

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

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(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.

C1

The BC number concentration distributions were fitted in our baseline calculations using a Gaussian distribution to account for particles smaller than the SP2 detection limit (Ditas et al., 2018). This extrapolation resulted in an increase of the BC mass concentration by 3-8 percent, so its effect on the reported results (e.g., the observed MAC) was minor. This information has been added to the revised paper together with a graph (in the Supplementary Information) with a few representative mass distributions. A discussion of other SP2 uncertainties has been also added (Lack et al., 2012). This SP2 issue is discussed together with the rest of the uncertainties of both the measurements and the modeling in a new uncertainty analysis section that has been added to the revised paper.

(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 a 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 “deltaMAC”. Related, the conclusions and calculations regarding the brown carbon imaginary RI, as determined.

This is a valid point but it is due to a misunderstanding of this rather poorly placed sentence. Our calculations are self-consistent. The MAC of 9.9 m²/g was never used in any of the calculations and should not be part of the discussion here. It was mentioned

C2

at this point just to support the argument that the measured value of 16.3 m²/g is too high compared to what would be expected for pure uncoated BC. We have moved the discussion of the MAC values of pure, uncoated BC to the introduction of the paper stressing that its value at a specific wavelength depends both on the size distribution of the particles but also on their degree of aging (fresh aggregates versus collapsed more spherical structures). We just make the point now that the measured value of 16.3 m²/g is far outside the range expected for pure, uncoated BC particles.

The details of all the Mie theory calculations are now provided at one place in the paper. Some of them were in different parts of the original work. The predicted average BC MAC405 using the measured BC size distribution and assuming pure uncoated spherical particles was 7.2 m²/g varying from 6.1 to 7.8 m²/g during the study (hourly averages). This is consistent with the expected 5.3-9.2 m²/g for BC core diameters in the 10-350 nm size range. This information has been also added to the paper.

We should also stress that the 16.3 m²/g is the average measured value based on the PAX and the SP2 measurements. It is not based on an assumed reference value for the pure, uncoated BC MAC value. Thus, there is no issue regarding the consistency of the predicted and the measured values. The uncertainty of both is analyzed in the new uncertainty analysis section. Please note that the differences of the measured and the predicted MAC405 were as high as 7 m²/g and we argue that this difference cannot be explained by the corresponding uncertainties in the measurements and the modeling.

(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 2 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*

C3

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 MAC405 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 MAC405 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.)

The uncertainty of the estimated value of the absorption of the BC is addressed in the new uncertainty analysis section. We test the hypothesis that this absorption has been underestimated and that this can explain the difference in measured and predicted absorption of the particles. We show that while increasing the absorption of the BC cores can explain the average observed absorption it cannot explain its variability.

The second point of the reviewer is that our calculations are based on the assumption that all particles of the same size contain the same BC (internally mixed aerosol population). This is correct and it does provide the upper limit for the lensing effect and

C4

therefore the minimum of the unexplained absorption that could be assigned to BrC. All the air masses sampled during the campaign were quite aged so it is reasonable to assume that all the BC particles were coated. In order to provide a better constraint for our method we calculated the coating thickness of the rBC cores using the leading-edge-only (LEO) fit method (Gao et al. 2007) and the SP2 data. The thicknesses as expected were lower than those resulting from the internal mixing assumption but were still significant. We have repeated our calculations using this estimate of the coating thickness and tested the robustness of the link between the unexplained absorption and the ELVOC concentrations but also for the rest of our results.

We have followed the reviewer's suggestion and investigated the relationship between MAC405 and the ratio of non-refractory PM1 and rBC. There is a positive correlation between the two ($R=0.31$) and the intercept is $12.8 \text{ m}^2/\text{g}$. This analysis provides, as the reviewer suggests, limited support to our argument, but has been added to the paper nonetheless.

(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 Aethalometer. Is the R^2 value larger at longer wavelengths than it is at shorter wavelengths?*

We followed the reviewer's suggestion and examined the values of the R^2 between the MAC and the rBC concentration at different wavelengths. Indeed, the R^2 at 370 nm was 0.67, a value lower than the R^2 at 405 nm (equal to 0.74). This is consistent with the presence of some BrC. However, the first is based on the Aethalometer and the second on the PAX measurements. Moving at higher wavelengths the R^2 at 450 nm was 0.68, at 520 nm 0.67, at 590 nm 0.65, and at 660 nm 0.65. These values provide

C5

a mixed picture. Part of the explanation for this behavior could be that a fraction of the BrC is associated with rBC either from the emissions or from the associated gas-phase pollutants that react in their way to the site. This information has been added to the revised paper and the corresponding figures to the Supplementary Information.

