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Replies to referee #1

We thank the referee for the careful revision of the manuscript 'Direct observations of molecular clusters and nucleation mode particles in the Amazon'.

The comments improve the current manuscript. We will address all the comments and concerns in detail as shown below/ as in the following paragraphs.

General comments.
We thank the reviewer for suggesting the comparison of the two research sites. This issue has been addressed carefully in the revised manuscript.

The identity of specific sentences in the current manuscript were a mistake. We have re-phrased the identical sentences from previous publications in the revised manuscript.

We address the specific comments of the referee here below.

Referee comment:
There are specific sentences and complete text passages which are identical to Martin et al., 2016. The following list is not necessary complete. The authors should make sure that further text passages similar to other work are referenced correctly. I encourage to use the similarity report provided by the iThenticate plagiarism screening service.

Reply: All the identical text passages to previous publications have been re-phrased in the revised manuscript.

Specific comments:
Page 4, lines 134:
The authors state that T3 is located in a pristine environment. According to e.g., Martin et al., 2016 T3 (time points three) is located downwind of the pollution in a pasture area. I suggest to not use 'pristine' in this context.
Reply: We agree with the referee. The term pristine has been removed from the revised manuscript

Page 4, lines 118:
"T0t is mostly unaffected by the Manaus pollution and is surrounded by dense rainforest. It allows the characterization of an almost completely undisturbed natural environment"
- Did the authors filter for pollution affected periods? If so, what are the filter criteria?
Reply: In the general data analysis, we did not filter for pollution affected periods, since we report average values for the whole measurement period and wet/dry season specifically.
However, for the analysis of the NPF events, pollution events would appear in the NAIS/SMPS data as elevated aerosol concentrations in the accumulation mode. Also, the calculation of the condensation sink gives a good criterion for polluted days, which is clearly higher on non NPF days. Since we observed two nucleation events, with GR of approximately 10-20 nmh^{-1} and about 1 nmh^{-1}, it might be that the days with the higher GR are days which are more influenced by the Manaus pollution plume. Since the sulfuric acid concentrations seemed to be about the same on days with

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high and low GR, we may assume that the Manaus pollution is not the main factor influencing the air masses.

Page 4, lines 124:

The introduced DMPS measurements are performed using an inlet line above canopy. Nevertheless, the section is called ’inside canopy measurements’ which is confusing. I further wonder if there are any comparisons of the DMPS and NAIS during the 3-year period to confirm the quality of measurements.

Reply: The section has been re-named to ‘Measurements inside the rainforest’ to avoid confusion. We changed the classification of the two sites in the whole manuscript accordingly. T0t is called inside rainforest site and T3 pasture or outside rainforest site.

The instrumentation was calibrated before shipping to the campaign and regular maintenance including flow adjustments and zero checks were performed.

Page 5, lines 136:

"The site is located in a clearing of the rainforest." According to Martin et al., 2016 the site is located in a pasture area (2.5 x 2 km) outside the rainforest. I suggest to rephrase the text accordingly from ’outside canopy’ to ’outside forest’ or ’pasture site’.

Reply: We thank the referee for the suggestion. The text has been rephrased accordingly, ***line 177-180****:*

‘The site is an open pasture site, where the Manaus pollution plume regularly intersects and the rainforest canopy did not hinder mixing. Due to the site location, T3 is either a pristine environment or highly influenced by the Manaus pollution plume, mainly depending on the wind direction.’

Page 6, lines 180:

A description of the applied inlet system for the PSM would be interesting for future studies under high rh conditions.

Reply: We agree with the referee. A description has been added to the revised manuscript, ***line 236-243:***

The inlet system consists of a core sampling probe combined with a sintered tube. The core sampling probe consists of two cylindrical tubes with different outer diameters (10 mm and 6 mm). The larger diameter of the outer tube allows up to 10 Lpm total laminar flowrate, to minimize diffusional losses. The inner tube is directly attached to the PSM with an airflow of 2.5 Lpm. The excess airflow is discarded into an exhaust line (Kangasluoma et al, 2016). Downstream of the core sampling line is a sintered tube where dry pressurized air is introduced. The water molecules in the sample flow are pushed towards the outer walls of the sinter material by diffusion, drying the airflow.

