## Answers to the third referee

General comments

1. I also agree with reviewer #2 that the title should be made broader since the current title does not accurately represent the focus of this paper. I recommend adding information such as winter/summer comparison of OOA sources and oxidation using f43 and f44 and the relationship to OX.
*See comments to the 2nd referee to the first general consideration*

2. PMF of ACSM data is relatively new. This paper could have a larger impact if it elaborated more on how and why the specific type of PMF was run on this dataset. References to any previous PMF of ACSM data should be included if available.
More specifically, it is not clear why the primary factors (HOA, COA, BBOA) were constrained. Was it not possible to get PMF results with similar mass spectral profiles to previous results and could be supported by other measurements with their time series? I would suggest adding to the experimental methods section why PMF was run the way it was, with constraining the primary factors. If it is not possible to get representative and supportable PMF results from ACSM data without constraining the primary factors.
*A full discussion of the PMF method is presented in response to the comments of the 2nd referee to the fourth general consideration.*
*In particular, we note that the studies of Lanz et al. (2008) and Canonaco et al. (2013) have shown improved model performance, i.e. higher correlations between factor time series and factor profiles with relevant tracers, when including a priori information in form of known POA factor profiles in the PMF model using the ME-2 solver.*

3. It appears that the COA diurnal cycle is relatively flat. Without comparing it with other measurements, how can you be sure COA is present within this dataset? Was PMF run without COA to compare the fit and resulting time series of the PMF factors? Winter COA and BBOA appear to have similar mass spectral signatures – can you be certain both are needed to explain and/or present in this data? Perhaps previous measurements of HR-ToF-AMS measurements (and PMF analysis) from Zurich could be referenced to support the use of the 3 primary factors for this data set.it would be noteworthy for the community to know.
*The COA factor was introduced in order to explain the meal activities (bump at noon and evening dinner peak, especially for the summer case). A PMF run without a COA factor is not able to capture this information that would remain in the diurnal residual, as was previously discussed in Canonaco et al 2013 for the winter case.*
*There are no published HR-ToF-AMS PMF analyses of measurements conducted in Zurich.*

4. Are LV-OOA and SV-OOA PMF results supported by other measurements in order to verify their representation of different OOA's? Usually, PMF factors are plotted alongside other measurements to substantiate how they are believed to represent

different OA types/sources. If this is not deemed necessary or no longer required by the community since the factors have become more "standard" due to their mass spectral signatures alone, the reasons for this should be stated. Why wasn't a single OOA factor used?

*Figure 1 shows the f44/f43 for SOA (i.e. OOA) in winter and summer. From visual inspection, it is evident that the points do not form a simple "cloud", but rather suggest a line. This indicates that a single factor is inadequate to represent the spectral variability in OOA. On increasing the number of (OOA) factors, we retrieve factors consistent with previously published spectral and temporal characteristics of LV-OOA and SV-OOA. Further, the different location (and apparent slope) of the data points in the f44/f43 space indicates that the winter and summer cases each require unique LV-OOA and SV-OOA profiles. These points are now clarified in the text as follows:*

*"Visual inspection of Fig. 1 indicates that the SOA points do not form a cloud, but rather suggest a line. This indicates that a single OOA factor cannot adequately represent SOA spectral variability in both seasons and at least two OOA factors with consistent characteristics of SV-OOA and LV-OOA are required. Note that the different location (and apparent slope) in the f44/f43 space of the winter and summer data indicates that a combined winter/summer PMF would fail to capture the seasonal variability in OOA."*

5. Most of the paper looks at f43 and f44 from the summed OOA factors. What would the results look like if the two OOA factors were constrained in the same way as the primary factors? The diurnal profile for the factors are not correlated with any other measurements to substantiate their representation of different "sources". SVOOA does increase when NOx does (Fig. S.3), however, the LV-OOA appears to have no diurnal cycle. I have a hard time following the idea of conversion of SV-OOA to LVOOA, when the diurnal profile of LV-OOA is flat. This seems to indicate LV-OOA could just be representing a well mixed (regional?) background aerosol.

