Response to reviews

Reviewer comments are in **bold**. Author responses are in plain text. Excerpts from the manuscript are in *italics*. Modifications to the manuscript are in *blue italics*. Page and line numbers in the responses correspond to those in the ACPD paper.

Review #1

The presented paper by de Sá et al, 'Urban influence on the concentration and composition of submicron particulate matter in central Amazonia' gives a very clear overview of the aerosol particle composition during the wet season in the Amazon region. The authors use two different methods to analyse AMS data. PMF, which gives an overview of the particle composition and fuzzy c-means algorithm to study the anthropogenic influence on the aerosol in Amazon. I have few minor comments which are addressed in the following:

We thank the reviewer for the input, and the revised manuscript takes into account the comments and questions, as detailed in the responses below.

1. in the Introduction line 30, information on isoprene emissions compared to other biogenic or even anthropogenic VOCs could be added. Eg., how much isoprene is estimated to be emitted globally, how much of it is emitted by the amazon rainforest?

We thank the reviewer for this suggestion. Information on the importance of isoprene emissions, especially in the Amazon, is added to the revised manuscript, as follows:

Line 36:
~~*For tropical forests, isoprene emissions are especially important in PM production (Martin et al., 2010a; Chen et al.,*~~ *2015Isoprene accounts for half of global BVOC mass emissions, and tropical forests are responsible for about 80% of terpenoid emissions (Guenther et al., 2012). In the Amazon, isoprene is the dominant BVOC emitted by vegetation and is estimated to contribute to about half of the organic PM concentrations under background conditions (Kuhn et al., 2010; Chen et al., 2015; Yáñez-Serrano et al., 2015) (Kuhn et al., 2010; Chen et al., 2015; Yáñez-Serrano et al., 2015).*

2.a Also in the Introduction,, in line with the measurement period that you are describing here, how many days of data did you collect during the IOP1.

The whole duration of IOP1 (Feb 1 to Mar 31, 2014) was the nominal operation time for all instruments including the AMS. The AMS data coverage is shown in Figure 1. The referred sentence in the introduction is clarified, as follows:

Line 60:
The analysis employs data sets collected in the wet season from February 1 to March 31, 2014, corresponding to the first Intensive Operating Period (IOP1) of the GoAmazon2014/5 experiment (Martin et al., 2016). ~~, corresponding to the wet season during the period of February 1 to March 31, 2014.~~

2.b How frequently was the site influenced by the Manaus pollution during the time period presented in the manuscript?

We appreciate the suggestion, and the revised text includes this information as follows.

Line 72:
The site was situated in a pasture of 2.5 km × 2 km surrounded by forest. Based on modeled flow trajectories of the pollution plume, the T3 site intercepted the plume about 40% of the time (Martin et al., 2017).

3. in Methodology you mention 'V' and 'W' mode data. Maybe this is common knowledge but in my opinion it is useful to add a short description of what that means at least in the supplementary material.

The text is adjusted to restrict the use of these technical terms to the Supplementary Material, and an explanation of what these modes mean is included there.

Line 95:
Organic, sulfate, ammonium, nitrate, and chloride PM mass concentrations were ~~obtained from "V-mode" data. The choice of ions to fit was aided by "W-mode" data, which were collected for one of every five days.~~ quantified.

Line 208:
Positive-matrix factorization was applied to the time series of the organic component of the high-resolution ~~"V-mode"~~ mass spectra (Ulbrich et al., 2009).

Supplementary material, line 3:
Quantification of mass concentrations by the AMS was obtained from "V-mode" data, which corresponds to the shorter ion time-of-flight path and is therefore the more sensitive mode. The choice of ions to fit was aided by "W-mode" data, which corresponds to the longer ion time-of-flight path and is therefore the mode with higher mass resolution. V-mode data were collected continuously, and W-mode data were collected for one of every five days. The time series of organic mass spectra measured by the AMS in V-mode was analyzed by positive-matrix factorization (PMF) using a standard analysis toolkit (Ulbrich et al., 2009). ~~High-resolution "V-mode" data were used.~~

4. in Auxiliary measurements and datasets, l. 124: it would be nice also for the supplementary measurements to add information for what time period that data was taken and how much of data was collected during each set of measurements.

