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Interactive comment on "Molecular composition of organic aerosols in central Amazonia: an ultra-high resolution mass spectrometry study" *by* I. Kourtchev et al.

Anonymous Referee #2

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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?

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. 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.

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.

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.

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.

Lines 371-373: It would be relevant to mention 4-nitrocatechol and isomeric methyl-nitrocatechols 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.

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. 9,

273-284, 2012.

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-E-hexenal, and 3-hexenal, and have recently been characterized as isomeric 3-sulfooxy-2-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.

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.

Figure SI5: What do the large grey circles at around m/z 180 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.

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 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 (C7H6NO4) 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.

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 interest-

ing (but less abundant) biomass burning SOA markers are m/z 182 ($C_8H_8NO_4$) compounds, corresponding to isomeric dimethyl-nitrocatechols.

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, 277-285, 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.

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