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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Aerosol light absorption and the role of extremely low volatility organic compounds" *by* Antonios Tasoglou et al.

Anonymous Referee #1

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The authors provide an analysis of measurements of light absorption, particle composition & volatility, and black carbon concentrations wherein they aim to establish the contribution of non-BC absorption to the total absorption and establish relationships with the observed particle composition. They conclude that the observed absorption is in great excess of that expected by uncoated black carbon alone and attribute this difference, based on comparison with Mie theory calculations, to a combination of the lensing effect for BC and to brown carbon. They conclude that that the lensing effect varies little over the campaign. The also conclude that the brown carbon absorptivity correlates with the absolute concentration of ELVOCs in their SOA. Unfortunately, I find their analysis and interpretation contains some fundamental flaws and misunderstandings regarding the relationship between Mie theory and observations. While I wish I

could be more positive, I do not think that this paper can be accepted in its current form and I question whether it would be acceptable at any point. My reasoning follows below.

1. The authors measure BC concentrations using an SP2. Not shown are any size distributions, which are important to consider as the measurements may have a negative bias owing to BC particles that are outside the detection window. This contribution may be small, but it should be considered if it has not been (it is not clear from the presentation). One way this has been dealt with in the literature is through single- or multi-modal fitting. This is another reason that the observed MAC might be higher than an expected value for pure BC (see line 278). This links to a question about measurement uncertainties, which are not reported. The authors must provide a discussion of uncertainties, that includes potential biases owing to factors such as BC outside of the measurement size window.

2. A major concern that I have about this paper relates to their interpretation of their absorption measurements. They state that the MAC of pure, uncoated BC at 405 nm should be 9.9 m2/g, but that they observe an average of 16.3 m2/g. However, they conclude later that their predicted value of 14.1 m2/g is a factor of two greater than it should be. This implies an MAC of 7.05 m2/g for pure BC from the calculations, much smaller than the 9.9 m2/g. This is because Mie theory generally leads to underestimates of the BC absorption. Thus, the calculated MAC is biased low. The extent of the underestimate depends on the details of the calculations (refractive index, particle size), which are not provided. The amount of information regarding the calculations is insufficient to allow clear judgement of their appropriateness. Regardless, it is evident that the authors are not making a fair comparison; the 14.1 m2/g value cannot be compared to the 16.3 m2/g value as they are starting from different reference values. Thus, the authors conclusion on L290 that there must be non-refractory absorbing material is not justified, nor are any subsequent calculations of the "delta_MAC". Related, the conclusions and calculations regarding the brown carbon imaginary RI, as determined

via closure, are not justified, in my opinion.

3. I do not find that the inputs to their calculations are sufficiently constrained to allow for accurate calculation of the absorption. Certainly, their calculated value cannot be directly compared to the observations (as the authors do) owing to my point in comment 3 that they undoubtedly underestimate the absorption by BC in their calculations. Beyond that, the authors seem to make a very poor assumption regarding the coatings on BC. The note that they use the ratio of the total aerosol mass divided by BC mass to estimate coating thickness. This is not appropriate. The BC-containing particles likely make up a small fraction of the total particles. Thus, some unknown fraction of the total non-BC material is internally mixed with BC. Quite often this fraction can be quite small, although it depends explicitly on the history of the air mass. If the authors are unable to provide constraints on the actual amount of coating on their BC, their calculated Eabs must be taken as an upper limit, with the actual value falling somewhere between 1 and the upper limit (2.07); unfortunately, no tighter constraint is possible without additional information regarding the true coating state. It is evident that the assumption that all material coats BC is a poor assumption, as the variability in the calculated MAC is negligible; this is simply because the particles always have "thick" coatings, in the plateau of the Mie curve, and thus little variability in the calculated MAC. The calculated MAC cannot be compared to the observations in any sort of quantitative manner. The conclusion that the lensing-induced enhancement is 2.07 is not justified. The authors might consider comparing the observed MAC_405 versus the NRPM to BC ratio; if the authors assumption that there is a substantial absorption enhancement and that all NRPM material is coated on BC were valid they should see a strong relationship between the MAC_405 and the NRPM/BC ratio that trends towards the expected pure BC value as the NRPM/BC ratio declines. (There may still be a relationship between the coating amount and the total NRPM/BC ratio, and thus even if a relationship is observed it is not definitive proof. Nonetheless, it might provide guidance for the interpretation.)

4. The authors report a strong correlation between the MAC at 405 nm and the BC concentration. They do not report the relationship at other wavelengths. If BrC is making a major contribution, and if it does not come from primary emissions that are associated with the BC emissions, then there should be a stronger relationship at longer wavelengths. The authors have measurements at longer wavelengths from the Aethelometer. Is the Rˆ2 value larger at longer wavelengths than it is at shorter wavelengths?

5. One of the conclusions of Karnezi et al. (2014) is that "Our results indicate that existing TD-based approaches quite, often cannot estimate reliably the OA volatility distribution, leading to large uncertainties, since there are many different combinations of the three properties that can lead to similar thermograms." Yet, this is exactly what the authors have done here. It is thus unclear how the authors know that they have a unique solution, especially with respect to the co-variation between the derived volatility distribution and accommodation coefficient.

6. Why would one expect that an intensive property (the delta_MAC) should correlate with an extensive property (the ELVOC concentration)? Typically, intensive properties should correlate with some other intensive property (for example, the ELVOC fraction of total OA). Extensive properties should correlate with extensive properties (for example, the estimated unexplained absorption vs the absolute ELVOC concentration). I do not see a justification for why an intensive measurement should correlated with an extensive. The authors highlight this relationship in their abstract, yet spend a total of 7 lines presenting and discussing it. This is, in my opinion, insufficient. Does the delta_MAC correlate with any other measured properties, as but one thing that it would be useful for the authors to consider? That said, I'll note again that I do not believe the delta_MAC values are valid for the reasons discussed above, and thus, in my opinion, this entire analysis is suspect.

7. Also, what might be the source of these low-volatility absorbing organic components in this environment? This is not discussed. Why would the low-volatility components from LO-OOA have the same absorptivity as those from MO-OOA, as implied in the

equation at line 300. It is generally thought that OA from biogenic sources is relatively non-absorbing. Certainly, I am unaware of any measurements that indicate that SOA from biogenics, which presumably dominate this site, can have an RI as large as 0.4, which the authors indicate was measured. The authors need to provide justification via comparison to the literature.

8. The authors measured light absorption coefficients using an aethelometer and a PAX. As best I can tell, the authors have not compared the measurements from these two instruments to establish whether the aethelometer suffers from any positive biases that are known to impact filter-based absorption measurements. That said, such biases are less likely to influence the wavelength dependence measurements than they are the absolute absorption values.

Additional comment:

The authors must place their data in an appropriate repository.

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