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Atmospheric
Chemistry
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Discussions

# *Interactive comment on* "Spectral absorption of biomass burning aerosol determined from retrieved single scattering albedo during ARCTAS" *by* C. A. Corr et al.

**C. A. Corr et al.**

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We thank the reviewers for their thoughtful and thorough comments, questions, and suggestions. We have responded to the general comments from each reviewer. Technical/editorial comments have all been addressed in the paper and will not be explicitly discussed here. Comments from reviewers 1, 2, and 3 will be denoted as 'RC1', 'RC2', and 'RC3', respectively. Author comments will be denoted as 'AC.'

RC1: In Tables 3 and 4, the contributions of OA to absorption are listed. Table 3 shows absorption derived from actinic flux measurements; table 4 from the scattering and absorption measurements made aboard the aircraft. Why are the absorption numbers

so different between the tables? On line 26 of page 13983, the authors state that the OA contributions [to absorption] compare well [between the two tables]. The comparison does not look very good to me. Some additional explanation is needed here.

AC: The "good" comparison refers to the trends in the PSAP data, not the percentages themselves. The percentages calculated from both the PSAP and the retrieval data indicate OA absorption is greater in the 17 April plume and is high at shorter wavelengths (as discussed on page 13983, lines 28-29). We will add a note that we are aware of the large difference in magnitude of the percentages in the text to emphasize this point. Additionally, we will reword line 26 on page 13983 to state: "Despite the possible influence of absorbing trace gases, OA contributions showed similar trends to those calculated using PSAP b(abs) values at 470nm and 532nm…" The large differences between the percentages is unclear for the same reason we're suspicious of the percentages calculated using the retrieval data (e.g., trace gases not accounted for in the spectra – page 13983, lines 11-16 and lines 20-25).

RC2: The authors state that the errors associated with the extrapolation of the AE from 2 visible wavelengths into the UV are likely small (page 13974, ln 16-28). However, the results reported in Table 2 and page 13981 (ln 5-10) show that the AAE results are much different if calculated in the visible versus the UV range. In fact, the authors use this discrepancy as a possible explanation of the very high AAEs reported in this study compared with values reported previously (page 13982). A much more detailed assessment of the errors associated with the extrapolation of the AE from the 450/550 nm pair into the UV needs to be included.

AC: The Angstrom exponent used to extrapolate AOD at 450 and 550nm to AOD at UV wavelengths was one calculated using the AOD values (i.e., "AOD AE"). As AOD (and total extinction) are dominated by aerosol scattering, enhancements at shorter wavelengths due to the presence of OA are much less pronounced than for absorption alone. Instead, variability in the AOD AE with wavelength range is much more sensitive to particle size, as evident from the work of Eck et al. (1999). Further, the sensitivity analysis of the Eck et al. (1999) data described on page 13974 (line 20-24) shows that, even for biomass burning plumes with presumably high concentrations of OA, extrapolation to 380nm using the AOD AE between 440 and 500nm reproduces AERONET AOD at 380nm within ∼3%.

RC2: Although the actinic flux measurements extend to 600 nm, SSA values were only calculated to 550 nm. The data sets were also truncated at 500 nm due to unexpectedly low SSA values below this point on Apr 17 (Fig. 3). This was attributed to low AODs. However, it would seem that low AODs would result in a noisier data set not in a systematically low error. Therefore discarding the data below 500 nm seems arbitrary. Since a major goal of the work is to present spectrally resolved aerosol optical properties, the SSA aerosol absorption determinations should be extended to include all the applicable actinic flux data (350 – 600nm) and results should not be discarded simply because they are unexpected.

