Responses to the Comments of Reviewer 1

(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.

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%, 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 m^2/g, but that they observe an average of 16.3 m^2/g. However, they conclude later that their predicted value of 14.1 m^2/g is a factor of two greater than it should be. This implies a MAC of 7.05 m^2/g for pure BC from the calculations, much smaller than the 9.9 m^2/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 m^2/g value cannot be compared to the 16.3 m^2/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.

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 m^2/g was never used in any of the calculations and should not be part of the discussion here. It was mentioned at this point just to support the argument that the measured value of 16.3 m^2/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 m^2/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 MAC_{405} using the measured BC size distribution and assuming pure uncoated spherical particles was 7.2 $m^2 g^{-1}$ varying from 6.1 to 7.8 $m^2 g^{-1}$ during the study (hourly averages). This is consistent with the expected 5.3-9.2 $m^2 g^{-1}$ 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 m^2/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 MAC_{405} were as high as 7 m^2/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 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.)

The uncertainty of the estimated value of the absorption of the BC is addressed in the new uncertainty analysis section where we try additional values of the BC refractive index (both high and low). We test indirectly 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 link between this variability and the ELVOC concentrations remains robust for both the low and high values of the refractive index.

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 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 MAC_{405} and the ratio of non-refractory PM_1 and rBC. There is a positive correlation between the two (R=0.31) and the intercept is 12.8 m^2/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 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 are 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 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.

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 b_{abs} 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 ΔMAC 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 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 revised paper including two new figures in the Supplementary Information. 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 $b_{abs,370}$ measured by the aethalometer was higher than the $b_{abs,405}$ of the PAX. Their relationship is described by the equation y=3.32x - 3.24. Similarly, the $b_{abs,450}$ 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.

References

Cappa, C., Lack, D., Burkholder, J., and Ravishankara, A.: Bias in filter based aerosol light absorption measurements due to organic aerosol loading: Evidence from laboratory measurements, Aerosol Sci. Technol., 42, 1022–1032, 2008.

Cain, K. P., Karnezi, E., Pandis, S. N.: Challenges in determining atmospheric organic aerosol volatility distributions using thermal evaporation techniques, Aerosol Sci. Tech., doi: 10.1080/02786826.2020.1748172, 2020.

Ditas, J., Ma, N., Zhang, Y., Assmann, D., Neumaier, M., Riede, H., Karu, E., Williams, J., Scharffe, D., Wang, Q., Saturno, J., Schwarz, J. P., Katich, J. M., McMeeking, G. R., Zahn, A., Hermann, M., Brenninkmeijer, C. A. M., Andreae, M. O., Pöschl, U., Su, H., and Cheng, Y.: Strong impact of wildfires on the abundance and aging of black carbon in the lowermost stratosphere, P. Natl. Acad. Sci. USA, 115, 11595–11603, 2018.

Drosatou, A. D., Skyllakou, K., Theodoritsi, G. N., and Pandis, S. N.: Positive matrix factorization of organic aerosol: insights from a chemical transport model, Atmos. Chem. Phys., 19, 973–986, https://doi.org/10.5194/acp-19-973-2019, 2019.

Gao, R. S., Schwarz, J. P., Kelly, K. K., Fahey, D. W., Watts, L. A., Thompson, T. L., Spackman, J. R., Slowik, J. G., Cross, E. S., Han, J. H., Davidovits, P., Onasch, T. B., and Worsnop, D. R.: A novel method for estimating light-scattering properties of soot aerosols using a modified single-particle soot photometer, Aerosol Sci. Technol., 41, 125–135, 2007.

Karnezi, E., Riipinen, I. and Pandis, S. N.: Measuring the atmospheric organic aerosol volatility distribution: A theoretical analysis, Atmos. Meas. Tech., 7, 2953–2965, 2014.

Lack, D. A., J. M. Langridge, R. Bahreini, C. D. Cappa, A. N. Middlebrook, and J. P. Schwarz.: Brown carbon and internal mixing in biomass burning particles. Proc. Natl. Acad. Sci. USA, 109, 14802–14807, 2012.

Lack, D. A., Cappa, C. D., Covert, D. S., Baynard, T., Massoli, P., Sierau, B., Bates, T. S., Quinn, P. K., Lovejoy, E. R., and Ravishankara, A. R.:Bias in filter based aerosol light absorption measurements due to organic aerosol loading: Evidence from ambient measurements, Aerosol Sci. Technol., 42, 1033–1041, 2008.

Louvaris, E. E., Florou, K., Karnezi, E., Papanastasiou, D. K., Gkatzelis, G. I., and Pandis, S. N.: Volatility of source apportioned wintertime organic aerosol in the city of Athens, Atmos. Environ.,158, 138-147, 2017.

Saleh, R., Robinson, E. S., Tkacik, D. S., Ahern, A. T., Liu, S., Aiken, A. C., Sullivan, R. C., Presto, A. A., Dubey, M. K., Yokelson, R. J., Donahue, N. M., and Robinson, A. L.: Brownness of organics in aerosols from biomass burning linked to their black carbon content, Nat. Geosci., 7, 647–650, 2014.

Wong, J. P. S., Tsagkaraki, M., Tsiodra, I., Mihalopoulos, N., Violaki, K., Kanakidou, M., Sciare, J., Nenes, A., and Weber, R. J.: Atmospheric evolution of molecular-weight-separated brown carbon from biomass burning, Atmos. Chem. Phys., 19, 7319–7334, https://doi.org/10.5194/acp-19-7319-2019, 2019.

Responses to the Comments of Reviewer 2

(1) Overview: The paper is focused on presenting observations from a ~3 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% and for the MO-OOA concentrations was 3%. 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 ~1 consistent with expectations for significant BrC absorption? In fact, can any significant absorption be attributed to low volatility species?

The observation of an average AAE ~ 1 is not inconsistent with the presence of some BrC especially during selected periods. 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% increase of the campaign average b_{abs} 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% and for the MO-OOA concentrations was 3%. 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 PM_1 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 PM_1 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?

An uncertainty analysis has been added to the revised paper to address these issues. The PAX has an uncertainty of less than 10% 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%, so its effect on the reported results (e.g., the observed MAC) was minor. The average propagated uncertainty of the MAC_{405}, based on the measurements of rBC and b_{abs} at λ=405 nm is approximately 20%. 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 $b_{abs,370}$ measured by the aethalometer was higher than the $b_{abs,405}$ of the PAX. Their relationship is described by the equation y=3.32 x - 3.24. Similarly, the $b_{abs,450}$ 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 MAC_{405} was calculated by dividing the $b_{abs,405}$ 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%, 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 PM_1 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 %, 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. Less than 20% 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% of particles larger than 50 nm is lost. The uncertainty introduced by the correction ranged was approximately 20% (Gkatzelis et al., 2016; Louvaris et al., 2017).

The above points have been added to the manuscript.

(11) d) 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 PM_1 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 was assumed of 1.55 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 ◦C.

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 n_{rBC}=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.

(19) L249: “average calculated saturation concentration of 0.016 ug/m^3”.
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 showing the individual measurement points.

(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 PM_1 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 b_{abs} 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% 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.

References

Arnott, W.P., Moosmüller, H., Sheridan, P. J., Ogren, J. A., Raspet, R., Slaton, W.V., Hand, J. L., Kreidenweis, S. M. and Collett Jr., J. L.: Photoacoustic and filter-based ambient aerosol light absorption measurements: instrument comparison and the role of relative humidity, J. Geophys. Res., 108, 4034–44, 2003.

Bond, T. C., and Bergstrom, R. W.: Light absorption by carbonaceous particles: An investigative review, Aerosol Sci. and Technol., 40, 27–67, 2006.

Bond, T. C., Habib, G., and Bergstrom, R. W.: Limitations in the enhancement of visible light absorption due to mixing state, J. Geophys. Res., 111, D20211, 2006.

Cappa, C., Lack, D., Burkholder, J., and Ravishankara, A.: Bias in filter based aerosol light absorption measurements due to organic aerosol loading: Evidence from laboratory measurements, Aerosol Sci. Technol., 42, 1022–1032, 2008.

Gkatzelis, G. I., Papanastasiou, D. K., Florou, K., Kaltsonoudis, C., Louvaris, E. and Pandis, S. N.: Measurement of nonvolatile particle number size distribution, Atmos. Meas. Tech., 9, 103–114, 2016.

Lack, D. A., Langridge, J. M., Bahreini, R., Cappa, C. D., Middlebrook, A. N., and Schwarz, J. P.: Brown carbon and internal mixing in biomass burning particles, Proc. Natl. Acad. Sci. USA, 109, 14802–14807, 2012.

Lack, D. A., and Cappa, C. D.: Impact of brown and clear carbon on light absorption enhancement, single scatter albedo and absorption wavelength dependence of black carbon, Atmos. Chem. Phys., 10, 4207–4220, 2010.

Lack, D. A., Cappa, C. D., Covert, D. S., Baynard, T., Massoli, P., Sierau, B., Bates, T. S., Quinn, P. K., Lovejoy, E. R., and Ravishankara, A. R.:Bias in filter based aerosol light absorption measurements due to organic aerosol loading: Evidence from ambient measurements, Aerosol Sci. Technol., 42, 1033–1041, 2008.

Lee, B. H., Kostenidou, E., Hildebrandt, L., Riipinen, I., Engelhart, G. J., Mohr, C., Decarlo, P. F., Mihalopoulos, N., Prévôt, A. S. H., Baltensperger, U., and Pandis, S. N.: Measurement of the ambient organic aerosol volatility distribution: Application during the Finokalia Aerosol Measurement Experiment (FAME-2008), Atmos. Chem. Phys., 10, 12149–12160, 2010.

Liu, C., Chung, C. E., Yin, Y., Schnaiter, M.: The absorption Ångström exponent of black carbon: from numerical aspects, Atmos. Chem. Phys., 18, 16409–16418, 2018.

Louvaris, E. E., Florou, K., Karnezi, E., Papanastasiou, D. K., Gkatzelis, G. I., and Pandis, S. N.: Volatility of source apportioned wintertime organic aerosol in the city of Athens, Atmos. Environ.,158, 138-147, 2017.

Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L.: Interpretation of organic components from positive matrix factorization of aerosol mass spectrometric data, Atmos. Chem. Phys. 9, 2891–2918, 2009.

Aerosol light absorption and the role of extremely low volatility organic compounds

Antonios Tasoglou[1,5], Evangelos Louvaris[2,3], Kalliopi Florou[2,3] Aikaterini Liangou[2,3], Eleni Karnezi[1] Christos Kaltsonoudis[4], Ningxin Wang[1], Spyros N. Pandis[1,2,3]

[1]Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh
[2]Department of Chemical Engineering, University of Patras, Patras, Greece
[3] Institute of Chemical Engineering Sciences (ICE-HT), FORTH, Patras, Greece
[4]Department of Mechanical Engineering, Carnegie Mellon University, Pittsburgh, United States
[5]RJ Lee Group, Inc., Monroeville, United States

Abstract

A month-long set of summertime measurements in a remote area in the Mediterranean is used to quantify aerosol absorption and the role of black and brown carbon. The suite of instruments included a high-resolution Aerosol Mass Spectrometer (HR-ToF-AMS), and a Scanning Mobility Particle Sizer (SMPS) both coupled to a thermodenuder and an aethalometer, a photoacoustic extinctiometer (PAX_{405}), a Multi-Angle Absorption Photometer (MAAP), and a Single Particle Soot Photometer (SP2).

The average refractory black carbon (rBC) concentration during the campaign was 0.14 μg m^{-3}, representing 3% of the fine aerosol mass. The measured light absorption was two or more times higher than that of fresh black carbon (BC). Mie theory indicated that the absorption enhancement due to the coating of BC cores by non-refractory material could explain only part of this absorption enhancement. The role of brown carbon (BrC) and other non-BC light-absorbing material was then investigated. A good correlation (R^2=0.76~~65~~) between the unexplained absorption and the concentration of extremely low volatility organic compounds (ELVOCs) mass was found.

1. Introduction

Atmospheric aerosol may influence climate in two ways: directly through scattering and absorbing radiation, and indirectly through acting as cloud condensation nuclei (IPCC, 2011) Black carbon is the dominant light absorbing aerosol component. BC is a distinct type of carbonaceous material that is formed mainly during combustion processes. In addition, some organic aerosol (OA) has the ability to absorb sunlight. The OA with strong light absorption is called brown carbon (BrC) (Andreae et al., 2006).

