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Discussions

Interactive comment on "Measurement of size dependent single scattering albedo of fresh biomass burning aerosols using the extinction-minus-scattering technique with a combination of cavity ring-down spectroscopy and nephelometry" *by* Sujeeta Singh et al.

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REFEREE COMMENTS: The author should go over and recheck every single reference that they site, and make sure it is sited correctly. The introduction includes at least 5 references which were sited either wrong or in a misleading way. P3 line 105-109: This sentence implies that, Riziq et al., 2007;Riziq et al., 2008 and Dinar et al., 2008 were using extinction minus scattering technique alternatively measuring both extinction and scattering. These 3 papers where measuring only extinction using the

CRD, and retrieved the scattering/abortion via Mie theory calculation. Same comment applies to the flowing 2 references Butler et al., 2007; Miller and Orr-Ewing, 2007. The authors claim that these papers measure the SSA of isolated aerosol particles. However, both the Butler et al., 2007 and the Miller and Orr-Ewing, 2007 were measuring/determining only the extinction of light by single aerosol particles. Additionally, this paragraph is almost an exact copy of a paragraph in the group's previous paper (Singh at al., 2014 aerosol science and Technology, page 1345 last paragraph).

AUTHORS RESPONSE: We thank the referee for pointing the errors in the references: we are checking all the references to make sure citations are relevant and appropriate in the final manuscript.

Regarding Page 3 line 105-109, the authors don't feel this at all implies what the referee concluded. We only stated that they used the extinction minus scattering technique, but we didn't state they measured both extinction and scattering. However, to avoid confusion and in response to the comment the paragraph will be modified in the revised manuscript, and will read as:

"The extinction-minus-scattering technique has been used for airborne ambient measurements (Hallar et al. 2006), for studies involving optical properties of biomass aerosols and humic- like aerosols using CRD for measurement of extinction and Mie theory calculations to determine scattering and absorption (Riziq et al. 2007, 2008; Dinar et al. 2008), and for determining the extinction of isolated aerosol particles (Butler et al. 2007; Miller and Orr-Ewing 2007)."

REFEREE COMMENTS: Same comment for the paragraph stating at P4 line 132-140, is almost identical to a paragraph in p 1346 in Singh at al., 2014). The authors should address these issues.

AUTHORS RESPONSE We will revise the paragraph and refer the readers to the earlier paper for details. The paragraph will be revised in the manuscript and will read as "Details of the experimental method and derivation of key equations for particle optical properties and CRDS analysis have been described by Singh et al. (2014) and references therein. Here, we only summarize the main points and encourage the reader to see the reference cited for details. The key equation for CRDS measurement is the extinction coefficient αext (m-1) is defined by Equation 1

Where cair is the speed of light in air and RL is the ratio of mirror-to-mirror distance d to the length of the cavity occupied by the sample, resulting in a unitless value >1. The ring-down time is τ0 for an empty cavity and τ in the presence of a sample. Extinction coefficient is the product of the cross section ïĄşext (m2/particle) and number density of particles NCRD (particles/cm3) in the CRD cavity. A unit conversion factor has been omitted for simplicity." REFEREE COMMENTS: P12 line 416-418: The Beyersdorf, 2013 reference is not a peer reviewed paper, this data was presented after the flight and represents very preliminary data from a meeting. The authors should remove this reference.

AUTHORS RESPONSE The authors are aware that this was a preliminary meeting presentation, but would like to keep the reference and change the text in the manuscript as below:

"In preliminary data presented in a meeting following NASA measurements during SEAC4RS, involving in situ sampling of the smoke from the Yosemite Rim Fire, the initial SSA of smoke was 0.92 and increased in the first 0–7 hrs. to 0.96, and was nearly constant after that (up to two days)." In the references it is cited as a meeting presentation. Sadly, no Rim Fire results on aerosol optical properties have been published from a peer-reviewed source; the closest being a publication that focused entirely on molecular emissions from the Rim Fire (doi 10.1016/j.atmosenv.2015.12.038).

