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.*

o *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-PM$_1$ 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 <u>most</u> of the SFOA$_{PMF}$ mass measured by the cToF-AMS is being assigned to OO2$_{PMF}$ 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 OOAs 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.
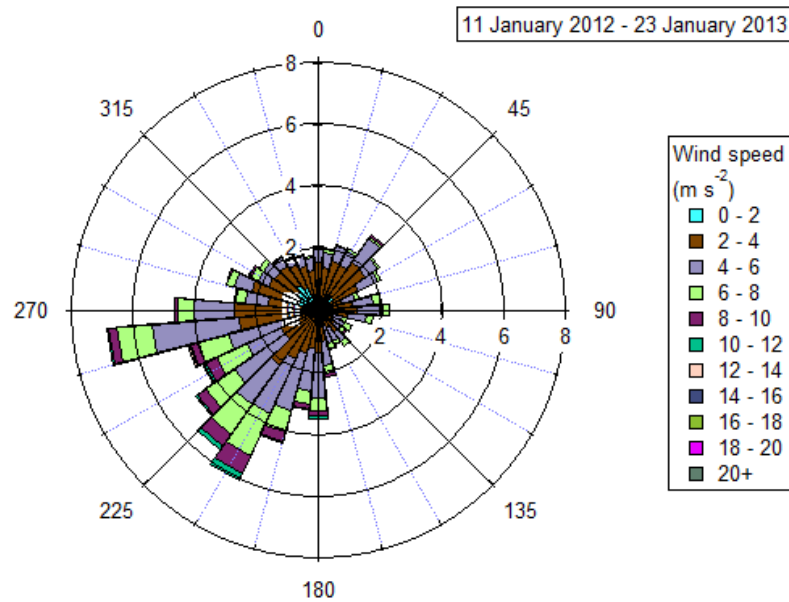
In addition, 1 day back trajectories using outputs from the UK Met. Office's NAME (Numerical Atmospheric Dispersion Modelling Environment - (Jones et al., 2007 - Air Pollut. Model. Appl. XVII 17, 580–589.; Ryall and Maryon, 1998 - doi:10.1016/S1352-2310(98)00177-0) dispersion model described in Fleming 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 (± one standard deviation) was 24.1 ppb (± 12.1) and for 20 July-24 August (the period of data removed from PMF analysis) was 26.1 (± 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).*