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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.

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(1) *Overview: The paper is focused on presenting observations from a âĹij3 week measurement campaign at a Cretan site with little direct local influence. Measurements of rBC, aerosol light absorption, gas phase tracers, and bulk aerosol composition were complied to answer a primary focus topic: connecting observed aerosol absorption and potential BrC influences via the proxy of low volatility compounds. Publication of this kind of work falls within the aims of ACP, and contributes to the broad understanding of aerosol absorption. The manuscript does not yet make a strong enough case for its conclusions. The major reasons for this are 1) the lack of uncertainty analysis 2) un-discussed conflict between conclusions and observations, and 3) lack of details provided about interpretation and work such that the reader is not sure what was done*

and what it means. In my opinion, the paper is a good start towards a publication ready manuscript, but more analysis work and explanation is still required to make a solid contribution to establishing distilled conclusions from the observations.

We appreciate the constructive comments and suggestions of the reviewer. To address them we have: (1) performed additional uncertainty analysis of the results focusing on the robustness of our conclusions. A new uncertainty analysis section has been added; (2) addressed the apparent conflict between the value of the angstrom exponent and the conclusion about the brown carbon levels; and (3) provided additional details about the approach used. Our detailed responses (in regular font) follow each reviewer's comment (in italics).

General Comments

(2) *Uncertainty: throughout the manuscript consideration and discussion of uncertainty should be expanded. Comparison of MAC from theory and measurement depends critically on the uncertainties of the various approaches. To the extent that there is validating information about the PMF, this could also be considered in terms of uncertainty in drawing associations between bulk composition (which is all that the PMF is indicating) and the BC sources/microphysics (which also can affect MAC).*

We have added a new section in the paper describing our uncertainty analysis of the results. This takes into account both the uncertainty of the measurements but also the uncertainty introduced by the various assumptions during the theoretical analysis. We have followed the reviewer's suggestion and addressed the uncertainty of the PMF analysis. We used the bootstrapping approach (Ulbrich et al., 2009) performing ten additional simulations. The estimated uncertainty for the LO-OOA concentrations was 2 percent and for the MO-OOA concentrations was 3 percent. These relatively small uncertainties suggest that the PMF uncertainty regarding the determination of these factors does not affect our conclusions. The corresponding results have been added to the Supplementary Information and are discussed in the new uncertainty analysis section. We have also looked at the correlations between the concentrations of MO-OOA, LO-OOA and BC. The R^2 between the hourly concentrations of MO-OOA and rBC was 0.12, and for LO-OOA and rBC 0.17. This is not unexpected given that Finokalia is far away from the corresponding sources of both BC and organic compounds and significant physical and chemical processing has taken place during the transport of the aerosol from the sources to the receptor. The R^2 between the hourly concentrations of the ELVOCs and rBC was 0.25. This information has been added to the revised paper.

(3) *Some issues have not been sufficiently addressed. They include: a) how is the observation of AAE of around 1 consistent with expectations for significant BrC absorption? In fact, can any significant absorption be attributed to low volatility species?*

The observation of AAE around 1 is not inconsistent with the presence of some BrC. For example, Lack and Cappa (2010) argued that an AAE<1.6 does not exclude the possibility of BrC; rather BrC cannot be confidently assigned unless AAE>1.6. The AAE of coated BC is highly sensitive to particle size distribution and it decreases as particle size increases (Liu et al., 2018). This last study shows that relatively low values of AAE should be expected in a site like Finokalia and demonstrated the importance of various parameters on the BC AAE and the potential problems introduced by assuming BC AAE as being equal to 1.0. Finally, please note that based on our estimates BrC led to a 15 average increase of the campaign average babs at 405 nm. This increase is on average modest and is not inconsistent with the relatively low AAE observed in this remote site with relatively large, heavily processed particles. The finding that this unexplained absorption increases as the concentration of the ELVOCs increases is probably the most interesting finding of our work. We have added discussion of these points in the revised paper.