(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.*

This is a valid point. The comment of Karnezi et al. (2014) referred to a detailed volatility distribution in the Volatility-Basis-Set framework. We have recently shown (Louvaris et al., 2017; Cain et al., 2020) that the uncertainty of volatility classes (e.g. ELVOCs, LVOCs, SVOCs) is significantly less than the uncertainty of individual volatility bins. The uncertainty of these concentrations is provided by the fitting algorithm used in the paper and is shown in Figure 4 of the paper. We have repeated the analysis of the links between the unexplained absorption and the ELVOC levels. The results are discussed in the new uncertainty analysis section and show that our original conclusion is robust.

(6) *Why would one expect that an intensive property (the deltaMAC) 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*

C6

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 deltaMAC 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 deltaMAC values are valid for the reasons discussed above, and thus, in my opinion, this entire analysis is suspect.

This is a valid point and we agree with the reviewer that it is preferable to correlate either intensive properties or extensive properties to each other. We have examined the correlation of the unexplained absorption and the ELVOC concentration and found an $R^2=0.76$. This actually strengthens our argument regarding the contribution of the ELVOCs to the unexplained absorption by removing the other factors entering into the calculation of the intensive property the MAC. We have revised Figure 7 accordingly.

Please note that we devote two pages in the original manuscript explaining the estimation of the ELVOC concentrations and a few more pages discussing the calculation of the unexplained absorption.

We have examined the correlations of Δ MAC with the rBC, with other parameters and found that they were all much lower than those for the ELVOCs (0.76). For example the R^2 with the rBC was 0.38 (rBC), with the LO-OOA 0.44 and with the MO-OOA 0.29. There was a relatively high R^2 with the sulfate levels (0.59) that could be interesting as high sulfate levels in this area correspond to high aerosol acidity which has been shown to promote formation of oligomers in secondary organic aerosol. This analysis has been added to the paper.

(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

C7

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.

The OA in the site is the result of long range transport from other areas and is not due to local sources (including biogenics). During the period of the study the area near the station has almost no vegetation (mainly dried out bushes). The average O:C of the OA in the site (around 0.83 on average) during the campaign is a lot higher than that of fresh biogenic SOA. Air mass came to the site from continental Greece and Balkans, Turkey, Africa and central Mediterranean. The OA in the Eastern Mediterranean during the summer has significant contributions from both anthropogenic and biogenic sources but their contributions remain uncertain. Based on our recent work (Drosatou et al., 2019) the LO-OOA and MO-OOA do not reflect different sources, but rather different degrees of chemical aging. ELVOCs can be produced both by primary sources (combustion of fossil fuels but also biomass burning) and secondary processes. Given the intense chemical processing of the organic compounds from all sources in their way to Finokalia, we cannot assign based on our measurements to a specific source or sources. The association of BrC with material of lower volatility away from its sources has been reported in a number of studies focusing on biomass burning (Saleh et al., 2014; Wong et al., 2019). This discussion has been added to the revised paper.

(8) The authors measured light absorption coefficients using an aethalometer and a PAX. As best I can tell, the authors have not compared the measurements from these two instruments to establish whether the aethalometer 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.

A comparison of the aethalometer and the PAX measurements has been added to the Supplementary Information of the revised paper. We compared the absorption coeffi-

C8

lients measured by the aethalometer at 370 nm and at 450 nm with that measured by the PAX at $\lambda=405$ nm. The measurements of the two instruments were highly correlated with $R^2=0.9-0.91$. The babs₃₇₀ measured by the aethalometer was higher than the babs₄₀₅ of the PAX. Their relationship is described by the equation $y=3.32x - 3.24$. Similarly, the babs₄₅₀ measured by the Aethalometer was higher than that of the PAX at 405 nm and their relationship was described by the equation $y=1.85x - 0.93$. These discrepancies could possibly exist due to the artifacts associated with OA loadings on the filter (Cappa et al., 2008; Lack et al., 2008). A brief discussion has been added in the main paper and the corresponding figures have been added to the SI.

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C9

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C10