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

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 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. 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 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 a-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 a-values does not imply a high variation, ranging between 1.88-2.2, suggesting that all the solutions are mathematically 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/Qexp 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/Qexp 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 *a*-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, 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, NOx 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/Qexp? 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: uconstrained 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/Qexp 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 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 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

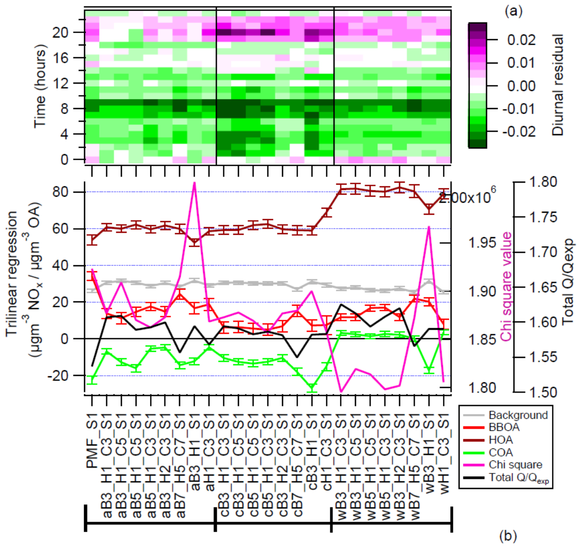
Comment 8 from Referee.

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.

author's changes in manuscript



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

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 added to the supplement.

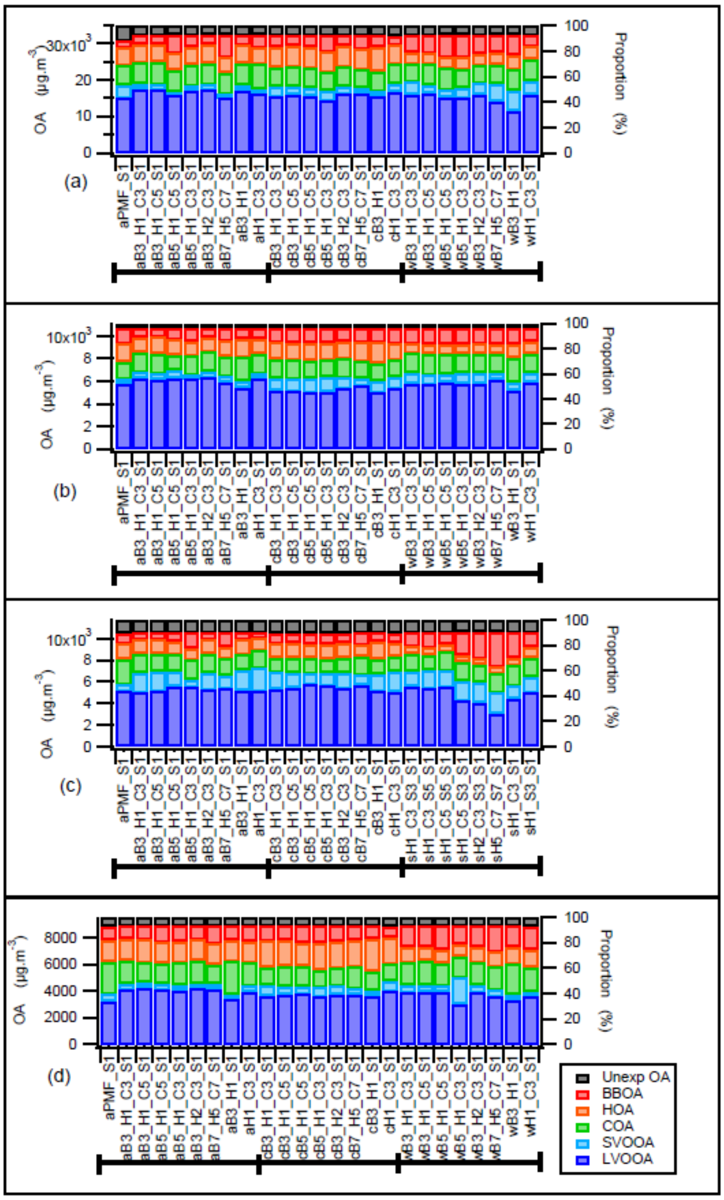


Figure S1: OA concentrations and proportions of the different OA sources to the total OA. March-Dec (a), spring (b), Summer (c) and autumn (d).

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 correlated 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 multivariate 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.

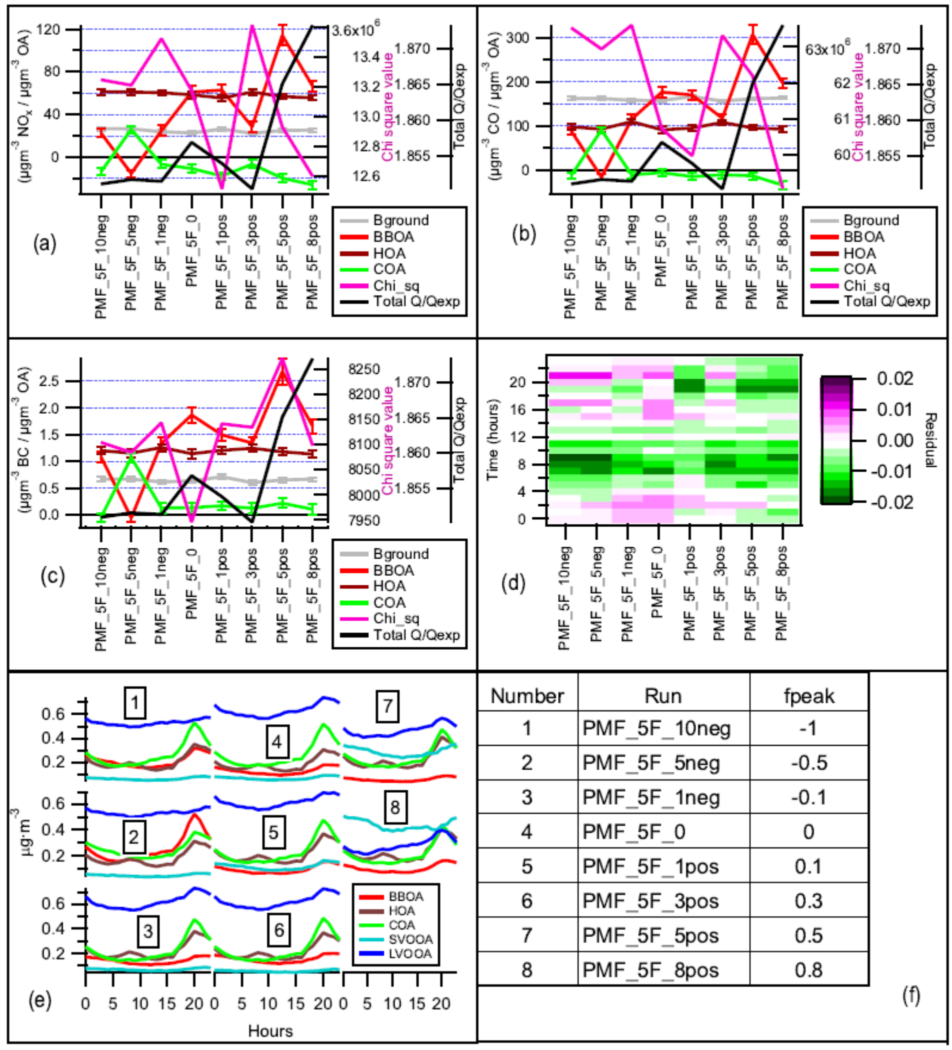
Section 2.3 fourth paragraph.

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.



Number	Run	fpeak
1	PMF_5F_10neg	-1
2	PMF_5F_5neg	-0.5
3	PMF_5F_1neg	-0.1
4	PMF_5F_0	0
5	PMF_5F_1pos	0.1
6	PMF_5F_3pos	0.3
7	PMF_5F_5pos	0.5
8	PMF_5F_8pos	0.8

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

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

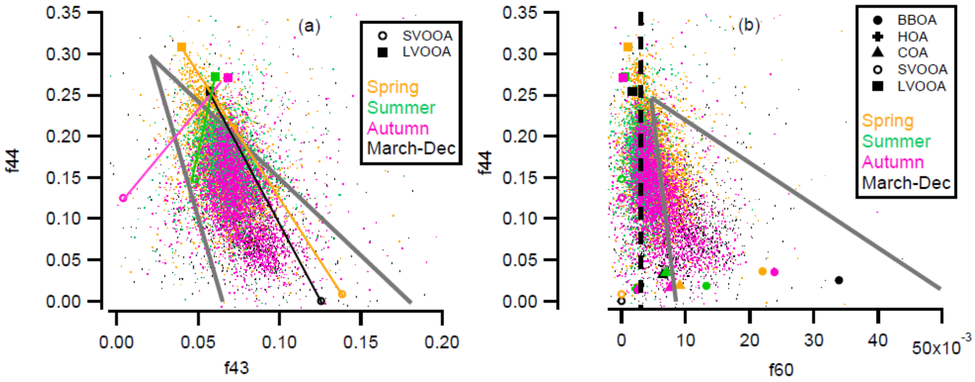


Figure 4: f44 vs f43 (a) and f44 vs f60 (b) plots for different periods of time.

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 PM_1 is composed mainly of OA, SO_4, NO_3, NH_4 and BC, it is possible to analyse the PM_1 composition during $PM_{2.5}$ high concentrations (Fig. 6.b). Episodes with moderate and high $PM_{2.5}$ concentrations were observed with low wind speeds (Fig. S8), being NO_3 and LVOOA the main PM_1 contributors. High NO_3 concentrations were observed during spring as found in a previous study performed by Young et al. (2015a) who determined that NO_3 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 (g_i) and a range of a-values (a) to constrain OA sources in different runs ($g_{i,run}$)

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

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 avalues approach, minimizing Q/Qexp, and trilinear regression analysis. However, the criteria of determining best solution are not clearly explained in each analysis (Figure S4_Figure S7).

