

Interactive comment on “Organic Aerosol source apportionment in London 2013 with ME-2: exploring the solution space with annual and seasonal analysis” by Ernesto Reyes-Villegas et al

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Response to comments of referee # 1

Comment 1 from Referee.

Abstract line 19: the phrase “seasonal data sets showed a higher seasonal variability” is confusing. After reading the rest of the paper, I think I understand what the authors are saying, but this should be rephrased for clarity. I believe the point is that some sources are seasonal, and therefore the seasons should be evaluated independently rather than running PMF or ME-2 on the full data set.

author’s response

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The paragraph was rephrased.

author’s changes in manuscript

ME-2 analysis of the seasonal datasets (spring, summer and autumn) showed a higher variability in the OA sources that was not detected in the combined March-December dataset; this variability was explored with the triangle plots f44:f43 f44:f60, where a high variation of SVOOA relative to LVOOA was observed in the f44:f43 analysis. Hence, it was possible to conclude that, when performing source apportionment to long-term measurements important information may be lost and this analysis should be done to short periods of time such as seasonally.

Comment 2 from Referee.

Line 156: Use of target profiles from AMS and not ACSM may hinder this work, given that Ng et al. 2011 reported a markedly different collection efficiency for HOA and OOA by the ACSM, leading to underestimation of HOA by the ACSM. Further, Ng et al. 2011 reported that when HOA containing particles are externally mixed from OOA particles, this differential collection efficiency could be significant. Do the authors have any insight as to whether this could be important for the London work? At the very least, this shortcoming should be presented clearly at the outset of the work. If ACSM target profiles are available, those would be preferable to test the performance of ME-2.

author’s response

This situation was taken into consideration when first defining the way to analyse this dataset. For this reason, it was decided to run ME-2 with different α -values and target profiles from a variety of studies, in order to explore the solution space and select the solution that best identified the OA sources, according to the statistical tests applied. As shown in section 4, the use of AMS mas spec as target profiles, while giving a wide range of possible solutions with different target profiles, delivered successful results. The ACSM was specifically designed to deliver mass spectra that were equivalent to

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the AMS and so there is every reason to expect that using AMS spectra is appropriate, as they are not just comparable but should have a higher signal-to-noise ratio. Given that the purpose of this work is to systematically assess the suitability of target profiles, it would be remiss of us not to consider AMS-generated target profiles, especially considering there are more of these available, including ones obtained from the same site. Frolich, et al. (2015) used AMS mass spectra as target profiles to deconvolve OA measured with 14 ACSM and one AMS during an intercomparison, being able to successfully separate 4 different sources by partially constraining COA and HOA.

A new section in the supplement (section S3) has been added with a PMF analysis with different f-peaks in order to show how the PMF solution was chosen for the further comparison with ME2 solutions showing that ME-2 analysis improved the OA source identification compared to PMF solutions. For all these reasons we do not consider that using AMS TP has a negative effect on the ME-2 source apportionment.

author's changes in manuscript

This paragraph will be added at the end of the first paragraph in section 2.2.1

The ACSM was specifically designed to deliver mass spectra that were equivalent to the AMS; with the AMS having a higher signal to noise ratio, it is expected the use of its mass spectra as TP to be appropriate. Moreover, we consider AMS-generated TP to be convenient to use especially considering there are more of these available, including the ones obtained from the same site. In this study, the suitability of different TP will be systematically assessed in the determination of OA sources using a wide range of α -values.

Comment 3 from Referee.

