

We would like to thank both referees for their helpful comments and suggestions. We would like to provide the following responses, where referee comments are in normal font and our responses are italicised.

Anonymous referee #1

The paper summarizes almost year-long measurements of aerosol composition in the suburbs of London using aerosol mass spectrometry. The period of study overlaps with two intensive measurement periods in winter and summer. Seasonal trends in aerosol composition are discussed and measurements are compared with previous data. In addition, PMF analysis is performed on 2 sets of organic mass spectra. The uniqueness of the paper is the PMF analysis for source characterization of organic aerosol in the region. In other words, to me, the inorganic data presented don't add any new and significant scientific knowledge to the literature. However, I am troubled with the fact that the PMF results from a c-ToF and HR-ToF mass spectrometers during the winter period are not the same. This brings me to question the validity of PMF analysis for the rest of the period. It is obvious that the authors have worked hard to present the PMF analysis; however, I'm not sure if the analysis is justified because two similar instruments result in different solutions and could lead to two different conclusions. To strengthen the paper (in addition to addressing the major and minor comments listed below), I recommend including auxiliary gas phase data and backtrajectory analysis to support and explain the observed patterns in inorganic and organic composition. Otherwise, the paper appears to be just another AMS paper with a summary of observations, without real meaningful context to it. I recommend accepting the manuscript after major revisions.

- *We would like to thank the referee for taking the time to review the manuscript and providing some very interesting and thoughtful comments. We would like to offer the responses below to each of the comments. Firstly, we would like to emphasise the uniqueness of the conclusions reached in this manuscript as it would not have been possible to reach such conclusions by previous studies.*
 - *This is the first time that analysis of this nature has been performed; this is the first time PMF has been applied to a year-long dataset, specifically a long-term chemical composition dataset from an AMS in an urban environment. The results from this study show new data that concern the aerosol processes in London on a year-round basis. Analysis of the inorganic species adds to the conclusions from this study as the importance of regional and transboundary pollution is highlighted. Furthermore, nitrate is found to be a key component of high pollution events in London, which is important to consider when considering the EU Air Quality Directive limits for 24 hour and annual PM limits.*
 - *During the period of a calendar year, the concentration of SOA varied yet the oxygen content of the organic mass did not despite the variety of different air masses and range of temperatures that were experienced at the site. Furthermore, during the year the type and concentration of SOA precursors vary, along with photochemical activity, so it is expected that SOA properties would reflect these changes but in this study they did not. Without a year-long aerosol chemical composition dataset it would not have been possible to evaluate the extent to which SOA formation,*

properties, and evolution are influenced by meteorological parameters and precursor emissions.

- *Together, secondary inorganic and organic aerosols were found to account for a significant fraction of the submicron aerosol burden in London where local, regional, and transboundary pollution played an important role in influencing London's total submicron aerosol burden. This 12 month dataset also enabled the particulates responsible for high concentration events in London to be identified and compared during different seasons. Furthermore during winter the high concentration events were found to be governed by primary organic particulate emissions, notably from vehicles, cooking, and solid fuel organic aerosols, as well as by nitrate formation, whereas during the summer high concentrations were driven by SOA formation. It would not have been possible to provide recommendations on specific ways to improve air quality without these data, particularly on which sources need to be targeted and be the focus of future pollution abatement strategies.*

1. Calling the measurements background measurements is misleading in my opinion. If the sampling site is located 7 km west of central London, it qualifies as more of a suburban area and not background environment. Please consider rephrasing throughout the manuscript (including tables and figures).

- a. *North Kensington is approximately 5 km from the West End of London, which is generally considered as the centre of London, whereas it is about 15 km from the outer suburbs to the west and south-west. The authors would like to refer the reviewer to the definition of a background site as provided by the Department of Environment, Food and Rural Affairs: "Located such that its pollution level is not influenced significantly by any single source or street, but rather by the integrated contribution from all sources upwind of the station e.g. by all traffic, combustion sources etc. upwind of the station in a city, or by all upwind source areas (cities, industrial areas) in a rural area. These sampling points shall, as a general rule, be representative for several square kilometres. At rural background sites, the sampling point should not be influenced by agglomerations or industrial sites in its vicinity, i.e. sites closer than five kilometres." (<http://uk-air.defra.gov.uk/networks/site-types>). Further, literature based on studies from this location such as Bigi and Harrison (2010, doi:10.1016/j.atmosenv.2010.02.028) list the reasons as to why the North Kensington site is classed as urban background. Therefore we will not be rephrasing in the revised manuscript as suggested. The following has been included at line 12, page 18744 in the revised manuscript: "A background site is defined by DEFRA as being located such that its pollution level is not influenced significantly by any single source or street, but rather by the integrated contribution from all sources upwind of the station" and "be representative for several square kilometres".*

2. Line 12 of abstract: considering that the site is more of a suburban area and not background or true urban, the conclusions from this study cannot explain urban behavior of OA, so if indeed, SOA oxidation at the site is not changing in the year, this doesn't explain how SOA in an urban environment will behave. This sentence in the abstract and last paragraph in section 5.2 need to be removed.

