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 #1:

General comments:

This paper shows data of biomass burning aerosols from above the USA, with the optical properties measured using two complementary techniques, optical analysis of liquid filter extracts and in situ PSAP measurements. The authors attempt to achieve closure between these and estimate the instantaneous direct radiative forcing using a radiative transfer model. This is a highly relevant field, as the exact effect that brown carbon (BrC) has on the earth's radiative budget is currently a hot topic of debate, with estimates varying by a large amount. In situ data such as this is vital to constraining models and improving our understanding.

The methods used seem to be both sound and state-of-the-art. The fact that the two techniques were able to agree to such an extent I regard as a highly significant achievement in its own right. The article was well put together and I'm pleased to say that I found it a joy to read. I've only a few comments, but these are of a technical nature and won't affect the conclusions. Other than that, I wholeheartedly recommend publication.

Technical comments:

P5965, L12: 'Fisherbrand' is asterisked but it is not clear why.

The asterisk has been changed to "TM" (superscript), in accordance with the manufacture page.

P5966, L8: What is meant by 'N'?

"N" means the number of samples used in the comparison between methanol extraction and sequential extraction results. The text has been changed from "N=18" to "sample number = 18".

P5967, L12: The AMS uncertainty seems a little high. Is this capturing any collection efficiency uncertainty? How was the collection efficiency estimated anyway? Also, was a pressure-controlled inlet used?

The AMS was operated with a setup similar to that described in Dunlea et al. (2009) and using a pressure-controlled inlet (Bahreini et al., 2008). The AMS collection efficiency was estimated using the composition-dependent formulation of Middlebrook et al. (2011) as implemented in the standard AMS data analysis software (Sueper, 2015, http://cires1.colorado.edu/jimenez-group/wiki/index.php/ToF-AMS_Analysis_Software), and applied with a 1-min time resolution to reduce the effect of high-frequency noise. The AMS uncertainty for OA (2 sigma = 38%) is estimated as described in Bahreini et al. (2009) and Middlebrook et al. (2011) and is dominated by the uncertainty in collection efficiency and relative ionization efficiency of OA.

Refs:

E.J. Dunlea, P.F. DeCarlo, A.C. Aiken, J.R. Kimmel, R.E. Peltier, R.J. Weber, J. Tomlison, D.R. Collins, Y. Shinozuka, C.S. McNaughton, S.G. Howell, A.D. Clarke, L.K. Emmons, E.C. Apel, G.G. Pfister, A. van Donkelaar, R.V. Martin, D.B. Millet, C.L. Heald, and J.L. Jimenez. Evolution of Asian Aerosols during Transpacific Transport in INTEX-B. Atmospheric Chemistry and Physics, 9, 7257-7287, 2009.

R. Bahreini, E.J. Dunlea, B.M. Matthew, C. Simons, K.S. Docherty, P.F. DeCarlo, J.L. Jimenez, C.A. Brock, and A.M. Middlebrook. Design and Operation of a Pressure Controlled Inlet for Airborne Sampling with an Aerodynamic Aerosol Lens. Aerosol Science and Technology, 42: 465–471, 2008.

A.M. Middlebrook, R. Bahreini, J.L. Jimenez, and M.R. Canagaratna. Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer using Field Data. Aerosol Science and Technology, 46, 258–271, DOI:10.1080/02786826.2011.620041, 2011.

R. Bahreini, B. Ervens, A.M. Middlebrook, C. Warneke, J.A. de Gouw, P.F. DeCarlo, J.L. Jimenez, E. Atlas, J. Brioude, C.A. Brock, A. Fried, J.S. Holloway, J. Peischl, D. Richter, T.B. Ryerson, H. Stark, J. Walega, P. Weibring, A.G. Wollny, F.C. Fehsenfeld. Organic Aerosol Formation in Urban and Industrial plumes near Houston and Dallas, TX. Journal of Geophysical Research-Atmospheres 114, D00F16, doi:10.1029/2008JD011493, 2009.

P5977, L6: A recent paper by Liu et al. (doi: 10.1002/2014GL062443) found an even bigger potential range than this by invoking a Rayleigh-Debeye-Gans approximation.

The authors thank the reviewer for this comment, and have modified the text to include the result in this recent-published paper.

P5977, L8: I'm a little confused by this line of discussion. The previous sentences discuss the effect of morphology on AAE, which can cause both negative and positive discrepancies from unity, but then an 'enhancement' is discussed. The main focus of the Cappa et al. (2012) is the enhancement of bulk absorption, not AAE.

The authors thank the reviewer for this comment. The text has been modified for clarification, as below:

More random mixtures, or mixtures containing absorbing material, such as BrC, can significantly alter the range of AAE_{BC} (Lack and Cappa, 2010). Recent ambient data do not show significant enhancement of aerosol light absorption at lower wavelengths that would be indicated by deviation of an AAE_{BC} from 1 (Cappa et al., 2012).

P5985, L13: For consistency with the rest of the text, use '1' rather than 'one'.

The text has been modified.

Table 3: Please be consistent in the unit notations for the denominator; having µg/m3 rather than µg m-3 looks odd next to Mm-1.

The text has been modified.

Figures 8 and 9: I would not denote the 1:1 lines with 'y=x' because y and x do not refer to variables used here. I think '1:1' would suffice.

The annotation in figures 8 and 9 has been changed.

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.

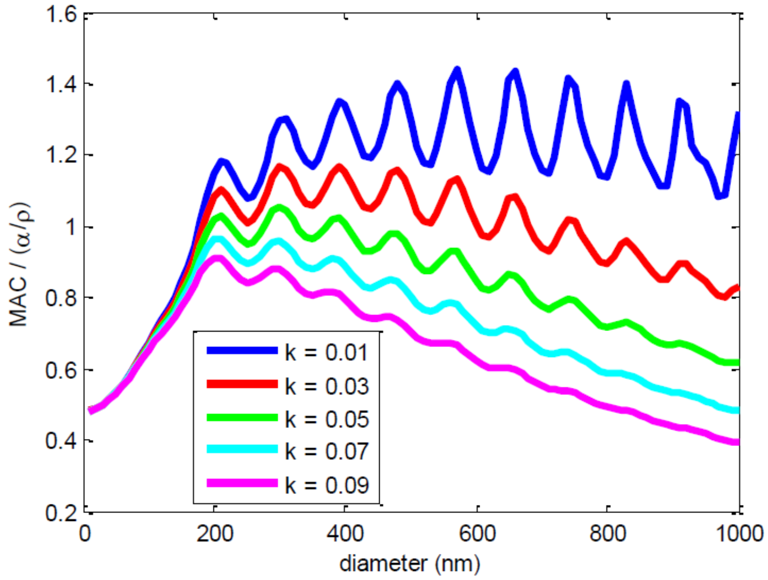


Figure 1: conversion factor as a function of particle size and for different imaginary part of the refractive index (k) values.

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." *<u>Sci. Rep.</u>* ***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).

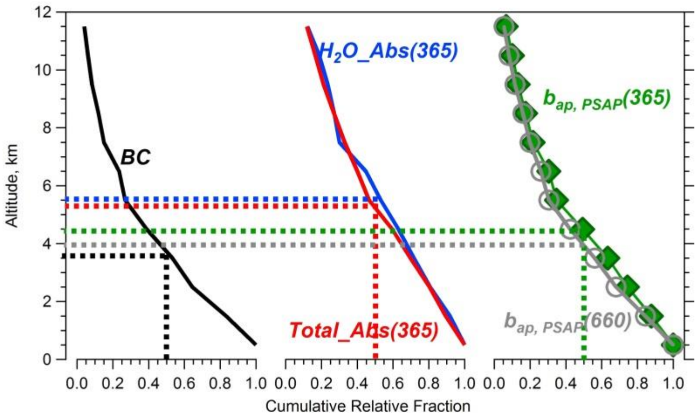
de Gouw, J.A., C. Warneke, D.D. Parrish, J.S. Holloway, M. Trainer, and F.C. Fehsenfeld (2003a), Emission sources and ocean uptake of acetonitrile (CH3CN) in the atmosphere, J. Geophys. Res., 108 (D11), 4329, doi: 10.1029/2002JD002897.

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

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 #3:

General comments:

This well-written manuscript presents results obtained from aircraft measurements on brown carbon (BrC) in aerosol samples collected over central U.S. during a summer period that was impacted by several biomass burning events. Approximately 600 filter samples were collected over a range of altitudes (1 - 12 km) and extracted in water and methanol to measure H2O_Abs(365) and total_Abs(365), where the latter includes absorption data from samples extracted in both water and methanol. This filter extraction procedures are solid and provides a lot of insight into the chemical nature of the BrC constituents. During biomass burning periods, H2O_Abs(365) and total_Abs(365) were highly correlated with other known emissions from biomass burning plumes, including CO, ACN, and BC. Under background conditions, H2O_Abs(365) was somewhat correlated with smoke tracers, but the total_Abs(365) was not well correlated with any specific tracers, but most correlated with WSOC, possibly due to BrC evolving to a more water-insoluble state as it ages. Importantly, these data seemed to be well supported by the online measurements. Further, they estimated the BrC contribution to climate forcing using a radiative transfer model (SBDART). From these model calculations, they find that overall negative TOA aerosol scattering is reduced by ~20% due to BrC presence.

This manuscript is really important to appear in Atmospheric Chemistry and Physics, especially since there has been a lot of interest and uncertainty in BrC formation and its potential abundance in the atmosphere. I tend to agree with the other comments made by the other 2 reviewers and also agree this should be published with minor revisions noted. My main questions below relate to the sources of BrC since that is an area that my group and many others have been interested in. One item I hope that the authors will consider in the future is to have their filters analyzed off-line by mass spectrometric techniques to provide more insights into the potential sources of BrC in both the biomass burning and background conditions. That would make this an even better paper, BUT please note I think is is already a GREAT paper. The molecular-level data would have only made this a "dream" paper. I hope they will consider this in future work if it is possible.

The authors thank the reviewer for insightful comments. We agree that a molecular-level analysis would provide more insights into the chemical nature of BrC constituents, but it is beyond the scope of this paper, which we should definitely consider in future work.

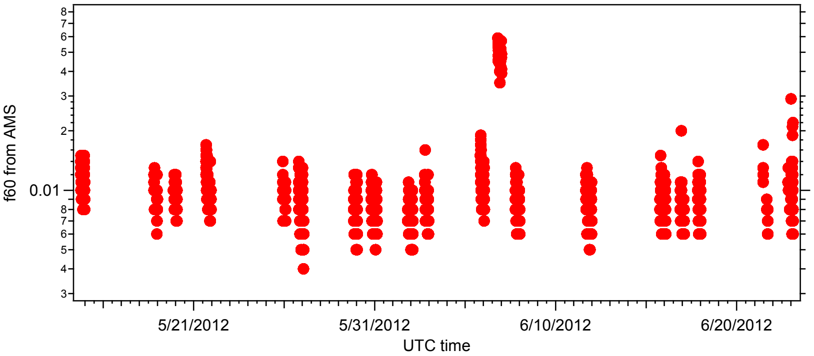
A few minor questions/comments:

1.) In discussing the correlation of Total_Abs(365) data with other datasets, I found it interesting that the authors also didn't consider the possibility of SOA constituents aging to produce BrC that is more soluble in the methanol extracts. For example, Lin et al. (2014, ES&T) showed that IEPOX-derived oligomers that absorb in the BrC region are more soluble in methanol. Further, one could consider aldehydes from

BVOC oxidations yielding BrC oligomers through cloud droplet formations and evaporation, similar to work of DeHaan, McNeill, Turpin, Noziere, and other groups. I'm especially curious to know how BVOCs in this region may play a role in the BrC signals observed in the background air? Could this be important or is what you measure in the background air really just aged biomass burning?