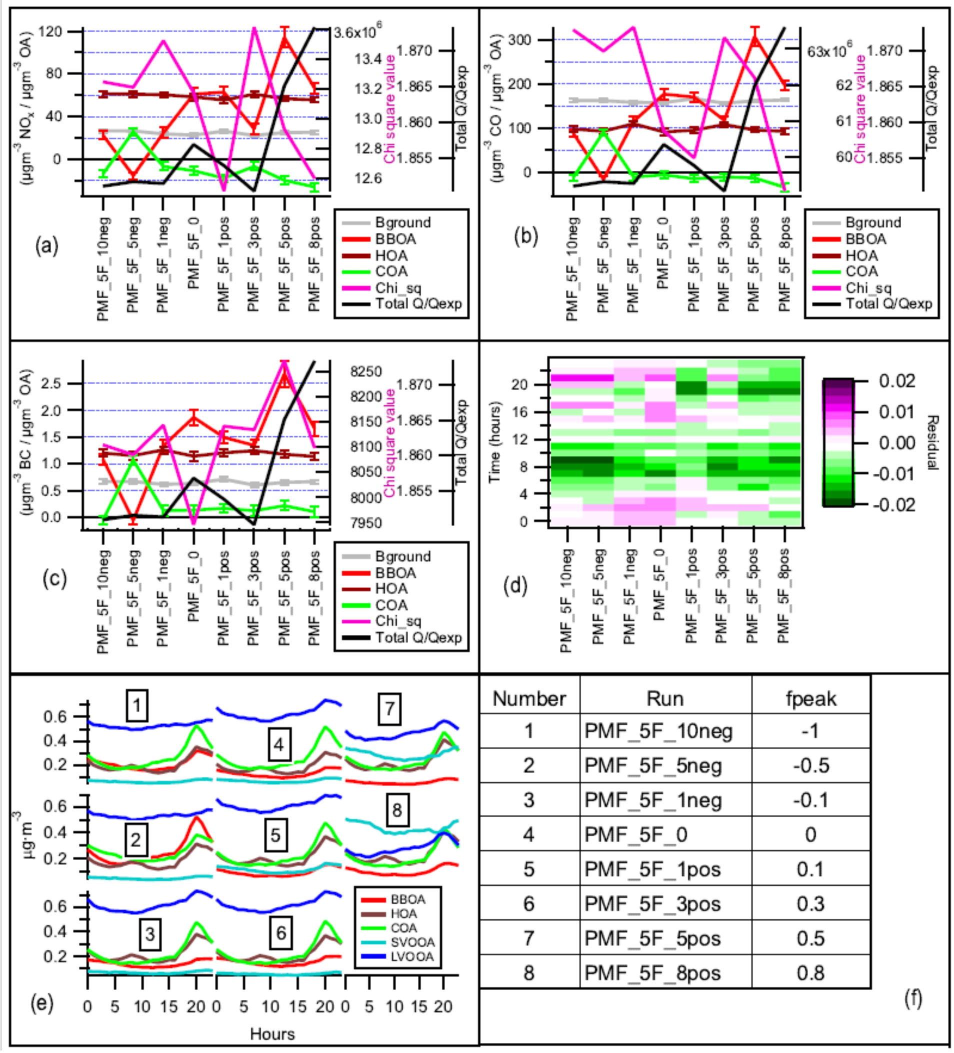
author's response

The description has been further explained in supplement S3.

author's changes in manuscript

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

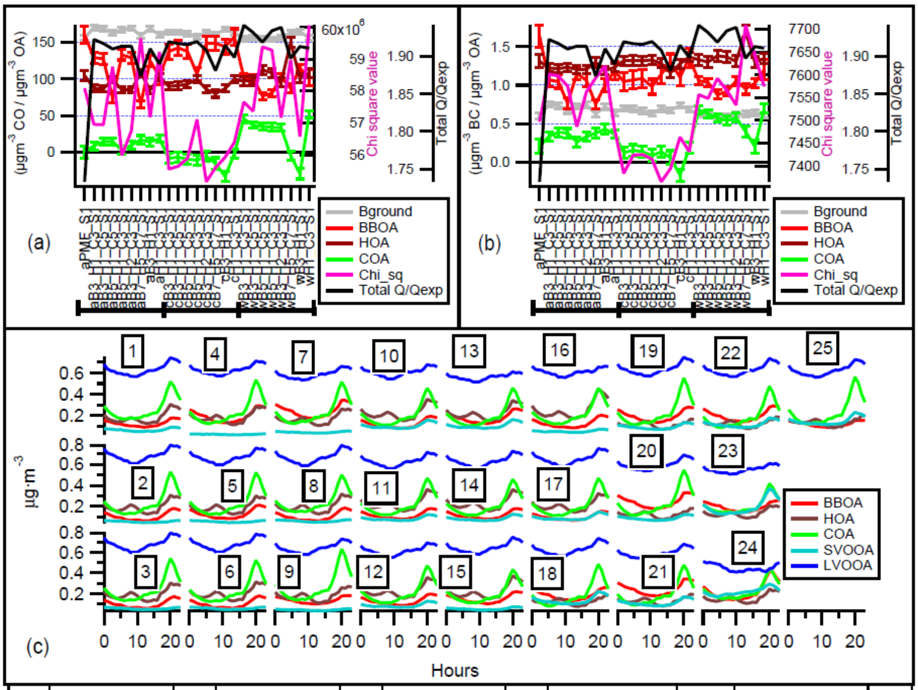
PMF runs were performed, for the March-December period, from fpeak -1 to 1 with steps of 0.1. Figure 4 shows the comparison of the runs that converged (some of the fpeaks did not converge) in order to determine the PMF solution that better identified the OA sources to be compared to the ME-2 solutions. 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.



Number	Run	fpeak
1	PMF_5F_10neg	-1
2	PMF_5F_5neg	-0.5
3	PMF_5F_1neg	-0.1
4	PMF_5F_0	0
5	PMF_5F_1pos	0.1
6	PMF_5F_3pos	0.3
7	PMF_5F_5pos	0.5
8	PMF_5F_8pos	0.8

Figure S3 : NOx, CO and BC trilinear regression (a, b, c), diurnal residual (d), diurnal concentrations (e) and solution list for March-Dec PMF analysis (f).

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 NOx (Figure 2.b) and CO (Figure S5.a) trilinear regression and low diurnal residual (Figure 2.a).

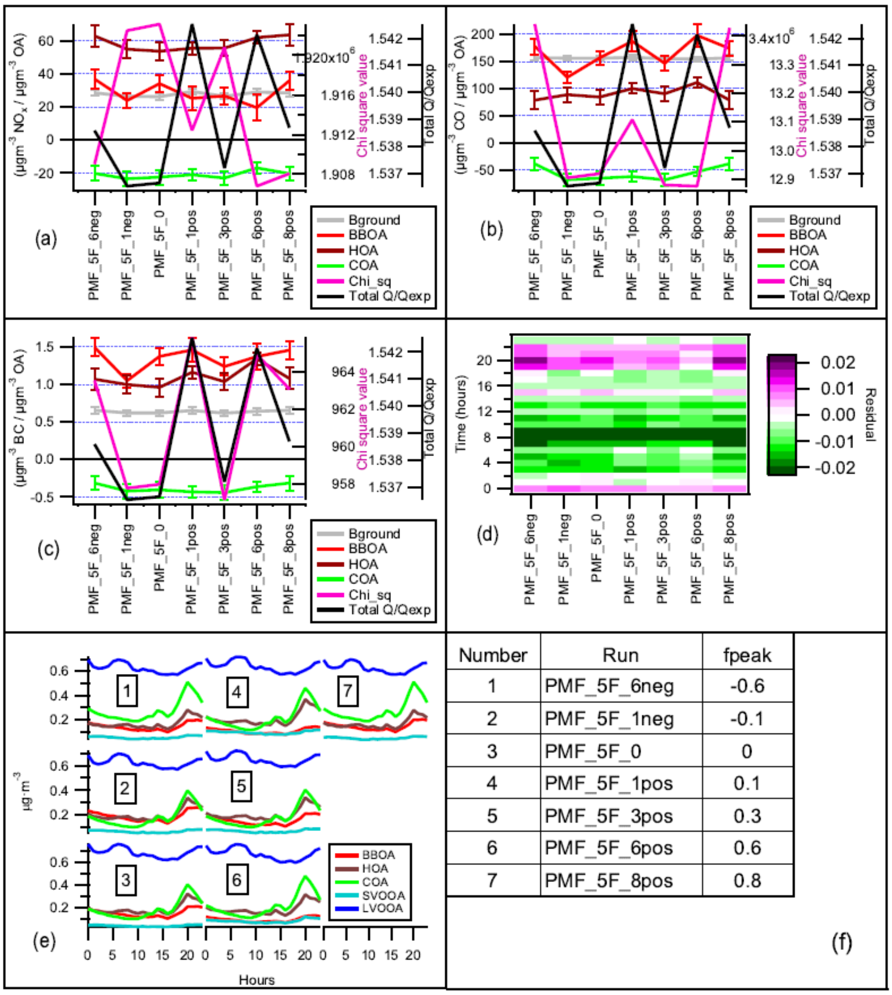


1	aPMF_S1	6	aB3_H2_C3_S1	11	cB3_H1_C5_S1	16	cB3_H1_S1	21	wB5_H1_C3_S1
2	aB3_H1_C3_S1	7	aB7_H5_C7_S1	12	cB5_H1_C5_S1	17	cH1_C3_S1	22	wB3_H2_C3_S1
3	aB3_H1_C5_S1	8	aB3_H1_S1	13	cB5_H1_C3_S1	18	wB3_H1_C3_S1	23	wB7_H5_C7_S1
4	aB5_H1_C5_S1	9	aH1_C3_S1	14	cB3_H2_C3_S1	19	wB3_H1_C5_S1	24	wB3_H1_S1
5	aB5_H1_C3_S1	10	cB3_H1_C3_S1	15	cB7_H5_C7_S1	20	wB5_H1_C5_S1	25	wH1_C3_S1

(d)

Figure S4: CO and BC trilinear regression (a, b), diurnal concentrations (c) and solution list for March-Dec analysis (d).

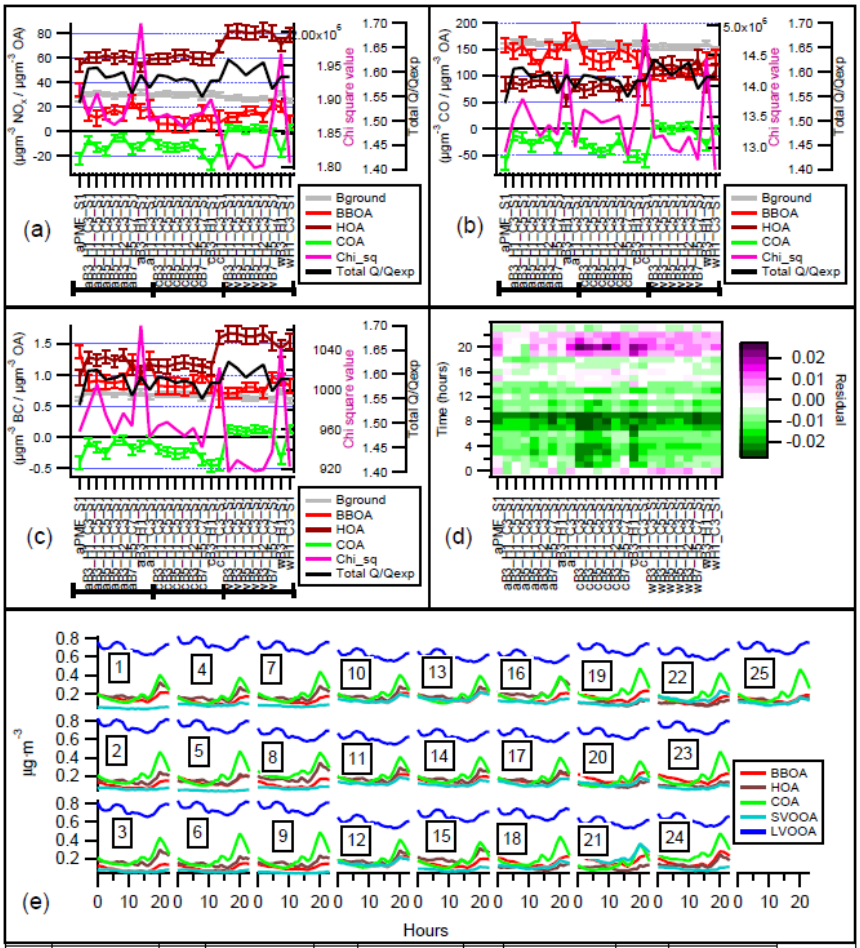
Figure S6 shows the PMF analysis for the spring period. All solutions show similar diurnal concentrations with negative COA slope fo the three trilinear regressions. Solutions 2 and 3 have the lower Q/Qexp, Solution 3 was chosen to be compared with ME-2 solutions.



