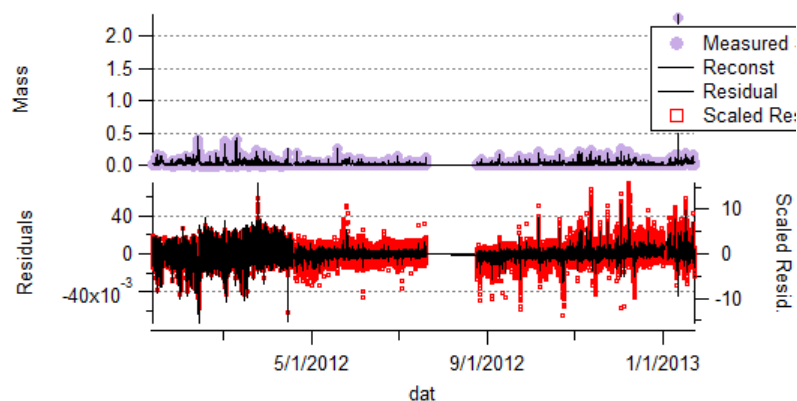


Anonymous referee #2

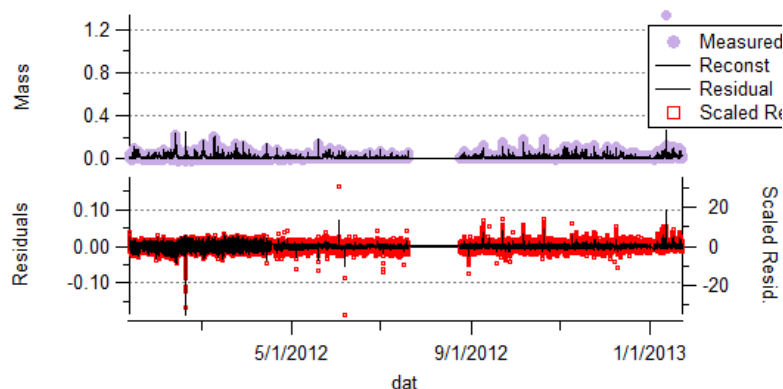
In the present manuscript Young et al. present data and source apportionment results from one of the longest AMS measurement campaigns so far. The paper focuses mainly on secondary aerosols. The authors take great care in documenting their PMF analysis, which is commendable. Anyhow, my main concerns 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 NO₃ 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 NO₃ 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 ng m^{-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 CO₂⁺ 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