

Review of “Simultaneous Aerosol Mass Spectrometry and Chemical Ionisation Mass Spectrometry measurements during a biomass burning event in the UK: Insights into nitrate chemistry” by Reyes-Villegas et al.

In this study, the authors use cToF-AMS, I<sup>-</sup> HR-ToF-CIMS, and Aethalometer to characterize one biomass burning event. The authors identified both primary and secondary particulate organic nitrate (PON) in the biomass burning event. The secondary PON is proposed to arise from NO<sub>3</sub>• chemistry. Further, it is found that while primary PON can absorb light at 470nm, the secondary PON does not. The topic is clearly of interest to the community. However, I have some concerns about the PMF analysis, particularly regarding that the concentrations of all factors increase during the biomass burning event. Also, the discussions on the relationship between absorption and different OA components need substantial revisions. For example, all the r<sup>2</sup> values in section 4.4 do not match the values in table 1, which makes the discussion difficult to follow. At this time, I recommend accept with major revisions.

#### Major Comments

##### 1. PMF results.

It has been challenging to perform source apportionment on a dataset including a special event with high concentrations. This study takes an important step to address this issue. However, the PMF results are still not satisfactory. My major concern is that all OA factors show significant increase during the biomass burning event (Figure 5 and 6). LV-OOA increases by ~30 μg m<sup>-3</sup>. Since fresh biomass burning unlikely contribute to LV-OOA, the increase in LV-OOA suggests PMF artifacts. The COA and HOA increase by ~8 μg m<sup>-3</sup> and ~20 μg m<sup>-3</sup> during the biomass burning, respectively. These enhancement magnitudes cannot be explained by the inversion at night. The enhanced concentrations of LV-OOA, COA, and HOA during the biomass burning event are likely interference from biomass burning.

Using the suggested two-step approach, a clean BBOA factor still cannot be resolved. For example, BBOA\_1 is a mixed factor between LV-OOA and BBOA. Have the authors tried PMF2 solver on the whole dataset? Including the biomass burning event would be useful to get a clear BBOA factor, which helps to identify the BBOA concentration during the non-biomass burning

period. However, the disadvantage of this method is that the concentrations of all OA factors would falsely decrease during the biomass burning.

The authors have done careful evaluation on PMF results. PMF results from two different tests (test 2 and test 2\_ON) are presented, but the PMF results are different. This causes many confusions. For example, why does the mass spectrum of BBOA change between test 2 and test 2\_ON (i.e., BBOA-2 vs BBOA)? Why are two BBOA factors are resolved in test 2, but only one BBOA factor in test 2\_ON? Why is SV-OOA only resolved in test 2, but not in test 2\_ON? I suggest the authors to present only the most reasonable/best solution in the manuscript to avoid confusion.

Details about PMF analysis are included details in the SI. However, I suggest that some key points should be briefly discussed in the main text as well. For example, Line 222, it should be justified that why test 2 is the best. What criteria do the authors look at?

2. Discussions on the light absorbing properties of OA components are confusing and require substantial revisions.

(1) The most important issue is that the  $r^2$  values in the manuscript do not match those in table 1.

(2) What's the rationale behind eqn. 6? Why is the partial slope used? In MLR3, there is no sPON\_ME2. Then how is the light-absorption of sPON\_ME2 evaluated?

(3) In the abstract, it is stated that LV-OOA absorb light at 470nm over that of black carbon. Where is the justification for this conclusion?

(4) Line 278, the authors state that after modifying the fragmentation table, the correlation between  $b_{\text{abs}_{470\text{wb}}}$  and BBOA is improved. I wonder if the improvement is mainly because that there are only one BBOA is resolved in test 2\_ON, but two BBOA factors in test 2? In other words, is the improved correlation simply due to that modifying the fragmentation table somehow helps to separate the BBOA factor? What's the  $r^2$  between  $b_{\text{abs}_{470\text{wb}}}$  and the sum of BBOA and BBOA\_1 in test 2?

(5) Line 374, the authors need to be cautious that not all organic nitrates can absorb light. Most identified light-absorbing organic nitrate are nitro aromatic compounds (Lin et al., 2016; Mohr et al., 2013).

3. The separation of primary PON (pPON) and secondary PON (sPON).

(1) How do the authors identify pPON and sPON? In Figure 6, the sPON\_ME2 has more evident signal at  $m/z$  30 than pPON. What does the mass spectrum of organics that associate with sPON

look like? Where are the organic signals associated with pPON\_ME2 from? Fresh biomass burning? More discussions regarding pPON\_ME2 and sPON\_ME2 are required.

(2) The authors use two methods to differentiate pPON and sPON. However, there are discrepancies in the results (Figure 7 vs. 8). For example, pPON\_ME2 decreases slower than BBOA in Figure 8. Could the authors directly compare the results from these two methods (i.e., scatter plot)?

(3) Previous studies have attempted to run PMF analysis on combined organic and nitrate mass spectra (Sun et al., 2012; Xu et al., 2015). The authors should compare to other literature.

#### Minor Comments

1. Line 68. It should be “Ng et al., 2017”.
2. Line 212. What’s the  $\text{NO}_2^+/\text{NO}^+$  value of organic nitrate used in this study? This information should be mentioned in the main text.
3. Line 227. The mass spectrum of factor 4 is very similar to that of SV-OOA in step a. Then how do the authors justify “SV-OOA” in step a?
4. Line 392, please cite Washenfelder et al. (2015), which showed that biomass burning OA is light absorbing.

#### Reference

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