

Response to comments of Referee 1.

As a general point, we agree that PMF/ME-2 analysis was probably not a perfect representation of the aerosol, however we argue that the factorisation given represents a ‘best estimate’ based on the testing and validation work performed. We consider that, while BBOA concentrations could be mixed with other OA sources implying a decrease on BBOA concentrations, the represents the best estimate of the temporal trend biomass burning OA emissions. This is supported by the good correlation BBOA shows with  $b_{abs\_470wb}$   $r^2=0.880$ . Thus we consider BBOA time series to be accurate enough to determine primary and secondary PON concentrations.

Through discussions outside of this review, we have considered that the term Particulate Organic Nitrate (PON) is not the most appropriate as this could include nitro compounds in addition to organic nitrates. Hence, we have decided to refer to the acronym as Particulate Organic Oxides of Nitrogen (PON) which include both nitrate and nitro organic compounds. Furthermore, because the chemistry community do not strictly consider these compounds primary, the term ‘primary’ here should include the qualifier in that it is not necessarily produced in the fire, but on a short enough time scale that its temporal trend is indistinguishable from the actual primary emissions, so is therefore considered ‘primary’ within the receptor model.

Comments from referee are in blue and response from co-authors is in black.

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  $\sim 30 \mu\text{g m}^{-3}$ . Since fresh biomass burning unlikely contribute to LV-OOA, the increase in LV-OOA suggests PMF artifacts. The COA and HOA increase by  $\sim 8 \mu\text{g m}^{-3}$  and  $\sim 20 \mu\text{g m}^{-3}$  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.

We agree that during bonfire night, LV-OOA, COA and HOA may be mixed with BBOA concentrations. We mention in section 4.1 that this would be the case. Conclusions will be modified mentioning that even when using the methodology of first analysing the period before and after bonfire night and then analyse the bonfire night period, it was not possible to completely separate the OA sources. We run PMF and ME-2 for the whole dataset (test1). However, when we compared solutions from different tests, analysing first the period without bonfire emissions and then the bonfire night event, was best way to do source apportionment.

The following paragraph has been added to the end of section 4.1 OA source apportionment during bfo event:

Here we show the importance of performing OA source apportionment using different approaches in order to identify the best way to deconvolve OA sources. PMF and ME-2 source apportionment tools could not completely deconvolve OA sources during the bfo event. However, due to the high correlation between for  $b_{abs\_470wb}$  and BBOA\_2 ( $r^2 = 0.880$ ) we consider that while BBOA\_2 might not represent the total OA concentrations from the bonfire night event, it does represent the trend of OA emitted from 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.

We agree two solutions in the manuscript to be confusing. The manuscript has been edited, leaving only one solution on the main manuscript (Test2\_ON). The other solution has been moved to the appendix, as one of the objectives of this paper is to assess ME-2 under different tests in order to study its performance.

This paragraph has been added to section 3.3 OA source apportionment:

Test2\_ON was the optimal 'best estimate' solution, a brief description is given here after being compared to the other tests (Section S7.2 in supplement). From this analysis, test2 was the best way to deconvolve OA sources, with the lowest parameters analysed: residuals, Q/Qexp values and Chi square. After modifying the fragmentation table, Test2\_ON still shows a good performance with low parameters (Fig. S6-S8). Refer to section S7 in supplementary material for detailed information about source apportionment strategy and analysis performed to determine the optimal solution.

2.

(1) The most important issue is that the r2 values in the manuscript do not match those in table 1.

The r2 values on table 1 are the correct r2 values. The values mentioned on the paragraph were not updated from a previous version. r2 values have been updated.

(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?

We have expanded the explanation of the multilinear equation. There is sPON\_ME2 in MLR3, the following two paragraphs have been added to explain equation 6.

$$b_{abs\_470wb} = A + B * x1 + C * x2 \quad (6)$$

When the parameter s<sup>"D"</sup> and x3 are used it means a trilinear regression was performed. MLR1 x1=BBOA, x2=PON. MLR2 x1=BBOA\_2, x2=PON. MLR3 x1= BBOA\_2, x2=sPON\_ME2, x3=LVOOA in HSC and x3=pPON in bfo. A is the origin and the partial slopes B, C and D represent the contribution of x1 ,x2 and x3 to  $b_{abs\_470wb}$ , respectively.

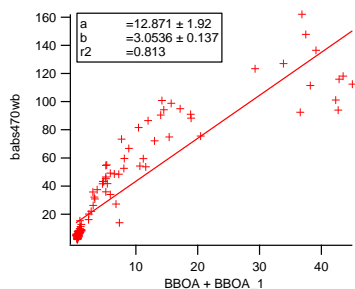
As used in previous studies (Elser et al., 2016;Reyes-Villegas et al., 2016), multilinear regression analysis allows to determine the relationship between one parameter and two or more variables. Here we are analysing the partial slopes and origin to determine the correlation of babs\_470wb with the other variables.

(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?

Sorry to be ambiguous, the abstract has been edited as follows:

Our results suggest that sPON\_ME2 does not absorb light at 470 nm while pPON\_ME2 and LVOOA absorb light at 470 nm.

(4) Line 278, the authors state that after modifying the fragmentation table, the correlation between babs\_470wb 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 r2 between babs\_470wb and the sum of BBOA and BBOA\_1 in test 2?



We still consider OA source apportionment improves after modifying the fragmentation table. During the bonfire night  $r^2$  values between  $b_{abs\_470wb}$  and BBOA is 0.839 before the modification and 0.880 after the modification, while  $r^2 = 0.813$  is obtained between  $b_{abs\_470wb}$  and the sum of BBOA+BBOA\_1. The  $r^2 = 0.813$  will be mentioned in the manuscript

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

We have decided to change our definition of PON from “particulate organic nitrate” to “particulate organic oxides of nitrogen” which will involve both nitro and nitrate organic compounds.