Good point.

First, observational data suggest that the campaign observations are largely impacted by biomass burning. The plot below shows the time series of f60 from AMS, which is an indicator of biomass burning.



From the plot we see, f60 from AMS is around 1% during the whole campaign, while Cubison et al. (2011) has suggested that a level of f60 ~0.3%±0.06 % is an appropriate background level for this tracer. Therefore we consider the BrC signals observed is largely impacted by biomass burning, although the relative contribution is difficult to estimate.

On the other hand, our observation did suggest that aged BrC tends to be more soluble in methanol, and light-absorbing IEPOX-derived oligomers could be a possible explanation. We believe that some fractions of the campaign observations are certainly impacted by IEPOX chemistry, especially the southeastern US where the isoprene emission is rich. However, a recent study showed that at a remote surface site in the southeast significantly impacted by BSOA, biomass burning dominated the source of BrC (Washenfelder et al., 2015), whereas BSOA had no discernible impact. Therefore, we believe aged biomass burning is the main source of the ubiquitous BrC, but that biogenic SOA cannot be ruled out. We have added this discussion into the main text, section 3.3 (Page 5970-5971).

Refs.

Lin, Y.-H., et al. (2014). "Light-Absorbing Oligomer Formation in Secondary Organic Aerosol from Reactive Uptake of Isoprene Epoxydiols." Environmental Science & Technology 48(20): 12012-12021.

Cubison, M. J., Ortega, A. M., Hayes, P. L., Farmer, D. K., Day, D., Lechner, M. J., Brune, W. H., Apel, E., Diskin, G. S., Fisher, J. A., Fuelberg, H. E., Hecobian, A., Knapp, D. J., Mikoviny, T., Riemer, D., Sachse, G. W., Sessions, W., Weber, R. J., Weinheimer, A. J., Wisthaler, A., and Jimenez, J. L.: Effects of aging on organic aerosol from open biomass burning smoke in aircraft and laboratory studies, Atmos. Chem. Phys., 11, 12049-12064, doi:10.5194/acp-11-12049-2011, 2011.

Washenfelder, R. A., et al. (2015), Biomass burning dominates brown carbon absorption in the rural southeastern United States, Geophys. Res. Lett., 42, 653–664, doi:10.1002/2014GL062444.

2.) In addition to Limbeck et al. (2003) study cited in the introduction, I think the authors should also highlight work done by Lin et al. (2014, ES&T) that demonstrated isoprene epoxydiols can yield oligomeric species that can absorb light at short wavelengths, and thus, act as a BrC. Some of these oligomers were identified in SE USA fine aerosol collected at the ground sites.

The reference has been added into text.

Brown Carbon Aerosol in the North American Continental Troposphere: Sources, Abundance, and Radiative Forcing

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For submission to ACP

Keywords: Brown carbon, aerosol absorption, vertical profiles

Abstract

Chemical components of organic aerosol selectively absorb light at short wavelengths. In this study, the prevalence, sources, and optical importance of this so-called brown carbon (BrC) aerosol component are investigated throughout the North American continental tropospheric column during a summer of extensive biomass burning. Spectrophotometric absorption measurements on extracts of bulk aerosol samples collected from an aircraft over the central USA were analyzed to directly quantify BrC abundance. BrC was found to be prevalent throughout the 1 to 12 km altitude measurement range, with dramatic enhancements in biomass burning plumes. BrC to black carbon (BC) ratios, under background tropospheric conditions, increased with altitude, consistent with a corresponding increase in the Absorption Ångström Exponent (AAE) determined from a 3-wavelength Particle Soot Absorption Photometer (PSAP). The sum of inferred BC absorption and measured BrC absorption at 365 nm was within 3% of the measured PSAP absorption for background conditions and 22% for biomass burning. A radiative transfer model showed that BrC absorption reduced top of atmosphere aerosol forcing by ~20% in the background troposphere. Extensive radiative model simulations applying this studies background tropospheric conditions provided a look-up chart for determining radiative forcing efficiencies of BrC as a function of surface-measured BrC-BC ratio and single scattering albedo (SSA). The chart is a first attempt to provide a tool for better assessment of brown carbon's forcing effect when one is limited to only surface data. These results indicate that BrC is an important contributor to direct aerosol radiative forcing.

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1. Background

Carbonaceous components of atmospheric aerosols are known to affect climate through direct scattering and absorption of solar radiation. The most prevalent carbonaceous aerosol component is the organic aerosol fraction (OA), which until recently was assumed to only scatter light and act to cool the climate (*Koch et al*, 2007; *Myhre et al*, 2008). The black carbon (BC) fraction efficiently absorbs light and substantially warms the atmosphere (*Bond et al.,* 2013). Globally, BC forcing is ranked the third most important anthropogenic climate-warming agent after carbon dioxide and methane (*IPCC,* 2013), considering both direct and indirect effects. Recent studies have shown, however, that components of OA also contribute to light absorption (e.g., *Yang, et al.*, 2009; *Zhang et al.*, 2011, 2013) and that their influence on climate may be substantial (*Bahadur et al.*, 2012; *Chung et al.*, 2012; *Feng et al.*, 2013; *Park et al.*, 2010). These compounds are referred to as Brown Carbon (BrC hereafter) because they tend to absorb light most efficiently at short wavelengths.

A variety of studies have investigated the sources for BrC. Primary BrC is known to be emitted directly from incomplete combustion of fossil or biomass fuels (*Hoffer et al.*, 2006; *Lukacs et al.*, 2007; *Andreae and Gelencser,* 2006), and secondary organic aerosol (SOA) formed from combustion emissions may also be brown (*Saleh et al.*, 2013; *Zhang et al.*, 2013). Laboratory studies find that light-absorbing secondary compounds (chromophores) can be formed by a variety of mechanisms, including aromatic-SOA production under high levels of nitrogen oxides (NO_x), and through various aqueous phase reactions, such as lignin (*Hoffer et al.*, 2006) and isoprene oxidation (*Limbeck et al.*, 2003), or form light-absorbing oligomers from reactive uptake of isoprene epoxydiols (*Lin et al.*, 2014). They can also be formed from reactions of carbonyls (e.g., glyoxal, methylglyoxal) in acidic solutions (*Sareen et al.*, 2010), with amino acids (*de Haan et al.*, 2009), methyl amines (*de Haan et al.*, 2009), or ammonium salts (*Sareen et al.*, 2010). Concentrating of solutes during droplet evaporation can also enhance BrC formation (*Zarzana et al.*, 2012). While BrC can be lost by wet and dry deposition, analogous to OA, atmospheric aging of aerosols may also lead to a loss of BrC due to photo-bleaching (*Lee et al.*, 2014; *Zhong et al.*, 2014; *Forrister* et al., 2015).

BrC can be difficult to identify with aerosol optical instruments. *Lack and Langridge* (2013) suggested that the use of an observed wavelength dependence of light absorption, described by the Absorption Ångström Exponents (AAE), to predict BrC absorption leads to substantial uncertainties. Difficulties arise because optical instruments cannot measure BrC independently of BC. Typically, BrC is determined based on differences between the observed absorption at low wavelengths, where BrC absorption is effective, to what is expected from BC alone. Both factors in the difference calculation are uncertain. There have also 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). However, one of the main uncertainties is related to what BC absorption should be, independent of other absorbers. Some studies indicate that BC mixing state with non-absorbing materials can lead to substantial shifts in AAE relative to pure BC (*Lack and Langridge* (2013)), making it difficult to attribute enhanced light absorption at low wavelengths to BC mixing state or BrC, if based solely on AAE.

A more definitive and sensitive approach for identifying BrC is possible by directly measuring chromophores in aerosol solution extracts, since the method can isolate BrC from other absorbers (BC and mineral dust) and long-path absorption cells provide a measurement with high sensitivity. 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.). These direct measurements of BrC show that it is ubiquitous. BrC has been shown to be strongly linked to biomass burning and HUmic-Like Substances (HULIS) throughout Europe (*Lukacs et al.*, 2007). In the southeastern U.S., BrC has been found in rainwater from continental sources (*Kieber et al.*, 2006), while BrC in $PM_{2.5}$ was associated with biomass burning in winter and summer, along with possible contribution from SOA formation (*Hecobian et al.,* 2010; *Zhang et al.,* 2012; *Washenfelder et al.,* 2015).

Chromophores in the ambient aerosol that produce the observed BrC optical properties are not well characterized. *Zhang et al.* (2013) identified a number of water-soluble nitro-aromatic compounds responsible for BrC in Los Angeles SOA, but they only accounted for ~4% of observed BrC absorption at 365nm. 4-nitrocatechol ($C_6H_5NO_4$) was identified as the largest contributor at roughly 1.4%. Similar nitro-aromatic chromophores have been identified in fogs (*Desyaterik et al.*, 2013) and aerosols (*Mohr et al.*, 2013) impacted by biomass burning.

Although studies of BrC based on aerosol extracts have been used to investigate the sources, extent and chemistry of fine particulate BrC, it is difficult to use this method to assess optical properties of BrC-containing particles. To estimate optical properties from solution data, *Liu et al.* (2013) used size-resolved measurements of aerosol extract light absorbance from several sites to estimate light absorption (b_{ap}) by BrC-containing particles, assuming that the BrC was externally mixed with other absorbers. In this study, we apply these results to aircraft-based filter measurements and use the direct measurements of chromophores in solutions to estimate the extent and sources of BrC throughout the U.S. continental troposphere (up to ~12km altitude). A closure analysis is performed comparing the sum of light absorption at 365nm from BC and BrC to measurements extrapolated from a 3-wavelength PSAP, averaged over filter sampling intervals, to assess our method for inferring BC and BrC. The importance of BrC is then determined through a radiative transfer model using altitude-resolved BC and BrC data to delineate absorbing aerosol forcing in the continental troposphere from these two components. Since column measurements are rare, the average background tropospheric vertical profile measured in this study is used to create a chart that allows estimation of BrC top of atmosphere (TOA) forcing based on surface measurements of aerosol optical properties and aerosol optical depth.

2. Method

2.1. NASA DC-8 research aircraft measurements during the DC3 campaign

Filters were collected from the NASA DC-8 research aircraft, based out of Salina, KS, between May and June 2012 as part of the Deep Convective Clouds and Chemistry (DC3) campaign (*Barth et al.*, 2014). The study area focused on the central USA and filter samples were obtained from near-surface to an altitude of roughly 12 km a.s.l. (pressure altitude). Fig. 1a shows the locations of filter sampling periods during the study, color-coded by altitude.

2.2. Filter Sampling, Extraction and Analysis

The filter sampling system captured particles nominally smaller than 4.1 μm aerodynamic diameter (*McNaughton et al.*, 2007) onto 1μm pore, 90mm diameter, Teflon (EMD Millipore) filters. Sampling was generally done during level flight legs with typically 5 min integration times. In total, 609 filter samples were obtained from 22 flights, along with 2 field blanks per flight. Data were corrected by subtraction of the average blank for each flight. Over the course of the study, filters were not uniformly collected over the measurement column. Fig. 1b shows the filter sampling frequency (number of filters collected/total filters) as a function of altitude.