- a. *Further to the response to comment 1, the site is classed as urban background so the sentence in the abstract and last paragraph in section 5.2 in the manuscript will not be changed as suggested.*
3. Have you tried running PMF on different seasons separately to see how similar/different the factors are?
 - a. *PMF has been run on the different seasons separately with relatively similar factors found in each season i.e. some combination of HOA, COA, SFOA, and OOA depending on the season where a SFOA factor was not derived from the summer run and only one OOA factor was derived from the winter runs. However, more extensive analyses would be required to fully compare the factors derived from the seasonal split PMF run and those from the annual PMF run, which would likely lead to another manuscript. However, the premise for looking at an annual dataset was to obtain information on the contributions of the factors to the total organic aerosol concentration throughout an annual cycle rather than the detailed sources under a specific condition, which is what the PMF runs on the individual seasons would be more useful for. Furthermore, the sources would differ by season such as the source types of primary organic aerosol, particularly the sources of SFOA. In the summer, the OOA factor would likely be different to OOA derived from PMF runs on other seasons due to the different precursors and photochemistry during the summer. Consequently, there would be an issue of how to stitch the factors together from the different seasons in order to obtain information about the annual trends, which is the point of our paper. The mass spectrum and chemical composition of SFOA in particular is known to vary substantially depending on a variety of conditions thus interpretation of seasonal trends could be flawed. We appreciate the comments and questions from the reviewer on this point but as we wanted to look at the trends across the entire year we feel that the approach we have taken was the most suitable for what we wanted to investigate.*
4. Table 2: there is no discussion in the discrepancy between PMF winter COA estimates from c-ToF and HR-ToF analysis (slope of only 0.52). In addition, there was no discussion on why only 1 OOA is resolved for HR-ToF and 2 OOAs for c-ToF. Since it seems OOA2(mod) has a very small concentration, the logic of considering a 5-factor solution for c-ToF analysis doesn't seem to hold true. This is not good news that the PMF results from winter from two co-located AMS instruments is not the same.
 - a. *The main focus of this manuscript is the secondary inorganic and organic aerosols rather than the primary organic aerosols or the comparison between the two instruments. However, there are a few main reasons for why different PMF results were derived from the two instruments:*
 - i. *Firstly, PMF is not without uncertainties and ambiguities due to rotations and model errors e.g. Paatero and Tapper, 1994 (DOI: 10.1002/env.3170050203), Lanz et al., 2007 (doi:10.5194/acp-7-1503-2007), Ulbrich et al., 2009 (doi:10.5194/acp-9-2891-2009), Allan et al., 2010 (doi:10.5194/acp-10-647-2010). The HR-ToF-AMS has a greater resolving power and produces more detailed spectral data than the cToF.*

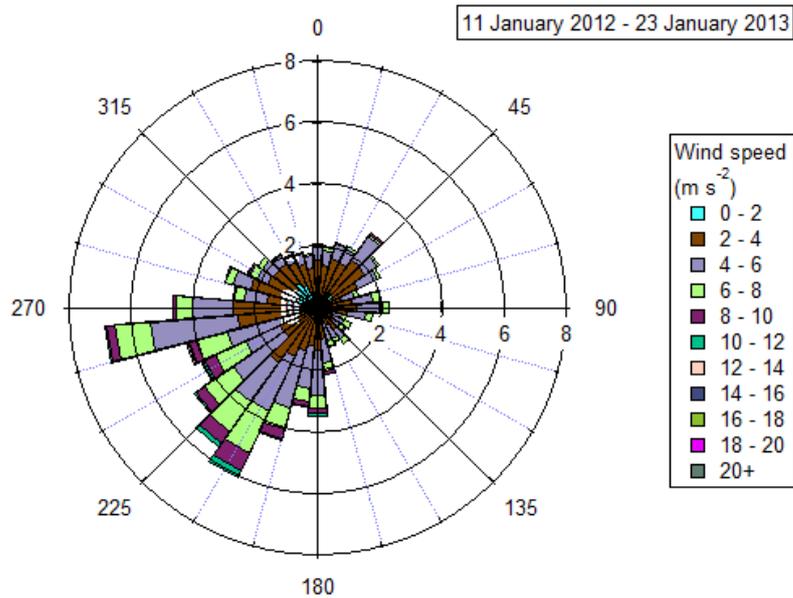
Furthermore, as the cToF data is of unit mass resolution (UMR), key peaks are not explicitly separated and therefore contribute to rotational ambiguity under normal PMF analysis. A greater number of different factors may therefore be expected to be resolved from PMF analysis of the HR-ToF data. In comparison to solutions from the cToF, HR-ToF PMF solutions are better constrained thus their rotational ambiguity is reduced (Zhang et al., 2011 - DOI 10.1007/s00216-011-5355-y). Consequently, this does not mean that the PMF analysis of the cToF data is wrong but rather the HR-ToF data are more detailed. It may therefore not be necessarily expected that the same factors, and same concentrations, be obtained from two co-located AMSs when they have different resolving powers. In addition an important aspect of PMF analysis is choosing the optimum number of factors, which has been assessed accordingly for each individual instrument in this study. When PMF is run on the January-February 2012 cToF dataset and on the December 2012-January 2013 dataset, 4 factors are derived: HOA, COA, SFOA, and OOA. A second SFOA factor was derived from the winter HR-ToF data but it is not completely unexpected that a fifth factor was not derived from the cToF dataset because only UMR data are available. Reasons for the differences in the factorisation of the two datasets are also discussed in the complementary paper (doi:10.5194/acp-15-2429-2015).

