Response to the comments of anonymous Reviewer 1

We would like to thank the referee for the immense work invested. The review is very helpful and we will follow the remarks in order to improve the publication.

Comment 1: However, given the rich dataset, I would have expected that the authors could try calculating fluxes from concentration gradients using current models, e.g. k-theory, or inverse Lagrangian models.

Response 1: Unfortunately we did not have sufficient 3D micrometeorology data to efficiently calculate the fluxes, although this matter was thoughtfully discussed as all authors agreed it would have been ideal to report fluxes if we have the needed micrometeorology data. See response 3 from Referee 2.

Comment 2: I would also have appreciated more correlation of observed concentration dynamics with meteorological parameters and concentration of ozone, NOx and CO measured at the site.

Response 2: Concentration dynamics will be investigated in a separate study (Wolff et al., in preparation). Therefore, we would prefer to keep the manuscript as is, by reporting the ambient mixing ratios in a vertical and seasonal aspect only.

Comment 3: Pag 29160 lines 22-23: Unclear what you meant to say: what are the differences between wet and dry seasons?

Response 3: As the name implies, the dry and wet season are characterized by huge differences in the amount of rainfall. In the abstract, we will define in brackets the months of each period. Further clarification will be done to the sentence in line 22.

Pag 29160 line 10 [this numeration is according to the ACPD publication page numbering]: "(February/March 2013 as wet season and September 2013 as dry season)"

Pag 29160 lines 22-23*:* "The increased contribution of oxygenated volatile organic compound (OVOC) above the canopy patterns indicated a transition from dominating forest emissions during the wet season (where mixing ratios were higher within the canopy) to a blend of biogenic emission, photochemical production, and advection during the dry season as mixing ratios were higher above the canopy."

Comment 4: Pag 29161 line 14-15: unclear what you meant to say, please rephrase.

Response 4: The sentence will be rephrased to:

Pag 29161 line 14: "One of these ecosystem interactions is the emission of BVOC by the forest, which can influence the ecosystem at a number of spatial scales from the cell, tissue, organism, and whole ecosystem."

Comment 5: Pag 29162 line 15-16: What about ozone? Isoprene has a high ozone forming potential and this may also impact radiative forcing.

Response 5: Provided the low NOx present in the Amazonian atmosphere (Andreae et al., 2002), the ozone formation potential should not be very effective.

Comment 6: Pag 29164 line 15-17: Under pristine environmental conditions as in your experimental site with low concentration of nitrogen oxides, isoprene hydroperoxides (ISOPOOHs) have been characterized as the dominant first-generation isoprene oxidation products, and these compounds are observed with PTR-MS at a nominal mass weight (m/z) = 71 (Rivera-Rios et al. 2014). This important contribution should also be mentioned here.

Response 6: Thank you for the comment. The contribution will be mentioned in the text.

Pag 29164 line 17: "Moreover, increasing evidence of an isoprene hydroperoxide dominated chemistry under low NOx conditions, such as in the Amazon, has become available. Thus these hydroperoxides must be considered a major isoprene oxidation product in these environments (Liu et al., 2013; Rivera-Rios et al., 2014)."

Comment 7: Pag. 29166 line 1: Having different tubing lengths and different resident times of the air, how can you discriminate between atmospheric reactions at the sampling heights and reactions inside the tubing walls? Wouldn't it be better to just have the lines all of the same length?

Response 7: Due to logistical difficulties we could not have all tubing at the same length. However, due to the high flow of the Teflon pump (16lpm) and the low residence time of an air sample in the lines (maximum residence time of 25 sec), the compounds quantified in this study should have minimum losses as reactivity is not that fast. A wall loss experiment was set up in order to see how much of a known concentration would be lost to the lines at different heights. We found no differences between the different line length and a loss-rate that was within the PTR-MS error (≈10%). We will add a comment to the text.

Page 29166 line 2: "We performed a retention time experiment by injecting calibration gas at a known concentration at the different inlet heights. No significant differences between the different line lengths was found, and the average % loss for each compound was within PTR-MS measurement uncertainty (≈10%). Thus we regard line losses to have a negligible effect on our measurements."

Comment 8: Pag. 29167: how much volume of air was sampled through the cartridges? How did you calculate uncertainties? Or just provide a reference.

Response 8: We sampled 3.3L. Uncertainties for the GC were obtained from Kesselmeier et al., 1997, which will be added to the text. In addition we will explain the sampling error uncertainty in text, which was due to memory effects [losses to adsorbent due to time between sampling and analyzing].

Pag 29167 line 9: "On chosen days, 3.3 L samples were collected continuously at selected heights using a GSA SG-10-2 personal sampler pump."

Pag 29167 line 16: "The analytical uncertainty of the measurements by GC-FID was less than 10% (Kesselmeier et al., 1997), furthermore, due to memory effects (losses to adsorbent due to time between sampling and analyzing), the sampling error was determined to be less than 20%. The uncertainty of the PTR-MS was calculated according to the error propagation method (Doerffel, 1984) taking into account the uncertainty of the calibration (including multicomponent gas standard and mass flow controllers errors), of the PTR-MS itself and the background error."

Comment 9: Pag. 29168 lines 26-27: From the title it seems that you are showing continuous measurements over the seasons, but indeed you only show data for 10 days in the dry and wet periods. In section 3.2 you mention 4 field campaign. This is a bit misleading, I would suggest dedicating a small section in the Material & Methods right after subsection 2.1 where you describe measurement period.

Response 9: We appreciate the suggestion. A new 2.2 section describing the measurement period will be added to the revised version.