Line 216: The authors write, "When analysing different solutions from the same dataset (Fig. 2.b), it is possible to observe that the use of different α -values does not imply a high variation, ranging between 1.88-2.2, suggesting that all the solutions are mathe-

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matically acceptable." I do not understand the point of this sentence, and I think the main issue is the phrase "does not imply a variation." Please clarify.

author's response

The idea here is that Q/Q_{exp} in isolation does not identify the best solution and more parameters need to be analysed in order to determine the solution that separates better the different OA sources. The variation mentioned is comparing these Q/Q_{exp} values with the ones in the literature (section 4.1.1)

author's changes in manuscript

For an ideal solution a Q/Q_{exp} value of 1.0 would be expected. However, there is not a standard criterion to define a satisfactory Q/Q_{exp} value as a certain amount of 'model error' will cause it to be systematically higher than unity (Ulbrich et al., 2009). When comparing different solutions from the same dataset (Fig. 2.b), it is possible to observe that there is not a significant variation on the Q/Q_{exp} (ranging between 1.88-2.2) when using different α -values, suggesting that all the solutions are mathematically acceptable. The unconstrained solution is the one with the lowest total Q/Q_{exp} with a value of 1.88, which is expected, as PMF calculates the solution by minimising this value; however, the PMF solution has a high Chi square and negative slope for COA (Fig. 2.a), implying that this solution is not environmentally acceptable, thus it is necessary to analyse all the different parameters in fig. 2 in order to select the solution that best identifies the OA sources.

Comment 4 from Referee.

Line 220: The authors write "however, [the] PMF solution has a high Chi square and negative slope for COA (Fig. 2.a), suggesting that this solution is not environmentally acceptable, thus it is necessary to analyse all the different parameters in fig. 2 in order to select the solution that best identifies the OA sources." It is useful to use the trilinear regression to determine if the PMF factors are environmentally realistic. However,

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the authors should provide more detail here if they intend to use this justification to eliminate the PMF solution. Specifically, for which “y” is the slope negative? BC, CO, NO_x or all three? Please indicate here. And, was this true for all the PMF solution rotations under 5 factors? Or just the one with the lowest Q/Q_{exp}? What about seeds? Was this negative slope true for those as well?

author's response

The explanation about how to determine the best solution has been explained with further details. In general: unconstrained runs with three seeds were performed with different number of factor in order to determine the most suitable number of factors, after defining 5 factor to be the most adequate number of factors, unconstrained analysis exploring the f-peak from -1 to 1 with steps of 0.1 (Fig. S4, S6, S8 and S10) was performed to determine the PMF solution to be compared with the ME-2 solutions.

author's changes in manuscript

Section 3.1.1 Unconstrained runs with f-peak = 0 and 3 different seeds were performed in order to determine the number of OA sources, being five (BBOA, HOA, COA, SVOOA, LVOOA) the most adequate number of sources (Fig. S1.b) as it was possible to split the SOA into SVOOA and LVOOA. Further unconstrained analysis was performed by running five factor solutions with different f-peaks, from -1 to 1 with steps of 0.1 (Fig. S4) in order to select the PMF solution to be compared with the ME-2 analysis.

Section 3.1.3 Diurnal concentrations for all the solutions (Supplement S3) were analysed to determine the main sources. Here, it was possible to observe that solutions with undesirable outputs in the residual, total Q/Q_{exp} and/or trilinear regression were likely to have mixed diurnal concentrations between two sources. For example in the case of “c” TP solutions, CO and BC trilinear regressions (Fig. S5.a and S5.b) show better COA slopes with values close to zero, however due to the high diurnal residual (Fig. 2.a) and HOA with high concentrations during the evening (Fig. S5.c), suggesting

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mixing with BBOA, “c” TP solutions are not considered acceptable solutions.

Comment 5 from Referee.

Line 292 (first entire paragraph in 4.1.2): I could not parse this paragraph. I think the term “variation” is misused and causes confusion. I understand the value of using the trilinear regression, but this description is nearly incomprehensible. Please revise.

author's response

The paragraph has been edited in the manuscript

author's changes in manuscript

Looking at the trilinear outputs for the different periods of time analysed (Figure 3.a), NO_x/HOA ratios present higher variability with values of 50.0 for March-Dec, 81.0 for spring, 41.0 for summer and 85.5 for autumn. The different NO_x/BBOA and NO_x/HOA slopes for spring, summer and autumn suggest that when looking at March-Dec solution only, there are seasonal variations that this solution does not completely capture. With regard to background and NO_x/COA slopes, they are well identified and relatively constant over the different periods of time analysed.

