

# ***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 # 3

Comment 1 from Referee.

The authors use ME-2 tool to analyze ACSM data to further explore the OA sources and find the best solutions, and the criteria for selecting best solution are using a values approach, minimizing  $Q/Q_{exp}$ , and trilinear regression analysis. However, the criteria of determining best solution are not clearly explained in each analysis (Figure S4\_Figure S7).

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The description has been further explained in supplement S3. Moreover, a description how the PMF was chosen has been added with the Figure S4.

author's changes in manuscript

S3. Analysis to determine the best solution for the different periods of time.

PMF runs were performed, for the March-December period, from  $f_{\text{peak}} -1$  to 1 with steps of 0.1. Figure 4 shows the comparison of the runs that converged (some of the  $f_{\text{peaks}}$  did not converge) in order to determine the PMF solution that better identified the OA sources to be compared to the ME-2 solutions. Run number 4 is chosen to be the best solution, according to the statistical tests applied, with low diurnal residual and positive COA for CO and BC trilinear regressions.

Figure S5 shows the analysis performed to determine the best solution for the March-December period. As mentioned in the main text of this paper, “c” and “w” target profiles (TP) show the less desirable results; “c” TP show a high positive residual (Figure 2.a) and “w” TP show a high chi-square and COA slope. (Figures C1.a and S4.b). From the “a” TP, aB3\_H2\_C3\_S1 solution is chosen to present the best results from this analysis due to COA slope close to zero for NO<sub>x</sub> (Figure 2.b) and CO (Figure S5.a) trilinear regression and low diurnal residual (Figure 2.a).

Figure S6 shows the PMF analysis for the spring period. All solutions show similar diurnal concentrations with negative COA slope for the three trilinear regressions. Solutions 2 and 3 have the lower Q/Q<sub>exp</sub>, Solution 3 was chosen to be compared with ME-2 solutions.

Figure S7 shows the analysis performed to determine the best solution for spring period. Solutions with “a” and “c” TP show the less desirable results with negative slopes for COA and high chi-square in the trilinear regression (Figures S5.a, S5.b and S5.c), “c” TP also show high diurnal residuals. The solution wB3\_H1\_C3\_S1 is chosen to present the best results from this analysis with low chi-square and diurnal residuals.

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Figure S8 shows the PMF analysis for the summer period. Solution 4 has a high Q/Q<sub>exp</sub> but as it shows a COA slope close to zero in the three trilinear analyses and a low diurnal residual compared to the other PMF solutions, it has been chosen to be compared with ME-2 solutions.

Figure S9 shows the analysis performed to determine the best solution for summer period. Solutions with “c” and “s” TP show the less desirable results. “s” TP show low chi-square values, however, they present high negative residuals in the morning and at night. “c” TP show a high positive residual around 15:00-18:00 hrs. The solution aB5\_H1\_C3\_S1 is chosen to present the best results from this analysis due to the low diurnal residual, COA slope close to zero and the low BBOA slope in the NO<sub>x</sub>, BC and COA trilinear regressions (Figures S9.a, S9.b and S9.c).

Figure S10 shows the PMF analysis for the autumn period. Solution 4 has been the chosen solution to be compared with ME-2 solutions because of its low Q/Q<sub>exp</sub> and a COA slope close to zero for the NO<sub>x</sub> trilinear regression and a lower diurnal residual compared to the other PMF solutions.

Figure S11 shows the analysis performed to determine the best solution for autumn period. Solutions with “a” TP show the less favourable Chi square results in the three trilinear regression figures (Figures S11.a, S11.b and S11.c). wB3\_H1\_S1 solution is chosen to present the best results from this analysis with low chi-squares and COA slope close to zero in the trilinear regression with NO<sub>x</sub> (Figures S11.a).

Comment 2 from Referee.

