We would like to thank Reviewer# 1 for very helpful comments and suggestions. All comments and suggestions have been considered. Point by point responses to these comments are listed below.

General comments The manuscript presents UHRMS data of PM2.5 aerosol samples collected in central Amazonia during both the 'wet' and 'dry' seasons. Several tracer compounds corresponding to sources of biogenic and anthropogenic organic aerosol (OA) have been tentatively identified and UHRMS visualisation tools such as the Kendrick mass defect, Van Krevelen diagrams etc have been plotted to obtain further information of the differences in molecular composition between samples. The work presented is very interesting, in particular the demonstrated change in the OA chemical composition with increasing number of incident fires. As the authors note, higher time resolution filter collection would have led to a better understanding of the various factors affecting aerosol sources and formation at their sampling site. However, I do believe that this work offers new and interesting data. The manuscript did however suffer from inaccuracies with the incorrect use of acronyms, spelling mistakes and wording, which is in some places, is rather difficult to understand. I recommend that this manuscript should be published but only after the manuscript has been thoroughly checked for errors and the comments below, particularly specific comments 1 and 2 which are imperative to the work, have been addressed.

Specific comments 1. Lines 259 - 272. It appears that the identification of all of the tracer compounds with the exception of IEPOX (which is mentioned in the experimental section) was confirmed using only UHRMS via MS2. As stated, UHRMS does not differentiate between structural isomers. The authors should be able to confirm if the tracer compounds are present in the samples through the comparison of the ion fragmentation patterns to the literature or authentic standards of the tracer compounds, providing the fragmentation patterns are not too 'messy' (i.e. multiple fragmentations of different structural isomers). I suspect the fragmentation data of m/z 161.0456 consisting of four tracer compounds and possibly other structural isomers may be particularly difficult to interpret and this should be mentioned in the manuscript. In addition, I don't believe the authors can attribute the entire ion abundance of m/z 203.05611 to 3-MBTCA, unless the fragmentation data shows no indication of any other possible structural isomers. Finally, how do the authors know that other possible structural isomers are not largely contributing to the ion abundance of the other tracer compounds (i.e. C6H5NO4 etc)? The authors need to provide more justification/evidence for the identification of these compounds and the use of their ion abundances in Figure 4.

We would like to mention that we were very cautious in interpreting direct infusion results. For instance, we initially stressed the fact that '*The structural or isomeric information is not directly obtained from the direct infusion analysis….'* (lines 259-260 in the original text). We also stated that *'It must be noted that due to competitive ionisation of analytes in the direct infusion ESI analysis of the samples with a very complex matrix (i.e., aerosol extracts), the ion intensities do not directly reflect the concentration of the molecules in the sample; therefore, data shown in this work is semi-quantitative'* (lines 157-160). *Moreover, we stated that 'Direct infusion analysis suffers from competitive ionisation in the complex matrices and thus comparing ion intensities across samples has to be done with caution'* (lines 275-277). It must be noted that there is a large number of publications indicating and justifying the use of the direct infusion analysis for semi-quantitative purposes (see review by Nizkorodov et al., 2011). While the term "nitrophenols" does include all

possible isomers, we agree that other compounds may contribute to a molecular formula assigned as 3-MBTCA. As confirmed by the LC/MS analysis of selected samples the compound assigned to $C_8H_{12}O_6$ molecular formula corresponds to MBTCA. However, in the revised version of the manuscript we emphasised again that molecular formula assigned as 3-MBTCA may also include other compounds: *'Moreover, other compounds with similar molecular composition present in the aerosol matrix may also contribute to the ion intensities of the discussed above compounds.'* We also replaced 'MBTCA' by a molecular formula $C_8H_{12}O_6$ in the Fig 4.

2. Were the IOP1 and IOP2 samples analysed on the same day, or was the detector variation of the UHRMS monitored during the analysis period? The UHRMS will vary in sensitivity. Running samples days or weeks apart may result in a variation in the amount of species observed due to fluctuations in the UHRMS sensitivity (e.g. as the mass spectrometer becomes 'dirty', the detector sensitivity will decrease, affecting the ion intensity and subsequently the amount of species observed). This is particularly important in Figures 2 and 4 where the molecular formulae and ion abundances, respectively, are compared. If the samples were not analysed at the same time or if the detector sensitivity was not monitored, the authors would not be able to compare the ion abundance of the tracer compounds as shown in Figure 4. This is also likely to affect the comparison of the molecular formulae in Figure 2. The work presented here would then be only qualitative (rather than semi-quantitative). Were any attempts made to account for variations in detector sensitivity?