Number	Run	fpeak
1	PMF_5F_6neg	-0.6
2	PMF_5F_1neg	-0.1
3	PMF_5F_0	0
4	PMF_5F_1pos	0.1
5	PMF_5F_3pos	0.3
6	PMF_5F_6pos	0.6
7	PMF_5F_8pos	0.8

Figure S5: NOx, CO and BC trilinear regression (a, b, c), diurnal residual (d), diurnal concentrations (e) and solution list for spring PMF analysis (f).

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.

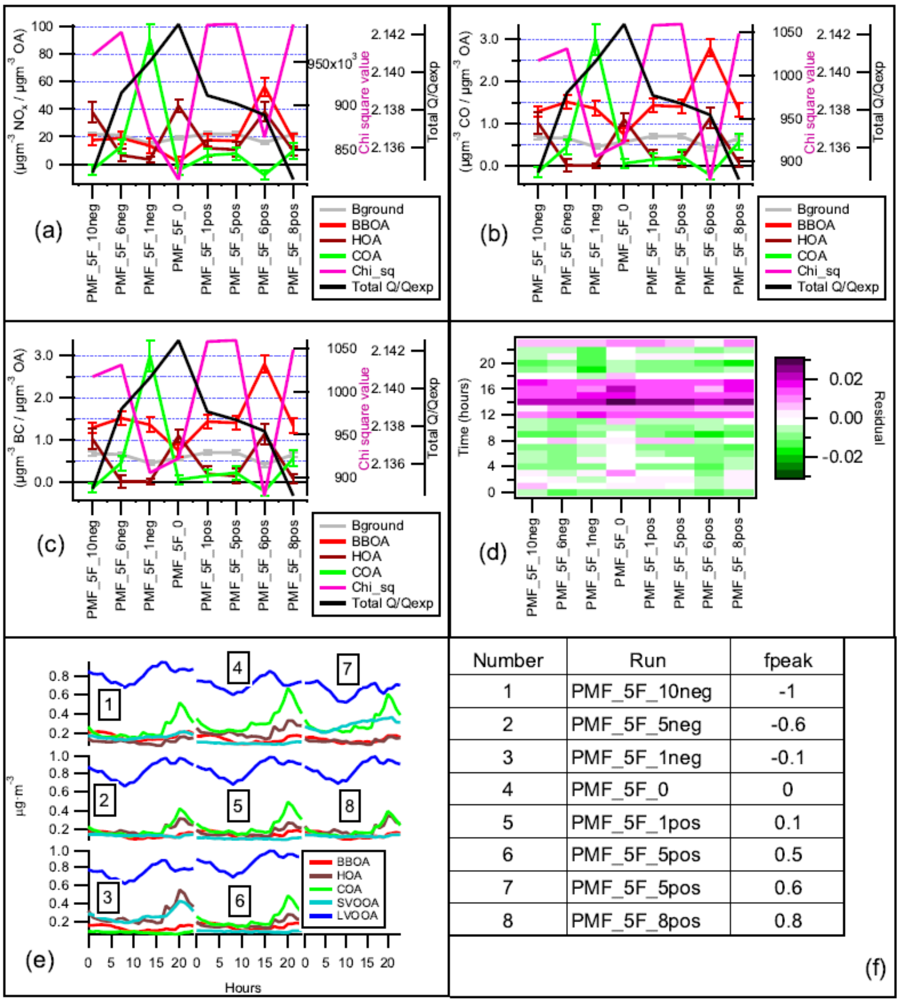


1	aPMF_S1	6	aB3_H2_C3_S1	11	cB3_H1_C5_S1	16	cB3_H1_S1	21	wB5_H1_C3_S1
2	aB3_H1_C3_S1	7	aB7_H5_C7_S1	12	cB5_H1_C5_S1	17	cH1_C3_S1	22	wB3_H2_C3_S1
3	aB3_H1_C5_S1	8	aB3_H1_S1	13	cB5_H1_C3_S1	18	wB3_H1_C3_S1	23	wB7_H5_C7_S1
4	aB5_H1_C5_S1	9	aH1_C3_S1	14	cB3_H2_C3_S1	19	wB3_H1_C5_S1	24	wB3_H1_S1
5	aB5_H1_C3_S1	10	cB3_H1_C3_S1	15	cB7_H5_C7_S1	20	wB5_H1_C5_S1	25	wH1_C3_S1

(f)

Figure S6: CO and BC trilinear regression (a,b,c), diurnal residual (d),diurnal concentrations (e) all the solutions for spring analysis (f).

Figure S8 shows the PMF analysis for the summer period. Solution 4 has a high Q/Qexp 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.



Number	Run	fpeak
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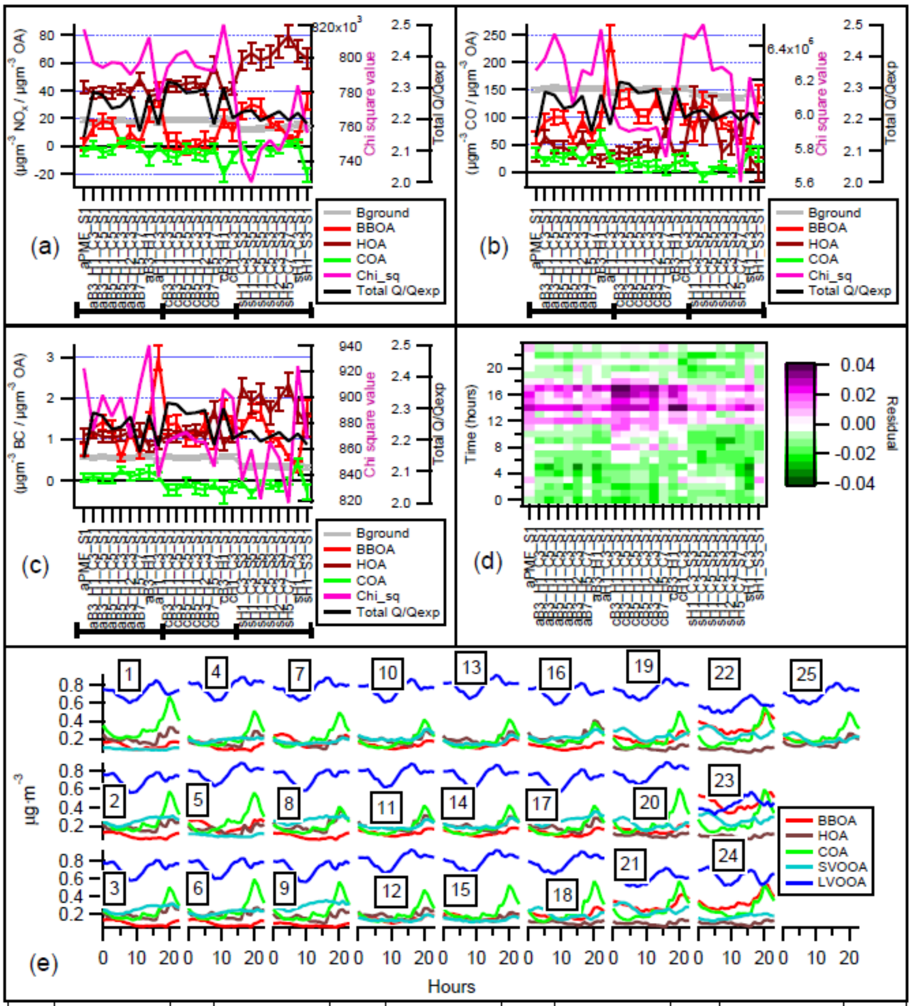
4	PMF_5F_0	0
5	PMF_5F_1pos	0.1
6	PMF_5F_5pos	0.5
7	PMF_5F_5pos	0.6
8	PMF_5F_8pos	0.8

Figure S7: NOx, CO and BC trilinear regression (a, b, c), diurnal residual (d), diurnal concentrations (e) and solution list for summer PMF analysis (f).

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 dueto the low diurnal residual, COA slope close to zero and the low BBOA slope in the NOx, BC and COA trilinear regressions (Figures S9.a, S9.b and S9.c).

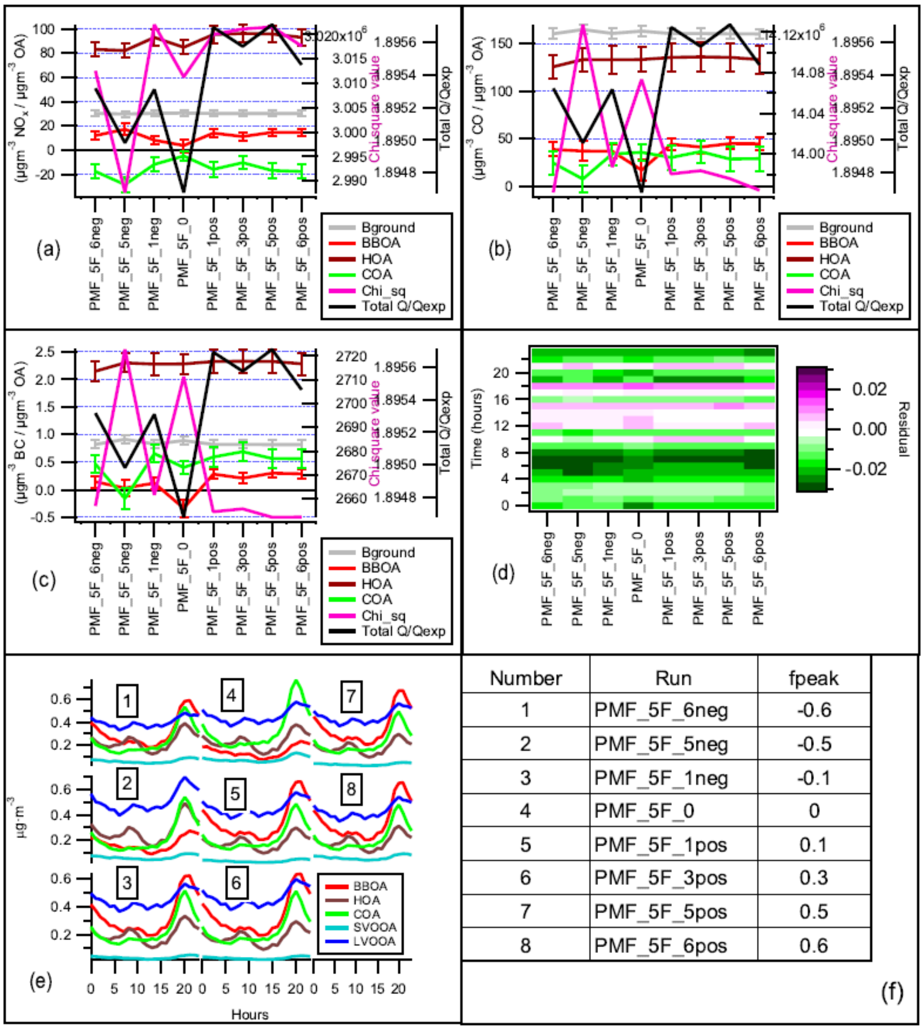


1	aPMF_S1	6	aB3_H2_C3_S1	11	cB3_H1_C5_S1	16	cB3_H1_S1	21	sH1_C5_S3_S1
2	aB3_H1_C3_S1	7	aB7_H5_C7_S1	12	cB5_H1_C5_S1	17	cH1_C3_S1	22	sH2_C3_S3_S1
3	aB3_H1_C5_S1	8	aB3_H1_S1	13	cB5_H1_C3_S1	18	sH1_C3_S3_S1	23	sH5_C7_S7_S1
4	aB5_H1_C5_S1	9	aH1_C3_S1	14	cB3_H2_C3_S1	19	sH1_C3_S5_S1	24	sH1_C3_S1
5	aB5_H1_C3_S1	10	cB3_H1_C3_S1	15	cB7_H5_C7_S1	20	sH1_C5_S5_S1	25	sH1_S3_S1

(f)

Figure S8: CO and BC trilinear regression (a,b,c), diurnal residual (d),diurnal concentrations (e) all the solutions for summer analysis (f).