Filters were extracted first in 15 mL of high purity water (18.3 MΩ) by 30 minutes of sonication. The liquid extracts were then filtered via a 25mm-diameter 0.45 µm pore syringe filter (Fisher Scientific, Fisherbrand^{TM} Syringe Filters) to remove insoluble components. Water extracts were transferred into a Liquid Waveguide Capillary Cell coupled to a Total Organic Carbon (LWCC-TOC) analyzer. The combined system quantifies the water-soluble UV-Vis (nominally 200 to 800nm wavelength range) light absorption spectra (referred to here as, *H_2O_Abs (λ)*) and water-soluble organic carbon (WSOC) mass following the method by *Hecobian et al.* (2010). (See Table 1 for a list of acronyms). The limit of detection (LOD) was determined as 3 times the SD of field blanks. At 365 nm the LOD of the solution light absorption measurement (*H_2O_Abs (365)*) was 0.031 Mm^{-1}, whereas the WSOC LOD is estimated at 0.084 µgC m^{-3}. Measurement uncertainties are estimated at 20% for *H_2O_Abs (365)* and 9% for WSOC, based on uncertainties and variability in water blanks, field blanks, standards, and duplicate measurements.

Following water extraction, the extraction vial and filter were drained and dried by inverting, then the filter was re-extracted in 15 mL of methanol (VWR International, A.C.S. Grade) following the same procedure as the water extract, however in this case only the UV-Vis absorption spectra were measured. The estimated LOD for methanol-soluble light absorption at a wavelength of 365nm (*MeOH_Abs (365)*) is 0.11 Mm^{-1} with an uncertainty of 27%. Here, total solution absorption due to BrC (*Total_Abs (λ)*) is determined from the sum of water-soluble and methanol-extracted

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absorption from the sequential extraction process, under the assumption that this process dissolves all chromophores (*Chen and Bond*, 2010) (*Total_Abs (365)* uncertainty is roughly ±34%). Tests with filters loaded with ambient particles from urban Atlanta show that the methanol extraction, by itself, tends to also include most water-soluble compounds and that the sequential extraction is comparable to methanol extraction alone; the sum of light absorption from extractions of water plus methanol in series were within ~10% of just methanol extraction (sample number= 18).

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2.3. Online Measurements

2.3.1 Gases

A number of gases were used in this study as emissions tracers. Biomass burning was identified using acetonitrile (CH_3CN) and carbon monoxide (CO). Acetonitrile was measured via PTR-MS (uncertainty of ±20%) and CO by a Diode laser spectrometer (uncertainty of ±2% or 2 ppbv).

2.3.2 Aerosols

Particle light absorption coefficients (b_{ap}) were measured with a Particle Soot Absorption Photometer (PSAP, Radiance Research) at wavelengths of 470, 532, and 660 nm. The inlet had an intrinsic 50% cut size of 4.1 µm, consistent with the filter collection, and the sample air was dried (RH typically less than 40%). As a filter-based optical instrument, where particle absorption is determined from light attenuation through a filter being loaded with particles, the PSAP suffers from various artifacts (*Bond et al.*, 1999; *Petzold et al.*, 2005). This includes multiple scattering by the filter fibers and by aerosols embedded on or within the filter; the latter increases with filter loading. Reported PSAP b_{ap} data were adjusted using *Virkkula et al.* (2010). Based on the operation of the instrument, the PSAP absorption coefficients are estimated to have an uncertainty of 20% or 0.2 Mm^{-1}, whichever is larger. Artifacts that depend on aerosol composition, however, may increase this uncertainty (*Lack et al.*, 2008). All PSAP data used in the following analyses have been averaged to filter sampling times.

Refractory black carbon (rBC, here referred to just as BC to minimize confusion with BrC) mass concentrations were measured with a SP2 (Single Particle Soot Photometer) and corrected to account for accumulation-mode BC at sizes outside the detection range of the instrument (*Schwarz et al.*, 2008). The instrument was calibrated with fullerene soot (Alfa Aesar Lot #F12S011), the accepted calibration material for the instrument (*Baumgardner et al.*, 2012). Estimated uncertainty is 30% from flow and BC mass calibrations and aspiration efficiency. OA was measured with a high resolution time-of-flight Aerodyne Aerosol Mass Spectrometer (AMS) (*DeCarlo et al.*, 2006). The AMS was operated with a setup similar to that described in Dunlea et al. (2009) involving a pressure-controlled inlet (Bahreini et al., 2008). Collection efficiency was estimated using the composition-dependent formulation of Middlebrook et al. (2011) as implemented in the standard AMS data analysis software (Sueper, 2015,

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http://cires1.colorado.edu/jimenez-group/wiki/index.php/ToF-AMS_Analysis_Software), and applied with a 1-min time resolution to reduce the effect of high-frequency noise. AMS uncertainty for OA (2 sigma = 38%) is estimated as described in Bahreini et al. (2009) and Middlebrook et al. (2012) and is dominated by the uncertainty in collection efficiency and relative ionization efficiency of OA. In the following analysis, online data were averaged to filter sampling times and included in the analysis if the online data covered greater than 75% of the sampling time. All aircraft data are blank corrected and reported at standard temperature and pressure (273 K & 1013 mb).

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The ambient light scattering coefficients (b_{sp}), used in the subsequent radiative transfer model, were measured by a TSI Integrating nephelometer at wavelengths of 450 nm, 550 nm, and 700 nm. The inlet cut-point was the same as other instruments (aerodynamic diameter of 4.1 µm). Scattering coefficients at three wavelengths were first averaged over the filter-sampling period, if more than 75% of the period was covered by measurements. The averaged scattering coefficients were then extended to other wavelengths based on a scattering Ångström exponent (SAE) by equations (1) and (2).

$$SAE = -\frac{\ln(b_{sp}(700)) - \ln(b_{sp}(450))}{\ln(700) - \ln(450)} \quad (1)$$

$$b_{sp}(\lambda) = b_{sp}(550) \cdot \left(\frac{\lambda}{550}\right)^{-SAE} \quad (2)$$

Excluding biomass burning plumes, the study mean ± SD SAE was 1.27±0.74, Scattering data were reported to have a 10% uncertainty for measurements at all three wavelengths, therefore the combined uncertainty in estimated scattering coefficients at various wavelengths, based on equations (1) and (2), was estimated at roughly 20%.

3. Results

In the following analysis, we first use data on light absorption of the aerosol extracts to investigate sources and distributions of BrC. Following this, the solution data are converted to estimates of BrC aerosol absorption coefficients and the optical effects of BrC are investigated.

3.1. Identifying biomass burning plumes

During the DC3 campaign, 2 out of 22 aircraft flights were specifically targeted to investigate biomass burning emissions, and in six other flights at least one biomass burning plume was encountered. For this work, the data are simply delineated between clearly evident biomass burning sampling periods and all else, the latter being referred to as background tropospheric conditions. To identify biomass burning plumes, CO and CH_3CN were used as tracers following the method of *de Gouw* et al. (2004). First, enhancements in CO in time-series plots were identified. For these episodes, if r^2 values for CO and CH_3CN were higher than 0.5, the plume was designated as biomass burning. Identified biomass burning sampling periods are listed in Table 2. If greater than 75% of the filter sampling integration time was identified as a biomass burning plume, it was characterized as biomass burning. By this criterion roughly 12% of collected filters were identified as biomass burning. Filters not identified are referred to as background measurements, but may still have been influenced, to some extent, by biomass burning due to small-duration plume intercepts. Residual impacts from dispersed biomass burning emissions may also account for some fraction of the ambient aerosol throughout the troposphere during this study. However, the majority of filters were collected under what could be considered more typical continental tropospheric conditions, albeit during a summer of extensive burning.

3.2. Study Statistical Summary

A summary of the DC3 BrC solution measurements, together with other relevant species, is given in Table 3. BrC in filter extracts was observed throughout the study region, with over 85% of the data above the LOD.

Comparing with background conditions, biomass burning plumes were notable by significantly higher BrC levels. Average *H_2O_Abs(365)* in the identified biomass burning plumes was 5 times higher than background conditions, while *Total_Abs(365)* was approximately 4 times higher. In contrast, the enhancements in other species were smaller; WSOC was only ~ 1.3, OA 2.8 and BC 2.6 times higher than background conditions. The differential enhancement of WSOC and *H_2O_Abs(365)* or *Total_Abs(365)* indicates that biomass burning aerosol is browner on a per mass basis (higher mass absorption efficiencies) than the background aerosol, as seen in other

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studies (*Hecobian et al.*, 2010). These results confirm that biomass burning is a strong source for both water- and methanol-soluble BrC and are consistent with studies using different methods to identify BrC and biomass burning (*Lack et al.*, 2013).

The proportion of water to methanol soluble BrC was different in background versus biomass burning plumes. In background air masses, the water-soluble BrC fraction was roughly 25 to 33% (i.e., $H_2O\_Abs(365)$ / $Total\_Abs(365)$), similar to previous studies (*Zhang et al.*, 2013; *Liu et al.*, 2013). However, the water-soluble BrC fraction was higher in biomass burning plumes, where $H_2O\_Abs(365)$ comprised ~ 45% of the $Total\_Abs(365)$. These data suggest that primary smoke emissions contain or form more water relative to methanol-soluble BrC compared to aged BrC.

3.3. Correlations

Associations between various species in both the biomass burning plumes and under background conditions are investigated based on correlations. Results are summarized in Table 4. Correlations are shown for $H_2O\_Abs(365)$ and $Total\_Abs(365)$. Since, for background conditions, two thirds to three quarters of the BrC absorption is associated with the methanol extract, $Total\_Abs(365)$ correlations with various other species are driven primarily by the methanol-soluble BrC (for brevity, we do not show correlations for just the methanol-soluble BrC). Note that for airborne measurements, temporal correlations imply spatial correlations between species.

For biomass burning samples, species expected from the smoke plumes (e.g., CO, acetonitrile, OA, WSOC, BC and PSAP b_{ap} at all three wavelengths) are highly correlated with each other, and all are highly correlated with both *H_2O_Abs(365)* and *Total_Abs(365)*, consistent with a common source. The least correlated were WSOC and BC (r=0.70), and *H_2O_Abs(365)* and BC (r=0.72), possibly because some fraction of the water-soluble compounds may be secondary and not as likely to be correlated with a primary component (BC).

In contrast, for background conditions there was a poor correlation between *H_2O_Abs(365)* and *Total_Abs(365)* (r = 0.32) and they were correlated with a different set of species. *H_2O_Abs(365)* was correlated mostly with the PSAP measurements of absorption (r = 0.66 at 470 nm) or with BC (r = 0.64), but not well correlated with WSOC (r = 0.34). But, *H_2O_Abs(365)* was somewhat correlated with OA (r = 0.57) and acetonitrile (r = 0.57), suggesting that the water-soluble faction in the background troposphere could be more strongly related to primary emissions and possibly linked to aged biomass burning.