The instrument was routinely calibrated before the analysis. It must be noted that in the current study we used a nanoESI source where each sample is processed using a separate ESI tip and nozzle, so there is no carryover between samples. All samples were analysed in a random order and within 48-hours after extraction (to minimise possible methylation; therefore, the observed differences could not be attributed to the instrument contamination.

3. Line 217 states that the number of molecular formulae of species containing CHO increased by ~ 20% from IOP1 to IOP2, but Figure 2 shows that this increase is within the standard deviation of the three replicate measurements. Please can the authors state in line 217 that this ~ 20% difference is based on the average number of molecular formulae. Can the authors demonstrate that these differences are statistically significant? Do the ratios of the compounds classes differ between wet and dry season?

The t-test demonstrated that there is a significant difference for individual subgroups (e.g., CHO) between two compared seasons (p=0.0092 and p=0.00007).

As requested the following statement has been added to the text: '*The Student's t-test showed that the observed difference for CHO (p=0.0092) and CHON (p=0.00007) subgroups between two seasons is statistically significant.'*

4. The experimental section needs to be separated into sections to make it clearer. Currently, the direct infusion flow rate follows the LC-MS parameters after UHRMS has already been discussed (line 140). Sub-headings such as 'LC-MS analysis', 'ESIUHRMS analysis' and 'data processing' would make the experimental section easier to understand.

As suggested the subheadings '*Direct infusion UHRMS analysis*' and '*LC-MS analysis*' have been added to the experimental section.

5. Line 157, competitive ionisation is not the only reason why ion intensities do not re- flect the concentration of the compounds when using ESI. The ionisation efficiency of species will also vastly differ depending largely on their chemical structure and composition (see Oss et al (2010)). Please can the authors acknowledge this in the manuscript?

This phenomenon, which is true for all mass spectrometry ionisation techniques, including hard ionisation techniques such as electron ionisation, is already covered by the matrix statement in the same sentence. As suggested by the reviewer, Oss et al reference has been added to the text.

6. The authors use very strict molecular formulae constraints, along with other parameters such as O/C ratio ≥ 1.3, 0.3 ≤ H:C ratio etc. This is likely to remove a large proportion of the observed peaks from further analysis. I understand why the authors have done this, but please can they include the percentage of the observed mass spectral peaks which are assigned molecular formulae in the manuscript (i.e. 57 % of the observed mass spectral peaks were assigned a molecular formulae using the constraints; as shown in Woznaik et al 2008)?

As suggested, we added a table SI2 (analogous to that in Wozniak et al., 2008) showing % occurrence of formula groups to all peaks assigned molecular formulae in the mass spectra during the two sampling periods.

7. The authors refer to Kourtchev et al (2013) and (2015) for further details regarding the processing of the UHRMS data. From these papers, it appears that the background ions are subtracted from samples. If so, please can the authors include this in this manuscript? This is an important part of the data processing and needs to be mentioned in this manuscript too.

As suggested, the following statement has been added to the text: '*The background spectra obtained from the procedural blanks were also processed using the rules mentioned above. The formulae lists of the background spectra were subtracted from those of the ambient sample and only formulae with a sample/blank peak intensity ratio ≥ 10 were retained'*. Lines 179-182 (see revised text)

8. Line 228-229. The authors state that the daytime %RH during IOP1 was 89%. This seems a little high based on the data shown in Figure SI2. Please state in the manuscript whether this is the average %RH or maximum. Also, have the authors calculated the %RH only during the filter sampling time periods? Given that the authors are justifying why there is increased number of organonitrates in the IOP1 samples the %RH should only refer to the filter sampling time periods.

Yes, the values correspond to the maximum and the minimum RH during the filter sampling periods. This has been now clarified in the text.

9. Line 251 states that wet deposition of aged or processed aerosol cannot be only reason for the observed differences in OSc. If the aerosol had wet deposited, how would the authors of sampled this?

Unfortunately, we do not fully understand this remark but we assume that this comment is a misunderstanding: we did not collect any precipitation or aerosol deposited due to wet deposition but only particles that were not scavenged by cloud or rain droplets.

10. Can the authors add the isoprene gas-phase measurements into Figure 4? Use of replicate figures with 'a' (benzene overlaid) and 'b' (isoprene overlaid) may prevent the data from looking too busy.