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/Qexp and a COA slope close to zero for the NOx trilinear regression and a lower diurnal residual compared to the other PMF solutions.

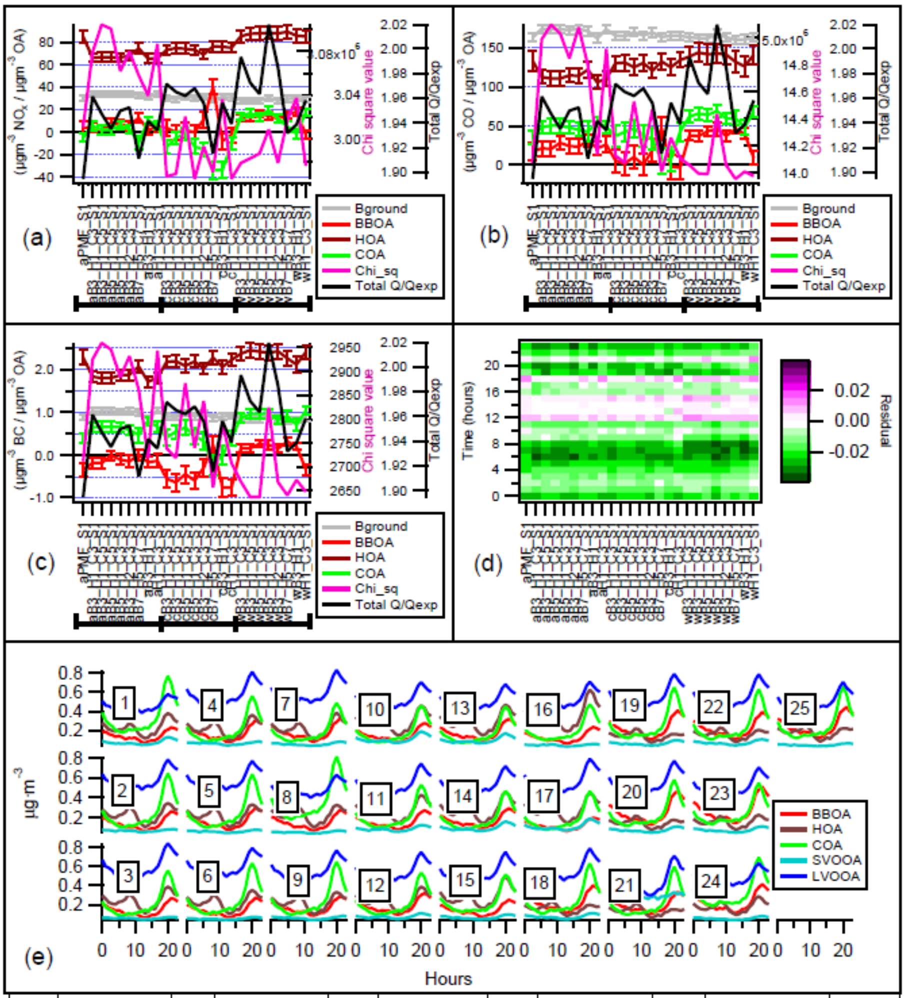


Number	Run	fpeak
1	PMF_5F_6neg	-0.6
2	PMF_5F_5neg	-0.5
3	PMF_5F_1neg	-0.1
4	PMF_5F_0	0
5	PMF_5F_1pos	0.1
6	PMF_5F_3pos	0.3
7	PMF_5F_5pos	0.5
8	PMF_5F_6pos	0.6

(f)

Figure S9: NOx, CO and BC trilinear regression (a, b, c), diurnal residual (d), diurnal concentrations (e) and solution list for autumn PMF analysis (f).

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 NOx (Figures S11.a).



1	aPMF_S1	6	aB3_H2_C3_S1	11	cB3_H1_C5_S1	16	cB3_H1_S1	21	wB5_H1_C3_S1
2	aB3_H1_C3_S1	7	aB7_H5_C7_S1	12	cB5_H1_C5_S1	17	cH1_C3_S1	22	wB3_H2_C3_S1
3	aB3_H1_C5_S1	8	aB3_H1_S1	13	cB5_H1_C3_S1	18	wB3_H1_C3_S1	23	wB7_H5_C7_S1
4	aB5_H1_C5_S1	9	aH1_C3_S1	14	cB3_H2_C3_S1	19	wB3_H1_C5_S1	24	wB3_H1_S1
5	aB5_H1_C3_S1	10	cB3_H1_C3_S1	15	cB7_H5_C7_S1	20	wB5_H1_C5_S1	25	wH1_C3_S1

(f)

Figure S10: CO and BC trilinear regression (a,b,c), diurnal residual (d),diurnal concentrations (e) all the solutions for autumn analysis (f).

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 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 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.

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.

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 µg.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 µg.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 µg.m^{-3} or less are low compared with diurnal concentrations of the OA sources, which concentrations ranged 0.1-0.6 µg.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 section 4.1 where we show how seasonal solutions present different values of Q/Qexp, 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 explantion 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" 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 NOx/HOA, CO/HOA, and NOx/ _CO to determine the weekdays 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 NOx 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 NOx 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 NOx concentrations and HDD emitting higher HOA concentrations.

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

author's changes in manuscript

Considering that PM_1 is composed mainly of OA, SO_4, NO_3, NH_4 and BC, it is possible to analyse the PM_1 composition during $PM_{2.5}$ high concentrations (Fig. 6.b). Episodes with moderate and high $PM_{2.5}$ concentrations were observed with low wind speeds (Fig. S8), being NO_3 and LVOOA the main PM_1 contributors. High NO_3 concentrations were observed during spring as found in a previous study performed by Young et al. (2015a) who determined that NO_3 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.

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 *a*-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 f44:f43 values for SVOOA (Fig. 4.a) and f60 values ranging from $13x10^{-3}$ for summer to $24x10^{-3}$ for autumn (Fig. 4.b). These variations support the importance of running ME-2 during periods of time where weather conditions and 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.

author's changes in manuscript

None

Technical correction

Figure S1: Please label significant m/z peaks, O/C and H/C ratios in each solution.
“(c)” was missing in the end of the caption of Figure S1.

author's response

The figure has been updated.

author's changes in manuscript

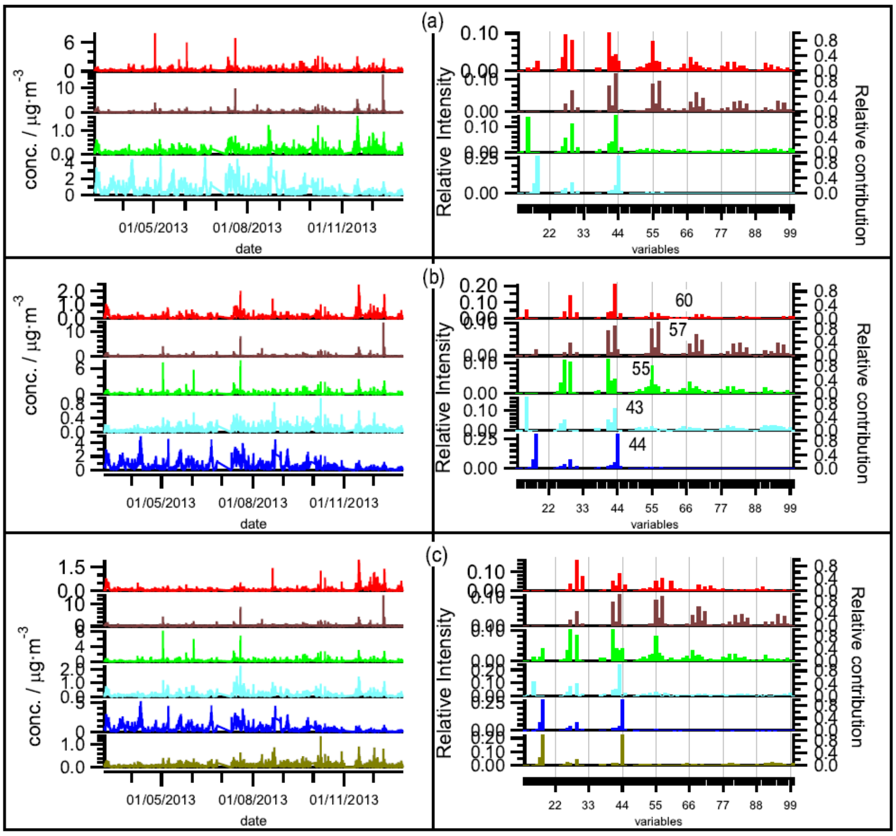


Figure S11: PMF solutions: four-factor solution (a), five-factor solution (b) and six-factor solution (c) to determine the number of OA sources.

Response to comments of referee # 4

Comment 2 from Referee.

Lines 47-49 – add Takahama et al., Organic Functional Groups in Aerosol Particles from Burning and Non-burning Forest Emissions at a High-Elevation Mountain Site, Atmos. Chem. Phys., 11, 6367–6386, 2011.

author's response

The citation has been added to the manuscript.

author's changes in manuscript

In particular, the Aerosol Chemical Speciation Monitor (ACSM), which has been recently developed (Ng et al., 2011), has been used to carry out long-term measurements of non-refractory submicron aerosols around the world, for instance an industrial-residential area in Atlanta, Georgia (Budisulistiorini et al., 2013), a high-elevation mountain in Canada (Takahama et al., 2011), at background locations in South Africa, (Vakkari et al., 2014) and Spain (Minguillón et al., 2015a;Ripoll et al., 2015), a semi-rural site in Paris (Petit et al., 2015) and at an urban background site in Switzerland (Canonaco et al., 2015).

Comment 3 from Referee.

Line 110 – what is the difference between PM and aerosols?

author's response

PM refers specifically to solid and liquid particles and aerosols are these liquid and solid particles in a gas (usually air). There are not main differences between these two terms and PM is used when the particle size is taken into consideration. The intention with this paragraph was to show different studies carried out at the North Kensington site and the particle size is important to mention to compare different studies. The paragraph has been rewritten to compare the different studies based on the particle size.

author's changes in manuscript

Different studies have been carried out at this site such as analysis of elemental and organic carbon concentrations in offline measurements of particulate matter with a diameter less than 10 micrometres (PM10) (Jones and Harrison, 2005), PM_{10} and NO_x association with wind speed (Jones et al., 2010), properties of nanoparticles (Dall'Osto et al., 2011), PM_{10} and $PM_{2.5}$ (Liu and Harrison, 2011) and in aerosol chemical composition (Beccaceci et al., 2015) in the atmosphere. The first long-term study of the behaviour of non-refractory inorganic and organic aerosols (PM_1) at the North Kensington site was carried out analysing cToF-AMS data collected from January 2012 to January 2013 (Young et al., 2015a) where source apportionment analysis was carried out applying unconstrained PMF runs, with five sources identified: HOA, COA, solid fuel OA (SFOA), SVOOA and LVOOA.

