-Vis spectra.

1.3. Using a single conversion factor of 2 for all data points is not convincing. Ideally, the authors could explicitly calculate the conversion factor for each data point using Mie theory based on the measured size distribution. They need to at least quantify the uncertainty associated with the constant conversation factor and/or show that their conclusions hold in light of this uncertainty. The Mie calculations shown in Figure 1 below suggest that this uncertainty is rather larger. The conversion factor (MAC / [alpha/rho]) calculated at 365 nm varies considerably with particle size and the imaginary part of the refractive index (k).

The reviewer makes a good point. Ideally, Mie theory should be applied with size-resolved data, but for this specific campaign we only have size distribution data of organic aerosol mass determined by AMS, whereas the light absorption was measured from bulk filter samples and was not size-resolved.

The use of a single conversion factor is based on measurements of BrC size distributions at a number of ground-based sites (rural, urban, road-side) (Liu et al., 2013). In that paper we reported that although the size distribution of OA varied (mass median diameters ranged from 0.37 to 0.72 µm between sites) the distribution of BrC was stable (mass median diameters ranged from 0.49 to 0.54 for methanol extracts, with similar results for water extracts). In the paper, we also discussed the similarity of aerosol size distribution in this study and the study in the paper mentioned above, to explain why we can use this conversion factor of 2 to estimate BrC aerosol light absorption. We've also cited the uncertainty of 30% for this conversion factor (Page 5976, lines 1-2), determined in Liu et al. (2013) paper.

In response to this comment, although a "real" Mie theory application onto each data point was not available due to lack of size-resolved information, we instead assume that BrC is evenly distributed among all OA, and estimated the light absorption by applying Mie theory to retrieved refractive indices and measured OA size distributions (detailed method described in Washenfelder et al., 2015). The conversion factor is 2.08±0.14, similar to the conversion factor of 2 cited from Liu et al. (2013).

1.4. The authors acknowledge the uncertainty associated with their mixing state assumption (they assume BrC and BC are externally mixed), but they can do more to quantify the uncertainty. They can perform calculations (at least for some of the data points) using the internally mixed assumption and account for absorption enhancement by lensing as a bounding case. The core-shell sizes can be assumed based on OA/BC ratios obtained from AMS/SP2 measurements. This can be done either explicitly using Mie theory, or the approximation given by Bond et al. (2006).

In response to this point, a Mie theory calculation using the internally mixed assumption was made. Core-shell sizes were estimated based on OA/BC ratios. BC core refractive index was set at 1.95-0.79i, from Bond et al. (2013). OA shell refractive index was set at 1.55-0.00156i at 365 nm, in which 1.55 was from literature (e.g., Bond and Bergstrom, 2006; McMeeking et al., 2005), and the imaginary part was determined from bulk measurements of BrC absorption at 365 nm and OA mass concentration measured by AMS using the equation below, following the method in Liu et al. (2013),

$$k = \frac{\rho \cdot \lambda \cdot MAC(\lambda)}{4\pi} = \frac{\rho \cdot \lambda \cdot Total\_Abs(\lambda)}{4\pi \cdot OM}$$

Based on the assumptions mentioned above, the light absorption estimated for the core-shell is 3.3 times of that by the BC core only, and will be 2.44 times of the aerosol light absorption estimated by PSAP. In this case, we believe the external mixing assumption provides a more reasonable closure on light absorption. We have added one paragraph to the main text discussing the assessment of internal-mixing assumption.

References:

Bond, T. C., et al. (2013). "Bounding the role of black carbon in the climate system: A scientific assessment." Journal of Geophysical Research: Atmospheres 118(11): 5380-5552.

Bond, T. C. and R. W. Bergstrom (2006). "Light Absorption by Carbonaceous Particles: An Investigative Review." Aerosol Science and Technology 40(1): 27-67.

McMeeking, G. R., et al. (2005). "Observations of smoke-influenced aerosol during the Yosemite Aerosol Characterization Study: 2. Aerosol scattering and absorbing properties." Journal of Geophysical Research: Atmospheres 110(D18).