The absorption of BC depends on its mixing state (Liu et al., 2015, 2017). Usually, BC is coated with scattering material causing its light absorption to increase due to the lensing effect (Fuller et al., 1999; Jacobson, 2001; Bond et al., 2006; Lack and Cappa, 2010). The absorption enhancement (E_{abs}) is defined as the ratio of the aerosol absorption coefficient (b_{abs}) over the b_{abs} of the pure BC particles. This enhancement can also be calculated by the ratio of the equivalent mass absorption cross-sections (MAC). The MAC is defined as the ratio of b_{abs} over the BC mass. The MAC of pure, uncoated BC at a specific wavelength depends both on the size distribution of the particles, but also on their morphology (fresh aggregates versus collapsed more spherical structures). Based on Bond et al. (2006) pure BC particles in the 10-350 nm diameter range have an expected MAC_{550} =3.9-6.8 m^2 g^{-1} or MAC_{405} =5.3-9.2 m^2 g^{-1}. The E_{abs} can be measured by using a thermodenuder (TD) for the removal of the non-refractory coating material from the BC containing particle, or it can be estimated using a theoretical model (for example Mie or Rayleigh-Debye-Gans theory) if the particle morphology is known. Incomplete removal of the non-refractory material in the TD can lead to underestimation of the E_{abs} (Healy et al., 2015; McMeeking et al., 2014).

Commented [SP1]: REVIEWER 1, Comment 2; REVIEWER 2, Comment 22

Previous studies have demonstrated that lensing has a strong effect on the light absorption of BC. Liu et al. (2015) found a campaign average E_{abs} of 1.3 at wavelength (λ) equal to 405 nm and 1.4 at 781 nm in a rural area near London during the winter. They also suggested that the lower volatility BrC has stronger absorption than the semi-volatile BrC. Knox et al. (2009) performed measurements in downtown Toronto, during the wintertime using a TD at 340 °C. They reported an E_{abs} of 1.43 for fresh particles, based on thermal OC/EC and photoacoustic measurements. Liu et al. (2017) combined laboratory experiments with diesel exhaust emissions and ambient measurements to show that particles with a ratio of non-refractory PM to BC mass (R_{BC}) less than 1.5 (typical for traffic emissions) had a negligible lensing effect. When the R_{BC} was above 3, lensing caused significant enhancement of the absorption of BC. Zhang et al. (2018a) presented three years of measurements in a suburban cite outside Paris, France, influenced by both fresh and aged air masses. On average they found an E_{abs}=2.07 at 370 nm, and an E_{abs}=1.53 at 880 nm. They calculated the E_{abs} by measuring the absorption coefficient (b_{abs}) with an aethalometer, while the elemental carbon (EC) was measured with thermal methods using daily filters. Zhang et al. (2018b) presented measurements in Beijing, China during wintertime. Using aethalometer measurements, refractory and non-refractory particle size distributions and Mie theory, they calculated that the lensing effect led to an E_{abs} ranging from 1.5 to 2 on average at 880 nm. Zanatta et al. (2018) found an E_{abs}=1.54 at 550 nm for measurements at the Zeppelin Arctic Station. Lack et al. (2012) analyzed measurements of biomass burning plumes near Boulder, CO during summertime. Using a TD at 200 ^{o}C, they found E_{abs} values as large as 2.5 at 404 nm and 1.7 at 532 nm. Using the absorption Angström exponent (AAE) and Mie theory calculations they showed the presence of BrC.

Some studies have argued that Mie theory may overestimate the E_{abs}. Cappa et al. (2012) suggested that the absorption enhancement of BC in California in the summertime was low with values equal to 1.13 at 405 nm and 1.06 at 532 nm for R_{BC}>10. For their measurements they used a TD operated at 225 ^{o}C and 250 ^{o}C. Hearly et al. (2015) also reported practically no enhancement in the BC absorption at 781 nm and E_{abs}=1.19 at 405 nm in Toronto, Canada during summertime. During a period associated with wildfires the same authors measured R_{BC}=6.9 and E_{abs}=1.39 at 405 nm. They argued that there was little evidence of the lensing effect, and that BrC was driving the E_{abs}. Cappa et al. (2019) performed measurements in Fresno, CA during wintertime and Fontana, CA during summertime. They found that in Fresno there was absorbing OA, BrC, which was related to biomass burning OA and nitrate-associated OA. In Fresno, they reported average E_{abs} of 1.37, 1.22 and 1.1 at wavelengths equal to 405, 532, 781 nm, respectively, for R_{BC} ranging from 1 to 4. In Fontana the E_{abs} was lower with values of 1.1 at 405 nm and 1.07 at 532 nm. Laboratory measurements of McMeeking et al. (2014) for biomass burning aerosol indicated higher absorption in lower wavelengths compared to higher ones and thus the presence of BrC. No enhancement of absorption was observed at R_{BC}<1. On average they found an E_{abs} equal to 1.25 at 781 nm with a maximum value of E_{abs}=4 for R_{BC}>10.

Recent studies have suggested that the absorption efficiency of OA could be related to its volatility. Saleh et al. (2014) in their laboratory biomass burning experiments showed that almost all absorbing OA was associated with extremely low volatility compounds (ELVOCs), with an effective saturation concentration C^* of 10^{-4} μg m^{-3}. In addition, Saleh et al. (2018) using controlled combustion experiments showed that the absorption activity of BrC is proportional to its molecular size.

Despite the significant progress in understanding the absorption of atmospheric fine aerosol there are still remaining questions regarding both the absorption enhancement of black carbon and the absorption of OA as the aerosol evolves in the atmosphere. In this study we try to address these issues for aerosol that has been aged in the atmosphere for at least a few days before arriving at the island of Crete in the Eastern Mediterranean.

2. Experimental Methods

A remote location in the Eastern Mediterranean was used for the study of the absorption and volatility of aged carbonaceous aerosol. The area is characterized by intense photochemistry, especially during the summer (Pikridas et al., 2010) and is affected by pollutants transferred from continental Europe, Turkey, Greece and Africa (Mihalopoulos et al., 1997; Lelieveld et al., 2002; Kalivitis et al., 2011; Bougiatioti et al., 2014). Previous measurements have shown that the OA reaching the area is highly oxidized regardless of its origin (Hidlebrandt et al., 2010; 2011). Lee et al. (2010) showed that these oxidized organic compounds have much lower volatility than fresh SOA. Long-term measurements in the region have revealed relatively high light absorption and scattering by aerosol during the summer (Kalivitis et al., 2011; Vrekoussis et al., 2005).

The FAME-16 field campaign took place from May 9 to June 2, 2016. Measurements were conducted at the Finokalia Station (*35^o 20' N, 25^o 40' E*, 250 m asl), a remote site on the island of Crete in Greece (Mihalopoulos et al., 1997). The nearest large city is Heraklion with 150,000 inhabitants located 50 km west of Finokalia (Kouvarakis et al., 2000). There are no local sources near the station, allowing the investigation of aged OA from different source regions. During this study, two Saharan dust events occurred from May 12 till May 15 and May 21 till May 22.

A Scanning Mobility Particle Sizer (SMPS, TSI classifier model 3080, CPC model 3775) was used to measure the number and the size distribution of the particles. The aerosol flow was set at 1 L min^{-1} and the sheath flow at 5 L min^{-1}. The sampling time was 3 min.

The mass concentration and the chemical composition of the particles were monitored using a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, Aerodyne Research, Inc.). SQUIRREL 1.56D and PIKA v1.15D were used for the data analysis, while for the elemental ratio calculations the improved ambient calculation approach of Canagaratna et al. (2015) was used. The HR-ToF-AMS was operated in V-mode with a sample time of 3 min. The collection efficiency of the HR-ToF-AMS was calculated using the algorithm of Kostenidou et al.

(2007). The average CE was 0.64±0.2. Positive matrix factorization (PMF) analysis (Lanz et al., 2007; Paatero and Tapper, 1994; Ulbrich et al., 2009) was performed using as input the high resolution OA mass spectra and the mass-to-charge ratios (*m/z*) from 12 to 200.

A Single Particle Soot Photometer (SP2, Droplet Measurement Technologies) was used to measure the BC size distribution and concentration. The SP2 had ~~was an~~ 8-channels and included a 1064 nm ~~type, equipped with a~~ Nd:YAG l~~L~~aser ~~: 1064 nm~~ operating~~ed~~ at 4 V and~~,~~ 3400 A. The instrument was calibrated using fullerene soot (Alfa Aesar, stock 40971, lot L20W054) (Gysel et al., 2011). 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 with an ~~,~~ R^2=0.99 (Saliba et al., 2016). ~~(Saliba et al., 2016).~~ The data were analyzed using the Probe Analysis Package for Igor. In our measurements, the number concentration of BC was low (<10,000 particles cm^{-3}), and thus it was assumed that there were no coincidence artifacts in our measurements. The scattering measurement was calibrated using monodisperse polystyrene latex (PSL) spheres. The BC number concentration distributions measured by the SP2 were fitted using a Gaussian distribution to account for particles smaller than the SP2 detection limit of approximately~~,~~ 50 nm (Ditas et al., 2018). This extrapolation resulted in an increase of the BC mass concentration by 3-8% (Figure S9), therefore the uncertainty introduced by BC outside the measurement window was minor.~~. The estimated measurement uncertainty of the SP2 is 40% (Lack et al., 2012).~~

A photoacoustic extinctiometer (PAX, Droplet Measurement Techniques) with a blue (405 nm) laser was used to measure the absorption (b_{abs}) and the scattering (b_{scat}) coefficients. Fullerene soot and PSL spheres were used to calibrate the absorption and scattering signals, respectively. An activated carbon denuder was placed in front of the PAX to remove NO_2. The PAX has an uncertainty of less than 10% for the b_{abs} measurement (Lack et al., 2012). Furthermore, a seven wavelength aethalometer (AE31, Magee Scientific) was used to measure the b_{abs} at 370, 470, 520, 590, 660, 880 and 950 nm and to calculate the absorption Angstrom exponent (AAE), which describes the wavelength dependence of the b_{abs}. The aethalometer measurements were corrected for scattering and multiple scattering artifacts following Saleh et al. (2014) and Tasoglou et al. (2017) using the corrections suggested by Weingartner et al. (2003) and Kirchstetter and Novakov (2007). High relative humidity (>70%) can introduce measurement artifacts in the measurement absorption coefficient by filter- based techniques or photoacoustic methods (Arnott et al. 2003). A

Commented [AT2]: REVIEWER 2 Comment 9

Commented [AT3]: REVIEWER 2 Comment 9

Commented [AT4]: REVIEWER 1 comment 1 ; Reviewer 2 comment 9

Commented [AT5]: REVIEWER 2 Comment 7

diffusion drier was used upstream of the optical measurements. The campaign average temperature and relative humidity were 22±4 °C and 53±19 %, respectively. The measurement station had ~~an AC unit~~a temperature-control system maintaining the temperature at approximately 25 °C. ~~A diffusion drier was used upstream of the optical measurements.~~

The thermodenuder (TD) used in this study, was placed upstream of the HR-ToF-AMS and the SMPS. The TD design was similar to that developed by An et al. (2007) and is described by Louvaris et al. (2017). The TD was operated at temperatures ranging from 25 °C to 400 °C using several temperature steps from 25 °C to 200 °C over several hours and then rapidly (in 20 min) increasing its temperature to the 375-400 °C to investigate the presence of ELVOCs. One complete cycle from 25 to 400 °C and back to 25 °C lasted approximately 10 h. ~~The temperature was increasing from ambient to 200^{O}C for approximately 6 hours. Then the temperature was increased to a higher temperature 400^{O}C in order to investigate the existence of ELVOCs. The increase from 200 ^{O}C to 400^{O}C was approximately 20 min.~~ Sampling was alternated between the ambient line and the TD line every 3 minutes using computer-controlled valves. Changes in particle mass concentration, composition, and size due to evaporation in the TD were measured by the HR-ToF-AMS and the SMPS resulting in thermograms of OA mass fraction remaining (MFR) as a function of TD temperature. The OA MFR was calculated as the ratio of organic mass concentration of a sample passing through the TD at time t_i over the average mass concentration of the ambient samples that passed through the bypass line at times t_{i-1} and t_{i+1}. The sample residence time in the centerline of the TD was 14 s at 25 °C, corresponding to an average residence time in the TD of 28 s. The MFR values were corrected for particle losses in the TD due to diffusion and thermophoresis. To account for these losses, 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. Less than~~Up to~~ 20% of the particulate matter was lost in the TD~~,~~ at temperatures up to 100°C.~~,~~ T~~while t~~he losses increased at~~for~~ higher temperatures. ~~For a temperature equal to~~and at 400 °C approximately~~almost~~ 50% of particles~~ulates~~ larger than 50 nm was~~is~~ lost. The uncertainty introduced by the loss correction was approximately~~ranged from~~ 20~~ to 30~~% (Gkatzelis et al., 2016; Louvaris et al., 2017). The final step of the data analysis was to average the corrected for CE and TD losses MFR data based on temperature bins of 10°C. The MFR calculation assumes implicitly that the OA concentration remains constant during the measurement period. To ensure that this condition is satisfied, if two consecutive OA ambient

Commented [AT6]: REVIEWER 2 comment 10

Commented [SP7]:

Commented [SP8R7]: REVIEWER 2, Comment 12

Formatted: Superscript

Formatted: Superscript

Formatted: Superscript

Commented [AT9]: REVIEWER 2 comment 13

Commented [AT10]: REVIEWER 2 comment 10

mass concentrations differed by more than 25%, the corresponding MFR was not included in the analysis. Also, in order to ensure that the temperature was constant during the measurement, the absolute difference between the two samples had to be less than 5ºC. If this difference for a TD sample was higher, then the sample was not included in our analysis. The same approach was used also for the factors resulting from the PMF analysis of the AMS spectra. However, in this case a minimum concentration threshold of 0.1 μg m^{-3} was used for the ambient concentrations together with the criterion of the stability of the ambient concentrations during the sampling period. MFR values corresponding to concentrations of the PMF factors below this threshold were not included in the dataset. Approximately 75% of the OA samples satisfied all these constraints and were used in the analysis. The corresponding percentages were 65% and 70% for the two identified PMF factors. In the present work the complete datasets will be analyzed together, averaging the corresponding measurements. More details regarding the data analysis and the sensitivity tests of the TD measurements are provided in the supplementary information.

