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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.

Anonymous Referee #2

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The manuscript presents a valuable dataset which provides vertical gradients of BVOC volume mixing ratios within and above a Amazonian rain forest canopy and describes vertical gradient changes between different seasons. Quantification of BVOCs by means of proton transfer reaction - mass spectrometry and the validation of compounds by GC are convincing. Given that data sets including seasonal and vertical information above an Amazonian rain forest are rare this data will contribute significantly to the understanding of the vertical and seasonal BVOC distribution in a tropical environment and is certainly worth publishing. However, the manuscript offers some room for improvements described below:

General Remarks:
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.
Language: 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. I just mentioned some examples in the technical details below. Although this is no scientific issue it makes the paper partially hard to read and understand.
Results: 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.

Details:

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

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

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).

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.

Introduction: See general remarks

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. . .

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?

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

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.

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.

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)'

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

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.

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.
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'
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.
Page 29171, line 22: are you talking about the rsquare or the Pearson correlation coefficient?
Page 29171, line 25/26: be precise – how did you take transport and chemistry into account?
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.
Page 29172, line 14-15: I don't understand the sentence. . . Consider rewriting.
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!
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. . .
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.
Page 29173, line 27-28: Would this behaviour refer to a difference in dominating sources necessarily? What about a difference in sinks (stronger photochemistry at the canopy top) or stronger vertical mixing?
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.
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.
Page 29175, line 6-12: This belongs into the discussion. Additionally the statement that Acetonitrile typically originates from biomass burning requires a reference.
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.
Page 29176, line 9: I guess you mean an increase in the variability of BVOC mixing ratios? Please clarify.
Page 29176, line 13-14: The second part of the sentence is hard to understand. Consider rewriting!
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.
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.
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.
Page 29177 line 11: 'the rise of ozone and NOx' do the authors refer to the personal communication here? See comment above.
Page 29177 line 15: '. . .and vertical patterns. . .' as you refer to differences during the wet and dry season as well please include that.
Page 29177 line 18ff: It is well known that isoprene emissions are light dependent. . . Please insert a reference.
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.
Page 29178 line 18: If you refer to previous studies please include the corresponding references here.
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.
Figure 2: Please include measurement altitude into the figure, e.g., write Isoprene levels at 24 m (ppbv) as y label.
Units: I would suggest to change ppb to ppbv throughout the whole manuscript.
Figure 4 -10: The coloured 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.
Page 29178 line 26ff: A switching of the metabolic processes? I think this sounds very speculative. . . Do you have any references?
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.
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!
Page 29181 line 27- Page 29182 line 5: Please rewrite the corresponding sentences they read odd.
Page 29182 line 12: What do you mean by 'to improve our understanding of BVOC'?? Do you mean 'BVOC emission, transport and chemistry'?
Page 29182 line 20-23: The two sentences are unclear. Do you mean something like 'Marked seasonality and diurnal behaviour 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 BVOC mixing ratios were attributed. . .'
Page 29183 line 1. 'This indicates a mixture of sources. . . ' What about sinks?
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. . .

Technical issues:
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.
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.
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.
Page 29165, line 20 and Page 29166, line 9: The acronym for volatile organic compounds was already introduced before.
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 analysing absorbent tubes by GC-FID (Fig.2)'
Page 29170, line 23: Suggest rewording to 'During daytime isoprene showed highest mixing ratios. . .'
Page 29170, line 26/27: Suggest rewording to 'Strong gradients towards the ground were seen especially for the dry season. . .'
Page 29171, line 2: you write 'In addition, the variability increased during the dry season. . .' variability increased compared to what? Be precise.
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)'
Page 29171, line 7: What do you mean with relatively stronger? And compared to what? Be precise.

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.
Page 29173, line 1-2: 'The minimum of the MVK+MACR-to- isoprene ratio was located inside the canopy. . .'???
Page 29173, line 17-18: The mixing ratios remained much lower compared to what?
Page 29178 line 19: Better: 'Among those factors' instead of just 'Among those'
Page 29179 line 10: Please insert 'compared to isoprene' after 'proportionally'
Page 29179 line 12: Please insert 'production' after 'MVK + MACR'
Page 29180 line 6: Change to 'MEK, however, showed a less pronounced increase above the canopy.'
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.
Page 29181 line 23: Please change 'This compares. . .' to 'The values compare. . .'
Page 29182 line 7: Change to: 'Among the studies listed in table 2 we reported highest mixing ratios. . .'
Page 29183 line 4: '. . .site, height and season. . .'

References:
Fall, R., T. Karl, A. Hansel, A. Jordan, and W. Lindinger, Volatile organic compounds emitted after leaf wounding: On-line analysis by proton-transfer-reaction mass spectrometry, J. Geophys. Res., 104(D13), 15963–15974, 10.1029/1999JD900144, 1999.
Laffineur, Q., Aubinet, M., Schoon, N., Amelynck, C., Müller, J. F., Dewulf, J., Van Langenhove, H., Steppe, K., and Heinesch, B.: Abiotic and biotic control of methanol exchanges in a temperate mixed forest, Atmos. Chem. Phys., 12, 577-590, 10.5194/acp-12-577-2012, 2012.
Karl, T. G., Spirig, C., Rinne, J., Stroud, C., Prevost, P., Greenberg, J., Fall, R., and

Guenther, A.: Virtual disjunct eddy covariance measurements of organic compound fluxes from a subalpine forest using proton transfer reaction mass spectrometry, Atmos. Chem. Phys., 2, 279-291, 10.5194/acp-2-279-2002, 2002.

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