The triangle plot of f43: f44 and f44:f60 was introduced to compare the seasonal differences. The authors also pointed out that it's an oversimplification tool to address the chemical complexity of LVOOA and SVOOA component, and further work is needed to completely address the OA chemistry difference in seasonal changes. Please clarify it or add more details how this triangle plot addresses the results and conclusion. In the abstract, the authors write “the seasonal variability was explored with triangle plots of

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f43:f44 and f44:f60, with HOA and COA being the most suitable sources to constrain.” The COA is mainly characterized by m/z 55 and m/z 57, but here the f60 is low for COA. Is it more appropriate to look at f55 and f57 for COA in seasonal differences?

author’s response The paragraph in the abstract has been modified. The main idea here is to describe the seasonal variation mainly observed in SVOOA rather than mentioning the most suitable sources to constrain. More details about the f44:f43 variation in the triangle plot have been added to the manuscript. author’s changes in manuscript abstract: 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. Section 4.2 This analysis shows that the factors derived for SOA do not always conform to the model of LVOOA and SVOOA proposed by Jimenez et al. (2009). Furthermore, the fact that the lines are going in different directions with the seasons of year means that the factorisation is identifying different aspects of the chemical complexity, as LVOOA and SVOOA rather than being originated from primary emissions are part of continuous physico-chemical processes involving gases, aerosols and meteorological parameters among others. This serves to highlight that a 2-component model (LVOOA and SVOOA) is an oversimplification of a complex chemical system as concluded by Canonaco et al. (2015) who found significant f44 vs f43 difference for summer and winter analyses. Minor comments Comment 1 from Referee. Line 188 : Equation (4) B and C parameters were not defined.

author’s response B and C parameters have been defined in the manuscript. author’s changes in manuscript B, C and D slopes represent the contribution of BBOA, HOA and COA to “Y” and the intercept A is representative of the “Y” background concentration.

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Comment 2 from Referee. Line 288-290: The authors write “The summer is overestimated and a strong variation of the source profiles, a situation that ME-2 is not able to capture.” If there is a strong variation of the source profile, how does the ME-2 confirm the data accuracy?

author’s response The comparison here is with the diurnal residual for the different analyses (March-Dec, Spring, Summer and Autumn). As mentioned in the manuscript, PMF considers the sources to be constant over time which is not true and more in daytime during summer when more photochemistry is happening, affecting the source apportionment. We can see this effect on the diurnal residual with positive concentrations between 12:00 to 17:00 UTC. However, the concentrations in the residuals of 0.018 are low compared to the diurnal concentrations of the different sources (Fig S6e). author’s changes in manuscript It is in the diurnal residual where we can observe a high variation (Fig. 3.b), with autumn proving to be the most overestimated with negative residuals of  $-0.033 \mu\text{g.m}^{-3}$  mainly in the morning and at night. On the other hand, summer shows to be the most underestimated solution with values of  $0.018 \mu\text{g.m}^{-3}$  particularly between midday and 17:00 UTC. The fact that summer is underestimated from 12:00 to 17:00 UTC is probably related to the increase on photochemical activity, a situation that ME-2 is not able to capture as considers the mass spectra to remain constant over the period analysed. It is important to notice that these diurnal residuals of  $0.03 \mu\text{g.m}^{-3}$  or less are low compared with diurnal concentrations of the OA sources, which concentrations ranged  $0.1\text{-}0.6 \mu\text{g.m}^{-3}$ .

Comment 3 from Referee. Line 296: The authors write “ the March-Dec dataset solution does not completely capture”. What range of variability for thrilinear regression? The authors write there are seasonal variations that the dataset solution does not completely capture. How does this method completely capture it and avoid failures?

author’s response

The paragraph has been edited to better explain the seasonal variations. It is in all the

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section 4.1 where we show how seasonal solutions present different values of  $Q/Q_{exp}$ , residuals and POA slopes suggesting that there is a seasonal dependency on the different OA sources which would not be possible to determine when running ME-2 for long periods of time (March-Dec).