The concentrations of gas-phase pollutants were measured using a Proton-Transfer Reaction Mass Spectrometer (PTR-QMS 500, Ionicon Analytik) and gas monitors. The PTR-MS was calibrated with a standard gas mixture of VOCs. The concentration of O_3 was measured using a continuous O_3 analyzer (Thermo Scientific, 49i) and the concentrations of nitrogen oxides were measured using a $NO/NO_2/NO_x$ analyzer (Thermo Scientific, 42i-TL).

Formatted: English (United States)

3. Theoretical Analysis Methods

The dynamic TD evaporation model of Riipinen et al. (2010) together with the uncertainty estimation algorithm of Karnezi et al. (2014) were used for the determination of the OA volatility distribution. Inputs for the model included the ambient OA concentration, the OA density calculated by the algorithm proposed by Kostenidou et al. (2007), the initial average particle size, TD temperature, the MFR values, and TD residence time. In the volatility basis set framework of Donahue et al. (2006), the volatility distribution is represented with a range of logarithmically spaced C^* bins along a volatility axis. In this study 6 bins with variable mass fractions were chosen. For this 6-bin solution, the best 2% of the mass fraction combinations with the lowest error were used to estimate the average mass fraction along with their corresponding standard deviation for the uncertainty of each bin. Additionally the parameters that affect indirectly the calculated volatility such as the effective vaporization enthalpy (ΔH_{vap}), and the effective accommodation coefficient (a_m) were estimated following Karnezi et al. (2014). Additional information regarding the data analysis of the TD measurements are in the supplemental information (sections S1 and S2).

A Mie theory model based on the work of Bohren and Huffman (1983) was used to calculate the theoretical MAC and ~~E_{abs}~~ E_{abs} at 405 nm assuming a spherical core-shell morphology (China et al., 2015). The assumption that all BC particles were coated and had obtained a relatively spherical shape ~~of internal mixture~~ can be justified by the lack of any local sources and the fact that all particles reaching the site had been heavily processed in the photochemically active summertime atmosphere of the Eastern Mediterranean. ~~All the air masses sampled during the campaign were quite aged, so it is reasonable to assume that all the BC particles were coated.~~ PMF analysis of the OA AMS spectra did not show any fresh emissions like HOA or BBOA and no acetonitrile was detected. FLEXPART analysis confirmed that the air masses measured were transferred from long distance areas (30% continental Greece and the Balkans, 13% Aegean, 24% Africa, 33% Italy/Sicily). The measurements ~~also~~ suggested a positive correlation (R=0.31) ~~internal mixture the relationship~~ between the MAC_{405} and the ratio of non-refractory PM_1 to ~~and~~ rBC with an ~~. There is a positive correlation between the two, (R=0.08) and the~~ intercept of ~~is~~ 12.1 m^2 g^{-1} (Figure S10).

~~Mie theory describes the extinction of light by spherical particles due to an incoming planar electromagnetic wave. Mie theory calculations can underestimate the absorption even up to 30% due to the morphology and mixing of the BC related particles (Bond et al., 2006). The calculations were based on the SMPS and SP2 size distributions.~~ For the BC core we assumed a refractive index of the core n_{rBC}=1.85+0.71i (Bond ~~and Bergstrom,~~ et al., 2006) and a density of 1.8 g cm^{-3} (Mullins and Williams, 1987; Park et al., 2004; Wu et al., 1997). A non-absorbing coating of the BC core was assumed, with a refractive index of n_{OA} = 1.55 (Bond and Bergstrom, 2006). The total aerosol effective density used was calculated based on the SMPS and HR-ToF-AMS distributions. The average effective density for the campaign was 1.66±0.11 g cm^{-3}. The size distribution of the BC cores was provided by the SP2 and the corresponding measured rBC size distributions including the extrapolation to smaller sizes outside the SP2 measurement window.

The coating thickness in the base case calculation was estimated based on the assumption that the BC material is internally mixed with the non-refractory aerosol species (Saliba et al., 2016). The SMPS size distributions were used to estimate ~~is assumed based on the rBC size~~

Commented [SP11]: REVIEWER 2 Comment 17

Commented [AT12]: REVIEWER 2 comment 15

Commented [AT13]: REVIEWER 2 comment 14

Commented [SP14]: REVIEWER 2 Comment 23

Commented [SP15]: REVIEWER 1, Comment 2

~~distribution.~~~~The other inputs of the model were the measured BC size distributions from the SP2 and~~ the ratio of the total aerosol mass over the BC mass as measured. ~~by the SMPS and the SP2, respectively.~~ 1-hour averaged data were used as inputs in the model. ~~The size of the core is assumed based on the rBC size distribution.~~ ~~The total aerosol mass divided by BC was used to estimate the coating thickness based on the assumption that the BC material is internally mixed with the non-refractory aerosol species (Saliba et al., 2016).~~

Commented [SP16]: REVIEWER 1, Comment 2

~~The assumption of internal mixture can be justified by the lack of any local sources. All the air masses sampled during the campaign were quite aged, so it is reasonable to assume that all the BC particles were coated. PMF analysis did not show any fresh emissions like HOA or BBOA and no acetonitrile was detected. FLEXPART analysis confirmed that the air masses measured were transferred from long distance areas (30% continental Greece and the Balkans, 13% Aegean, 24% Africa, 33% Italy/Sicily). The measurements also suggest internal mixture the relationship between MAC_{405} and the ratio of non-refractory PM_1 and rBC. There is a positive correlation between the two, (R=0.08) and the intercept is 12.1 m^2 g^{-1} (Figure S10).~~In order to provide a better constraint for the analysis~~method~~ ~~an additional calculation of~~ the coating thickness of the rBC cores was also estimated 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 (Figure S11). Repeated Mie theory calculations using the coating thickness based on the LEO fit method are presented in the uncertainty analysis section.

Commented [AT17]: REVIEWER 1 Comment 3

~~The MAC values of pure, uncoated BC at a specific wavelength depend both on the size distribution of the particles but also on their degree of aging (fresh aggregates versus collapsed more spherical structures). A previous study has shown that pure BC core diameters in the 10-350 nm size range have an expected MAC_{550} =3.9-6.8 m^2 g^{-1} or MAC_{405} =5.3-9.2 m^2 g^{-1} (Bond et al., 2006). In this study the MAC_{405} predicted by Mie theory and the MAC_{405} calculated by the ratio of $b_{abs,405}$ over the rBC measured by PAX_{405} and SP2 were compared. The comparison was used to identify the absorption enhancement due to the lensing effect as well as the existence of an absorbing coating.~~

4. Results and discussion

The average rBC concentration of the campaign was 0.14 μg m^{-3} and the average OA concentration was 1.5 μg m^{-3} (Figure 1). The two major Saharan dust events affected, as expected, the aerosol optical properties. In the present study we focus only on the non-dust periods. The dominant PM$_1$ components were sulfate and OA, accounting for 46% and 34% of the PM$_1$, respectively. The O:C ranged from 0.65 to 1, with an average value of 0.83~~.~~, revealing the absence of fresh OA. These values are typical in Finokalia during the spring and summer periods (Hidlebrandt et al., 2010).

4.1 OA Volatility

The estimated volatility distribution for the total OA in Finokalia during FAME-16 is depicted in Figure 2. Use of OA with $C^* = 10^{-8}$ μg m^{-3} was needed to capture the behavior of the OA at 400 ^{o}C. Almost 40% of the OA consisted of semi-volatile organic compounds (SVOCs), 35% of low volatility organic compounds (LVOCs), and the rest was extremely low volatility organic compounds (ELVOCs).

The estimated value of the effective vaporization enthalpy was 80 ± 20 kJ mol^{-1}. This value was in agreement with the reported value by Lee et al. (2010) of 80 kJ mol^{-1} for the FAME-08 campaign. The estimated accommodation coefficient was 0.27, ranging from 0.1 to 0.8. This value was a little higher than the 0.05 value reported in the earlier study. However, both suggest only moderate resistances to mass transfer during the evaporation in the TD.

The corresponding measured and predicted thermograms are depicted in Figure 3. Almost 30% of the OA had not evaporated even after heating at 400 ^{o}C. The temperature at which half of the OA evaporated was T_{50}=120 ^{o}C, a value similar to that observed by Lee et al. (2010). The composition of the OA leaving the TD changed significantly as temperature increased according to the model. At 125 ^{o}C the LVOCs and ELVOCs contributed equally to the remaining OA mass. For further temperature increases the LVOC fraction was reduced until 375 ^{o}C, at which point only the ELVOCs remained.

PMF analysis resulted in a two-factor solution (Florou et al., in prep.). Factor 1 corresponded to more oxidized oxygenated OA (MO-OOA) and Factor 2 to a less oxidized component (LO-OOA). The average contribution of the two factors was 47% for the MO-OOA and 53% for the LO-OOA. The O:C for the MO-OOA was 0.95 (OS_C = 0.59) and for the LO-OOA it was 0.56 (OS_C = -0.27). ~~Both the MO-OOA and the LO-OOA were increasing with the increase of the rBC mass.~~ There was a weak positive correlation between LO-OOA, MO-OOA and rBC. The R^2 between the hourly concentrations of MO-OOA and rBC was 0.12 (Figure S12), and for LO-OOA and rBC 0.17 (Figure S13). 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.

Commented [AT18]: REVIEWER 2 comment 2

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.

The Finokalia area is characterized by the absence of local sources and as result the absence of fresh OA. The area is characterized by dry land and dry vegetation (dry bushes), thus no high biogenic emissions are expected. The OA during FAME-08, was also found to consist entirely of OOA with no primary OA (POA) present (Hildebrandt et al., 2010). POA evaporates and gets oxidized rapidly in the photochemically active environment of the Eastern Mediterranean during its transport from its sources to this remote site. FLEXPART simulations during the measurement campaign revealed that the air masses arriving at the site during the study were originating ~~studied were transferred~~ from ~~30%~~ continental Greece and the Balkans (30% of the time), ~~13%~~ Aegean (13% of the time), ~~24%~~ Africa (24%), and ~~33%~~ Italy/Sicily (33%). ~~In this remote location there are no anthropogenic activities. No fresh biogenic OA (BOA) was detected either. The area is characterized by dry land and dry vegetation (dry bushes), thus no high biogenic emissions are expected.~~

Formatted: Indent: First line: 0"

The volatility distributions of the two PMF factors were estimated following the same approach as that for the total OA. The measured thermograms for the two PMF factors are shown in Figure 4. Almost 50% of both the MO-OOA and the LO-OOA evaporated at 150 °C. Almost 30% of the MO-OOA mass, and about 20% of the LO-OOA did not evaporate even at temperatures as high as 400°C. The model reproduced the observed MFR values for both factors. Both factors contained components with a wide volatility range. The MO-OOA exhibited a bimodal volatility distribution with peaks at effective saturation concentrations of 10^{-8} and 10 μg m^{-3}. Its effective enthalpy of vaporization was approximately 90 ± 35 kJ mol^{-1} and its accommodation coefficient was 0.27. The estimated volatility distribution of the LO-OOA was a little more uniform peaking at an effective saturation concentration of 1 μg m^{-3}. The average calculated ~~average~~ saturation concentration~~volatility~~ of LO-OOA at 298 K was 0.016 μg m^{-3}, an order of magnitude higher than that of the MO-OOA. The LO-OOA enthalpy of vaporization was 70 ± 20 kJ mol^{-1}, 20 kJ mol^{-1} lower than that of the MO-OOA. Its accommodation coefficient was approximately 0.1 indicating small mass transfer resistances. MO-OOA consisted of approximately 40% SVOCs, 30% LVOCs, and 30% ELVOCs. On the contrary, LO-OOA consisted of almost 45% SVOCs, 40% LVOCs and only 15% ELVOCs. 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 process~~sources~~.