Total_Abs(365) was not well correlated with any of the other parameters in the background samples. This lack of correlation suggests that much of the background tropospheric BrC had undergone some form of processing or evolution (e.g., photobleaching). A similar situation is observed for WSOC, which was also not generally correlated with any of the other variables in Table 4. In a ground-based study, *Liu et al.* (2013) observed higher relative levels of water to methanol-soluble BrC near sources compared to aged aerosol, consistent with an aging process that preferentially depletes water soluble fraction of BrC. Other chemical processes are possible, e.g., *Lin et al.* (2014) showed that IEPOX-derived oligomers that absorb in the ultra-violet region are more soluble in methanol, suggesting the potential contribution of biogenic SOA, especially in biogenic-rich regions. However, a recent study showed that at a remote surface site in the southeast US, significantly impacted by biogenic SOA, biomass burning was the dominant BrC source (*Washenfelder et al.*, 2015). Therefore, we believe aged biomass burning is the main source of the ubiquitous BrC, but that biogenic SOA cannot be ruled out.

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3.4. Altitude profiles of light absorbing aerosols

These data show that BrC is detected throughout the continental troposphere. Vertical profiles of $H_2O\_Abs(365)$ and $Total\_Abs(365)$ are given in Figs. 2a and 2b for both the biomass burning plumes and background conditions. The profiles were constructed by sorting the two data sets into 1-km bins and plotting the bin median. Error bars represent the inter quartile ranges for each bin and demonstrate the large variability in the data, especially for the biomass burning plumes.

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BC concentration and PSAP b_{ap} at 660nm are also plotted. BrC, BC and PSAP absorption show large differences between biomass burning events and background conditions, with the biomass burning plumes dominant at a few altitudes where the aircraft encountered and pursued specific plumes. The biomass burning altitude profiles for BrC, BC and PSAP absorption are all somewhat similar, indicating that biomass burning contributes to all carbonaceous aerosol components that absorb light, as previously shown by the high correlations amongst these species. This is less true for background conditions where differences between the light absorbing components can be seen, for example, BC concentrations are generally more elevated closer to the surface.

To compare vertical distributions of aerosol light absorbing components in background air masses, the cumulative column fraction of light absorption coefficient or BC concentration is plotted in Fig. 3. At a given altitude, the cumulative fraction is the light absorption coefficient, or concentration, integrated over all altitudes above, relative to the total column. Note that the integral of the actual absorption occurring would depend on the vertical profile of actinic flux; this is independent of the relative distributions that we explore here. Half the column BC concentration occurs at approximately 3.5 km a.s.l., while for water or total (water plus methanol extract) BrC, this occurs between 5 and 6 km, indicating a more uniform vertical distribution and not as dominated by surface emissions compared to BC. PSAP-determined aerosol absorption at 660 nm and light absorption extrapolated to 365 nm is also shown (the method for extrapolating is discussed below, see Eq. 7). For PSAP absorption efficiency at 365 nm, the 50% altitude is 4.5 km a.s.l., which is between BC and BrC, suggesting contributions to light absorption by a mixture of BC and BrC at 365nm, while the 50% altitude for PSAP absorption efficiency at 660 nm is ~4 km a.s.l., closer to BC, as expected, since at 660nm BC should dominate the total light absorption (i.e., BrC does not effectively absorb at high wavelengths, see next section).

The ratio of BrC (*Total_Abs(365)*) to the SP2-measured BC mass also increases with altitude, (see Supplemental Fig. S1), further demonstrating the differences in vertical distributions of BrC and BC for the background troposphere. These results suggest there is in-situ BrC production or possibly preferential loss of BC with increasing altitude. Higher BC at the surface may reflect greater contributions from fossil fuel combustion sources for BC. Vertical profiles of aerosols greatly affect overall radiative forcing.

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3.5. Absorption Ångström Exponents for BrC and bulk light absorbing aerosols

The wavelength (λ) dependence of light absorption is often fit with a power law of the form:

$$Abs(\lambda) = K \cdot \lambda^{-AAE} \qquad (3)$$

Where *Abs(λ)* is the light absorption at a given wavelength (λ) for light passing through a region of light absorbing species (example, the waveguide with liquid extracts, or an aerosol layer in the ambient atmosphere), and *AAE* is the Absorption Ångström Exponent, (the factor *K* is not important in this analysis). For the high spectral resolution data available with spectrophotometric measurements of absorption in the water or methanol aerosol extracts, the AAE (in this case AAE for

BrC, AAE_{BrC}) is determined from a linear regression fit of $log(Abs(\lambda))$ vs $log(\lambda)$ between 300 and 450 nm. Examples of the solution light absorption spectra for a biomass burning sample and typical background sample are shown in Fig. 4, along with the regression fit to determine an AAE_{BrC}. Above roughly 450nm, in both background and biomass burning plumes, the BrC absorption levels out or increases, which may be due the chemical nature of the chromophores. This range is excluded from the AAE_{BrC} calculation. In the following analysis *AAEs* for ambient aerosols are assumed to be the same as the solution-measured BrC *AAE* (*Moosmuller et al.*, 2011; *Liu et al.*, 2013).

The BrC absorption Ångstöm exponents were somewhat similar for background conditions and biomass burning samples, however, there were significant differences between water and methanol extracts. For water extracts the mean ± stdev of AAE_{BrC} was 6.82±2.63 for background conditions and 8.95±1.73 for biomass burning. Methanol extract AAE_{BrC} was on average 4.54±3.07 for background conditions and 5.04±2.61 for biomass burning plumes. Lower AAE_{BrC} for methanol versus water extracts (also see Fig. 4) may be related to differences in solubility of the chromophores (*Zhang et al.*, 2013; *Chen and Bond*, 2010). BrC chemical speciation by *Zhang et al.* (2013) found that larger molecular weight PAHs absorbed more toward the visible range (i.e., have a lower AAE) and have a lower water-solubility. Methanol extract lower AAE_{BrC} could result from higher molecular weight chromophores not soluble in water.

The AAE for the overall light absorbing ambient aerosol can also be calculated from the more limited spectral data (three wavelengths) associated with the PSAP. Here, AAE_{PSAP} is calculated using absorption measured at the wavelength pair, 470 and 660 nm by;

$$AAE_{PSAP} = -\frac{\ln\left(b_{ap,PSAP}(660)\right) - \ln\left(b_{ap,PSAP}(470)\right)}{\ln(660) - \ln(470)} \tag{4}$$

AAE altitude profiles are plotted in Fig. 5. On average, there is no significant variability in the vertical profiles of background air-mass mean AAE_{BrC}, for either water or methanol extracts (Fig. 5a). There is however, much more variability within each altitude layer. The cause of this variability could be due to aerosol chemistry, but investigating it is beyond the scope of this analysis.

AAE_{BrC} considers only BrC absorbers, whereas AAE_{PSAP} includes all absorbers (BrC and BC). Average AAE_{PSAP} for the biomass burning periods was 2.15 ± 0.88 (mean ± stdev) and 1.60 ± 0.61 for background conditions. Differences can also be seen in the vertical profiles (Fig. 5b), where for the most part, the AAE_{PSAP} was higher in the biomass burning plumes compared to background conditions. Qualitatively, the higher AAE_{PSAP} for the biomass burning air masses is consistent with significant contributions from BrC, although light absorption enhancements due to mixing state cannot be ruled out. Another noteworthy feature of Fig. 5b is that a trend in AAE_{PSAP} may also be evident in the vertical profile for background conditions, where AAE_{PSAP} tends to increase with altitude. This is consistent with the greater fraction of BrC to

BC with altitude. Note, that for both biomass burning and background air masses the AAE_{PSAP} is closer to 1 near the surface where BC appears to be more dominant. Overall, the independent measurements of BrC and aerosol AAEs are consistent and suggest that the observed AAEs greater than one are mostly due to BrC and not enhancements due to BC mixing state.

3.6. Light Absorption Calculations: BrC, BC and PSAP

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In the previous analysis, BrC solution light absorption data was presented. Now, BrC solution data is converted to optical absorption to quantify the separate contributions of BrC and BC as a function of altitude. The sum of BC and BrC absorption are then compared to the PSAP data (total BrC and BC). The analysis could be done at any wavelength, however, 365 nm is chosen since it is in a wavelength range where a reliable BrC measurement is possible, e.g., at lower wavelengths, other non-BrC species begin to impact the data, such as nitrate, but sufficiently low that BrC, if present, should have a significant optical effect (i.e., BrC absorption drops off rapidly with increasing wavelength, as seen above, Fig. 4).

3.6.1 BrC Light Absorption

To convert the solution absorbance to light absorption by an aerosol, knowledge of both particle morphology and how the chromophores are distributed amongst particle size is needed. In the past, studies have often assumed a small particle limit when making this conversion, where light absorption by BrC aerosol is taken as 0.69 to 0.75

times the light absorption of the solution (e.g., *Sun et al.* 2007). This likely gives a lower limit for BrC absorption since BrC is not associated with sub-nm size particles. *Liu et al.* (2013) measured the size distribution of BrC and showed that the chromophores were consistently found in the accumulation mode in both fresh vehicle emissions and for more aged background aerosols (BrC geometric mass mean diameter was ~0.5 µm). It is likely that this is more representative of the BrC size distribution of the background troposphere, given that the aerosols are aged. This assumption is supported by the AMS size-resolved OA data. OA was predominantly in the accumulation mode throughout the atmospheric column, excluding biomass burning plumes. For background conditions OA geometric mass mean diameters were 0.38±0.02 µm for the altitude range 0-5 km, and 0.37±0.08 µm for 5 km and above.

From Mie theory calculations, assuming that the BrC was externally mixed with other absorbers, *Liu et al.* (2013) found that aerosol absorption is approximately 1.8 to 2 times higher than the bulk absorption measured in the extracts. *Washenfelder et al.* (2015) used bulk measurements of BrC absorption at 365 nm to estimate the OA refractive index and used OA size distributions and Mie theory and also found a conversion factor of two for aerosols at a rural site. In this study, by applying Mie theory to AMS-measured size-resolved OA assuming that the BrC is evenly distributed amongst all OA (details described in *Washenfelder et al.*, (2015)), we obtain a conversion factor of 2.08±0.14, consistent with the conversion factor of 2 obtained from *Liu et al.* (2013). Thus the aerosol BrC absorption at 365 nm is estimated for the two solvent extracts simply as,

$$b_{ap,H_2O\_BrC}(365) = 2 \cdot H_2O\_Abs(365) \qquad (5)$$

$$b_{ap,Total\_BrC}(365) = 2 \cdot \left[H_2O\_Abs(365) + MeOH\_Abs(365)\right] = 2 \cdot Total\_Abs(365) \qquad (6)$$

Considering the known uncertainty in the conversion factor of 2 (estimated to be at least 30% (*Liu et al.*, 2013)) and the liquid absorption measurements, the overall uncertainty of these coefficients is estimated to be at least 30 and 45%.

