

## ***Interactive comment on “Measuring Light Absorption by Organic Aerosols: Correction Factors for Solvent Extraction-Based Photometry Techniques” by Nishit Shetty et al.***

### **Anonymous Referee #1**

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While I appreciate that the authors have looked into differences between suspended and solution-phase absorption by OA, and have been waiting for someone to do this in more detail, I am ultimately not in support of the publication of this paper in its current form. For one, I am concerned about the suggestions for such a wide range of scaling factors for water extracts. This combines too many factors, specifically size and solubility. If not all of the material is soluble, then the correction factors are forcing agreement for something that was not even measured, that is the amount of material extracted. While this might have worked for these particular test samples, I have serious doubts about the robustness of the scaling factors. They talk about the need for scaling factors as a function of SSA. But, as these sampled particles are aged in the atmosphere,

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or mix with other sources should I expect the relationships determined here to hold? I am skeptical. After reading through a few times, I've actually become increasingly skeptical. Or at least the presentation of the results. In my view, this study points out that one should take caution when using water or methanol extracts to determine absorption. Most likely it will lead to a low bias compared to the atmosphere. While we already knew this, this study adds by showing the issue more explicitly than many previous studies. But I don't actually think we should be presenting "correction factors" that might be used because I think that these are likely to lack robustness, especially in the case of water as a solvent. Ultimately, I unfortunately do not think that this paper should be published in its current form. My concern is that the casual reader might just apply these scaling factors to their data without understanding that they very well might not apply at all due to differences in their system. I suggest that the authors refocus the paper, drawing out the distinction between a bias (which results from extraction) versus the difference between solvent and particles as an explicitly optical issue (i.e. the need for Mie theory or something similar). Additionally, the authors need to provide a more robust uncertainty analysis.

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%).

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.

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 in-

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creasing.

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).

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).

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?

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.

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.

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

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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.

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.

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

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?

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.

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.

\*\*L231: These are not “fluctuations.” They are simply uncertainties. However, the error

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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.

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.

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

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 ( $r^2 = 0.81$ , Figure 5b) than water-soluble BrC ( $r^2 = 0.40$ ), 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 be-

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tween 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.

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.

As a general comment, throughout I suggest that the authors get rid of the "bulk" language and refer to these as liquid-extracted samples. Or "solution phase." Or something else similarly descriptive. "Bulk" is not especially descriptive, since particles also contain "bulk" material.

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.

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.

The Mie theory section is fine, but I think that to some extent it shows the overall inadequacy of this paper. If the issue is that e.g. water extraction does not extract all absorbing organic species, then a correction factor is not what is necessary, better extraction is necessary. The idea that there might be some universal correction factor

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that can account for solubility differences among the many different sources and types of OA in the atmosphere is, in my view, not realistic.

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