Commented [AT19]: REVIEWER 2 comment 19

The fitting of the individual factor thermograms implicitly assumes that each factor had the same size distribution as the total OA and also that the two factors were externally mixed. The uncertainty introduced by these two assumptions was implicitly evaluated comparing the estimated total OA of volatility distribution with the composition-weighted average of the volatility distributions of the two OA factors. The two distributions agreed within a few percent for $10^{-3}<C^{*}<10^{0}$ and within 10% for the lowest and highest volatility bins.

4.2 Aerosol optical properties

The PAX was used to measure the b_{abs} and b_{scat} at 405 nm. The measured $b_{scat,405}$ ~~at 405 nm~~ ranged from 11.5 to 47 Mm^{-1} with an average campaign value of 26.5 Mm^{-1} (Figure 5). ~~In addition,~~The corresponding ~~Similarly,~~ $b_{abs,405}$ ~~at 405 nm~~ ranged from 0.64 to 5.6 Mm^{-1} with an average value of 2.1 Mm^{-1}.

Commented [AT20]: REVIEWER 2 comment 21

The absorption coefficients measured by the aethalometer at λ=370 nm and at λ=470 nm, were compared with the absorption coefficient 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 $b_{abs,370}$ measured by the aethalometer was higher than the $b_{abs,405}$ of the PAX. Their relationship is

Formatted: Font: Italic

described by the equation y=3.32x - 3.24. Similarly, the $b_{abs,450}$ measured by the a~~A~~ethalometer was higher than that of the PAX at 405 nm and their relationship was described by ~~*the equation*~~ y=1.85x – 0.93 (Figure S14). Part of these differences are due ~~These discrepancies could possibly exist due~~ to the artifacts associated with filter-based absorption measurements ~~OA loadings on the filter~~ (Cappa et al., 2008; Lack et al., 2008).

Commented [AT21]: Reviewer 1 Comment 8 ; Reviewer 2 comment 8

Acetonitrile is a known biomass burning marker and can help identify the potential influence of the site by biomass burning events or wildfires during the campaign. The acetonitrile concentration measured by the PTR-MS remained close to 0.4 ppb during the campaign, which is the local background level. This together with the low BC levels indicate that the site was not impacted by nearby biomass burning during the study.

The $b_{abs,405}$ variation followed that of the rBC (R^2=0.74 for the hourly averages). The R^2 at λ=370 nm was lower at 0.67 than that at 405 nm. ~~, a value lower than the R^2 at λ= 405 nm.~~ This is consistent with the presence of some BrC. However, the $b_{abs,370}$ is measured by the aethalometer and the $b_{abs,405}$ by~~on~~ the PAX ~~measurements~~. For the b_{abs} at higher wavelengths measured by the aethalometer the R^2 at λ=450 nm was 0.68, at λ=520 nm 0.67, at λ=590 nm 0.65, and at λ=660 nm 0.65 (Figure S15). These values are rather inconclusive regarding~~cannot justify~~ the existence or absence of BrC. 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.

Commented [AT22]: REVIEWER 1 Comment 4

The ratio of the $b_{abs,405}$, measured by the PAX, over the rBC mass, was equal to dMAC$_{405}$=16.3±4.2 m^2 g^{-1}~~The ratio of the $b_{abs,405}$ over the rBC, MAC$_{405}$, was equal to 16.3±4.2 m^2 g^{-1}.~~ ~~Using the definition of the AAE,~~

$$\cancel{AAE = -\frac{\ln\left[MAC_{405}/MAC_{532}\right]}{\ln\left[405/532\right]},}$$

~~we can calculate the MAC of freshly generated BC 405 nm.~~ . In this study the average rBC size distribution had ~~diameter ranged from 10 to 350 nm with~~ a number mode diameter of~~in~~ 67 nm and a mass mode diameter equal to ~~mean at~~ 185~~106~~ nm. T~~It is clear that t~~he measured MAC$_{405}$ is clearly higher~~bigger~~ than the expected MAC$_{405}$ of uncoated BC particles (Bond et al., 2006). ~~Previous studies have shown that freshly generated BC has a MAC$_{532}$ of 7.5 m^2 g^{-1} (Clarke et al., 2004; Bond and Bergstrom, 2006). Using the definition of the AAE,~~

~~$\mathrm{AAE} = -\frac{\ln\left[\mathrm{MAC}_{405}/\mathrm{MAC}_{532}\right]}{\ln\left[405/532\right]}$,~~

~~we can calculate the MAC of freshly generated BC 405 nm. Assuming that the AAE is equal to unity for BC particles, we find that the MAC$_{405}$ of BC was approximately 9.9 m^2 g^{-1}.~~ The difference between the measured and the theoretical value of MAC$_{405}$ can be due to the coating of BC by other PM components (lensing effect) and/or the existence of other absorbing material. These two potential explanations~~is~~ will be explored in the following paragraphs~~below~~.

Commented [SP23]: REVIEWER 1, Comment 2

The AAE of the aerosol was calculated ~~by~~ using ~~calculated by~~ a power-law fitting of the b_{abs} measured by the aethalometer in all seven wavelengths (370, 470, 520, 590, 660, 880, 950 nm). The campaign average AAE ~~of PM for wavelengths ranging from 370 to 950 nm~~ was 0.97±0.22. Lack and Cappa (2010) suggested that an AAE>1.6 should confirm the presence of non-BC absorbing material, however an AAE<1.6 does not exclude its presence. The AAE of coated BC cores can deviate from the typical AAE=1 with values greater or lower than unity (Gyawali et al., 2009). ~~In addition, Lack and Cappa (2010) suggested that an AAE>1.6 should confirm the presence of non-BC absorbing material, however an AAE<1.6 does not exclude its presence.~~ Liu et al. (2018) ~~Another study~~ showed that the AAE of coated BC is highly sensitive to particle size distribution and demonstrated that AAE decreases as particle size increases (Liu et al., 2018). The same study 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. Based on the relatively large aged particles present in Finokalia~~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. Therefore the relatively low average AAE does not preclude the presence of some absorbing organic aerosol.~~ in a site like Finokal ia 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.~~

Commented [AT24]: REVIEWER 2 comment 24

Commented [AT25]: Reviewer 2 comment 3

Commented [AT26]: REVIEWER 2 comment 3

Mie theory calculations were performed in order to estimate the MAC$_{405}$ and the E_{abs} due to the lensing effect of the shell covering the BC core. Initially, a non-absorbing shell was assumed. The predicted MAC$_{405}$ had an average value of 15.4 m^2 g^{-1}. The average E_{abs} due to lensing effect was 2.13. The predicted average MAC$_{405}$ using the measured BC size distribution and assuming pure uncoated spherical particles was 7.2 m^2 g^{-1} varying from 6.1 to 7.8 m^2 g^{-1} during the study (hourly averages). This is consistent with the expected 5.3-9.2 m^2 g^{-1} for BC core diameters in the

10-350 nm size range (Bond et al. 2006). The average predicted MAC_{405} was lower than the average measured MAC_{405} =16.3 m^2 g^{-1}. There were several periods during which the measured MAC was much higher than the ~~difference between the measured and the~~ predicted values with the differences ~~was~~ as high as 8.5 m^2 g^{-1} ~~.~~ (Figure 6). These discrepancies suggest the potential presence of high levels of absorbing OA during these periods. ~~The predicted MAC_{405} had an average value of 14.1 m^2 g^{-1}. The average E_{abs} due to lensing effect was 2.07. The average predicted MAC_{405} was 13% lower than the measured suggesting the existence of non-refractory absorbing material (Figure 6).~~ ~~The measured MAC_{405} was higher than the predicted MAC_{405} in 47% of the cases, suggesting the existence of absorbing material (Figure 6).~~

Commented [AT27]: REVIEWER 1 comment 2

Commented [AT28]: REVIEWER 1 comment 2

In the next step, the Mie theory calculations were repeated assuming an absorbing shell with a refractive index of $n_{OA} = 1.55 + ki$, where the imaginary part, *k*, was allowed to vary from 0 to 0.4. This range of *k* values was selected based on previous literature (Kirchstetter et al., 2004; Alexander et al., 2008; Chakrabarty et al., 2010; Chen and Bond, 2010; Saleh et al., 2014; Chakrabarty et al., 2016, Li et al., 2016; Saleh et al., 2018). ~~One third~~~~53%~~Approximately half of the resulting *k* values during the campaign were zero, suggesting a non-absorbing shell, while the other half were ~~two thirds~~ were positive. More specifically, 23~~2~~% of the estimated *k* values ranged from 0.01 to 0.1, 7~~22~~% from 0.11 to 0.2, ~~1~~3~~9~~% from 0.21 to 0.3, and 14% of the *k* values ranged from 0.31 to 0.4. During these periods, the campaign average $b_{abs,405}$ was equal to 2.4 Mm^{-1}. BrC was estimated to lead to a 15% increase of the campaign average $b_{abs,405}$.

Commented [AT29]: REVIEWER 2 comment 3

4.3 The role of ELVOCs

ELVOCs can exhibit substantial larger light absorption than LVOCS or SVOCs. 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). The hypothesis that the presence of ELVOCs could explain the higher aerosol light absorption was tested. The unexplained MAC (ΔMAC) difference of measured and predicted values was compared with the total ELVOC mass concentration. The ELVOC concentration was estimated based on the results on the volatility analysis of the two PMF factors:

$$[ELVOC]= 0.15\ [LO\text{-}OOA] + 0.3\ [MO\text{-}OOA]$$

The unexplained $b_{abs,405}$ ~~least squares fit between~~ (~~the~~ 3 ~~-hour~~ average values) was well correlated with the estimated ~~d unexplained $b_{abs,405}$ and~~ ELVOC concentrations with an~~was~~ R^2=0.76 (Figure

7). The corresponding R^2 between the 3-h average ~~The least squares fit between the 3 hour averaged~~ ΔMAC and the ~~and~~ ELVOCs was ~~had R^2=~~0.66~~5~~ (Figure S16~~7~~). ~~The least squares fit between the 3-hour averaged unexplained $b_{abs,405}$ and ELVOC was R^2=0.76 (Figure 7).~~ The~~i~~se results suggest~~s~~ that the ELVOCs were probably contributing to the total absorption and could explain the difference in the MAC.

Correlation of the ΔMAC with the rBC, and with other parameters ~~and~~ were lower than those for the ELVOCs. 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 correlation with the sulfate levels (R^2=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. A comparison of the difference of measured and the predicted $b_{abs,405}$ and the ELVOC was also conducted for all the periods including those in which no BrC was present (k=0). The correlation was R^2 = 0.52. During the k=0 periods the predicted $b_{abs,405}$ was equal or higher than the measured $b_{abs,405}$. This difference was due to overestimation of the absorption values by the Mie theory or due to the uncertainties in the measurements of the b~~b~~$_{abs,405}$.

Commented [AT30]: REVIEWER 1 comment 6

5. Uncertainty analysis

The analysis presented in the previous sections has been based on a series of assumptions and, as expected is affected, by measurement uncertainties. We have tested the robustness of our conclusion about the link between the unexplained absorption and ELVOC levels by repeating the analysis for several cases. We focused on the estimation of the coating thickness of the BC particles, the~~The calculations were repeated in order to test how the different type of uncertainties can affect the relationship of the ELVOC and the unexplained absorption. The analysis tested the assumption of the coating thickness of the shell, the assumed~~ refractive index of black carbon, the uncertainty of the measurements by the SP2 and PAX_{405}, ~~and~~ the uncertainty of the results from the PMF analysis and finally the uncertainty of the thermodenuder ~~as well as from the TD dynamic evaporation~~ model. The results of the corresponding tests are summarized in the following paragraphs.

