

## Answers to the second referee

### General comments

1. The authors may consider to modify the title, as the overall discussion is not focus on the relationship between the degree of oxygenation of OOA and the levels of oxidants. Rather, the manuscript is likely to improve our understanding of biogenic secondary organic aerosol (BSOA) formation due to enhanced BVOCs emission at high temperature. Furthermore, based on the f44/f43 space and diurnal cycles analysis, it is clear that the observed relationship can be only applied to the data observed in annual basis. The high loading of more oxygenated LV-OOA is clearly observed in the afternoon due to active photochemistry or high temperature (Figures shown in supplementary information). The authors should take extra care to deliver this message to the reader.

*We agree with the reviewers 2 and 3, in that the current title doesn't completely cover all presented results. We reformulated the title as follows:*

*"Seasonal differences in oxygenated organic aerosol (OOA) composition: implications for emissions sources and factor analysis"*

2. Abstract: It is recommended to remove the second paragraph of the abstract because it is a speculation without further support throughout the manuscript. Furthermore, the authors should clearly state the key findings from the interpretation of f44/f43 space in the third paragraph. Otherwise, it can be removed as well.

*The speculative sentence has been removed. The sentence about the f44/f43 space has been rewritten and better embedded into the abstract:*

*"...f44 for ambient SOA is not higher but is rather similar or lower than on days with low OX. On the other hand, f43 (representing less oxidized ions) increases. These changes are discussed in the f44/f43 space frequently used to interpret ACSM and aerosol mass spectrometer (AMS) data."*

3. Introduction, Page 28081, line 25-26: Please provides appropriate references to support the argument that "LV-OOA results mostly from photochemical and/or aqueous aging of SV-OOA: ". Please also clarify whether aging of primary organic aerosol (i.e. hydrocarbon-like OA and biomass burning OA) can produce LV-OOA significantly especially in the urban environments.

*The LV-OOA/SV-OOA sentence has been referenced and slightly modified:*

*"SV-OOA usually represents freshly formed OOA, whereas LV-OOA may result from photochemical aging of SV-OOA, direct gas-phase to LV-OOA conversion, or aqueous-phase chemistry, all of which lead to a net increase of OOA f44 with atmospheric age (Hallquist et al. 2009)."*

4. Section 2.2, Page 28085, line 12-24: It is uncommon to perform PMF analysis of standard AMS measurements with factor profile (i.e. mass spectra) constraints. Please clearly state 1) the reasons to run the PMF by constraining the primary sources but 2)

not secondary oxygenated organic aerosols. It is directly related to the estimation of OOA f43 and f44 described in Section 2.3.

*In the current study, mass spectral constraints serve as a means of exploring the rotational ambiguity of the PMF solution. Rotational ambiguity, i.e. the possibility that different combinations of factor profiles and time series yield a similar goodness of fit to the data, is a well-known complication of PMF analysis. Most of the past AMS/ACSM PMF analyses explored the solution space with the global fpeak that provides a lower estimate of the rotational ambiguity (Paatero et al 2014). As a consequence, it is possible (even likely) that the environmentally optimal PMF solution might be inaccessible and mixed factor time series and/or factor profiles would need to be accepted. The ME-2 algorithm used herein can access the entire solution space. To achieve this in a computationally efficient way, we constrain selected factor profiles using our a priori knowledge of site characteristics and the large body of existing AMS/ACSM PMF analyses. This strategy was introduced for ACSM data in Canonaco et al 2013 and further discussed in Crippa et al 2014 for AMS data. This approach has only recently seen wide application to AMS/ACSM data, but several publications already demonstrate its feasibility and/or superiority to conventional PMF analyses (e.g. Lanz et al. 2008, Canonaco et al. 2013, Crippa et al., 2014, Poulain et al., 2014, Minguillón et al., 2015).*

*The reviewer touches on an important point in noting that we constrain POA sources but not SOA. PMF analyses empirically define POA as being directly emitted from a source, e.g. traffic or cooking and therefore independent from chemical conversion processes and/or meteorological parameters. A number of previous (unconstrained) PMF analyses have shown that POA profiles (e.g. HOA, COA, and to some extent BBOA) have similar factor mass spectra independent of the site. It is therefore reasonable to draw on this previous work to set boundary conditions on the profiles of one or more of these species at a new site, if they are inferred to be present.*

*In contrast to POA, the SOA mass spectrum depends on many parameters, e.g. precursor gases, photochemical age, oxidation mechanism, and atmospheric conditions (e.g. temperature-driven partitioning). Meaningful constraints on one or more SOA profiles would require consideration of all these factors and knowledge of their links to spectral characteristics, which is not possible given the current state of the science.*

*In order to clarify these thoughts we added the following sentences to the main text at the end of subsection 2.2:*

*“Generally, primary aerosol components are assumed to be unaffected by meteorological and chemical aging processes, since they represent fresh emissions. This assumption is empirically supported by the similarities in POA profiles retrieved in PMF analyses at many sites, e.g. in Ng et al. 2011a. This allows the model to be constrained using POA factor profiles from other PMF studies and allowing dataset-specific optimizations with the ME-2 solver using the  $\alpha$ -value technique. In contrast to POA, OOA profiles (i.e. SOA composition) depend on many parameters, e.g. precursor gases, aging processes and atmospheric conditions. To appropriately constrain an OOA profile, the effect of these considerations on the spectral profiles must be known, but this is not*

*currently possible. Therefore, OOA factors are not constrained but rather allowed to be modeled by PMF.”*

5. Section 3.1, page 28068:

1) Line 17: The cooking factor has a stronger peak at night (i.e. dinner time) in both seasons as shown in Figure S3 and S6. Please modify the sentence.