AC: Low AOD does indeed result in noisier SSA retrievals, which ultimately results in systematically low mean retrieved SSA (the average of all possible retrieved SSA values, the values used in this work to determine AAE). A contour plot of actinic flux as a function of SSA and AOD is shown in Figure 1 of this response (also attached as a supplement). As can be seen in Figure 1, as AOD drops below 0.1 (even 0.15), actinic flux approaches a constant value: the actinic flux under aerosol-free conditions. At these low AODs, changes in actinic flux are much less sensitive to changes in aerosol properties, including SSA. This means that for a given AOD, there are more possible SSA values that could produce the same actinic flux value in TUV. This increases the range in retrieved SSAs. As the range in SSA increases, the mean SSA approaches 0.75, or the average of all possible SSA values examined here (0.5-1.0). While this value could be higher than retrieved SSA values in other plumes (e.g., plumes with a lot of BC), for the 17 April biomass burning plume, 0.75 is lower than the ∼0.8-0.9 retrieved at wavelengths less than 500nm. In order to clarify this in the text, a more detailed discussion on the relationship between AOD and actinic flux and a description

of Figure 1 will be included. This will be inserted in the discussion of the tailing (page 13979, lines 14-24).

RC2: Aerosol absorption (Fig 5) is calculated from the SSAs and aerosol extinction (Equation 4). How was aerosol extinction calculated? If extinction was calculated by using the AEs from the 2 visible wavelength pairs, (as in page 13974, ln 6-9), how does this bias the results, especially in the UV?

AC: As with AOD, extinction was calculated by extrapolating to UV wavelengths using the extinction Angstrom exponent. Similar to the AOD AE discussed above, the extinction is much more influenced by scattering (as evident from SSA values larger than 0.5 retrieved here) and is therefore more influenced by particle size than composition. Significant deviations from the 450-550 extinction Angstrom exponent are therefore unexpected.

RC2: The authors state that "the b(abs) values in the UV wavelengths are much higher than those calculated at the visible wavelengths. . ." How was this determined? Were values simply averaged over the entire range (350-400nm; 400-500nm)? If so how were the sharp bands attributed to interferences treated?

AC: b(abs) values calculated for 350-399nm were averaged and compared to b(abs) averaged over 400-500nm to examine the broad spectral characteristics of b(abs). This was done in part because of the high frequency variability in question. It is unclear whether these sharper features in spectral b(abs) (Fig 5) are, in fact, due to additional gas phase absorption not presently accounted for or if they are related to instrument variability or non-aerosol/non-gas absorption bands inherent to the solar spectrum (e.g., Fraunhofer lines). For this reason, no attempt has been made to remove these dips or to correct the AAEs for them. Since the AAE fit is a linear fit in log-space through all the data, removal of these spikes is not expected to change the AAE values greatly. A quick check was performed on the April 17th case to confirm this. When all major spikes were removed in this instance, AAE decreased from 6.78 to 6.32.

RC2: The absorbance plots in Fig. 5 seem to have an enhanced absorption appearing as a broad band from 410-455 nm in both events. Is this considered real? How does this affect the calculation of AAEs?

AC: It is difficult to say whether the apparent enhanced absorption between 410-455nm is real or just an illusion caused by the sharp decrease that precedes it (∼410nm). Regardless, it appears to be negligible compared to the overall spectral trend in b(abs) and thus would not significantly impact the calculated AAEs. A decrease in absorption over this band would act to increase the AAE, though again, this increase would likely be small.

RC2: It can only be assumed that the Retrieved AAE reported in Table 2 is calculated across the entire wavelength range of Fig 5 (350-500nm), although this is not explicitly stated. How was this determined? Were all data used exactly as shown in Fig 5? What AAEs are obtained from the data sets if only absorbances at 450 and 550 nm are used - analogous to the PSAP calculations? 470/532 (Table 2)? 470/660 nm (Table 2)? Table 2 should be expanded to include AAEs calculated for different wavelength ranges including those used by other authors (page 13981 - 13982). Standard deviations and goodness of fit (r2) of the logarithmic plots should also be included in the Table.

