The authors want to kindly thank all reviewers for their very fruitful comments and thoughts. We include below a point by point response to their suggestions.

**Answers to the first referee**

Specific comments

1. Introduction Page 28081, Line 2 – Suggest adding have before generally
   done
2. Page 28082, Line 1 – Suggest adding experiments after chamber
   done
3. Page 28082, Lines 13, 15, and 18 – The chemical formulas used have not been defined
   All formulas are now defined in the text.
4. Acknowledgements Page 28092, Line 4 – Suggest changing author to authors
   done
5. References Page 28092, Line 11 – Accent marks are missing from Prevot, Page 28093, Line 20 – Accent marks are missing from Prevot, Page 28093
   done
6. Line 26 – Believe levels Of O-3 should be levels of O3
   done
7. Page 28093, Line 27 – Believe NO chi should be NOx
   done
8. Page 28094, Line 10 – Accent marks are missing from Prevot, Page 28094, Line 25 – Accent marks are missing from Prevot, Page 28095, Line 18 – Accent marks are missing from Prevot, Page 28095, Line 32 – Accent marks are missing from Prevot, Page 28096, Line 16 – Accent marks are missing from Prevot, Page 28097, Line 26 – Accent marks are missing from Prevot
   done
9. Figure 2 - Believe f43 on the y-axis of plot c should be in italics, Figure 4 - Believe f44 and f43 on the y- and x-axes should be in italics
   done
10. Figure 5 - It looks like there is something overlapping with the units on the y-axis of plot
    corrected
11. Supplementary Material Winter 2011 Page 1, Line 1 – Suggest removing the the before Winter
    done
12. Supplementary Material Winter 2011 Page 1, Line 3 – Suggest changing peak a to peak at
    done
13. Supplementary Material Winter 2011 Page 1, Figure S1 caption – In first line of caption suggest changing for the winter to during winter
    done
14. Supplementary Material Winter 2011 Page 2, Figure S2 caption – Suggest changing for the winter to during winter
    done
15. Supplementary Material Summer 2011 Page 3, Line 1 – Suggest removing the the before summer
    done
16. Supplementary Material Summer 2011 Page 3, Figure S4 caption – In first line of caption suggest changing over the winter to over summer
    done
17. Supplementary Material Summer 2011 Page 4, Figure S5 caption – In first line of
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 aqueousphase 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 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 a-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 NOx 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 α-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 α-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 f44/f43 relationship to α-pinene SOA. Although we cannot rule out the possibility that SOA from other monoterpenes may somewhat perturb the f44/f43 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 a-pine ne (Pfaffenberger et al. 2013). The data from these two studies are represented with orange rectangles in Figs. 1a and 1b, respectively.”


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 BBBOA. 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 $^{14}$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 $^{14}$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 SVOOA

and LV-OOA. Hence, SV-OOA will likely contain to some extend 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.


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 f44 / f43 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 NOx 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 lot 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".

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”. SV-OOA 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 LV-OOA, 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 2nd 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 f44 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 LVOOA conversion route and the two sentences read now:

These sources emit VOCs which 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 conversion rate generating LV-OOA from either SV-OOA or directly from VOC’s, typically occurring on a timescale of hours (Jimenez et al., 2009), is rather small.

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 which has high statistical uncertainty due to the small number of measurements it contains) 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 f44 (LV-OOA) is rather flat with increasing OX at the expense of the bulk OOA f43 (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 SOA f44 is rather flat with increasing OX in favor of the total OOA f43 (SV-OOA), 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 10th and 90th 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).