- ii. The cToF dataset covers a full calendar year thus a range of conditions, particularly meteorological conditions, influence the data, this includes a wide range of temperatures and photochemistry which enable the two OOA subtypes to be identified. Furthermore, the dataset covers two winter periods where primary organic aerosols are predominant so the SFOA factor, for example, is identified throughout the year. The HR-ToF dataset only covers two separate 4-week periods; one in the winter and one in the summer. The resolution of the HR-ToF and the intensive observation periods allow for more detailed investigation into the sources of aerosols, which are known to vary with season but measurements only covering 4 weeks will not likely be as influenced by such a range in temperature and photochemistry.
- iii. Although both the 4- and 5-factor solutions were deemed valid, the 5-factor solution better separated the factors in terms of their mass spectra and several of the diagnostics used to determine the most suitable number of factors were improved in the 5-factor solution compared to the 4-factor solution. We believe the approach used in this study with the 5-factor solution delivers more accurate data than the 4-factor solution.

5. Is the summer data removed from yearly averages as well because of bad tuning of the mass spec? for example line 24, p. 18757 that indicates 38% contribution to primary OA from SFOA doesn't include summer months? If yes, it's better to re-emphasize that again when discussing 'annual' averages. (also in Figures, e.g, Fig. 2-3). To me, it makes sense to have all the inorganic and total organic data removed from the paper for summer as well because the heater bias may affect detection efficiency of different ions differently.

- a. *The comment regarding removal of the summer data from the annual averages of the OA factors has been addressed in the revised manuscript as suggested. Line 1 on page 18758 in the revised manuscript now reads: “The greatest contribution of the organic components to total OA mass, which does not include some of the summer period (see Sect. 4.1), is from OOA1 (31%), followed by SFOA_{mod} (25%), HOA (21%), and COA (19%).” All relevant figure captions have also been amended accordingly. The summer data are not removed from the inorganics or the organics when the total NR-PM₁ are averaged because there was no evidence that the concentrations of these species were specifically affected by the change in tuning of the mass spectrometer. For example, there were no obvious step changes in the time series of the concentrations of each of the species. In contrast, when PMF was run on the organic fraction it was evident that the tuning of the mass spectrometer had affected some of the organic aerosols by way of step changes in the mass concentrations thus we were able to justifiably remove these data. In other words, there is no evidence that the total ion count from organic fragments changes with the change in tuning as the total mass loading of organic aerosol does not seem to be affected. However, there is evidence that the peak shapes and/or intensities change as PMF resolves differences in the factors with the change in tuning.*
6. Line 15, p. 18756 is confusing. From reading the previous section, I was under the impression that SFOA factor from HRTof is double that of SFOA of c-ToF. So why is it stated here that ‘nearly all’ of SFOA factor is assigned to OOA2? Do the authors mean that all of OOA2 is in fact SFOA (as is suggested by the very low OOA2(mod)? If yes, line 15 here needs clarification.
- a. *Not all of the SFOA factor is assigned to OOA2 as there is some mass of OOA2 without an SFOA influence (termed OOA2_{noSF} in the manuscript), albeit a small mass concentration. We feel it would be misleading to state that all of the mass of SFOA is convolved with OOA2. For consistency, line 18 of page 18755 has been edited in the revised manuscript to become the following: “This suggests that most of the SFOA_{PMF} mass measured by the cToF-AMS is being assigned to OOA2_{PMF} in PMF; the total SFOA mass could therefore be up to a factor of two greater than previously estimated.”*
7. In applying eqn 1, I’m not convinced that investigating the daily averages of OOA2 vs. SFOA is better than analyzing the recorded data as is, i.e., before averaging for longer periods.
- a. *As OOA2 and SFOA have very similar diurnal profiles using the recorded data it is unlikely that a meaningful correlation between the two factors to deduce the fraction of SFOA convolved with OOA2 would be achieved using these data. As described in Section 4.3 of the manuscript, the concentrations of both SFOA and OOA2 are likely to increase in the evening due to the semi-volatile nature of OOA2 and the association of SFOA with domestic space heating activities. We feel that averaging the data to 24 hours enables any differences in their temporal behaviour other than those expected during the day to be observed.*
8. According to eqns 1 and 3, OOA2(mod) is the same as intercept in eqn 1, i.e., OOA2(noSF)?