We intentionally did not show isoprene data in this manuscript because it will be published as an independent work.

11. Line 443. Can the authors give more justification as to why they think the observation of these highly oxygenated species are likely to be associated with molecules produced through homogenous photochemical ageing reactions? Compounds with ~ 10 oxygen atoms are likely to be of relatively low volatility residing mainly in the particulate phase. Heterogeneous reactions would seem likely here.

In this sentence we are referring to a literature study which also observed highly oxygenated species and suggested that they could be produced through homogenous photochemical ageing reactions. The exact formation mechanism for these species is still highly debatable as for most of them there are no chemical standards. We agree that heterogeneous reactions could possibly also lead to formation of such compounds. To clarify this, we removed the word 'homogeneous' from the statement.

12. Can the authors show the data points from IOP1 and IOP2 in different colours/shapes in Figure SI3?

As suggested different markers were used for IOP1 and IOP2 data points in Fig SI3.

13. Can the authors draw the categorises/sources of aerosol (i.e. SV-OOA, BBOA etc) onto Figure 3 as shown in Kroll et al (2011). This will make the data much easier to visualise when describing in the results section.

The main emphasis of the figure 3 is to show the shift in the carbon oxidation state from dry to wet seasons in organic aerosol *throughout the whole mass range*. Addition of the categories would make the plot very busy and difficult to visualise the shift in the OSc. However, as suggested by the reviewer, we added these categories to another carbon oxidation state plot in the revised Fig. 7 and updated the figure caption accordingly.

Reference - Oss et al., (2010) Anal. Chem. 82. 2865-2872

Technical corrections 1. OH should be written as OH or 'OH radical'

Corrected

2. Line 67, the use of 'participate in heterogeneous chemical reactions in the atmosphere' doesn't make an awful lot of sense in this sentence, re-word or remove.

The word 'heterogeneous' has been removed

3. Line 70, for the most part, precursor and oxidant types will determine the composition of SOA formed, which will in turn determine the light absorbing properties of the SOA. Remove 'precursor and oxidant types' from this sentence or re-word.

As suggested by the reviewer 'precursor and oxidant types' has been removed from this statement.

4. NOx should be written as NOx (use of subscript)

Corrected

5. Line 75, remove 'for example', this sentence does not follow the above.

We disagree with this comment, reaction between anthropogenic nitrogen oxides (NO_x) and sulfur dioxide (SO_2) with a range of BVOCs leading to formation of organic nitrates is an example of anthropogenic/biogenic interactions discussed in the above sentence.

6. Line 89, 'UHRMS have a mass resolution...' should be, 'UHRMS has a mass resolution....'

We are discussing several techniques here (e.g. Fourier transform ion cyclotron resonance MS and Orbitrap MS). To address the reviewer's comment, we replaced 'MS' with 'mass spectrometers'.

7. Line 97, need a comma after Shanghai.

Corrected

8. Line 98, this sentence would read better as; 'UHRMS has proven to be extremely useful or a value tool/technique for assessing.....'

As suggested, the sentence has been changed to '*UHRMS has proven to be extremely useful in assessing chemical properties of the SOA*'

9. Line 104, Martin et al 2015 is not in the references, do you mean Martin et al 2016?

Corrected

10. Line 105, the T3 site is 69.4 km from Manaus (Martin et al 2016), not 70 km. Change to ~ 69 km or 69.4 km.

Corrected

11. Line 113, could you make this a little clearer? '...passed over the single large city (Manaus)'

Corrected

12. Supplementary material Table SI1, is there a reason why the time is reported as, for example, 7H47? If not, change column header to 'Time (UTC, HH:MM)' and remove 'H'. 13.

Corrected

Line 121, this sentence reads as if the sampling flow rate changes during sample collection. Re-word.

The sentence has been change to *'The airflow through the sampler was approximately 10 L min^{-1}'* .

14. Line 123, how were the samples stored at -4 ËŽC?

The sentence has been extended to *'...and stored in the freezer at –4°C until analysis.'*

15. Line 127, 'optima' is the name of the product not the grade, the grade is LC-MS. Change.

Optima is a trademark name of the Fisher LC/MS grade solvents which is different from the regular LC/MS grade solvents available on the market. The 'TM' and 'LC/MS' have been added to the revised version of the manuscript.

16. Line 128, how was the sample reduced to a volume of 200 µL, via a nitrogen line or evaporator? If the latter, please give details of manufacturer etc.

