

Interactive comment on “Processing of biomass burning aerosol in the Eastern Mediterranean during summertime” by A. Bougiatioti et al.

Anonymous Referee #1

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The paper of Bougiatioti et al. provides evidence of significant atmospheric processing of biomass burning aerosol in Eastern Mediterranean during summer time leading to significant underestimation of the biomass burning source based on traditional PMF source apportionment. While atmospheric processing of biomass burning aerosol has been established few studies exist about the implications of the processing using traditional source apportionment techniques. Having said that, the quantitative assessment of the processed BBOA aerosol needs a better reasoning and more thorough discussion or some of the conclusions should be played down mainly due to the fact that the aerosol chemical speciation monitor was designed mainly for monitoring purposes rather than being a truly scientific instrument. There is simply too much information lacking - high resolution fragmentation pattern, mass size distribution, inference of mix-

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ing state – to make the unambiguous conclusions. My biggest concern is the claim that almost half of OA can be attributed to biomass burning. While that may be true in particular region and particular air masses, especially the ones associated with fire plumes, the conclusion is clearly overblown out of proportions. Other than that the paper is pretty well written and easy to follow though there were many details lacking as well. The paper can be recommended for publication after addressing the above major and many minor comments below.

The main argument in the paper for the existence of OOA-BB factor is a 3 factor solution and consideration of Sicilian fires lacking direct biomass burning traces. It may look statistically correct, but there are few important questions remaining before the OOA-BB factor can be considered established and quantified. BBOA and OOA factors are indeed pretty obvious; the former associated with fire plumes and the other correlating with sulphate and processed down to m/z 44 mainly. It does not mean, however, that OOA factor has one source origin, but rather it has been processed to the highest degree of oxygenation becoming an end product of atmospheric transformation of organic matter. Naturally, OOA-BB factor looks like an intermediate product, but the details are ambiguous. For instance, why BBOA and OOA-BB should be correlating with nitrate? Is nitrate and not sulphate produced in biomass burning plumes? Or is it a regional phenomenon, but then both nitrate and sulphate should be equally present in internally mixed aerosol? Moreover, why OOA-BB is poorly correlating with BC if atmospheric processing is supposedly processing OA, but not splitting with BC? In the absence of wet scavenging, atmospheric processing alone should not break the correlation between BBOA and BC. Even considering OOA-BB coming from multiple diffused fire plumes it should still be correlating with the originally present BC. The breakdown of correlation suggests to me that the OOA-BB factor is not unique and is a combination of additional factor even if processed BBOA is dominating OOA-BB factor. Based on purely statistical terms, R square value is not a correlation (r is the correlation), but rather the variance which shows a fraction of the total variance of the two variables explained by the common source. Hence, $R^2=0.48$ of OOA-BB and BC

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suggests that biomass burning can explain 48% of the variance with the rest of the variance due to other sources or reasons. Even BBOA and BC have 62% of the common variance which is large, but not overwhelming.

The diurnal patterns presented in Figure 5c need more thorough consideration. Why OOA has peculiar diurnal pattern if this type of OM should be already processed to the highest possible degree and no photochemical activity can enhance the concentration in the afternoon? What was the diurnal pattern of sulphate? Typically, factors representing regional sources (background) do not exhibit diurnal patterns except the ones related to boundary layer dynamics. Possibly the factor is not unique either. Quite contrary, OOA-BB doesn't show any pronounced diurnal pattern with only a small peak coinciding with the morning BBOA peak. Also, why would BBOA peak in the morning? It must be due to specific transport time as biomass fires typically burn day and night. Authors should try estimating transport time from identified fires by backward trajectories to check for the consistency. Based on the above it can be argued that in absolute terms processed BBOA amounts to the difference between the background OOA-BB and the morning peak concentration ($\sim 0.2-0.3 \text{ ug/m}^3$) limiting its significance.

Biomass burning fires in Sicily need much better reasoning as they constitute the concluding argument in favour of significant OOA-BB. The associated evidence of fires in Sicily is rather loose and ambiguous (lines 12-14, page 25978; was it a fire or not a fire event?). As already noted above, the heavy processing of BBOA originating in Sicily should not break correlation with BC. Air mass back trajectories including their vertical evolution should be presented and discussed.

Minor comments:

Authors should normally use past tense as a common expression and only occasionally a present tense.

P25972, line 11-14. The PMF factor analysis is primarily based on temporal variation of all the fragments included, not just 44 and 43. Have authors tried to assign different

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weighting to the dominant m/z, especially m/z 44?

P25974, line 3. Authors clearly state they focus on specific clearly identified fires, but the main conclusion refers to the overall Eastern Mediterranean region. I would like to note that the measurements only covered two month of a single year.

Line 12. Spell ACSM for the first time and then use the acronym.

Line 16. Correct to "particle flash vaporisation in high vacuum".

Line 19. How relevant is the referral to PM10 inlet if ACSM aerodynamic lens limit particle transmission to PM1 – misleading information to uninformed reader.

Line 22. Different collection efficiency for sulphate is wrong. Authors possibly refer to relative ionisation efficiency (REI) which was not estimated by calibration. Or was it? Otherwise I don't understand applying arbitrary CE for sulphate and only then comparing to filter measurements.

P25975, line 6. Spell oxalate for the first time.

Line 19. If acronym is ME, spelling should be multilinear engine, not solver.

Line 25. Statistical tool is not a model, better use "mathematically extracted" instead of "modelled".

P25976, line 10. Discrepancies can also be attributed to different sampling devices because 1um cut off function is slightly different in aerodynamic lens compared to atmospheric sampling devices.

Line 11. Sentence about parameterisation is awkward and sounds out of context.

Line 23, 26. SMPS and gravimetric measurements were not introduced in Experimental section.

Line 24. Density of particles is very low considering densities of sulphate/nitrate (~ 1.7), organics (1.4) and any dust ($\sim 1.8-2.0$). My guess is that the density estimated in refer-

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enced paper included water. By the way, was SMPS fully dried (often SMPS systems run at around 40% RH which is not low enough to evaporate water completely)? Hence, the density of 1.35 could have worked because SMPS was not completely dried.

P25977, line 10. Wrong expression “at the expense of sulphate”, otherwise explain how sulphate may be substituted/replaced.

P25978, line 12-16. I am confused about the second period of 25-30 of September. What for was it mentioned? I am confused whether Sicilian biomass burning events were fires or not. Section 3.3. Conclusions based on O/C ratio are overstated considering very indirect estimation of the ratios based on studies from often different continents. To me 2 decimal places of the estimated O/C ratios are not justified based on the above uncertainty. I suggest stating uncertainties after introducing the calculations and then presenting and discussing ratios with a single decimal point without error.

P25980, line 2. It should be noted that PMF was run on OM mass spectra only. There are studies when PMF was run on all fragments.

Line 3. 1 factor solution is not a solution – it’s the total OM. Discussion should start from 2 factor solution.

Line 10. Provide number for “relatively well”.

Line 12-13. Replace “splitting behaviour” to “split factors”.

Line 13. “new factor profile” to “unique factor profile”.

Table 1. 2 decimal places are optimal considering precision. Make numbers uniform.

Figure 2. Daily filter measurements should be presented as a step line, not a point. A step line will make it clearer for the visual agreement/disagreement.

Figure 5c. Make order of factors from top to bottom same as in 5b.

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