We thank the reviewers for their extremely insightful suggestions. Based on the reviewer's comments we've made substantial changes to the manuscript including modifications to the data analysis and conclusions. We have also made changes to the title and abstract and provided a more robust uncertainty analysis. We have made modified the conclusions of the manuscript and are not purporting our findings as correction factors any more. Many studies which are now referenced in the updated manuscript have used such "correction factors" without regard to artifacts associated with individual system biases. We believe this manuscript provides the necessary critique for the use of such factors and elaborates upon AÅE based artifacts in solvent extract measurements which has not been actively studied in past work in this field.

Below are our responses to specific concerns brought up by the reviewers:

Reviewer 1:

In Fig. 2a and 4a (which are related), the data to me seem to just show a step function for the water extracts. There are a subset of measurements where the OA/bulk are relatively low and then a step up to a bunch of measurements with higher ratios. This does not look like a power law to me at all. Also, what should I make of the measurements where OA/bulk = 1? The authors have made a case that the particle/solution difference should give a minimum difference of a factor of 2 (if extraction were 100%).

We had considered the use of a step function over a power law, the reason for selecting the power law fit was to keep the equation consistent through all regressions. It would appear that a step function is better than the power law for the water extracts, but the gradual slope with OC/TC ratios and SSA is more prominent in the methanol and acetone extracts. In addition to this, the root mean square error (RMSE) values for the power law fit were consistently lower than their step function counterparts. The power law fit can also mimic a step function with a steeper slope and can also have a curve with a gradual slope depending on the value of the power law exponent. None of our OA/bulk values for water were below 2, hence we had suggested a range from 2 to 11 for water extracts, and 1 to 4 for methanol/acetone extracts. We realize now that touting these as correction factors without measurements for extraction efficiency and particle size distribution would be misleading and have removed these suggestions all together.

L47: The authors should decide whether this statement is in reference to observational studies or model studies and cite accordingly. They mix observation with model here, making it less clear what their point is. If observational, they should cite the now famous Kirchstetter paper.

The citation has been added and all citations are now referencing observation studies

L52: The authors might consider citing the work from the Heald group and from Saleh. They will find the list of studies that intentionally include absorbing OA is rapidly increasing.

Citations have been added and the sentence modified from "have a few global modeling studies…" to "have global modeling…"

L56: Suggest changing to "ideally excludes. . .EC." It is possible that EC can break through filters and impact measurements. See the work by Geoff Smith (Phillips and Smith, AS&T, 2017).

The sentence has been changed. The authors were familiar with the AS&T paper by Phillips and Smith, and avoided ultrasonication of the filters to prevent mechanical dislodging of deposited BC aggregates

L57: I strongly suggest modifying this statement about this being a "good" analytical method to state right up front that it does not measure "only the OC absorption spectra." It measures the absorption spectra of the OA that is extracted into the solvent. If the method were "good" and measured "only the OC absorption spectra" then there would be no dependence on solvent (or pH).

The original intent of using different solvents in our experiments was to quantify the difference in biases for this method due to varying extraction efficiencies of different solvents. Perhaps we were not clear in conveying the intent for the use of different solvents in the previous iteration of the manuscript. We have modified the entire paragraph to distinguish between extraction related biases and limitations due to size measurement errors.

L62: One must also assume something about the real component. Suggest changing to "complex refractive index." Also, why an "assumed" number distribution. Why not a measured one?

The sentence has been changed to reflect that an assumed real part as well as the measured imaginary part of the refractive index are used together to calculate the Mie based absorption coefficient. An "assumed" number distribution was written to justify that the extracted organics could/would have a distinct size distribution than the organic aerosol (OA). Scientists can use an SMPS based size distribution or a PM based size distribution for OA, each with their own assumptions. We have however, changed the sentence to reflect that the distributions can be measured or assumed.

L64: In mentioning "past studies," it is not clear whether the authors here are referring to some issue with the samples not being suspended particles or to issues associated with extraction of only a subset of the total OA material. The former is a method limitation. The latter is a bias. These should be distinguished here. Related, in the next sentence the authors mention past studies obtained different correction factors for water and methanol. But if Mie theory were the only issue then there would be no difference. This again emphasizes that the issue of incomplete extraction must be brought up and made a central part of this discussion.

We agree with the reviewer completely and thank them for pointing out the insufficiency in our arguments for this case. We have restructured and reconstructed the entire paragraph to emphasize the reason for these biases. Citations have been modified to reflect differences both due to incomplete OC extraction as well as size-dependent absorption properties.

L78: It is not clear to me that either the Zhang paper or Saleh paper address the issue of "the types and fractions of organics extracted by a given solvent" and how these relate to SSA or

EC/OC. They address variability in properties, yes. But I don’t think they address what the authors purport.

The authors thank the reviewer for pointing this out. We have modified the sentence to “…such as the EC/OC ratios, and single scattering albedo (SSA), even though these properties have shown to be well correlated with OA optical properties.” to signify that the EC/OC ratios are correlated with the “brownness” of organics with production of more ELVOCs, and these in turn could impact the amount of OC extracted by traditional solvents. The meaning of the sentence seems to have altered over subsequent iterations to the manuscript hence the mismatch in citations.

L84: It is not necessarily correct to state that a single-wavelength PAS cannot separate OC from BC absorption. One can, at least in theory, evaporate OC to just determine the BC absorption. Alternatively, if one can make high quality measurements of the MAC at a single wavelength, then this can be compared to an appropriate reference value. These are both as valid as extrapolations from multiple-wavelength measurements. (All must be interpreted with caution and attempt to account for coating effects.) I find this sentence and the ones that follow to be overstating the case and pushing a particular view of how things should be measured, but stating it as an objective fact. This should be revised.

We have changed the sentence to state that a single-wavelength PAS on its own cannot separate OC and BC absorption. In the Conclusion section of the earlier manuscript, the technique mentioned by the reviewer and a few more were stated as potential alternatives for measuring BC absorption. We have conditioned the language of the paper to reflect that this is one of the potential methods with which BC and OC absorption can be separated. The authors are confident with this method as it is free of biases related to thermophoretic particle losses as seen with most thermodenuders (Stevanovic et al., 2015), and can account for light absorption enhancement due to “lensing effect”, if absorption enhancement is considered independent of wavelength (Liu et al., 2015). The equations supporting this would be:

$$b^{\lambda}_{abs,IPN} = b^{\lambda}_{abs,BC} . E^{\lambda}_{MAC_{BC}}(Lens) + b^{\lambda}_{abs,BrC}$$

Where, $E^{\lambda}_{MAC_{BC}}(Lens)$ is the coating related absorption enhancement, and $b^{\lambda}_{abs,BrC}$ (OA absorption) is zero at 1047 nm. The absorption coefficient measured at 1047 nm will account for the coating related absorption enhancement and this is what is extrapolated to the lower wavelength, giving us a representative value for BC absorption at those wavelengths.

L142: Was a sonicator used? It would be surprising to find out that the samples were not sonicated during extraction.

The authors should report the extraction efficiency for the water solvent, as they can do this from the WSOC and OC measurements. What fraction of OA was extracted? It presumably must be small, or the correction factor for water versus methanol would not be all that large.

No, a sonicator was not used during extraction due to concerns of mechanically dislodging BC from the filters (Phillips and Smith, 2017). We had initially thought of sending extracted and unextracted filters for EC/OC analysis to characterize extraction efficiency and determine mass absorption efficiencies but did not go through with it due to constraints with shipping filters. For justifying the validity of extractions without sonication, we would like to point the reviewer to work by Cheng et al. (2016), where they've performed methanol extractions without sonication and concluded that most organics were extracted. We allowed for longer dissolution times than Cheng et al. (2016), though they had larger solvent volumes for extraction.

We conducted the experiments in two sets, the first included water extraction along with TOC analysis of the extracts and the second set of experiments included extraction using all the plotted solvents. Data from the first set of experiments was used for the Mie calculations and as proof of concept that the extraction technique works and gives reasonable absorbance. The fraction of OA extracted by water had a broad range with values varying from 32-74% which are close to those observed by Chen and Bond (2010) for primary organic emissions.

L178: "OC/TC ratios were assumed constant. . .". Was this assumption tested in any way?

Yes, the assumption was tested by conducting experiments where two or more filters in a given burn were sent for EC/OC analysis. The EC/OC values were consistent and within error for all fuels except for Douglas fir. The instability for douglas fir emissions was noted early on as it was not possible to achieve a stable absorption coefficient signal for burns using this fuel. Consequently, douglas fir emissions were not extracted in any solvent, however data from these burns were used as points in the SSA v/s OC/TC plots. Table S2 now details the number and purpose of each filter collected in a given burn.

L198: For the blacker samples (lower OC/TC), the BC will absolutely impact the retrieval of the real refractive index. How was this accounted for?

The Mie calculations were performed for samples with OC/TC values of 1 to avoid assumptions for separating BC and OC size distributions from SMPS data. Hence, we did not have problems in retrieving real refractive indices. The retrieved real index for the sage burns was 1.61 ± 0.12 which is a reasonable estimate for OA emissions (Dinar et al., 2008; Sumlin et al., 2018).

L212: The Cheng et al. reference is to a computational study. As much as those can shed insights, I suggest using an observational or lab study to make the case of the value for the SSA for BC. With the exception of some recent results from NIST (Radney et al., 2014, ES&T), I think that most experimental studies suggest lower values than stated here are possible.

We have added a range of values for the expected SSA and made variations to the citations while also mentioning that SSA is highly sensitive to monomer size.

L222: Presumably this power law was arbitrarily chosen? Were other forms explored? What is the predictive power of this, especially at high OC/TC? See the above comment about the data seeming to look more like a step function, than a power law.

See response to the first comment where we explain the reason for using a power law over the step function. The predictive power of these parametrizations is not high, but better than equivalent step function counterparts. As these parametrizations are not predicting correction factors, we believe the low predictive powers for the parametrizations should not be a concern. The parametrizations in the updates manuscript are only provided to give some form of mathematical visualization to the data.