Page 29165 line 19: "2.1.1 Measurement period

We measured for two different campaigns which represent the two extremes of seasonality (more information about seasonality can be found in section 3.2. The wet season campaign took place from February 20th to March 6th of 2013. The dry season campaign took place from the 20th to the 30th of September 2013. This site generally experiences dry season conditions from August to October, during which cumulative precipitation is less than 100 mm/month (Restrepo-Coupe et al., 2013)."

Comment 10: Pag. 29169 line 10-15: Do you exclude possible Monoterpene overestimation by PTRMS instead due to overlapping of some isomer masses at m/z 81?

Response 10: We will modify the text in order to clarify the comment.

Page 29167 line 2: "We rule out a large interference on m/z 81 due to the fact that the observed concentrations are similar to those observe in other studies (Rinne et al., 2002; Jardine et al., 2011) and the 1:10 ratio between isoprene and monoterpene mixing ratios has been previously reported in Rondonia (Kesselmeier et al., 2002b).

Page 29169 line 15: "For more information about uncertainty see section 2.4."

Comment 11: Pag. 29170 line 26: Why didn't you include wet season dynamics in fig 4 as you did in figures 6 for isoprene oxidation compounds?

Response 11: We will include in figure 4 the wet season diel cycle of isoprene. The wet season diel cycle of monoterpenes is not available since all data point were below the LOD.

Comment 12: Pag. 29171 lines 20-26: it is unclear how you tested emission algorithms based on temperature only and on light + temperature dependencies if you only have concentration data rather than fluxes. Did you just correlate modeled fluxes with ambient concentration? This does not seem to be feasible.

Response 12: We just wanted to illustrate that there might be a relation between the modelled fluxes and mixing ratios as these can be a reflection of emissions. We decided that we will remove that part from the manuscript.

Comment 13: Pag. 29174 lines 11-12: Did you try to calculate air retention time inside the canopy? This may help understanding the reaction time of emitted VOC.

Response 13: As the focus of the paper was on characterizing the diurnal and seasonal dynamics of the vertical BVOC ambient concentrations at the ATTO site, we were not able to calculate air retention time inside the boundary layer. However, we agree this could provide important information on BVOC chemistry and transport interactions.

Comment 14: Pag. 29175 line 22: I would add also ISOPOOH as possible above-canopy reaction product. Perhaps you may use a term (e.f. iox) to generalize isoprene oxidation products recorded at m/z 71.

Response 14: Thank you for the comment. We will integrate this information.

Page 29167 27: "It should be noted that recent research has shown the possibility of ISOPOOH (isoprene hydroperoxy radicals) which could interfere in m/z 71, especially under low NOx conditions, in which isoprene hydroperoxides are the dominant first-generation oxidation products. This is why m/z 71 within this study should be considered in reality as MVK+MACR+ISOPOOH (Liu et al., 2013; Rivera-Rios et al., 2014). From now on, all references in this study to isoprene oxidation products can be MVK, MACR or, most likely, mostly ISOPOOH, but since we are not able to analytically separate them, we report them as one."

Comment 15: Pag. 29177 lines 10: Measurements of NOx and O3 are mentioned in the M&M section. Showing a graph with vertical distribution of NOx and O3 may help in the discussion of results. At the moment the discussion is very speculative since you are not showing atmospheric oxidants and you are not showing vertical profiles of turbulence. Concentrations of CO may also help understanding the anthropogenic emissions during the dry season.

Response 15: See response to comment 1 to referee 1 and response to comment 3 to reviewer 2.

Comment 16: Pag. 29177 line 20-25: Diurnal dynamics of O3 have been often described to peak at 3PM, this matches with your MAC+MVK concentration dynamics. Possible O3-isoprene interactions?

> **Response 16:** Due to the overall low NOx environment, we assume this interaction should not be really strong.

Comment 17: Pag. 29178 line 25: I find difficult to imagine a switching in a metabolic process which turn plants from emitting de-novo monoterpenes (light+temperature dependencies) to plants emitting monoterpenes from storage organs (temperature dependency only). I would rather think that Amazon is a highly biodiverse ecosystem and perhaps the plant species in the tower footprint are prevalently T-dependent emitters and diverge from plants described by Bracho-Nunez et al. in 2003.

> **Response 17:** Yes we agree with you and we will delete the sentence. Now it will read as following:
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> **Page 29178 line 23:** "They seemed to more closely follow the diurnal temperature than the radiation cycle. Furthermore, as the PTR-MS measures the sum of monoterpenes, it is possible that the monoterpene composition changes seasonally along with their reactivities and vertical patterns (Kesselmeier et al., 2002b; Kuhn et al., 2004).

Comment 18: Pag. 29179 lines 4-17: I would spend some discussion of the recent paper from Rivera-Rios et al. 2014 in GRL which demonstrate relevant ISOPOO production under low NOx conditions.

> **Response 18:** We understand that by the new comment in the methodology in which we say (Page 29167 line 2) "From now on, all references in this study to isoprene oxidation products can be MVK, MACR or, most likely, mostly ISOPOOH, but since we are not able to analytically separate them, we report them as one." We are acknowledging this issue, and since we are not able to analytically separate we will talk at them as a whole.

<u>Response to comments from anonymous reviewer # 2.</u>

We would like to thank anonymous reviewer 2 for his detail comments and suggestions that would substantially improve the final version of the manuscript. We deeply appreciate and acknowledge his concerns and efforts with the aim to improve the manuscript in an optimum way, which would help the future readers and BVOC scientists.