(4) *b) how is absorption of internal mixtures with rBC separated from bulk phase absorption?*

The assumption in our baseline analysis is that the non-refractory absorbing material is coating the BC particles. All the air masses sampled during the campaign were quite aged so it is reasonable to assume that all the BC particles were coated. Our baseline calculations are based on the assumption that all particles of the same size contain the same BC (internally mixed aerosol population). This provides the upper limit for the lensing effect and therefore the minimum of the unexplained absorption that could be assigned to BrC. We have performed an additional calculation using the coating estimated by the SP2 measurements to test the robustness of our conclusions. Additional assumptions are examined in the added uncertainty analysis section.

(5) *c) How is the PMF validated? Did rBC concentration (not deviation in MAC) correlate or anti-correlate with either factor?*

We used the bootstrapping approach (Ulbrich et al., 2009) performing ten additional simulations. The estimated uncertainty for the LO-OOA concentrations was 2 percent and for the MO-OOA concentrations was 3 percent. These relatively small uncertainties suggest that the PMF uncertainty regarding the determination of these factors does not affect our conclusions. Both MO-OOA and LO-OOA were positively correlated with rBC with the corresponding correlation coefficient R being 0.35 for MO-OOA and 0.41 for LO-OOA. These correlations between the absolute concentrations of the various PM components are in general expected in remote sites that are affected sometimes by more polluted air masses (leading to increases of the major PM components) and cleaner air masses processed by rain (leading to decreases of the major PM components. For example, the R of the non-refractory PM1 and the rBC was 0.55. The corresponding results have been added to the Supplementary Information and are discussed in the new uncertainty analysis section.

(6) *d) How are coating thicknesses constrained for rBC?*

Two different approaches are now used for the calculation of the coating thicknesses.

In the first approach used in the original paper the coating of the BC core was calculated using the PM1 mass and the rBC distribution as it was measured by the SP2. This approach corresponds to the internal mixing assumption. In order to provide constraints in our method we also calculated in the revised paper the coating thickness of the rBC cores using the leading-edge-only (LEO) fit method (Gao et al. 2007) of 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.

(7) *e) How high is confidence, based on measurement and theoretical uncertainties, that the range of MAC is not solely associated with 1) rBC and PAS uncertainties or 2) lensing enhancements?*

A detailed uncertainty analysis has been added to the revised paper to address these issues. The PAX has an uncertainty of less than 10 percent for the aerosol absorption measurement (Lack et al. 2012). Part of the uncertainty of the rBC mass by the SP2 is related to the detection limit of the smaller BC particles. The BC 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. The average propagated uncertainty of the MAC405, based on the measurements of rBC and babs at λ=405 nm is approximately 20 percent. Mie theory calculation can underestimate the absorption due to BC morphology and mixing. These uncertainties are discussed together with the rest of the uncertainties of the measurements and the modeling in a new uncertainty analysis section that has been added to the revised paper.

(8) *The reader needs more information about what was done in order to understand the*

results: a) How did the PAS and Aethalometer compare? Which was used to generate MAC405? How significant were the differences between them?

A comparison of the aethalometer and the PAX measurements has been added to the Supplementary Information of the revised paper. We compared the absorption coefficients measured by the aethalometer at 370 nm and at 450 nm with that measured by the PAX at λ=405 nm. The measurements of the two instruments were highly correlated with R^2=0.9-0.91. The babs,370 measured by the aethalometer was higher than the babs,405 of the PAX. Their relationship is described by the equation y=3.32 x - 3.24. Similarly, the babs,450 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. The MAC405 was calculated by dividing the babs,405 measured by the PAX and the rBC mass. This point is clarified in the revised manuscript to avoid confusion.