Major comment 2:

The discussion of the spectrophotometric absorbance measurements is not adequate. The authors discard the data at wavelengths longer than 450 nm, where Figure 4 shows absorbance leveling out. The authors attribute this to the "chemical nature of the chromophores" which I take to mean that there exist chromophores that absorb significantly at wavelengths longer than 450 nm. If this is true, then the data should not be discarded! When they calculate AAE values based on data at wavelengths smaller than 450 nm, then they use this AAE to extrapolate to longer wavelengths, this would introduce major bias.

The authors need to think more about the shape of absorbance curves in Figure 4 and how to interpret the measured absorption at wavelengths > 450 nm.

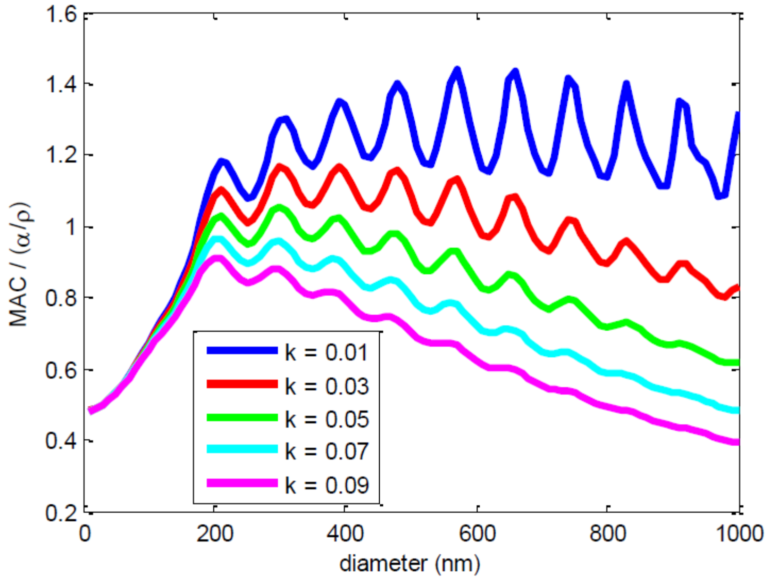


Figure 1: conversion factor as a function of particle size and for different imaginary part of the refractive index (k) values.

The reviewer may have confused AAE from PSAP with BrC AAE determined from the spectra (shown in figure 4). For BrC, we estimated AAE in wavelength range of 300-450 nm, based on the measured spectra as shown in Figure 4. Whole spectra (200-800 nm) of BrC were available for all data points so we did not extrapolate the BrC absorption to longer wavelengths when performing the radiative transfer analysis, so no error is introduced due to poor AAE fitting of data. We just did not include higher wavelengths in BrC AAE since the power law fit would have been poor. For PSAP, we did use the AAE to extrapolate light absorption to longer wavelengths, while the PSAP AAE has been determined based on measurements at 470 and 660 nm, the smallest and longest wavelength PSAP covered.

In the description of radiative forcing model inputs, we did incorrectly state that all absorption and scattering values were extrapolated throughout the 300-700 nm, which was not accurate. The text has been modified, from:

“BrC was based on the AAEs from the total (water + methanol) solution data”,

to

“BrC was determined based on the whole measured spectra of total (water+methanol) solution data”.

Major comment 3:

The radiative transfer calculations.

3.1. The authors state that they include scattering aerosols. What types, and how were their concentrations and vertical profiles obtained? The same for gases.

The ambient aerosol and gas light scattering was measured by nephelometer on board, with the measurement and the extrapolation of scattering coefficient at different wavelengths described in the method part (section 2.3.2).

The SBDART model was run assuming an atmospheric profile for a standard mid-latitude summer (described in Page 5982, line 19), with default parameters (including gases) already incorporated into the model.

3.2. Also, they do the calculations with and without BrC and find that BrC reduces the overall cooling by 20% (from -24.84 to -19.33). A couple of points: 1) is that the overall effect of BrC or is it the effect of "brownness"? In other words, when they do the calculations without BrC do they take the OA out or keep it but assuming it's non-absorbing? 2) This 20% is only meaningful when compared to the BC effect. What is the difference in cooling with and without BC? If it is much larger than the 20% effect of BrC (which still needs to be better defined), then the BrC effect cannot be considered significant.