*Sentence has been modified to read:*

*“Note that the solutions are environmentally reasonable, e.g. the traffic factor correlates with NO<sub>x</sub> and EC, the cooking factor peaks during mealtimes (noon and evening), BBOA is higher at night and lower during the day accounting for nocturnal heating in winter and barbecuing and possible local fire events in summer, the daily cycle of SV-OOA is anticorrelated with temperature for the winter and summer data (Fig. S.3 and S.6).*

*This underlines the fact that this factor was tagged as cooking factor due to the present lunch activity around noon.*

2) Line 20-22: The conversions of SV-OOA to LV-OOA was observed in the summer time only. Instead, the SV-OOA diurnal cycle correlates with HOA and COA quite well in the winter, indicating that the formation of SV-OOA might be related to other human activities. Please clarify.

*The visible diurnal correlation between SV-OOA and the other primary sources encountered in winter is mainly due to boundary layer effects (e.g. the diurnal cycle of CO (not shown) is similar to SV-OOA). Therefore, we believe this correlation does not imply a direct source relationship.*

6. Section 3.1, page 28087, line 7-10: Which biogenic compounds are studied by Pfaffenberger et al. (2013)? If they only investigated alpha-pinene (from Figure 1 caption), can the authors provide further evidence to demonstrate that the OOA observed in the summer dominated by alpha-pinene SOA?

*Oderbolz et al (2013) showed that monoterpenes are the major biogenic precursors for SOA in central Europe; isoprene SOA is also expected to contribute, and sesquiterpene SOA is negligible. Steinbrecher et al. (2009) found that  $\alpha$ -pinene is the most abundant monoterpene. In addition, a very recent study by D’Andrea et al. (2015) found that in Central Europe, monoterpene SOA is higher than isoprene and sesquiterpene SOA combined. Therefore, the  $\alpha$ -pinene experiments of Pfaffenberger et al. (2013) are likely a reasonable surrogate for biogenic SOA. Further, Chhabra et al. (2011) demonstrated that isoprene SOA has a similar f<sub>44</sub>/f<sub>43</sub> relationship to  $\alpha$ -pinene SOA. Although we cannot rule out the possibility that SOA from other monoterpenes may somewhat perturb the f<sub>44</sub>/f<sub>43</sub> behavior of ambient biogenic SOA, the observed ambient SOA is consistent with that of the major biogenic SOA precursors expected in Switzerland. This interpretation is also consistent with the observation that summer OA in Zürich is mostly non-fossil (Szidat et al., 2006).*

*The sentence introducing the alpha-pinene study at the end of subchapter 3.1 now reads as follows:*

*“The winter SV-OOA lies more on the left side of the triangular space, whereas the summer SV-OOA is on the right side of the triangular space. These locations are comparable with the location of SOA from smog chamber studies conducted with biomass burning (Heringa et al 2011) and for  $\alpha$ -pinene (Pfaffenberger et al. 2013). The data from these two studies are represented with orange rectangles in Figs. 1a and 1b, respectively.”*

*Chhabra, P. S., Ng, N. L., Canagaratna, M. R., Corrigan A. L., Russel L. M., Worsnop2, D. R., Flagan, R. C., Seinfeld, J. H.: Elemental composition and oxidation of chamber organic aerosol, *Atmos. Chem. Phys.*, 11, 8827-8845, 2011.*

*D’Andrea, S. D., Acosta Navarro, J. C., Farina, S. C., Scott, C. E., Rap, A., Farmer, D. K., Spracklen, D. V., Riipinen, I., Pierce, J. R.: Aerosol size distribution and radiative forcing response to anthropogenically driven historical changes in biogenic secondary organic aerosol formation, 15, 2247–2268, 2015.*

*Oderbolz, D. C., Aksoyoglu, S., Keller, J., Barmpadimos, I., Steinbrecher, R., Skjøth, C. A., Plaß-Dülmer, C., and Prévôt, A. S. H.: A comprehensive emission inventory of biogenic volatile organic compounds in Europe: improved seasonality and land-cover, *Atmos. Chem. Phys.*, 13, 1689-1712, doi:10.5194/acp-13-1689-2013, 2013.*