The coating thickness was recalculated applying the ~~using~~ LEO algorithm~~calculations from~~ on the SP2 measurements. The average coating thickness calculated by this approach was

Commented [SP31]: REVIEWER 2, Comment 4 approximately half of that calculated using the internal mixture assumption (Fig. S11). This resulted in lower predicted absorption and therefore a larger gap between measurements and predictions assuming that the organic aerosol was not absorbing. The unexplained absorption increased by approximately 35% (from 0.24 to 0.32 Mm^{-1}). ~~With the new coating thickness MIE theory calculations were repeated and a new theoretical MAC$_{405}$ and babs$_{405}$ were found.~~ The calculations indicated~~showed~~ that 71% of the samples had a k>0 suggesting an absorbing shell. The correlation between the unexplained absorption and the ELVOC concentration remained high ~~least square fit between the averaged ΔMAC and ELVOC was R2=0.51 while the one for the Δbabs and ELVOC was~~ R^2=0.69 (Fig. S17), suggesting that despite the uncertainty in the coating thickness our results are quite robust.~~.~~

Commented [SP32]: REVIEWER 2 Comments 9 and 11

Commented [SP33]: REVIEWER 2, Comment 6

The effect of the assumed BC refractive index on our results was tested by repeating the Mie theory calculations for two additional values: a relatively high value of 1.95 +0.679i and a relatively low value 1.5 + 0.5i were assumed (Bond and Bergstrom, 2006). For the high refractive index, the predicted average MAC$_{405}$ using the measured BC size distribution and assuming pure uncoated spherical particles was 7.7 m^2 g^{-1} varying from 6.3 to 8.2 m^2 g^{-1} during the study (hourly averages). Even if the unexplained absorption was reduced its R^2 with the ELVOCs remained high and equal to 0.72 (Fig. S18). For the low refractive index, the predicted average MAC$_{405}$ of the uncoated BC particles was 6.2 m^2 g^{-1} (range of 5.2-6.5 m^2 g^{-1} during the study). The R^2 between the unexplained absorption, $\Delta b_{abs,405}$ and the ELVOC concentration was R^2=0.55 (Fig. S19). So the link between the unexplained absorption and the abundance of ELVOCs is quite robust with respect to the assumed value of the BC refractive index.

We estimated that 92-97% of the BC mass concentration was inside the SP2 measurement window therefore given that we also corrected for it fitting the measured size distribution, the uncertainty introduced by this limitation of the SP2 was minor. Lack et al. (2012) estimated an uncertainty of the aerosol absorption measurement $b_{abs,405}$ measurements by the PAX of less than 10%. Both of these uncertainties did not have an important effect on the link between the unexplained absorption and the ELVOC concentrations.

Commented [SP34]: REVIEWER 2 Comment 7

~~In addition, Mie theory calculations were repeated for more refractive indexes of the BC core. A maximum a refractive index $n_{rBC,max}$ = 2.0 +1.0i and a minimum $n_{rBC,min}$ = 1.5 + 0.5i were assumed (Bond and Bergstrom, 2006). For the maximum refractive index, the calculations showed that 17% of the samples had a~~ ~~k>0 suggesting an absorbing shell. The least square fit between the~~

~~averaged ΔMAC and ELVOC was R^2=0.49 while the one for the Δb$_{abs}$ and ELVOC was R^2=0.71. For the minimum refractive index, the calculations showed that 95 % of the samples had a k>0 suggesting an absorbing shell. The least square fit between the averaged ΔMAC and ELVOC was R^2=0.31 while the one for the Δb$_{abs}$ and ELVOC was R^2=0.55.~~

~~As mentioned in a previous section the estimated measurement uncertainty of the SP2 is 40%. In addition. The PAX has an uncertainty of less than 10% for the aerosol absorption measurement b$_{abs,405}$ (Lack et al. 2012). The average propagation uncertainty of the MAC$_{405}$, based on the measurements of rBC and b$_{abs}$ at λ=405 nm, is 20%. An upper and lower measured MAC$_{405}$ was calculated using this propagated uncertainty. For the upper limit of the measured MAC$_{405}$, 89% of the samples had an absorbing shell. The relationship of the ELVOCs with the ΔMAC was R^2=0.23, and the relationship with the Δb$_{abs}$ was R^2=0.47. Furthermore, for the lower limit of the measured MAC$_{405}$, only 15% of the samples had an absorbing shell. The relationship of the ELVOCs with the ΔMAC was R^2=0.49, and the relationship with the Δb$_{abs}$ was R^2=0.75.~~

An assessment of the uncertainty of the concentrations of the two OA- factors determined by the PMF analysis was performed~~took place~~ by bootstrapping 10 ~~runs~~ simulations (Ulbrich et al., 2009). ~~The results showed that the statistical uncertainties were small indicating the accuracy of the two factors (Figure S17).~~ The estimated uncertainty for the LO-OOA concentrations was 2% and for the MO-OOA concentrations was 3% (Fig. S20). These relatively small uncertainties suggest that the PMF uncertainty regarding the determination of these factors does not affect significantly~~t the~~ conclusions of this study. ~~As I was stated in a previous section, both MO-OOA and LO-OOA were positively correlated with rBC with the corresponding correlation coefficient R^2 being 0.17 for MO-OOA and 0.12 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. The R^2 of the non-refractory PM$_1$ and the rBC was 0.3 (Figure S18).~~

The uncertainty related to the volatility distributions determined by the thermodenuder results was assessed by estimating low and high limits of the ELVOC concentrations:~~In addition, the~~ ELVOC$_{low}$ and ELVOC$_{high}$. These~~ concentrations~~ were estimated based on the extreme mass fractions that were calculated during~~in~~ the sensitivity analysis of the TD model (Supplemental information Section S2). The LO-OOA ELVOC mass fraction~~s~~ ranged from 0.09 to~~ (ΔH$_{vap}$= 50 kJ~~

Commented [SP35]: REVIEWER 2 Comment 5

~~mol^{-1} and a_m=0.19) and~~ 0.25 while that of the MO-OOA from 0.13 to 0.47. For the low ELVOC case we thus assumed that:~~(ΔH$_{vap}$= 100 kJ mol^{-1} and a_m=0.02) (Table 2). Similarly, the MO-OOA ELVOC mass fractions ranged from 0.13 (ΔH$_{vap}$= 50 kJ mol^{-1} and a_m=0.59) and 0.47 (ΔH$_{vap}$= 150 kJ mol^{-1} and a_m=0.09) (Table 1).~~

~~For the lowest case:~~

$$[ELVOC_{low}]= 0.09\ [LO\text{-}OOA] + 0.13\ [MO\text{-}OOA]$$

The R^2 between the ~~1~~

~~The least square fit between the 3-hour averaged ΔMAC and ELVOC$_{low}$ was R^2=0.68. Similarly, the least squares fit between the 3-hour averaged~~ unexplained $b_{abs,405}$ and ELVOC$_{low}$ was R^2=0.79 (Fig. S21).

For the high ELVOC~~est~~ case:

$$[ELVOC_{high}]= 0.25\ [LO\text{-}OOA] + 0.47\ [MO\text{-}OOA]$$

Once more the correlation between the unexplained absorption at 405 nm and the ELVOCs was quite high with R^2=0.78 (Fig. S22).

Commented [SP36]: REVIEWER 1 Comment 5

~~The least square fit between the 3-hour averaged ΔMAC and ELVOC$_{high}$ was R^2=0.66. Similarly, the least squares fit between the 3-hour averaged unexplained $b_{abs,405}$ and ELVOC$_{low}$ was R^2=0.78. These results suggest that the ELVOCs were probably contributing to the total absorption and could explain the difference in the MAC.~~

Commented [AT37]: Reviewer 2 Comment 2

~~5.~~6.Conclusions

A month-long campaign was conducted at a remote site, in Finokalia, Crete during May of 2016. The dominant PM$_1$ components were sulfate and aged organics with O/C=0.81. The average ambient OA concentration was 1.5 μg m^{-3} and the rBC was 0.14 μg m^{-3}. Continuous monitoring of biomass burning markers revealed that there w~~as~~ere no periods of enhanced biomass burning influence~~no detectable impact of wildfires~~ on the site during the campaign. PMF analysis resulted in two secondary OA factors: one more oxidized (MO-OOA) and one less oxidized (LO-OOA). Total OA consisted on average of 40% SVOCs, 35% LVOCs and 25% ELVOCs. Both OA components with a wide range of volatilities. Approximately 30% of the MO-OOA was ELVOCs, 30% LVOCs and 40% semi-volatile material. The LO-OOA was more volatile on average with 40% consisting of LVOCs and 45% of SVOCs and 15% of ELVOCs.

Commented [AT38]: REVIEWER 2 Comment 26

Aerosol optical properties were measured. The average b_{scat} at 405 nm was 26.5 Mm^{-1} and the average b_{abs} at 405 nm was 2.1 Mm^{-1}. Furthermore, the average AAE was 0.97 and the MAC_{405} was 16.3. Mie theory calculations were able to reproduce ~~one third~~less than half of the measured MAC_{405} values assuming core-shell morphology and a non-absorbing shell (k=0). We estimated that the non-absorbing shell was causing an enhancement of the absorption by a factor of 2.1~~207~~. For the other ~~two thirds~~half of the measurements the presence of an absorbing shell with an average k of 0.18~~21~~ was needed to explain the measurements.

The ELVOCs mass concentration was estimated using the volatility distributions of the two factors. The ELVOC concentration was highly correlated with the unexplained MAC_{405} (R^2=0.66) and the unexplained $b_{abs,405}$ (R^2=0.76), defined as the differences of the parameters measured and the ones predicted by Mie theory for k=0. These results suggest that the unexplained absorption in this remote site could be due to a large extent to the extremely low volatility components of the organic aerosol.~~The ELVOC concentration was highly correlated (R^2=0.65) with the difference of the unexplained MAC_{405}, defined as the difference of the measured MAC_{405} the measured and the one predicted by Mie theory for k=0.~~

Data availability. The data in the study are available from the authors upon request (spyros@chemeng.upatras.gr).

Author contributions. AT conducted the absorption measurements, analysed the results and wrote the paper. EL performed the thermodenuder measurements and analysed the results. KF performed the AMS measurements and analysed the results. AL performed the PTR-MS measurements and analysis. EK was responsible for the OA volatility analysis. CK coordinated the field campaign and assisted with all measurements. NW assisted with all measurements SNP was responsible for the design and coordination of the study and the synthesis of the results. All co-authors contributed to the writing of the manuscript.

Competing interests. The authors declare that they have no conflict of interest.

Acknowledgements

This work was supported by U.S. Environmental Protection Agency STAR program [grant number R835035]. Travel support was provided by the European Research Infrastructure ACTRIS. The authors would like to thank the Finokalia station personnel for the accommodation and for providing the aethalometer measurements.

References

Alexander, D. T. L., Crozier, P. A., and Anderson, J. R.: Brown carbon spheres in East Asian outflow and their optical properties, Science, 321, 833–836, 2008.

An, W. J., Pathak, R. K., Lee, B. H., and Pandis, S. N.: Aerosol volatility measurement using an improved thermodenuder: Application to secondary organic aerosol, J. Aerosol Sci., 38, 305–314, 2007.

Andreae, M. O., and Gelencser, A.: Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols, Atmos. Chem. Phys., 6, 3131–3148, 2006.

Arnott, W.P., Moosmüller, H., Sheridan, P. J., Ogren, J. A., Raspet, R., Slaton, W.V., Hand, J. L., Kreidenweis, S. M. and Collett Jr., J. L.: Photoacoustic and filter-based ambient aerosol light absorption measurements: instrument comparison and the role of relative humidity, J. Geophys. Res., 108, 4034–44, 2003

Bond, T. C., and Bergstrom, R. W.: Light absorption by carbonaceous particles: An investigative review, Aerosol Sci. and Technol., 40, 27–67, 2006.

Bond, T. C., Habib, G., and Bergstrom, R. W.: Limitations in the enhancement of visible light absorption due to mixing state, J. Geophys. Res., 111, D20211, 2006.

Bohren, C. F., and Huffman, D. R.: Absorption and scattering of light by small particles. Research supported by the University of Arizona and Institute of Occupational and Environmental Health, New York: Wiley Interscience, 1983.

Bougiatioti, A., Stavroulas, I., Kostenidou, E., Zarmpas, P., Theodosi, C., Kouvarakis, G., Canonaco, F., Prévôt, A. S. H., Nenes, A., Pandis, S. N., and Mihalopoulos, N.: Processing of biomass burning aerosol in the eastern Mediterranean during summertime, Atmos. Chem. Phys., 14, 4793–4807, 2014.

Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Hildebrandt Ruiz, L., Fortner, E.,Williams, L. R., Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J. T., and Worsnop, D. R.: Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications, Atmos. Chem. Phys., 15, 253–272, 2015.