The sentence has been extended to *'..using a nitrogen line'*.

17. Line 154, define CID

Corrected

18. Line 154, 'MSMS' should be written as MS/MS or MS2

Corrected

19. Line 156, include the word 'time' in 'chromatographic elution' (i.e. chromatographic elution time or retention time)

Added

20. Line 184, define E/N before abbreviating

'a field density ratio' has been added before *'E/N'*

21. Supplementary material SI1, explain what 'MP14-06' etc (displayed on the figures) refers to in the figure caption.

As suggested, this has been now clarified in the figure caption: *'72 h back air mass history ('footprints') arriving at the T3 station for the periods of the analysed filters (labelled as e.g., MP14-06, MP14-16, MP14-17).*'Lines 37-39

22. Line 209, states that the majority of ions were associated with molecules less than 500 Da but Figure 1 only goes up to m/z 500. Either show the full m/z scan range in Figure 1 or re-phase Line 209 (e.g. the majority of species were observed between m/z 100 to 400).

The line 209 (in the original text) has been rephrased to *'……were associated with molecules below 500 Da although the measured mass goes up to 900 Da.'*

23. Line 212, 'fragile compounds'. Why are some compounds fragile? Please expand

The sentence has been extended to *'…(e.g. highly oxygenated compounds)'*.

24. Line 213 is difficult to read. Re-word.

As suggested the sentence has been rephrased to: '*The largest group of identified molecular formulae in all samples were attributed to molecules containing CHO atoms only (1051±141 formulae during IOP2 and 820±139 during IOP1), followed by CHON (537±71 during IOP2 and 329±71*

during IOP1), CHOS (183±34 during IOP2 and 137±31 during IOP1) and CHONS (37±11 during IOP2 and 28±10 during IOP1) (Fig. 2).'

25. Figure 2; include 'IOP1' and 'IOP2' next to 'wet' and 'dry' season respectively in Figure 1 or the opposite in the figure caption.

Corrected

26. Supplementary material Table SI1, make clear which samples are from wet and dry season.

This has been now clarified in the Table SI1 footnote*: The samples MP14_06 to MP14_28 correspond to 'wet' (IOP1) period and MP14_128 to MP14_153 to 'dry' (IOP2) period.*

27. Line 223, Table SI1, NOy should be written as NO_y (use of subscript).

Corrected

28. Line 227 and Figure SI2 caption, define 'RH'.

Defined

29. Figure SI2 caption, what is 'ARM'? Define. Should this be in the references?

The ARM has been defined and the link to the website is provided: '*Figure SI2. Relative humidity (RH) at the T3 sampling site during (a) IOP1 and (b) IOP2 The arrows indicate sample collection periods. Atmospheric Radiation Measurement (ARM) data source http://www.archive.arm.gov. '*

30. Figure SI2, what are the dashed lines displaying? Explain in caption.

The explanation has been added to the figure legend: *'The continuous dashed line indicates the lowest and highest RH vales during both seasons'*

31. Line 228, use of 'IOP1' then 'wet season'. Please use either wet and dry or IOP1 and IOP2.

For consistency we have added IOP2 to this sentence: *'In this respect, while night time maximum RH during both filter sampling periods was very similar (~90%), day-time RH during IOP1 was higher (89%) compared to that from the IOP2 period (66%) (Fig. SI2).'*

32. Line 230 and elsewhere, 'OSc' should be written as 'OSc'

We do not understand this comment.

33. Figure 3, please give a starting number of carbon atoms on the x-axis or start from zero.

Done

34. Line 256, move reference to the end of the sentence.

Corrected

35. Line 273, SO_x should be written as SO_x (use of subscript).

Corrected

36. Line 390, change to ’a reduced number of ’ or ’decreased number of’

As suggested we replaced ‘r*educed’* by *‘decreased’*

37. Lines 400 and 401 are difficult to understand. Be more precise (e.g. ....difference in OSc is more pronounced with compounds containing more than 7 carbon atoms). ’Affected ions’? Re-word.

Yes, in this sentence we are discussing figure 7 and thus OSc differences associated with the carbon atoms in the molecular formulae. For clarity we expanded this sentence to *‘The difference in OSc becomes even more pronounced with increased numbers of carbons (e.g. >7 carbon atoms) in the detected molecular formulae’.*

38. Line 375, change ’nitroartomatic’ to ’nitro-aromatic’

Done

39. Line 376, ’overplayed’?

Changed to ‘overlaid’