Comment 1: Introduction: The introduction is quite long and unfortunately it misses to guide the reader to the point: Why are we interested in studying biogenic VOCs exactly in the Amazonian rain forest? Isn't this the question which has to be answered to the reader before stating the objective in the last paragraph of the introduction? After reading the objective the reader asks, 'Yes, but why exactly is this study important?' – Most likely because this question was not answered completely before. While the first paragraph of the introduction goes into the right direction the further paragraphs serve to introduce every single VOC. However, this information needs to be set into the right

context. I would suggest to condense the introduction and close the circuit why the study will contribute significantly to the scientific understanding of the atmospheric distribution of BVOCs and their role in atmospheric chemistry before stating the objective.

Response 1: For better explanation we will add a comment after the first paragraph on why are we interested in studying biogenic VOCs in the Amazonian rainforest. We understand that by explaining of page 29161 the pristine conditions of the Amazon environment allowing the study of continental regions with similar atmospheric condition regimes to before the industrial revolution. We also explain the Amazonian atmospheric photo-reactor (Andreae et al., 2002). At last, in the following page [29162] we explain the importance of BVOC at the different ecosystem levels, detailing their impact in the atmosphere by the possible production and formation of secondary organic aerosols, thus influencing radiation properties as well as cloud processes. We will make two subchapters 1.1 in which we will describe the VOC species [of interest] in the Amazonian environment. In addition, we will include a clearer objective of our research study in the Amazon in the introduction.

Page 29162 line 2 [this numeration is according to the ACPD publication page numbering]: "Having in view all these issues it is acknowledged that field observations of BVOCs in the tropics are rare likely due to logistical and technical problems including site access, power requirements, and high ambient humidity and temperatures."

Page 29164 line 24: "The objective of this study is to provide a detailed description of BVOC in-canopy mixing ratios and fluctuations, which can indicate heterogeneous sources within the canopy and can be related to the exchange between the forest and the atmosphere under dry and wet season conditions. Furthermore, the measurements give insight for a new forest site with data obtained at the new Amazonian Tall Tower Observatory (ATTO) site on an 80 m tower."

Comment 2: I would strongly advise to have a proper language check on the manuscript I figured out a couple of oversights. Some parts of the manuscript – especially in the Results section - are hard to understand because of imprecise statements or improper use of words.

Response 2: We gratefully acknowledge the advice and we will carefully rechecked the document for language mistakes.

Comment 3: I wondered why the authors did not try to measure or calculate fluxes. With a shorter dwell time for the VOCs e.g. 0.2 s (as e.g. in the case of methanol) one could try to calculate above canopy fluxes e.g. by means of the virtual disjunct eddy covariance method (Karl et al., 2002) given that 3D wind measurements are available at the corresponding altitude. Although I understand that the switching between different altitude levels and sequential measurements (using a single PTR-MS) make continuous flux measurements challenging. However, it would have been valuable to have at least an imagination of the BVOC fluxes during the different seasons especially for the discussion. Further, I expected to see measurements of other atmospheric pollutants like ozone or NOx to support the discussion part of the manuscript which is partially quite

speculative. Were there any ozone and NOx measurements at the site? If yes it would be good to integrate them to support the discussion.

Response 3: We have had many discussions regarding ecosystem-scale flux calculations amongst the authors and arrived at the decision that flux calculations under these circumstances would result in large uncertainties due to the unconstrained turbulence conditions within and above the forest canopy. See response to comment 1 from reviewer 1. Measurements of other pollutants at the site, such as ozone and NOx will be discussed in detail in a future manuscript (Wolff et al, in preparation). However, our observations represent the first BVOC measurements at the ATTO tower site and include other novel aspects such as diurnal and seasonal dynamics as well the first vertical gradient observations of methyl ethyl ketone demonstrating biogenic emissions and acetonitrile demonstrating anthropogenic uptake.

Comment 4: Title: As the authors refer to the forest with the words 'within and above' please remove the word site from the title.

Response 4: We will remove the word "site".

Comment 5: Page 29160, line 10: '(February/March 2013 and September 2013)', please insert wet season and dry season to clarify which seasons are meant.

Response 5: We will do as suggested. See response to comment 3 from reviewer 1.

Comment 6: Page 29160, line 21-25: This part is rather cryptic. Specify why 'OVOC patterns' indicate this transition. The word pattern is not meaningful. The sentence: 'This was inferred from the high mixing ratios found within the canopy, and those obtained above the canopy for the wet and dry season, respectively' does not clarify which patterns the authors refer to (a reader doesn't know the figures at this stage of the manuscript).

Response 6: We will rewrite this sentence more clearly. See response to comment 3 of reviewer 1.

Comment 7: Page 29160, line 28: The last sentence of the abstract does not relate to anything what was written before although the start 'In addition,' indicates this. Consider rewriting or clarify the connection between this sentence and the one before.

Response 7: We will change the text to:

Page 29160 line 28: "Considerable differences in magnitude of BVOC mixing ratios, as compared to other reports of Amazonian BVOC, demonstrate the need for long-term observations at different sites and more standardized measurement procedures in order to better understand the natural exchange of BVOC between the Amazonian rainforest and the atmosphere."

Comment 8: Page 29165, Site description: The main part of the information which is given in section 3.2. (Time series) would be important to have in the site description. In

my opinion a site description is also thought to introduce site, climatic conditions, and characteristics in the seasonality.

Response 8: Yes we agree and we will include a 2.2 section in the materials and methods explaining the time of measurements. See response 9 to reviewer 1.

Comment 9: Page 29166, line 19: The authors write: 'Humidity dependent calibrations (using bubbled synthetic air, regulated as close as possible to ambient humidity conditions) were performed' why did you not use the zero air to dilute your gas standard? Which dilution steps did you use for your calibration? What were typical sensitivities for your PTR-MS?

Response 9: We used humidified zero air to dilute the standard. We will insert the different calibration steps as well as the wet and dry season sensitivity for each calibrated compound. Please note, that the limit of detection (LOD) is already described just before.