Comment 6 from Referee.

Line 322: This finding, that SVOOA is not always in the same position in the triangle relative to LVOOA seems BIG. Perhaps it could be emphasized more, or earlier? In the abstract?

author's response

This finding has been added to the abstract.

author's changes in manuscript

ME-2 analysis of the seasonal datasets (spring, summer and autumn) showed a higher variability in the OA sources that was not detected in the combined March-December

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dataset; this variability was explored with the triangle plots f44:f43 f44:f60, where a high variation of SVOOA relative to LVOOA was observed in the f44:f43 analysis. Hence, it was possible to conclude that, when performing source apportionment to long-term measurements, this analysis should be done to short periods of time such as seasonally.

Comment 7 from Referee.

Table 1: This would be far more useful if the acronyms were avoided or defined.

author's response

The acronyms description is shown in the section 2.2.1 where the table will be displayed in the final manuscript.

author's changes in manuscript

None.

Comment 8 from Referee.

Figure 2 (a): The color scale is useful to compare residuals, though I question the use of different colors to indicate positive and negative residuals. It would be easier to read the graph if either the best solutions were darkest (since the dark pink looks close to the dark green) OR if the same color was use for both positive and negative. It would also be useful to separate or demarcate the break between "a" and "c" as well as "c" and "w." This would make it clearer that we are comparing those larger groups instead of individual factors.

author's response

The use of different colours for negative and positive residuals is useful in the way that it tells the reader if the solution is overestimated (negative residual) or underestimated (positive residual). About using a break to separate solutions with different target profiles is a reasonable suggestion; this will be modified in the updated manuscript.

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author's changes in manuscript

Figure 2 Diurnal residual, y axis represents the 24 hours and x axis the different solutions with a variety of target profiles and a-values (a). NO_x trilinear regression for solutions with different target profiles (b). BBOA represents the slope of μgm^{-3} of NO_x per μgm^{-3} of BBOA. The same applies for HOA and COA. Whiskers represent the 95% confidence interval.

All the technical corrections were taken into account and modifications were done in the manuscript

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-465, 2016.

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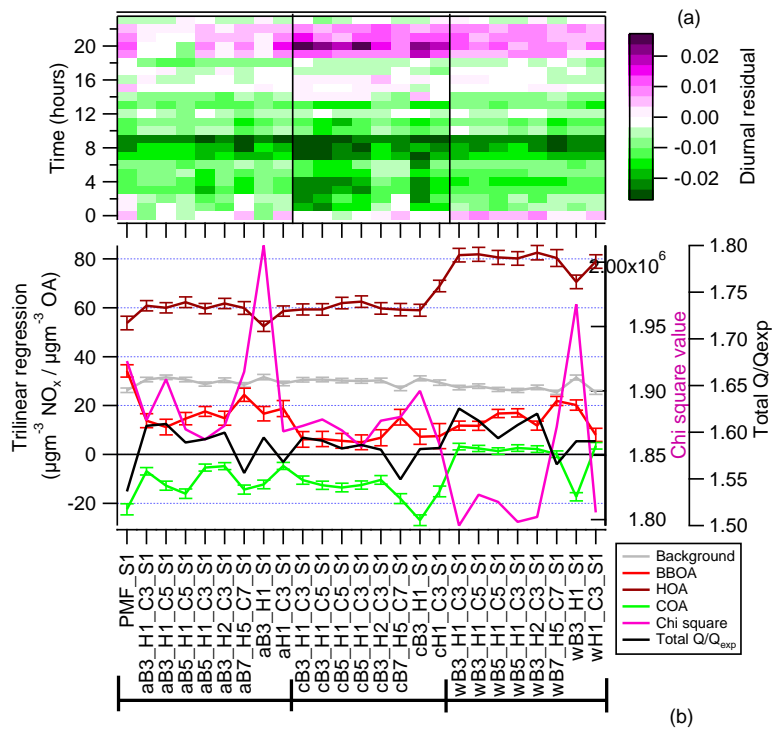


Fig. 1. Figure 2