Cappa, C. D., Zhang, X., Russell, L. M., Collier, S., Lee, A. K. Y., Chen, C.-L., Betha, R., Chen, S., Liu, J., Price, D. J., Sanchez, K. J., McMeeking, G. R., Williams, L. R., Onasch, T. B., Worsnop, D. R., Abbatt, J. and Zhang, Q.: Light Absorption by Ambient Black and Brown Carbon and its Dependence on Black Carbon Coating State for Two California, USA, Cities in Winter and Summer, J. Geophys. Res.,124, 1550−1577, 2019.

Cappa, C. D., Onasch, T. B., Massoli, P., Worsnop, D. R., Bates, T. S., Cross, E. S., Davidovits, P., Hakala, J., Hayden, K. L., Jobson, B. T., Kolesar, K. R., Lack, D. A., Lerner, B. M., Li, S. M., Mellon, D., Nuaaman, I., Olfert, J. S., Petäjä, T., Quinn, P. K., Song, C., Subramanian, R., Williams, E. J., and Zaveri, R. A.: Radiative absorption enhancements due to the mixing state of atmospheric black carbon, Science, 337, 2012.

Cappa, C., Lack, D., Burkholder, J., and Ravishankara, A.: Bias in filter based aerosol light absorption measurements due to organic aerosol loading: Evidence from laboratory measurements, Aerosol Sci. Technol., 42, 1022–1032, 2008.

~~Chakrabarty, R. K., Moosmuller, H., Chen, L.-W. A., Lewis, K., Arnott, W. P., Mazzoleni, C., Dubey, M. K., Wold, C. E., Hao, W. M., and Kreidenweis, S. M.: Brown carbon in tar balls from smoldering biomass combustion, Atmos. Chem. Phys., 10,6363–6370, 2010.~~

Chakrabarty, R. K., Gyawali, M., Yatavelli, R. L. N., Pandey, A., Watts, A. C., Knue, J., Chen, L.-W. A., Pattison, R. R., Tsibart, A., Samburova, V., and Moosmüller, H.: Brown carbon aerosols from burning of boreal peatlands: microphysical properties, emission factors, and implications for direct radiative forcing, Atmos. Chem. Phys., 16, 3033–3040, 2016.

Chakrabarty, R. K., Moosmuller, H., Chen, L.-W. A., Lewis, K., Arnott, W. P., Mazzoleni, C., Dubey, M. K., Wold, C. E., Hao, W. M., and Kreidenweis, S. M.: Brown carbon in tar balls from smoldering biomass combustion, Atmos. Chem. Phys., 10,6363–6370, 2010.

Chen, Y. and Bond, T. C.: Light absorption by organic carbon from wood combustion, Atmos. Chem. Phys., 10, 1773–1787, 2010.

China, S., Scarnato, B., Owen, R. C., Zhang, B., Ampadu, M. T. , Kumar, S., Dzepina, K., Dziobak, M. P., Fialho, P., Perlinger, J. A., Hueber, J., Helmig, D., Mazzoleni, L. R., and Claudio Mazzoleni, C.: Morphology and mixing state of aged soot particles at a remote marine free troposphere site: Implications for optical properties, Geophys. Res. Lett., 42, 1243–1250, 2015.

Clarke, A. D., Shinozuka, Y., Kapustin, V. N., Howell, S., Huebert, B., Doherty, S., Anderson, T., Covert, D., Anderson, J., Hua, X., Moore, K. G., McNaughton, C., Carmichael, G., and Weber, R.: Size distributions and mixtures of dust and black carbon aerosol in Asian outflow: Physiochemistry and optical properties, J. Geophys. Res., 109, D15S09, doi.org/10.1029/ 2003JD004378, 2004.

Ditas, J., Ma, N., Zhang, Y., Assmann, D., Neumaier, M., Riede, H., Karu, E., Williams, J., Scharffe, D., Wang, Q., Saturno, J., Schwarz, J. P., Katich, J. M., McMeeking, G. R., Zahn, A., Hermann, M., Brenninkmeijer, C. A. M., Andreae, M. O., Pöschl, U., Su, H., and Cheng, Y.: Strong impact of wildfires on the abundance and aging of black carbon in the lowermost stratosphere, P. Natl. Acad. Sci. USA, 115, 11595–11603, 2018.

Donahue, N. M., Robinson, A. L., Stanier, C. O., and Pandis, S. N.: Coupled partitioning, dilution, and chemical aging of semivolatile organics, Environ. Sci. Technol., 40, 2635–2643, 2006.

Drosatou, A. D., Skyllakou, K., Theodoritsi, G. N., and Pandis, S. N.: Positive matrix factorization of organic aerosol: insights from a chemical transport model, Atmos. Chem. Phys., 19, 973–986, https://doi.org/10.5194/acp-19-973-2019, 2019.

Florou, K., Liangou, A., Louvaris, E., Kaltsonoudis, C., Tasoglou, A., Patoulias, D., Kouvarakis, G., Vlachou, A., Kourtchev, I. and Spyros N. Pandis, S. N.: The Finokalia Aerosol Measurement Experiment (FAME-16): Atmospheric processing of organic aerosol in the Eastern Mediterranean, in prep.

Fuller, K. A., Malm, W. C., and Kreidenweis, S. M.: Effects of mixing on extinction by carbonaceous particles, J. Geophys. Res., 104, 15941–15954, 1999.

Gao, R. S., Schwarz, J. P., Kelly, K. K., Fahey, D. W., Watts, L. A., Thompson, T. L., Spackman, J. R., Slowik, J. G., Cross, E. S., Han, J. H., Davidovits, P., Onasch, T. B., and Worsnop, D. R.: A novel method for estimating light-scattering properties of soot aerosols using a modified single-particle soot photometer, Aerosol Sci. Technol., 41, 125–135, 2007.

Formatted: Font:

Gkatzelis, G. I., Papanastasiou, D. K., Florou, K., Kaltsonoudis, C., Louvaris, E. and Pandis, S. N.: Measurement of nonvolatile particle number size distribution, Atmos. Meas. Tech., 9, 103–114, 2016.

Gyawali, M., Arnott, W. P., Lewis, K., and Moosmueller, H.: In situ aerosol optics in Reno, NV, USA during and after the summer 2008 California wildfires and the influence of absorbing and non-absorbing organic oatings on spectral light absorption, Atmos. Chem. Phys., 9, 8007–8017, 2009.

Gysel, M., Laborde, M., Olfert, J. S., Subramanian, R., and Gröhn, A. J.: Effective density of Aquadag and fullerene soot black carbon reference materials used for SP2 calibration, Atmos. Meas. Tech., 4, 2851–2858, 2011.

Healy, R. M., Wang, J. M., Jeong, C.-H., Lee, A. K. Y., Willis, M. D., Jaroudi, E., Zimmerman, N., Hilker, N., Murphy, M., Eckhardt, S., Stohl, A., Abbatt, J. P. D., Wenger, J. C., and Evans, G. J.: Light-absorbing properties of ambient black carbon and brown carbon from fossil fuel and biomass burning sources, J. Geophys. Res., 120, 6619–6633, 2015.

Hildebrandt, L., Engelhart, G. J., Mohr, C., Kostenidou, E., Lanz, V. A., Bougiatioti, A., DeCarlo, P. F., Prévôt, A. S. H., Baltensperger, U., Mihalopoulos, N., Donahue, N. M., and Pandis, S. N.: Aged organic aerosol in the eastern Mediterranean: The Finokalia aerosol measurement experiment 2008, Atmos. Chem. Phys., 10, 4167–4186, 2010.

Hildebrandt, L., Kostenidou, E., Lanz, V. A., Prévôt, A. S. H., Baltensperger, U., Mihalopoulos, N., Laaksonen, A., Donahue, N. M., and Pandis, S. N.: Sources and atmospheric processing of organic aerosol in the Mediterranean: Insights from aerosol mass spectrometer factor analysis, Atmos. Chem. Phys., 11, 12499–12515, 2011.

Jacobson, M. Z.: Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols, Nature, 409, 695–697, 2001.

Kalivitis, N., Bougiatioti, A., Kouvarakis, G., and Mihalopoulos, N.: Long term measurements of atmospheric aerosol optical properties in the Eastern Mediterranean, Atmos. Res., 102, 351–357, 2011.

Karnezi, E., Riipinen, I., and Pandis, S. N.: Measuring the atmospheric organic aerosol volatility distribution: a theoretical analysis, Atmos. Meas. Tech., 7, 2953–2965, doi:10.5194/amt7-2953-2014, 2014.

Kirchstetter, T., Novakov, T., and Hobbs, P.: Evidence that the spectral dependence of light absorption by aerosols is affected by organic carbon, J. Geophys. Res., 109, D21208, doi.org/ 10.1029/2004JD004999, 2004.

Kirchstetter, T. W., and Novakov, T.: Controlled generation of black carbon particles from a diffusion flame and applications in evaluating black carbon measurement methods, Atmos. Environ., 41, 1874–1888, 2007.

Knox, A., Evans, G. J., Brook, J. R., Yao, X., Jeong, C.-H., Godri, K. J., Sabaliauskas, K., and Slowik, J. G.: Mass absorption cross-section of ambient black carbon aerosol in relation to chemical age, Aerosol Sci. Tech., 43, 522-532, 2009.

Kostenidou, E., Pathak, R. K., and Pandis, S. N.: An algorithm for the calculation of secondary organic aerosol density combining AMS and SMPS data, Aerosol Sci. Tech., 41, 1002–1010, 2007.

Kouvarakis, G., Tsigaridis, K., Kanakidou, M., and Mihalopoulos, N.: Temporal variations of surface regional background ozone over Crete Island in the Southeast Mediterranean, J. Geophys. Res., 105, 399–407, 2000.

Lack, D. A., Langridge, J. M., Bahreini, R., Cappa, C. D., Middlebrook, A. N., and Schwarz, J. P.: Brown carbon and internal mixing in biomass burning particles, Proc. Natl. Acad. Sci. USA, 109, 14802–14807, 2012.

Lack, D. A., and Cappa, C. D.: Impact of brown and clear carbon on light absorption enhancement, single scatter albedo and absorption wavelength dependence of black carbon, Atmos. Chem. Phys., 10, 4207–4220, 2010.

Lack, D. A., Cappa, C. D., Covert, D. S., Baynard, T., Massoli, P., Sierau, B., Bates, T. S., Quinn, P. K., Lovejoy, E. R., and Ravishankara, A. R.: Bias in filter based aerosol light absorption measurements due to organic aerosol loading: Evidence from ambient measurements, Aerosol Sci. Technol., 42, 1033–1041, 2008.

Lanz, V. A., Alfarra, M. R., Baltensperger, U., Buchmann, B., Hueglin, C., and Prévôt, A. S. H.: Source apportionment of submicron organic aerosols at an urban site by factor analytical modelling of aerosol mass spectra, Atmos. Chem. Phys., 7, 1503–1522, 2007.

Lee, B. H., Kostenidou, E., Hildebrandt, L., Riipinen, I., Engelhart, G. J., Mohr, C., Decarlo, P. F., Mihalopoulos, N., Prévôt, A. S. H., Baltensperger, U., and Pandis, S. N.: Measurement of the ambient organic aerosol volatility distribution: Application during the Finokalia Aerosol Measurement Experiment (FAME-2008), Atmos. Chem. Phys., 10, 12149–12160, 2010.

Lelieveld, J., Berresheim, H., Borrmann, S., Crutzen, P. J., Dentener, F. J., Fischer, H., Feichter, J., Flatau, P. J., Heland, J., Holzinger, R., Korrmann, R., Lawrence, M. G., Levin, Z., Markowicz, K. M., Mihalopoulos, N., Minikin, A., Ramanathan, V., de Reus, M., Roelofs, G. J., Scheeren, H. A., Sciare, J., Schlager, H., Schultz, M., Siegmund, P., Steil, B., Stephanou, E. G., Stier, P., Traub, M., Warneke, C., Williams, J., and Ziereis, H.: Global air pollution crossroads over the mediterranean, Science, 298, 794–799, 2002.

Li, X., Chen, Y., and Bond, T. C.: Light absorption of organic aerosol from pyrolysis of corn stalk, Atmos. Environ. 144, 249–256, 2016.

Liu, S., Aiken, A. C., Gorkowski, K., Dubey, M. K., Cappa, C. D., Williams, L. R., Herndon, S. C., Massoli, P., Fortner, E. C., Chhabra, P. S., Brooks, W. A., Onasch, T. B., Jayne J. T., Worsnop, D. R., China, S., Sharma, N., Mazzoleni, C., Xu, L., Ng, N. L., Liu, D., Allan, J. D., Lee, J. D., Fleming, Z. L., Mohr, C., Zotter, P., Szidat, S., and Prévôt, A. S. H.: Enhanced light absorption by mixed source black and brown carbon particles in UK winter, Nat Commun., 6, 843, 2015.