Page 29166 line 19: Humidity dependent calibrations (using bubbled zero air to dilute the standard, regulated as close as possible to ambient humidity conditions) were performed using a gravimetrically prepared multicomponent standard including methanol (m/z 33; ncps/ppb =$10.73_{\text{wet season}}$ and $9.11_{\text{dry season}}$), acetonitrile (m/z 42; ncps/ppb = $22.82_{\text{wet season}}$ and $19.07_{\text{dry season}}$), acetaldehyde (m/z 45; ncps/ppb = $21.71_{\text{wet season}}$ and $18.41_{\text{dry season}}$), acetone (m/z 59; ncps/ppb = $22.69_{\text{wet season}}$ and $19.88_{\text{dry season}}$), isoprene (m/z 69; ncps/ppb = $6.03_{\text{wet season}}$ and $8.51_{\text{dry season}}$), MVK+MVK (m/z 71; ncps/ppb = $20.34_{\text{wet season}}$ and $16.37_{\text{dry season}}$), MEK (m/z 73; ncps/ppb = $16.95_{\text{wet season}}$ and $17.91_{\text{dry season}}$) and α-pinene (m/z 137; ncps/ppb = $0.029_{\text{wet season}}$ and $0.52_{\text{dry season}}$ and m/z 81; ncps/ppb = $4.98_{\text{wet season}}$ and $5.63_{\text{dry season}}$) with dilution steps ranging from 22 to 0.8 ppb (Ionicon, Austria for the wet season and Apel and Riemer for the dry season).

Comment 10: Page 29166, line 19: Please exchange 'multicomponent standard of formaldehyde' by 'multicomponent gas standard including formaldehyde.'

Response 10: We will be modified accordingly.

Comment 11: Page 29166, line 25: Ionimed does not exist anymore. Ionimed and Ionicon consolidated under the name Ionicon. Did I understand it right and the standard was bought at Ionicon but originally it was from Apel and Riemer? Please note: write 'Apel and Riemer' not 'ApelandRiemer' and consider including the habitat.

Response 11: Two different calibration cylinders were used, one for the wet season which was the Ionicon one, and another one for the dry season. This will be specified in the text and the wording for Apel and Riemer will be modified accordingly. See response to comment 9.

Comment 12: Page 29166, line 25 and following lines: The authors write: 'Monoterpenes were monitored at m/z 81 (mass calibrated independently for alpha-pinene, Pearson coefficient for m/z 81 against m/z 137: 0.71), its main fragment, instead of the unfragmented m/z 137' A Pearson correlation coefficient of 0.71 is quite low (Rsquare of approximately 0.5) which means that only 50 % of the variability on mass

channel 81 is explained by m/z 137. You are aware that on m/z 81 there are also other compounds, e.g. a fragment of the leaf wound compounds (Fall et al., 1999)? With such a low Pearson correlation coefficient it would be better to cope with the lower detection limit and quantify monoterpenes directly using the m/z 137.

> **Response 12**: We understand your concern and we take it as ours. We had a relatively low correlation between m/z 137 and m/z 81 likely due to the noise of m/z 137 rather than overlapping of compounds. We will include this information in the text as specified in response to comment 10 from reviewer 1.

Comment 13: Page 29167, line 3-9: 'The PTR-MS technology allows for fast sampling at very low mixing ratios, but the system relies solely on mass-over-charge (m/z) for compound specification. As such, cross validation with another compound selective technique, such as Gas Chromatography is strongly advised. This was performed using the GC-FID (Gas Chromatography-Flame Ionisation Detector) technique for monoterpenes () and isoprene.' I advise to write: 'The PTR-MS technology allows for fast sampling at very low mixing ratios, but the system relies solely on the mass to charge ratio (m/z) for compound specification. To cross validate compounds gas chromatography was performed for monoterpenes (.) and isoprene using a GC-FID (gas-chromatography-flame ionization detector)'.

> **Response 13:** We appreciate the suggestion and we will modify the specific part accordingly.

> **Page 29167 line 3: "**The PTR-MS technology allows for fast sampling at very low mixing ratios, but the system relies solely on mass-over-charge (m/z) for compound specification. To cross validate compounds gas chromatography was performed for monoterpenes (α-pinene, camphene, 1-octen-3-ol, sabinene, β-pinene, myrcene, α-phellandrene, 3-carene, α-terpinene, ρ-cymene, limonene and δ-terpinene) and isoprene using a GC-FID (Gas chromatography-flame ionization detector)."

Comment 14: Page 29167, line 19-22: How did you estimate the uncertainties? Did you, for example, include errors of flow controllers during the calibrations?

> **Response 14:** Yes we did include mass flow controllers' uncertainties, calibration gas uncertainties, etc. We used the theory of propagation of error and it will be added to the text.

> **Page 29167 line 17:** "The uncertainty of the PTR-MS was calculated according to the error propagation method (Doerffel, 1984) taking into account the uncertainty of the calibration (including multicomponent gas standard and mass flow controllers errors), of the PTR-MS itself and the background error."

Comment 15: Page 29168, line 19-21: 'Finally, butanal could also have been a contributor, but GC-FID values for butanal had a mean of 0.01+-0.04 ppb (n=104) and thus we considered it as negligible. Therefore, we regarded m/z 73 as representing MEK.' You wrote before that you did not perform compound specification by GC-FID for m/z 73. Thus the sentence is confusing.

Response 15: Yes we agree it is confusing and thus we will remove the sentence and leave as final sentence for that paragraph:

Page 29168 line 19: "Thus, despite the possible contributions from other compounds to m/z 73 are plausible, we regard MEK as a major contributor to the signal."