3.6.2 BC and PSAP Light Absorption

To estimate light absorption by the ambient aerosol at 365nm, PSAP measurements at higher wavelengths are extrapolated to 365 nm using a calculated AAE_{PSAP}. Particle absorption at a certain wavelength, $b_{ap,PSAP}(\lambda)$, is calculated from the AAE_{PSAP} from Equation (4) and the light absorption measured at 660nm;

$$b_{ap,PSAP}(\lambda) = b_{ap,PSAP}(660) \cdot \left(\frac{\lambda}{660}\right)^{-AAE_{PSAP}} \qquad (7)$$

It is noted that AAE_{PSAP}, given in Eq, 4, could have been determined from different wavelength combinations (i.e., 470-532 nm, 532-660 nm). For this data set, the other wavelength pairs led to a predicted $b_{ap,PSAP}(365)$ systematically different by roughly 20% of that predicted by equations (4) and (7). The wavelength pair of 470 and 532 results in a $b_{ap,PSAP}(365)$ that was ~20% higher (regression slope = 1.19, r^2 = 0.98, intercept = -0.02 for $b_{ap,PSAP}(365)$ predicted from 470-532 vs $b_{ap,PSAP}(365)$

predicted from 470-660 wavelength pair). Whereas the other combination produces a systematically 20% lower $b_{ap,PSAP}(365)$ (regression slope = 0.80, r^2 = 0.94, intercept = 0.04 for $b_{ap,PSAP}(365)$ from 532-660 vs $b_{ap,PSAP}(365)$ predicted from 470-660 wavelength pair). Thus, the 470-660 pair gives the middle value between what is predicted by other possible combinations (see *Liu et al.,* (2014) for how the choice of wavelength pair influences the vertical distribution of AAE_{PSAP}).

Since data on light absorption by BC is not available, it was estimated. A number of possible methods are available. In the first case, BC absorption at a certain wavelength ($b_{ap,BC1}(\lambda)$) is calculated from light absorption coefficients recorded at high wavelengths, where contributions from BrC should be minimal, and extrapolated to lower wavelengths using an assumed BC AAE (AAE_{BC}),

$$b_{ap,BC1}(\lambda) = b_{ap,PSAP}(660)\cdot(\frac{\lambda}{660})^{-AAE_{BC}} \qquad (8)$$

Aged BC aerosol is likely to be internally mixed with other aerosol components, which, based on simplified models, such as spherical clear shells over absorbing BC cores (*Bond et al.*, 2006), and limited laboratory data (*Schnaiter et al*., 2005; *Slowik et al*., 2007), could lead to a significantly different AAE_{BC}, for example, ranging from ~0.6 to 1.6 (*Kirchstetter and Thatcher*, 2012; *Feng et al.,* 2013; *Lack and Cappa*, 2010; *Liu et al.*, 2015). More random mixtures, or mixtures containing absorbing material, such as BrC, can significantly alter this enhancement (*Lack and Cappa*, 2010). Recent ambient data do not show significant enhancement of aerosol light absorption at lower wavelengths, which would be indicated by deviation of an AAE_{BC}

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from 1 (*Cappa et al.*, 2012). In the following analysis, an AAE_{BC} of 1 is used as the default case.

Instruments that measure light absorption based on particles deposited on a filter, such as the PSAP, can also be significantly biased high due to artifacts (*Lack et al.*, 2008). To avoid this, an alternative approach to calculate BC absorption is to estimate the light absorption coefficient at high wavelengths, where BrC does not absorb light, using the BC mass concentration and an assumed characteristic BC mass absorption cross-section (MAC) at a given wavelength. BC absorption at other wavelengths can be determined using the AAE_{BC}. *Bond and Bergstrom* (2006) have suggested a MAC_{BC} = 7.5 ± 1.2 m^2g^{-1} at 550 nm for pure uncoated (i.e., fresh) BC. Here, we use this as a possible lower bound for BC light absorption and refer to this second method of calculating the BC absorption with a subscript 2,

$$b_{ap,BC2}(\lambda) = MAC_{BC} \cdot BC \cdot \left(\frac{\lambda}{550}\right)^{-AAE_{BC}} \qquad (9)$$

For consistency, this prediction of BC absorption is compared to the ambient aerosol absorption (b_{ap2}), which is estimated by extrapolating from this MAC-determined light absorption coefficient ($b_{ap,\,BC2}$) using the PSAP AAE,

$$b_{ap2}(\lambda) = b_{ap,BC2}(\lambda) \cdot \left(\frac{660}{\lambda}\right)^{-AAE_{BC}} \cdot \left(\frac{\lambda}{660}\right)^{-AAE_{PSAP}} \qquad (10)$$

A schematic showing the various optical calculations is given in Fig. 6.

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In this data set, the second approach leads to a lower prediction of BC absorption compared to the first method (i.e., $b_{ap,BC2} < b_{ap,BC1}$, see Fig. 6) due to differences between the assumed MAC_{BC} and the PSAP-measured MAC. For this data set, the non-biomass burning study-average MAC at 660nm is 10.9 m^2g^{-1} (see Supplementary Material Fig. S2). This is roughly 75% higher than the assumed pure BC MAC_{BC}, where MAC_{BC} at 550 nm was converted to a MAC_{BC} at 660 nm, by assuming an AAE_{BC} of 1, resulting in MAC_{BC} at 660nm = 6.3 m^2g^{-1}. Observed MACs are often found to vary substantially (*Chan et al.*, 2011), and some of this variability is thought to be due to internal mixing of BC. (see *Bond et al.*, (2013) for a review). In summarizing observations of ambient aerosol BC MACs, *Bond et al.*, (2013), suggests that a MAC_{BC} 50% greater than that of pure BC is reasonable (*Bond et al.,* 2013), which is not significantly different from what we observed. This suggests that the PSAP data for background conditions may not be highly skewed by artifacts.

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The schematic in Fig. 6 suggests that light absorption by the ambient aerosol at 365nm (e.g., $b_{ap,\ PSAP}(365)$) is higher than that predicted at the same wavelength for BC (e.g., $b_{ap,\ BC1}(365)$). This is often interpreted to be due to additional absorption by BrC (*Kirchstetter et al.*, 2004; *Sandradewi et al.*, 2008; *Chen and Bond*, 2010; *Sun et al.*, 2007; *Clarke et al.*, 2007) and is due to the ambient AAE (AAE_{PSAP}) being greater than AAE_{BC} (i.e., 1). However, as noted above, due to uncertainties associated with these various calculations, such as possible variability in AAE_{BC}, definitively attributing the difference to be due to BrC is highly uncertain. However, in this case we have a direct measurement of BrC and an optical closure analysis can be performed to assess if BrC is a reasonable explanation for the difference.

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

In the following we focus on BC absorption based on the PSAP measurements and an assumed AAE_{BC} of 1 (i.e., $b_{ap,\ BC1}$). Results using the other measure of BC absorption ($b_{ap,\ BC2}$) are discussed, but not plotted.

3.7.1 Background Conditions

Vertical profiles of altitude-binned median data of the light absorption coefficients at 365nm for BC ($b_{ap,BC1}$), plus either water soluble BrC ($b_{ap,\ H2O\_BrC}$) (Fig. 7a), or total BrC ($b_{ap,\ Total\_BrC}$), are shown in Fig. 7, along with the PSAP data extrapolated to 365nm ($b_{ap,\ PSAP}$) representing the ambient light absorption coefficient. Fig. 7 shows that absorption drops off with increasing altitude. It is also evident that the absorption of just black carbon ($b_{ap,\ BC1}$) is always significantly less than the overall ambient aerosol absorption determined from the PSAP, at 365nm ($b_{ap,PSAP}$). Water-soluble brown carbon absorption, $b_{ap,\ H2O\_BrC}(365)$, is small relative to BC and the sum of the two is always lower than the observed absorption ($b_{ap,\ PSAP}$), which is reasonable as the water-soluble fraction is only a portion of the light-absorbing organics. Total BrC absorption, $b_{ap,Total\_BrC}$(365), on the other hand, is more comparable to BC absorption over most of the altitude range, and when the two are summed, the BC+BrC tends to agree with the observed absorption. (Note, measurement uncertainties are roughly 28 to 45% for the various light absorption coefficients).

A more quantitative assessment of closure for background conditions can be seen in a scatter plot with orthogonal distance regression of the sum of the estimated BC and BrC versus PSAP absorption (Fig. 8). From Fig. 8a, on average for background tropospheric conditions, at 365 nm BC accounts for roughly 74% of the ambient absorption. When the water-soluble BrC is added, a slope of 0.90 (Fig. 8b) indicates that the BC plus water-soluble BrC improves the closure, but still slightly under-predicts the light absorption coefficient. When the total BrC is used (water + methanol extractions) the sum of BC and BrC results in a slope near 1 (0.97), but with a positive intercept at 0.56 Mm^{-1}. If the regression is forced through zero, the slope is 1.16. If the low particle limit is used in the conversion of solvent extracts absorption to ambient particle absorption (instead of the factor of 2 (*Liu et al.* 2013)), the slope would be 0.76 for BC + water-soluble BrC, and 0.85 for BC + total BrC vs. ambient. These comparisons have assumed an AAE_{BC} of 1, but a range of values are possible (i.e., *Gyawali et al.,* 2009). In this case, an AAE_{BC} value of 0.82 would result in regression slope of 1 between the sum of BC and BrC absorption versus $b_{ap,\ PSAP}$ at 365 nm, for a solution conversion factor of 2. One cannot definitively attribute all enhanced light absorption at low wavelengths to BrC; some combination of enhancement due to BC mixing and BrC is possible. In this data set, however, an enhancement in light absorption at low wavelengths is most consistent with just BrC.

Light absorption closure was carried out based on the assumption that BrC is externally mixed with BC. Mie theory calculations were performed using the internally mixed assumption, with core-shell sizes estimated from OA/BC ratios obtained from AMS and SP2 measurements. BC core refractive index was set at 1.95-0.79i (*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),

$$k = \frac{\rho\cdot\lambda\cdot MAC(\lambda)}{4\pi} = \frac{\rho\cdot\lambda\cdot Total\_Abs(\lambda)}{4\pi\cdot OA} \qquad (11)$$

Based on these assumptions, the light absorption estimated for the core-shell is 3.3 times that of only the BC core, and 2.4 times the aerosol light absorption measured by the PSAP. In contrast, assuming BrC and BC are externally mixed (no shell-core enhancements), estimated light absorption at 365 nm from the PSAP was within roughly 25% of that assuming external mixtures (see Figures 8 and 9). In this case, we believe the external mixing assumption provides a more reasonable closure on light absorption.

Finally, in the previous sections we showed the prevalence of BrC increases relative to BC with increasing altitude, based on solution data. Now that the closure analysis provides some support for the BrC absorption coefficients at 365 nm, the fractional

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contribution of brown carbon absorption (both water and total BrC) relative to ambient absorption can be assessed as a function of altitude. Fig. 7c shows that the fraction of BrC substantially increases with increasing altitude, with absorption due to total BrC (at 365nm) accounting for > 80% of total absorption above ~7.5 km, a region where ambient absorption coefficients are low.

3.7.2 Biomass burning events

Applying a vertical distribution analysis is not possible for biomass burning plumes, since there were limited data points for some of the altitudes, but closure analysis based on the combined data is shown in Fig. 9. The conversion factor from solution BrC to ambient aerosol absorption has not been studied for biomass burning events (*Liu et al.,* (2013) did not include a size-resolved measure of biomass burning BrC), leading to some uncertainty in this closure analysis. As before a multiplication factor of 2 is used as the base case, recognizing there is uncertainty in this assumption.

Biomass burning is known to be a strong source for BrC, and Fig. 9a shows that on average, at 365nm BC only accounted for roughly 57% of the light absorption, substantially lower than that for background conditions. For BC plus water-soluble BrC the slope is 77% and, for BC plus total BrC the slope is 122%, in this case over-predicting the observed values. An AAE_{BC} value of 0.82, which resulted in slope of 1 for background conditions, results in a smaller (9%) over-estimation for the biomass burning plumes. More studies of individual biomass burning plumes would provide greater insight into possible roles of both BC mixing and BrC in light absorption enhancements.