AC: AAE was calculated as the slope of a linear fit to a plot of ln(wavelength) versus ln(b(abs)). This fit included all b(abs) values between 350 and 500nm (as in Fig. 5). This will be stated prior to the discussion on the AAE values (page 13980, ∼line 27). While we appreciate the suggestion to include a direct comparison between the PSAP AAE values and those determined from retrieved b(abs), we feel such a comparison would not be meaningful. As discussed on page 13979 (lines 14-24) and in above comment responses, it is unclear how reliable the SSA data above 500nm are due to the decrease in AOD at these wavelengths. For this reason, b(abs) at wavelengths greater than 500nm have not been calculated. Therefore, we feel there would be considerable uncertainty in two-wavelength AAEs that rely on b(abs) at wavelengths greater than 500nm and that reporting such values would not improve the current conclusions. Additionally, as demonstrated in numerous SSA and AAE retrieval studies (e.g., Bergstrom et al., 2007, Marley et al., 2009, Russell et al., 2010), aerosols have a broadband absorption signature in radiometric datasets. Therefore, in order to truly capture aerosol spectral absorption, AAE calculations from radiometric data are performed using a fit to a number of wavelengths rather than just using different wavelength pairs. This is at least in part due to the “unexplained” high frequency variability seen in results from retrievals using radiometric datasets (especially actinic flux as discussed in this work). Such non-aerosol absorption may result in falsely high (or low) AAE values depending on the wavelength chosen.

RC2: The retrieved AAE reported for Apr 17 is very high (6.78)!! Values this high have not been reported for whole aerosols. Although AAEs greater than 6 have been reported for water soluble species extracted from biomass burning aerosol samples, these extracts were composed primarily of humic-like substances, which have been estimated to be 35% of the whole aerosol and the AAEs for the whole aerosol samples from which they were extracted were much lower ( 3). The retrieved AAE for Jun 29 (3.3) is more in line with those reported previously in both fresh and aged biomass burning plumes. The aerosol absorbances reported for Apr 17 were a factor of 10 lower than on Jun 29 and showed strong high frequency variations in the UV which would not be expected for absorption due to aerosols. The authors attribute this variance to absorption by atmospheric gasses. Whatever the reason, these interferences render the very high retrieved AAE for Apr 17 suspect. If the lines observed in Fig 5 on Apr 17 are indeed absorption from interfering gasses, an attempt should be made to identify and remove them or at the very least report the AAEs +/- one sigma.

AC: We agree that the high values retrieved for 17 April are suspicious as we note on page 13981 (lines 17-27). However, very high AAEs (∼7-11) have been reported by Chen and Bond (2010) for methanol extracts of biomass burning aerosol, which, according to their figure 4, include nearly 100% of the initial OC. Further, as noted above, the removal of the largest “dips” in the spectral b(abs) only reduced the AAE by ~7%, suggesting the high frequency variability plays a minor role in the AAE. It should also be noted that these AAE values were determined for plumes with significant contributions from biomass burning OA (see Fig. 2), rather than "traditional" whole aerosol samples which are likely more diffuse and influenced by background aerosol. Nonetheless, the retrieved AAE for 17 April is much higher than those retrieved or measured for other ambient biomass burning aerosol and should indeed be interpreted somewhat cautiously. This will be stated more firmly following the discussion of the 17 April AAE (page 13981, ~line 27). Additionally, uncertainty associated with the AAE values as a result of uncertainty in the SSA retrievals as well as the r-squared values will be reported.

RC2: The contributions of OA to the absorption profiles were determined by subtracting a 1/wavelength profile extrapolated from absorbance at 660 nm determined by the PSAP. This assumes no absorbance at 660 by OC. Is this assumption valid? The AAEs reported from the OC absorbance profiles for Apr 17 (Fig 6) are unreasonably high (9.59 for the UV and 7.56 for the visible). What are the standard deviations and r2 for these results? Using this same procedure for the PSAP measurements, what would be the b(abs) for OC at 470? 532?

AC: OA is noted to be strongly scattering at most visible wavelengths as evident from measurements of aerosol optical properties of biomass burning aerosol at visible wavelengths (e.g., Abel et al., 2003). Given this, absorption by OA at 660nm is expected to be small. However, as Review 3 highlights, the internally mixed nature of most particles complicates this assumption. Therefore this method should be taken as a means to simply estimate the contribution of OA to absorption, rather than provide an undisputed actual contribution. This point will be made more clear on page 13983 (lines 1-6). Additionally, error and r-squared values for these OA-only AAE values will be included in the discussion.