author's changes in manuscript Looking at the trilinear outputs for the different periods analysed (Figure 3.a), HOA slopes 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 BBOA and HOA slopes for spring, summer and autumn suggest that when looking at March-Dec solution only, there are seasonal variations, perhaps affected by changes on the inhabitants' daily activities (i.e. domestic heating) and meteorological conditions, that the March-Dec solution does not completely capture. With regard to COA slopes and background concentrations, they are well identified and relatively constant over the different periods analysed. Comment 4 from Referee. Line 320-322: "The fact that the lines are going in different directions with the seasons of year means that the factorization is identifying different aspects of the chemical complexity." It seems that the "chemical complexity" is not clear explained why the LVOOA and SVOOA lines are different directions.

author's response

The paragraph was edited adding explanation about what we mean of "chemical complexity" author's changes in manuscript Furthermore, the fact that the lines are going in different directions with the seasons of year means that the factorisation is identifying different aspects of the chemical complexity, as LVOOA and SVOOA rather than being originated from primary emissions are part of continuous physicochemical processes involving gases, aerosols and meteorological parameters among others. This serves to highlight that a 2-component model (LVOOA and SVOOA) is an oversimplification of a complex chemical system as concluded by Canonaco et al. (2015) who found significant f44 vs f43 difference for summer and winter analyses. Comment 5 from Referee. Line 330: "The fresh OA during autumn and highly oxygenated BBOA during summer"

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seems not convinced. It would be good if the authors could provide O/C ratios or any indicators (f44 or f43) that supports the “highly oxygenated BBOA” during summer. author’s response paragraph has been edited on the manuscript author’s changes in manuscript BBOA evolution has been frequently observed with high f44 and low f60 values due to due to aging, oxidation and cloud processing (Huffman et al., 2009; Cubison et al., 2011). Thus, it was possible to obtain a variety of BBOA for the different seasons of the year, ranging from a fresh BBOA with a high f60 during autumn to a more oxidised BBOA with a low f60 during summer.

Comment 6 from Referee. Line 343-345 : Please add reference for this paragraph. The authors use the ratios of NO<sub>x</sub>/HOA, CO/HOA, and NO<sub>x</sub>/ \_CO to determine the week-days and weekend ratios. However, there is no strong evidence show that these ratios are best indicators to analyze the impact of diesel or petrol emissions contribution. Also, when the authors conclude the heavy-duty diesel vehicle emissions are possible contributions during weekdays, but it seems not strongly supportive to conclude this.

author’s response

The paragraph has been edited and more references have been added.

author’s changes in manuscript

Diesel emits higher NO<sub>x</sub> and HOA concentrations compared to petrol, while petrol emits higher concentrations of CO, according to the National Atmospheric Emissions inventory (NAEI, 2016), during 2014 the emission factors (units in kilotonnes of pollutant per Megatonne of fuel used) were: 11-12 for diesel and 1.9-4.3 for petrol in the case of NO<sub>x</sub> and 2.4-5.6 for diesel and 11-50 for petrol in the case of CO. Moreover, there are variations between Light Duty Diesel (LDD) and Heavy Duty Diesel (HDD) emissions (LAEI, 2013), with LDD emitting higher NO<sub>x</sub> concentrations and HDD emitting higher HOA concentrations.

It is possible to qualitatively analyse the impact of different fuels on air pollution by

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looking at weekday/weekend ratios (WD/WE), as previously done in several studies (Bahreini et al., 2012; Tao and Harley, 2014; DeWitt et al., 2015) and stating the hypothesis that different fuels will have different pollutant contribution during the week.

Comment 7 from Referee.

Line 375 : “ The main PM1 contributors to moderate and high PM2.5 concentrations are NO3 and LVOOA.” It would be supportive if the authors could provide more information about NO3.

author’s response

The paragraph has been edited.

author’s changes in manuscript

Considering that PM1 is composed mainly of OA, SO4, NO3, NH4 and BC, it is possible to analyse the PM1 composition during PM2.5 high concentrations (Fig. 6.b). Episodes with moderate and high PM2.5 concentrations were observed with low wind speeds (Fig. S8), being NO3 and LVOOA the main PM1 contributors. High NO3 concentrations were observed during spring as found in a previous study performed by Young et al. (2015a) who determined that NO3 concentrations in spring depend on air mass trajectory, precursors and meteorology. Different contributions from OA sources were identified: in the episode in March, high BBOA concentrations were observed, whereas during the episodes in April and September, higher concentrations of LVOOA were detected.