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


Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland

Abstract

Aerosol chemical speciation monitor (ACSM) measurements were performed in Zurich, Switzerland for 13 months (February 2011 through February 2012). Many previous studies using this or related instruments have utilized the fraction of organic mass measured at $m/z$ 44 ($f_{44}$), which is typically dominated by the $\text{CO}_2^+$ ion and related to oxygenation, as an indicator of atmospheric aging. The current study demonstrates that during summer afternoons, when photochemical processes are most vigorous as indicated by high oxidant OX ($\text{O}_3$+NO$_2$), $f_{44}$ for ambient SOA is not higher but is rather similar or lower than on days with low OX. On the other hand, $f_{43}$ (less oxidized fragment) tends to increase. These changes are discussed in the $f_{44}/f_{43}$ space frequently used to interpret ACSM and aerosol mass spectrometer (AMS) data. This is likely due to the formation of semi-volatile oxygenated aerosol produced from biogenic precursor gases, whose emissions increase with ambient temperature. In addition, source apportionment analyses conducted on winter and summer data using positive matrix factorization (PMF) yield semi-volatile oxygenated organic aerosol (SV-OOA) factors that retain source-related chemical information. Winter SV-OOA is highly influenced by biomass burning, whereas summer SV-OOA is to a high degree produced from biogenic precursor gases. These sources contribute to substantial differences between the winter and summer $f_{44}/f_{43}$ data, suggesting that PMF analysis of multi-season data employing only two OOA factors cannot capture the seasonal variability of OOA.
1. Introduction

Atmospheric aerosols are at the center of scientific and political discussions due to their highly uncertain direct and indirect climate effects (IPCC, 2007), their adverse impacts on human health (Peng et al., 2005), and their influence on our inhabited (Watson, 2002) and agricultural areas (Matson et al., 2002). Reliable identification and quantification of aerosol sources is essential for developing control strategies. The concentrations of particulate matter have generally decreased in the last 10-20 years in Europe and Switzerland but legal thresholds are still often exceeded (Barmpadimos et al., 2011; Barmpadimos et al., 2012). Atmospheric aerosols are classified based on their formation processes as primary and secondary aerosols, which are directly emitted into the atmosphere and formed from gas to particle conversion, respectively. Recently, the scientific focus has shifted towards submicron particulate matter (PM1) (Hallquist et al., 2009), especially the organic fraction, which typically comprises 20-90% of the total submicron aerosol mass (Jimenez et al., 2009).

Aerodyne aerosol mass spectrometers (AMS), including the aerosol chemical speciation monitor (ACSM), have become important and widely employed instruments for the chemical characterization of submicron organic aerosol (Canagaratna et al., 2007; Ng et al., 2011b). These instruments provide on-line quantitative mass spectra of the non-refractory (inorganic and organic) aerosol composition with high time resolution. Frequently, the organic fraction is further analyzed (Lanz et al., 2007; Ulbrich et al., 2009; Zhang et al., 2011) using the positive matrix factorization algorithm (PMF) proposed by Paatero and Tapper (1994), which represents the organic mass spectral matrix as a set of source/process-related factor mass spectra and time series. Compilation and comparison of northern hemispheric datasets led to the characterization of secondary organic aerosol (SOA)-related factors as semi-volatile and low volatility oxygenated organic aerosol (SV-OOA and LV-OOA) (Jimenez et al., 2009; Ng et al., 2010). The SV-OOA mass spectra have a higher fraction of $m/z$ 43 to organic mass ($f_{43}$) and a lower fraction of $m/z$ 44 to organic mass ($f_{44}$) relative to LV-OOA. SV-OOA and LV-OOA factors derived from ambient PMF analyses yield a triangle in the $f_{44}/f_{43}$ space (Ng et al., 2010). 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 (Ehn
et al., 2014), or aqueous-phase chemistry, all of which lead to a net increase of OOA \( f_{44} \) with atmospheric age (Hallquist et al., 2009).

Evidence from several smog chamber and ambient studies suggests that the location in the \( f_{44}/f_{43} \) space could carry information on the source of SV-OOA. The generation of SOA from smog chamber experiments indicates that for a given \( f_{44} \), SOA formed from wood burning experiments (Hennigan et al., 2011; Heringa et al., 2011) yields lower \( f_{43} \) than from biogenic precursors (Alfarra et al., 2012; Chhabra et al., 2011; Ng et al., 2010; Pfaffenberger et al., 2013). Recently, some ambient studies also showed that the \( f_{43} \) and \( f_{44} \) points lie in specific regions in the triangular space depending on the season (Crippa et al., 2014; Freney et al., 2011; Freney et al., 2014; Ge et al., 2012). However, the ambient studies showing the raw data points consider the total \( f_{43} \) and \( f_{44} \) fraction rather than the model-derived OOA. Thus, the position of these points is affected by the contribution of the primary sources, whereas in Ng et al. (2010) the triangular space referred to the modelled OOA factors, i.e. SV-OOA and LV-OOA only.