*Steinbrecher, R., Smiatek, G., Koble, R., Seufert, G., Theloke, J., Hauff, K., Ciccioli, P., Vautard, R., and Curci, G.: Intra- and inter-annual variability of VOC emissions from natural and seminatural vegetation in Europe and neighbouring countries, *Atmos. Environ.*, 43, 1380–1391, doi:10.1016/j.atmosenv.2008.09.072, 2009.*

*Szidat, S., Jenk, T. M., Synal, H.-A. Kalberer M., Wacker, L., Hajdas, I., Kasper-Giebl, A. , Baltensperger, U.: Contributions of fossil fuel, biomass-burning, and biogenic emissions to carbonaceous aerosols in Zurich as traced by  $^{14}\text{C}$ , *J. Geophys. Res.*, 111, D07206, doi:10.1029/2005JD006590, 2006.*

7. Section 3.2, page 28087, line 17-26: This is related to comment #5. The reviewer agrees that m/z 60 can be used as an indicator of biomass burning related POA and SOA. However, two points have to be clarified.

1) Why the SV-OOA diurnal cycle correlates well with HOA and COA (e.g. peaked at 10 am and 8 pm)? If the SV-OOA is secondary in nature (i.e. oxidation of biomass burning related VOCs as mentioned in the manuscript), its diurnal cycle should be better correlated with BBOA. This suggests that the SV-OOA formation might be somewhat influenced by other anthropogenic emissions.

*The correlation of the SV-OOA diurnal cycle with that of HOA and COA is related to boundary layer dynamics, as discussed in detail in response to question 5.2. The relationship of anthropogenic sources to SV-OOA is further investigated using  $^{14}\text{C}$  measurements in response to question 7.2.*

2) Even though the authors exclude the SV-OOA formation from traffic emissions based on the contributions of primary traffic emission to the observed total organic aerosol mass, is it possible that a significant amount of traffic-related VOCs (in addition to BB VOCs) involved the SV-OOA formation via gas-phase chemistry?

*We exclude traffic (POA and SOA) as a major source of SV-OOA based on the <sup>14</sup>C source apportionment analysis (Zotter et al 2014), which estimates that around 20% of the total organics are of fossil origin during winter in Zurich. Thus the sum of traffic-related POA and SOA cannot be higher than 20% of OA. The present study models 12% to the traffic POA (25% to SV-OOA, 40% to LV-OOA) leaving no more than 8% for traffic-derived SV-OOA and LV-OOA. Hence, SV-OOA will likely contain to some extent traffic SOA, but it is minor compared to the non-fossil contributions in winter. For summer, Szidat et al. (2006) showed that the organic aerosol in summer is also mostly non-fossil.*

*Szidat, S., Jenk, T. M., Synal, H.-A. Kalberer M., Wacker, L., Hajdas, I., Kasper-Giebl, A. , Baltensperger, U.: Contributions of fossil fuel, biomass-burning, and biogenic emissions to carbonaceous aerosols in Zurich as traced by <sup>14</sup>C, J. Geophys. Res., 111, D07206, doi:10.1029/2005JD006590, 2006.*

8. Section 3.3.2, page 28089: In addition to the condensation of freshly formed SVOOA, the diurnal cycle of LV-OOA peaked at the afternoon (Figure S6) is likely due to active photochemistry (i.e. OH oxidation). This may be another reason to make the day-time organic aerosol more oxygenated. Please clarify.

*We agree with the referee and added the following sentence:*

*“Moreover, oxidation processes enhancing the LV-OOA fraction during the afternoon, as highlighted by the diurnal cycle in Figure S6 will increase the daytime f<sub>44</sub> / f<sub>43</sub> ratio leading to an increased separation of the day versus night points.”*

#### Specific comments

1. Section 2.1, page 28083, line 14: The sampling period (January 2011 to February 2012) is different to those described in the abstract and introduction. Please correct.

*“January” has been replaced by “Feb.” and now the sampling time reads: “Feb. 2011 to Feb. 2012.”*

2. Section 2.1, page 28083, line 24: Please provide the instrument model for NO<sub>x</sub> measurement.

*The instrument name and model type were added (Horiba APNA 360)*

3. Section 3.1, page 28068, line 17: The cooking factor has a stronger peak at night (i.e. dinner time) in both seasons as shown in Figure S3 and S6. Please correct the sentence.

*Sentence has been modified to read: “...,the cooking factor peaks during the meal activities (lunch and evening peak) in the diurnal cycle, ...”*

*This underlines the fact that this factor was tagged as cooking factor due to the present lunch activity around noon.*

4. Page 28088, line 1-2: There are a lots of previous studies suggest that heterogeneous oxidation can also lead to LV-OOA formation.

*We added references to studies of heterogeneous oxidation of ambient OA (George et al 2008 and Slowik et al 2012).*

5. Page 28088, line 18-19: Please add references to support the relationship between biogenic emission and elevated temperature.

*We added the reference to Gunther et al 1997*

6. Figure S4 caption: It should be "....source apportionment over the summer...".

*"Winter" has been replaced with "summer".*