Liu, C., Chung, C. E., Yin, Y., Schnaiter, M.: The absorption Ångström exponent of black carbon: from numerical aspects, Atmos. Chem. Phys., 18, 16409–16418, 2018.

Liu, D., Whitehead, J., Alfarra, M. R., Reyes-Villegas, E., Spracklen, D. V., Reddington, C. L., Kong, S., Williams, P. I., Ting, Y.-C., Haslett, S., Taylor, J. W., Flynn, M. J., Morgan, W. T., McFiggans, G., Coe, H., and Allan, J. D.: Black-carbon absorption enhancement in the atmosphere determined by particle mixing state, Nat. Geosci., 10, 184–188, 2017.

~~Liu, S., Aiken, A. C., Gorkowski, K., Dubey, M. K., Cappa, C. D., Williams, L. R., Herndon, S. C., Massoli, P., Fortner, E. C., Chhabra, P. S., Brooks, W. A., Onasch, T. B., Jayne J. T., Worsnop, D. R., China, S., Sharma, N., Mazzoleni, C., Xu, L., Ng, N. L., Liu, D., Allan, J. D., Lee, J. D., Fleming, Z. L., Mohr, C., Zotter, P., Szidat, S., and Prévôt, A. S. H.: Enhanced light absorption by mixed source black and brown carbon particles in UK winter, Nat Commun., 6, 843, 2015.~~

Louvaris, E. E., Florou, K., Karnezi, E., Papanastasiou, D. K., Gkatzelis, G. I., and Pandis, S. N.: Volatility of source apportioned wintertime organic aerosol in the city of Athens, Atmos. Environ., 158, 138-147, 2017.

McMeeking, G. R., Fortner, E., Onasch, T. B., Taylor, J. W., Flynn, M., Coe, H., and Kreidenweis, S. M.: Impacts of nonrefractory material on light absorption by aerosols emitted from biomass burning, J. Geophys. Res., 119, 12272–12286, 2014.

Mihalopoulos, N., Stephanou, E., Kanakidou, M., Pilitsidis, S., and Bousquet, P.: Tropospheric aerosol ionic composition in the eastern Mediterranean region, Tellus, 49B, 314–326, 1997.

Mullins, J., and Williams, A.: The optical properties of soot: A comparison between experimental and theoretical values, Fuel, 66, 277–280, 1987.

Paatero, P., and Tapper, U.: Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values, Environmetrics, 5, 111–126, 1994.

Park, K., Kittelson, D. B., Zachariah, M. R., and McMurry, P. H.: Measurement of inherent material density of nanoparticle agglomerates, J. Nanopart. Res., 6, 267–272, 2004.

Pikridas, M., Bougiatioti, A., Hildebrandt, L., Engelhart, G. J., Kostenidou, E., Mohr, C., Prevót, A. S. H., Kouvarakis, G., Zarmpas, P., Burkhart, J. F., Lee, B.-H., Psichoudaki, M., Mihalopoulos, N., Pilinis, C., Stohl, A., Baltensperger, U., Kulmala, M., and Pandis, S. N.: The Finokalia Aerosol Measurement Experiment – 2008 (FAME-08): an overview, Atmos. Chem. Phys., 10, 6793–6806, 2010.

Riipinen, I., Pierce, J. R., Donahue, N. M., and Pandis, S. N.: Equilibration time scales of organic aerosol inside thermodenuders: Kinetics versus equilibrium thermodynamics, Atmos. Environ., 44, 597–607, 2010.

Saleh, R., Cheng, Z., and Atwi., K.: The brown–black continuum of light-absorbing combustion aerosols, Environ. Sci. Technol. Lett. 5, 508–13, 2018.

Saleh, R., Robinson, E. S., Tkacik, D. S., Ahern, A. T., Liu, S., Aiken, A. C., Sullivan, R. C., Presto, A. A., Dubey, M. K., Yokelson, R. J., Donahue, N. M., and Robinson, A. L.: Brownness of organics in aerosols from biomass burning linked to their black carbon content, Nat. Geosci., 7, 647–650, 2014.

Saliba, G., Subramanian, R., Saleh, R., Ahern, A. T., Lipsky, E. M., Tasoglou, A., Sullivan, R. C., Bhandari, J., Mazzoleni, C., and Robinson, A. L.: Optical properties of black carbon in cookstove emissions coated with secondary organic aerosols: Measurements and modeling, Aerosol Sci. Technol., 50, 1264–1276, 2016.

Tasoglou, A., Saliba, G., Subramanian, R., and S. N. Pandis S. N.: Absorption of chemically aged biomass burning carbonaceous aerosol, J. Aerosol. Sci., 113, 141–52, 2017.

Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L.: Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data, Atmos. Chem. Phys., 9, 2891–2918, 2009.

Vrekoussis, M., Liakakou, E., Koçak, M., Kubilay, N., Oikonomou, K., Sciare, J., and Mihalopoulos, N.: Seasonal variability of optical properties of aerosols in the eastern Mediterranean, Atmos. Environ., 39, 7083-7094, 2005.

Weingartner, E., H. Saathoff, M. Schnaiter, N. Streit, B. Bitnar, and U. Baltensperger: Absorption of light by soot particles: Determination of the absorption coefficient by means of aethalometers, J. Aerosol. Sci. 34, 1445–63, 2003.

Wong, J. P. S., Tsagkaraki, M., Tsiodra, I., Mihalopoulos, N., Violaki, K., Kanakidou, M., Sciare, J., Nenes, A., and Weber, R. J.: Atmospheric evolution of molecular-weight-separated brown carbon from biomass burning, Atmos. Chem. Phys., 19, 7319–7334, https://doi.org/10.5194/acp-19-7319-2019, 2019.

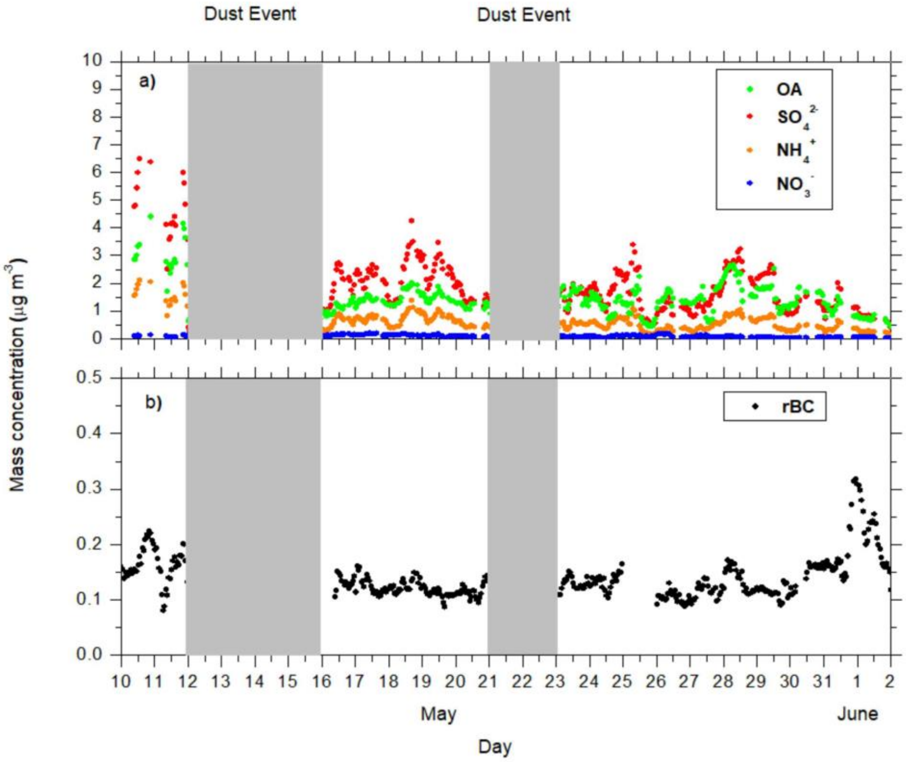
Wu, J.-S., Krishnan, S. S., and Feath, G. M.: Refractive indices at visible wavelengths of soot emitted from buoyant turbulent diffusion flames, J. Heat Transfer, 119, 230–237, 1997.

Formatted: Adjust space between Latin and Asian text, Adjust space between Asian text and numbers, Pattern: Clear (White)

Zanatta, M., Laj, P., Gysel, M., Baltensperger, U., Vratolis, S., Eleftheriadis, K., Kondo, Y., Dubuisson, P., Winiarek, V., Kazadzis, S., Tunved, P., and Jacobi, H. W.: Effects of mixing state on optical and radiative properties of black carbon in the European Arctic, Atmos. Chem. Phys., 18, 14037-14057, 2018.

Zhang, Y.; Favez, O.; Canonaco, F.; Liu, D.; Močnik, G.; Amodeo, T.; Sciare, J.; Prévôt, A. S. H.; Gros, V., and Albinet, A.: Evidence of major secondary organic aerosol contribution to lensing effect black carbon absorption enhancement, NPJ Climate and Atmospheric Science, 1, doi.org/10.1038/s41612-018-0056-2, 2018a.

Zhang, Y., Zhang, Q., Cheng, Y., Su, H., Li, H., Li, M., Zhang, X., Ding, A., and He, K.: Amplification of light absorption of black carbon associated with air pollution, Atmos. Chem. Phys., 18, 9879–9896, 2018b.


Dust Event
Dust Event
a)
OA
SO_4^{2-}
NH_4^+
NO_3^-
b)
rBC
Mass concentration (μg m^{-3})
0
1
2
3
4
5
6
7
8
9
10
0.0
0.1
0.2
0.3
0.4
0.5
10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 1 2
May
June
Day

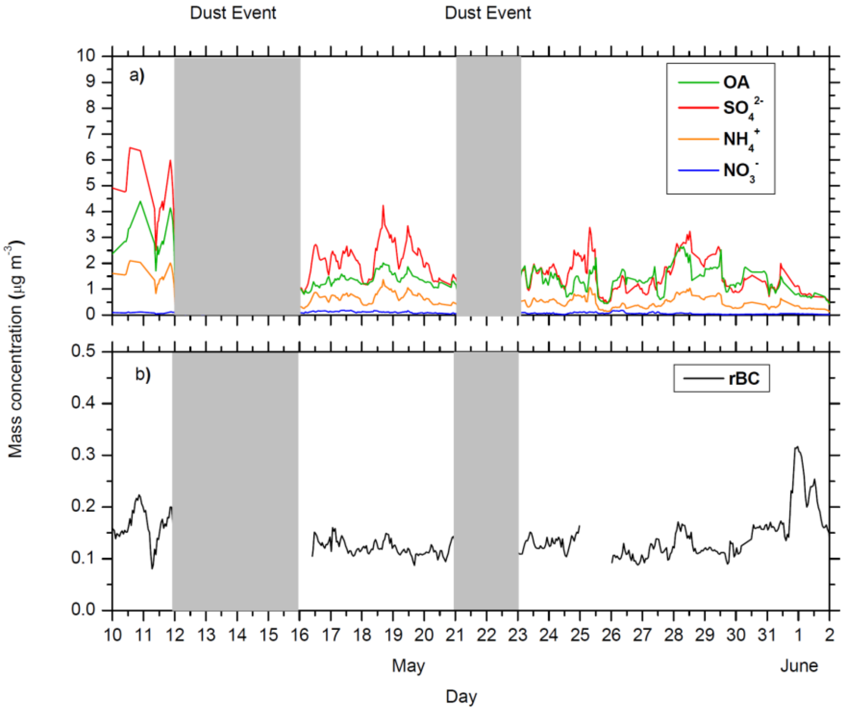


Figure 1: Evolution of the aerosol chemical composition based on the HR-TOF-AMS and SP2 measurements during FAME-16: a) the non-refractory aerosol components; b) rBC concentration. The shaded areas represent the dust events periods~~.~~

Commented [SP39]: REVIEWER 1 Comment 20

Formatted: Justified

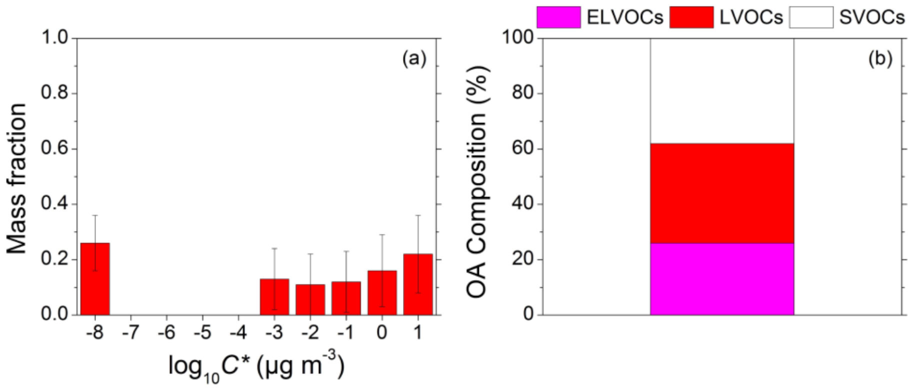


Figure 2: (a) Total OA volatility distribution along with its uncertainty estimated by the Karnezi et al. (2014) approach. The error bars represent the corresponding variability (± 1 standard deviation). (b) OA composition. Magenta color represents the ELVOCs, red the LVOCs, and white the SVOCs.