Page 6, lines 183:

"Laboratory studies have shown that the RH affects the counting efficiency of the PSM drastically" - Please provide references.

Reply: the sentence has been rephrased as follows:

Line 244-246: Laboratory studies have shown that the RH affects the counting efficiency of the PSM drastically (higher sensitivity at smaller sizes at higher RH; Kangasluoma et al. 2013, Iida et al, 2009).

Page 7, lines 203:

"The DMPS data reported here is qualitative but not quantitative." - Please specify if

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there were problems with this instrument. Quantitative SMPS data are discussed in e.g., section 3.2.

Reply: the issue is addressed more precisely in the revised manuscript. Since the particle losses in the sampling line due to diffusion are not precisely known, the SMPS data has not been corrected for those losses. Hence, for the data shown in Figure 7, where the concentrations of 6-10 nm and 10-20 nm are shown, we feel comfortable only at making assumptions based on the trend of the data but not absolute numbers.

We added the following sentence to the revised manuscript:

Page 7, lines 264-267: 'The DMPS data reported here are qualitative, not quantitative, as the losses due to diffusion in the sampling line are not precisely known and therefore not taken into account in the data presented later in this manuscript.'

Page 7, lines 220:

The planetary boundary layer development is probably different for pasture and rainforest sites. Can you please comment on that?

Reply: The local features and land-use affect the development of convective boundary layer as well as their emission spectra in terms of volatile organic compounds are different. In the morning, the boundary layer develops more rapidly in the pasture area due to lower evapotranspiration and the sensitive heat flux is dominating. This induces a more rapidly growing mixed layer, causing more efficient vertical mixing of precursors and aerosols. Also, photochemistry is more pronounced in (semi) open area than under the canopy. However, during the daytime the small-scale variability in boundary layer dynamics and in VOC concentrations tends to even out. The rapid oxidation chemistry remains characteristic for each site.

We added a sentence in the revised manuscript. ***Page 8, line 293-297****: '*The boundary layer development is also different at the two different measurement sites. It develops more rapidly in the pasture area, causing a more efficient vertical mixing compared to the site enclosed by rainforest. From our observations, we conclude that the main differences in the dynamics of the aerosol particle population at the two measurement sites is due to the 'umbrella effect' of the rainforest canopy.

Page 8, lines 234:

"We observed an unexplained increase in the concentrations of the cluster ions in the NAIS towards the end of October 2013 to January" - Can you please comment on possible reasons for that drift? Is it possible that this drift continued after moving to T3?

Reply: we carefully looked at the flow rates and other NAIS technical data that could give some input, but we could not find any clear indicator of an instrumental drift. The drift continued after moving to T3, which is why we corrected all the data after we observed the drift for the first time accordingly. We attribute the drift is caused by a slow change in the differential mobility analyzer flow rates and charger ion filtration that cause erroneously some of the corona charger generated ions to penetrate into the detectors.

We explain this with the following sentences on ***page 8, lines 306-323*** *in the revised manuscript:*

'We observed an unexplained increase in the concentrations of the cluster ions in the NAIS towards the end of October 2013 to January 2014 at the T0t site. This increased level continued when the NAIS was taken to the T3 site. We consider this drift instrumental. By comparing the 2014 concentrations of the NAIS channels to those prior to the increase (January 2012 and 2013), a correction factor of 1.8 was applied to the 4 smallest size channels of the NAIS (0.8-1.25 nm) to account for the drift for the subsequent data.'

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Page 9, lines 276:

"the biomass burning during the dry season is expected to increase large ion concentrations"
- Please provide a reference

Reply: we rephrased the sentence as follows:

Page 9, lines 361-365:

'Additionally, the wet and dry seasonality characteristic for the Amazon (Rissler et al. 2006, Martin et al. 2010a) can be observed in the concentration of the large ions (4-20nm): the biomass burning during the dry season seems to increase large ion concentrations, whereas during the wet season their concentrations decreased, most likely due to wet deposition and reduced source strengths.

Page 10, lines 287:

"Figure 2 shows the seasonal variability of ions and particles in the three size ranges (0.8-2nm, 2-4 nm and 4-20 nm)" - the lowermost panel in Fig. 2 is missing.