L231: These are not "fluctuations." They are simply uncertainties. However, the error bars reported do not seem to reflect these uncertainties properly. There is no notable decrease in the size of the error bars below/above the thresholds identified. This begs the question, how were the uncertainties determined? The currently reported uncertainties in Fig. 2 are clearly underestimated, based on the potential for a 200% bias. Ultimately, the uncertainty is likely a direct function of the OC/TC, since the BC contribution will be larger when this ratio is smaller, and thus it will become increasingly difficult to separate OC from BC contributions. More than that, any uncertainty in the AAE will create a systematic, but OC/TC-dependent, bias in the key ratio determined here. I think that these issues need to be discussed in much greater detail.

We have modified the paragraph to represent the importance of uncertainties due to AÅE. The error bars in Fig. 2 and Fig. 4 do not contain uncertainties associated with AÅE as is mentioned in the text. This was when we were presenting our results as correction factors instead of biases and had hence separated out "correction factors" with high errors from those with relatively low errors for potential use in different systems. We have revised this and added errors associated with AÅE uncertainties to our plots. The revised manuscript uses Monte Carlo simulations to estimate errors by assuming each value follows a normal probability distribution with certain standard deviations and have calculated errors based on that. We have also expanded our discussion on the role of OC/TC in these uncertainties.

L242: This statement by the authors, that if they translate data from another study to the parameter space used here (OC/TC) they find different results, suggests that the premise of this study might be flawed. This suggests that the results here might not translate well to other settings, and thus the fit function determined in Fig. 2 is not robust beyond the current study. The authors need to address the issue of how robust they expect their parameterization to be, and how extensible to other systems. Also, the fact that the current study and a previous study disagree so much seems to limit the statement on L253 that the SSA can be predicted from the OC/TC. The prediction from the fits in this study may simply not be robust.

We have added to the section by using our fit to predict values from another study and have suggested reasons for possible mismatch between the fits obtained from our study and those by Pokhrel et al., (2016). We hypothesize that the main reason for the difference in fit parameters could be the result of potential difference in EC/OC ratios obtained by different instruments even though the same thermal protocol was used in both studies (Panteliadis et al., 2015). The reason for comparison with Pokhrel et al., was to show that even though the parameters for the fits were different, both studies obtained linear correlations between SSA and OC/TC (or EC/TC) indicating that some form of systematic linear trend between the two parameters exists.

L279: The authors need to clarify how specifically an OC/TC dependence of the OA absorptivity explains the apparent difference in methanol versus water.

We hypothesize that the temperature for burns which lead to high EC fractions in the aerosol also lead to the release of larger amounts of ELVOCs (Saleh et al., 2014) or polycyclic aromatic hydrocarbons (PAHs) which might not be completely extractable by water but are more readily extracted by methanol. These compounds have been shown to have high absorption efficiencies which could lead to the observed difference in absorption even though extraction efficiencies might not be drastically different. Thus, absorption coefficients for WSOC are lower than MSOC and corresponding AÅE values are higher as these compounds are expected to absorb light at longer wavelengths as well . The text has been modified to represent this.

L284: Are the authors deriving their conclusion that the Zhang et al. (2013) results support the findings here from the following sentence in Zhang: "The water-insoluble BrC, calculated as the difference between methanol- and water-extracted BrC, exhibited a tighter correlation with ambient EC concentrations ($r2 = 0.81$, Figure 5b) than water-soluble BrC ($r2 = 0.40$), suggesting that the water-insoluble BrC components and EC have similar sources (e.g., incomplete combustion from vehicle emissions and wood burning)." As best I can tell, this is the only sentence that might connect. But I am skeptical of the relevance, since in the Zhang case the distinction is largely between primary and secondary OA, not different types of primary OA. I suggest that the authors' argument needs to be strengthened if it is to be kept.

We have removed the Zhang et al. (2013) citation and modified our argument for the increase in $b_{abs,OA}/b_{abs,bulk}$ with increasing EC fractions of our aerosol. The argument now reads:

"The differences in the magnitudes of the correction factors between acetone/methanol extracts and water extracts increase as the EC composition of the aerosols increases. An increase in extremely low volatility organic compounds (ELVOCs) with increasing EC/OC ratios was observed by Saleh et al. (2014) and we hypothesize that these ELVOCs which have high mass absorption efficiencies (Saleh et al., 2014; Di Lorenzo and Young 2015) could have a lower solubility in water than methanol or acetone which would explain the increasing difference in $b_{abs,OA}/b_{abs,sol}$ values between water and methanol/acetone extracts."

L294: It is not clear how the authors come to the conclusion that "higher molecular weight" compounds are responsible here. This seems like speculation and should be posed as such.

We have changed our hypothesis for lower AÅE of methanol to as shown below:

"Experiments by Zhang et al., (2013) observed absorption by polycyclic aromatic hydrocarbons (PAHs) at longer wavelengths close to the visible region. Organic compounds such as methanol have a higher extraction efficiency for these compounds than water leading to higher absorption by methanol extracts at longer wavelengths which results in lower AÅE (Zhang et al., 2013)."

L288 and AAE discussion: The authors do not present an error analysis here, and the uncertainties on the lower OC/TC samples will be very large if propagated appropriately. This is especially important for any of the conclusions reached regarding comparison between particle and solution-phase differences.

We have propagated the uncertainties and included corresponding errors to our results. The conclusions have been modified to reflect this. We used a Monte Carlo simulation to estimate the mean and errors for the particle phase.

L300: The authors state that the particle phase AAE are "close to" those in the solution phase at high OC/TC. But then in the next sentence they state that the particle phase and solution-phase "deviate significantly." These seem contradictory. I actually do like this general aspect of the analysis (especially at higher OC/TC, where uncertainties from extrapolation are smaller). But, without a robust error analysis and a more quantitative discussion of the comparison I don't think the authors can arrive at their conclusions. At minimum, there should be something like a t-test to check for statistical differences between the particle- and solution-phase AAE values. I suspect that if the authors include all data (not just dung) they will find that the methods give statistically indistinguishable AAE values.

We carried out a t-test for differences in water and particle phase AÅE for 12 samples with OC/TC ratios ≥ 0.90 and differences are significant with p values < 0.05. The difference is however not statistically significant for water when all samples are compared ($p \approx 0.15$, 18 data points) excluding those with OC/TC ratios < 0.7 as these data points have high errors in AÅE. The differences are extremely statistically significant when comparing all samples with OC/TC ratios ≥ 0.95 (11 data points) and > 0.7 (18 data points) with p values < 0.0005 when comparing particle phase AÅE with acetone and methanol.

Reviewer 2:

Lines 114/116: The ratio of OC/TC were reported of ranges 0.55-1 but figure 3 (line 489) shows that ratios observed are only in the specific data ranges such as 0.55, 0.6, and 0.7. 0.8, and 1. It is not clear why the OC/TC data of ratios in between those ranges, such as of ratios 0.65, 0.75, and 0.85, were not observed and not reported. Are these ratios were rounded? And also, there is no excess data of ratios about 0.55 and 0.6 which contribute for analysis. I have the impression that the significant correlation, ~0.95 of SSA vs OC/TC is mainly driven by some outliers. I strongly recommend presenting error analysis on these data sets

The different OC/TC mass ratios were obtained by prematurely extinguishing the flame and this did not give us much power over the exact value of OC/TC ratios that were generated. The ratios were not rounded and the fact that we could not observe values such as 0.65, 0.75 and 0.85 was just a matter of chance and something that was out of our control. We have made new plots for Figure 3 which represent the errors in the OC/TC ratios and SSA along with 95% confidence intervals for our fits. We are now reporting the RMSE for the fit instead of the r values thereby removing any effects of outlier points. We have also modified the regression from a least square method to an orthogonal distance regression to account for uncertainties in the OC/TC ratio.

Lines 124/126: Why was SMPS not used for all of the experiment? Please clarify this. Also, give a reference or a brief explanation of how the geometric mean size distribution was determined?

The experiments were conducted in two batches, once by only performing water extractions as a proof of concept and the other set where organics were extracted in water, methanol and acetone. The SMPS measurements along with the TOC analysis were done on samples collected during the first batch of experiments and data from these were used in the Mie calculations. We have added text in the manuscript to indicate this difference. The geometric mean was evaluated by the TSI software using the general formula for geometric mean size. We did not find it necessary to include a description for calculating the geometric mean as it is not relevant to the following discussion.

Line 151: There are no references or derivation of mathematical equations used in the manuscript, for example, Eqn.1, babs, bulk (λ). Please provide the references or derivations to support the validity of the mathematical equations used in the manuscript.

Citations have been added to corresponding references for the different equations used throughout the manuscript.

Line 154: Explain why absorbance at a given wavelength is normalized to the absorbance at 700nm.

We have provided an explanation which states that the absorbance is normalized to values at 700 nm to account for any signal drift within the UV-Vis spectrophotometer signal.

Lines 183/185: What is the range of assumptions made along with Mie theory, as stated in the text? Reference is recommended to include for determining the imaginary complex refractive index

Mie Theory assumes that the particles are uniform and isotropic with a spherical shape, and that these particles are fully illuminated in an infinite dielectric medium. In addition to this, the real part of the complex refractive index needs to be assumed as well. We have modified the sentence to read:

"…absorption, using Mie Theory along with assumptions regarding the shape of the particles and the real part of its complex refractive index."

A reference to the equation has been added.

Line 223: How were the RMSE values calculated? Please include the reference/formula or name of software which was used to get RMSE values in Table 1, such as excel MATLAB, or Igor Pro.

The RMSE values were calculated using Excel. We have added a sentence in the manuscript to reflect this.

Lines 223/224: Please add a line to justify the impact of BC AAE on conversion factor for particles with SSA smaller than 0.7 at 375nm and smaller than 0.825 at 405 nm.