- a. *The following line has been inserted into the revised manuscript on line 5, page 18757 for clarification: “where $OOA2_{mod}$ in equation 3 is equivalent to $OOA2_{noSF}$ in equation 1.”. Different terminology is used in the two equations to highlight that $OOA2_{mod}$ is a concentration estimated from the calculations described whereas $OOA2_{noSF}$ emphasises that the concentrations calculated here are believed to have no influence from SFOA.*
9. Typically OOA2 represents ‘locally’ produced SOA, which one might expect to depend strongly on photochemical processing whereas OOA1 is the strongly oxidized, long range transported OA. Since concentration of OOA2 is very small throughout the analyzed months, it appears that contribution of locally produced SOA to total OA at this site is small. How is the transport pattern of urban pollutants over the site? If the site is mostly upwind of London urban emissions, then it is not surprising that OOA2 and contribution of locally processed OA is small, and also not surprising that the oxidation characteristic of OA is not varying throughout the year. In addition, because summer months were not included in the PMF analysis of C-ToF data, ‘yearly’ discussion of SOA oxidation, which is expected to depend strongly on photochemical activity, is fruitless. These are important points that need to be addressed in the abstract and conclusion.
 - a. *In response to the comment about the contribution of locally produced SOA to total OA at the site being small, we would like to note that the OOA2s are not two discrete types of OA but rather a continuum of OA evolution where the two subtypes represent end members. Although some sites do exhibit the behaviour described in the referee’s comment (Jimenez et al., 2009 – doi: 10.1126/science.1180353; Ng et al., 2010 - doi:10.5194/acp-10-4625-2010) the analyses of the dataset presented in this manuscript show that this behaviour is not observed at the site in London.*
 - b. *Please see response 1a. Due to the location of the site, air reaching North Kensington from the west or south-west has already travelled over a substantial part of London. Due to the location of the North Kensington site (http://uk-air.defra.gov.uk/networks/site-info?site_id=KC1), it is widely accepted as being representative of background urban air quality in central London (Bigi and Harrison, 2010 - doi:10.1016/j.atmosenv.2010.02.028; http://uk-air.defra.gov.uk/assets/documents/reports/cat05/1312100920_Particles_Network_Annual_report_2012_AS_83.pdf). Furthermore, the location in London means sources would be expected from all directions. To emphasise this point, wind data from the station at Heathrow airport is used in the following plot showing the transport of pollutants over the site during the measurement period and is found to be predominantly from the southwest although air mass trajectories from all directions are observed. Heathrow wind data are used rather than data obtained at the site for two reasons: long-term data are available for the Heathrow station whereas only the data from the two IOPs are available from the North Kensington site and the surrounding buildings strongly influence the meteorological data at the site whereas this is not the case at Heathrow airport.*



In addition, 1 day back trajectories using outputs from the UK Met. Office's NAME (Numerical Atmospheric Dispersion Modelling Environment - (Jones et al., 2007 - Air Pollut. Model. Appl. XVII 17, 580–589.; Ryall and Maryon, 1998 - doi:10.1016/S1352-2310(98)00177-0) dispersion model described in Fleming et al. (2012, doi:10.1016/j.atmosres.2011.09.009), show that during the period the AMS was measuring i.e. 11 January 2012-23 January 2013, air masses arriving at the site in North Kensington had spent 32.1% of their last 1 day below 100m in London (see table below). This further indicates that the site is influenced by a number of different sources, both from outside London and within London itself.

Sector	%
Atlantic	9.4
North France	6.9
Benelux	3.0
Channel	5.7
North Sea	7.1
Ireland	3.6
Scotland	0.5
North East UK	1.1
North West UK	1.0
Wales	2.4
Midlands	10.6
East Anglia	2.0
South West UK	6.8
London	32.1
South East UK	7.8
Scandinavia	0.2

- c. *Only a period of approximately 5 weeks during July and August were excluded from the PMF analysis. A range of photochemical activity was still experienced throughout the year. The full month of June and some periods of both July and August were still included in the analysis, where June, July, and August are typically considered summer months. The average ozone mixing ratio for June through to the end of August (\pm one standard deviation) was 24.1 ppb (\pm 12.1) and for 20 July-24 August (the period of data removed from PMF analysis) was 26.1 (\pm 15.2). Consequently the mean and standard deviation of the ozone mixing ratio are not statistically significantly different from the whole June, July, and August period. This suggests that the data we do have from the AMS is representative of the 5 week period that has been removed. Furthermore, substantial photochemical activity would have also occurred at other times such as during the heat wave in March 2012. The following has been included in the revised manuscript page 18758, line 7: “However, the mean (and standard deviation) ozone mixing ratio was not found to be statistically significantly different between the 5 week period not included in PMF analysis and the whole June, July, and August period, suggesting the data that is included in the analysis is representative of the data that were removed.”*
- d. *Regarding the comment on annual trends of SOA oxidation, the analysis performed and shown in figure 7 was based on the full organic aerosol dataset with the contributions from the primary organic aerosols removed thus shows the oxidation of SOA as a whole throughout the year and not just of the two OOA factors derived from PMF. Irrespective of the contributions of OOA1 and OOA2 to total SOA during the year, one would expect SOA oxidation to vary with the time of year due to the availability of precursors, differences in the precursors with season, and photochemical activity. For example, differences in SOA oxidation would be expected between late spring and winter. However, as no obvious trends in SOA oxidation with temperature or time of year were evident from the plots in figure 7, we feel that our conclusion that there is no variability in the extent of SOA oxidation holds.*
10. Line 4, p. 18761: since temperature affects the boundary layer mixing height and therefore concentration of pollutants, it is not straightforward to consider concentrations across different seasons without normalizing to correct for dilution. Isn't there CO (or CO₂) measurements available at the site which can be used to normalize OA (or SOA) by (e.g., in Fig. 6)?
- a. *The sentence at line 4, page 18761 does not refer to the absolute magnitude of the pollutants but rather it specifically refers to changes in the f_{43} and f_{44} of the calculated SOA. f_{43} and f_{44} are ratios thus the absolute concentration effects do not need to be considered.*
- b. *High quality CO measurements are available at the site but only until the end of August 2012. Although longer-term CO measurements are available from the site as part of the AURN monitoring station, these are of lower resolution and therefore may not be of sufficient quality to enable a reliable normalisation to be performed. Furthermore, any long-term CO data would also need de-trending for long-range transport as its atmospheric lifetime is longer than that of aerosols, which in itself is a very non-trivial exercise.*