Photochemical oxidation constitutes a major production pathway for OOA. The tropospheric ozone concentration is mainly generated from the oxidation of volatile organic compounds (VOCs) initiated by the OH radical and is thus a useful indicator for photochemical activity. The net oxidation of the simplest VOC, methane (\( CH_4 \)) with oxygen (\( O_2 \)) leading to carbon monoxide (\( CO \)), water (\( H_2O \)), hydroxyl radical (\( OH \)) and ozone (\( O_3 \)), is represented in the presence of \( NO_x \) as follows (Seinfeld and Pandis, 2006):

\[
CH_4 + 8O_2 \rightarrow CO + H_2O + 2OH + 4O_3
\]  

The ozone molecules produced by these oxidation reactions participate in a rapid equilibrium between NO and \( NO_2 \), involving the photolysis of \( NO_2 \), summarized by:

\[
NO + O_3 \leftrightarrow NO_2 + O_2
\]

The sum of \( O_3 \) and \( NO_2 \) concentrations, defined as the oxidant OX (Alghamdi et al., 2014; Clapp and Jenkin, 2001; Jenkin, 2014), is therefore a proxy for atmospheric aging in the troposphere.

Lagrangian studies investigating the evolution of air parcels moving downwind from a city have shown an increase of the LV-OOA to SV-OOA ratio (implying an increase in total OOA \( f_{44} \)) as a function of the distance from the city center.
(Jimenez et al., 2009). However, field campaigns and monitoring networks typically rely on stationary measurements, representing Eulerian studies instead, for which the relationship between aging (i.e. OX) and $f_{44}$ is not strictly given.

In this study, ACSM aerosol mass spectra measured in Zurich between February 2011 and February 2012 were analyzed using the PMF algorithm in the multilinear engine (ME-2) implementation (Paatero, 1999). The transformation of OOA during the aging processes in summer is related to OX and temperature. Moreover, the OOA composition is characterized in terms of $f_{44}$ and $f_{43}$, investigating the extent to which precursor sources can be inferred from these values.

2. Materials and Methods

2.1. Measurements

The instruments and the methods employed for this study were described in detail by Canonaco et al. (2013), and only a brief overview is presented here. An ACSM (Aerodyne Research, Inc., Billerica, MA, USA) was deployed at the Kaserne station, an urban background station in the city center of Zurich (Switzerland), from February 2011 to February 2012. The ACSM is a compact aerosol mass spectrometer designed for long-term measurements of non-refractory particulate matter with vacuum aerodynamic diameters between approximately 60 and 600 nm, typically denoted as NR-PM1. The instrument is described in detail by Ng et al. (2011b). For a detailed description of AMS operation and analysis principles, the reader is referred to Jayne et al. (2000), Jimenez et al. (2003), Allan et al. (2003), Allan et al. (2004), and Canagaratna et al. (2007).

The meteorological data and trace gases were measured with conventional instruments by the Swiss National Air Pollution Monitoring Network, NABEL (Empa, 2011). The time resolution of all these instruments was ten minutes. NO$_x$ was measured by chemiluminescence spectroscopy (Horiba APNA 360), whereas UV absorption was employed to measure the concentration of ozone (Thermo Environmental Instruments (TEI) 49C, Thermo Electron Corp., Waltham, MA). An aethalometer (AE 31, Magee Scientific Inc.) was utilized to retrieve the concentration of equivalent black carbon (EBC).

2.2. The multilinear engine (ME-2)
ME-2 (Paatero, 1999) is an engine for solving the positive matrix factorization algorithm (Paatero and Tapper, 1994) where a measured matrix $X$ is deconvolved into two matrices $G$ and $F$ and the remaining residual matrix $E$:

$$X = GF + E$$  \hspace{1cm} (3)

In the measured matrix $X$, the columns $j$ are the m/z's and each row $i$ represents a single mass spectrum per unit time. Note that $p$ is defined as the number of factors of the chosen model solution, i.e. the number of columns of $G$ and the number of rows of $F$. Each column of the matrix $G$ represents the time series of a factor, whereas each row of $F$ represents the factor profile (mass spectrum).

