We would like to thank Reviewer# 2 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: This manuscript deals with the molecular characterization of PM2.5 aerosol collected in Manaus, Brazil, which is impacted by regional biomass burning, mainly during the dry season, and anthropogenic pollution from the city. Advanced analytical ultra-high resolution MS-based tools are applied, which allow a comprehensive MS data evaluation and identification of molecular formulae. Several comments were already formulated in a first review, with which I could agree. This review will therefore be limited to additional comments. The manuscript contains indeed interesting and novel data on Amazonian fine aerosol, which could be elaborated and is worth publishing after suitable revision. What I miss in the manuscript is a comparison with previous studies dealing with the detailed molecular characterization of Amazonian fine aerosol.

A first example: the 2-methyltetrols have been measured in several studies (e.g., Claeys et al., ACP 10, 9319-9331, 2010); the highest levels were observed during the dry period which is characterized by biomass burning (and higher particle concentrations of sulfuric acid). This observation is in agreement with the results obtained in the present study, taking into account that 2-methyltetrol sulfates were converted to 2-methyltetrols during the GC/MS procedure with prior trimethylsilylation?

In the current study we concentrated on direct infusion mass spectrometry analysis and therefore we intentionally limited our comparison mainly to the literature that employed similar techniques. As suggested by the reviewer comparison to previous studies by Claeys et al. (2010) has been added to the text: *'This is also in agreement with previous studies from Amazon where the highest levels of 2-methyltetrols were observed during the dry period which was characterised by biomass burning (and higher particle concentrations of sulfuric acid) (Claeys et al., 2010). Considering that Claeys et al (2010) employed alternative GC/MS procedure with prior trimethylsylilation, 2-methyltetrol sulfates were converted to 2-methyltetrols and not detectable as separate OS compounds.'* Lines 339-344 (see revised text)

A second example: A study on Amazonian biomass burning aerosol (Claeys et al., Environ. Chem., 9, 273-284, 2012) using LC/MS led to the molecular characterization of several strongly UV-absorbing nitro-aromatic compounds, with 4-nitrocatechol and isomeric methyl-nitrocatechols being the most abundant ones. Nitrocatechols are mentioned in the current manuscript but no mention is made of the methyl-nitrocatechols, which are very important markers for biomass burning secondary organic aerosol (SOA), formed from m-cresol emitted during the fires.

As suggested discussion of methyl-nitrocatechols has been added to the text: '*… and methyl-nitrocatechols ($C_7H_7NO_4$, m/z 168.03023) are important markers for biomass burning OA, formed from m-cresol emitted during biomass burning (Iinuma et al., 2010)*' Lines 283-285

In addition, also several biogenic SOA markers were identified in the study of Claeys et al. (2012), including MBTCA, terebic acid, terpenylic acid, 2-hydroxyterpenylic acid, and azelaic acid.

Please see our response below.

Specific comments Lines 129-131: Part of the samples was used for LC/MS analysis but no LC/MS results are presented in the current manuscript. It would be very relevant to provide LC/MS results and as such support molecular assignments. It would also be relevant to see whether the major compounds found in LC/MS correspond to the major ones with the semi-quantitative direct infusion approach used in the present work. Figure 1: The base peak in panel (a) is at m/z 171 (terpenylic acid?), but this ion is not discussed in the manuscript. Has this ion been assigned? There are also other abundant ions of the CHO type in the region below m/z 200 which merit attention, such as m/z 157 (terebic acid?) and m/z 187 (2-hydroxyterpenylic acid, or azelaic acid?), and are likely biogenic SOA markers.

To be able to compare mass spectral intensities from different aerosol samples, as well as to minimise matrix effect, we aimed to have similar aerosol loading of the sample extracts for the direct infusion analysis. Since we aimed for approximately 0.3 µg µL^{-1} of particulate matter in each sample extract, there was enough aerosol material only for direct infusion analysis for most of the samples. Only a few aerosol samples had sufficient loading for both direct infusion and LC/MS analyses. Therefore, the later technique was only used to confirm the assignments of a few marker compounds observed in direct infusion analysis. This now has been clarified in the text:

'Depending on the aerosol loading of the analysed samples a part (1/2 to whole) of the filter was extracted in methanol (Optima R LC/MS grade, Fisher Scientific) in a chilled ice slurry, filtered through a Teflon filter (0.2 µm, ISODiscTM Supelco) and reduced by volume using a nitrogen line to achieve approximately 0.3 µg of aerosol per µL methanol. Several samples with the highest aerosol loading were divided into two parts for both direct infusion and LC/MS analyses, while the samples with the lowest loading were only analysed using direct infusion analysis.' Lines 126-132

With direct infusion analysis we identified more than a thousand molecular formulae, therefore the main emphasis was placed on a bulk molecular composition of the OA rather than identification of all possible marker compounds and which would be a study different to the one presented here. The discussion of the individual compounds was limited to a few known marker compounds that corresponded to the most intense ions.