3.7.3 Use of the MAC in closure calculations for background conditions

A similar analysis, but where BC and ambient light absorption are based on an assumed BC MAC, SP2-measured BC concentrations, and PSAP AAE (i.e., see Fig. 6, $b_{ap,BC2}$ and b_{ap2})), can also be performed. As discussed in a previous section, this approach leads to a lower prediction of BC absorption compared to the first method (i.e., $b_{ap,BC2} < b_{ap,BC1}$), and therefore a lower b_{ap2} than $b_{ap,\,PSAP}$ at 365 nm (Fig. 6). In this case the closure analysis for BC versus ambient light absorption (b_{ap2}) results in a slope of 0.73, whereas BC + water-soluble BrC the slope is 0.97 and for total BrC the slope is 1.40. Thus, unlike when the PSAP absorption coefficients at 660nm are used directly, the sum of BC and BrC light absorption generally exceeds the ambient total absorption. This happens because using a MAC of pure BC results in substantially lower absorption coefficients, making the proportion of BrC higher. It appears that the use of the MAC_{BC} (7.5 at 550 nm or 6.3 m^2g^{-1} at 660 nm) in this case does not produce as reasonable a result as absorption coefficients based on the PSAP data (observed study MAC of 10.9 m^2g^{-1} at 660 nm) and so this method is not considered in the radiative forcing calculations that follow.

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3.8 Radiative Forcing

The Santa Barbara DISORT Atmospheric Radiative Transfer (SBDART) model was used to assess the role of BrC in direct radiative forcing for background conditions in the continental troposphere. Vertically resolved optical properties were used, including light absorption coefficients for BC, BrC and total absorption based on the PSAP, along with measurements of the light scattering coefficients from the multi-wavelength nephelometer. Absorption and scattering coefficients were calculated for 10 wavelengths, over the 300-700 nm range, and average values were determined for each 1-km altitude bin. BC absorption was determined using Equation 8 and AAE_{BC} = 1, BrC was determined based on the complete measured spectra of total (water+methanol) extract, and overall ambient aerosol light absorption was based on Equation 7 and inferred AAE_{PSAP}. Scattering coefficients were determined from Equation 2. The scattering is based on measurements and independent of the light absorption used (i.e., just BC or BC plus BrC). The wavelength-dependent single scattering albedo (SSA) was then calculated as input to the SBDART model. Aerosol optical depth (AOD) was also calculated using absorption and scattering data. The SBDART model interpolated from these data over the wavelength range of 250 to 4000 nm. A third input needed for SBDART is the asymmetry parameter (g), of which a uniform value of 0.65 (*Carrico et al.*, 2003) was used across all wavelengths. An atmospheric profile for a standard mid-latitude summer was assumed and tested with albedo resulting from surface types of both sand and vegetation. The model was run with solar zenith angle (SZA) ranging from 0-85 degrees, at 5-degree increments. Daily average forcing is the integrated instantaneous radiative forcing averaged over a 24-hour period.

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To assess the influence of BrC relative to BC, forcing was calculated based on the estimates of BC optical properties (AAE_{BC}=1), then compared to forcing for BC+BrC. Four groups of wavelength-dependent inputs were generated for each altitude bin; no aerosol (gases only), scattering aerosols only, BC as the only absorbing aerosol, and BC+BrC as absorbing aerosols. Only background data were used (i.e., biomass burning plumes were excluded), to better represent typical continental atmospheric conditions. At a SZA of 40°, considering all aerosol direct optical effects, but delineating absorption by BC and BrC, the instantaneous forcings at top of atmosphere (TOA) were -19.33 W m^{-2} and -24.84 W m^{-2} for BC+BrC and BC, respectively, with vegetation as surface type, and -23.35 W m^{-2} and -28.57 W m^{-2} for a surface of sand. Integrated over 24-hour period, diurnally averaged forcings at TOA were -14.79 and -11.82 W m^{-2} for BC and BC+BrC, vegetation surface type, and -16.94 and -14.11 W m^{-2}, respectively, for a surface type of sand. The overall negative TOA forcing is due to cooling by aerosol scattering; however, BrC absorption appreciably changes the TOA forcing relative to BC only, resulting in roughly 20% less cooling compared to only BC. The forcings at the surface are discussed in *Liu et al.* (2014).

Alternatively, we could use the PSAP data to estimate total light absorption by aerosols instead of BC+BrC, in which case we get light absorbers other than BC (eg, BrC, dust) contributing ~17%, similar to the values reported above. Other combinations of the analyses are possible, but all give similar results. Therefore, for the aerosol loadings recorded in this study, we find that BrC increased the shortwave solar absorption in the atmosphere by approximately 20%, demonstrating the importance of BrC as a climate forcing agent.

Most measurements of BrC and other aerosol optical properties are made at the surface. To allow estimates of TOA forcing due to contributions of aerosol BrC throughout the column, the average distributions of single scattering albedo and optical depth observed under background conditions is used to generate a chart relating aerosol radiative forcing efficiencies (RF_{eff}) as a function of the aerosol absorption coefficient of BrC relative to BC at 365nm and SSA measured at the surface. The RF_{eff} is defined as the TOA aerosol radiative forcing divided by aerosol optical depth (AOD) at 500 nm. Fig. 10 was generated through multiple runs (N=4320) of SBDART and shows that RF_{eff} values of BrC increase with decreasing SSA and increasing BrC/BC ratio, as both factors result in higher BrC at a given AOD. The circle in the Fig. represents the average background conditions during this campaign, with a value of 16.71 W m^{-2} per unit optical depth at 500 nm, with a surface of vegetation. In comparison, the forcing efficiency is -88.64 W m^{-2} per unit optical depth at 500 nm for BC+scattering, which is in agreement with previous research (e.g., *Bush and Valero* (2003)).

If the vertical profiles applied in SBDART represents typical background tropospheric

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conditions in the continental US, application of Fig. 10 is not limited to this campaign. Further airborne studies similar to this one are needed to assess this assumption. As noted, the SSA and BrC/BC absorption ratios plotted in the Fig. are surface values at 365 nm, while column AOD could be easily retrieved from remote sensing techniques, for example, AOD at 500 nm is available from AERONET. Therefore, the Fig. can serve as a look-up chart to estimate radiative forcing contributions by BrC, when altitude-resolved parameters are not available. For example, a data point for surface measurements at a rural site in the southeastern US (*Washenfelder et al.*, 2015) is also shown in Fig. 10. In addition, large-scale models require substantial number of computations, the patterns shown in this Fig. could be considered as a simplified module and incorporated into models with minimal computational costs.

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4. Summary

Direct measurements of BrC were made on solvent extracts from filters collected at altitudes ranging from approximately 1 to 12 km over the central US during summer. The data were segregated into periods of sampling in biomass burning plumes and more typical background tropospheric conditions. The filters were extracted sequentially; first in water, then in methanol, and the sum of the water plus methanol extract BrC assumed to represent the total BrC.

During biomass burning periods, both water- and methanol-soluble BrC were highly correlated with other known emissions from biomass burning plumes, including CO, acetonitrile and BC. Under background conditions, the water-soluble fraction of BrC was somewhat correlated with smoke tracers, whereas the methanol-soluble BrC was not well correlated with any specific tracers, but most correlated with WSOC, possibly due to the BrC evolving to a more water-insoluble state as it aged. BrC was 4 to 5 times higher in biomass burning plumes relative to the background conditions and more water-soluble (45% of the total, at 365nm, in the biomass burning plumes versus 30% in background air).

BrC was found throughout the tropospheric column. For background conditions, BrC was more evenly distributed throughout the column than BC, resulting in an increasing proportion of BrC relative to BC, with increasing altitude. This was consistent with an observed increasing AAE from the 3-wavelength PSAP data.

Estimates of BC and BrC absorption coefficients at 365nm were compared to observed PSAP absorption. For background air masses, a closure between BC + BrC versus ambient absorption coefficients derived from the PSAP resulted in a slope within 3% of one. For biomass burning plumes the closure was within 22%. Reasonable closure suggests that PSAP AAEs greater than one were mainly due to the presence of BrC and not due to enhancements from BC internal mixing with other compounds, although the data do not definitely prove this.

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To estimate the BrC contribution to climate forcing, the vertically-resolved data were applied to a radiative transfer model (SBDART). The overall negative TOA forcing by aerosol scattering was reduced by approximately 20% due to BrC absorption. Thus, for the aerosol loadings recorded during this study under background conditions, BrC increased the shortwave solar absorption in the atmosphere by roughly 20% over what would occur if it were not present. These results demonstrate that BrC is an important climate forcing agent and should be considered in global climate models.

Because there are differences in BC and BrC sources and vertical distributions, the latter has an impact on the radiative forcing (*Samset and Myhre*, 2011), BrC cannot be accurately represented by a simple scaling of BC. Furthermore, this study and others (*Lee et al.*, 2014; *Zhong et al.*, 2014) show that BrC is dynamic with significant changes possibly occurring with photochemical aging, making predicting BrC levels and optical effects of BrC absorption complex. Instead a look-up chart was developed based on the average vertical profile for atmosphere background conditions in this study. The chart provides estimates of BrC radiative forcing based on three surface-measured aerosol parameters. The look-up chart is an important first attempt at developing a tool to assess the role of BrC radiative forcing and aid in including BrC in global models. Measurements of well aged BrC vertical profiles similar to those of this study are needed in other locations to improve the predictability of this type of model.

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Table 1: Nomenclature:

PSAP	Particle Soot Absorption Photometer
b_{ap}	light absorption coefficient for fine particles (M/m)
BC	Black Carbon
BrC	Brown Carbon
WSOC	Water-Soluble Organic Carbon (µgC m^{-3})
OA	Organic Aerosol (µgm^{-3})
AAE	Absorption Ångström Exponent
AAE_{BrC}	Absorption Ångström Exponent for brown carbon from solution data
AAE_{BC}	Absorption Ångström Exponent for black carbon
AAE_{PSAP}	Absorption Ångström Exponent based on the PSAP data
$A(\lambda)$	light absorbance measured by the spectrophotometer, (unitless)
$Abs(\lambda)$	light absorption measured in a solution at wavelength λ (Mm^{-1})
$H_2O\_Abs(\lambda)$	light absorption measured in water-extract at wavelength λ (Mm^{-1})
$MeOH\_Abs(\lambda)$	light absorption measured in methanol-extract at wavelength λ (Mm^{-1})
$Total\_Abs(\lambda)$	sum of $H_2O\_Abs(\lambda)$ and $MeOH\_Abs(\lambda)$ for a filter extracted sequentially using the two solvents (water then methanol).
$b_{ap,\ H2O\_BrC}(\lambda)$	Mie predicted fine particle brown carbon absorption from water extracts (Mm^{-1}), wavelength is specified in text.
$b_{ap,\ Total\_BrC}(\lambda)$	Mie predicted fine particle brown carbon absorption from the sum of water and methanol extracts (Mm^{-1}), wavelength is specified in text.
$b_{ap,PSAP}(\lambda)$	Light absorption coefficient of fine particles at wavelength λ (Mm^{-1}) determined from the PSAP data.
$b_{ap,BC1}(\lambda)$	Light absorption coefficient of BC at wavelength λ (Mm^{-1}), estimated from PSAP absorption at 660 nm, assuming non-BC light absorbers are minimal at 660 nm and an AAE_{BC} of 1
$b_{ap,BC2}(\lambda)$	Light absorption coefficient of BC at wavelength λ (M/m), estimated using a mass absorption cross section of 7.5 m^{2}g^{-1} at 550 nm and an AAE_{BC} of 1
$b_{ap2}(\lambda)$	Light absorption coefficient of fine particles at wavelength λ (Mm^{-1}) determined from $b_{ap,BC2}(660)$ and AAE_{PSAP}
MAC	Mass Absorption Cross-section
SZA	Solar Zenith Angle
TOA	Top of Atmosphere
a.s.l.	Above sea leveled
SD	Standard Deviation

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Table 2. Periods of identified biomass-burning plumes.