The next two sentences in the manuscript justify the impact of BC AÅE on $b_{abs,OA}/b_{abs,bulk}$. The uncertainty in BC AÅE could lead to uncertainties close to 200% at smaller SSA values. We have added a sentence explaining that the increase in uncertainty would be due to an increase in BC mass concentrations with decreasing SSA.

Line 225: What is sensitivity analysis as stated in the text? Please explain briefly

The sensitivity analysis is performed to observe how sensitive the measurements are to variations in certain variables ($ÅE_{BC}$ here). To perform the analysis, the value of $AÅE_{BC}$ was varied from 0.85 to 1.1 and we noted the corresponding change in $b_{abs,OA}/b_{abs,bulk}$. The differences were compared to values where $AÅE_{BC}$ is 1 and the differences are indicative of how sensitive the result is to given variable.

Line241/242: Briefly describe why the two different studies, Pokhrel et al. (2016) and the current studies give different slopes and intercepts of the resulting fits?

We hypothesize that the main reason for the difference in fit parameters could be the result of potential difference in EC/OC ratios obtained by different instruments even though the same thermal protocol was used in both studies (Panteliadis et al., 2015). A section where we compare our fit to another study has also been added to this section.

Line 276: What does SI represent for?

SI stands for Supplementary Information and has been expanded as so in the manuscript.

Lines 292/295: Briefly explain why the higher molecular weight compounds absorb more light?

We have changed our hypothesis for differences in AÅE between water and methanol extracts and have added text explaining that this may be due to increased extraction of polycyclic aromatic hydrocarbons (PAHs) by methanol. These PAHs absorb more light at longer wavelengths which would result in lower AÅE values for methanol when compared to water.

Lines 296: AAE values for OA are significantly high with wide ranges of 4.4 -14.61. How are these values related to wavelengths? Please provide some references, if there are any, to support these values

Few studies look at AÅE of OA in the UV range making it difficult to find relevant citations. However, our AÅE values are similar to those observed by Chen and Bond 2010 for OC extracted in methanol and water. Pokhrel at al. 2016 observed AÅE ranging from 3.7 to 10.4 for wavelengths 405/532/660 which are close to the values observed in this study.

Lines 296/297: It is reported that overall AAE for OA decreases with increased EC. Please add a graph/or a brief note to show AAE for OA measurements with the concentration of EC.

We have removed this argument from the manuscript.

Line 342: Authors' names are not clearly reported: RKC, SB, WMH, NS, AP, are not previously reported with these names in the authors' list. I think it is not relevant to include author contributions in the manuscript once a list of authors is reported.

The author contribution list was added as it is a requirement for publication in ACP.

Reviewer 3:

(1) The authors effectively define the in-situ shortwave absorption coefficient for organic aerosol, babs,OA, as the excess of the PAS-measured total over the BC contribution. They extrapolate the necessary shortwave BC value from a longwave PAS measurement, via an assumed unit AAE. This BC contribution is the proverbial 'elephant in the room', appearing nowhere in the results but providing essential context for their interpretation. What are the relative contributions of OA to total absorption at short wavelengths, and how do they vary with fuel type and burn conditions? Extended AAEs (AAE405-1047 or AAE375-1047), from which a curious reader could derive an answer, are nowhere indicated. A related question is how longwave absorption and TOR EC relate to each other, since they are independent proxies for the same BC. Figure 3 plots only ratios against ratios, shortwave bscat/(bscat+babs) from the in-situ IPN measurement against OC/TC from the filter TOR analysis. It would seem at least equally instructive to compare the concentration values directly, longwave babs against TOR EC

The relative contribution of OA absorption ranged from 23 to 97% at 375 nm and from 7 to 96% at 405 nm. The fraction of OA absorption decreases with increasing EC fraction of the aerosol. In Figure 3 we plotted SSA with OC/TC to compare the results with similar trends observed by Pokhrel et al. (2016). TOR EC was converted to EC mass concentrations based on the sampled volume and b_{abs} at 1047 nm was plotted against the EC mass concentration. The plot showed an increase in the b_{abs} with increasing EC mass fraction as expected, however, the scatter was high with a few outlier points at high EC mass concentrations. We have added a Table with extended AÅEs, both $AÅE_{375-1047}$ and $AÅE_{405-1047}$ in the Supplementary Information, but believe that adding the plot for $b_{abs}(1047)$ against TOR EC might not be as helpful due to the lower correlation as compared to the trend between SSA and OC/TC.

(2) Two SVOC denuders sit between the burn chamber and the holding tank (Figure 1), but we can expect some phase re-equilibration to occur within the holding tank before samples are drawn. Adsorption of re-volatilized organic species by the quartz sampling filters will then generate artifacts in the TOR and extraction measurements that are not present in the IPN optics measurements. Did the authors collect and analyze quartz blanks to quantify these artifacts, using a (non-adsorbing) PTFE filter between the smoke-filled holding tank and sampling port to exclude the particle phase?

We did not account for phase partitioning of the of the SVOCs within the holding tank. We have modified the text to indicate that this might lead to positive artifacts in the OC measurements and could lead to an increase in solution phase absorption coefficients. However, the contribution to absorption by SVOCs is small compared to the non-volatile organics (Chen and Bond 2010) and should not affect our measurements by a lot with adsorption artifacts contributing an OC error of 1-3% (Pokhrel et al., 2016).

(3) It is hard to relate and reconcile the experimental data shown or listed in the different figures and tables. Not all IPN- and TOR-characterized burn samples were filter-extracted for OA, and not all water extracts were analyzed for TOC. It would be helpful to make these

experimental layers clearer to the reader, along with some indication of criteria for inclusion/exclusion. For example, Table S1 lists 53 filters collected from 28 burns. I infer that this (53) counts just the filters consumed for TOR OC/TC analysis, each paired with another filter collected for extraction (lines 133-134). (If the 7 filters from dung burns instead represented all TOR and extraction filters together, then we would have at most 3 pairs yielding complete records, contra the 4 observations listed in Table 4.) It appears from Table 4 that only 21/53 ~ 40% of the other filters were selected for quartering and extraction. Does Figure 3 show all 53 observations from Table S1? Do Figures 2 and 4 show those 21 observations from Table 4? It would be helpful to be told the total number of observations appearing in each figure and table.

We conducted the experiments in two sets, the first included water extraction along with TOC analysis of the extracts and the second set of experiments included extraction using all the plotted solvents. Data from the first set of experiments was used for Mie calculations and as proof of concept that the extraction technique works and gives reasonable absorbance. Data plotted in all graphs and the AÅE table were analyzed during the second set of experiments. We thank the reviewer for pointing out the confusion regarding this and have added Table S2 which details how each filter was used and corresponding OC/TC ratios. We have also added the number of data points used in each plot. As for dung, all dung burns had no visible flaming combustion phase and smoldered throughout the combustion process and the one odd sample without a corresponding OC/TC filter was just assumed to have an OC/TC value of 1. Removing this data point does not affect the fit coefficients and conclusions by a lot and we believe that assuming the dung emissions to be purely organic is justified.

(4) Is it true that the TOR analyses were performed AT Sunset Laboratories (line 238), and not locally with an instrument manufactured BY Sunset Laboratories?

Yes, the TOR analysis was performed at Sunset Laboratories.

(5) In addition to flowrate and sampling time (line 133), filter area is a relevant experimental factor and should be specified.

We agree with the reviewer, a 47 mm diameter quartz fiber filter was used for sampling and then quartered and used for analysis. The same has been added to the text as well in Section 2.2.1 “Quartz filters (Pallflex Tissuquartz, 47 mm diameter) collected during sampling were split…”

Reviewer 4:

Given the comments already made by the other three anonymous reviewers, I will refrain from repeating what they have stated. I agree with Reviewer #1’s assessment that the conclusions from this work are not sufficiently general to be of use for correcting bulk, solvent-based absorption measurements. As the other reviewers have pointed out, the measured correction factors incorporate not just geometric differences in bulk and particle absorption but also solvent- and constituent-specific factors, including solubility. And, there are correction factors measured at nearly identical SSA or OC/TC values that differ by factors of 2-3 (Figures 2 and 4) – such scatter is too great to draw a meaningful conclusion

about the dependence of the correction factors on SSA or OC/TC ratio. It appears as if no dependence, i.e. a horizontal line, would describe the trends about as well as the arbitrarily-chosen power law function.

Based on comments by the other reviewers, we have made substantial changes to the manuscript and modified the conclusion as well and are not purporting our findings as correction factors any more. We had considered the use of a step function over a power law, the reason for selecting the power law fit was to keep the equation consistent through all regressions. It would appear that a step function is better than the power law for the water extracts, but the gradual slope with OC/TC ratios and SSA is more prominent in the methanol and acetone extracts. In addition to this, the root mean square error (RMSE) values for the power law fit were consistently lower than their step function counterparts. The power law fit can also mimic a step function with a steeper slope and can also have a curve with a gradual slope depending on the value of the power law exponent.

In short, the main conclusion from this study is that there are different correction factors for water and methanol/acetone with water extracting less absorption than the other solvents. This conclusion is not new and may not be general to other types of absorbing organic aerosols or even other types of biomass burning aerosols. What is more, the extent of scatter makes potential use of these factors problematic. Hence, the factors measured here are not broadly applicable. Furthermore, the purported dependence of these factors on SSA or OC/TC is overstated making that conclusion suspect as well.

The conclusions have been changed.