11. line 13, p. 18761: it has not been shown that the aerosol observed at the site is really London SOA.

a. *It is not clear what the referee means by “London SOA”, whether it is that which is measured in London or formed within London. However, the location of North Kensington is such that it would be a suitable place to measure either or both. Please also see our responses 1a and 9b above. In addition, as the North Kensington site is classed as being an urban background site it is widely accepted as representative of background air quality in central London thus the aerosol observed at the site is considered to be London SOA. However, as an increment relative to a rural site, such as Detling or Harwell, is not yet available to show whether or not the aerosol is London SOA, this statement is a speculative hypothesis rather than a proven conclusion. Line 10, page 18761 in the revised manuscript has been amended to: “The f_{44} and f_{43} for the two OOA components identified from PMF analysis in this study are therefore also plotted within the f_{44} vs. f_{43} space to further constrain the degree of oxidation of what is hypothesised to be London SOA.”*

12. line 19, p. 18761: The O/C ratios of OOA1 don't make sense to me. From the c-ToF data, O/C for all months except summer is 0.79, but for HR-ToF, the O/C for summer (which should represent the highest degree of oxidation) is just 0.52. I believe the HRToF PMF analysis is not separating out the factors properly either such that there is some contribution of less oxygenated factors to OOA1. Wasn't there an OOA2 factor resolved for HR-ToF analysis?

a. *The analysis presented in this manuscript did not separate out OOA1 and OOA2 according to the Jimenez model (Jimenez et al., 2009 –DOI: 10.1126/science.1180353). This does not mean that PMF analysis is not factorising the OA ‘properly’, but rather it means that something other than the progressive oxidation of SOA is the driving factor of the OOA split at this site. As is shown in the analysis and discussed in the manuscript, the oxidation level doesn't vary that much at this site so it must be that some other chemical variability is driving the split.*

b. *An OOA2 factor was resolved for HR-ToF analysis, which had an O:C ratio of 0.52 (line 18, page 18761). The authors agree that this observation is surprising but as the HR-ToF is able to separate out key peaks, as discussed in response to comment 4, rotational ambiguity is not as much of a problem with PMF analysis of HR-ToF data. Correlations between the mass spectra from the HR-ToF and cToF for OOA1 and OOA2 are shown in Section 6 of the supplementary material, where the OOA1 and OOA2 mass spectra are from PMF analysis of the year-long cToF data and only from the summer HR-ToF dataset as it was only possible to derive both OOA factors from PMF analysis of the summer data. Nevertheless, strong correlations were observed with a Pearson's r of 0.82 for OOA2 and 0.93 for OOA1, although it must be borne in mind that the two OOA subtypes are not necessarily the same. In addition, the HR-ToF dataset only covers a period of approximately 4 weeks between July and August whereas a greater dynamic range in photochemical conditions and ambient temperature will have been experienced across the year for the cToF dataset. As the latter includes a heatwave in March amongst other meteorological conditions, it may explain the higher overall O:C ratio for OOA1 from the cToF. The lower O:C ratio*

of OOA1 from the HR-ToF may also suggest that the peak in OOA production and oxidation was not during the 4 week measurement period in 2012.

