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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 #2**

Received and published: 7 January 2015

General comments:

The manuscript reports the Aerosol chemical speciation monitor (ACSM) measurements performed in Zurich from February 2011 to February 2012, and in particular, investigates the relationship between the degree of oxidation of OOA (oxygenated organic aerosol) and the oxidants (Ozone + NO2) in summer 2011. The high temperature in summer enhanced the emission of biogenic volatile organic compounds (BVOCs) and the levels of atmospheric oxidants, leading to a significant formation of



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biogenic secondary organic aerosol (i.e. SV-bSOA identified by PMF analysis in the manuscript). The SV-bSOA is generally less oxidized than the LV-OOA. The mass fraction of SV-bSOA increased as a function of total OOA loading. The inverse relationship between the degree of oxidation of OOA and the oxidant levels (or temperature) suggests that the formation kinetic of SV-bSOA from BVOCs is faster than that of LV-OOA from BVOCs/SV-bSOA.

Overall, this manuscript provides a good illustration of SOA formation due to biogenic influence. I recommend this work to be published in Atmospheric Chemistry and Physics after addressing the specific comments below:

Specific 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.

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.

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,



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especially in the urban environments.

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.

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. 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.

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?

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 $\sim$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. 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?



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8. Section 3.3.2, page 28089: In addition to the condensation of freshly formed SV-OOA, 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.

Minor comments and Technical corrections:

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.

2. Section 2.1, page 28083, line 24: Please provide the instrument model for NOx measurement.

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.

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

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

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

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