Comment 6 from Referee.
Line 317 – I don’t see BBOA, HOA or COA in Figure 4a.
author's response

Figure 4.a shows only SVOOA and LVOOA values. The caption on the plot has been modified. The clouds of dots show the f44:f43 and f44:f60 values for the OA measurements (the adding of these clouds was required for another referee).

author's changes in manuscript

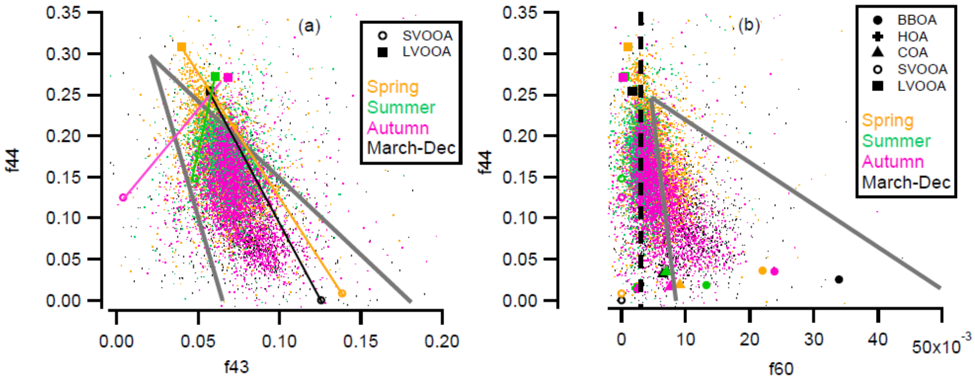


Figure 4: f44 vs f43 (a) and f44 vs f60 (b) plots for different periods of time.

Comment 7 from Referee.
Lines 318-319 - How do the connecting lines display variability? Are they intended to make the differences between the cluster of LVOOA and the wider spread of SVOOA points more obvious?

author's response

Yes, this is has been explained with more detail in the manuscript.

author's changes in manuscript

Figure 4.a shows that LVOOA, while having different values between solutions, is found in distinct areas of the plot (connecting lines are used to make the SVOOA variability clearer), whereas SVOOA shows values of f44 vs f43 with high variability.

Comment 8 from Referee.
Lines 328-329 – could cloud processing also contribute to the higher 44 and lower 60?
author's response

Yes, paragraph has been edited in 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 11 from Referee.
Lines 359 – 363 – you use "possible to observe" in a couple of places in this paragraph. I suggest re-writing those segments.
author's response

The paragraph has been edited on the manuscript.

author's changes in manuscript

Figure 5 shows the WD/WE ratios, where it is possible to observe NOx/ΔCO ratios of 1.25, 1.35 and 1.136 for March-Dec, summer and autumn, respectively, suggesting diesel with a higher contribution during WD compared to petrol. These findings are confirmed by the CO/HOA ratios, which for the same periods of time, are lower than one (0.8, 0.45 and 0.9) suggesting a lower contribution of petrol during weekdays compared to diesel. In spring, there are no considerable changes to the WD/WE ratios, although a higher contribution of petrol is shown during WD with values of 1.28 for CO/HOA and low diesel contribution.

Comment 13 from Referee.
Line 375 –How do you derive PM1? It is a large unstated assumption if you mean that the ACSM measures PM1. It will measure a larger fraction of the PM1, but it is not a PM1 measurement.
author's response

PM_1 composition is mainly conformed by OA, SO_4, NO_3, NH_4 and BC, these components were mentioned on the manuscript. Also, Fig. 6 has been updated.

author's changes in manuscript

Considering that PM_1 is composed mainly of OA, SO_4, NO_3, NH_4 and BC, it is possible to analyse the PM_1 composition during $PM_{2.5}$ high concentrations (Fig. 6.b).

Comment 14 from Referee.
Line 379 – Another unsubstantiated claim. Explain how you come to the conclusion that secondary aerosols are the main contributors to PM2.5 from particles smaller than the upper limit of the ACSM. Which components of Figure 6 do you consider secondary and which do you consider primary?
author's response

BBOA, HOA COA and BC are considered primary while SVOOA, LVOOA, NO_3, NH_4 and SO_4 are considered secondary. The text and figure in the manuscript have been modified.

author's changes in manuscript

Defining BBOA, HOA COA and BC as primary and SVOOA, LVOOA, NO_3, NH_4 and SO_4 as secondary aerosols, the main PM1 contributors to $PM_{2.5}$ concentrations are secondary aerosols with a total contribution of 61% (Fig. 6.c).

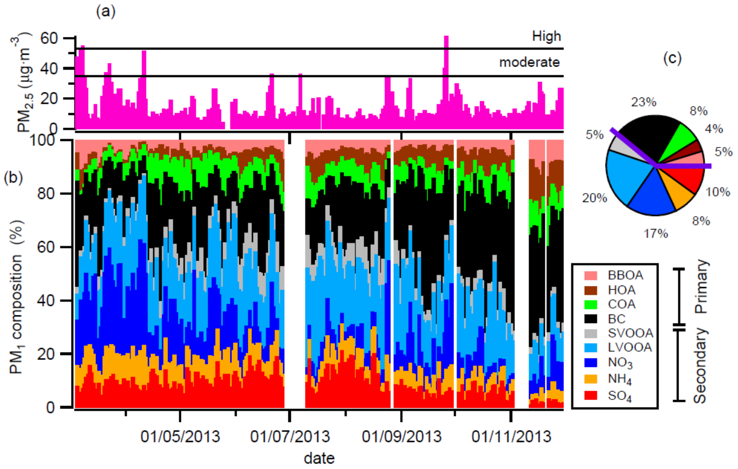


Figure 6: Daily PM2.5 concentrations (a) daily (b) and total PM1 composition (c), purple line in Fig. 6.c separates secondary and primary aerosols.

Organic Aerosol source apportionment in London 2013 with ME-2: exploring the solution space with annual and seasonal analysis

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Abstract. The Multilinear Engine (ME-2) factorisation tool is being widely used following the recent development of the Source Finder (SoFi) interface at the Paul Scherrer Institute. However, the success of this tool, when using the a-value approach, largely depends on the inputs (i.e. target profiles) applied as well as the experience of the user. 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. Aerosol Chemical Speciation Monitor (ACSM) measurements were carried out at the urban-background site of North Kensington, London from March to December 2013, where for the first time the behaviour of OA sources and their possible environmental implications are studied using an ACSM. Five OA sources were identified: biomass burning OA (BBOA), hydrocarbon-like OA (HOA), cooking OA (COA), semivolatile oxygenated OA (SVOOA) and low-volatility oxygenated OA (LVOOA). 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. Further analysis on the atmospheric implications of these OA sources was carried out, identifying evidence of the possible contribution of heavy-duty diesel vehicles to air pollution during weekdays compared to those fuelled by petrol.

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Deleted: A strategy to explore the solution space is proposed to objectively determine the solution that best deconvolves the organic aerosol (OA) sources where trilinear regression has proven to be a useful tool to compare different ME-2 solutions.

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Keywords: Aerosol sources, matrix factorization, air quality, PM$_1$, ACSM, SoFi.

1. Introduction

Developed countries have made great improvements in air quality. However, air pollution still represents a significant air quality issue, mainly in urban cities, due to the sheer number of inhabitants and the associated anthropogenic emissions resulting from the inhabitants' daily activities (transportation, energy production and industrial activities). In particular, aerosols have significant effects on air quality (Watson, 2002;Pope III and Dockery, 2006;Keywood et al., 2015).

Organic aerosols (OA) are one of the main constituents of submicron particulate matter, composing 20–90% of the total submicron particle mass (Zhang et al., 2007). OA are classified according to their origin as primary OA (POA) or secondary OA (SOA). POA are directly emitted from a range of sources while SOA are produced from gaseous precursors (VOCs) by chemical reactions in the atmosphere. POA sources range from traffic emissions (hydrocarbon-like OA, HOA), biomass burning OA (BBOA), to OA emissions from cooking (COA) among others. Kupiainen and Klimont (2007) determined that the main sources of POA in Europe were emissions from traffic and the residential combustion of solid fuels. Allan et al. (2010) identified three POA sources: transport, burning of solid fuels and cooking in Manchester and London. SOA are the main constituents of OA ranging from 64% in urban areas to 95% in rural sites (Zhang et al., 2007). Previous source

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apportionment studies (Zhang et al., 2011) often identified a highly oxygenated fraction with low volatility (LVOOA) and a less oxygenated and more volatile species (SVOOA). In general, SVOOA represent fresh SOA, which, after photochemical processing, evolve into LVOOA (Jimenez et al., 2009). POA and SOA concentrations vary over seasons and years, thus in order to study the OA sources and processes as well as their impacts on air quality, it is necessary to carry out long-term measurements and subsequent source apportionment data analysis.

Aerosol mass spectrometry has been widely used for measuring aerosol concentrations in a wide range of ground based measurements (Hildebrandt et al., 2011;Mohr et al., 2012;Saarikoski et al., 2012;Young et al., 2015b). In particular, the Aerosol Chemical Speciation Monitor (ACSM), which has been recently developed (Ng et al., 2011), has been used to carry out long-term measurements of non-refractory submicron aerosols around the world, for instance an industrial-residential area in Atlanta, Georgia (Budisulistiorini et al., 2013), a high-elevation mountain in Canada (Takahama et al., 2011), at background locations in South Africa, (Vakkari et al., 2014) and Spain (Minguillón et al., 2015a;Ripoll et al., 2015), a semi-rural site in Paris (Petit et al., 2015) and at an urban background site in Switzerland (Canonaco et al., 2015).

Source apportionment techniques have been widely used to quantitatively determine aerosol sources. The main source apportionment models include: chemical mass balance (CMB) and positive matrix factorization (PMF).

CMB uses prior knowledge of source profiles and assuming that the composition of all sources is well defined and known (Henry et al., 1984). This technique is ideal when changes between the source and the receptor are minimal, although this barely happens in real atmospheric conditions and the constraints may add a high level of uncertainty.

PMF is a least-squares approach based on a receptor-only multivariate factor analytic model (Paatero and Tapper, 1994) . The main difference between PMF and CMB is that PMF does not require any information as input to the model and the profiles and contributions are uniquely modelled by the solver (Paatero et al., 2002). PMF was applied to OA data measured with an AMS for the first time by Lanz et al. (2007), using measurements taken at an urban background site in Zurich in the summer of 2005, where six OA sources were determined: LVOOA, SVOOA, HOA, Charbroiling-like OA, BBOA and COA. Subsequently, PMF was successfully applied to other datasets, acquired from a wide range of sampling sites and with different techniques, Ng et al. (2010) compiled and analysed 43 studies carried out at different sites around the world. This study provided a broad overview of aerosol composition and the importance of SOA as well as BBOA and HOA sources. In other PMF studies, it was possible to find other relevant sources such as COA (Allan et al., 2010;Huang et al., 2010;Liu et al., 2012;Mohr et al., 2012;Sun et al., 2013;Crippa et al., 2013a).

ME-2 is a multivariate solver that determines solutions using the same equations as PMF (Paatero, 1999), with the possibility of using previous knowledge (factor time series and / or factor profiles) as inputs to the model, to partially constrain the solution, thereby reducing the rotational ambiguity (Paatero et al., 2002) and leading to more interpretable PMF solution(s) as shown in Lanz et al. (2008) where three sources of OA were successfully determined (traffic related, solid fuel and secondary OA) during winter in an urban-background site in Zurich. Here unconstrained PMF runs failed to identify the environmental solution. This was most probably due to a high degree of temporal co-variation in the OA sources driven by low temperatures and periods of strong inversion.