Comment 8 from Referee.

Line 390: In the conclusion, the author write “ higher variation mainly in the SVOOA mass spectra and the BBOA; less variability was observed in LVOOA, COA and HOA.” The “variability” term was used in this manuscript many times, but there is no clear range for these variations.

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author's response

The paragraph has been rewritten to better explain these variations.

author's changes in manuscript

ME-2 proved to be a robust tool to deconvolve OA sources. This study highlighted the importance of using appropriate mass spectra as target profiles and  $\alpha$ -values when exploring the solution space. With the implementation of new techniques to compare different solutions, it was possible to systematically determine the solution with the best separation of OA sources, mathematically and environmentally speaking. The comparison carried out between the solution for the March-December dataset and the seasonal solutions showed high variations mainly in the SVOOA and the BBOA sources, with wide range of  $f_{44}:f_{43}$  values for SVOOA (Fig. 4.a) and  $f_{60}$  values ranging from  $13 \times 10^{-3}$  for summer to  $24 \times 10^{-3}$  for autumn (Fig. 4.b). These variations support the importance of running ME-2 during periods of time where weather conditions and  $\text{NH}_3$  emissions from human activities are less variable, such as seasonal analyses.

Comment 8 from Referee.

Table 1 : As mentioned by reviewer 1, please define clearly for the sets of target profiles.

author's response

The set of target profiles were previously described in the section 2.2.1 of the manuscript were this table will be part of in the final version. We do not consider necessary to repeat the description in the table.

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None.

Technical correction

Figure S1: Please label significant  $m/z$  peaks, O/C and H/C ratios in each solution.

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“(c)” was missing in the end of the caption of Figure S1.

author's response

Figure S1 has been updated.

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

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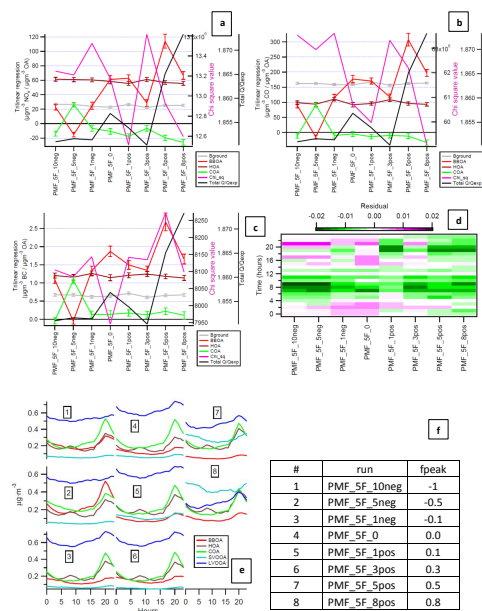


Figure S4 : NO<sub>x</sub>, CO and BC trilinear regression (a, b, c), diurnal residual (d), diurnal concentrations (e) and solution list for March-Dec PMF analysis (f).

Fig. 1. Figure S4

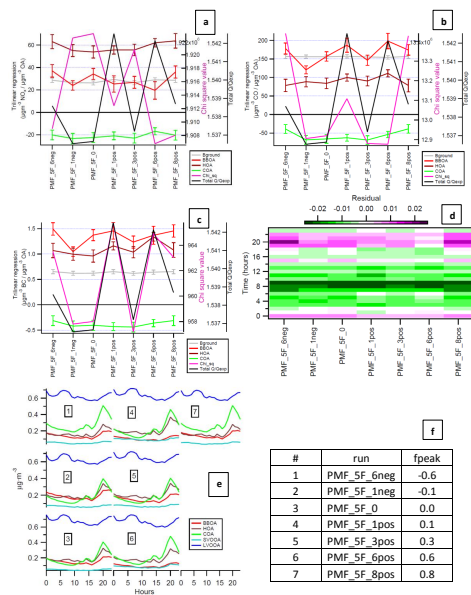


Figure S6: NO<sub>x</sub>, CO and BC trilinear regression (a, b, c), diurnal residual (d), diurnal concentrations (e) and solution list for spring PMF analysis (f).