13. Lines 27-29, p. 18761: Because of the comment above, I don't think the authors can comment on seasonality of SOA oxidation. There is no consistent dataset throughout the year to assess how oxidation of SOA components had changed.
 - a. *Please see our response to comment 9 above.*

14. Line 27, p. 18762: do the authors mean in the summer high concentration events are dominated by OA? Please clarify. Also, because of mistuning of the mass spec, how would the summer data be jeopardized.
 - a. *Line 27, p. 18762 has been amended accordingly in the revised manuscript.*
 - b. *The summer data will have an improved S/N compared to the other periods (see response to Referee #2, comment regarding P18745 L18, where, on average, a 40% decrease in S/N was estimated for 'detuned' periods which were those surrounding the summer 'tuned' period).*

Anonymous referee #2

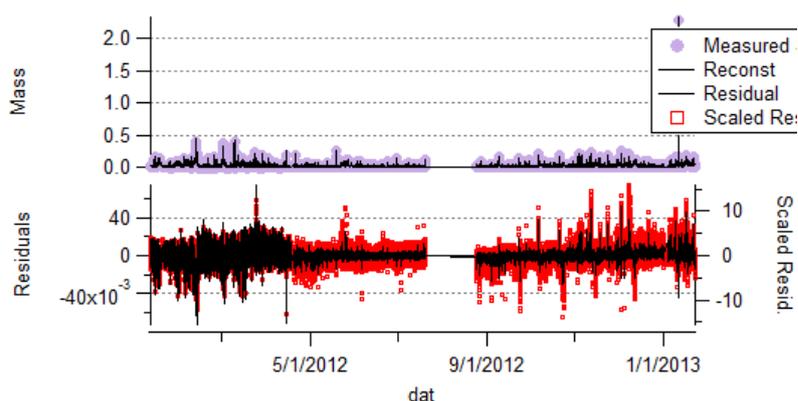
In the present manuscript Young et al. present data and source apportionment results from one of the longest AMS measurement campaigns so far. The paper focuses mainly on secondary aerosols. The authors take great care in documenting their PMF analysis, which is commendable. Anyhow, my main concerns concern the PMF. I think that the approach to do the SA over the whole period gives rise to several of the discussed issues: Factor mixing and difference between HR and CTOF. I got the impression that maybe the CTOF OOA2 actually is an overlap of what is LVOOA in summer and aged BBOA in winter. Both usually have (as mentioned in the text) similar diurnal cycles and a relatively large overlap of their spectra. Indications could be: is the correlation of OOA2 with NO₃ larger in summer than in winter (and vice versa for levoglucosan)? Or if one looks at the time series of the PMF residuals is there some m/z which have larger residuals in summer and others in winter. Also the fact that the HR PMF does not find a second OOA in winter and no SFOA in summer points in this direction. Was a separation in seasons tried and compared (e.g. division of the data according to average daily temperature)? The presented approach to deconvolve the OOA2 factor may solve that issue to some extent but a seasonwise approach or the application of the increased rotational control provided by the ME2 may improve the solution. In the discussion of the different factor solutions in the supplement an inclusion of the residuals time series instead of just the sum of Q/Q_{exp} is desirable, if possible.

- *Although ME2 may improve the solution in the ways described by the reviewer, the first stage of performing ME2 analysis is to run an unconstrained apportionment by way of PMF analysis thus the analysis presented in this study will be used in further analyses including ME2. In addition, the methods presented in Crippa et al., 2014 (doi:10.5194/acp-14-6159-2014) may not necessarily be relevant to urban environments, especially as only two out of the 17 measurement sites were in urban locations and consequently much work will be needed to validate the methods for this use. More importantly, in order to use ME2 one*

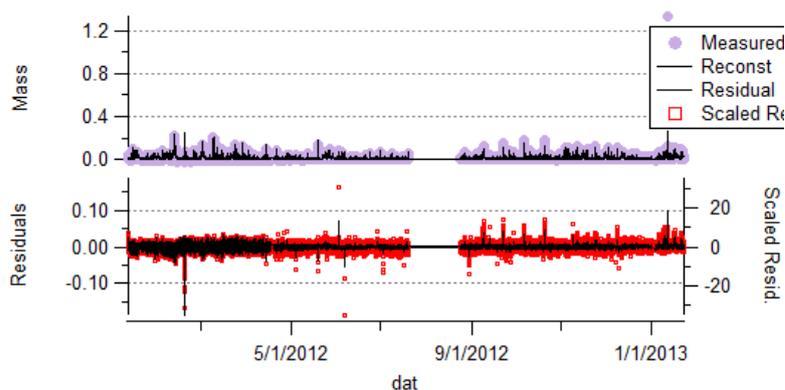
would need to employ source profiles and as it is likely that these are not constant from place to place, one would need to use suitable profiles i.e. source profiles specifically for London.

- The suggestion that OOA2 is an overlap of LVOOA in the summer and aged BBOA in the winter is a very interesting one and we thank the referee for their comments and analysis suggestions. The r^2 (Pearson's r) for OOA2 vs NO_3 in the summer is 0.08 (0.28), whereas for the winter it is 0.19 (0.43) where winter is January-February 2012, December 2012, and January 2013. Separately, the r^2 for JF is 0.16 and for DJ it is 0.22. Unfortunately no levoglucosan measurements are available during the summer. However, the correlations between OOA2 and NO_3 for the two different periods suggest that OOA2 is not likely to be an overlap of LVOOA and aged BBOA depending on the season. The following has been added at line 4, page 18756: "The possibility that OOA2_{PMF} could be an overlap of what is OOA1 in the summer and an aged SFOA in the winter has been explored but correlations between OOA2_{PMF} and nitrate suggest that this is not likely to be the case."
- Regarding the residuals, see plots below. The two key m/z 's for SFOA are shown. Apart from the noise, it is not particularly clear that there is any significant difference between winter and summer for these m/z 's.