The development of the Source Finder (SoFi) interface (Canonaco et al., 2013) written on the software package Igor Pro (WaveMetrics, Inc.) together with a further standardised approach developed by Crippa et al. (2014), allowed different OA source apportionment studies to be undertaken such as a study at a suburban background site in Paris, France during January-March 2012 (Petit et al., 2014); laboratory studies analysing atmospheric ageing from the photo-oxidation of α-pinene and of wood combustion emissions in smog chambers and flow reactors (Bruns et al., 2015); long-term measurements (February 2011-February 2012) carried out at an urban background site in Zurich, Switzerland studying differences in oxygenated OA

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during summer and winter periods (Canonaco et al., 2015). As part of the ACTRIS project (Aerosols, Clouds, and Trace gases Research InfraStructure network) (Fröhlich et al., 2015) an intercomparison between 14 ACSM and one high resolution time of flight aerosol mass spectrometer (HR-ToF-AMS) was carried out at the SIRTA site in Gif-sur-Yvette near Paris, being able to identify 4 sources: hydrocarbon-like OA (HOA), OA related to cooking activities (COA), biomass burning related OA (BBOA) and oxygenated organic aerosol (OOA). These four sources were successfully identified from HR-ToF-AMS measurements with unconstrained PMF analysis. However, in the case of the ACSM datasets, it was necessary to partially constrain solutions via ME-2 analysis; probably due to the low signal to noise ratio of ACSM data compared to the AMS and the rural site type. Furthermore, new ME-2 source apportionment studies have been published this year (Bozzetti et al., 2016;Fountoukis et al., 2016;Milic et al., 2016;Elser et al., 2016), and even more are expected to come due to the successful application of SoFi. Thus, new strategies to systematically explore the solutions are needed.

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This study includes data analysis of the first ACSM instrument deployed in the UK at the North Kensington site from March to December 2013, using the recently developed graphical interface SoFi, to perform non-refractory OA source apportionment analysis with the ME-2 factorization tool, implementing a strategy to determine the solution that best identifies OA sources, according to the statistical tests applied, and with further subsequent discussion of the various identified OA sources.

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2. Methodology

The data used in this analysis (5th March – 30th December 2013) were obtained using an Aerosol Chemical Speciation Monitor (ACSM), deployed at the urban-background site in North Kensington, London. This instrument is owned by The Department for Environment, Food and Rural Affairs (DEFRA) and is part of the Aerosols, Clouds, and Trace gases Research InfraStructure Network (ACTRIS).

Source apportionment of OA was carried out using the PMF model implemented through the Multi-linear Engine tool (ME-2) and controlled via the Source Finder (SoFi) graphical user interface version 4.8, developed at the Paul Scherrer Institute (PSI), Switzerland (Canonaco et al., 2013).

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2.1 Site and instrumentation

North Kensington (51.5215°, -0.2129°) is an urban background site located adjacent to a school, 7 Km to the west of central London. There is a residential road 30 metres to the east with an average traffic flow of 8,000 vehicles per day (Bigi and Harrison, 2010). This monitoring site is part of the DEFRA Automatic Urban and Rural Network (http://uk-air.defra.gov.uk/networks/network-info?view=aurn).

As an urban background site, North Kensington is not significantly influenced by a single source or street, and concentrations may be analysed as an integrated contribution from all sources upwind of the site in London. This site is widely accepted as representative site of background air quality in central London and has a large set of long-term measurements for various pollutants (Bigi and Harrison, 2010). Different studies have been carried out at this site such as analysis of elemental and organic carbon concentrations in offline measurements of particulate matter with a diameter less than 10 micrometres (PM_{10}) (Jones and Harrison, 2005), PM_{10} and NO_x association with wind speed (Jones et al., 2010), properties of nanoparticles (Dall'Osto et al., 2011), PM_{10} and $PM_{2.5}$ (Liu and Harrison, 2011) and in aerosol chemical composition (Beccaceci et al., 2015) in the atmosphere. The first long-term study of the behaviour of non-refractory inorganic and organic aerosols (PM_1) at the North Kensington site was carried out analysing cToF-AMS data collected from

January 2012 to January 2013 (Young et al., 2015a) where source apportionment analysis was carried out applying unconstrained PMF runs, with five sources identified: HOA, COA, solid fuel OA (SFOA), SVOOA and LVOOA.

The Aerosol Chemical Speciation Monitor (ACSM) measures, in real time, the mass and chemical composition of particulate organics, nitrate (NO_3), sulphate (SO_4) , ammonium (NH_4) and chloride (Cl) ions, with a detection limit of 0.2 µgm^{-3} for an average sampling time of 30 min (Ng et al., 2011). These chemical species measured by the ACSM are determined according to the same methodology used in the AMS as defined by Allan et al. (2004). In principle, the ACSM is designed and built under the same sampling and detection technology as state-of-the-art Aerosol Mass Spectrometer (AMS) instruments. However, the ACSM is better suited for air quality monitoring applications due to its lower size, weight, cost, and power requirements; it is also more affordable to operate and is capable of measuring over long periods of time without supervision (Ng et al., 2011).

Time series of pollutants such as BC, CO, NO_x, OC, EC were downloaded from the DEFRA website for the North Kensington monitoring site. Wind speed and direction data were obtained from the meteorological station at Heathrow airport (located 17 Km from the sampling site). Wind data from this site was used due to its representativeness of regional winds without being affected by surrounding buildings.

2.2 Source apportionment (ME-2)

The multilinear engine algorithm (Paatero, 1999) is a multivariate solver that is typically used to solve the PMF model, which is based on a receptor-only factor analytic model (Paatero and Tapper, 1994). The bilinear representation of PMF solves Eq. (1), written in matrix notation, which represents the mass balance between the factor profiles and the concentrations.

$$X = G * F + E \qquad (1)$$

The elements g_{ik} of matrix G represent the time series and the elements f_{kj} of matrix F represent the j elements of the profile (for example, mass spectrum) and E is the model residual.

The parameters f and g are fitted using a least squares approach that iteratively minimizes the variable Q (Paatero et al., 2002).

$$\mathrm{Q}(f, g) = \sum_{i=1}^{m} \sum_{j=1}^{n} \left(\frac{e_{ij}}{\sigma_{ij}}\right)^2 \qquad (2)$$

Where, e_{ij} represent the residuals and σ_{ij} the estimated uncertainty for the points i and j.

The variable Q depends on the number of selected factors and the size of the data matrix, hence it is necessary to normalize Q by the degree of freedom of the model solution (Q_{exp}) (Paatero et al., 2002) to monitor solutions.

$$Q_{exp} \cong n * m - p * (m + n) \qquad (3)$$

Where p is the number of factors chosen, n number of samples and m the mass spectra. Ideally, if the model accurately captured the variability of the measured data, it would be expected to have a value of $Q/Q_{exp} = 1$, still this value depends on fluctuations in the source profiles, over- or underestimation of input data errors and from the model error.

Solutions using a least squares approach to solve a factor analysis problem may have linear transformations, also known as rotations (Paatero and Hopke, 2009). One advantage of ME2 over PMF is that the rotational ambiguity can be reduced by using previous knowledge of profiles (for example mass spectra) or time series of different pollutants using the *a*-value approach. 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 ($g_{i,run}$)

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

The *a*-value is a parameter that represents the degree of variability of the target profile, which typically ranges from zero to one, the closer to zero the more constrained the solution is (Lanz et al., 2008). The user should keep in mind that partially constrained solutions are carried out by compromising the Q/Q_{exp} value, which should be monitored to determine the feasibility of the solutions.

2.2.1 Target profiles and levels of constraint

In this study, solutions obtained with ME-2 were constrained using the *a*-value approach, by using four different sets of mass spectra from previous studies as target profiles (TP) (Table 1). The "a" set of TP represent BBOA and HOA average factor profiles obtained from an analysis carried out on different mass spectra from a variety of monitoring sites across Europe (Crippa et al., 2014) and COA obtained from a study in Paris (Crippa et al., 2013a). "c", "s" and "w" sets of TP were provided by Young et al. (2015a) from a PMF analysis carried out on AMS measurements at the North Kensington site in London, 2012. "c" TP were obtained from an analysis performed on annual OA measured with a cToF-AMS (11 January 2012 – 23 January 2013). "s" and "w" TP were obtained from summer and winter measurements were taken with an HR-AMS (January–February 2012 and July–August 2012, respectively). 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.

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A wide range of combinations of TP and *a*-values were used during this analysis, all of them being run with three random initial values (seeds), to determine the stability of the solutions. Constraints were applied using one, two and three TP; in all the solutions, there were at least two unconstrained factors. Figure 1 shows the coding used to identify the different solutions, for example when constraining three factor profiles: wB5_H2_C3_S1.

2.3 Strategy to explore the solution space

The success of ME-2 relies on the additional use of *a priori* information in form of constraints. However, without a well-defined strategy or a limited analysis of the solution space, it may lead to a subjectively and inaccurately selected solution. Moreover, where possible, target profiles from different studies should be tested in order to determine which set of target profiles are the most adequate. Therefore, the following sections show the results of the analysis carried out on the dataset March-December 2013, where the considerations provided by Crippa et al. (2014) were applied. Moreover, new analysis techniques were developed to explore the solution space.

PMF solutions are run to determine the number of factors (sources) in the solution; this is carried out by running PMF for a different number of factors. Once the number of possible sources has been chosen, different combinations of *a*-values and constrained factors are tested to determine the solution that better identifies the OA sources. The residual of the solution provides important information; it is possible to determine if the solution is over estimated (negative residual) or under estimated (positive residual). When a structure on the diurnal residual is observed, it allows the factor which is affecting the residual to be determined (Crippa et al., 2014) and a decision to be made if the *a*-value should be modified or even if the target profile is the appropriate or not for this dataset. Together with the residual, it is recommended to look at the total

Q/Q_{exp}, which is a parameter used to monitor solutions, the best solution, according to the statistical tests applied, will be the one with values closest to one.

Trilinear regression is used as a new technique to explore the solution space in ME-2 analysis. Multilinear regression has been previously applied to analyse the relationship between POA and combustion tracers (Allan et al., 2010;Liu et al., 2011;Young et al., 2015b) as well as polycyclic aromatic hydrocarbons (Elser et al., 2016). This is used instead of simple linear regression because many of the combustion related variables will have multiple sources such as biomass burning and traffic. Eq. (4) shows the trilinear regression equation used to analyse the relationship between POA and combustion tracers.

$$Y = A + B[BBOA] + C[HOA] + D[COA] \quad (5)$$

Where "Y" is NO_x, BC, or CO.

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. 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, NO_x 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). A nonzero value would indicate correlation with combustion tracers and thus the possibility that it is receiving interference from HOA, which has a similar mass spectrum. Chi-square is used as a "goodness of fit" where the lower the value the better fit between the analysed pollutants.

3. Results

3.1 Exploring the solution space for March-December dataset

This section shows the results from the analysis applied to determine the solution that best represents the OA sources for the complete dataset March-December 2013, according to the statistical tests applied, where a total of eight unconstrained and 25 constrained solutions were analysed.

3.1.1 Solutions, *a*-values and stability

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. ME-2 is run using a range of *a*-values, these *a*-values were selected after trial and error and according to the literature (Lanz et al., 2008;Crippa et al., 2014;Petit et al., 2014), which suggests that *a*-values depend on the similarity of the target profile and the factor profile being analysed: HOA mass spectra do not show high variability when compared with different sites, thus it is possible to restrict the constraint with *a*-values of 0.1-0.2. On the other hand, COA and BBOA mass spectra from different sites show high variability and a looser constraint should be applied (for example *a*-values 0.3-0.5 or higher).