REFEREE COMMENTS: P6 lines 202-204: The author's state that, the samples were diluted and sonicated prior the introduction to CRDS and nephelometer, they also report that the size distribution changed after nebulization. Was this size distribution change a result of just atomizing problems, or is it a change in morphology or/and

chemistry? The authors need to address this question as part of this paper's framework. The authors claim that their measurement would represent fresh soot that has undergone cloud processes, however sonication and atomization may or may not, change the soot's morphology. If the authors wish to make this statement, it should be supported by measurement (e.g. electron microscopy). Chemical analysis is also required to make any statement about this measurement. Does this measurement represent coated particle or un-coated aerosols? The authors clearly state in p15 lines 537-538, that composition and morphology, have the most significant effect on fresh BB aerosols. While, these properties are indeed dependent on the burning stage particle size fuel type and condition; one needs to show that these properties do not change in water solution and atomization/ solicitor. The authors mention that a future work will be addressing changes in the mixing state and morphology, these issues should be addressed as part of the current manuscript.

AUTHORS RESPONSE We believe the change in the size distribution is mainly a result of an atomizing problem though change in morphology cannot be ruled out. The re-aerosolized particles will likely have a near spherical core-shell morphology. The samples were kept in distilled water and not exposed to the environment. As we stated in our previous response to a similar comment, we have several reasons for comparing our values to fresh BB soot. While some changes in the particle size distribution were observed upon impingement, this sampling scheme (or, really, any offline sampling scheme) is unlike any natural atmospheric processing. No photochemical changes were allowed to take place. The system would be too dilute for SOA formation via acid chemistry. Semi-volatile species would be almost immediately put into the condensed phase, though solubility would be a more important factor in determining their interactions with the particulate phase. As indicated in our previous response, further clarification on these issues will be included in the revision.

Addressing changes in morphology upon impingement and re-aerosolization, along with changes due to atmospheric aging, is no small task. We are in the process of building an indoor smog chamber. The characterization of this chamber and conducting optical and chemical properties measurements will probably take another year to address, and will result in at least two distinct publications. For considerations of time, publication length, and narrative flow, the authors do not believe these requests are feasible for the current manuscript. The authors are more than willing to revisit the conclusions of this paper when future results become available.

REFEREE COMMENTS: When comparing to their results to literature values, the authors refer to the MCE as an explanation for agreement/disagreement with the literature values. For example: 1) p11 line 394, 2) P13 line 436. However, the MCE was not measured in this work. This makes the [comparison] to [literature values] be very speculative.

AUTHORS RESPONSE The authors are examining their results in light of what is currently known about SSA and AAE of BB aerosols. Not to do this would be negligent. Specifically, there are schemes that relate SSA and AAE to either MCE or EC/(EC+OC). If these schemes are robust, new data should also fit within their trends. The authors disagree that this comparison is speculative. Indeed, this is, essentially, a “two equations, one unknown” problem. The two equations are trends (relationships) of SSA with MCE and AAE with MCE (or with EC/(EC+OC) in Pokhrel’s case). The unknown, MCE or EC/(EC+OC), can be solved precisely.

REFEREE COMMENTS: Also how could the authors show difference between fuel types without making sure that similar MCE is shown for all cases?

AUTHORS RESPONSE While the authors are attempting that level of control in future work, no work to date has tried to control MCE. But what gives rise to differences in MCE? The authors state, in the manuscript, that it is influenced by fuel type, fuel state, and burning conditions. Examples can be found on line 27 of the abstract and line 524. It is likely that MCE is varying with fuel type, and that these are not independent variables.

REFEREE COMMENTS: I agree with P.Pokhrel comment claiming that: “They concluded burn condition does not control the SSA and AAE and mention as a one of the major findings in abstract but have not tested SSA and AAE correlation with either MCE or BC/OA ratio.” The authors responded that they are currently working to address these important aspects of BB aerosols, including chemical analysis and optical properties as a function of aging using an indoor smog chamber in forthcoming work, this should be done (at least partially) as part of this manuscript framework.

AUTHORS RESPONSE: The authors, in their response, went on to state that at no time did we conclude that combustion conditions and MCE have no effect on SSA or AAE. If the reviewer could point out where in the manuscript this was stated (either explicitly or implied), the authors will rectify this misunderstanding. However, the authors are unable to find such an occurrence.