The base peak in the panel (a) at *m/z* 173.0454 corresponds to $C_7H_{10}O_5$, which is different from that of terpenylic acid. Unfortunately, this molecule was not clearly identified by the LC/MS analysis. With regards to the other abundant ions of the CHO type in the region below *m/z* 200, an ion at *m/z* 187.0612 corresponds to a deprotonated molecular formula $C_8H_{12}O_5$, which is neither 2-hydroxyterpenylic acid nor azelaic acid. An ion at *m/z* 157.01425 corresponds to a deprotonated molecular formula $C_6H_6O_5$, which is also different from terebic acid. Unfortunately, due to the absence of standards for the above mentioned compounds, the discussion of these molecular formula would be highly speculative.

Lines 209-229: As already mentioned above, LC/MS results would be very useful to support the molecular assignments, more useful in my opinion than MS/MS data, which in the case of 2-methyltetrolsulfates provide limited structural information (only the bisulfate anion). Quite some emphasis is given to the number of molecular formulae containing CHO, CHON, CHOS, and CHONS. More emphasis could be given to the molecular characterization of the major species, taking into account that LC/MS analysis has been performed and reference can be made to the literature. This type of information will be of great interest to readers dealing with molecular characterization.

Please see our response above.

Lines 279-286: Here, the origin of benzene is discussed and it is argued that benzene has mainly an anthropogenic origin because it correlates well with CO. It is not very clear what is meant by "anthropogenic origin". Biomass burning for domestic purposes (e.g., cooking) in urban locations can also be regarded as an anthropogenic activity and this must be clarified in the manuscript. Benzene could very well have mainly a biomass burning origin. More detailed insights could be obtained by measuring other aromatic compounds, such as cresols, and acetonitrile, which are characteristic for biomass burning; a good correlation between benzene and cresols/acetonitrile would point to a biomass burning origin. A differentiation between an anthropogenic and a tropical biomass burning origin cannot easily be made and will remain problematic. See the following article and references cited therein: Iinuma et al., Environ. Sci. Technol. 2010, 44, 8453–8459.

We agree that the correlation between benzene and cresols/acetonitrile would provide more information on the aerosol sources; unfortunately, cresols/acetonitrile data is not available for our study. In Manaus for heating and cooking purposes people mainly use natural gas; therefore, a significant contribution from these activities to the biomass burning OA at the site is highly unlikely. This statement has been added to the text: *'In Manaus natural gas is mainly used for heating and cooking and therefore, the contribution from these activities to biomass burning OA at our site is highly unlikely'.* Lines 310-312

Lines 371-373: It would be relevant to mention 4-nitrocatechol and isomeric methylnitrocatechols in the group of nitroaromatic compounds, since they are characteristic of biomass burning SOA; see Iinuma et al., Environ. Sci. Technol. 2010, 44, 8453– 8459.

As suggested by the reviewer, the following statement has been added to the text: *'Nitro-aromatic compounds, such as nitrophenols (DBE=5) and N-heterocyclic compounds including 4-nitrocatechol and isomeric methyl-nitrocatechols are often observed in the OA from the biomass burning sources (Kitanovski et al., 2012a,b; Iinuma et al., 2010) and have been suggested as potential contributors to light absorption by brown carbon (Laskin et al., 2015).'* Lines 405-409

Lines 393-396: In addition, the CHON molecules identified by LC/MS in biomass burning OA from Amazonia showed O/C ratios below 0.7, i.e., 4-nitrocatechol (C6H5O4N; O/C = 0.67), isomeric methyl-nitrocatechols (C7H7O4N; O/C = 0.57), and isomeric dimethyl-nitrocatechols (C8H9O4N; O/C = 0.50). Ref: Claeys et al., Environ. Chem. 9273-284, 2012.

As suggested, the following statement has been added to the text: *'In addition, the CHON molecules identified by LC/MS in biomass burning OA from Amazonia showed O/C ratios below 0.7, i.e., 4-nitrocatechol ($C_6H_5NO_4$; O/C = 0.67), isomeric methyl-nitrocatechols ($C_7H_7NO_4$; O/C = 0.57), and isomeric dimethyl-nitrocatechols ($C_8H_9NO_4$; O/C = 0.50) (Claeys et al., 2012).'* Lines 434-437

Lines 436-437: Species with molecular formulae C5H10O7S (m/z 213) could also be due to organosulfates formed from the green leaf volatiles 2-E-pentenal, 2-Ehexenal, and 3-hexenal, and have recently been characterized as isomeric 3-sulfooxy2-hydroxypentanoic acid and 2-sulfooxy-3-hydroxypentanoic acid. Ref. Shalamzari et al., ACP 16, 7135-7148, 2016. See also the corresponding discussion document, where the issue is raised that C5H10O7S species could be oxidation products of isoprene.

The following statement has been added to the text: '*This molecular formula could also be associated with organosulfates (e.g., isomeric 3-sulfooxy-2-hydroxypentanoic acid and 2-sulfooxy-3-hydroxypentanoic acid) formed from the green leaf volatiles 2-E-pentenal, 2-E-hexenal, and 3-hexenal(Shalamzari et al., 2016)'* Lines 482-485

Figure 5: What do the large grey circles between m/z 120 – 240 represent? Please, explain in the legend of the figure and discuss in the main text.