RC2: How were percentages in Tables 3 and 4 calculated? Do the numbers represent averages of the absorbances over the entire wavelength ranges (350-399nm; 400-

500nm)? Since the absorbances vary according to the AAEs, averages over a wide wavelength range are meaningless. Tables 3 and 4 should be combined and values reported only for single wavelengths, or narrow wavelength ranges, with standard deviations included. Also, a direct comparison should be added between retrieved data and that calculated from the PSAP measurements, both at the same wavelengths.

AC: The percentages were calculated by averaging the contribution of OA to total absorption in the UV range (350-399nm) and visible range (400-500nm). As these b(abs) values were calculated using AAE determined from a linear fit through all the data, the dependence of b(abs) on the wavelength range used to calculate AAE, should be minimal. Indeed, if the AAE were to be extended to longer wavelengths, it is likely the magnitude of the contribution of OA to total absorption would decrease. However, the OA contribution would still be greater in the UV than visible. This is supported by the similar trends seen in the PSAP data. Tables 3 and 4 will be combined. For reasons mentioned above, narrower bands and single wavelengths (e.g., those associated with the PSAP) are not necessarily useful to examine trends in absorption data retrieved with radiometric datasets. As such, they will not be added to the combined Table 3.

RC2: An attempt is made to correlate enhanced UV absorption and higher AAEs by calculating the extent of OC oxidation (OSc). However, values reported from +0.3 to -.4 on the 2 events have little meaning without previous results for comparison. A better approach would be to compare AAEs with EC/OC measurements or OA from the AMS.

AC: Currently, O/C ratios estimated from the AMS are discussed along with of the oxidation state values to provide context for the oxidation state values (page 13985, lines 22-26). Additionally, OA/BC ratios are presented on page 13984 (lines 4-6). EC/OC measurements were not made aboard the DC-8 during ARCTAS. Table 5 (to be Table 4 in the revised manuscript) will be modified to include both O/C ratios and OA/BC ratios to improve the visibility of these more commonly used parameters and to better provide context for the oxidation state values.

RC2: The paper should be shortened, focusing on the results as an example of obtaining aerosol absorption from actinic flux data with a more in-depth error analysis and detailed comparison to in-situ measurements as a means of validating the results. Omit the attempt to predict the extent of aerosol oxidation (Table 5; section 4.2) or aerosol composition as this is not substantiated by the data as presented.

AC: While we appreciate this suggestion, we respectfully disagree. We recognize the limitations of this work in that significant conclusions cannot be made from the results of two case studies as noted on page 13987 (lines 19-20). However, we do not feel our results are simply coincidental and have no value. As it is currently presented, this work highlights a potentially interesting connection between aerosol aging/oxidation and spectral absorption, one that we feel should be further explored by the atmospheric research community. We will emphasize this point in the final manuscript rather than absolute results. Additionally, a more in depth error analysis will be included in the discussion and/or tables.

RC2: Table 1 is difficult to read and should be expanded for clarity. In-plume and profile means should be listed in separate columns. List ranges instead of deviations, again in separate columns. Add distance of aircraft travel and number of points averaged. It would also be helpful to include any EC/OC results, and measurements of greenhouse gasses expected to be interferences (O3, NO, PANs, CH4).

AC: Table 1 will be expanded and ranges of values will be substituted for deviations. As spiral profiles were used in this analysis, there is no net horizontal aircraft motion, as described on page 13974 (lines 5-6). With the exception of O3, interference from greenhouse gases is not expected over the wavelength range considered here (350-500nm). However, concentrations of both NO2 and O3 can be included, though it should be noted that only column concentrations are used in the retrieval as discussed on page 13973 (lines 19-27).

RC2: Include PSAP measurements of absorption in Fig 5.

AC: PSAP b(abs) at 470nm will be included in Fig 5. for comparison. PSAP b(abs) at 532 and 660nm are outside the range of retrieved b(abs) for reasons mentioned above and will not appear in Fig. 5.

RC2: Figs 6 and 7 (log axis) are difficult to reconcile with Fig 5 (linear axis). Portions of the data have been omitted without explanation. The AAEs calculated from these data should be accompanied with standard deviation and goodness of fit criteria.

