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

Anonymous Referee #2

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Review for: 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.

This paper describes the measurements of the chemical composition and absorption of aerosols during the bonfire night event in Manchester with particular focus on primary and secondary particulate organic nitrate. While the topic of this paper is interesting to the community, it has some major issues resulting from (1) the use of the C-ToF-AMS and not an HR-AMS for the quantification of PON and (2) the PMF not being able to

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resolve the biomass burning event from all the other factors without crosstalk between the different factors. In general, the various steps of the PMF are poorly explained and are very difficult to follow, especially for a “non-AMS reader”. (3) There are also various parts of the paper that are redundant and others are missing, for example there were different PMF tests performed, but only one was used. So why describe the first test at all. On the other hand a description of the AMS instrument and quantification or a description of the PMF factors is missing. With all those issue, I cannot recommend this paper for publication in its current form without major improvement to the PMF analysis and results.

Major Comments:

Quantification of PON from biomass burning using a CToF-AMS: The m/z 46:30 ratio is used for the quantification of PON, which is based on a method done by Farmer et al 2010 that used an HR-AMS and did not include any biomass burning emissions. The large fraction of OA from biomass burning certainly will produce a large $CH2O+$ contribution and will make the quantification of PON very different compared to the Farmer et al paper. On page 7 line 250 the authors say that the m/z 30 interference is likely small, but this might be very different in biomass burning and needs to be shown or given a reference. In addition it is written on page 6 line 206 that the interference of $CH2O+$ is discussed in section 3.4.1, but no such section exists in the paper. So it is not clear, how the authors deal with the m/z 30 interference and how large the uncertainty or error estimate on the quantification of PON is. In addition in the later section, where the primary versus secondary PON is discussed, it is certainly possible that the m/z 30 interference is different as the composition changes during the later part of the night, when the authors claim that they observed secondary PON.

A section needs to be added, where the interference is clearly explained and the effect needs to be quantified. This should result in an uncertainty range for the m/z 30:46 ratio and error estimate for PON. All of this should be added to the instrumentation section, where there needs to be a description of the AMS added as well that includes a discussion on the calibration for NH4NO3 and, if available, for PON compounds. Here it should be made clear what m/z 30:46 ratio NH4NO3 has in this particular instrument? The resulting error estimate needs to be taken into account for the following discussions.

For biomass burning the fragmentation tables need to be modified, which the authors do later in the paper. It does not make sense to me to run PMF on not-corrected data as was done in Section 3.3, when you know you are using incorrect data.

The section on the FragPanel modification is very specific to AMS users and all the three bullet points cannot be understood by anybody else without explaining all the abbreviations and acronyms. Especially sentences like on page 7 line 238: time series of PON:mz30 were calculated with the equation PON:mz30=PON/mz30, where PON=m/z 46:30. This makes mathematically no sense. Again all of this need to be included in the instrument section together with the quantification of PON and clearly will increase the already large uncertainty in the PON quantification during the biomass burning event.

The description of PMF and the ability of PMF to resolve the biomass burning event: In my opinion, PMF is pushed way too far in this manuscript given the quality of the data. It is well known that PMF has difficulties to resolve large individual peaks and this becomes very clear in this paper as well.

First of all this paper is clearly tailored to the AMS community, but it should at least be somewhat understandable to anybody else, especially when some of the main findings are related to the absorption of PON. None of the factors that are used such as HOA, COA or LVOOA are explained anywhere or even a reference given. What are those factors, how are they characterized, how do they relate to any of the other measured tracers and how do the ones determined in this manuscript compare to the AMS data base?

The next issue is that PMF was done in many different ways in this manuscript, many tests were performed and a lot of these tests were subsequently discarded. So why do you describe all the tests that have not worked. As it is written, this is very confusing and really hard to follow. Furthermore, two different PMF tests were actually used in the manuscript and they are very clearly different and the results that fit the story the best were used for no apparent reason. Even the number of BBOA factors changes between the two tests.

It is very clear that PMF, even in the way as done here with separating the biomass burning event from the rest of the time series, cannot resolve the single event. In Figure 6 the combined increase of LVOOA, COA, and HOA is about twice as large as the combined BBOA_2, sPON_ME and pPON_ME signals. One might argue that during bonfire night activities such as cooking and traffic might increased as well, but certainly not to such large extents. Especially the LVOOA signal, which is larger than the BBOOA signal, has to be from biomass burning as well. So it seems that the interferences in the biomass burning event are larger than the BBOA signal itself.

Given this large uncertainty and interferences on the PMF results, it seems clearly a step too far to try to separate sPON from pPON with two different methods that have large uncertainties and are not even fully consistent with each other. The I-CIMS measures some primary and secondary ON tracers, some of which are specific to biomass burning such as nitroaromatics, why have those measurements not been used to correlate with the sPON signal? It is not clear from the text on page 9, what compounds from the I-CIMS have actually been used, except some of the inorganic tracers.

Minor Comments:

There are a large number of minor issues mostly about missing Tables, wrong numbering of Sections and typos in axis labels and such, so I only point out the two most obvious ones.

- I mentioned that before, but all the references to other sections are wrong in the manuscript. Most importantly there are references to sections that don't even exist

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such as Section 3.4.1, in which supposedly the interference of m/z 30 is discussed. -- Another glaring omission is Table 1 mentioned on page 9 line 325. This Table could be the most important evidence to support the separation of sPON from pPON, but is unfortunately missing.

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