Fig. 2. Figure S6

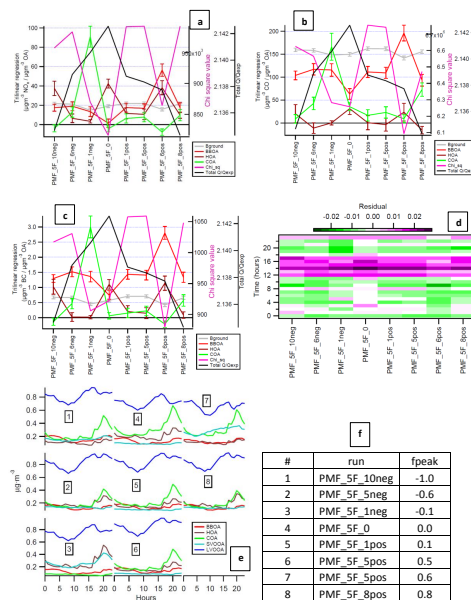


Figure S8: NO<sub>x</sub>, CO and BC trilinear regression (a, b, c), diurnal residual (d), diurnal concentrations (e) and solution list for summer PMF analysis (f).

Fig. 3. Figure S8

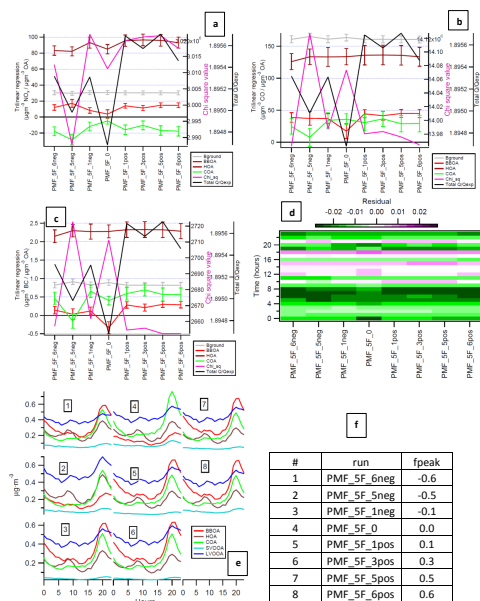


Figure S10: NO<sub>x</sub>, CO and BC telluric regression (a, b, c), diurnal residual (d), diurnal concentrations (e) and solution list for autumn PMF analysis (f).

Fig. 4. Figure S10

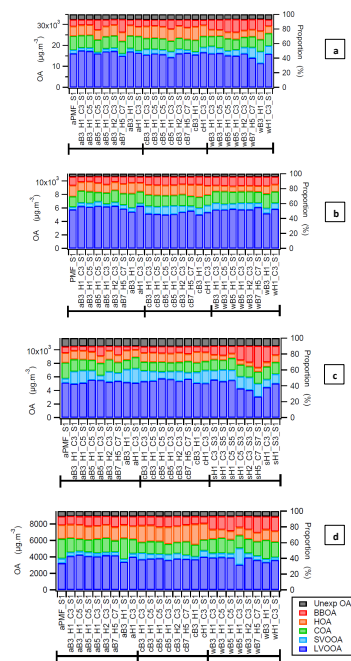


Figure S12: OA concentrations and proportions of the different OA sources to the total OA. March-Dec (a), spring (b), Summer (c) and autumn (d).

Fig. 5. Figure S12