Following this suggestion, the text is improved as follows.

Line 104:
In complement to the AMS data set, the analysis herein incorporated auxiliary gas and particle measurements ~~from~~ collected during IOP1 at T3 (Martin et al., 2016).

Line 124:
At T2, non-refractory particle composition and concentration were measured by an Aerosol Chemical Speciation Monitor (ACSM~~; Brito et al., in preparation).~~) during the wet season from March 9 to April 30, 2014 (Cirino et al., submitted). ACSM measurements were ~~also~~ made at T0a during the wet season of 2015 ~~(Carbone et al., in preparation).~~, from February 1 to March 31 (Andreae et al., 2015). Further AMS datasets collected ~~by AMS~~ at T0t during the wet season of 2008 (February 6 to March 22; AMAZE-08 campaign) were used in the analysis (Chen et al., 2009;Schneider et al., 2011). ~~AMS measurements made onboard the G-1 aircraft of the ARM Aerial Facility (AAF) during IOP1 also supported the analysis herein (Shilling et al., in preparation).~~

5. in Results and discussion, in line 180 it is important to mention here again that the measurements at T0 sites were taken in a different year. It helps the reader.

The reviewer raises a good point, and the text is adjusted as follows. (The reviewer mentioned line 180, but the information about T0 was at line 163, and we think this is what the reviewer meant.)

Line 163:
The NR-PM_1 mass concentrations at the T0 sites upwind of Manaus, although measured in different years, were consistently around ~~approximately~~ 1 $\mu g\ m^{-3}$.

6. Fig.3: This Figure contains too many data points, most of the points are hidden. I suggest to split the Figure into few sub-Figures, which enclose different time periods of the day. That allows to see any temporal trend of the particle evolution and to distinguish better what is happening at the different sites.

Based on this feedback, the figure is revised to provide a better visualization of the data points. The caption of Figure 3 is adjusted as follows:

Gray and blue circles correspond, respectively, to measurements at T3 and T2 during IOP1, in the wet season of 2014. For visualization purposes, the two datasets are plotted separately in panels a and b.

The intention of the authors for this figure is to provide a general comparison of the PM oxidation at both sites. For the reviewer's suggestion in relation to plume evolution, we think that a more elaborate analysis beyond the scope of the authors' intention would be necessary to take into account (i) the transport time between the sites for each individual data point, (ii) whether the plume passed over both sites, and (ii) meteorological factors. Cirino et al., submitted focused on this kind of complex plume analysis. The text is adjusted to reflect these important points.

Line 198:
The comparison depicted in Figure 3 ~~illustrates the effects of the plume over the 4 h of transport from T2 to T3 (Cirino et al., submitted).~~ indicates the effects of the plume over the 4 h of transport from T2 to T3, which were investigated in detail by Cirino et al. (submitted).

7. Fig.5: This Figure is easier to read and more informative, if the variables on the x-axis are grouped according to their source (biogenic, anthropogenic, background, biomass burning) other than the instrument they were measured with.

We appreciate this suggestion. Based on it, the authors prepared both possible figures for internal discussion. In the end, the authors believe that the original figure is better for presentation. The reason is that most of the tracers have contributions from several different and in some cases unknown sources so that a definitive classification would be uncertain, and the revised figure would be a scientific over-stretch. The exceptions, such as levoglucosan which is a specific tracer for biomass burning, are explicitly mentioned in the text.

8. Fig. 7: the airmass back-trajectories are more valuable if they are calculated as ensembles rather than single trajectories. Ensemble gives you a group of trajectories which are all equally likely.

We thank the reviewer for this thoughtful comment, which generated significant internal discussion among the authors. Although the idea is appreciated, the use of ensembles did not seem the most appropriate or necessary tool for the analysis of Figure 7.