Reply: This is a mistake. During the writing process, we decided not to show the 4-20 nm size range as it does not add any additional valuable information. The sentence was changed in the revised manuscript as follows:

Page 10, lines 373-374:

'Figure 2 shows the monthly variability of ions and particles in two size ranges (0.8-2nm, 2-4 nm) for the 2011-2014 period.'

Page 10, lines 305:

In this paragraph it is not clear to which figure or table the authors refer to. Some examples:
"Positive and negative cluster ion concentrations were, on average, higher during the wet season compared to the dry season."
"Additionally, cluster ions (0.8-2 nm) showed slightly higher concentrations in the morning and evening, compared to other times of the day"
"A dip in the median ion concentration after midday coincides with a higher median concentration of large ions, which is a sign of a larger sink for cluster ions."
"Lastly, 4-20 nm ions peaked at around midday during the wet season, while their diel pattern was more irregular during the dry season."

Reply: this paragraph has been deleted from the revised manuscript. The numbers refer to a Figure that has been removed from the final manuscript, as we decided to only show the particle concentrations, as the data shows a very similar behavior as the ion data. The ion data does not add any additional information to the manuscript.

Page 11, lines 343:

"The median total particle concentrations were about a factor of two higher during dry season (about 1500 cm-3) compared with the wet season (about 700 cm-3)." - In table 1 different values are shown. Furthermore, large particle (4-20 nm) concentrations are very similar to CPC measurements (> 10 nm), implying that on average all particles are in the size range between 10 and 20 nm.
Also, the average particle concentrations (4-20 nm) at T0t (250-800, for the wet season) compares well to total particle concentrations (e.g., in 10-500 nm size range) reported in earlier studies (e.g., Martin et al., 2010a, Martin et al., 2010b, Zhou et al., 2002).
This again implies that the size distribution is dominated by nucleation mode particles, which is in contrast to the same mentioned references.

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*Reply: The numbers reported in the text are a mistake. The sentence has been re-phrased as follows (**page 11, lines 426-428** in the revised manuscript)*: The median total particle concentrations were about a factor of 1.5 higher during wet season (about 1000 cm^{-3}) compared with the dry season (about 700 cm^{-3}).

The presented manuscript is (to our knowledge) the first comprehensive study of small ions and particles in the Amazon basin. We agree with the referee that from looking at those numbers, we could conclude that the aerosol particle population in the Amazon is dominated by the nucleation mode.

Nevertheless, we should be careful since previous studies have not been focusing on nucleation mode particles. All the numbers presented in the current manuscript for the T0t site are directly from the measurements with the NAIS. Whereas the previous results have been using different instrumentation and the measurement locations have been different. We think that from our current knowledge we cannot conclude that the aerosol particle population in the Amazon is dominated by the nucleation mode.

Page 12, lines 361:

"The rain events were more common during the wet season (Fig. 5) when also the median rain intensity was higher." According to Fig 5, the median rain intensity is highest in August.

*Reply: The sentence has been rephrased as follows: **p. 12, lines 482-483** in the revised manuscript:* 'The rain events were more common during the wet season, peaking in August which can be considered as transition season (Fig. 5; Martin et al, 2010) when also the median rain intensity was higher.'

Page 11, lines 377 and following:

In section 3.2 the authors describe a very interesting and scientifically significant phenomenom of increased particle and ion concentrations during rain. Concentrations increase by 2 orders of magnitute towards more than 10000 particles/ions per cubic centimeter. In the following discussion, the authors mention that the particle concentration (nucleation mode size) above canopy (SMPS) does not increase accordingly.

Instead, particle concentration increases only by 20 particles per cubic centimeter (6-20 nm size range), strongly contrasting the conditions below. They conclude that the high particle/ion concentration is a below canopy phenomenom. Furthermore, these nucleation mode particles are not able to leave the canopy which is acting as an umbrella preventing mixing.

In contrast, the presented diurnal variation suggests that mixing and planetary boundary layer development is efficient (although less efficient as compared to the pasture site). Also, the authors argue that they are able to measure ions and particles related to transported biomass burning plumes (page 9, lines 275). Why are those particles able to be mixed into the canopy. It is hard to believe that the forest canopy can maintain such a strong gradient of particle number concentration.

Please justify your statement.