Time (UTC)
2012/5/25, 22:00-22:26
2012/5/26, 21:20-21:40, 2012/5/27, 00:09-00:21
2012/6/6, 21:27-21:37, 2012/6/7, 00:19-00:36
2012/6/11 16:24-16:57, 17:56-18:11, 21:56-22:06
2012/6/15, 19:51-20:10
2012/6/16, 21:18-21:26, 2012/6/17 01:36-02:13
2012/6/17, whole flight
2012/6/22, whole flight

Table 3. Statistical summary of observed species throughout all flights during DC3 separated into three categories: All samples, samples during identified biomass burning events and samples for background conditions (periods when data could not be clearly identified as biomass burning). For statistical purposes, ½ the LOD value is substituted for data below LOD. All data have been merged to the nominally 5-min filter sampling time.

All samples	**LOD**	**% above LOD**	**Mean**	**Median**	**Std Dev**	**Min**	**Max**
WSOC[a]	0.084	95	1.24	0.81	1.83	0.042	31.37
OA [b]	0.30	89	3.48	2.82	10.85	0.15	208.53
BC [b]	0.01	84	0.069	0.036	0.189	0.005	3.75
H_2O_Abs(365)[c]	0.031	87	0.33	0.11	1.93	0.016	39.50
Total_Abs(365)[c]	0.11	86	0.94	0.44	3.89	0.055	67.19
Biomass Burning events							
WSOC	0.084	94	1.52	0.77	3.93	0.042	31.37
OA	0.30	88	7.55	3.73	25.95	0.15	208.53
BC	0.01	83	0.144	0.052	0.47	0.005	3.75
H_2O_Abs(365)	0.031	92	1.03	0.32	4.66	0.016	39.50
Total_Abs(365)	0.11	93	2.37	0.86	8.67	0.055	67.19
Background conditions							
WSOC	0.084	95	1.19	0.82	1.28	0.042	10.68
OA	0.30	93	2.69	2.01	2.69	0.15	12.79
BC	0.01	88	0.056	0.035	0.060	0.005	0.399
H_2O_Abs(365)	0.031	86	0.20	0.10	0.53	0.016	7.52
Total_Abs(365)	0.11	85	0.64	0.36	1.38	0.055	15.44

[a] unit: μgC m^{-3}; [b] unit: μg m^{-3}; [c] unit: Mm^{-1}

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Table 4. Pearson rank correlations (r) for biomass burning plumes and background conditions. Bold values above the matrix diagonal are from biomass burning plumes (69 data points), while italic numbers below the matrix diagonal are from background conditions (334 data points). All data were averaged to filter sampling times.

	WSOC	H_2O_Abs(365)	*Total_Abs(365)*	OA	CO	BC	Acetonitrile	$b_{ap,PSAP}(470)$	$b_{ap,PSAP}(532)$	$b_{ap,PSAP}(660)$
WSOC	1	**0.99**	**0.97**	**0.96**	**0.93**	**0.70**	**0.97**	**0.75**	**0.75**	**0.75**
H_2O_Abs(365)	*0.34*	1	**0.98**	**0.98**	**0.94**	**0.72**	**0.98**	**0.7**	**0.78**	**0.78**
Total_Abs(365)	*0.13*	*0.32*	1	**0.995**	**0.97**	**0.83**	**0.99**	**0.87**	**0.87**	**0.87**
OA	*0.28*	*0.57*	*0.20*	1	**0.97**	**0.85**	**0.99**	**0.89**	**0.89**	**0.89**
CO	*0.15*	*0.48*	*0.17*	*0.76*	1	**0.85**	**0.97**	**0.87**	**0.87**	**0.87**
BC	*0.20*	*0.64*	*0.30*	*0.86*	*0.75*	1	**0.82**	**0.99**	**0.99**	**0.99**
Acetonitrile	*0.11*	*0.57*	*0.23*	*0.48*	*0.52*	*0.57*	1	**0.86**	**0.86**	**0.86**
$b_{ap,PSAP}(470)$	*0.27*	*0.66*	*0.31*	*0.80*	*0.72*	*0.95*	*0.58*	1	**0.9999**	**0.9997**
$b_{ap,PSAP}(532)$	*0.27*	*0.63*	*0.31*	*0.80*	*0.72*	*0.95*	*0.55*	*0.99*	1	**0.9999**
$b_{ap,PSAP}(660)$	*0.28*	*0.59*	*0.29*	*0.80*	*0.70*	*0.93*	*0.51*	*0.98*	*0.99*	1

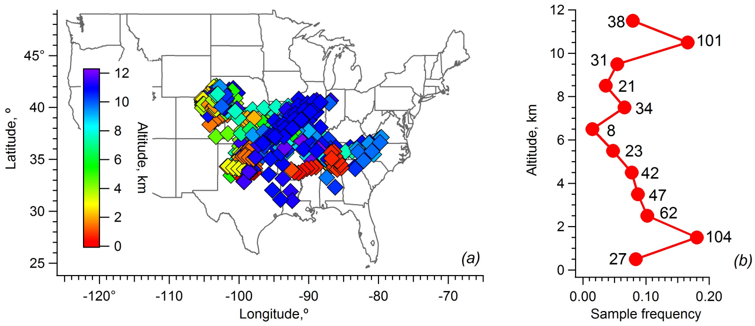

Fig. 1. (a) Filter collection sampling locations, color-coded by altitude, and (b) sampling frequency versus altitude for the complete DC3 mission, with number of filters for each altitude bin given.

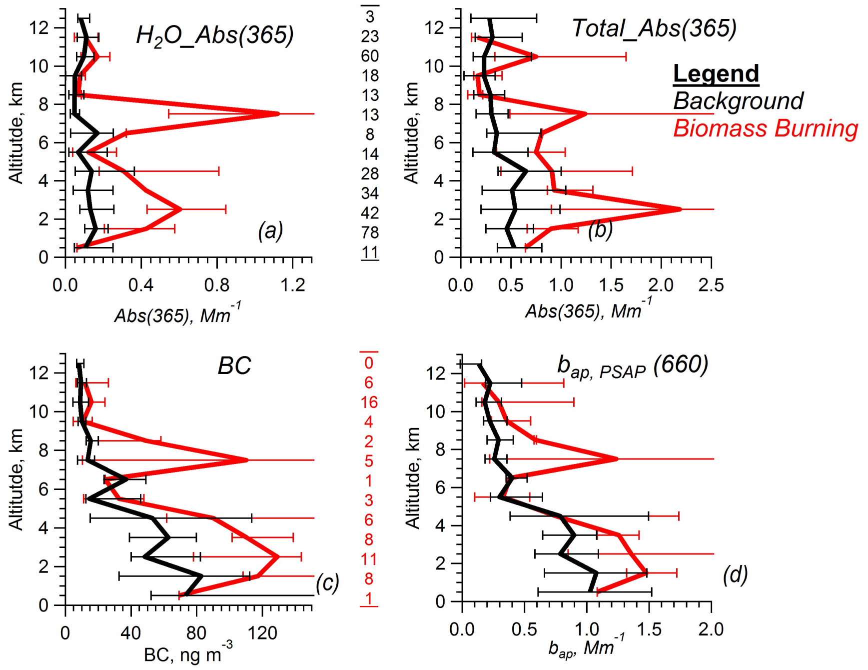

Fig. 2. Vertical profiles of absorption measured in filter water extracts and the sum of water and methanol extract (total), both at 365nm, SP2 BC concentration, and PSAP absorption at 660 nm. Data are binned into 1km ranges and the median values are shown. Error bars indicate inter-quartile ranges. The column in the middle shows the number of data points in each altitude bin, with black for background conditions (upper) and red for biomass burning (bottom row).

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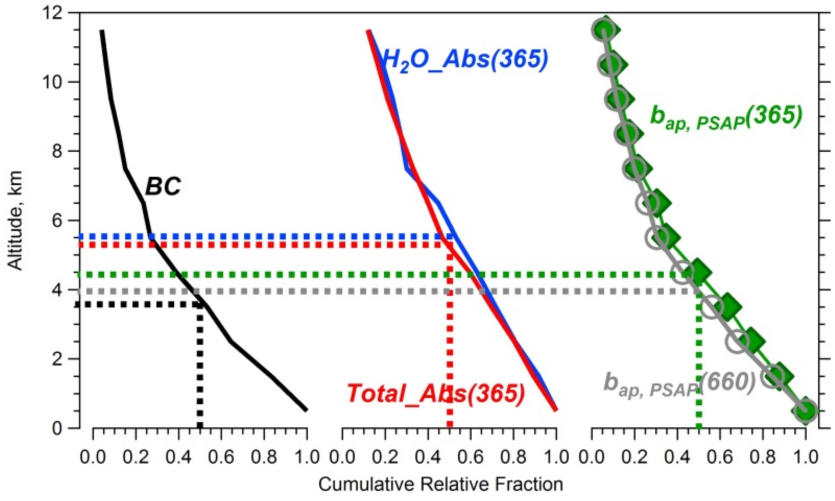

Fig. 3. Vertical profile of the relative cumulative fraction (summed over all altitudes above vs. the total column), for BC (SP2), brown carbon at 365 nm based on extract solution absorption, PSAP absorption at 660 nm, and estimated PSAP total aerosol absorption at 365 nm, during background tropospheric conditions.

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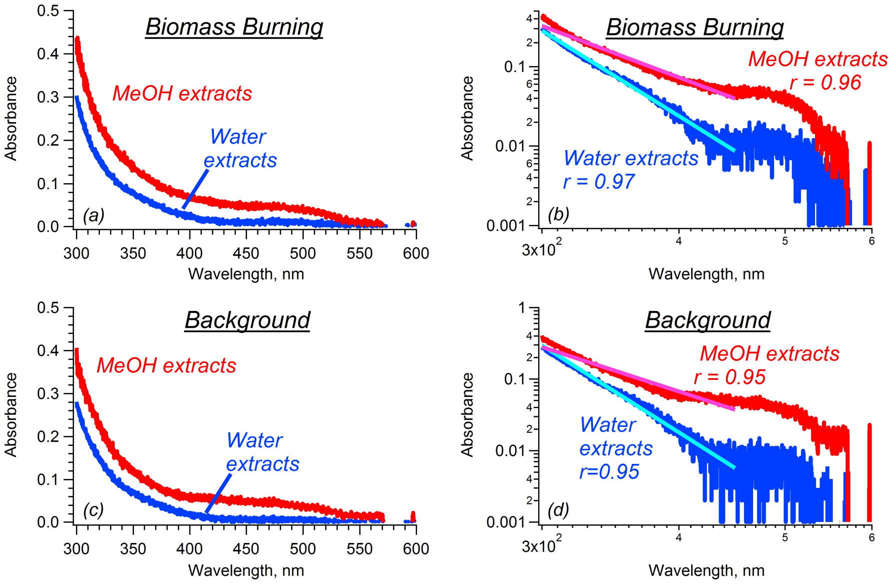

Fig. 4. Example solution spectra of H_2O and MeOH (methanol) extracts for biomass burning as well as background tropospheric conditions. Absorption Ångström exponent is calculated by a linear regression fit to logAbs vs logλ in the wavelength range of 300-450nm, with an average r value of 0.87 for water extracts, and 0.84 for methanol extracts for background data, and larger than 0.9 r value for biomass burning filter extracts, for both water and methanol.