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Measuring Light Absorption by Primary Organic Aerosols: Optical Artifacts in Traditional Solvent Extraction-Based Methods

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Abstract

Recent studies have shown that organic aerosol (OA) could have a non-trivial role in atmospheric light absorption at shorter visible wavelengths. Good estimates of OA absorption are therefore necessary to accurately calculate radiative forcing due to these aerosols in climate models. One of the common techniques used to measure OA light absorption is the solvent extraction technique from filter samples which involves the use of a spectrophotometer to measure bulk absorbance by the solvent-soluble organic fraction of particulate matter. Measured solvent phase absorbance is subsequently converted to particle-phase absorption coefficient using scaling factors. ~~varying scenarios of organic carbon (OC) to total carbon (TC) mass ratios has been an unexplored~~ The conventional view is to apply a correction factor of 2 to absorption coefficients obtained from solvent-extracted OA based on Mie calculations. The appropriate scaling factors are a function of biases due to incomplete extraction

of OC by solvents and size-dependent absorption properties of OA. ~~conversion under varying scenarios of organic carbon (OC) to total carbon (TC) mass ratios has~~ The range for these biases along with their potential dependence on burn conditions is an unexplored area of research.

Here, we performed a comprehensive laboratory study involving three solvents (water, methanol, and acetone) to investigate the bias in absorption coefficients obtained from the solvent extraction-based photometry techniques as compared to in-situ particle phase absorption for primary OA emitted from biomass burning. We correlated the bias with OC/TC mass ratio and single scattering albedo (SSA) and observed that the conventionally used correction factor of 2 for water and methanol-extracted OA might not be extensible to all systems and suggest caution while using such correction factors to estimate particle-phase OA absorption coefficients. ~~recommend using $b_{abs,OA}/b_{abs,bulk}$ values between 2 and 11 for water extracts and values between 1~~ Furthermore, a linear correlation between SSA and OC/TC ratio was also established. Finally, from the spectroscopic data, we analyzed the differences in Absorption Ångström Exponents (AÅE) obtained from solution- and particulate-phase measurements. We noted that AÅE from solvent phase measurements could deviate significantly from their OA counterparts.

1 Introduction

Carbonaceous aerosols constitute a major short-lived climate pollutant, and even though they have been studied extensively in recent years, estimates of their contribution to shortwave radiative forcing remains highly uncertain (IPCC, 2013). Based on their thermal-refractory properties, carbonaceous aerosols are categorized as elemental carbon (EC) or organic carbon (OC) (Chow et al., 2007b; Bond et al., 2013), and the sum of OC and EC is referred to as total carbon (TC). When defined optically, the refractory EC component is approximately referred to as black carbon (BC) (Chow et al., 2007b; Bond et al., 2013); BC aerosol constitute the strongest of the light absorbing aerosol components in the atmosphere (Ramanathan and Carmichael, 2008; Andreae and Gelencsér, 2006; IPCC, 2013). While BC absorbs strongly in the visible spectrum, the contribution of OC towards absorption has largely been neglected, even though many studies have demonstrated significant OC absorption at lower visible wavelengths (Yang et al., 2009; Chen and Bond, 2010; Chakrabarty et al., 2010; Kirchstetter 2012). The atmospheric mass of OC can be 3-12 times larger than that of BC (Husain et al., 2007; Zhang et al., 2008) which warrants its inclusion as an atmospheric light absorber. Only recently have global modeling studies started incorporating radiative forcing by organic aerosol (OA) absorption (Wang et al., 2014; Saleh et al., 2015; Lin et al., 2014; Wang et al., 2018). Thus, having accurate estimates for OA absorption is necessary to help improve climate models.

A convenient and prevalent methodology of measuring OA absorption is based on collecting aerosol particles on a filter substrate followed by extracting the organic compounds into a solvent. This analytical method is used in many studies as it ideally excludes any interference from EC and primarily provides the absorption spectra of extracted OC (Mo et al., 2017; Chen and Bond, 2010; Liu et al., 2013). The absorbance of organic chromophores in the solvent extract is measured using an ultraviolet-visible (UV-Vis) spectrophotometer and measured absorbance values can be converted to corresponding solvent phase absorption coefficients ($b_{abs,sol}$). However, this methodology has limitations as it is unable to represent size-dependent absorption properties of the extracted OA (Liu et al., 2013; Washenfelder at al., 2015; Moosmüller et al., 2011). To correct for this limitation, the complex refractive index (RI) of OC is estimated by assuming the real part and calculating the imaginary part for extracted OC using $b_{abs,sol}$ and dissolved OC concentration, ~~The absorbance values can be converted to corresponding bulk phase absorption coefficients (b-~~ the complex RI is then used along with a number size distribution as inputs to Mie theory for calculating the particle-phase absorption coefficient for dissolved OC. In addition to discrepancies between particle and solvent phase optical properties, the method suffers from biases due to incomplete extraction of organics by different solvents (Chen and Bond, 2010; Liu et al., 2013) which lead to differences in values of $b_{abs,sol}$ obtained from different solvents. The significance and extent of this bias varies based on the OC extraction efficiency of a given solvent and would be negligible for solvents extracting 100% of organic chromophores. A combination of inefficient organic carbon extraction and the methods inability to measure size-dependent OA absorption properties can result in significant errors to optical properties obtained using this method. Despite the low OC extraction efficiency of water (Chen and Bond, 2010) and large potential for errors, past studies have used light absorption by water soluble organic carbon (WSOC) as a surrogate for OA optical properties (Bosch et al., 2014; Kirillova et al., 2014a; Kirillova et al., 2014b). However, the use of water as an OA surrogate is decreasing with more recent studies using methanol to extract OC (Cheng et al., 2016; Shen at al., 2017; Xie et al., 2017). While methanol has a higher OC extraction efficiency than water (Chen and Bond, 2010), its efficiency is limited ranging from 85-98% (Cheng et al., 2016; Xie et al.,

2017) which can lead to misrepresentation of OA optical properties if the unextracted fraction correspond to extremely low volatility organic carbon (ELVOCs) or similar organic chromophores which have large light absorption efficiencies (Saleh et al., 2014), underscoring the need for a more complete extraction protocol. In addition to problems with incomplete OC extraction, previous studies have attempted to correct for size-dependent biases using absorption coefficients determined with Mie theory and provided a narrow range of solvent-dependent scaling factors from 2 for water extracts to 1.8 for methanol extracts, all corresponding to a mean particle diameter of 0.5 µm (Liu et al., 2013; Liu et al., 2016; Washenfelder et al., 2015). Sun et al. (2007) performed theoretical calculations and postulated a correction range of 0.69 - 0.75 for OC particles with diameters much smaller than the wavelength of light. These correction factors while applicable to these individual systems, might not be extensible to aerosol emissions from other combustion events. However, many studies have used scaling factors from such studies on absorption coefficients obtained from solvent phase optical measurements despite potential differences in system dependent biases for each experiment (Kim et al., 2016; Zhang et al., 2017; Wang et al., 2018). To the authors knowledge, no attempts have been made to explicitly study or quantify these biases with varying aerosol intrinsic properties, such as the EC/OC ratios, and single scattering albedo (SSA), even though these properties have shown to be well correlated with OA optical properties (Zhang et al., 2013; Saleh at al., 2014; Bergstrom et al., 2007).

In-situ measurement of particulate-phase absorption coefficient is commonly and accurately accomplished using a photoacoustic spectrometer (PAS) (Lack et al., 2006; Arnott et al., 2005; Arnott et al., 2003). However, on its own, a single-wavelength PAS cannot distinguish between absorption by OC and BC aerosol and it typically measures the total particle-phase absorption coefficient ($b_{abs,tot}$) of the aerosol population in the cell (Moosmüller et al., 2009). One can make use of a multi-wavelength PAS using which the OA absorption coefficient ($b_{abs,OA}$) could be separated out from that of BC absorption, based on the difference in BC and OA Absorption Ångström Exponent (AÅE) (Washenfelder et al., 2015; Arola et al., 2011; Kirchstetter and Thatcher; 2012). The AÅE for pure BC is well-constrained at 1 in the visible and near-infrared wavelengths (Moosmüller et al., 2009). The value of $b_{abs,OA}$ is calculated as the difference between $b_{abs,tot}$ and the BC absorption coefficient. A possible technique to measure the bias between particle and solvent phase organic absorption ($b_{abs,OA}/b_{abs,sol}$) can thus be established by carrying out simultaneous measurements of solution-and particle-phase absorption properties during a study. Determining $b_{abs,OA}$ using this method gives large errors when BC absorption coefficient is large or comparable to $b_{abs,tot}$ as $b_{abs,OA}$ would be a small number obtained by the subtraction of two large numbers limiting the use of this technique for relatively low EC/OC ratios.

Here, we burnt a range of different biomass fuels under different combustion conditions and the resulting aerosol emissions were passed through various in-situ instruments while simultaneously being collected on quartz-fiber filters. The particle phase absorption coefficient was obtained using integrated photoacoustic-nephelometer spectrometers (IPNs) at wavelengths 375, 405 and 1047 nm. Organics collected on quartz-fiber filters were extracted in water, acetone, and methanol, and corresponding $b_{abs,sol}$ values were calculated. These values were compared with corresponding $b_{abs,OA}$, and the change in $b_{abs,OA}/b_{abs,sol}$ with varying single scattering albedo (SSA) values and OC/TC ratios was examined. SSA was parametrized with the OC/TC ratios with trends similar to those observed by Pokhrel et al., (2016). AÅE from spectroscopic data for solution and particle phase measurements were compared, and the Mie Theory based correction factor was also investigated for a few samples.

2 Methods:

2.1 Sample generation and collection

Fig. 1 is a schematic diagram of our experimental setup, which consists of a sealed 21 m^3 stainless-steel combustion chamber housing a fan for mixing and recirculation (Sumlin et al., 2018b). Aerosol samples were generated by burning several types of biomass including pine, fir, grass, sage, and cattle dung (~~sources~~ details are ~~given~~provided in the Supplementary Information). During a chamber burn, 10-50 g of a given biomass was placed in a stainless-steel pan and ignited by a butane lighter. The chamber exhaust was kept closed for the duration of a given experiment. The biomass bed was either allowed to burn to completion or it was prematurely extinguished and brought to a smoldering phase by extinguishing the flame beneath a lid. ~~The~~ D~~d~~ifferent combustion conditions were used to generate samples with varying properties: OC/TC ratios ranged from 0.55-1, and SSA values ranged from 0.56-0.98 for wavelengths of 375, 405, and 1047 nm.