The backtrajectories are employed in this study in a supportive rather than central role to the clustering analysis, i.e., trajectories are not used to generate clusters but rather to help in their interpretation. In each panel of Fig. 7, trajectories are representative of the case studies shown in Fig. 6. It is visually clear that trajectories within those time periods are already clustered. Calculating ensembles for all observation times (every 12 min) over the course of the two months of the study period would have added a very large computational time and human expense that could not be afforded. Hence,

the cost-benefit of a more complex trajectory analysis was not justified, while the single trajectories still added value to the data interpretation.

Review #2

1. [T]his manuscript provides an overview of particle mass and chemical composition, with a focus on organic species in the Amazon. The authors strive to understand the anthropogenic contribution(s) to mass and influence on speciation and approach this with 2 different statistical approaches applied to online measurements. The work is interesting but seems premature. The paper relies on and cites several manuscripts that are "in preparation" to justify some arguments and conclusions and this is problematic. For example, comparison among different data sets (and presented in Figure 1) includes data not previously published, nor fully explained here.: data from ATTO sampling location "T0a-2015" is from Carbone et al., in preparation and "T2-2014" is from IOP1 Brito in preparation.

We thank the reviewer for reading the manuscript and providing valuable feedback.

For the references "in preparation", the following revisions are made.

(i) Carbone et al. (in preparation) is replaced by Andreae et al. (2015), which already published the T0a-2015 data used in this study.

(ii) Brito et al. (in preparation) is replaced by Cirino et al. (submitted). This manuscript is in the final stages of peer review, and we expect that "submitted" can be replaced with a full citation for the ACP publication of the present manuscript. Both Brito and Cirino, responsible for ACSM data collection and analysis at T2, are co-authors in the present study.

For changes made to the text to address (i) and (ii) please see reply #4 to review #1. The references in the caption of Figure 1 are also accordingly updated.

We believe that these updates satisfy the reviewer's concern about "premature". Importantly, the comparison of the T3 composition to other sites only appears in one section of the manuscript (lines 155-205). The main conclusions, by contrast, largely come from the combined analysis of PMF and FCM on the data collected at T3, which is completely original and presented in detail in the following sections of the manuscript (lines 206-514).

2. Organic mass variability in relation to meteorology seems to be an important finding and necessary to the arguments in this manuscript but Cirino et al. 'in prep' is the provided proof and readers are not left with sufficient information to understand the reasonableness of the argument.

This reference was adjusted as follows:

Line 174:
This influence waxes and wanes with small northerly or southerly shifts of the trade winds as well as other changes in regional circulation tied to daily meteorology (~~*Cirino et al., in*~~ *preparationdos Santos et al., 2014; Martin et al., 2017).*

3. The authors also cite de Sá et al 'in prep' to explain why a certain analysis is beyond the scope of this paper and not presented here and explain that the analysis is currently underway (e.g., biomass burning influence (presumably screened here?)) will be discussed in the literature later and I think that is ok.

The current manuscript focuses on the wet season. As stated in the introduction (line 48), the influence of biomass burning is minimal during the wet season. The reference to de Sá et al. (in preparation) in the introduction (line 64) was intended to highlight that there is a separate manuscript under way for the dry season (to also be submitted to the GoAmazon2014/5 Special Issue of ACP). Although related, these studies are independent.

4. Many journals would not even accept 'in prep' References at all. To use such References for conclusions seems unreasonable to me. Prior to acceptance for publication I think the 'prior' work must first be published or properly backed up here.

We understand the reviewer's concerns. Please see replies 10 and 11.

5. specific comments: Line 19/20: The choice to cite Weber et al., 2007 and Goldstein et al., 2009 here is curious. Weber et al. state in that paper: "Although NOx may be another precursor that could be influencing this system, NOx-WSOC… was weakly correlated" The R2 is <0.2 I acknowledge time scales for complex chemistry matter and correlation for instantaneous values can be low even though there is a dependence, however the work by Weber does not provide support for NOx or SO2 dependence as suggested by the authors here. The work by Weber et al does demonstrate a link to CO. The Goldstein analysis for particles is limited to satellite-AOT. Seasonal and spatial patterns have found these AOT observations are not due to organic fine particle mass (Ford and Heald, ACP 2013; Nguyen et al. GRL, 2016) The authors cite Xu et al., 2015 later in the manuscript and that would be a good citation here. Because the authors are talking in the manuscript here about the Southeast US, citing recent findings from the Southeast field campaigns (e.g., SOAS as in the Xu paper) and making a link with the context of those field campaigns would improve the paper.