1) This is the effect of "brownness", or say the absorption by BrC. Page 5982, Lines 11-13 state: "The scattering is based on measurements and independent of the light absorption used (i.e., just BC or BC plus BrC)." Thus the radiative transfer model always includes aerosol scattering, only the light absorption parameter is changed. Therefore "BC" and "BC+BrC" in the discussion of radiative forcing are descriptions of light absorption parameters used in SBDART. To minimize confusion, we have changed "the effect of BrC" to "the effect of BrC absorption" in relevant places (e.g., Pg 5985, line 28).

2) The 20% effect is determined by comparing to the effect of only BC. Take SZA of 40° and vegetation surface as an example (Page 5983, lines 3-5), the difference in cooling with and without BC is -24.84 W m^{-2}, and for absorbing aerosols including both BC and BrC the instantaneous forcing is -19.33 W m^{-2}. We have also stated in Page 5983, Lines 9-10 that "BrC absorption appreciably changes the TOA forcing relative to BC only, resulting in roughly 20% less cooling compared to only BC." Since BC forcing is ranked the third most important anthropogenic climate warming agent, 20% of BC effect would not be considered as negligible.

3.3. The aerosol radiative effect numbers (-20'ish W/m2) seem to have a very large magnitude, at least compared to the global average aerosol DRF in say the IPCC report (close to -0.5 W/m2). How do the authors' numbers compare to other studies that calculate regional aerosol DRF over the US?

Several studies have suggested that the direct aerosol radiative forcing estimated from one specific study might be one or even two orders of magnitude higher than values suggested for global mean aerosols by IPCC report (e.g., Xu et al., 2003; Bates et al., 2006), which might be due to (1) the difference in what is included in the mean, e.g., between daily and annual means, measurements at one latitude vs planetary average, etc., and (2) large variety of aerosol optical properties and abundance at different locations, especially the land-ocean difference. Specifically for this work, our radiative effect numbers might be enhanced due to biomass burning impacts, as discussed in the paper. The inherent property, radiative forcing efficiency (DRE), defined as DRF/AOD, is more appropriate for the assessment of DRF.

Furthermore, the DRE values are 88.64 W m^{-2} for BC. The value falls within the ranges reported in the literature, i.e., 22-216 W m^{-2} for BC (Chung et al., 2012; Wang et al., 2014; Yu et al., 2013). Meanwhile, DRE values of organic aerosols have been reported in a range of -5 to -38 W m^{-2} (Yu et al., 2013), while our estimation at -20 W m^{-2} also agrees with literature data. Therefore, we believe our assessment of aerosol DRF originated from this specific study is reasonable.

References

Xu, J., et al. (2003). "Direct aerosol radiative forcing in the Yangtze delta region of China: Observation and model estimation." Journal of Geophysical Research: Atmospheres 108(D2)

Bates, T. S., et al. (2006). "Aerosol direct radiative effects over the northwest Atlantic, northwest Pacific, and North Indian Oceans: estimates based on in-situ chemical and optical measurements and chemical transport modeling." Atmos. Chem. Phys., 6, 1657-1732, doi:10.5194/acp-6-1657-2006, 2006.

Wang, Q., et al. (2014). "Global budget and radiative forcing of black carbon aerosol: Constraints from pole-to-pole (HIPPO) observations across the Pacific." Journal of Geophysical Research: Atmospheres 119(1): 195-206.

Chung, C. E., et al. (2012). "Observationally constrained estimates of carbonaceous aerosol radiative forcing." Proceedings of the National Academy of Sciences 109(29): 11624-11629.

Yu, H., et al. (2013). "A multimodel assessment of the influence of regional anthropogenic emission reductions on aerosol direct radiative forcing and the role of intercontinental transport." Journal of Geophysical Research: Atmospheres 118(2): 700-720.

3.4. The chart to extrapolate surface measurements to TOA effect of BrC is not well-supported. The authors need to provide evidence/arguments that the vertical profile measurements done in this study (thus the chart) can be generalized.