In PMF, the entries in $G$ and $F$ are fit using a least squares algorithm that minimizes iteratively the quantity $Q^m$, defined as:

$$Q^m = \sum_{i=1}^{m} \sum_{j=1}^{n} \left( \frac{e_{ij}}{\sigma_{ij}} \right)^2$$  \hspace{1cm} (4)

Here $e_{ij}$ are the elements of the residual matrix $E$ and $\sigma_{ij}$ are the measurement uncertainties for the input points $x_{ij}$.

It is well known that PMF solutions suffer from rotational ambiguity (Paatero et al., 2002), i.e. multiple combinations of $G$ and $F$ can be found that yield similar $Q^m$. Thus, the solution space needs to be explored in order to find the most environmentally reasonable and interpretable solution according to the recommendations discussed in Ulbrich et al. (2009), Canonaco et al. (2013) and Crippa et al. (2014).

In this study, rotations are explored using the $\alpha$-value approach, which was first introduced by Lanz et al. (2008) for AMS data, employed for ACSM data in Canonaco et al. (2013) and systematically tested on 25 AMS data sets in Crippa et al. (2014). Within this method, the user directs the algorithm towards useful rotations by constraining factor profiles (as done here) and / or factor time series based on a priori information (Paatero and Hopke (2009)).

Briefly, the $\alpha$-value determines the extent to which a given factor profile ($f_{j,\text{solution}}$) is allowed to vary with respect to its predefined profile value ($f_j$) during the model iteration:

$$f_{j,\text{solution}} = f_j \pm \alpha \cdot f_j$$  \hspace{1cm} (5)
where the index $j$ denotes a measured variable (i.e. $m/z$) and the $\alpha$-value is its scalar product. As an example, an $\alpha$-value of 0.1 allows for a variability of approximately $\pm 10\%$.

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.

For this study we conducted the source apportionment employing the ME-2 solver and constraining the primary aerosol components, i.e. traffic (HOA), cooking (COA) and biomass burning (BBOA) using the $\alpha$-value approach and allowed for two additional free factors representing the secondary components. HOA and COA anchor profiles were taken from Crippa et al. (2013), where these primary sources were successfully resolved in an unconstrained PMF run. The BBOA anchor is the averaged BBOA mass spectrum reported in Ng et al. (2011a). The employed $\alpha$-values are 0.1 for HOA and COA and 0.3 for BBOA. This was based on different sensitivity tests performed on the winter and summer data set separately, similar to those presented in Canonaco et al. (2013). The higher $\alpha$-value for BBOA accounts for the fact that the biomass burning sources are more variable, as they depend strongly on the burning material and burning conditions (Hennigan et al., 2011; Heringa et al., 2012; Weimer et al., 2008).

2.3. Estimating OOA $f_{43}$ and $f_{44}$

The approach used in this study for estimating $f_{43}$ and $f_{44}$ for OOA involved the subtraction of the contributions from the primary sources arising at $m/z$ 43 and $m/z$ 44. This is slightly different from the method of Ng et al. (2010), where only the modeled $f_{43}$ and $f_{44}$ for SV-OOA and LV-OOA were considered. The two methods produce slightly different results because specific
sources/processes are not perfectly represented by individual factors, as evidenced by the residual matrix $E$. In the current method, the variability not captured by the model (i.e. residuals), propagates into the calculated $f_{43}$ and $f_{44}$. This means that the total OOA variability is more fully captured by the current method, but at the cost of unintentionally including variability due to imperfectly modeled POA.

3. Results and Discussion

3.1. Source apportionment in winter and summer 2011

Source apportionment was conducted separately for winter (February and March) and summer (June to August) 2011. These two seasons represent extreme cases, whereas spring and fall may be conceptualized as intermediate cases. A complete source apportionment analysis of the ACSM data of 2011 / 2012 is in preparation (Canonaco et al., in prep.). The summer / winter 2011 results are summarized in the supplementary material. Note that the solutions are environmentally reasonable, e.g. the traffic factor correlates with $NO_x$ and EBC, 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. S3 and S6). 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.