Comment 16: Page 29169 line 22, section 'Time series': The information given here fits more to the site description or site characterization. Consider moving this part accordingly. Moreover, the title time series is meaningless - it does not refer to the information given in this section.

Response 16: We agree and we will add a 2.2 section at the M&M to describe the measurement periods. However we believe that some of the information in the section 3.2 is part of the results as it is the analysis of the meteorological conditions among seasons. We also decided to change the time series title to "Analysis of meteorological parameters". See response to comment 9 from reviewer 1.

Comment 17: Page 29170, line 25: Suggest rewording to 'During the night (median for the time period 00:00-03:00 LT), however, isoprene mixing ratios above the canopy were considerably higher than within canopy'.

Response 17: We will rephrase accordingly.

Page 29170 line 24: "During the night (median of the period of 00:00-03:00 LT), however, isoprene mixing ratios above the canopy were considerably higher than within the canopy (Figure 4)."

Comment 18: Page 29171 ff: You refer to the vertical profiles always within special time periods. I guess referring to them as midday, afternoon, night (after a proper definition) would make it easier for the reader and probably also for the authors as one already has to cope with the different altitudes.

Response 18: We understand that time periods for statistics do not represent a general daylight period (i.e. the whole afternoon, the whole midday period), and therefore we prefer to use the exact time range as used for statistics.

Comment 19: Page 29171, line 22: are you talking about the rsquare or the Pearson correlation coefficient?

Response 19: This specific text will be removed (See comment response to comment 12 from reviewer 1) but we meant Pearson.

Comment 20: Page 29171, line 25/26: be precise – how did you take transport and chemistry into account?

Response 20: As transport and chemistry was not directly treated, this text will be removed.

Comment 21: Page 29172, line 5-7: Do you mean: 'Dry and wet season data of MVK + MACR showed a clear seasonality and large differences magnitude'? Please rewrite accordingly.

Response 21: Thank you for the suggestion. This sentence will be rewritten for clarity.

Page 29172 line 5: "Dry and wet season data of isoprene oxidation products showed a clear seasonality and large differences in magnitude between the seasons."

Comment 22: Page 29172, line 14-15: I don't understand the sentence Consider rewriting.

Response 2: We will rewrite to:

Page 29172 line 14: "Mixing ratios below the canopy were usually 0.1 ppb lower than above the canopy throughout the day".

Comment 23: Page 29172, line 21: 'During this time of the year' it is not clear to which season you refer to. I guess the dry season? Please clarify!

Response 23: We will modify it to "dry season" instead of this time of the year.

Comment 24: Page 29173, line 15-16: 'Although the highest mixing ratios were found at the canopy top, the diurnal cycle with a pronounced increase around noon suggested a biogenic origin. ' Although'? The one does not exclude the other. Why would it be unusual to believe in a biogenic origin of the OVOCs just because ratios at the top of the canopy (and not within the canopy) were highest? I guess the insulation is strongest at the canopy top.

Response 24: To clarify, we will exchange the word "although" with "with".

Page 29173 line 15: With the highest mixing ratios found at the middle of the canopy, the diurnal cycle with a pronounced increase around noon is consistent with biogenic emissions from canopy vegetation.

Comment 25: Page 29173, line 19-20: where is the difference between above the canopy and at the top of the canopy? Comparing to Fig 1. 24 m is more inside the canopy than at the top. It would be easier to have the proper altitude in brackets (the corresponding figure only shows 0.5,24 and 79m). Reading through the last paragraph I have the feeling that different terminologies are used for the same altitudes (which is quite confusing) please define a uniform terminology for each altitude and use that consistently. Maybe include a proper definition to Figure 1 next to the altitude.

Response 25: The terms ground, middle of the canopy and above the canopy can be easily derived from the figure and set into context with the height. We will carefully use a uniform terminology in the revised

version. In addition we will change “top of the canopy” for “middle of the canopy” (see response to comment 24).

Comment 26: Page 29173, line 27-28: Would this behavior refer to a difference in dominating sources necessarily? What about a difference in sinks (stronger photochemistry at the canopy top) or stronger vertical mixing?

Response 26: Yes you are right. After “dominating sources” we will include “and sinks, as well as possible differences in the vertical mixing”.

Page 29173 line 27: “Such difference clearly indicated a seasonal change in the dominating sources and sinks, as well as possible differences in the vertical mixing for this species.”

Comment 27: Page 29174, line 15: You refer here to the limit of detection for methanol which is –by the way - exceptionally high... Referring to table 1, I found that the dwell time for methanol is just 0.2s instead of 1 s as for most of the other compounds. Is there a reason choosing this dwell time? Increasing dwell time means also decreasing the limit of detection.

Response 27: Due to the need to measure more masses per height during a vertical profile (only 2 min at each height), the dwell times for some masses were reduced. The tradeoff is an increased limit of detection for methanol.

Comment 28: Page 29174, line 20-24: This belongs more to the discussion than to the results. Additionally you write ‘could be the photochemical oxidation of VOCs’ Unclear – do you mean photochemical oxidation of other VOCs that degrade to methanol or do you mean a photochemical sink for methanol.

Response 28: We agree and we will remove this par as it is already mentioned in the discussion.

Comment 29: Page 29175, line 6-12: This belongs into the discussion. Additionally the statement that Acetonitrile typically originates from biomass burning requires a reference.

Response 29: We are agree and we will move it to the discussion.

Page 29181 line 2: “Distinct biomass burning plumes were not observed. This indicates that there was no biomass burning close-by impacting our measurements, and impact from long-range transport may be assumed. Such burning activities can be expected during this time of the year (Karl et al., 2007a). In addition the observation that levels decrease towards the ground could indicate a potential uptake by soil bacteria, although wet deposition cannot be excluded. The variability of the measurements especially inside the canopy occults a possible influence by plant emissions which has previously been reported (Bange and Williams, 2000; Nyalala et al., 2011).”