Lack of direct measurement of BrC vertical profile from previous studies is definitely a limitation to an accurate assessment of the role of BrC radiative forcing, which we have carefully stated and have suggested that direct in-situ measurements of BrC vertical profiles are needed in our main text (page 5986, lines 3-5). Meanwhile, the look-up chart was provided to make a full use of our highly unique observational data, with this limitation clearly stated. Some field campaigns have measured the vertical profiles of BC (e.g., Rahul et al., 2014; Samset and Myhre, 2011; Tripathi et al., 2005; Hodnebrog et al., 2014). The trend that BC decreases with altitude, similar to our observations, was observed in various environments including both urban atmosphere and aerosol from biomass burning plumes. While few studies have investigated and directly compared the vertical distribution of various light-absorbing components, including BC and BrC, Park et al. (2010) has suggested that the relative ratio of BrC to BC increases with altitude, by comparing GEOS-Chem model simulations with a set of input and observations from TRACE-P campaign. This conclusion is consistent with our direct measurement of in-situ BrC and BC vertical distributions, and supports that our chart on BrC radiative forcing could provide a generalized estimation based on surface measurements.

References:

Rahul, P. R. C., et al. (2014). "Double blanket effect caused by two layers of black carbon aerosols escalates warming in the Brahmaputra River Valley." Sci. Rep. ***4****.*

Samset, B. H. and G. Myhre (2011). "Vertical dependence of black carbon, sulphate and biomass burning aerosol radiative forcing." Geophysical Research Letters ***38****(24).*

Tripathi, S. N., et al. (2005). "Enhanced layer of black carbon in a north Indian industrial city." Geophysical Research Letters ***32****(12).*

Hodnebrog, Ø., et al. (2014). "How shorter black carbon lifetime alters its climate effect." Nat Commun ***5****.*

Park, R. J., et al. (2010). "A contribution of brown carbon aerosol to the aerosol light absorption and its radiative forcing in East Asia." Atmospheric Environment ***44****(11): 1414-1421.*

Minor comments

1) The authors state uncertainty bounds in measurements at several points in the manuscript without mentioning how these were estimated (e.g. p. 5965 line 21 and line 28, and many other places..)

For the measurement of WSOC and solution absorptions, we have stated in the text that "Measurement uncertainties are estimated at 20% for H2O_Abs(365) and 9% for WSOC, based on uncertainties and variability in water blanks, field blanks, standards, and duplicate measurements." (page 5965, line 21). For uncertainties related to other measurements, including PSAP bap, SP2 BC, and AMS Org, we have provided references which have detailed description of methods (e.g., page 5966, line 24; page 5967, line 9 and line 11).

2) PSAP measurements: The authors rightly mention that the PSAP is notorious for artifacts, however their statement about uncertainty (20%) is not convincing. The adjustment of data needs to be shown explicitly (maybe in SI) for at least one or more representative cases to show the extent of correction applied. For example, is the correction wavelength-dependent?

The PSAP bap data were corrected using method with details described in Virkkula et al. (2010), which was stated in Page 5966, lines 23-24. As described in the Virkkula paper, the correction is wavelength-dependent. We decline to expand on this in the paper because, as recognized by the reviewer, these issues are well known and fully addressed elsewhere.

Specific comments:

Abstract line 21: "BrC is an important component of.." should be something like "BrC is an important contributor to.."

The text has been changed.

p. 5962 line 6: there are many more studies that have investigated light absorbing OA – add e.g. to the reference list.

The text has been changed.

Paragraph starting p. 5962 line 26: the authors dismiss online optical instruments as a means to quantify BrC absorption, stating mixing with BC as a major issue. It's true that mixing with BC poses difficulties, but there have been attempts to decouple the effects of BC absorption (including enhancement due to internal mixing – lensing) and BrC absorption by integrating measurements with Mie theory calculations (e.g. Lack et al., 2012; Saleh et al., 2014). These methods should be acknowledged. Then they present offline measurements of OA extracts as the better alternative, which can be argued, but is not necessarily the case. These too suffer from issues, the most obvious being extraction efficiency. This should also be acknowledged.

We have modified the text to acknowledge those attempts. And for the offline measurements of extracts, we've added one sentence to discuss the extraction efficiency, as:

"Studies have shown that >85% of the organic aerosols could be extracted by methanol (e.g., Chen and Bond, 2010; Du et al., 2015, in prep.)".

Chen, Y. and T. C. Bond (2010). "Light absorption by organic carbon from wood combustion." Atmospheric Chemistry and Physics 10(4): 1773-1787.