The sample at issue is mainly white pine. It exhibits the following properties, based on Figures 1 and 4 of Pokhrel et al.:

1. The AAE is high, suggesting EC/(EC+OC) and MCE are low 2. SSA values are low, suggesting EC/(EC+OC) and MCE are high 3. There is a lack of SSA spectral dependence, suggesting EC/(EC+OC) and MCE are low Even if the authors were to measure MCE or EC/(EC+OC) for white pine, it cannot have an MCE both above and below 0.92 or an EC/(EC+OC) both above and below 0.2. It is either at the high end or the low end where the relationships of Liu et al. and Pokhrel et al. do not work well with our white pine observations.

That being said, further explanation is clearly warranted in the manuscript. The authors would have liked to provide a graphical comparison of our results with FLAME-4 results, but we were unable because Liu et al. did not provide their raw data used in their figures. However, Pokhrel et al., thanks to the encouragement of ACPD, did provide their data. While Liu et al. and Pokhrel et al. plot SSA and AAE against MCE, EC/OC, and EC/(EC+OC), neither publication plots SSA against AAE. We have done so here and Figure 1 and accompanying discussion will be included in the revised manuscript:

"As can be seen in Figure X, many of our measurements inhabit a distinct location in AAE/SSA space. The AAE is higher and the SSA is lower than most FLAME-4 observations. Part of this difference may be that previous measurements were done for the entire burn and all diameters below 2.5 μm, whereas measurements in this work were segregated by size and burning stage. When both data sets were combined and fit to a power law function, the y-offset increased and the fit had greater power dependence."

REFEREE COMMENTS: Same comment applies to the any of the possible explanations given in the last paragraph of p 13 (lensing, volatilize low molecular organics.) This explanation should be supported by some chemical analysis

AUTHORS RESPONSE: As stated in the last sentence, the aim of that paragraph was not truly an explanation of results. Indeed, we don't discuss our results at all in the paragraph. We are exercising due diligence, and mentioning potentially important effects that we could not constrain at the time this data was gathered. We will attempt to clarify this point, earlier in the paragraph, in the revised manuscript.

REFEREE MINOR COMMENTS: 1) The author could address the multiple charged particles issue, by performing a multiple charge corrections (see for example Flores et al., 2012 ACP)

AUTHORS RESPONSE The authors would like to thank the reviewer for reminding us of this factor. In earlier work on monodisperse polystyrene, it was not an important factor. While it's certainly possible for the authors to calculate the contribution of multiply charged particles, it is not altogether clear how it would be used. Flores et al. and many others need to account for particle size because of their use Mie theory fitting to determine RI. For 300 nm particles, the SSA of 400 nm particles could potentially approximate to the 424 nm particles that would have double the geometric cross section with twice the charge. However, there is not enough available information (measure-

ments of SSA and AAE at 566 and 707 nm diameters) to adjust the 400 or 500 nm particles. We will mention this in the "due diligence" paragraph, and will discuss its potential impact for the 300 nm particle case, where such an assessment can be made. Most troubling is the mention of "errata" by Flores et al. concerning the original paper by Wiedensohler, even though the authors were unable to locate any such errata.

REFEREE COMMENTS: 2) For all of the figures: please make sure all of the figures are consistent and clear. For example: The font size is different in every single figure. Figure 1: The drawing is cut on the left, figure 11: there is an axis on the right size (but other figure are open).Comparing figure 9 to 10: There have the same x –axis but one start with the actual Number 500 and doesn't have minor ticks. Figure 11: the number 0.6 is cut, the legend is 'smooshed' etc.

AUTHORS RESPONSE The figures will be corrected to address the concerns in the revised manuscript.

REFEREE COMMENTS: 3) Please provide an explanation to changes of the SSA with the particle size, for example: why is the Cedar smoldering 500nm has a lower SSA than the cedar smoldering 400nm?

AUTHORS RESPONSE We did respond to the similar comment by P. Pokhrel. It is likely that at small particle diameters, such as 300 nm, EC has a greater contribution to the particle mass than OC, giving rise to lower SSA values for the smoldering stage of this fuel at this size. To make up for this, larger particles could have a greater contribution of OC, resulting in its greater abundance in PM2.5. This is consistent with the larger observed SSA values for larger diameter particles in the smoldering stage of cedar combustion.

