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 # 2

Comment 1 from Referee.

Much of the variability in solutions are expressed in terms of fragment ratios. What is the range in OA mass estimated for the set of remaining plausible solutions?

author's response

The OA mass estimated for all the different solutions was practically the same, with summer being the period with less OA mass estimated (90%) and the other periods

with more than 95% of mass estimated from the total OA concentrations. Figure S12 has been added to the supplement.

author's changes in manuscript

at the end of section 3.2 It is worth to mention that all plausible solutions deconvolved a high percentage of the total OA mass (Fig. S12), with summer being the period with less OA mass estimated (90%) and the other periods with more than 95% of mass estimated from the total OA concentrations.

Figure S1 added to the supplement.

Comment 2 from Referee.

The conclusions regarding the superiority of the outlined approach are perhaps stated too strongly by the authors. For instance, in the abstract and conclusions: trilinear regression is said to "objectively determine" the solution, but it is perhaps not truly not objective in that the authors are imposing their prior assumption regarding the nature of cooking emissions and their relation to combustion tracers. And even then, the protocol does not uniquely determine the "best" solution. On this point, it would be useful to plot confidence intervals on the regression coefficients in Figure 2 (and Figure S6) as there are a number of solutions which fulfill this criterion.

Similarly, the statement about ME-2 being "robust" or "using appropriate mass spectra" being important may be revisited. As pointed out by Reviewer 1, there are some concerns about using AMS profiles to constrain ACSM. More generally, introducing source profiles can help reduce the range of solutions compared to PMF. However, it is not made clear in this manuscript that the solutions obtained by this approach are necessarily better than a subset of solutions that can be obtained by PMF (which are derived solely from the ACSM data). Some claims might be made regarding the appropriateness of AMS profiles to the extent that the physical expectations set forth by the authors are met using them (i.e., there are solutions for which COA is not corre-

lated with combustion tracers), but there are still many questions remaining to make too strong a conclusion.

author's response

By 'objective', we wished to convey that the tests being applied to the data were being performed in a quantitative and consistent manner with as little subjective inspection of the results as possible. This is to distinguish from many interpretations of multi-variate analyses, where there is often a tendency to approve solution sets based on criteria that are defined a posteriori. However, we concede that describing the tests as 'objective' may not have been appropriate. While the tests rely on the model that the factors behave according to a certain way relative to the tracers, we deem this appropriate if the factors are to be specifically assigned to physical sources such as traffic, cooking, etc. However, this is one of a number of tests, including Q/Qexp, diurnal residuals, diurnal concentrations and trilinear regression (Chi-square and slopes) for different number of seeds and a-values. By 'best' solution, we mean that this is the solution that we can deem optimal according to the results of the tests we have available. Confidence intervals were added to the trilinear regression plots.

About using AMS mas spec: 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 a-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. Frolich, et al. (2015) used AMS mass spectra as target profiles to deconvolve OA measured with 13 ACSM during an intercomparison, being able to successfully separate 4 different sources by partially constraining COA and HOA. While a high variability was found on the LVOOA mass spectra, minor effect was observed on the actual time series. PMF solutions were explored for different f-peaks from -1 to 1 with steps of 0.1 (Fig. S4, S6, S8 and S10) to show how one PMF solution was chosen to be compared with the ME-2 solutions and the improvement of the ME-2 solution compared with the unconstrained run. Fig. S4 is shown in the following

paragraphs.

author's changes in manuscript

The sentence in the abstract has been modified as follows: "A strategy to explore the solution space is proposed, where the solution that best describes the organic aerosol (OA) sources is determined according to the systematic application of predefined statistical tests. This includes trilinear regression, which proves to be a useful tool to compare different ME-2 solutions."

Sentences were paraphrased; when the word "objectively" was mentioned, it was changed in the manuscript for "systematically", for example:

. . .new strategies to objectively explore the solutions are needed.

was paraphrased for:

. . .new strategies to systematically explore the solutions are needed.

Sentences were also paraphrased in the manuscript. When we are indicating "the best solution" that deconvolves the OA sources, for example:

. . .consistent with the diurnal residual analysis that the best solution is with the solutions constrained with "a" target profiles.