Du et al., (2015), Optical properties of Beijing carbonaceous aerosol by the stepwise-extraction thermal–optical-transmittance (SE-TOT) method, in prep.

p. 5970 line 23: it's not clear how the conclusion that "water-soluble faction in the background troposphere could be more strongly related to primary emissions and possibly linked to aged biomass burning" follows from the data.

The conclusion comes from the stronger correlation between H2O_Abs(365) and acetonitrile, the latter has been considered as an indicator for biomass burning (e.g., de Gouw et al., 2003).

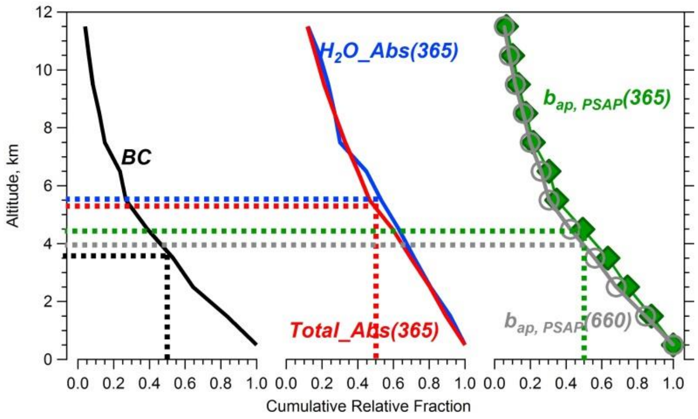
de Gouw, J.A., C. Warneke, D.D. Parrish, J.S. Holloway, M. Trainer, and F.C. Fehsenfeld (2003a), Emission sources and ocean uptake of acetonitrile (CH3CN) in the atmosphere, J. Geophys. Res., 108 (D11), 4329, doi: 10.1029/2002JD002897.

p. 5970 line 26: I don't see a reason to jump to the conclusion that there used to be BrC but got photobleached. The more straightforward conclusion is that there was not much BrC to begin with.

We believe that photobleaching is a very reasonable explanation for our observation of decreasing correlations between BB tracers and BrC absorption. Note that total_Abs(365) is the sum of water-soluble and methanol extractable solution absorption. We have identified water-soluble Abs(365) to be linked with primary emission markers such as BC and acetonitrile. The lack of correlation for total_Abs(365) in background air must be due to some secondary process. Bleaching certainly explains these observations.

p. 5972 line 5-10: the difference between PSAP_abs 365 and 660 50% mark is too small to support the conclusion that the authors make on the relative wavelength dependence of BrC vs BC absorption. In fact, from Figure 3, the 50% mark for 365 is closer to 4.2 km (the authors say 4.5 km in the text).

The plot was not reproduced accurately. If we draw the 50% line of $b_{ap,PSAP}$ *(365)* more carefully (see the plot below), it is 4.5 km, not 4.2 km. And we can also see the difference between $b_{ap,PSAP}$ *(365)* and $b_{ap,PSAP}$ *(660)* vertical profiles.



Reword section 3.5 title: BrC is a component of light absorbing aerosols.

Reword from

Absorption Ångström Exponents for BrC and light absorbing aerosols

to

Absorption Ångström Exponents for BrC and bulk light absorbing aerosols

Reword section 3.6 title: you don't compare BC to BrC, but compare certain properties of the two (mass, absorption, etc.)

Reword from

Light absorption calculations for comparing BrC to BC and PSAP data

to

Light absorption calculations: BrC, BC, and PSAP

p. 5974 line 25: it's not clear how nitrate (you mean inorganic nitrates?) would impact the data.

The inorganic nitrate ion absorbs ultraviolet radiation at 220 nm (i.e., Shaw et al., 2014), so if we choose a wavelength too low, it's hard to distinguish absorption by nitrate ion and organic matter.

Shaw, B. D., et al. (2014). "Analysis of Ion and Dissolved Organic Carbon Interference on Soil Solution Nitrate Concentration Measurements Using Ultraviolet Absorption Spectroscopy." Vadose Zone Journal 13(12).

Reword title of section 3.7: you can't compare to PSAP – it is an instrument not a measured quantity.

Reword from:

Optical importance of BrC relative to BC and a closure assessment by comparison to PSAP

to

Optical importance of BrC relative to BC and a closure assessment by comparison to PSAP absorption