For one set of experiments, the particles were directly sampled from the chamber; in another set, the sampling was done from a hood placed over the burning biomass. A diffusion dryer removed excess water from the sample stream, and the gas-phase organics were removed by a pair of activated parallel-plate semi-volatile organic carbon (SVOC) denuders. The gas-phase organics were stripped to reduce artifacts produced by the adsorption of organic vapors on the quartz filters. The aerosols were finally sent to a 208-liter stainless-steel barrel, from which they were continuously sampled by the three IPNs~~ and a scanning mobility particle sizer (SMPS, TSI, Inc.)~~.

Some phase repartitioning of condensed SVOC into the vapor phase may take place post the denuders in our holding tank and would introduce a positive bias to our filter-based measurements. The experiments were conducted in two sets, the first set included a scanning mobility particle sizer (SMPS, TSI, Inc.) and size measurements from this instrument were used in Mie Theory calculations detailed in Section 2.3. The SMPS was not used in the second set of experiments due to problems with aerosol flows in the system. However, the SMPS data from the first set of experiments gave us an estimate of the range over which the size distributions varied and was used to obtain the geometric mean of the size distribution. The real-time absorption and scattering coefficients were measured by the IPNs, and samples were simultaneously collected on quartz fiber filters once a steady state signal was achieved. The absorption and scattering coefficients were used to calculate the SSA, which is simply the scattering coefficient divided by the extinction coefficient. Radiative forcing calculations for absorbing OC require good estimates of OC absorption at different SSA values (Lin et al, 2014; Feng et al, 2013; Chakrabarty et al, 2010) underscoring the need to study OA absorption biases as a function of SSA. The particles were passed through the filter samplers at a flowrate of 5 lmin^{-1}, with sampling times ranging from 2-15 minutes. Two or more filters were collected for a given steady state condition. One of these filters was used to determine the OC and EC fractions of the deposited particles, and the other filters were used for the extraction experiments. The only exception to this case is one sample of emissions from dung combustion where the resultant aerosol was assumed to be purely organic based on a purely smoldering combustion phase and by comparing with optical properties from previous experiments.

2.2 Analytical Techniques

2.2.1 Absorption by solvent extracted OC

Quartz filters (Pallflex Tissuquartz, 47 mm diameter) collected during sampling were split into four quarters, and each quarter was extracted using either deionized water, acetone, hexane, or methanol. The absorption by hexane extracts were low and prone to errors, so data for its extracts were not analyzed. The filters were placed in 3-5 ml of the solvent for 24 hours. The filter was not sonicated to reduce artifacts from mechanical dislodging of BC particles (Phillips and Smith, 2017). The solvent volumes were measured both before and after the extraction and the differences between the two measurements were within 8%. The extracts were then passed through syringe filters with 0.22 μm pores to remove any impurities introduced by the extraction process.

The light absorbance of the extracts was measured using a UV-Vis spectrophotometer (Varian Inc., Cary 50) at wavelengths from 300 nm to 800 nm. To compare the absorbance ($A(\lambda)$) of chromophores in the solution with the absorption coefficient of the particles in the atmosphere, all absorbance values were converted to solution-phase absorption coefficients at given wavelengths ($b_{abs,sol}(\lambda)$) (Liu et al., 2013):

$$b_{abs,sol}(\lambda) = (A(\lambda) - A(700))\frac{V_l}{V_a * l} \,.\, \ln(10),$$

(1)

where V_l is the volume of solvent the filter was extracted into, V_a is the volume of air that passed over the given filter area, and l is the optical path length that the beam traveled through the cuvette (1 cm). The absorbance at a given wavelength is normalized to the absorbance at 700 nm to account for any signal drift within the instrument. The resulting absorption coefficient (m^{-1}) was multiplied by ln(10) to convert from log base 10 (provided by the UV-Vis spectrophotometer) to natural log.

2.2.2 Absorption by BC and OC in particle phase

To estimate the BC absorption at 375 nm and 405 nm, the absorption data from the IPN operated in the infrared regime at a wavelength of 1047 nm was converted to equivalent BC particulate absorption at the near UV wavelengths, using a BC absorption Ångström exponent ($AÅE_{BC}$) value of 1 (Kirchstetter et al., 2004; Andreae and Gelencsér, 2006). The assumption here being that all the absorption at 1047 nm could be attributed to BC aerosol (Bahadur et al., 2012). The BC light absorption coefficient at shorter wavelengths ($b_{abs,BC}(\lambda_1)$) was calculated by:

$$b_{abs,BC}(\lambda_1) = b_{abs,tot}(1047).\left(\frac{\lambda_1}{1047}\right)^{-AÅE_{BC}}, \tag{2}$$

where λ_1 is the wavelength at which the absorption will be calculated and AÅE is defined for a pair of wavelengths λ_1 and λ_2 as the exponent in a power law expressing the ratio of the absorption coefficients as follows (Moosmüller et al., 2009):

$$AÅE(\lambda_1\lambda_2) = \frac{ln\left[{b_{abs}(\lambda_1)}/{b_{abs}(\lambda_2)}\right]}{ln\left[{\lambda_2}/{\lambda_1}\right]} \tag{3}$$

AÅE is an optical descriptor of the inherent material property. For BC particles, typical values of AÅE ≈1, while for OC particles AÅE > 4 (Moosmüller et al., 2009). The value of $b_{abs,BC}$ at 375nm and 405nm was then subtracted from $b_{abs,tot}$ at those wavelengths to calculate $b_{abs,OA}$. The ratio $b_{abs,OA}(\lambda)/b_{abs,sol}(\lambda)$ was calculated to represent the scaling bias between the bulk solvent phase absorption coefficient and OA absorption coefficient.

The organic and elemental carbon compositions of the filters were measured with a thermal-optical OC/EC analyzer (Sunset Laboratory, Tigard, OR) using the Interagency Monitoring of Protected Visual Environments (IMPROVE)-A Thermal/Optical Reflectance (TOR) analysis method (Chow et al., 2007a). The OC/TC ratios were assumed to be constant for a given steady state IPN reading, which allowed us to relate the absorption data to the OC/TC data. The assumption was tested by performing EC/OC analysis of two filters collected during a given steady state for a burn. The OC/TC ratio remained unchanged or within experimental error for the burns and results for the EC/OC analysis of tested filters are provided in Table S1 and S2 of the Supplementary Information.

2.2.3 Uncertainty using Monte Carlo simulations

The uncertainties due to error propagation were evaluated using a Monte Carlo approach. The true measurement value was assumed to possess a Gaussian probability distribution with mean and standard deviation values corresponding to measured values and instrument specifications. Calculations were performed by randomly selecting values based on the probability distribution for the different variables and corresponding values for $b_{abs,OA}/b_{abs,sol}$ were estimated. A total of N = 10000 iterations was performed for each data point and each simulation was rerun 100 times till the $b_{abs,OA}/b_{abs,sol}$ value converged for the calculations. The propagated error due to the uncertainty in all variables was then calculated as the standard deviation of $b_{abs,OA}/b_{abs,sol}$ values obtained over all the simulations. A pseudocode for the Monte Carlo simulation is detailed in the Supplementary Information along with Table S3 which denotes typical mean and standard deviation values used for variables with uncertainties.

2.3 Mie Theory Calculations

A commonly used method to correct for differences between the chromophore absorption in solution and aerosol particle absorption is by using Mie Theory (Liu et al., 2013; Washenfelder et al., 2015). The imaginary part (k) of the complex refractive index $m = n + ik$ can be determined from bulk solution phase absorption data and converted to equivalent

OA absorption using Mie Theory along with assumptions regarding the shape of the particles and the real part of the particles complex refractive index.

To find k, the mass absorption efficiency (α/ρ) was determined using the absorbance data and the OC mass concentration in the solution (Liu et al., 2013):

$$\frac{\alpha(\lambda)}{\rho} = \frac{b_{abs,sol}(\lambda)}{M}, \tag{4}$$

where $b_{abs,sol}(\lambda)$ is the solvent-phase absorption coefficient determined in Eq. (1), and M is the mass concentration of OC in the solution. In the given study, the mass concentration was measured for some of the water extracts using a total organic carbon (TOC) analyzer (Shimadzu, TOC-L). The corresponding water-soluble organic carbon (WSOC) was then used to estimate α/ρ of the solution. The calculated α/ρ was then used to determine k for the WSOC by (Chen and Bond 2010):

$$k(\lambda) = \frac{\rho.\lambda.\left(\frac{\alpha(\lambda)}{\rho}\right)}{4\pi}, \tag{5}$$

where λ is the light wavelength at which k needs to be calculated, and ρ is the density of the dissolved organic compounds. A ρ value of 1.6 (Alexander et al., 2008) was used to calculate the k values, and was also used in all subsequent calculations using density. A Mie based inversion algorithm was used to extract the real part of the refractive index (n) using data from the SMPS and IPN (Sumlin et al., 2018a). A sensitivity analysis was performed by varying the n value from 1.4 to 2, and the change in Mie calculated absorption was within 18%. The size distribution for the WSOC was estimated assuming the same geometric mean and standard deviation as that of the original aerosol, but with number concentrations calculated based on the extracted mass. Calculations for the number concentration are provided in the Supplementary Information.

3 Results and discussion

3.1 Absorption bias correlated with Single Scattering Albedo

Fig. 2 shows the trends in $b_{abs,OA}(\lambda)/b_{abs,sol}(\lambda)$ for primary organic aerosol emissions with varying SSA. The error bars are estimated from the results of the Monte Carlo simulation and account for uncertainties in IPN measurements, UV-Vis spectrophotometer measurements, filter sampling flowrates, BC AÅE based uncertainties and extract volume measurements. Measured SSA for pure fractal BC aggregates have values between 0.1-0.4 (Schnaiter et al., 2003; Bond et al., 2013) depending on the size of the BC monomers (Sorensen 2001), and due to this particularly low SSA of BC compared to OC, an increase in the BC content of the aerosol composition would lead to decreasing SSA. This relationship is explored further in Section 3.2 and 3.3. Fig 2. indicates that the light absorbed by methanol and acetone extracts were almost identical and would imply that the amount and type of OC extracted by the two solvents were similar, as seen in other studies as well (Chen and Bond, 2010; Wang et al., 2014). The reason for observed differences in the bias between water and methanol extracts are discussed further in Section 3.3. The differences between the mean values of $b_{abs,OA}(\lambda)/b_{abs,sol}(\lambda)$ at 375 and 405 nm were less than or close to the errors associated with them, hence any trends with wavelength were not explored.