As suggested by the reviewer the following explanation has been added to the text and the figure: *'The largest grey circles in Fig 5(a-c) correspond to the ions at m/z 133.01425 (with neutral molecular formula $C_4H_6O_5$), m/z 187.0612 ($C_8H_{12}O_5$), m/z 201.07685 ($C_9H_{14}O_5$), m/z 203.05611 ($C_8H_{12}O_6$), m/z 215.05611 ($C_9H_{12}O_6$) with DBE<6.'* Lines 367-370 and 881-883

FigureSI5: What do the large grey circles at around m/z180 and 280 represent in panel (a)? What do the large grey circles between m/z 140 and 180 represent in panels (b) and (c)? Please, explain in the legend of the figure and discuss in the main text.

As suggested by the reviewer the following explanation has been added to the text and the figure legend:

'The largest grey circles in Figure SI5a correspond to the ions at m/z 187.11357 with a neutral molecular formula $C_9H_{17}NO_3$ *and m/z 281.26459 with a neutral molecular formula* $C_{18}H_{35}NO$*. The largest grey circles in Figure SI5 b and c correspond to the ions at m/z 154.0146, m/z 168.03023 and m/z 152.03532 with neutral molecular formulae* $C_6H_5NO_4$*,* $C_7H_7NO_4$ *and* $C_7H_7NO_3$*, respectively'*. Lines 398-402 (main text) and 82-86 (SI).

Figure SI6: It is evident from these figures that CHO compounds are present at significant abundances in the natural background. What species do the large grey circles represent in panels (a–c)?

Figure SI6 shows exactly the same ion distribution as in Figure 5, but expressed using aromaticity index. The large circles in both figures correspond to the same molecular formula; therefore, to avoid repetition we added the explanation for these ions to only one of these figures.

Figure SI7: I wonder what the large yellow circles (panels (b) and (c)) between m/z 150 and 200 represent. Do they correspond to m/z 168 ($C_7H_6NO_4$) compounds, due to isomeric methyl-nitrocatechols, which are expected to be very prominent and most abundant in the samples from the dry biomass burning period? Looking at panel (a) I wonder what the large grey circles around m/z 190 and 380 represent? Please, explain in the legend of the figure and discuss it in the main text.

As suggested by the reviewer the following explanation has been added to the figure legend: *'The largest grey circles in panel 'a' correspond to ions at m/z 186.11357 and m/z 280.26459 with neutral molecular formulae* $C_9H_{17}NO_3$ *and* $C_{18}H_{35}NO$*, respectively. The yellow circles in panels 'b' and 'c' correspond to the ions at m/z 154.0146, m/z 168.03023 and m/z 152.03532 with molecular formulae* $C_6H_5NO_4$*,* $C_7H_7NO_4$ *and* $C_7H_7NO_3$*, respectively, which are known biomass burning marker compounds (see discussion in the main text)'*. Lines 102-107 (SI)

I found Figures SI5, SI6 and SI6 the more interesting figures in the manuscript, but unfortunately they ended up in the supplement. Please, consider to include them in the main text, perhaps leaving out some other figures and putting some emphasis on methyl-nitrocatechols, specific SOA markers for biomass burning. Other interesting (but less abundant) biomass burning SOA markers are m/z 182 ($C_8H_8NO_4$) compounds, corresponding to isomeric dimethyl-nitrocatechols.

A very large diversity of the data was produced in this work resulting in a large number of figures, so we had to be very selective which figures could be kept in the man text. Our justification was based on the fact that some of the figures in the SI would be rather challenging for a general reader with little mass spectrometry background. Therefore, we prefer to keep SI5 and SI6 in the SI.

As suggested by the reviewer the following explanation has been added to the text: *'It is worth mentioning that aerosol samples affected by biomass burning contained another interesting ion at m/z 182.04588 with a neutral molecular formula* $C_8H_9NO_4$*, possibly corresponding to biomass burning OA markers isomeric dimethyl-nitrocatechols (Kahnt et al., 2013)'*. Lines 409-412 (main text)

Lines 473 – 477: Here, the authors indicate that future work is needed to better understand the quantitative contributions of the various factors to the aerosol composition at the T3 site and they suggest to analyze samples with higher sampling resolution. A better approach would be to also measure specific marker compounds more quantitatively by LC/MS or other methods, including biogenic SOA markers, and primary and secondary biomass burning markers, and apply a receptor modelling technique. See, for example, the recent study by de Oliveira Alves et al. (Atmos. Environ., 120, 277285, 2015), where for a site in western Amazonia, i.e., Porto Velho, a distinction could be made between contributions from biomass burning, fossil fuel combustion and a mixed source to the PM10 mass.

The following statement has been added to the text: *'The analysis of aerosol samples with higher sampling resolution or quantifying specific marker compounds and applying receptor modelling techniques (Alves et al., 2015) would allow separating these sources in more detail and thus improve understanding of the aerosol formation sources at the site.'* Lines 519-523 (main text)