Residuals for m/z 60:



Residuals for m/z 73:



- The residuals time series has been included in Figure S21 in the Supplementary as requested.

Some more minor comments:

- P 18741 L 26: Not sure if Zhang is a good citation here, I suggest to change to doi:10.1038/nature13774 or similar.
 - *The authors thank the reviewer for the link to the paper by Huang et al. (2014), which was published after this manuscript was published in ACPD. The Huang et al. (2014) paper is very interesting; however there is no specific mention on the build-up of primary organic aerosols during winter due to meteorological conditions. The citation has been included along with that of Zhang et al. (2007) to provide references for the full comment in the manuscript.*

- P 18749 L 5: Mention ACSM in this section? Since it is related and used for long-term measurements routinely.
 - We think the referee may have meant page 18743, line 2 in relation to this comment rather than page 18749, line 5. The following sentence has been included at line 2, page 18743 in the revised manuscript: “The related aerosol chemical speciation monitor (ACSM, Ng et al., 2011a), however, is routinely used for long-term measurements of aerosol chemical composition.” Consequently, only the acronym ACSM is used on page 18753, line 1 as it has now been written out in full earlier in the manuscript.

- P 18744 L1+10: As a non British it would be nice for me to know what DEFRA and NERC stands for.
 - *This comment has been addressed in the revised manuscript.*

- P18745 L18: Can you specify at what current the filament was run and did you estimate the effect on the S/N?
 - *The average filament emission from the full measurement campaign was 0.36 mA. By comparing the strength of the airbeam signal during this campaign with others running under normal conditions (where the emission current is typically around 0.5 mA), we can estimate that we had an overall reduction in the S/N of approximately 40%, although this also includes the reduction in S/N due to the detuning of the heater bias.*

- P 18743 L22 + 18751 L9: summarize or summarise?
 - *This comment has been addressed in the revised manuscript.*

- P18746 L1: I miss a description of the IE? Was an averaged IE used or did you adjust that over time? RIE: there were no significant changes in the RIE over the year? Even after major modifications (e.g. filament, vacuum pump, MCP change)
 - *An average IE determined from all of the calibrations was applied to the full dataset, which was 7.24×10^{-8} . No trends in the variation of the IE/MS airbeam during were apparent, nor was the variation systematic, indicating that the differences in IE from the different calibrations were not likely to be due to degradation of the components within the AMS, for example. However, the corresponding standard deviation was 1.76×10^{-8} indicating that there is some uncertainty in the average IE value used due to variations. The following sentence has been included on page 18745, line 23: “An*

average ionisation efficiency (IE) determined from all calibrations was applied to the full data set.”

- *The RIE for ammonium was found to be very consistent throughout the year. Unfortunately, it was only later in the year, following comparisons of the data from the cToF-AMS with the HR-ToF-AMS for the winter IOP, that sulphate calibrations were also performed when possible. Despite only a few calibrations being performed, the results were still very consistent between the different calibrations.*
- P18746 L 16: Was it not possible to correct for these step changes with the flowrate and airbeam signal
 - *Step changes evident in the flowrate were not necessarily reflected in the concentration data. For example, the longest period of time where the flowrate was lower than usual occurred was 5-22 June 2012 (see Fig. S3a) but there was no step change in the concentrations on the 5th. In fact, concentrations during this period were not too different from the period before any changes in the flowrate occurred. Consequently it was not clear what period of time any corrections could/should be applied to. However, some data were removed but this only totalled 0.08% of the data. Less than 5% of the data were flagged as suspect but even then the effect of the changes in flowrate on the concentrations were not obvious and were not highlighted as being problematic from other analyses, such as PMF.*
- P18752 L16: As mentioned above splitting into seasons may avoid some problems of factor mixing. Indeed, a split just according to dates may not be the best option but one could define better objective criteria like average daily temperature.
 - See response to similar comment from Referee #1 (comment 3).
- Why is information lost by splitting the data? I do not understand this argument. PMF works also well on shorter periods as it was shown in many studies and factor profiles, especially of the secondaries which have different precursors summer and winter may change a bit over time. With shorter periods one could capture that to some extent and gain (not loose) information on annual trends.
 - *If the data are split according to season, the equivalent factors may have different profiles between seasons and there will be step changes between the different periods. As such, this makes it difficult to directly compare factors from different seasons and thus assess year-round behaviour of these factors. Furthermore, unless the same factors were identified from all seasons, a true analysis of the temporal trends of each factor could not be performed. Indeed, analysis of shorter time periods could capture more information, but on the sources or precursors of the aerosols within that period, rather than the longer temporal trends. Please also refer to our response to reviewer 1, comment 3.*
- P 18752 L 24: No a priori knowledge is needed to run ME2. It is just possible to add additional constraints but not mandatory. Basically the addition of these additional constraints (i.e. factor profiles with some degree of freedom) gives you just a handle to explore more rotations (in a way similar, but much more complex than fpeak).