Comment 30: Page 29176, line 1-3: The statement is speculative the lower methanol mixing ratios could be a consequence of lower emissions as well (maybe because of

decreased insulation). That the reduced mixing ratios of methanol are a consequence of uptake at wet plant surfaces is a hypothesis which has to be supported by references (e.g. Laffineur et al., 2012). I would suggest to tone down and include references.

Response 30: We thank the referee for this contribution. We decided to include it as a reference rephrase as following:

Page 29176 line 1: "Finally, the mixing ratios of water soluble compounds, such as methanol, might also be influenced by the wet plant surfaces (Laffineur et al., 2012) emphasizing the seasonal trend that originated from reduced emissions."

Comment 31: Page 29176, line 9: I guess you mean an increase in the variability of BVOC mixing ratios? Please clarify.

Response 31: The clarification will be inserted.

Page 29176 line 9: "In addition, an increase in the variability of BVOC mixing ratios above the canopy was observed in the dry season, with mixing ratios inside the canopy sometimes reaching the above canopy levels."

Comment 32: Page 29176, line 13-14: The second part of the sentence is hard to understand. Consider rewriting!

Response 32: We agree and we decided to write the sentence as:

Page 29176 line 11: "Most likely this was due to the higher insolation during the dry season which results in high upper canopy leaf temperatures and turbulent mixing above the canopy during the day. Thus, this higher variability might also have been influenced by changing environmental conditions, seasonal differences in plant emission potential, variation in the oxidative capacity of the atmosphere influencing secondary BVOC production rates, and transport of air masses from other regions."

Comment 33: Page 29176, line 16 – Page 29177 line 6: The two paragraphs come out of the blue here and disturb the flow of reading especially as the next paragraph (starting at page 29177 line 7) connects well to the paragraph in front (ending at page 29176 line 15) of the two mentioned ones. I suggest to remove them here. If the authors think the information is required it needs to be included somewhere where it fits better.

Response 33: We agree but we believe the information is necessary for the discussion as it provides a climatic comparison with other forested ecosystems as well as a phenological link to climatic conditions in the Amazon region, important for understanding the seasonality of BVOC in the Amazon. Therefore, we will place those two paragraphs at the beginning of section 4.1 Diel and seasonal behavior (Page 29175 line 125).

Comment 34: Page 29177 line 7: The long range transport of what? You probably mean the long range transport of NOx enriched air masses? Please clarify. There are a couple of mistakes like that throughout the manuscript. Even if the reader can guess

what the authors mean it would improve the manuscript a lot if the authors state clearly what they mean.

Response 34: We will modify accordingly.

Page 29177 line 7: "During the dry season, long range transport of NOx enriched air masses from other regions, including biomass burning air masses, could have triggered a higher oxidative capacity of the air as indicated by higher ozone and NOx concentrations at the ATTO site during the dry season (Wolff, S. personal communication, 2014)."

Comment 35: Page 29177 line 7-17: It sounds like there are ozone and NOx measurements at this site. If measurements of ozone and NOx at this measurement site are available at the corresponding time they should be included to support the discussion about atmospheric degradation which is a bit speculative without measurements of other atmospheric pollutants.

Response 35: See response to comment 3.

Comment 36: Page 29177 line 11: 'the rise of ozone and NOx' do the authors refer to the personal communication here? See comment above.

Response 36: Yes we do refer to the personal communication from the study Wolff et al. In particular we refer to the increase in ozone and NOx mixing ratios consequent from higher mixing ratios during the dry season as compared to the wet season.

Comment 37: Page 29177 line 15: 'and vertical patterns' as you refer to differences during the wet and dry season as well please include that.

Response 37: We agree and we will include among seasons after vertical patterns.

Page 29177 line 14: "Summarizing, the different mixing ratios and vertical patterns among seasons can be related to changes in insolation, temperature, external sources (i.e. biomass burning air masses during the dry season) and leaf phenology, all related to seasonality."

Comment 38: Page 29177 line 18ff: It is well known that isoprene emissions are light dependent. Please insert a reference.

Response 38: We will include a reference here.

Page 29177 line 18: "Isoprene peaked together with light intensity just after midday inside the canopy during the dry and the wet season (Guenther et al., 1996)."

Comment 39: Page 29178 line 4ff: I think I didn't get the point of discussion here How efficiently isoprene can escape from the canopy by transport depends on the nocturnal boundary layer (NBL) height which is usually quite low. During the night there is

usually no or only very weak vertical mixing and horizontal transport below the NBL leads to the transport of air masses which originate as well from rain forest canopy. Please clarify what you want to state.

Response 39: We agree it may be unclear and we will modify to:

Page 29178 line 28: "This decrease just after sunset was too rapid to be explained exclusively by gas-phase chemistry due to a decrease in the levels of OH which does not have major sources in the dark (Goldan et al., 1995). Under these conditions a decrease in isoprene mixing ratios can be partially explained by ceasing photosynthesis. Ozonolysis of alkanes during the night can be neglected due to the low ozone levels (Paulot and Orlando 1996; Andreae et al., 2002). This potentially important process becomes more visible during the night, when the nocturnal boundary layer results in low transport rates (with a wind speed at 19m of 0.23±0.17m s-1) with diffusion being the main trigger. Under these conditions, the profile of isoprene with lower mixing ratios to the ground during the night clearly indicated a sink at the surfaces (such as leaves, soil and/or litter). Presumably isoprene was lost as well to microbial consumption (Goldan et al., 1995; Cleveland and Yavitt, 1997; Gray et al., 2014)."

