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Interactive comment on "Quantifying black carbon light absorption enhancement by a novel statistical approach" *by* Cheng Wu et al.

Anonymous Referee #2

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The manuscript presents a statistical analysis of black carbon light absorption enhancement based on observations made over roughly one year using a filter-based absorption instrument and a thermal-optical analysis OC/EC analyzer. They derive the absorption enhancement (Eabs) from the total mass absorption efficiency measured from the ratio of the absorption and EC measurements to that estimated for bare BC particles. To determine the bare BC MAE the authors employ a method that searches for an MAE value based on an assumed independence between EC and absorption due to BC coatings. While this approach presents a potential alternative to more expensive and labor-intensive methods to examine the important topic of BC light absorption enhancement, it is not clear to me that it works based on the information presented in the manuscript. First, while it does compare Eabs derived using this method to previ-

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ously reported values using other techniques, there is not a direct comparison between the results obtained using this technique and more established methods for the same site. As pointed out by Liu et al. (2015), the "influence of coatings on BC absorption may be source and regionally specific", so it is difficult to draw too much confidence in the approach based on similarities with other locations. Second, it is not obvious that the measurement of EC is independent of the amount of light absorbed by BC coatings. While it is true that the mass of primary BC should be independent of coating absorption, EC is an operationally defined quantity, and depending on how coatings interact with its measurement during thermal optical analysis, could in fact have a relationship with coatings and light absorption due to coatings. For these two principle reasons I do not recommend the manuscripts publication in ACP in its current form.

General comments

RH impacts

The manuscript does not clearly state whether air was dried prior to sampling with the instruments. Section 4.5, which discusses impacts of RH on the observations, implies that it was not. The methods section states that 2.5 um cyclones were used upstream of the Aethalometer and Sunset instruments, but does not specify a sizecut for the nephelometer or MARGA instruments. If the nephelometer and MARGA instruments did not have a sizecut, it is extremely difficult to compare results from those instruments to those from the AE-31 and Sunset due to potential differences from coarse mode particle contributions.

If the air was not dried prior to sampling more details need to be provided regarding the effective RH for the optical instruments (AE-31 and nephelometer), which may be different from ambient RH due to temperature differences between the ambient air and the instruments. In addition, if air was sampled at near ambient RH it could have a number of complicating factors on the subsequent analysis. Filter-based absorption instruments, as the authors acknowledge, are affected by artifacts, including the scat-

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tering and shadowing of light in the filter matrix by filter fibers and particles embedded on the filter. Varying sample RH can change the filter artifacts in difficult to account for ways. For example, if hygroscopic particles are present on the filter they can swell or shrink depending on the sample RH, changing the light transmission properties of the filter, artifacts affecting the absorption measurement and possibly the absorption measurement itself depending on how RH interacts with the correction methods applied. The manuscript should include a discussion of how well the correction methods applied can account for changes arising from changes in RH. In addition, the effective size cut of the cyclone will be affected by RH in that the aerosol sampled will be different depending on how much water is associated with it. This effect may be small depending on the aerosol distribution and makeup of the light-absorbing particles, but should be addressed.

Another potential issue related to RH affects some of the results presented in Section 4.5. First, it is not clear if the RH reported is ambient RH or instrument RH. If ambient RH, it needs to be established that the RH at the location of the measurement (the filter) is also at the same RH as the ambient. In addition, it is not clear that the absorption measured on the AE-31 filter represents the absorption in the ambient air. For example, if BC becomes coated on the filter (which can happen in the presence of liquid organic aerosol (e.g. Subramanian et al., 2007) it is not clear how water uptake by those organic films might alter the absorption by particles that were not originally coated. Non-BC containing material can also take up water, alter the optical properties of the filter, and change the apparent absorption attributed to BC. Also, since the AE absorption measurement is based on the change in attenuation over time if the hygroscopic properties of particles change with time the apparent absorption could be affected. For example, consider a situation where BC with a hygroscopic coating has been sampled onto the filter for some period of time. As the sample RH begins to decrease the water will evaporate from the filter, likely leading to a decrease in attenuation (there is a reduced enhancement of absorption, for example). At the same time consider what happens if additional BC is sampled to the filter. This acts to increase

attenuation, opposing the RH effect. As a result the BC measured during this time would be underestimated (its effect on attenuation is countered to some degree by the opposing RH effect). Note that the magnitude of these impacts would be difficult to account for, in that they depend on the hygroscopicity of the material on the filter and how that material and associated water interacts in the filter matrix.

Measurement biases and impacts on the analysis

Biases in filter-based absorption and OC/EC measurements are mostly associated with other materials mixed and/or co-sampled with BC/EC, so it is likely that errors in the measurements have a systematic relationship. For example, the presence of organic aerosol and organic films has been linked to both biases in filter-based measurements (e.g., Lack et al., 2008) as well as potential impacts on EC measurement via pyrolized carbon correction (Subramanian et al., 2007). The manuscript needs a detailed discussion of how correlations in biases between the methods affect the retrieved MAEp values and resulting Eabs calculations. Since the manuscript is seeking to establish a new method this potential issue needs much more attention. Several specific comments below are related to this general concern.

Specific comments

78-80: Missing from the list of field studies is Cappa et al. (2012), which found a weak enhancement for observations in California, US.