- *The first stage of running ME2 is to run it without constraint, which is in effect running PMF. Any additional constraints requires a priori knowledge of what is expected from the factors e.g. in the form of prescribed profiles. Basically, if no constraints are added in ME2 then one is effectively running PMF. If constraints are added then a priori assumptions need to be made. See Canonaco et al. (2013 - doi:10.5194/amt-6-3649-2013), particularly Section 2.2.5: “Here the elements of the F matrix (factor profiles) and/or of the G matrix (factor time series) can be constrained by the user. The user inputs one or more factor profiles (rows of F)/factor time series (columns of G) and a constraint defined by the scalar a that can be applied to the entire profile/time series or to individual elements of the profile/time series only.” Furthermore, we need to know the source profiles for London in order to be able to perform ME2 on the dataset from this study. Please also see the response to the first general comment regarding ME2.*

- P18754 L2: Even with your reduce S/N due to the lower filament setting you have much larger S/N than the ACSM?
 - *We think this comment refers to P18753, L2. Comparison of the detection limits quoted in Drewnick et al. (2009 - doi:10.5194/amt-2-33-2009) with those quoted in Ng et al. (2011 doi:10.1080/02786826.2011.560211), the ToF-AMS data averaged over 30 seconds has an organic detection limit of 30 ngm⁻³ while the equivalent statistic for the ACSM is 148 ng m⁻³ when averaged over 30 minutes. This makes for a factor of 40 difference in overall signal to noise. Line 2, page 18753 has been edited in the revised manuscript to: “Furthermore, several of the factorisation problems that ME-2 overcomes when applied to data from the ACSM (Ng et al., 2011a) compared to the AMS are related to the fact that the ACSM has much lower signal-to-noise ratio (approximately by a factor of 40).”*

- P18756 L 5-10: I have difficulties understanding this paragraph. Please clarify.
 - *This paragraph has been reworked in the revised manuscript to: “This is not to suggest that all OOA2 factors contain some contribution of SFOA. However, if SFOA is convolved with OOA2, as is the case in this study, it is possible to estimate the proportion of SFOA convolved with OOA2 with the support of additional measurements. In this study we have shown that comparisons of measurements from the two AMSs highlighted a large difference in SFOA concentrations, which was further supported by levoglucosan measurements and those from the cToF-AMS itself such as org60. Improved separation of OA factors may be achieved in the future, particularly in the absence of supporting measurements, from the application of ME-2 to similar datasets such as those from the ACSM.”*

- P18764 L9: How can you comment on the change of the oxidation of SOA. The SOA result you get from the PMF only gives you two fixed factors over the whole 1a period. Please clarify.
 - *In this analysis, the triangle plot is being used independently of the two SOA factors. The two SOA factors derived from PMF are plotted in figure 7 for reference and the conclusion on the oxidation of SOA was not based on the two fixed factors. The small*

squares in the plot are the daily averages of SOA as a whole, which was calculated by removing the contribution of the derived primary OA factors from the full organic aerosol matrix. The remainder was assumed to be secondary OA. No obvious trends in SOA oxidation with temperature or time of year are apparent in this plot. This has been described in the manuscript in Section 5.2, specifically page 18760, line 20 to page 18761, line 15. In addition, line 10 on page 18760 in the revised manuscript has been changed to the following: "The f_{44} and f_{43} for the two OOA components identified from PMF analysis in this study, which are fixed factors over the whole one year period, are therefore also plotted within the f_{44} vs. f_{43} space to further constrain the degree of oxidation of what is hypothesised to be London SOA." Please also see our response to reviewer 1, comment 9.

- Fig. 4: It is difficult to see anything in this plot on my printout. Is the OOA2 sometimes negative? PMF results should, as the name says always be positive
 - *The OOA2 in the plot in figure 4 is not the OOA2 derived from PMF analysis but rather the calculated $OOA2_{mod}$ and is thus not constrained to be positive. Although a concentration cannot physically be negative, the level of uncertainty in estimating the concentrations using the method described in Section 4.4 is provided by way of the standard deviation for the $OOA2_{mod}$ concentration ($0.46 \mu\text{g m}^{-3}$ for that particular period, the winter IOP, line 15, page 18757. For the whole campaign the standard deviation for $OOA2_{mod}$ was $0.29 \mu\text{g m}^{-3}$, line 17, page 18758).*
- Supplement P3: You don't downweight to reduce signal. You downweight to reduce the influence of some signals to the PMF solution in order avoid PMF to try explain noise. Also the modification of the m/z44 related channels is rather a "not upweighting" than a downweighting.
 - *This has been addressed in the revised Supplementary Information document on page 8 in paragraph 1 of Section 4.1 to be as follows: "Ions with a signal to noise ratio of less than 2 were deemed 'weak' and downweighted by a factor of 2. Downweighting was performed to reduce the influence of some signals to the PMF solution in order to avoid PMF trying to explain the noise. Those peaks related to the CO_2^+ ion (m/z 44) were also downweighted, or rather 'not upweighted', to reduce the influence from duplicated ions to the signal. "*

After these concerns have been addressed I recommend publication of this manuscript