Constraining only one or two factors of the five-factor solutions gave the least favourable results with high residuals and mixing factor profiles. When analysing the different seeds, these solutions also showed high variability between seeds; greater stability was found when three of the five factor solutions were constrained (Fig. S2), behaviour also observed by Crippa et al. (2014). As a result, in this analysis, five-factor solutions constraining three factors will be analysed for the first seed. One PMF solution and two solutions constraining two factors were also used during the exploration (Fig. 2) for three sets of TP.

3.1.2 Q/Q_{exp}, diurnal residual and trilinear regression

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 *a*-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.

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Figure 2.a shows the diurnal residual analysis where solutions constrained with "c" target profiles present high positive residual around 14:00-19:00 hrs. Solutions constrained with "w" target profiles have a negative residual during early morning with a positive residual at 21:00 hrs. Hence, the solution with a better diurnal residual is within the solutions constrained with "a" target profiles.

Figure 2.b shows the trilinear regression outputs between NO_x and POA for the different solutions (see supplement S3 for BC and CO trilinear regressions). All the solutions properly identified the background NO_x concentrations (grey line). Solutions with "c" and "w" target profiles showed similar undesirable results as in the diurnal residual analysis, with "c" target profiles presenting negative COA slopes and "w" presenting high COA slopes and Chi square values, 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. Additionally, trilinear regression outputs show variations between different solutions constrained with "a" target profiles with changes mainly in the Chi square and the BBOA.

3.1.3 Diurnal concentrations and mass spectra

OA sources have characteristic diurnal trends, and they may be used, together with their respective mass spectra, to analyse the solutions and determine if all the factors in the solution are suitable, environmentally speaking. BBOA showed low concentrations during the day, with high concentrations at night, mainly related to domestic heating (Alfarra et al., 2007); HOA presents two peaks during the day related to commuting, one in the morning and another one in the evening (Zhang et al., 2005); COA has two peaks related to OA emissions from cooking activities: one peak at noon and one peak in the evening (Allan et al., 2010). SVOOA is temperature dependent with low concentrations during the day increasing in the evening due to the condensation of gas phase pollutants. LVOOA, due to its regional origin, does not show high variations in its diurnal trend.

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

These undesirable outputs previously observed were also detected when analysing the mass spectra of the different solutions; Fig. S3 shows examples of diverse situations that were found: in the solution wB7_H5_C7_S1 it is possible to observe mixed factors where SVOOA has peaks of BBOA (m/z 60) and COA (m/z 55 and 57); one source with only one strong peak in its mass spectrum (SVOOA in solution cB3_H1_S1); The PMF solution was not able to properly identify a BBOA factor with low peaks at m/z 60 and 73 and a peak at m/z 60 for COA implying mixing with BBOA.

Finally, from this analysis, aB3_H2_C3_S1 was determined to be the solution that best represents the OA sources for March-December analysis, according to the statistical tests applied.

3.2 Seasonal analysis

When applying source apportionment, ME-2 considers that both target profiles and factor profiles remain constant over time, which may not be the case for long periods of time where meteorological conditions and pollutant emissions related to human activities vary greatly (Canonaco et al., 2015;Ripoll et al., 2015), thus the same analysis that was carried out on March-December data set was applied to data divided into seasons of the year: spring (March, April and May), summer (June, July and August) and autumn (September, October and November), see supplement S.3 for detailed information of the seasonal analysis.

Analysing the spring dataset (Fig. S7), solutions constrained with “a” and “c” TP were found to present the least favourable results with high Chi-square values and negative COA ratios in the trilinear analysis, as well as a higher negative diurnal residual; the solution wB3_H1_C3_S1 was deemed to be the best solution for spring analysis. Solutions constrained with “s” and “c” TP were the least favourable results for the summer analysis (Fig. S9) with low chi-square values in “s” target profiles, which show high negative residuals in the morning and at night. “c” target profiles show a high positive residual around 15:00-18:00 hrs; the solution aB5_H1_C3_S1 was found to be the best solution for the summer analysis. In the autumn analysis (Fig. S11), solutions constrained with “a” and “w” TP were found to be the least favourable results with high positive residuals in the morning, also “a” target profiles show high chi-square values. The solution cB3_H1_S1 was deemed the best solution for the autumn analysis, according to the statistical tests applied. 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.

4. Discussion and atmospheric implications

4.1 Annual and seasonal solutions

In the following subsections, the outputs of annual and seasonal solutions are compared in order to further explore the variability of the different OA sources.

4.1.1 Total Q/Q_{exp} and diurnal residual

Analysing the total Q/Q_{exp}, all the solutions obtained were mathematically acceptable and with small variations between their different values: 1.95 for March-December, 2.01 for spring, 1.95 for summer and 1.96 for autumn (Fig. 3.a).

Q/Q_{exp} values obtained in this study are compared to values obtained in different ME-2 studies, for example Petit et al. (2014), in a study using an ACSM, obtained a Q/Q_{exp} value of 6; studies carried out in Spain during winter and summer obtained 1.15 and 0.38 respectively (Minguillón et al., 2015b). Q/Q_{exp} values obtained with PMF are also comparable with values obtained in this study, for example (Young et al., 2015a) obtained a value of 1.35 from annual measurements carried out with a cToF-AMS at this site; (Allan et al., 2010) obtained different Q/Q_{exp} values for the analysis carried out to three different data sets: a value of 3.9 from measurements obtained using a HR-ToF-AMS and values of 10.5 and 16.7 using a cToF-AMS; also Crippa et al. (2013b) identified a Q/Q_{exp} value of 4.59, on HR-ToF-AMS measurements during July 2009 at the urban background site in Paris. Due to all this variability of Q/Q_{exp} values found in the literature, this parameter alone cannot be used as a criterion to determine the solution that best identifies the OA sources.

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 $\mu g.m^{-3}$ mainly in the morning and at night. On the other hand, summer shows to be the most underestimated solution with values of 0.018 $\mu g.m^{-3}$ 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 $\mu g.m^{-3}$ or less are low compared with diurnal concentrations of the OA sources, which concentrations ranged 0.1-0.6 $\mu g.m^{-3}$.

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4.1.2 Trilinear regression analysis

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.

The analysis presented in section 4 shows that seasonal analysis more accurately deconvolves OA sources, being possible to obtain more detailed information that will be lost when running ME-2 for long periods of time.

4.1.3 Target profiles (TP) and their impact on the solutions

As previously mentioned, the chosen solutions were: aB3_H2_C3_S1 for March-December, wB3_H1_C3_S1 for spring, aB5_H1_C3_S1 for summer and wB3_H1_S1 for autumn. The fact that March-December and summer solutions were obtained with "a" TP is possibly due to the fact that these TP represent an average from different mass spectra, becoming robust TP able to deal with the variations of these two datasets; one large dataset (March-Dec) and one dataset with concentrations affected by the different photochemical processes due to the high temperatures (Summer). On the other hand, spring and autumn do not show these variations and their OA sources may be apportioned using winter TP which were obtained under similar temperatures.

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Looking at the "c" and "s" TP, these were the ones with the least favourable results in all analyses carried out. This may be attributed to "c" being the only TP obtained with a cToF-AMS while the rest were obtained using a HR-AMS. In the case of "s" TP the unfavourable outputs are again related to the high variability present during this period of time. This analysis shows the importance of using the adequate TP when doing source apportionment as well as to explore solutions with different types of TP in order to determine the OA sources.

4.2 Variability of factor profiles

The variability of the different solutions previously obtained may be explored further with the triangle plots f44 vs f43 (Ng et al., 2010;Morgan et al., 2010) and f44 vs f60 (Cubison et al., 2011). The parameters f43, f44 and f60 represent the ratio of the integrated signal at m/z 43, 44 and 60, respectively, to the total signal in the organic component mass spectrum. Figure 4.a shows that LVOOA, while having different values between solutions, is found in distinct areas of the plot (connecting lines are used to make the SVOOA variability clearer), whereas SVOOA shows values of f44 vs f43 with high variability. 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 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.

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By analysing Fig. 4.b, it is possible to observe the variability in f60, with the lowest value obtained in summer (0.013) followed by spring, autumn and March-Dec (0.022, 0.024 and 0.034, respectively). Variability in biomass burning OA depends on the fuel type, burning conditions and level of processing (Weimer et al., 2008;Hennigan et al., 2011;Ortega et al., 2013;Young et al., 2015b). A study carried out by (Young et al., 2015b) in London, 2012, identified two types of solid fuel OA factors, attributed to differences in burning efficiency. 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.

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For all the solutions, COA presents an f60 value of approximately 0.01, which has been previously identified by Mohr et al. (2009) who obtained f60 values of 0.015 - 0.03 for different types of meat cooking. The fact that all the COA mass spectra present similar f44:f60 ratios suggest the COA footprint is relatively constant over the different seasons, being together with HOA the more adequate sources to constrain when applying the *a*-value approach.

4.3 Petrol and diesel contribution to traffic emissions

Traffic emissions contribute significantly to air pollution (Beevers et al., 2012;Carslaw et al., 2013;May et al., 2014). In order to better analyse traffic emissions and their impact on air quality, it is necessary to understand the fuel type and pollutant contribution from different vehicles. In particular, the United Kingdom has a considerable percentage of diesel-fuelled vehicles; according to the vehicle licencing statistics, the percentage of diesel-fuelled vehicles licenced has been increasing over the last few years from 22% in 2006 to 36.2% in 2014 respectively, while petrol-fuelled vehicles decreased from 77.7% to 62.9% (GOV.UK, 2015).

Diesel emits higher NO_x 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_x 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_x concentrations and HDD emitting higher HOA concentrations.

It is possible to qualitatively analyse the impact of different fuels on air pollution by 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. This analysis is performed considering WD as Monday to Friday and WE only Sunday to eliminate the mixed traffic on Saturday. Another consideration is that heavy duty/light duty emissions fleet ratio is higher during the week (Lough et al., 2006;Bahreini et al., 2012;Heo et al., 2015). It is also important to state that heavy duty vehicles are exclusively diesel fuelled whereas light duty vehicles are a mixture of diesel and petrol.

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Trilinear regression explained in section 2.3, was used with data divided into WD (Monday to Friday) and WE (Sunday) to analyse the WD/WE contributions. Subsequently, it was possible to determine WD/WE ratios for the slopes: NO_x/HOA and CO/HOA.

In order to compare these trilinear outputs with the WD/WE ratios between NO_x and CO, $NO_x/\Delta CO$ was calculated from average concentrations: there is a difference in lifetime between CO (lifetime of months) and NO_x (lifetime of hours), thus it is important to consider the background CO concentrations to be able to compare NO_x and CO concentrations. It is necessary to perform a linear regression between CO and NO_x and calculate ΔCO, which is the average CO concentration minus the intercept from the CO:NO_x linear regression.

Figure 5 shows the WD/WE ratios, where it is possible to observe $NO_x/\Delta CO$ ratios of 1.25, 1.35 and 1.36 for March-Dec, summer and autumn, respectively, suggesting diesel with a higher contribution during WD compared to petrol. These findings are confirmed by the CO/HOA ratios, which for the same periods of time, are lower than one (0.8, 0.45 and 0.9) suggesting a lower contribution of petrol during weekdays compared to diesel. In spring, there are no considerable changes to the WD/WE ratios, although a higher contribution of petrol is shown during WD with values of 1.28 for CO/HOA and low diesel contribution. Analysing the NO_x/HOA ratios, the seasonal ratios show values of 1.07, 1.06 and 1.05 suggesting a slightly higher contribution of LDD during WD than HDD.