. . .consistent with the diurnal residual analysis that the best solution, according to the statistical tests applied, is with the solutions constrained with "a" target profiles.

This paragraph will be added at the beginning 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 a-values.

Section 2.3 fourth paragraph. The following considerations should be taken into account: The slopes and intercepts should be positive as they represent air pollutant concentrations and the slope D is used as a validation parameter which should be close to zero, due to its low contribution to BC, NOx and CO, owing to the fact that most cooking in the UK uses electricity or natural gas as a source of heat (DECC, 2015;NAEI, 2016).

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.

Paragraph added to the supplement: PMF runs were performed, for the March-December period, from fpeak -1 to 1 with steps of 0.1. Figure 4 shows the comparison of the runs that converged (some of the fpeaks 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.

Minor comments Comment 1 from Referee.

In Figure 4, it would be helpful to plot points or contours for the range observed in ambient samples for comparison against ME-2 profiles.

author's response f43, f44 and f60 of the OA measurements were added to figure 4.

author's changes in manuscript

figure 4.

Comment 2 from Referee. Section 4.4: Some discussion of the NO3 and LV-OOA percentages in the text would be useful.

author's response

The paragraph has been modified.

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 3 from Referee.

The authors write the essential equations for PMF but not equations for how factor constraints are introduced using the "a-factor" by ME-2, while the rest of the manuscript is dedicated to presenting ME-2 solutions.

author's response

The basic equation to apply the a-value was added to the manuscript. author's changes in manuscript

The equation 4 was applied using different target profiles (gi) and a range of a-values (a) to constrain OA sources in different runs (gi,run).

$$g_{(i,run)} = g_i \pm a * g_i \quad (4)$$

(Equation 4 with proper symbols is shown at the end of the attached file with figures).
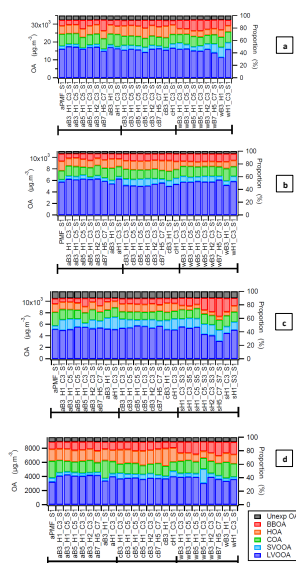
C7

Figure S1: OA concentrations and proportions of the different OA sources to the total OA. March-Dec (a), spring (b), Summer (c) and autumn (d).
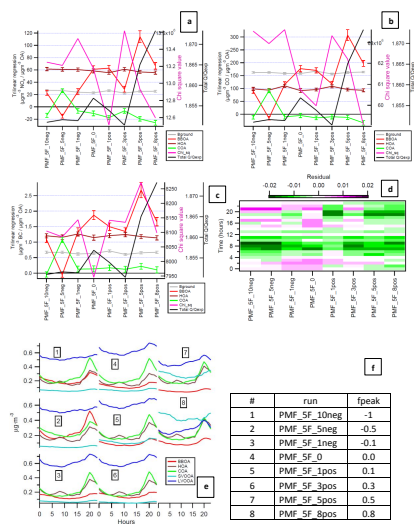
Fig. 1. Figure S1

C8

Figure S1 : NOx, CO and BC trilinear regression (a, b, c), diurnal residual (d), diurnal concentrations (e) and solution list for March-Dec PMF analysis (f).
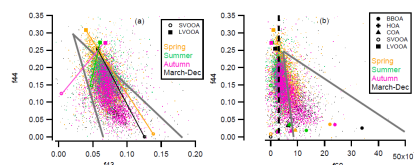
Fig. 2. Figure S2

Figure 4: f44 vs f43 (a) and f44 vs f60 (b) plots for different periods of time.

The equation 4 was applied using different target profiles (g_i) and a range of a-values (a) to constrain OA sources in different runs ($g_{i,run}$).

$$g_{i,run} = g_i \pm a * g_i \qquad (4)$$

Fig. 3. Figure S4_equation4