The value of $b_{abs,OA}(\lambda)/b_{abs,sol}(\lambda)$ approached a constant in the measured range of data. A power law ($y = k_0 + k_1 x^{k_2}$) was used to fit the points in Fig. 2, and the corresponding fit parameters, along with root mean square error (RMSE) values, are listed in Table 1. The fit was performed using the curve fitting tool in MATLAB and the RMSE values were calculated in Microsoft Excel. The power law fits were deficient in capturing the true behavior of the bias with SSA but performed better than corresponding mean values and step function curves. The parametrizations presented in this section are representative of laboratory-based biomass burning (BB) aerosol emissions in this study and are provided to mathematically visualize trends in the data. These parametrizations might not be extensible to other emissions and should not be used for determining OA absorption bias in other systems. There were large errors associated with the bias for SSA values smaller than 0.7 at 375 nm and smaller than 0.825 at 405 nm. These large uncertainties at lower SSA are a result of increasing BC mass fractions at these SSA values. BC absorption coefficients increase with larger EC concentrations which result in significant errors while extrapolating BC absorption from longer wavelengths due to uncertainties is BC AÅE. ~~change in $b_{abs,OA}(\lambda)/b_{abs,bulk}(\lambda)$ due to a change in BC AÅE from 0.85 to 1.1, which are typical values observed in other studies (Lack et al., 2008; Bergstrom et al., 2007; Lan et al., 2013). For the correction factors at 375 nm, on varying the AÅE we calculated a change of less than 14% for aerosols with SSA greater than 0.7, whereas a change as high as 200% was seen for particles with SSA less than 0.7. Similar changes in the correction factor were observed for SSA less than 0.825~~ The large uncertainties at lower SSA values indicate that the method described here is best suited to determine $b_{abs,OA}(\lambda)/b_{abs,sol}(\lambda)$ for particles with relatively higher SSA values.

3.2 SSA parametrized with OC/TC

A linear relationship between the SSA and the EC/TC ratio was observed by Pokhrel et al. (2016). To replicate the linear trends observed by Pokhrel et al., we studied the correlation between SSA and OC/TC ratio (which is simply the EC/TC ratio subtracted from 1). Fig. 3 shows the variation in SSA with change in the OC/TC ratio of the aerosol. The OC/TC ratio was determined using the IMPROVE-A TOR protocol with a thermal optical EC/OC analyzer at Sunset laboratories. The data was parametrized using an orthogonal distance regression (ODR) to account for errors in the OC/TC ratio and resulting fits along with data points are plotted in Fig. 3. ODR is different from a standard linear regression as it accounts for errors in both the independent and dependent variables by minimizing least square errors perpendicular to the regression lines rather than vertical errors as in standard linear regression. The ODR fits are linear with RMSE values of 0.04 and 0.02 for wavelengths 375 nm and 405 nm respectively.

~~ratio subtracted from 1) was also observed by Pokhrel et al. (2016). However, when the data from that study were converted to OC/TC values for comparison, it was noted that the slopes and intercepts of the resulting fits were different from those observed in this study. Table 2 has a list of the slope and intercept of fits for comparable wavelengths in both studies, along with the correlation coefficient.~~

A linear relation between the SSA and the EC/TC ratio (which is simply the OC/TC ratio subtracted from 1) was also observed by Pokhrel et al. (2016). However, when the data from that study were converted to OC/TC values for comparison, it was noted that the slopes and intercepts of the resulting fits were different from those observed in this study. Table 2 has a list of the slope and intercept of fits for comparable wavelengths in both studies, along with the RMSE for our fit. A likely reason for dissimilar slopes and intercepts between the two studies could be due to discrepancies in EC/OC ratios obtained using the same temperature protocol. Inter-comparison studies have shown that different labs using the same sample with identical thermal protocols may produce different results (Panteliadis et al., 2015). The instrument bias could be such that obtained OC/TC ratios would have a proportional offset between different instruments leading to similar linear trends but with different slopes which might be the case here. Another plausible reason for the discrepancy could be positive artifacts in EC/OC analysis due to gas phase SVOCs being adsorbed on the quartz surface because of phase portioning of these compounds in the holding tank. This reason seems less likely due relatively small sampling times for the aerosols. To assess the performance of our parametrizations, we compared our fit to data obtained by Liu et al. (2014) at 405 nm for BB aerosol. Data from the plots was extracted using Web Plot Digitizer (Rohatgi 2010) and is plotted with our fit in Fig. 4. We observed that our fits predicted SSA well at OC/TC ratios > 0.7 with a RMSE value of 0.06 compared to 0.08 by Pokhrel et al. (2016) but predictions were worse for 405 nm at lower OC/TC ratios as is also evident from the relatively high SSA value of 0.39 for BC obtained using our parametrization at OC/TC ratio of 0. Generally, OC/TC ratios are greater than 0.7 for laboratory and field BB (Xie et al., 2019; Akagi et al., 2011; Zhou et al., 2017; Xie et al., 2017) which reduces concerns about underperformance of our fits for 405 nm at low OC/TC ratios. It would be appropriate to use these parametrizations to determine a reasonable range for SSA values rather than use them as a surrogate to determine actual SSA for a given BB aerosol plume. A modification of Fig. 4 which compares the linear fits by Liu et al. (2014) and Pokhrel et al. (2016) with our parametrizations in provided in the Supplementary Information.

Despite the difference between our fits and those by Pokhrel et al. (2016), a useful conclusion from Fig. 3 is that the OC/TC ratio determined using the IMPROVE-A protocol and SSA of BB aerosol have a linear dependence. This dependence, however, has high variations at OC/TC ratios very close to 1, where fuel type and burn conditions dictate the composition and absorption properties (Chen and Bond, 2010; Budisulistiorini et al., 2017) of organics released and hence a larger range of SSA values exist at those OC/TC ratios. Further studies need to be conducted using more fuels with a variety of distinct size distributions and burn conditions to determine the validity and exact parameters for the fit.

3.3 Absorption bias correlated with OC/TC ratio

Fig. 5 depicts the variation in $b_{abs,OA}(\lambda)/b_{abs,sol}(\lambda)$ for primary OA with different OC/TC ratios. Because the OC/TC ratio and the SSA are well correlated, we expect to see a similar trend for Fig. 5 as in Fig. 2. Similar to Fig. 2, the bias in Fig. 5 increases with decreasing OC/TC ratio and approaches a constant for the three solvents .

A power law like the one in Fig. 2 was fit to the data in Fig. 5. The fit parameters for the different solvents at the two wavelengths, along with the RMSE value for each fit, are presented in Table 3. We reiterate that the parametrization for $b_{abs,OA}(\lambda)/b_{abs,sol}(\lambda)$ as a function of OC/TC ratio depicted here is applicable to our system and should not be used to calculate the bias in other systems. The exclusivity of depicted fit parameters to our system excuses their relatively poor RMSE while representing the bias with OC/TC ratio. The parametrizations are provided to represent some quantitative measure to the data rather than just analyze the trends qualitatively. The large error bars from the Monte Carlo simulations at high EC fractions are mainly due to uncertainties associated with the BC AÅE. At lower OC/TC ratios, the contribution of BC absorption to total particle-phase absorption coefficient is more pronounced, leading to high uncertainties while extrapolating the coefficient to shorter wavelengths. It is apparent from Fig. 5 that these errors in the bias are more prominent at OC/TC ratios below 0.75. The burns with relatively high EC fractions are not representative of typical laboratory or field BB. Typical laboratory BB have OC/TC ratios > 0.7 (Xie et al., 2017; Akagi et al., 2011; Pokhrel et al., 2016; Xie et al., 2019) and > 0.9 for field BB (Aurell et al., 2015; Zhou et al., 2017; Xie et al., 2017). Thus, data presented in Fig. 5 with relatively large errors and EC fractions > 0.25 are not representative of typical BB in either laboratory or field settings which may warrant their exclusion from most analysis. We have still included these data points in our plots and Tables but have excluded their use in data analysis due to the high errors associated with them.

In Fig. 5, the difference in magnitude of the bias between methanol/acetone extracts and water extracts increase as EC fraction of the aerosol increases. An increase in the emissions of ELVOCs with increasing EC/OC ratios was observed by Saleh et al. (2014) and we hypothesize that these ELVOCs which have high mass absorption efficiencies (Saleh et al., 2014; Di Lorenzo and Young 2016) could have a lower solubility in water than methanol or acetone which would explain the increasing difference in $b_{abs,OA}/b_{abs,sol}$ values between water and methanol/acetone extracts. Some of the generated ELVOCs might be insoluble in methanol and acetone as well which would lead to the observed increase in the OA absorption bias with decreasing OC fraction of the aerosol. ~~difference in absorbance between water and methanol with increasing EC content would indicate~~

3.4 Variations in AÅE with solvents and OC/TC ratios

The AÅE values, for organics extracted in different solvents and those obtained from $b_{abs,OA}$ are compared in Table 4. The AÅE values along with the errors for OA measurements were calculated between λ = 375 and 405 nm using the Monte Carlo simulation. The AÅE for OA extracts were calculated based on $b_{abs,sol}$ and corresponding errors were propagated based on uncertainties in the UV-Vis measurements. Consistent with previous studies (Chen and Bond, 2010; Zhang et al., 2013; Liu et al., 2013), the AÅE values of water extracts were larger than the AÅE of acetone and methanol extracts. Experiments by Zhang et al., (2013) observed that polycyclic aromatic hydrocarbons (PAHs) absorbed light at longer wavelengths close to the visible region. Organic compounds such as methanol have a higher extraction efficiency for these compounds than water leading to higher absorption by methanol extracts at longer wavelengths which results in lower AÅE (Zhang et al., 2013) ~~weight compounds than water, and they can thus absorb more light at longer wavelengths, leading~~ .