4.4 $PM_{2.5}$ daily concentrations and PM_1 composition

$PM_{2.5}$ has been widely studied due to its potential to cause negative effects on health (Pope III and Dockery, 2006;Harrison et al., 2012;Bohnenstengel et al., 2014). This adverse impact is directly connected to the size of the particles, making PM_1 more detrimental to health than $PM_{2.5}$ (Ramgolam et al., 2009). Moreover, analysing the aerosol contribution to PM_1 and its association with $PM_{2.5}$ concentrations allows the possible influence of PM_1 on $PM_{2.5}$ levels to be determined. According to the Daily Air Quality Index (DAQI), $PM_{2.5}$ concentrations are considered moderate when daily concentrations are between 35 and 52 μgm^{-3} and high when levels are between 53 and 69 μgm^{-3}. Daily $PM_{2.5}$ concentrations during the sampling period show that the majority of daily concentrations were considered to be low episodes (Fig. 6.a), with 10 episodes of moderate concentrations and only two episodes of high $PM_{2.5}$ concentrations (55.2 and 61.5 μgm^{-3}).

Considering that PM_1 is composed mainly of OA, SO_4, NO_3, NH_4 and BC, it is possible to analyse the PM_1 composition during $PM_{2.5}$ high concentrations (Fig. 6.b). Episodes with moderate and high $PM_{2.5}$ concentrations were observed with low wind speeds (Fig. S13), being NO_3 and LVOOA the main PM_1 contributors. High NO_3 concentrations were observed during spring as found in a previous study performed by Young et al. (2015a) who determined that NO_3 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.

Defining BBOA, HOA COA and BC as primary and SVOOA, LVOOA, NO_3, NH_4 and SO_4 as secondary aerosols, the main PM_1 contributors to $PM_{2.5}$ concentrations are secondary aerosols with a total contribution of 61% (Fig. 6.c). These findings agree with a previous study carried out in this same monitoring site carried out by (Young et al., 2015a) who found secondary aerosols to be the predominant source of PM_1 over the year, with different secondary inorganic and organic aerosol contributions between winter and summer.

5. Conclusions

This study presents the source apportionment carried out using ME-2 within SoFi 4.8 of OA concentrations, measured with an ACSM from March to December 2013 at the urban-background site in North Kensington, London; the first time it was deployed in the UK.

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 *a*-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 f44:f43 values for SVOOA (Fig. 4.a) and f60 values ranging from 13x10^{-3} for summer to 24x10^{-3} for autumn (Fig. 4.b). These variations support the importance of running ME-2 during periods of time where weather conditions and emissions from human activities are less variable, such as seasonal analyses.

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SVOOA presented a high variability in the oxidation state during the different seasons. This is due to the nature of SVOOA being affected mainly with high temperatures and ME-2 not being able to completely determine SVOOA concentrations. These results support the indication that is not an accurate practice to use SVOOA as a target profile when analysing solutions. Trilinear regressions deliver quantitative information about the ratios between combustion tracers and POA. These ratios may be used as a proxy for other urban background sites to estimate POA concentrations.

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From analysing heavy and light duty diesel emissions, the main contributor on weekdays was found to be from diesel emissions, particularly LDD emissions. Thus, in order to reduce traffic emissions on weekdays, LDD vehicles should be targeted. For the PM$_{2.5}$ analysis (March-December 2013), the main PM$_1$ contributors to these concentrations were secondary aerosols and BC, which means that PM$_1$ contributors to PM$_{2.5}$ concentrations are related to emissions from combustion activities and also from secondary pollutants produced in the atmosphere.

This study delivers mass spectra and time series of OA sources for a long-term period as well as seasons of the year that maybe used in future studies as TP. Furthermore, the scientific findings provide significant information to strengthen legislation as well as to support health studies in order to improve air quality in the UK.

Author contributions: D.C. Green, E. Reyes-Villegas and J.D. Allan designed the project; D.C. Green and M. Priestman operated, calibrated and performed QA of ACSM data; E. Reyes-Villegas performed the data analysis; E. Reyes-Villegas, F. Canonaco, D.C. Green, H. Coe, A.S.H. Prévôt, and J.D. Allan wrote the paper.

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Table 1: Sets of target profiles used in the study.

a	c	s	w
BBOA	SFOA	HOA	SFOA
HOA	HOA	COA	HOA
COA	COA	SVOOA	COA

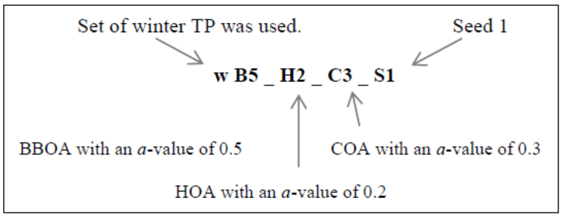

Figure 12: Coding used to identify the different runs.

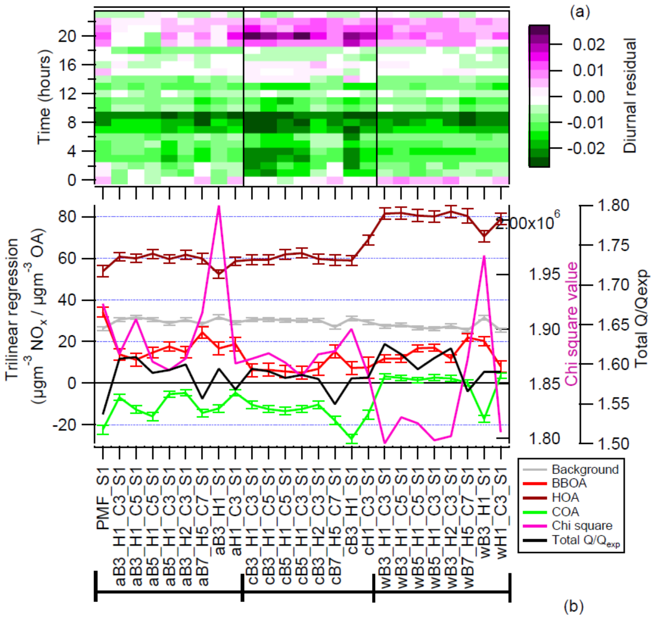

Figure 13 Diurnal residual, y axis represents the 24 hours and x axis the different solutions with a variety of target profiles and *a*-values (a). NO_x trilinear regression for solutions with different target profiles (b). BBOA represents the slope of μgm^{-3} of NO_x per μgm^{-3} of BBOA. The same applies for HOA and COA. Whiskers represent the 95% confidence interval.

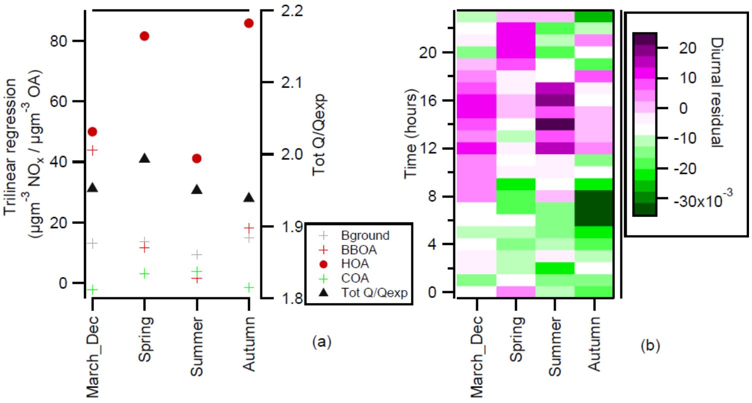

Figure 14: NO_x trilinear regression (a) and diurnal residual (b) for the different analyses.

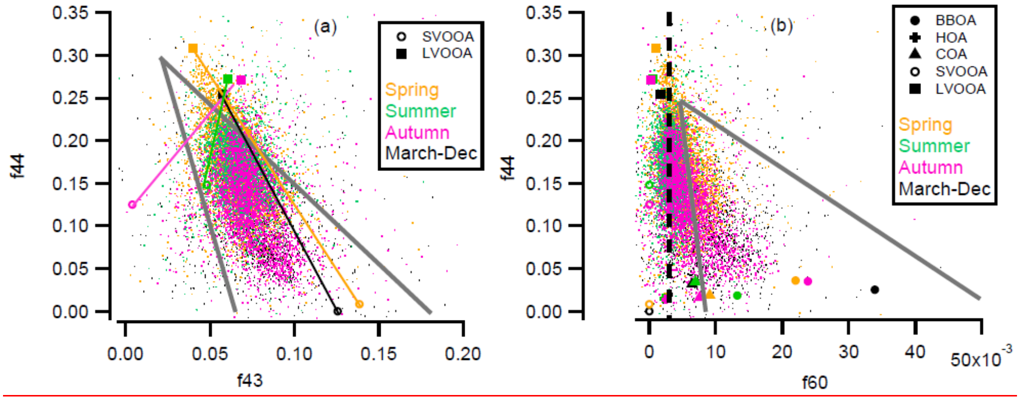

Figure 15: f44 vs f43 (a) and f44 vs f60 (b) plots for different periods of time.

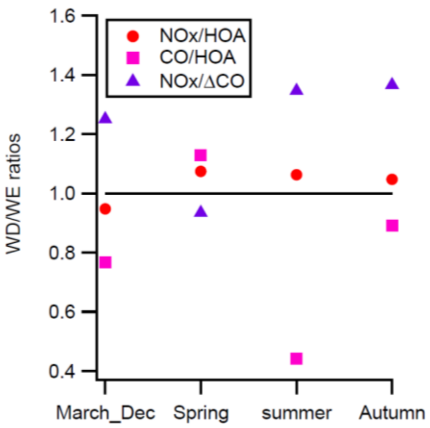

Figure 16: WD/WE ratios to analyse petrol and diesel contributions.

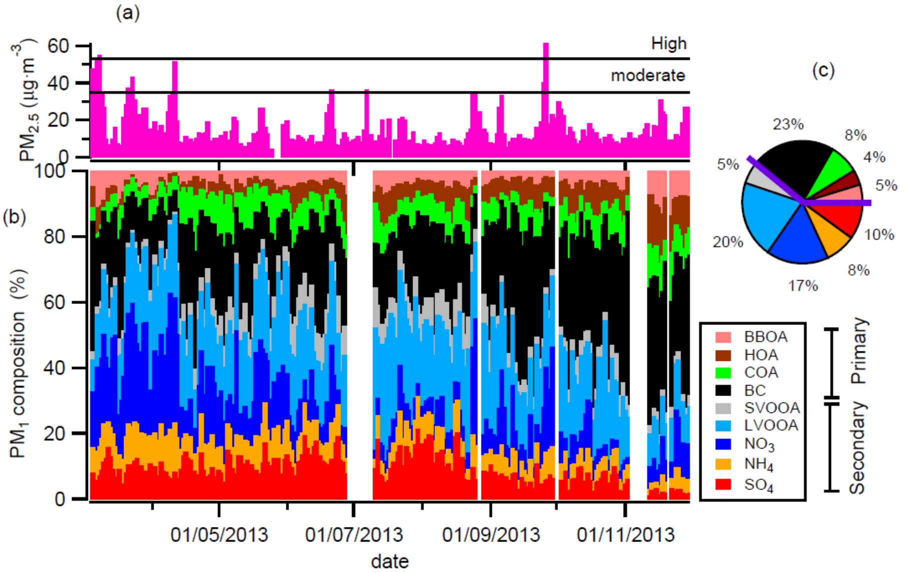

Figure 17: Daily PM$_{2.5}$ concentrations (a) daily (b) and total PM$_1$ composition (c), purple line in Fig. 6.c separates secondary and primary aerosols.