Figures S3 and S6 reveal an increase in concentrations for all factors except LV-OOA 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 which tends to concentrate all emissions. The OOA $f_{44}/f_{43}$ data together with the ratios of the SV-OOA and LV-OOA in the $f_{44}/f_{43}$ space are summarized for both seasons in Fig. 1. This figure highlights the fact that the majority of the OOA points, especially those with high masses (data with weak signal to noise is not expected to be explained by the model), are well-captured by the seasonal PMF run, since they are equally scattered (unimodal residual) around the connection line between SV-OOA and LV-OOA and hardly extend beyond these endpoints. Hence no major systematic
over- or underestimations occur. 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. 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 α-pinene (Pfaffenberger et al., 2013). The data from these two studies are represented with orange rectangles in Figs. 1a and 1b, respectively.

3.2. Variations in the f44/f43 space for winter 2011

The variation of the winter 2011 OOA points in the f44/f43 space shown in Fig. 1a is due to the linear combination between the winter LV-OOA and the biomass burning-related SV-OOA. Adopting the nomenclature convention proposed in Murphy et al. (2014) the winter SV-OOA, called SV-bbSOA (biomass burning SV-OOA), would be due to aging of biomass burning-related VOC’s emitted primarily by domestic heating, which peaks at night. Fig. S1 supports the interpretation of the winter SV-OOA as originating mainly from biomass burning emissions, due to the presence of m/z 60, the biomass burning tracer (Alfarra et al., 2007) that has been shown to be substantial in SV-OOA (Heringa et al., 2011). SV-OOA arising from traffic emissions is likely to be a minor contribution, as the total estimated contribution of the traffic source (combined POA and SOA) for Zurich winter 2011/2012 is on average less than 20% to the total OA (Zotter et al., 2014). In comparison, the PMF result in this study ascribed on average 12% of OA to primary traffic contributions, 25% to SV-OOA and 40% to LV-OOA. Even if the remaining traffic SOA contribution were completely assumed to be SV-OOA, this would still be a minor part of the total SV-OOA.

SV-OOA has a lower f44 compared to the SV-OOA in summer (see Sect. 3.3). Nonetheless, the f44 of LV-OOA in winter is higher than that of LV-OOA in summer despite reaching similarly low f43 values. A possible explanation could be aqueous-phase production of LV-OOA (either directly or via processing of
SV-OOA) in clouds or humidified aerosols, which are believed to increase oxygenation above that predicted by gas-phase reaction/condensation mechanisms (Ervens et al., 2011; George et al., 2008; Slowik et al., 2012). However, due to the lack of experimental data and ambient tracers for such mechanisms, this hypothesis remains speculative.

3.3. Variations in the $f_{44}/f_{43}$ space for the summer 2011

3.3.1. General trends

The variation of the summer 2011 OOA data in the $f_{44}/f_{43}$ space shown in Fig. 1 can be described as a linear combination of the summer LV-OOA and SV-OOA (see Sect. 3.2). The relation between temperature and OX for the measured data is shown in Fig. 2a. Note that OX is plotted as a function of the maximal daily temperature ± 2 hours to capture the period of highest photochemical activity. This strong relation implies that the photochemical oxidation is highest for days with high temperature. However, the relation between $f_{44}$ and OX is rather flat if not slightly inversely proportional as highlighted in Fig. 2b. On the contrary, $f_{43}$ shows a proportional dependence on the afternoon OX values (Fig. 2c). This is consistent with increased production of SV-OOA relative to LV-OOA, i.e. with increased VOC precursors in the atmosphere. Given the season and elevated temperatures, biogenic emissions are a likely source (Guenther, 1997). Fig. 3a illustrates the clustered afternoon data on top of the summer OOA data in the $f_{44}/f_{43}$ space. Only the values in the interval of four hours around the maximal daily temperature ($T_{max}$) were considered for the clustering. This figure elucidates the fact that the main horizontal movement of the $f_{44}/f_{43}$ OOA data is driven mainly by temperature and thus by biogenic emissions. Therefore, the modeled SV-OOA is predominantly of biogenic nature and has been referred to as SV-bSOA (biogenic SOA) by Murphy et al. (2014).