*See comments to the 2$^{nd}$ referee to the fourth general consideration regarding the difficulties in constraining OOA factors.*

*In summer LV-OOA is anticorrelated to SV-OOA pointing towards the possible SV-OOA to LV-OOA conversion (see Figure S6).*

*In winter the LV-OOA diurnal cycle is rather flat. However, this flat profile must compensate for the daily boundary layer dilution (CO is also decreasing by ~10% during the afternoon). Hence, there must be some production of LV-OOA, in order to keep the LV-OOA cycle flat (either gas-phase to LV-OOA or SV-OOA to LV-OOA transformation). The latter has been emphasized in the result section (3.1) and the sentence reads as following:*

*"In addition, the daily cycle of LV-OOA is rather flat (winter) or shows an increase during the afternoon (summer), representing either the conversion of SV-OOA to LV-OOA or direct LV-OOA formation from the gas-phase and thus compensating the effect of boundary layer dilution and / or advecting air masses containing background LV-OOA."*

6. Abstract: In agreement with referee #2 (comment 2), the Abstract needs to be revised. The second paragraph is speculative, and either needs further justification or

should be removed. It is not clear how aqueous processing is the likely reason for the higher f 44 values. The third paragraph should be elaborated upon or moved to the first paragraph since it is only one sentence. I think this is a large focus for this paper, therefore, would recommend adding more results to this section.
*See comments to the 2nd referee to the second general consideration*

7. Page 28081, Lines 15-18: The sentence mentions PMF being "frequently" used on AMS datasets but does not provide any citations for the previous work. I suggest citing the following paper: I.M. Ulbrich, M.R. Canagaratna, Q. Zhang, D.R. Worsnop, and J.L. Jimenez. Interpretation of Organic Components from Positive Matrix Factorization of Aerosol Mass Spectrometric Data. Atmospheric Chemistry and Physics , 9, 2891-2918, 2009.
*We agree and now cite the PMF studies of Lanz et al (2007) and Ulbrich et al (2009), as well as the source apportionment review of Zhang et al (2011).*

8. Page 28081, Lines 26-27: This sentence should be elaborated upon or removed, since it seems to be a tangential comment without further information as it is currently.
*We agree and have removed the sentence.*

9. Page 28082, Lines 16, 20: These reactions are simplified net chemical reactions. I recommend adding citations for readers interested in understanding the chemistry in more detail, especially for the VOC reaction.
*We agree and cited Seinfeld and Pandis (2006) for further reading.*

10. Page 28086, Lines 17: COA is mentioned to peak during noon. There is a peak at this time, but the larger peak for both seasons occurs in the evening. This could be hypothesized to be barbequing in the summer, but how is this peak explained for the winter?
*This point has been clarified by addition of the following sentence:*
*"Fig. S.3 and S.6 reveal an increase in contribution for all factors during the late evening and at night in winter and summer. This is mostly governed by a smaller boundary layer in the evening compared to midday that tends to concentrate all emissions."*

11. Page 28086, Lines 21-22: Is there information/references on timescales of conversion of SV-OOA to LV-OOA? References like this could further substantiate the theory that rapid conversion of SV-OOA to LV-OOA can occur and is the source of the increased LV-OOA observed in the afternoon. Without further discussion, this sentence stands as conjecture. It also needs to be stated that this is only for the summer data as this is not seen for during the winter.
*We agree with the reviewer and rephrased the three sentences dealing with the VOC to SV-OOA/LV-OOA transformation. In addition we also generalized the sentences and added besides the SV-OOA – LV-OOA conversion route also the general gas-phase LV-OOA conversion route and the two sentences read now:*

*"These sources emit VOCs that are transformed to SV-OOA and further to LV-OOA or directly to LV-OOA (orange arrows in the figure). Due to a substantial amount of VOCs and SV-OOA in summer, the production rate of LV-OOA from either SV-OOA or VOC's typically occurs on a timescale of hours (e.g. Jimenez et al 2009). The concentration of OX in the atmosphere is related to the net aging processes and is therefore linked to the conversion from VOC to SV-OOA and/or LV-OOA and from SV-OOA to LV-OOA.*

