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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Diel and seasonal changes of Biogenic Volatile Organic Compounds within and above an Amazonian rainforest site" *by* A. M. Ya nez-Serrano et al.

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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."

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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

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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

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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

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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

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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:

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

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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.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 29159, 2014.

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