3.3.2. Day and night variations

Fig. 3b shows the OOA data together with two grouped families. The red points are the same as in Fig. 3a, i.e. the afternoon values only. The blue points are the clustered points between 0 to 5 AM of the following morning. Only early morning points are considered to avoid dilution effects from a rising boundary layer after sunrise. The comparison of the two grouped families (afternoon and subsequent early morning) suggests that semi-volatile organics generated during the day condense to the aerosol phase at night, increasing $f_{43}$ and
decreasing $f_{44}$. This effect was already described Lanz et al. (2007) showing that the condensation of fresh oxygenated organic compounds (SV-OOA) was enhanced during the night and the early morning following hot summer days during a three-week campaign with the AMS in Zurich. The fact that the ACSM data from the entire summer season in Zurich in 2011 shows the same temperature-driven partitioning for SV-OOA reinforces the interpretation of the semi-volatile character of OOA2 from Lanz et al. (2007). As discussed in the previous section, the summer SV-OOA is likely governed by biogenic SV-OOA (SV-bSOA). Moreover, oxidation processes enhancing the LV-OOA fraction during the afternoon, as highlighted by the diurnal cycle in Figure S6, will increase the diurnal $f_{44} / f_{43}$ ratio leading to a stronger separation of the their day versus night points. Only a single pair of points in Fig. 3b, at the lowest temperature (and which has high statistical uncertainty due to the small number of measurements it contains) violates this trend.

3.3.3. SV-OOA vs LV-OOA

Figures 4a and 4b show summer SV-OOA and LV-OOA against the maximum afternoon temperature as calculated above (red bars) and the data between midnight and 5 AM of the following morning (blue bars). The SV-OOA concentration tends to increase as a function of temperature, both during the afternoon and early morning. LV-OOA shows a similar but less pronounced behavior. In Fig. 4c, the ratio (SV-OOA / total OOA) is plotted against the total OOA mass concentration. For low OOA concentrations, the fraction of SV-OOA increases with increasing total OOA. However, the fraction levels off for total OOA mass concentrations above 5 µg·m$^{-3}$. One possible explanation could involve the departure of the exponential dependency of the biogenic VOC’s emission rate from the temperature, which occurs at temperatures between 30 and 35°C (Smiatek and Steinbrecher, 2006).

Besides the positive trend of SV-OOA with respect to the summer afternoon temperature, the SV-OOA fraction increases as a function of total organic aerosol mass (OA), highlighted in Fig. 4c and Fig. S7. Recently, Pfaffenberger et al. (2013) showed that the partitioning of biogenic semi-volatile organic compounds (SV-OOA) to the aerosol phase is enhanced for increased aerosol mass concentrations, resulting in a decrease of $f_{44}$ and an increase in $f_{43}$. Fig. S7 shows $f_{44}$ and $f_{43}$ plotted as a function of total OA mass for the summer data together with the experimental data (Pfaffenberger, personal
communication). Our results in the higher mass range (above 5 µgm⁻³) suggest a similar behavior for f43, though less pronounced for f44. One reasonable explanation could involve a slightly higher total f44 value for the ambient data at low concentrations, due to higher photochemical aging. In addition, other reaction pathways, e.g. nitrate oxidation, or aqueous phase reactions might also affect the ambient composition and finally, the presence of other ambient VOCs than those tested in the above-mentioned smog chamber study, would also lead to a different slope of the ambient data.

3.3.4. SOA formation in summer

The main ambient emission and photochemical oxidation processes are summarized in Fig. 5. The four sources relevant for this study are represented at the bottom, i.e. biogenic, traffic, cooking and biomass burning. These sources emit VOCs which 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 conversion rate generating LV-OOA from either SV-OOA or directly from VOC’s, typically occurring on a timescale of hours (Jimenez et al., 2009), is rather small. 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. The strong relation between OX and temperature highlighted in Fig. 2a suggests that photochemistry is more active during the summer afternoon. However, Fig. 2b indicates that the SOA f44 is rather flat with increasing OX in favor of the total OOA f43 (SV-OOA), as also shown in Fig. 2c. Higher temperatures will enhance the biogenic emissions relative to the other emission rates. As a consequence the biogenic path will dominate and the resulting SV-OOA will most likely be predominantly of biogenic nature, i.e. SV-OOA, represented as the orange path in Fig. 5.