The AÅE calculated for OA ranged from 6.87 ± 1.73 to 15.57 ± 0.57 (excluding data with OC/TC > 0.75) which are slightly larger than AÅE values reported by most studies (Pokhrel et al., 2016; ; Lewis et al., 2008). However, these studies report AÅE values in the visible range, which might be lower than aerosol AÅE values in the UV range as observed by Chen and Bond (2010) for OA extracts. The range of AÅE observed for water, acetone and methanol extracts were similar to those observed by Chen and Bond (2010). A t-test for data presented in

Table 4 shows that AÅE values for OA were greater than their solution phase counterparts for both methanol ($N = 17$, $p = 0.0007$) and acetone ($N = 17$, $p = 0.0002$). The difference in AÅE of OA and water extracts were statistically insignificant ($N = 17$, $p = 0.25$), but these differences were statistically significant at OC/TC ratios ≥ 0.9 ($N = 12$, $p < 0.05$) where uncertainties due to BC absorption are lower. The reason for these differences could be a combination of artifacts due to inefficient extraction of organics absorbing light at lower wavelengths and the absence of size dependent absorption in the solvent phase which might not capture effects of enhanced particle phase absorption at lower wavelengths. These bulk solvent measurements of AÅE suggest that they might not be representative of spectral dependence of OC in the particle phase, and future studies and models should be cautious while using AÅE data from solvent-phase measurements to be representative of the particle phase.

3.4 Mie Calculations

The absorption coefficient determined from the bulk solvent absorbance using Eq. (1) was compared to absorption coefficients calculated using Mie theory for three samples of smoldering sage. The EC/OC analysis (IMPROVE-A protocol) determined that these samples consisted purely of OC, and because the SMPS measurements and TOC analysis were only performed on the first set of samples, the three samples of sage were considered optimum for the Mie calculations.

The Mie based scaling factors for converting solution phase absorption coefficients to particulate absorption for the three samples are presented in Table 5. The Mie calculated scaling factors at 375 nm and 405 nm are close to 2 as observed in previous studies (Liu et al., 2013; Washenfelder et al., 2015). The values for these scaling factor vary from 1.99 to 2.05 at 375 nm and 2.15 to 2.29 at 405 nm. However, it is important to note that these scaling factors are not representative of actual biases for determining OA absorption from solution phase as observed in Table 5. Thus, Mie based correction factor of 2 cannot be used for all conditions, as corroborated by observations from Fig. 2 and Fig. 5 ~~based correction factor might severely underestimate the absorption by the total absorbing OA~~. We advise researchers to avoid using such scaling factors for determining OA absorption without exact knowledge of OC extraction efficiencies and particle size distributions.

4 Conclusions

Under controlled laboratory conditions, we determined artifacts associated with optical properties of the solvent phase as compared to particle phase counterparts for primary OA emissions from biomass combustion. We combusted a range of different wildland fuels under different combustion conditions, generating a span of different SSA and OC/TC values. The SSA values ranged from 0.55 to 0.87 at 375 nm, and from 0.69 to 0.95 at 405 nm, the OC/TC values ranged from 0.55 to 1. We observed an increasing difference in $b_{abs,OA}/b_{abs,sol}$ for water and methanol extracts with increasing EC fraction of the aerosol. The decrease in water extracted absorption with decreasing OC/TC ratios was hypothesized to occur due to a decrease in extraction of ELVOC or similar compounds with high mass absorption efficiencies by water. ~~that the conversion factor tends towards a constant with increasing EC content for the range of SSA and OC/TC analyzed, and these factors were parametrized with the SSA and OC/TC of the~~ We also demonstrated that the SSA and OC/TC ratios can be well parametrized with a linear fit that captures the effects of brown carbon aerosol. We analyzed the validity of the conventionally used scaling factor of 2 for determining OA absorption coefficients from water extracts of organics and noted that, while the factor is reproducible, its use can misrepresent OA absorption coefficients. We recommend that future studies not use such scaling factors without knowledge of the OC extraction efficiency and particle size distributions as these scaling factors might not be extensible to organic aerosol emissions from all combustion processes. ~~and values between 1 and 4 for methanol extracts based on OC/TC ratios for EC mass fractions~~ A comprehensive technique which improves extraction efficiency with accurate knowledge of particle size distributions is necessary to determine correct scaling relations.

For future experiments, a better technique to quantify BC absorption at lower wavelengths, such as a thermodenuder to strip off all OC, or a single particle soot photometer along with core-shell Mie calculations can be used to determine BC absorption to decrease uncertainties for BC absorption observed during experiments using this technique. ~~Here, BC is assumed to be externally mixed with OC; correction factors accounting for BC~~ Zhang et al. (2013) observed lower AÅE for WSOC from a particle into liquid sampler (PILS) than for methanol extracts. The hypothesis was that the highly dilute environment in PILS increased dissolution of organics in water. This suggests that extraction of organics can be increased by heavily diluting the samples. This can be combined with highly accurate spectrometers similar to the technique used by Hecobian et al. (2010) to reduce some of the biases due to incomplete OA extraction.

Author Contributions

RKC conceived of this study and designed the experiments. SB and WMH collected the fuels for the experiments and performed EC/OC analysis on the sampled filters. NS and AP carried out the experiments and analysed the data. NS prepared the manuscript with input from all co-authors.

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Figures and Tables:

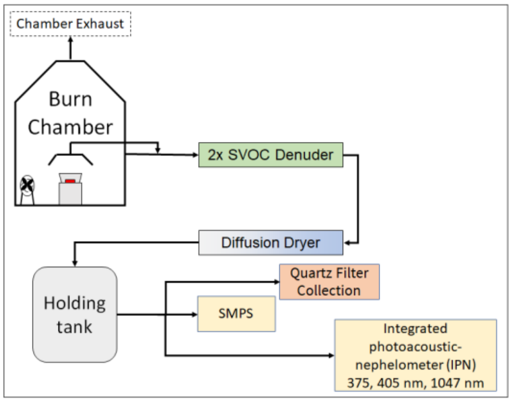

Fig. 1: A schematic representing the experimental setup. The aerosol emissions were either sampled directly from the chamber wall or through a hood placed directly above the combusting biomass.

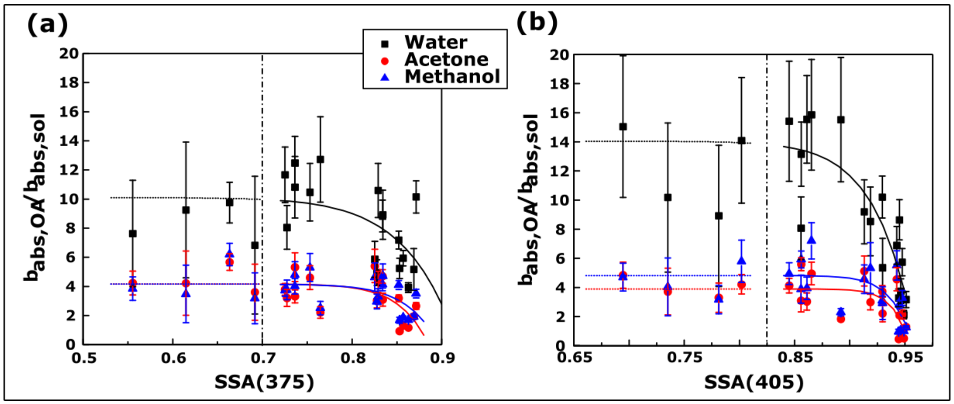

Fig. 2: Variation in $b_{abs,OA}/b_{abs,sol}$ with change in the SSA at (a) 375 nm and (b) 405 nm (N = 21). The error bars represent one standard deviation from the mean. The perforated lines separate points at lower SSA, which have high errors due to uncertainties in BC AÅE, from the data at high SSA.

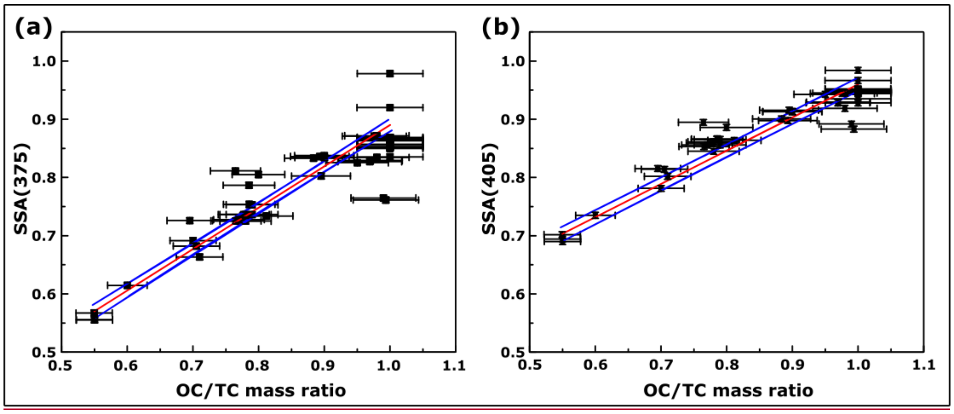

Fig. 3: SSA at (a) 375 nm and (b) 405 nm as a function of the OC/TC ratio (N= 49). The solid red lines are ODR fits to the data and the solid blue lines represent the 95% confidence intervals. The errors in OC/TC ratios were determined by the quadrature sum of uncertainties from EC/OC analysis and the error in SSA were negligible

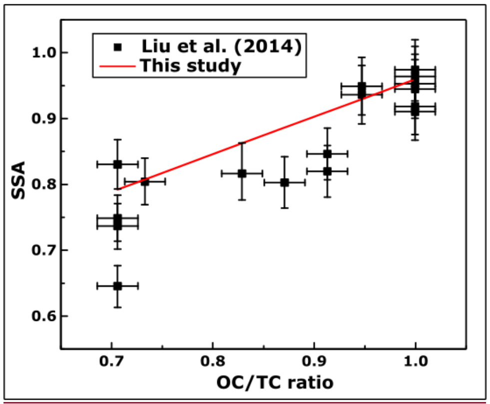

Fig. 4: Measured SSA values by Liu et al. (2014) for controlled laboratory combustion experiments plotted with the solid red line representing the ODR parametrization determined in this study.