We greatly appreciate that the reviewer pointed out this mismatch in citations. The text is updated as follows:

Line 15:
In the northeastern USA, de Gouw et al. (2005) showed that ~~organic PM concentrations correlated well with anthropogenic tracers, yet the concentrations of anthropogenic precursors were insufficient to explain the observed PM. In the southeastern USA, observations suggested that organic PM was produced mainly from BVOCs, however modulated by anthropogenic emissions of NOx and SO2 (Weber et al., 2007; Goldstein et al., 2009).~~concentrations of organic particulate matter (PM) correlated well with anthropogenic tracers, yet the concentrations of the anthropogenic precursors were insufficient to explain the observed PM concentrations. In the southeastern USA, radioisotope analysis of organic PM determined that 70% to 80% of the carbon mass had a modern origin even as correlations were observed between SOM mass concentrations and anthropogenic VOC and CO concentrations (Weber et al., 2007). This finding and those of further field studies in the region together suggested that the organic PM was produced mainly from biogenic VOCs (BVOCs) yet modulated by anthropogenic emissions of NO_x and SO_2 (Hu et al., 2015; Xu et al., 2015a; Xu et al., 2015b; Zhang et al., 2018).

6. I have no idea what "V" and "W" mode mean. The authors should provide an explanation if the distinction is important as they suggest.

Please see reply #3 to review #1.

7. Line 165: When talking about Figure 1 the authors state 'concentrations at the T2 site were more than three times higher on average' All of the presented averages in Figure 1b overlap within the uncertainty. Can it be stated that there is statistically significance to the difference? Figure 2 suggests a factor of 2, not 3.

The reviewer raises an important point that needs clarification. Firstly, the bars in Figure 1b do not represent uncertainty but rather variability in the measurements. Secondly, the variability of concentrations among sites can only be fairly compared by considering different times of day as was done in Figure 2, since the variability is largely driven by the diel trends. To clarify this point to the reader, we removed the bars in Figure 1b and emphasized in the caption of Figure 1 as well as in the text that a comparison of the variability across sites is presented in Figure 2, as follows.

Figure 1 caption:
~~Bars represent means and whiskers represent the standard deviation of measurements.~~ The variability of measurements across sites is evaluated in Figure Error! Reference source not found..

Line 170:

The diel trends of organic and sulfate mass concentrations as well as their variabilities across the four sites are shown in Figure Error! Reference source not found..

8. Figure 2 caption: Please correct the text: "Error! Reference source not found." The panels of Figure 2 have different y-axes and this should be mentioned explicitly.

We thank the reviewer for catching these two points, and corrections are made in the figure caption as follows:

*"… at four different sites (cf. Fig.**Error! Reference source not found.** and Fig. ~~Error! Reference source not found.~~ S1). The ordinate scale for the T2-2014 panel is twice that of the other panels. Mass concentrations were corrected to standard temperature and pressure (273.15 K and 105 Pa). Local time is (UTC - 4 h). Lines represent means, solid markers show medians, and boxes span interquartile ranges. ~~The ordinate scale for the T2 panel differs from the other three panels. Concentrations were adjusted to standard temperature (273.15 K) and pressure (105 Pa).~~*

9. Figure 4 is nice, but it's hard to read and digest.

We understand that the information content of Figure 4 is high. This study heavily relies on the PMF results, and Figure 4 provides an important summary of the PMF factors. The authors discussed several alternative representations for this figure and believe that the present version is the best option. Importantly, the text is optimized to accompany the figure. Lines 228 - 349 of the text are paired to the reading of Figure 4. The text explains the characteristics of the factors one by one in each paragraph and systematically refers to each of the panels in that figure.

10. Figure 9 is excellent!

Thank you!

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