4. Conclusions

This study shows that the SV-OOA modeled for ambient data by the means of the multilinear engine (ME-2) in winter and in summer retains some chemical information related to its precursor source(s). For a given f44, biomass burning-related SV-OOA exhibits lower f43 relative to biogenic SV-OOA (SV-OOA), locating these two SOA factors on the left and right-hand sides of the triangular space identified by Ng et al. (2010), respectively.
Periods of high photochemical activity in summer do not increase the SOA $f_{44}/f_{43}$ ratio because temperature-driven biogenic emissions and subsequent SV-OOA formation dominate over the conversion rate of SV-OOA to LV-OOA or direct formation of LV-OOA. The $f_{44}/f_{43}$ ratio is consistently lower at night than during the previous day due to the condensation of semi-volatile compounds produced during the day, predominantly from reaction of biogenic VOC’s.

In summer, the OOA composition depends strongly on temperature and mass concentration for values below 5 $\mu$g·m$^{-3}$. This highlights the importance of biogenic VOC emissions and of the biogenic SOA production.

In addition, there were substantial differences between the winter and summer $f_{44}/f_{43}$ data indicating that a PMF result over the whole data employing two OOA factors only would fail to fully represent the seasonal variability of OOA.

**Acknowledgements**

The ACSM measurements were supported by the Swiss Federal Office for the Environment (FOEN). The authors would like to thank L. Pfaffenberger and M. Heringa for compiling and providing their smog chamber results in the $f_{44}/f_{43}$ space, relevant for this publication. Thanks are also due to the Environmental group of the Swiss Federal Laboratories for Materials and Testing (EMPA) for their support and to M. Canonaco and S. Canonaco-Franceschini for a critical reading of this manuscript. J. Slowik acknowledges support from the Swiss National Science Foundation (SNF) in the form of Ambizione and Starting grants (PZ00P2_131673 and BSSG10_155846).

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Fig. 1  Estimated SOA $f_{44}$ and $f_{43}$ for winter 2011 (a) and summer 2011 (b). The data is color-coded based on the total OA mass concentration. The green points are the $f_{44}$ and $f_{43}$ ratios of SV-OOA (light green) and LV-OOA (dark green). Orange rectangles represent the composition of SOA from smog chamber experiments using biomass burning (a) and $\alpha$-pinene (b) precursors (Heringa et al. (2011), Pfaffenberger et al. (2013)).
Box plots for the summer data: a) OX as a function of afternoon temperature ($T_{\text{max}} \pm 2$ hours), b) SOA $f44$ as a function of afternoon OX and c) SOA $f43$ as a function of afternoon OX. The horizontal lines denote the median, the boxes span the quartiles and the whiskers represent the 10\textsuperscript{th} and 90\textsuperscript{th} percentiles.

**Fig. 2**
Fig. 3  SOA $f_{44}$ vs. $f_{43}$ for all data points in summer 2011 (gray dots) and LV-OOA/SV-OOA factors (green squares). a) Color-coded circles denote averages at the daily maximum temperature ($T_{\text{max}}$) ± 2 hours. b) Red circles denote daily $T_{\text{max}}$ ± 2 hours, while blue circles denote the average over the following midnight to 5 AM period. Black arrows connect corresponding day and night averages.
Box plots describing OOA composition, where horizontal lines indicate median values, boxes denote quartiles, and whiskers represent 10th and 90th percentiles. Quantities plotted are for the summer data: SV-OOA vs. temperature (a), LV-OOA vs. temperature (b), and SV-OOA fraction vs. total OOA mass (c). The afternoon and early morning points are estimated as $T_{\text{max}} \pm 2$ hours and midnight to 5 AM, respectively.
Fig. 5  The simplified scheme represents the emissions and aging processes occurring in ambient during the summer afternoons. The big arrows stand for the emission/conversion rates and the dashed arrows show qualitative dependencies, with the arrow pointing towards the dependent quantity. Higher temperatures in summer primarily enhance the biogenic path (highlighted in orange).