AC: Data should not have been omitted from the total b(abs) curve in Figure 6 and will be fixed. For 17 April, the subtraction of the b(abs,BC) extrapolated curve from the total b(abs) curve resulted in negative values of b(abs, OC) around the sharp dips in the total b(abs) curve. Due to their unphysical nature, these values were converted to 'NaN' in order to determine the AAE as a linear fit to a plot of ln(wavelength) versus ln(b(abs)). This will be explained in the text discussion of Fig. 6 as well as in the Fig. 6 caption. Figures 6 and 7 will be converted to a linear scale to be more visually compatible with Fig. 5.

RC3: pg 13978, line 22 - what are "non-aerosol spectral features inherent.." ?

AC Non-aerosol spectral features inherent to actinic flux measurements include Fraunhofer lines, sharp absorption lines produced from absorption by elements in the solar atmosphere. These features were referred to on page 13976 (line 26) but another reference will be added to the above sentence for clarity.

RC3: The decrease in SSA from 500-550 nm in Figs 3 and 4 is hard to understand. The authors discuss the possibility of the effects of a low AOD (for the April 17th case). This is actually a common problem as the AOD falls off considerably with wavelength. Perhaps the authors could come up with an estimate of the error in the SSA due to low optical depths.

AC: A similar issue was highlighted by Reviewer 2 and is addressed above. We propose clarifying this feature and its possible relationship to AOD by discussion of Figure

1 in this response, but do not intend to add this figure to the revised manuscript.

RC3: Subtracting off of a 1/wavelength absorption to estimate the absorption due to OC while not necessarily a bad idea, ignores the fact that most of the particles are made up of BC and OC in some combination. Thus, this is just a technique to estimate the effects of OC. (Also, Arola et al., might not be the best reference – Yang, M., Howell, S. G., Zhuang, J., and Huebert, B. J.: Attribution of aerosol light absorption to black carbon, brown carbon, and dust in China - interpretations of atmospheric measurements during EAST-AIRE, Atmos. Chem. Phys., 9, 2035–2050, doi:10.5194/acp-9-2035-2009, 2009 – might be better)

AC: We agree and will be sure to better emphasize that the OA contribution to absorption is an estimate, rather than ground truth. We will examine and likely include a reference to Yang et al. (2009).

RC3: I'm not a chemist but it seems to me that the AAE for organic aerosols is a function of the type of burning conditions more than aging. That's not to say that there aren't any effects of aging but in a cold, relatively dry atmosphere in the northern latitudes it seems unlikely. Again the AAE will be sensitive to the low AOD.

AC: Based on the plume sources discussed on page 13978 (lines 4-8) it is assumed the fuel type in both cases is boreal forest material which would make for similar burn conditions. However, as reported in Hornbrook et al. (2011), there are slight differences in the modified combustion efficiencies (MCE) determined for the two plumes; the 17 April plume has a higher MCE (0.97 +/- 0.02) than the 29 June plume (0.918 +/-0.009) suggesting the 29 June plume may have been produced from a slightly more smoldering fire. While these differences in burn conditions could certainly impact the AAE, they can still not explain the differences in the two cases. As shown in McMeeking et al. (2009), fires with lower MCE are associated with greater OC emissions than those that are pure flaming. It would therefore follow that the 29 June plume should actually have a higher AAE than a boreal forest fire plume of the same

age produced under more flaming conditions. In other words, if no processing of the 17 April plume has occurred, we should see a higher AAE on 29 June than on 17 April. As this is the opposite of what we see, we feel aging/oxidation is the best way to explain the differences in AAE.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/12/C6757/2012/acpd-12-C6757-2012-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 13967, 2012.

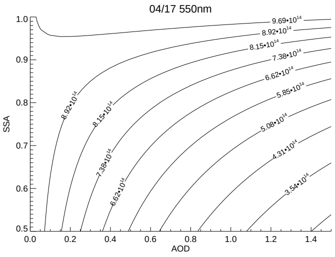

**Fig. 1.** Figure 1. Actinic flux as a function of SSA and AOD.