(9) *b) SP2 - laser intensity? size range of detection for rBC? Correction to account for total rBC accumulation mode concentrations? Type (8 channel?). Precision of cal with CPMA? Total uncertainty estimate in concentration (noting that different BC does have different response in SP2)? Calculation of coating thicknesses?*

The SP2 uses a Nd:YAG Laser at 1064 nm operated at 4 V and 3400 A. The calibration of the SP2 was verified in separate experiments using a centrifugal particle mass analyzer (CPMA, Cambustion). The SP2 mode mass and the CPMA mode mass were in good agreement, R^2=0.99 (Saliba et al., 2016). This information has been added to the experimental section.

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.

Two different approaches are now used for the calculation of the coating thicknesses. In the first approach used in the original paper the coating of the BC core was calculated using the PM1 mass and the rBC distribution as it was measured by the SP2. This approach corresponds to the internal mixing assumption. In order to provide constraints in our method we also calculated in the revised paper the coating thickness of the rBC cores using the leading-edge-only (LEO) fit method (Gao et al. 2007) of 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.

(10) *c) Sampling: was the aerosol dried? What temperature was the laboratory? If it was not dried, the whole analysis is likely questionable. How large were the corrections for diffusion and thermophoresis losses in the denuder (I expect likely negligible for Accum. mass).*

A diffusion drier was used upstream of the optical measurements to reduce any relative humidity-related measurement artifacts in the measurements (Arnott et al. 2003). The campaign average temperature and relative humidity were 22±4 C and 53±19 percent, respectively. The measurement station had an AC unit maintaining the temperature at 25 C.

To account for losses in the thermodenuder, sample flow rate as well as size- and temperature-dependent loss corrections were applied following Louvaris et al. (2017) corresponding to the operating conditions during the campaign. Up to 20 percent of the particulate matter was lost in the TD, at temperatures up to 100 C, while the losses increased for higher temperatures. For a temperature equal to 400 C almost 50 percent of particles larger than 50 nm is lost. The uncertainty introduced by the correction ranged was approximately 20 percent (Gkatzelis et al., 2016; Louvaris et al., 2017).

The above points have been added to the manuscript.

(11) *Mie theory tests: what constraints on coating thickness were used in the Mie Theory evaluation of index of refraction? Was this derived from SP2 data? How? This is a critical question if there is to be any conclusion drawn from this analysis. Note that SP2 determination of coating thicknesses are highly uncertain for thin coatings (e.g. Ohata et al. (2016). Hygroscopicity of materials internally mixed with black carbon measured in Tokyo, J. Geophys. Res. Atmos., 121, doi:10.1002/2015JD024153.)*

Two different approaches are now used for the calculation of the coating thicknesses. In the first approach used in the original paper the coating of the BC core was calculated using the PM1 mass and the rBC distribution as it was measured by the SP2. This approach corresponds to the internal mixing assumption. In order to provide constraints in our method we also calculated in the revised paper the coating thickness of the rBC cores using the leading-edge-only (LEO) fit method (Gao et al. 2007) of 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. A coating refractive index of 1.55 was assumed following previous studies (Bond and Bengstrom, 2006).

(12) *Line-level and specific comments L37 - averaged over a population. The literature review 34-83 - lensing enhancement is well written, but might give the reader the incorrect idea that similar work was done here. As only the AMS and SMPS were behind denuder this is not the case. (Note that it is a nice feature of your data set that initial brown carbon bleaching/evap should have already substantially occurred).*

In the literature review we wanted to summarize the finding of previous studies but also the different techniques used. We clarify that in our study only the AMS and the SMPS were behind the thermodenuder and that an interesting feature of the dataset is that the organic aerosol has been thoroughly processed.

(13) *TD - please provide more info about the temperature set points so that the reader isn't surprised by the lack of data between 200 and 375 âŮęC.*

We have added the detailed information about the temperature steps used in the thermodenuder explaining the change from 200 to approximately 375 C.

