

General comments

The manuscript presents UHRMS data of PM_{2.5} 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 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.

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?

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?

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', 'ESI-UHRMS analysis' and 'data processing' would make the experimental section easier to understand.

5. Line 157, competitive ionisation is not the only reason why ion intensities do not reflect 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?

6. The authors use very strict molecular formulae constraints, along with other parameters such as O/C ratio ≥ 1.3 , $0.3 \leq$ 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)?

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.

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.

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

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.

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.

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

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

Technical corrections

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

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.

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.

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

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

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

7. Line 97, need a comma after Shanghai.
8. Line 98, this sentence would read better as; 'UHRMS has proven to be extremely useful or a value tool/technique for assessing.....'
9. Line 104, Martin *et al* 2015 is not in the references, do you mean Martin *et al* 2016?
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.
11. Line 113, could you make this a little clearer? '...passed over the single large city (Manaus)'
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. Line 121, this sentence reads as if the sampling flow rate changes during sample collection. Re-word.
14. Line 123, how were the samples stored at -4 °C?
15. Line 127, 'optima' is the name of the product not the grade, the grade is LC-MS. Change.
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*.
17. Line 154, define CID
18. Line 154, 'MSMS' should be written as MS/MS or MS²
19. Line 156, include the word 'time' in 'chromatographic elution' (*i.e.* chromatographic elution time or retention time)
20. Line 184, define E/N before abbreviating
21. Supplementary material SI1, explain what 'MP14-06' *etc* (displayed on the figures) refers to in the figure caption.
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).
23. Line 212, 'fragile compounds'. Why are some compounds fragile? Please expand or reference.
24. Line 213 is difficult to read. Re-word.
25. Figure 2; include 'IOP1' and 'IOP2' next to 'wet' and 'dry' season respectively in Figure 1 or the opposite in the figure caption.
26. Supplementary material Table SI1, make clear which samples are from wet and dry season.
27. Line 223, Table SI1, NO_y should be written as NO_y (use of subscript).
28. Line 227 and Figure SI2 caption, define 'RH'.
29. Figure SI2 caption, what is 'ARM'? Define. Should this be in the references?
30. Figure SI2, what are the dashed lines displaying? Explain in caption.
31. Line 228, use of 'IOP1' then 'wet season'. Please use either wet and dry or IOP1 and IOP2.
32. Line 230 and elsewhere, 'OSc' should be written as \overline{OS}_c .
33. Figure 3, please give a starting number of carbon atoms on the x-axis or start from zero.
34. Line 256, move reference to the end of the sentence.

35. Line 273, SO_x should be written as SO_x (use of subscript).
36. Line 390, change to 'a reduced number of ' or 'decreased number of'
37. Lines 400 and 401 are difficult to understand. Be more precise (e.g.difference in \overline{OS}_c is more pronounced with compounds containing more than 7 carbon atoms). 'Affected ions'? Re-word.
38. Line 375, change 'nitroartomatic' to 'nitro-aromatic'
39. Line 376, 'overplayed'?