Reply: Earlier studies have shown that rain and particularly shattering of water droplets will result in high concentration of ions (e.g. Tammet et al., 2009). Typically, these effects are not seen with aerosol instruments as the ions are neutralized in the measurement process. Our main point here is that this increase in ion concentrations is mainly an effect that can be observed inside the canopy as the ions that we observe are produced by splashing of the water droplets on the tree leaves. Those ions will not survive until the measurements by the DMPS as it is sampling from above the

canopy and they ions are filtered out by the leaves before reaching the inlet of the DMPS. From the current measurements, we cannot make any statement of the source of the larger neutral particles that are seen by the DMPS above the canopy. It is likely that they are produced in cloud outflow regions and due to strong downdrafts entrained back into the mixing layer (Wang et al, 2016). Most likely the increase of 4-20nm ions during the dry season is a combination of local biomass burning sources and a decrease in wet deposition.
The sentence has been re-phrased in the revised manuscript:
***Page 9, lines 361-365**:*
'Additionally, the wet and dry seasonality characteristic for the Amazon (Rissler et al. 2006, Martin et al. 2010a) can be observed in the concentration of the large ions (4-20nm): the biomass burning during the dry season seems to increase large ion concentrations, whereas during the wet season their concentrations decreased, most likely due to wet deposition and reduced source strengths.

Page 15, lines 45

Please consider to show the results of your backward trajectory analysis in a map.

Reply: We thank the referee for the suggestion, as it improves the manuscript. We have added a Figure showing the map to clarify the back trajectory calculations

*We also rephrased the sentence as follows, **line 594-598: '***These air masses all originate from upstream of the Amazon river, where the NPF day air mass originate from further north, which is an area with dense rainforest. The results of the back trajectory calculations are shown in Figure 10. The red line shows the median of an ensemble or the non event days and the blue line for NPF days.

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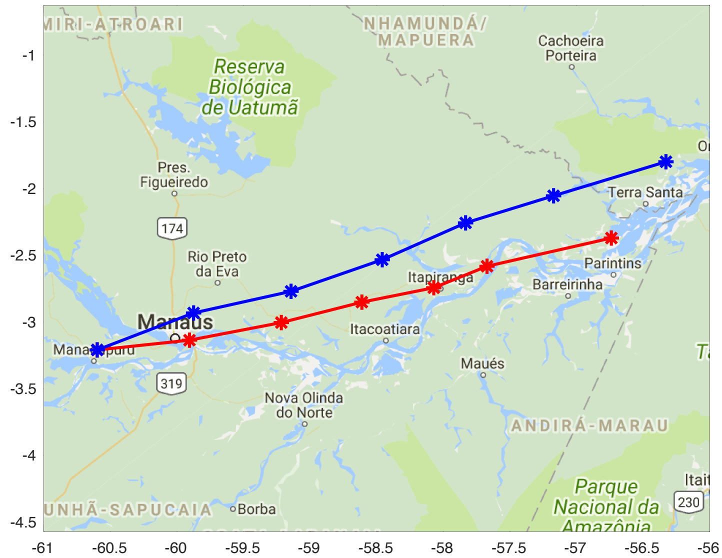

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Figure 10: median back trajectories for NPF (blue) and non NPF (red) days. The trajectories were calculated 24hours backwards arriving at 09:00 local time at 500m a.s.l. at the measurement site.

Page 15, lines 459:
In Fig. 10 a new particle formation event is shown: Please consider to add SMPS contour plots and SMPS particle number concentrations in the nucleation mode size range. Statistical information of SMPS nucleation mode particle number concentration will add further valuable information to Figure 9 and Tables 1 and 4.
The absence of the forest canopy at T3 gives the opportunity to combine NAIS and SMPS measurements, which allows to investigate the entire evolution of the submicron aerosol population.
Reply: we thank the referee for this suggestion. The SMPS Figure has been added to the Figure.