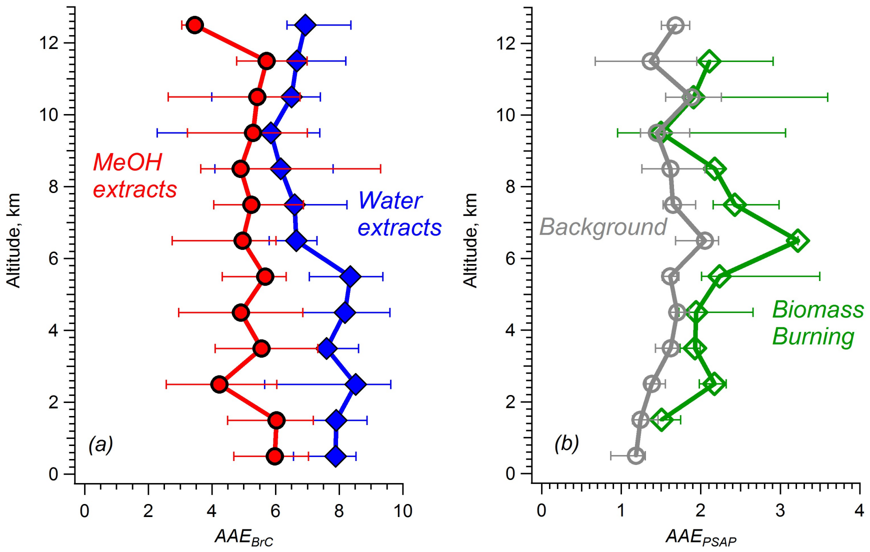

Fig. 5. Vertical profiles of Absorption Ångström Exponent (AAE) of (a) brown carbon from solution spectra of both water extracts (blue line) and methanol extracts (red line), for background conditions, and (b) PSAP absorption measurements based on the wavelength combination (470 nm, 660 nm), both background and biomass burning impacted periods. Data were binned by 1-km increments. Error bars indicated the inter-quartile range.

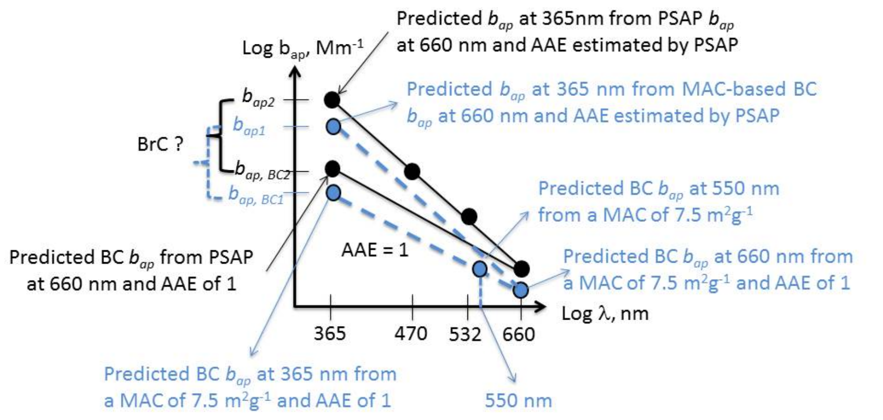

Fig. 6. Schematic of how ambient aerosol and BC absorption was extrapolated to lower wavelengths. Square data points represent PSAP measurement, which are used to estimate the ambient aerosol AAE (AAE_{PSAP}, not shown but slope of upper lines), and used to predict ambient aerosol absorption at 365 nm ($b_{ap,PSAP}$). Light absorption by black carbon ($b_{ap,BC}$) is estimated assuming an AAE_{BC} of 1 and extrapolating from the PSAP measurement at 660nm, a size where BrC absorption is minimal, or alternatively assuming a BC MAC of 7.5 m^2 g^{-1} at 550 nm and extrapolating to 365 nm with an AAE_{BC} of 1.

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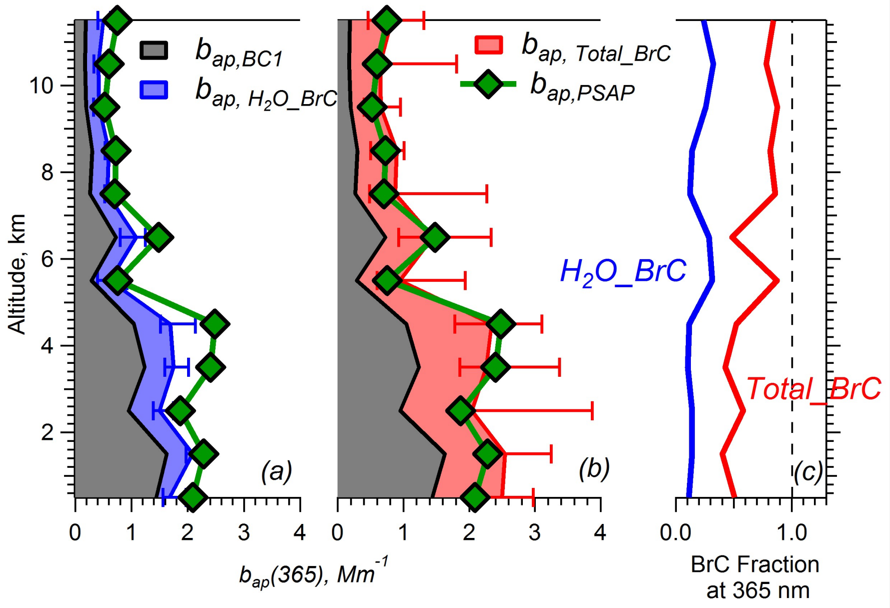

Fig. 7. Vertical profiles of estimated aerosol optical absorption at 365nm by BrC, BC, determined by an extrapolation from PSAP absorption at 660 nm ($b_{ap,BC1}$ shown in the schematic), and the sum of BrC and BC compared to total light-absorbing determined from the PSAP data. Fig. (a) shows water-soluble BrC (blue shaded), (b) the total BrC (red shaded) and (c) relative contribution of BrC to total aerosol absorption. In all plots, median values are shown and error bars indicate the inter-quartile range of estimated BrC absorption for each 1-km altitude bin. (Measurement uncertainties of the various absorption coefficients are estimated to be between ±28 and ±45%). Only background tropospheric data are plotted.

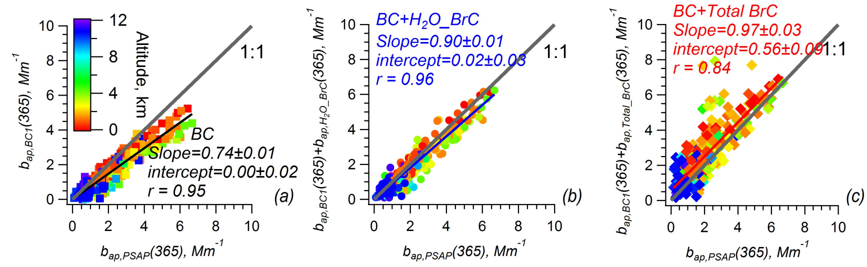

Fig. 8. Closure analysis of b_{ap} at 365 nm for background tropospheric conditions. Scatter plots of estimated (a) BC absorption, and (b) sum of BC absorption and water-soluble BrC absorption, and (c) sum of BC absorption and Total BrC absorption, compared with total aerosol absorption estimated by PSAP. Markers are color-coded by altitude. Orthogonal distance regression (ODR) fit results are shown. The 1:1 line is also included. (Measurement uncertainties of the various absorption coefficients are estimated to be between ±28 and ±45%).

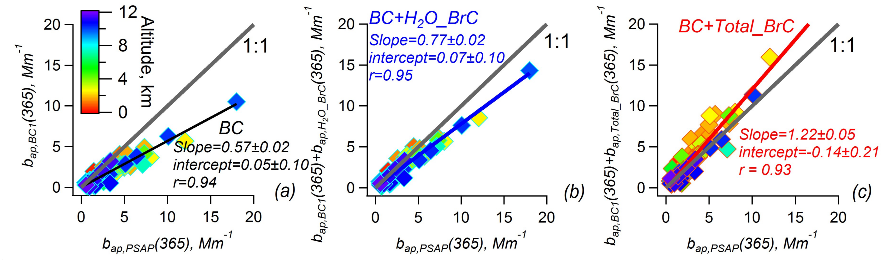

Fig. 9. Closure analysis of b_{ap} at 365 nm for biomass burning plumes via scatter plots of estimated (a) BC absorption, and (b) sum of BC absorption and water-soluble BrC absorption, and (c) sum of BC absorption and Total BrC absorption compared with total aerosol absorption based on PSAP data. Markers were color-coded by altitude. Orthogonal distance regression (ODR) fit results are shown. The 1:1 line is also included. (Measurement uncertainties of the various absorption coefficients are estimated to be between ±28 and ±45%).

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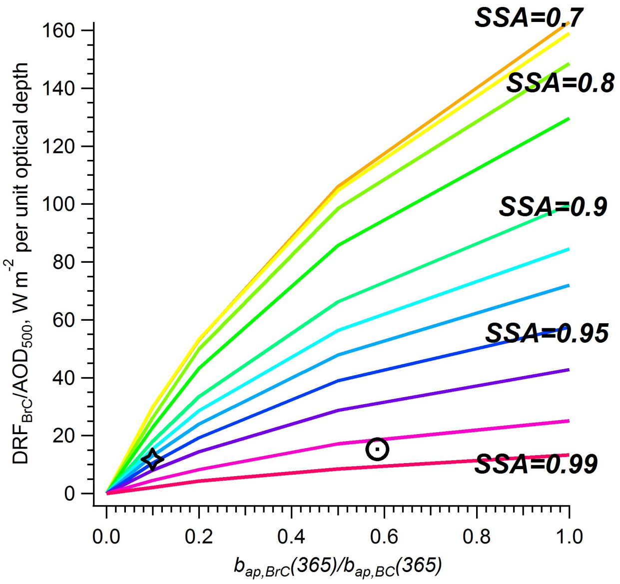

Fig. 10. BrC radiative forcing efficiencies, defined as the BrC TOA direct radiative forcing divided by AOD at 500 nm, as a function of BrC to BC absorption ratio and SSA measured at surface at 365 nm. The circle corresponds to average background conditions determined from the DC3 campaign. The star represents a surface measurement from southeast US, where altitude-resolved data were not available.