Comment 40: Page 29178 line 18: If you refer to previous studies please include the corresponding references here.

Response 40: We agree and we will include the reference.

Page 29178 line 17: "A few Amazonian tree species have been monitored for monoterpene emissions in previous studies, suggesting that more factors than solely meteorological influence the seasonality of monoterpene emissions (Kuhn et al., 2004; Bracho-Nunes et al., 2013)."

Comment 41: Table 2: The authors write 'values are reported as medians and means during daylight periods as reported in the references'. If you report the values here it should be stated for every value if it is mean or median and for which time period. I would suggest using footnotes.

Response 41: We agree, we will add a subscript specifying if the number it is a mean or a median in the table 2 caption.

Comment 42: Figure 2: Please include measurement altitude into the figure, e.g., write Isoprene levels at 24 m (ppbv) as y label.

Response 42: We will revise as suggested.

Comment 43: Units: I would suggest to change ppb to ppbv throughout the whole manuscript.

Response 43: After very careful discussions with all coauthors we do not agree on changing the unit as we are not talking about an ideal gas. In addition, only if the M is specified after ppb [ppbM] is referring to mass mixing ratios rather than that you are not talking about volume mixing ratios.

Comment 44: Figure 4 -10: The colored boxes around each plot to indicate if it is dry season or wet season data are redundant. It is written in words in each plot and already obvious without the boxes. Please remove the boxes.

Response 44: We will remove the colored frames.

Comment 45: Page 29178 line 26ff: A switching of the metabolic processes? I think this sounds very speculative Do you have any references?

Response 45: See response to comment 17 from reviewer 1.

Comment 46: Page 29180 line 18-20: Why not both? You stated above that NOx enriched air masses were transported to the site. These air masses could have been enriched in MeOH as well.

Response 46: We agree and we will modify to:

Page 29180 line 18: "For the dry season, the overall higher mixing ratios above the canopy is consistent with both enhanced photochemical production within the troposphere and transport of biomass burning impacted air masses"

Comment 47: Page 29181 line 11: The sentence sounds like the authors did investigate the plant species in the Amazonian rain forest among different seasons, which they did not. Please consider rewriting!

Response 47: We agree and we will clarify.

Page 29181 line 10: "Due to the immense area of the Amazonian ecosystem and the paucity of measurements, a great variability of plant species (Hans ter Steege et al., 2013) and atmospheric BVOC levels is observed in the Amazon basin."

Comment 49: Page 29181 line 27- Page 29182 line 5: Please rewrite the corresponding sentences they read odd.

Response 49: We agree they read odd and we will modify to:

Page 29181 line 27: "In agreement with Kanakidou et al., (2005), further efforts on monoterpene characterization in terms of abundance and reactivity in Amazonia are needed for a better understanding of SOA growth and formation processes, regionally as well as worldwide. In addition, the oxidative capacity of the atmosphere can be studied based on the oxidation products of isoprene. Across the Amazon region mixing ratios of isoprene oxidation products are always higher above the canopy and during the dry season (Table 2), especially when measured in the mixed layer by aircrafts (Karl et al., 2007; Kuhn et al., 2007) or tethered balloons (Kesselmeier et al., 2000) suggesting a higher oxidative capacity during the dry season above the canopy."

Comment 50: Page 29182 line 12: What do you mean by 'to improve our understanding of BVOC'?? Do you mean 'BVOC emission, transport and chemistry'?

Response 50: We meant that and we will modify it the text.

Page 29182 line 9: "Therefore more continuous measurements with a better representation in space and height are needed to investigate the seasonality of within and above canopy interactions with the atmosphere to improve our understanding of BVOC emissions, transport and chemistry over Amazonia."

Comment 51: Page 29182 line 20-23: The two sentences are unclear. Do you mean something like 'Marked seasonality and diurnal behavior of BVOC patterns was observed at the site as seen in their seasonal and vertical chances' You start the next sentence with 'This' and refer to the sentence in front. The text would be easier to follow if you would write something like: 'These changes in VOC mixing ratios were attributed'.

Response 51: We appreciate the detailed feedback. We agree it is unclear and we will change it to:

Page 29182 line 20: "Marked seasonality and diurnal behaviour was observed at the site, as seen in the BVOC mixing ratios seasonality and vertical profiles. These changes in BVOC mixing ratios were attributed to changing sources of these compounds mainly in relation to seasonal fluctuations of light, temperature and phenology."

Comment 52: Page 29183 line 1. 'This indicates a mixture of sources ' What about sinks?

Response 52: Yes, you are right. We will also include sinks in the sentence.

Page 29183 line 1: "This indicates a mixture of sources such as vegetation emissions, oxidation from primary emitted BVOCs and regional atmospheric transport as well as sinks."

Comment 53: Page 29183 line 4-7: Although the authors are right with the general statement I guess vertical profiles of mixing ratios in combination with ozone and NOx and maybe also BVOC flux measurements would be most useful and would leave much less room for speculation as BVOC mixing ratios alone.

Response 53: See response to comment 3.

Technical issues:
Comment 54: Throughout the manuscript: Sometimes you write oxidation capacity sometimes you write oxidative capacity. I guess oxidative capacity is the right terminology. Please check that and use a uniform terminology.

Response 54: We agree and we will modify all terms to oxidative capacity.

Comment 55: Page 29160, line 4: I suggest to write: 'biogenic volatile organic compounds', usually it is not necessary to capitalize each first letter to introduce an acronym. This refers also to other acronyms.

Response 55: We will modify all capital letters explaining an acronym.

Comment 56: Page 29160, line 7: 'Proton Transfer Reaction Mass Spectrometer': Please decide for a uniform notation all over the manuscript (compare page 29166 line 10 where you write 'Proton Transfer Reaction-Mass Spectrometer'). I would also suggest starting every word in small letters.