85: Suggest changing to “The TD approach is briefly discussed here.”

90: Some good points are raised in this discussion, but a few things are lacking. First, another major reason for use of PAS systems in the approach is that the technique does not have artifacts associated with filter-based methods for measuring light absorption, thus it provides an unambiguous measure of the light absorption coefficient in both heated and un-heated states. Also missing from the discussion is potential differences in BC core morphology being different for “fresh” versus “aged with coating removed”

conditions, or in other words, the TD may not be a perfect “time machine” to reverse the aging process and determine the effects of BC aging.

100-101: I realize this is not the focus of the manuscript, but it is worth noting here the logic presented here assumes a linear relationship between MAE and coated soot particle number fraction measured by SP2. This may not be the case due to limitations in the size of BC particles measured by the SP2, its ability to measure thin coatings, the potential impact of thin coatings on MA, the assumption of core-shell morphology, and the nature of the relationship between the fraction of coated particles (a parameter which ignores coating thickness, the physical driver of the absorption enhancement) and MAE.

133: What does the 5% uncertainty refer to? Is this before or after corrections? Are the uncertainties in the corrections as low as 5%? Also, the manuscript gives an uncertainty of 24% for the ECOC analyzer here, but then later states (line 153) up to a factor of 5 differences in EC measured by different protocols are possible. How is this to be reconciled?

166-169: The argument given here is only true if the errors in absorption measurement and EC mass measurement are independent and random. If some factor causes a positive bias in the filter-based absorption but a negative bias in the EC measurement they will not cancel, but instead there will be an apparent and potentially false apparent absorption enhancement. Or consider a situation where some co-sampled material affects the OC/EC split but not the filter-based absorption measurement, leading to an apparent change in Eabs.

187-188: Since EC is an operationally defined parameter based on a measurement technique there is not necessarily an inherent interdependency between it and the absorption due to coatings gained following emission.

Section 3.2: The results from the Mie simulations are not a new contribution and main points drawn from the discussion could be drawn from previous studies given in the

literature (e.g., Lack and Cappa, 2010; Bond et al., 2006).

260: Should note here that the AAE observed in measurement studies also includes absorption by potentially externally mixed brown carbon particles, not just those present in the form of shells on BC particles.

295: Suggest changing “concentrations” to “modes”.

299-302: Minor point here, but the MOUDI data also reflect differences in BC core equivalent diameters measured using LII and aerodynamic diameter of BC, so we would not necessarily expect similar sizing, even for uncoated BC. Worth mentioning here, though I do not disagree with the main argument given here.

303: Please state whether Tan et al. refer to BC only diameter or mixed particle diameter here.

314: I am curious as to why the 470 and 660 nm wavelength pairs were used to quantify AAE. Brown carbon tends to show much stronger impact at shorter wavelengths. Could the authors please include the AAE determined for the UV and 880 nm channels also measured by the AE-31?

321: I assume MAEp should be MAEp, 550 based on Table 1?

325-328: The Cappa et al. observation showing weak enhancement should also be included in this summary.

355: Use of “significantly” implies a statistically significant difference between the clusters. Please provide uncertainty estimates and confidence levels if this is intended, or omit.

360-361: I am curious how much the air mass trajectories were influenced by precipitation during the monsoon period/rainy season. It seems like aged/coated BC likely having higher Eabs would be more susceptible to removal compared to less-aged/coated BC with lower Eabs?

375-376: Could the authors clarify the reasoning given here? First, I believe the authors mean the MAEp determined in section 4.1, not 4.3, correct? I think this is arguing that because MAEp is, on average, higher than the MAE observed in the absence of BB influence there must be a large amount of BB influence on BC at this location? If so, I think some caution or caveats should be included in the discussion, since the BB influence tracer is not independent of the EC measurement. Further, I would expect there to be a much stronger effect on AAE if BB was such an important BC source, yet the later sections establish that AAE does not show a response.

381: Again I am curious as to the reasoning for selection of these wavelength pairs.

384-386: I do not quite follow the reasoning presented here. Why does the monthly average of 1.2 suggest variations in AAE are associated with thicker coatings than BrC contribution? To me the strongest evidence of minimal BB contribution is the lack of correlation with the K+/EC tracer. Does AAE show any correlation with Eabs? The manuscript asserts AAE is dominated by coating, so there should be a relationship based on the arguments presented.

413-415: The refractive index of the shell also changes as it takes up water. Is this accounted for in the modeling?

426: This approach requires that only BC and associated coatings affect Eabs and AAE, but AAE can also be affected by non-BC aerosol (e.g., brown carbon or dust) that is externally mixed with BC. I am not sure how this approach can work unless there is clear evidence that there are no other light-absorbing particles or that the relative abundance does not change with season.

Table 1, while convenient, could be omitted for length.

Figures 2-4 do not add much to the manuscript, in my opinion, and could be removed for length.

Figure 7: Minor, but x-axis is year and month, not just month. Replacing with “Date”

would be fine.

References:

Bond et al. (2006) Limitations in the enhancement of visible light absorption due to mixing state, J. Geophysical Research, doi: 10.1029/2006JD007315

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Liu et al. (2015) Enhanced light absorption by mixed source black and brown carbon particles in UK winter, Nature Communications, doi: 10.1038/ncomms9435

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