12. Page 28089, Section 3.3.2: It is mentioned that overnight more SV-OOA condenses from the previous day, which increases f43 and decreases f44. While this is overall true in the points shown in Figure 4, there is one day where only the f44 decreases, and more importantly one day where f44 increases. These opposing trends should be mentioned with potential explanations in the text.
*The following sentence has been added to the main text, in order to clarify the behavior of this point:*
*"Only a single pair of points in Fig. 3b, at the lowest temperature (and high statistical uncertainty due to few data points) violates this trend."*

13. Page 28090, Lines 5-11: This result seems very interesting. I strongly suggest adding a plot of your ambient data to show the trend visually for f44/f43 as a function of OOA mass loading, including also the fit lines for your data and the experimental data referenced.
*We share the opinion of the reviewer and therefore updated figure S7 containing now f44 and f43 as a function of total OA mass for the summer data.*

14. Page 28090, Lines 28 – Page 28091, Line 1: It is not clear to me what the authors mean when they say "the bulk OOA f 44 (LV-OOA) is rather flat with increasing OX at the expense of the bulk OOA f 43 (SV-OOA)". F44 does remain flat, while f43 increases with OX, however, what is meant by "at the expense" I am not clear on since f43 is changing while f44 remains constant, which to me means there is no effect. If a relationship is being mentioned here between f43 and f44 in response to changing OX, this needs to be explained in more detail.
*The sentence contained a wrong reference and the meaning was reversed. We updated the sentence which reads now:*
*"However, Fig. 2b indicates that the bulk OOA f44 (LV-OOA) is rather flat and the bulk OOA f43 (SV-OOA) is enhanced with increasing OX, as also shown in Fig. 2c."*

15. 2 and 5: Based on the text, I believe these figures are from summer only data. Please add the correct specification to the caption for the figure to make it clear to the reader which data is being shown. Why is only the median value included? Would it not be informative to also show the mean values?
*We now note that these figures include only summer data.*
*We agree with the reviewer in that reporting the mean value is also informative. However, we report the median, quartiles, the 10$^{th}$ and 90$^{th}$ percentiles, aiming to represent the distribution of the points under consideration. The authors have the*

*impression that the graphs would be too packed, when adding an additional symbol for the mean value.*

Specific comments

1. Page 28081, Line 10: The manufacturer's company name should be referenced in the experimental details, but is not necessary here.
*We agree with the reviewer and added the manufacturer's company name and the model type for the NOx monitor mentioned in the main text (Horiba APNA 360).*

2. Page 28083, Line 5: suggest adding a reference for PMF using ME-2
*We now reference Paatero 1999.*

3. Page 28083, Line 6: change "will be" to "are" or "are shown to be"
*changed*

4. Page 28084, Line 9: at the end of the sentence add " per unit time". In would be helpful to the reader to make clear that the rows are the time axis as well.
*added*

5. Page 28090, Line 3: Sentence references Figure S7 – should it not be Figure 5(c)?
*corrected and now the reference is to both Fig. 5(c) and S7*

6. Page 28091, Line 1: Should this be referencing Figure 2(c) instead of Figure 3? Since figure 3 does not include OX.
*corrected*

7. Figure 1: When printed, the very light grey points disappear. I would suggest adding a solid border to the points, changing to a color scale or a similar modification so the points are not lost. It also would be nice for comparison if both (a) and (b) had the same mass concentration scales.
*We have changed the color scale*

8. Figures 3 and 4: Suggest combining into one figure since the two plots are very similar,
and referencing them close together is beneficial.
*The figures have been combined.*

9. Figure S.3 and S.6: Move the figure Key box so that it is not covering any of the data. It is not possible to see the full diurnal profile of the LV-OOA where it is currently.
*done*

10. Figure S.4: Figure caption says "winter" in the text – change to "summer".
*done*