Response 56: We will modify to the initial one to Proton Transfer Reaction – Mass Spectrometer and thereafter we will refer to the instrument as PTR-MS.

Comment 57: Page 29165, line 20 and Page 29166, line 9: The acronym for volatile organic compounds was already introduced before.

Response 57: We will use the acronym.

Page 29165 line 20: "Measurements of VOC mixing ratios were accompanied by the determination of total OH reactivity, nitric oxide."

Page 29166 line 9: "Measurements of VOCs were performed using a PTR-MS."

Comment 58: Page 29169 line 5: I suggest to write: 'A cross validation for isoprene and monoterpene data obtained by in-situ PTR-MS measurements was performed off-line analyzing absorbent tubes by GC-FID (Fig.2)'.

Response 58: We will modify accordingly.

Comment 59: Page 29170, line 23: Suggest rewording to 'During daytime isoprene showed highest mixing ratios'.

Response 59: We will modify as specified.

Comment 60: Page 29170, line 26/27: Suggest rewording to 'Strong gradients towards the ground were seen especially for the dry season'.

Response 60: We will modify accordingly.

Comment 61: Page 29171, line 2: you write 'In addition, the variability increased during the dry season' variability increased compared to what? Be precise.

Response 61: We agree and we will modify the text to:

Page 29171 line 2: "In addition, the variability increases during the dry season compared to the wet season, as observed in the difference of IQR of 1.9 ppb during the wet season to 6.1 ppb during the dry season, at 24 m for the period 12:00-15:00."

Comment 62: Page 29171, line 4/5: 'Both seasons had similar vertical profiles' technically wrong please correct for example: 'Within canopy (24 m) similar vertical profiles of isoprene were seen for the dry and the wet season during midday (12:00-15:00)'.

Response 62: We agree and we will modify to:

Page 29171 line 4: "Within canopy (24 m) similar vertical profiles of isoprene were seen for the dry and the wet season during midday (12:00-15:00) and at night the highest values were found at the highest inlet."

Comment 63: Page 29171, line 7: What do you mean with relatively stronger? And compared to what? Be precise.

Response 63: We agree and we will modify the text to:

Page 29171 line 7: "However, the vertical profiles for isoprene during the wet season had a relatively stronger night-to-day variability at 24 m, as compared to the dry season, despite the overall lower mixing ratios during this period. The less pronounced vertical gradient during the dry season could be due to a stronger turbulent mixing (Figure 5)."

Comment 64: Page 29172, line 25: The ground levels cannot show a diurnal variability. I guess you mean mixing ratios at the ground level? Please check the manuscript properly! There are a couple of mistakes like that. Moreover it is not clear what the authors mean – do they mean a diurnal pattern with diurnal variability or do they mean that the variability shows a diurnal pattern? Use precise language.

Response 64: We agree and we will modify to:

Page 29172 line 25: "The ground level mixing ratios showed a night-to-day variability with respect to the wet season, though remained the lowest at this height."

Comment 65: Page 29173, line 1-2: 'The minimum of the MVK+MACR-to- isoprene ratio was located inside the canopy.'???.

Response 65: We will rephrase to:

Page 29173 line 1: "I_{ox}-to-isoprene ratios during the wet season were lowest in the middle of the canopy at 24m, and increased near the ground and above the canopy."

Comment 66: Page 29173, line 17-18: The mixing ratios remained much lower compared to what?

Response 66: We will modify to:

Page 29173 line 17: "The mixing ratios above the canopy and at the ground remained much lower than within the canopy (24m), throughout the measurement period, except for acetone."

Comment 67: Page 29178 line 19: Better: 'Among those factors' instead of just 'Among those'.

Response 67: We will change accordingly.

Page 29178 line 19: "Among those factors are the oxidative capacity of the atmosphere and phenological development, which may be accentuated during the dry season (Kuhn et al., 2004)."

Comment 68: Page 29179 line 10: Please insert 'compared to isoprene' after 'proportionally'.

Response 68: We will change it accordingly.

Page 29179 line 9: "Even though mixing ratios of isoprene oxidation products and isoprene rose during the dry season, they did not rise proportionally compared to isoprene."

Comment 69: Page 29179 line 12: Please insert 'production' after 'MVK + MACR'.

Response 69: We will insert the change.

Page 29179 line 10: "Whereas isoprene had a 4-fold increase from the wet to the dry season, isoprene oxidation products had a 10-fold increase, possibly indicating a faster depletion of isoprene than isoprene oxidation product production."

Comment 70: Page 29180 line 6: Change to 'MEK, however, showed a less pronounced increase above the canopy.'

Response 70: We will modify accordingly.

Comment 71: Page 29181 line 2-4: If you move the sentence 'Such burning activities' in front of the sentence 'As we did not observe' it fits better to the context.

Response 71: We will modify the text to:

Page 29181 line 2: "Distinct biomass burning plumes were not observed. This indicates that there was no biomass burning close-by impacting our measurements, and impact from long-range transport may be assumed. Such burning activities can be expected during this time of the year (Karl et al., 2007)."

Comment 72: Page 29181 line 23: Please change 'This compares' to 'The values compare'.

Response 72: We will change it accordingly.

Comment 73: Page 29182 line 7: Change to: ‘Among the studies listed in table 2 we reported highest mixing ratios’.

Response 73: We will change it accordingly.

Comment 74: Page 29183 line 4: ‘site, height and season’.

Response 74: We will change it accordingly.

Page 29183 line 3: “The summary of BVOC mixing ratios in the Amazonian ecoregion (Table 2) shows an enormous variation depending on site, height and season.”