SPECIFIC COMMENTS AND RESPONSES: 1) Figure 4: This figure is very confusing and difficult to follow, please make it more clear.

AUTHORS RESPONSE The figure will be modified for clarity and the caption will be more descriptive in the revised manuscript as below:

“Figure 4- The flow of the calculation for determining average values of σext, σscat, ω, and their errors. Variables with an asterisk represent individual measurements. σext for each experiment is derived from the αext and the number density within the cavity, via Equation 1. This number density is found using Equation set 3. The standard deviation of σext for each experiment is found using Equation 2. The RSD of σext for each experiment is found, averaged, and multiplied by the average σext to get the average standard deviation of σext. αscat for each experiment is corrected and σscat is found using the number density in the nephelometer. This is averaged and its standard deviation found from the run-to-run variability of σscat, the RSD of NNeph, and the correction factor error. The RSD of αscat is based on the run-to-run variability of αscat and the correction factor error. The SSA of each run is based on αscat and αext for each run and the number density relationship. This is averaged, and the run-to-run variability of SSA determined. This variability is used, along with the RSD of αscat and αext, to determine the SSA error.”

2) P8 line 255: Please change the period to comma. Avoid using ‘and’ after the period.

Change will be made in the manuscript.

3) P9 line 308: please add reference

The reference is added.

4) P9 line 313: “particles that have the same electrical mobility, but different mobility diameters were separated” This sentence is not clear did the authors mean: same electrical mobility but different mass selection?

This statement is correct. Mass of the particles is proportional to the product of the electrical mobility and mobility diameter and inversely proportional to the drag coefficient, which is also a function of the mobility diameter.

5) P9 lines 321-323: The authors state the SSA has a slope of zero over the range of

500-680nm, however the x-axis in the figure ends at 660nm. Please add the missing data to the figure.

The data was taken from 500-660 nm, 680 was an error. It will be corrected.

6) P12 line 405: please change Lewis to Lewis et al.,

This is done.

7) P12 line 406: please add reference

This was the same reference cited on line 405.

Figure Caption

Figure 1: Results of this work compared to FLAME-4 results (Liu et al, 2013; Pokhrel et al., 2016). A power law fit was performed in the form of AAE = a + bâĂćSSAc was performed for FLAME-4 and combined data. For FLAME-5, a = 2.402±0.296, b = 5.298±0.587, and c = 28.53±8.42. For the combined data set, a = 2.852±0.187, b = 4.961±0.599, and c = 36.965±11.300.

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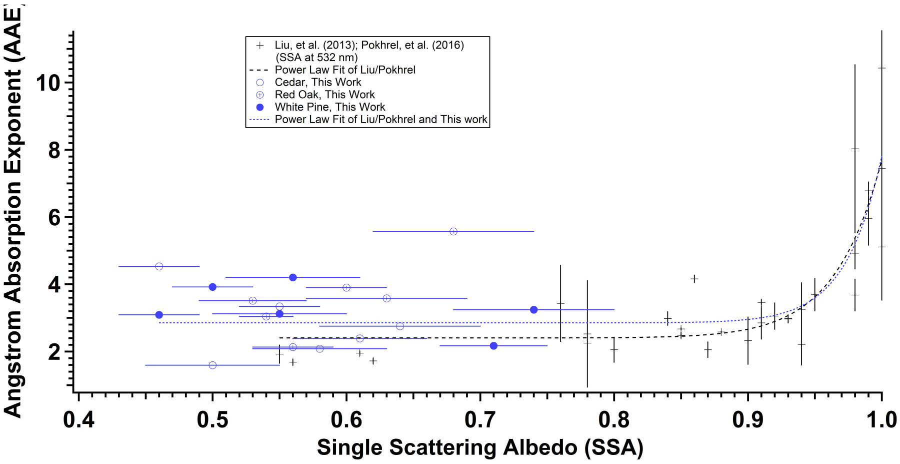

Fig. 1. Figure 1

$$\alpha_{ext} = \frac{R_L}{c_{air}}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right) = \sigma_{ext} N_{CRD}$$

Fig. 2. Equation 1