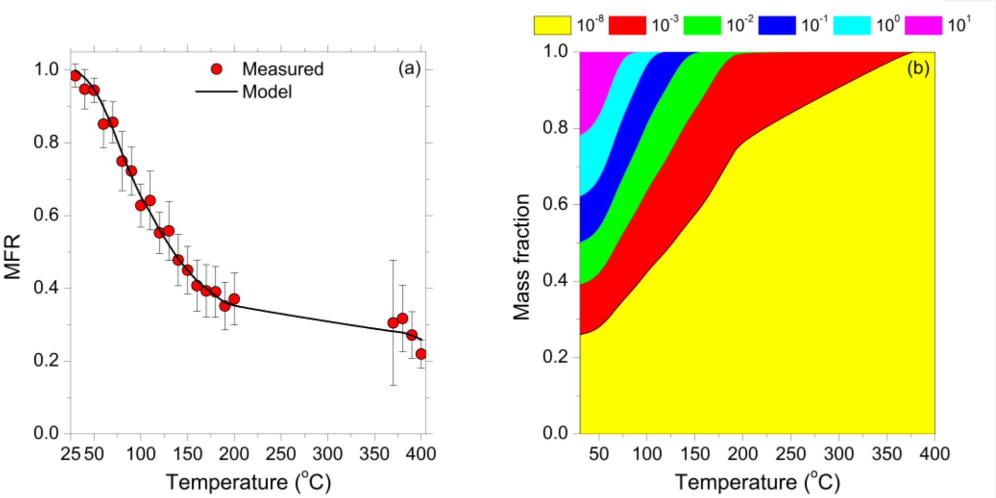


Figure 3: (a) Average loss-corrected total OA thermograms. Red circles represent the measured total OA MFR and the error bars the corresponding variability (±2 standard deviations of the mean). The solid lines are the model predictions (b) Mass fraction of the total OA for different effective saturation surrogate species with concentrations as a function of TD temperature. Yellow color represents the contribution of the effective saturation concentration $C^* = 10^{-8}$ μg m^{-3}, red the contribution of the $C^* = 10^{-3}$ μg m^{-3}, green the $C^* = 10^{-2}$ μg m^{-3}, blue the $C^* = 10^{-1}$ μg m^{-3}, cyan the $C^* = 10^{0}$ μg m^{-3}, and magenta the $C^* = 10$ μg m^{-3}.

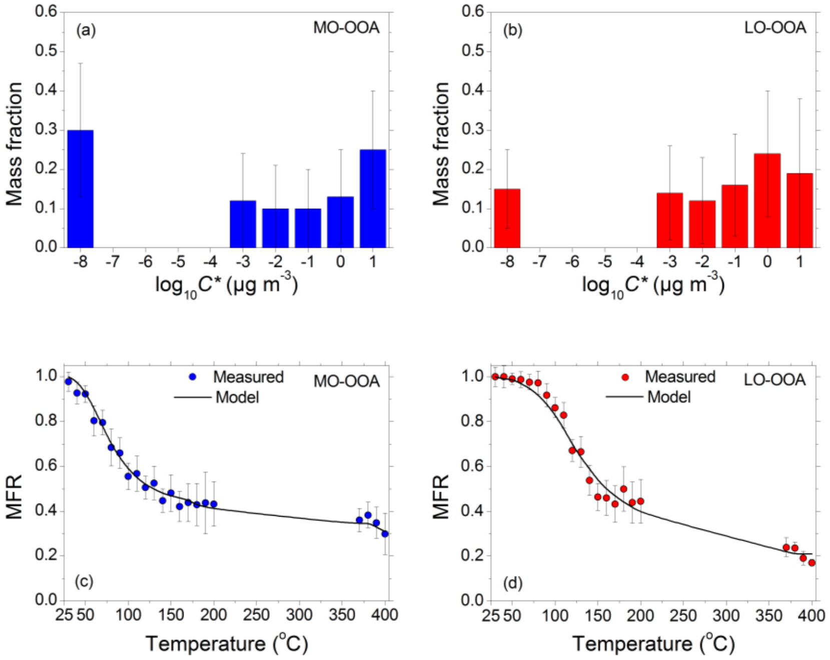


Figure 4: (a) Estimated volatility distribution of the MO-OOA factor along with its corresponding uncertainties by using the approach of Karnezi et al. (2014). (b) Estimated volatility distribution of the LO-OOA factor along with its corresponding uncertainties. (c) Measured (in circles) and predicted thermograms for the LO-OOA factor. The error bars represent ± 2 standard deviations of the mean. (d) Measured (in circles) and predicted thermograms for the LO-OOA factor. The error bars represent ± 2 standard deviations of the mean.

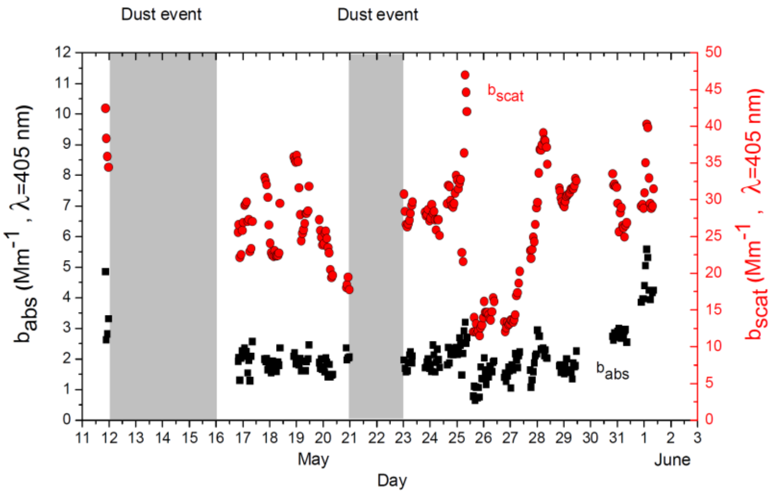


Figure 5: The timeseries of the aerosol optical properties at λ=405 nm. The black squares represent the absorption coefficient, b_{abs}, while the red circles represent the scattering coefficient, b_{scat}. The shaded areas represent the dust events periods.

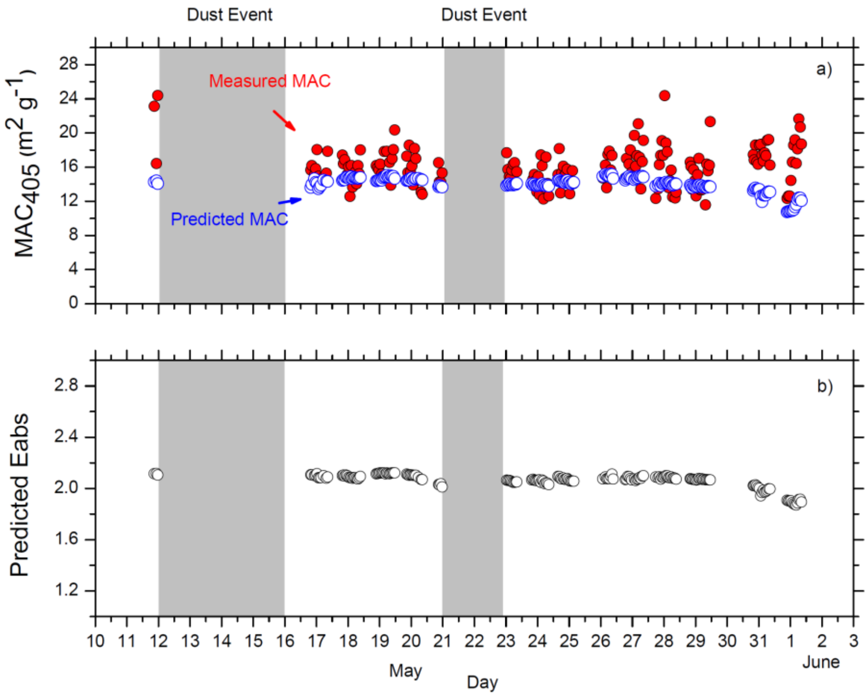


Figure 6: Hourly averaged ~~R~~results from the Mie theory calculations, assuming a non-absorbing shell (k=0): a) predicted (blue circles) and measured MAC_{405} (red circles). b) Hourly averaged Predicted E_{abs} values. The shaded areas represent the dust events periods.

Formatted: Left

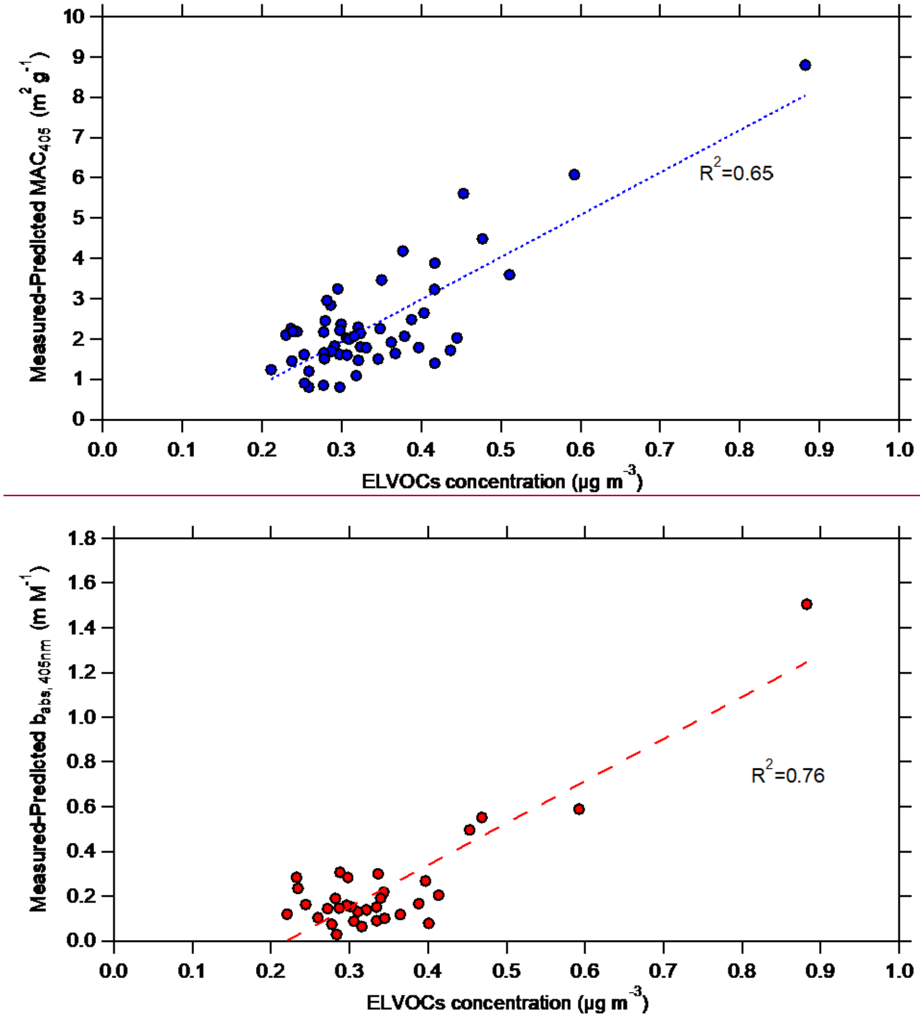


Figure 7: a) The difference between the measured and the predicted unexplained $b_{abs,405}$ as a function of the estimated concentration of the ELVOCs. The data shown represent 3-hours averaged values.~~Difference between the measured and the predicted MAC$_{405}$ as a function of the estimated concentration of the ELVOCs.~~

Formatted: Centered

Formatted: Subscript

Formatted: Subscript

Formatted: Justified