Atmos. Chem. Phys. Discuss., 14, C11122–C11127, 2015
www.atmos-chem-phys-discuss.net/14/C11122/2015/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Inverse relationship between the degree of oxidation of OOA (oxygenated organic aerosol) and the oxidant OX ($O_3 + NO_2$) due to biogenic emissions" *by* F. Canonaco et al.

Anonymous Referee #3

Received and published: 12 January 2015

General Comments:

This paper compares winter versus summer ACSM data collected during one consecutive year of measurements in Zurich. The differences between the organic aerosol (OA) composition between the winter and summer are the main focus of the paper. PMF using ME-2 results of the OA are presented along with the fraction of signal at m/z 43 and 44 from the total OA. The paper presents novel and noteworthy results, however, would benefit from more explanation in several places, including the reasons why the

particular type of PMF (with constrained primary OA factors) was chosen. Since PMF can be run in a lot of different ways and is relatively new for application to ACSM data, this seems to be an area where the community could learn more from this paper about how to run PMF on ACSM data. More detailed comments to this extent appear below. 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.

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, it would be noteworthy for the community to know.

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.

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

ACPD
14, C11122–C11127, 2015

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? 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.

Specific Comments:

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.

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.

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.

ACPD
14, C11122–C11127, 2015

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.

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?

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.

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.

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.

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 ïňĆat 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

ACPD
14, C11122–C11127, 2015

being mentioned here between f43 and f44 in response to changing OX, this needs to be explained in more detail.

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?

Technical Corrections:

Page 28081, Line 10: The manufacturer's company name should be referenced in the experimental details, but is not necessary here.

Page 28083, Line 5: suggest adding a reference for PMF using ME-2

Page 28083, Line 6: change "will be" to "are" or "are shown to be"

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.

Page 28090, Line 3: Sentence references Figure S7 – should it not be Figure 5(c)?

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

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.

Figures 3 and 4: Suggest combining into one figure since the two plots are very similar, and referencing them close together is beneficial.

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.

ACPD

14, C11122–C11127, 2015

Figure S.4: Figure caption says “winter” in the text – change to “summer”.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 28079, 2014.

ACPD

14, C11122–C11127, 2015