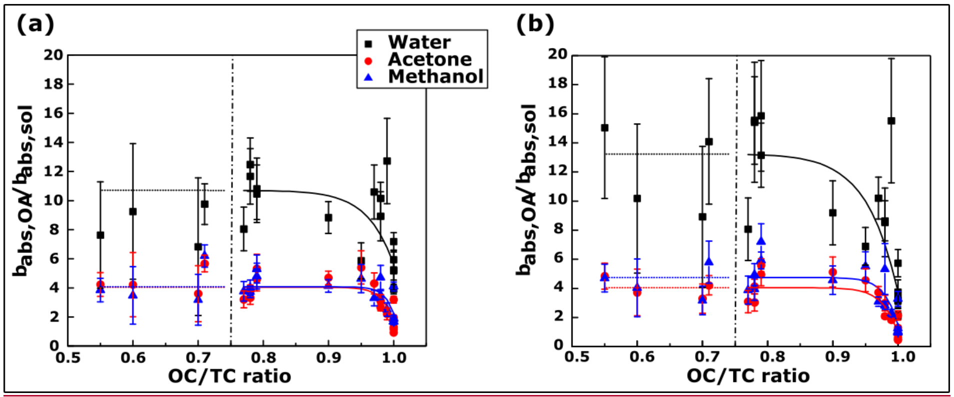

Fig. 5: The values of $b_{abs,OA}/b_{abs,sol}$ plotted with the OC/TC ratio, instead of the SSA, as in Fig. 2.

Table 1: Fit coefficients for $b_{abs,OA}(\lambda)/b_{abs,sol}(\lambda)$ as a function of SSA ($y = k0 + k1\ (SSA)^{k_2}$) for tested solvents and the fuels analyzed in this study along with the RMSE value for each fit.

	Wavelength (nm)	Solvent	Fit Parameters			
			k_0	k_1	k_2	RMSE
$\frac{b_{abs,O}}{b_{abs,\cancel{bulk}}}$	375	Water	10.1 (±2.1) ~~1.84~~	-~~19.09~~39.83 (±177.1)	~~8.43~~16.09 (±31.3)	2.2~~7~~1
		Acetone	~~4.28~~4.17 (±0.8)	-~~50.8~~117.4 (±36.9)	2~~4~~7.~~52~~46 (±37.5)	1.~~25~~12
		Methanol	4.~~34~~16 (±0.77)	-~~41.01~~69.12 (±451.6)	2~~1.41~~5.76 (±45.4)	1.06~~2.15~~
	405	Water	14~~3~~.0~~7~~4 (±4.2)	-4~~5~~2.37 (±70.5)	~~33.34~~27.42 (±35.5)	2.~~4~~6
		Acetone	3.89 (±1.12) ~~4.32~~	-~~18.69~~95.6 (±609.9)	~~35.19~~68.3 (±121.8)	1.~~17~~3
		Methanol	4.82 (±1.4) ~~5.00~~	-~~29.47~~49.05 (±250.3)	~~42.97~~53.07 (±98)	1.~~63~~48

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Table 2. ODR regression coefficients along with errors in brackets for plots of SSA v/s OC/TC ratios (y = m (OC/TC) + c) for the different biomass fuels used in this study, and parameters for ODR fit from Pokhrel et al. (2016) for 405 nm, along with RMSE values for our fits.

	Wavelength (nm)	m	c	RMSE~~r~~
This study	375	0.~~585~~71 (±0.04~~0~~)	0.~~2~~18~~1~~ (±0.03~~6~~)	0.04~~904~~
	405	0.~~47~~57 (± 0.02~~3~~)	0.~~475~~39 (± 0.02~~1~~)	0.~~948~~02
Pokhrel	405	~~0.874~~1.07 (±0.04) ~~(±0.049)~~	~~0.036~~-0.13 (±0.04) ~~(±0.042)~~	\~\~~~0.971~~

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Table 3: Fit parameters for ratios of the absorption coefficient of organics in the particle phase to the absorption coefficient of the solvent phase, as a function of the OC/TC ratio ($y = k_0 + k_1(OC/TC)^{k_2}$) for the fuels analyzed in this study, along with the RMSE value for each fit.

	Wavelength (nm)	Solvent	Fit Parameters			
			k_0	k_1	k_2	RMSE
$\frac{b_{abs,OA}}{b_{abs,bulk}}$	375	Water	10.7~~1~~ (±1.83)	-5.~~13~~05 (±2.54)	24.96 (±36.2) ~~32~~	2.~~1~~01
		Acetone	4.05 (±0.77) ~~26~~	-2.~~6~~37 (±1.21)	~~48~~57.~~11~~98 (±86.21)	0.98~~1.03~~
		Methanol	4.08 (±0.7) ~~26~~	-~~2~~1.82 (±1.11)	~~53.6~~71.54 (±139.6)	0.9~~2.14~~
	405	Water	~~12.89~~13.24 (±2.41)	-9.~~02~~46 (±3.15)	20~~1~~.~~06~~81 (±20.94)	2.~~3~~47
		Acetone	4.05 (±0.85) ~~29~~	-3.~~2~~08 (±1.29)	~~31.5~~43.29 (±49.62)	~~0~~1.~~97~~04
		Methanol	4.75 (±1.07) ~~96~~	-3.~~39~~24 (±1.65)	4~~0.85~~9.02 (±69.46)	1.33~~51~~

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Table 4: The AÅE of OA from various fuels extracted in water, acetone, and methanol, along with the AÅE calculated for $b_{abs,OA}$.

Fuel	OC/TC ratio	AÅE$_{375\text{-}405}$			
		OA	Water	Acetone	Methanol
Dung	1	13.74 ± 2.27~~13~~	8.00 ± 2.02	5.29 ± 1.43	5.21 ± 1.29
	1	1~~4~~5.~~44~~32 ± 2.36	8.95 ± 2.04	5.85 ± 0.44	7.75 ± 0.64
	1	1~~4~~5.57 ± 0.57~~61~~	7.48 ± 1.84	4.62 ± 0.31	4.5 ± 0.91
	1	14.~~08~~93 ± 2.73	8.55 ± 1.19	5.25 ± 0.2	6.8 ± 0.39
Sage	1	13.93 ± 1.91 ~~53~~	10.87 ± 1.19	8.62 ± 0.69	8.8 ± 1.12
	1	10.65 ± 1.47~~4~~	10.71 ± 4.54	6.29 ± 3.2	7.3 ± 2.9
	0.97	10.~~41~~58 ± 2.41	9.88 ± 1.42	5.2 ± 0.79	5.8 ± 0.69
	0.79	~~6.5~~7.36 ± 2.88	12.28 ± 2.4	8.62 ± 0.76	9.17 ± 1.2
	0.79	8~~7~~.~~6~~21 ± 2.40	10.58 ± 2.15	8.73 ± 0.83	8.3 ± 1.3
	0.71	10.36 ± 1.41~~8.23~~	7.5 ± 3.11	6.29 ± 1.71	6.4 ± 2.11
	0.55	9~~4~~.94 ± 4.21	6.48 ± 4.77	3.84 ± 1.97	3.6 ± 2.8
Grass	0.99	10~~9~~.~~8~~05 ± 2.43	12.08 ± 4.56	7.84 ± 0.93	7.5 ± 1.23
	0.78	9.~~35~~92 ± 3.11	10.15 ± 2.25	8.47 ± 0.47	9.6 ± 0.62
	0.78	6.87 ± 1.73~~3~~	9.7 ± 3.75	7.49 ± 0.81	7.3 ± 1.6
	0.77	8.99 ± 4.04~~22~~	8.21 ± 1.58	8.12 ± 0.62	8.4 ± 0.92
Pine	0.98	11.82 ± 1.04~~35~~	9.36 ± 2	8.55 ± 0.75	8.1 ± 1.08
	0.98	8.68 ± 1.89~~43~~	9.59 ± 3.39	8.36 ± 1.83	8.6 ± 1.53
	0.95	14~~3~~.~~97~~20 ± 3.53	16.44 ± 1.34	11.81 ± 0.91	12.8 ± 1.27
	0.9	8.24 ± 2.36~~7.51~~	9.09 ± 2.33	8.75 ± 1.63	8.7 ± 1.97
	0.7	15~~5~~.96 ± 10.87~~6~~	9.93 ± 3.13	6.33 ± 2.24	5.83 ± 2.08
	0.6	17~~5~~.~~0~~41 ± 10.81	6.36 ± 3.31	5.2 ± 2.81	5.4 ± 2.91

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Table 5: Correction factors for bulk solution absorption to particle phase absorption, based on Mie Theory calculations.

Fuel	Geometric mean (in nm)	Geometric standard deviation	Mie based ~~Correction~~ Scaling Factor		IPN based bias	
			375 nm	405 nm	375 nm	405 nm
Sage	397	1.3	2.04 ± 0.38	2.27 ± 0.41	2.6 ± 0.61	1.64 ± 0.55
	271	1.32	2.05 ± 0.38	2.29 ± 0.41	2.8 ± 0.57	1.87 ± 0.32
	159	1.59	1.99 ± 0.36	2.15 ± 0.39	2.81 ± 0.52	1.83 ± 0.37

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