(14) *L197 Bond and Bergstrom, 2006 suggest (1.95,-0.79) for the complex index at 1.8 g/cc. Not as stated.*

For the BC core we assumed a refractive index of the core nrBC=1.85+0.71i based on Bond et al. (2006). We have corrected the reference in the revised manuscript.

(15) *The paper by China et al., 10.1002/2014GL062404 will be useful for justifying use of Mie theory shell and core.*

We have added the suggested reference to the revised paper to further support the use of core and shell Mie theory for our site.

(16) *Please consider if Figure 2 is unnecessary given Figure 4a? Combine?*

We believe that the existence of Figure 2 is helping the reader for easy comparison between our study and previous studies in area (Lee et al., 2010). In addition, the plot is needed for comparison with other studies that use similar methods to calculate the OA volatility. Finally, the use of both Figure 2 and Figure 4 show how much each factor MO-OOA, and LO-OOA affects the total OA volatility.

(17) *Wavelength of Mie theory calcs? Note that RI for BC is likely low. Were the calculations carried out for observed core size dist? coating thickness? On what time scale were those calculated?*

The Mie theory calculation was performed at a wavelength of 405 nm in order to be able to compare our results with the measurements from the PAX. The sensitivity to the refractive index of BC was investigated and the results are discussed in the added uncertainty analysis section. The calculations were carried out based on the measured rBC core size distribution extrapolated so smaller sizes. Two different coating thicknesses were used. One based on the internal mixture assumption providing an upper limit for the calculation and one based on the thicknesses calculated by the SP2. One-hour averaged data were used as inputs in the model. The above information has been added to the revised paper.

(18) *Figure 7: negative Measure-Predicted not included - meaningless without all the data. It appears that some positive M-P data is also missing (based on the number of data points in figure 7 vs those in Figure 6a).*

Please note that the data in Figure 6a are one-hour averages while those in Figure 7 are 3-hour averages. This is now explained in the corresponding figure captions. The original Figure 7 has been redrawn using the unexplained absorption in the y-axis. We are now discussing the effect of the few negative unexplained values in the corresponding section and perform the corresponding statistical analysis both with and without them.

(19) *L249: "average calculated saturation concentration of 0.016 ug/m3".*

Corrected.

(20) *Time series not very helpful for understanding more than trends in extensive properties (amounts). Scatter plots would be more useful.*

We have converted Figure 1 of the original manuscript to a scatter plot and moved the original Figure 1 to the Supplementary Information.

(21) *L264: "similarly" - actually Babs and Bscat appear poorly correlated.*

We have rephrased this sentence.

(22) *L273 - please include the uncertainty on this value.*

A discussion has been in the introduction about the MAC values of pure, uncoated BC 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). The corresponding uncertainty is now discussed at this point of the paper.

(23) *L286: Not clear how coating thicknesses were constrained.*

Two different approaches are now used for the calculation of the coating thicknesses. In the first approach used in the original paper the coating of the BC core was calculated using the PM1 mass and the rBC distribution as it was measured by the SP2. This approach corresponds to the internal mixing assumption. In order to provide constraints in our method we also calculated in the revised paper the coating thickness of the rBC cores using the leading-edge-only (LEO) fit method (Gao et al. 2007) of the SP2 data. The thicknesses as expected were lower than those resulting from the internal mixing assumption, but were still significant. These methods are now explained clearly in the revised paper.

(24) *L281: AAE only described for 523 to 405. . . how the range calculated, averaged?*

The AAE was calculated by a power-law fitting of the babs measured by the aethalometer in all wavelengths (370, 470, 520, 590,660, 880, 950 nm). The information on the calculation of the AAE has been added in the revised manuscript.

(25) *L289: is 13 percent meaningful in the context of uncertainties?*

The new uncertainty analysis focuses on the robustness of this conclusion. Please note that the average was modest but there were periods of significant unexplained absorption.

(26) *L313 - I think you mean "no periods of enhanced BB influence"*

We have rephrased this sentence.

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