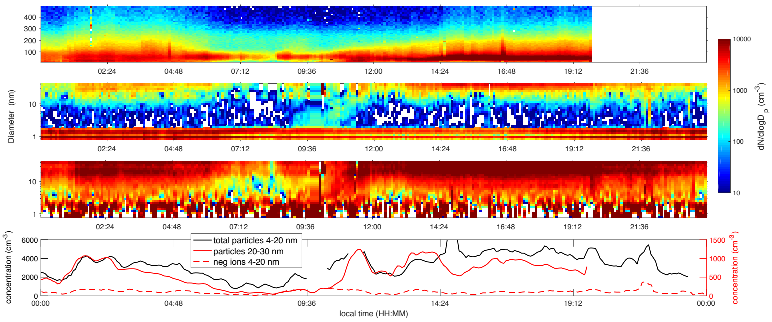

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Figure 11 One example NPF day as observed at the outside canopy (T3) site. (a) shows the surface Figure from the SMPS, (b) and (c) show the surface Figures from the NAIS, (b) for negative ions, (c) for total particles. The color code indicates the measured concentrations. Panel (d) shows concentrations for the 20-30nm size range from the SMPS (black line) and from the NAIS the negative ion (dashed red line) and total particle concentrations (solid red line) in the 4-20 nm size range.

Page 17, lines 510:
"Similar, but weaker, rain-events were found at the site outside the rainforest canopy (T3)." - weaker in terms of what?
Reply: We have re-phrased the sentence as follows in the revised manuscript:
Page 17, lines 679-683: 'Similar rain-events were found at the pasture site (T3). The production of small (0.8-2 nm) and intermediate ions (2-4 nm) during rain events reached a maximum of 10^4 cm^{-3} at the pasture site, where it was one order of magnitude higher at the T0t site. Large ion concentrations reached similar concentrations during rain events at both measurement sites.'

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Technical comments related to Figures

The boxes refer to the 25th-75th percentile.

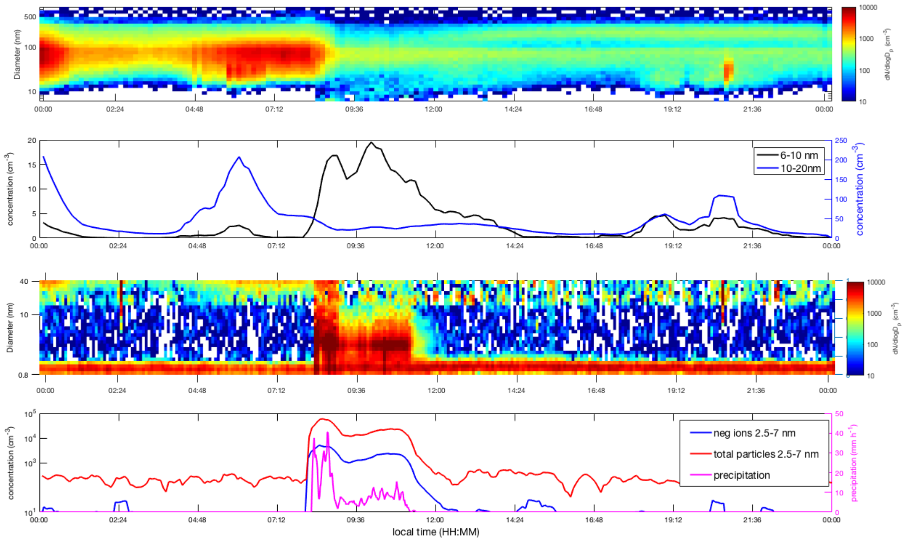
Reply: The whiskers show the extreme values of the data set which are not considered outliers.

The tables and Figures have been changed according to the suggestions of the referee in the revised manuscript.

Fig 4:

number concentration of small positive and negative ions disagrees by a factor of 2. According to Manninen et al., 2016 there should be an agreement within 20%. Please comment on the instrument performance and data quality.

Reply: Table 1 shows a very good agreement between the positive and negative ion concentrations. We believe that the difference seen in Figure 4 is due to a problem with the instrument performance, which might be different on certain days, but which does not affect the overall good instrument performance and data quality.



updated Figure 7

Figure 7. Example for a rain-induced event for total particles (DMPS). The DMPS measurements are taken above the canopy (60 m height), NAIS measurements are inside the canopy. Panel (a) shows the DMPS surface Figure. Panel (b) shows the particles measured by the DMPS for 6-10 nm (black line, left hand axis) and 10-20 nm (blue line, right hand axis). Panel (c) shows the surface Figure for the negative ions, measured by the NAIS. Panel (d) shows the negative ion concentrations for 2.5-7

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nm in blue and the total particle concentration in the same size range from the NAIS in red with the scale on the left axis. The pink trace shows the precipitation in mm h^{-1} on the right axis.

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