### 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.

The following paragraph has been added to the end of the section 3.3 OA source apportionment:

These two PON factors may have different sources; one may be secondary (sPON\_ME2) as it follows the trend of LVOOA concentrations (Fig. 5.a) and the other primary (pPON\_ME2) which has similar trend as BBOA (Fig. 5.b). Further details about pPON\_ME2 and sPON\_ME2 nature will be explored in section 4.2.

Moreover, the following paragraph has been added to the end of section 4.3:

During the bfo event, pPON\_ME2 showed high  $r^2$  values with carbon monoxide (0.78) as well as hydrogen cyanide (0.77), Methylformamide (0.65) and Dimethylformamide (0.63) which are typical primary pollutants related to combustion processes [(Borduas et al., 2015) and references therein]. sPON\_ME2 showed low correlations with CINO2 (0.52) and CINO3 (0.53). High  $r^2$  values were also observed during LC episode between CINO2 - CINO3 and LVOOA (0.67 - 0.66) and sPON (0.74 - 0.69) proving their secondary origin.

(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)?

This information will be added to supplement

Two methods have been used to determine primary and secondary PON. In the following plots we can see primary PON comparison has a good correlation with a pearson value of 0.7 while secondary PON comparison shows a different behaviour between them.

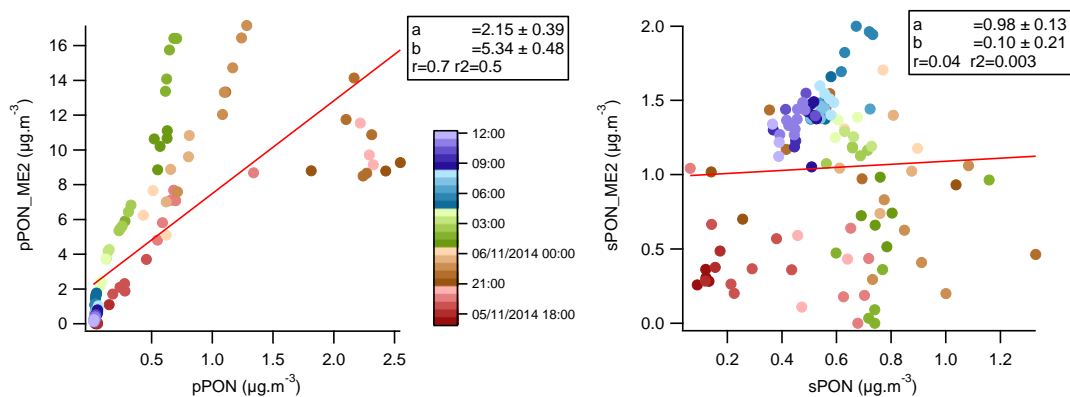


Figure S13: PON comparison for the two methods used.

(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.

This paragraph has been added to methodology in the section where we describe ME-2 PON analysis:

Previous studies have quantified PON concentrations from AMS-PMF analysis to both rural and urban measurements (Sun et al., 2012; Hao et al., 2014; Xu et al., 2015; Zhang et al., 2016).

This paragraph has been added to section 4.2 PON Primary/secondary:

Primary and secondary sources of PON have been previously identified from AMS-PMF analysis; Hao et al. (2014) identified PON to be secondary of nature, produced from the interaction between forest and urban emissions, while Zhang et al. (2016) determined PON to be related to primary combustion sources.

Minor Comments

1. Line 68. It should be “Ng et al., 2017”.

The citation has been edited.

2. Line 212. What’s the NO<sub>2</sub>+NO<sub>x</sub> value of organic nitrate used in this study? This information should be mentioned in the main text.

The following paragraphs have been edited in section 2.2.2 Particulate Organic Oxides of Nitrogen (PON):

Equation 5 calculates the PON fraction ( $X_{PON}$ ), using the signals at  $m/z$  30 and  $m/z$  46 to calculate  $m/z$  ratios 46:30 from AMS measurements ( $R_{meas}$ ), from ammonium nitrate calibrations ( $R_{cal}$ ), and from organic nitrogen ( $R_{ON}$ ) to quantify PON concentrations.

$$X_{PON} = \frac{(R_{meas} - R_{cal})(1 + R_{ON})}{(R_{ON} - R_{cal})(1 + R_{meas})} \quad (5)$$

Where ratios from ammonium nitrate calibrations  $R_{cal} = 0.5$ ;  $R_{meas} = m/z$  46:30 ratio from measurements;  $m/z$  46:30 ratio from ON  $R_{ON} = 0.1$ , Following Kostenidou et al. (2015) consideration,  $R_{ON} = 0.1$  was calculated as the minimum  $m/z$  46:30 ratio observed.  $R_{ON}$  value of 0.1 has been used in previous studies (Kiendler-Scharr et al., 2016; Tiitta et al., 2016).

$$PON = X_{PON} * NO_3^- \quad (6)$$

Finally, equation 6 calculates PON concentrations [ $\mu g.m^{-3}$ ] where  $NO_3^-$  is the total nitrate measured by the cToF-AMS.

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?

This figure has been moved to the appendix A. In this figure, we consider factor 4 mass spectra to be SVOOA in both (a) and (b).

4. Line 392, please cite Washenfelder et al. (2015), which showed that biomass burning OA is light absorbing. The citation has been added to the manuscript.

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