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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Speciated measurements of semivolatile and intermediate volatility organic compounds (S/IVOCs) in a pine forest during BEACHON-RoMBAS 2011" *by* A. W. H. Chan et al.

Anonymous Referee #1

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The article by Chan and coauthors entitled: "Speciated measurements of semivolatile and intermediate volatility organic compounds (S/IVOCs) in a pine forest during BEACHON-RoMBAS 2011" offers a novel great dataset for compounds barely measured before thanks to modifications on the already novel TAG-AMS, providing speciated measurements of sesquiterpenes, sesquiterpenoids, diterpenoids, alkanes, PAH, and PACs over a pine forest. These compounds due to their reactivity and volatility are very hard to measure and calibration is not trivial due to the lack of standards. A Positive Matrix Factorization is then used to extract information for a nice discussion of the possible sources and processes taking place for is factor grouping. The paper

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reads well, without language flaws. The methods are well described and the authentic calibrations and the derived calibrations are convincing. The dataset produced over this high altitude forest is important and certainly helps understanding the still unknown atmospheric chemistry due to (until now) unmeasured compounds. For these reasons, given the extraordinary data set on S/IVOC presented that will contribute significantly to the further understanding of atmospheric chemistry, this study is certainly worth publishing. However, there are some minor revisions to be done in order to improve the readers understanding.

General

In many places you give values only providing one unit (ng sm-3), but some others you give also pptv. I think this is highly enriching, so please add this conversion to the other values mentioned in the study.

Objective

You talk about the objective of BEACHON-RoMBAS, but that does not say it is the same as yours. Simply state that you have the same objective as the main campaign objective.

Methodology

You do not mention what is the real canopy height. Do so please. There is a general confusion about the instrument if I understood correctly. The whole system is called the SVTAG-AMS. This includes a HR-ToF-AMS within the system as well as SVTAG which is a custom made version of the TAG. In the methodology you give the impression of two systems, an SVTAG-AMS and a separate HR-ToF-AMS. This can be solved by changing the 2.3 of the HR-ToF-AMS to 2.2.1. Furthermore, in Page 22337 line 9 you mention you will focus on the gas and particle phase organics, but in reality I only see mention to compounds that are still in the gas phase, or at least the assumptions made seem to be regarding compounds in the gas phase. Please clarify. When explaining

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the HR-ToF-AMS, regarding figure S5 and S6; where are the AMS measurements coming from? A different AMS? Because if it is the same, I do not understand how can you take stand-alone measurements while sampling on the SVTAG-AMS. Please clarify. In the section for calibration you mention periodic zero air blanks and periodic calibrations. Can you mention how periodic? Can you also mention the source the zero air black? A catalytic convertor and brand, synthetic air...? In page 22340 line 21, I would give a short, more general description of PMF, such as a statistical tool, in order for people that have never heard of PMF to understand. The section of the PTR-TOF-MS is quite vague. Perhaps here it is wise to compare both inlets (i.e. PTR-TOF-MS vs. SVTAG-AMS). Mention that the PTR-TOF-MS was running in parallel as part of the BEACON-RoMBAS campaign and mention any publication of such data if available.

Results

In page 22343 line 1 you mention the dependency of SQT on light. While it is true that there might be some dependence of light, it is clear the dependence on temperature, which is not mentioned here. Please rephrase. I understand both diurnal cycles for the SVTAG-AMS and the PTR-TOF-MS are very similar, and that the inlets are in relative different locations, however is hard to think about such a big difference in concentration only due to the relative distance to the source. If we say that the source is the vegetation, one would expect higher mixing rations closer to the SVTAG-AMS inlet, which is still within the canopy, and closer to the top, where more leaf activity is supposed to happen. In order to help in this issue, the lower detection limit for the PTR-TOF-MS and the limit in terms of ppt for the SVTAG-AMS can be helpful. In figure 4, for the TAG, are all the speciated sesquiterpenes taken into account? Can it be that the PTR-TOF-MS is measuring some other sesquiterpene non-captured by the SVTAG-AMS, inferenced, for instance, to the discrepancy of both time series at the beginning of the campaign? In page 22346 line 4 you mention the surrogate standard. I completely understand the difficulty of getting SQT standards but it would be nice to expand on how these surrogates standards work, for someone that may like to replicate the method-

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ology. Furthermore, in the same page and same line you talk about a post-campaign calibration. I suppose this calibration was done prior to instrument transport away from site, right? If so please specify, if not, does not the MS get changed after transport so prior calibrations are not accurate any longer? Then this post-calibration would not be valid. In page 22346 you talk about the higher order terpenoids and mention that the diterpenoids found may come from resin acid. Please expand of what this resin acid is, and its role on the ecosystem. In page 22347 line 18 you mention that longicaamphenylone is more likely to be a primary product. Please expand why do you think so. In page 22352 line 14 you talk about the anticorrelation between factor 1 and isoprene and MBO, and since it is not a r2, that in not a good correlation at all. However what you mention is valid, simply say they are not correlated. In page 22355 line 27 you mention developed areas, do you mean areas with cleaner air? Please specify.

Figures and Tables

Figure 1: add diagram after schematic Figure 3: if you identify SQT204 and SQT202 why not identify the rest. Figure 4: In the diel profile are these averages? And the error bards, standard deviations? Figure 6: please expand on description. Figure 7: same as figure 6. In addition, mention what do dots and line represent. Page 22336 line 22: This sentence needs a reference.

Details

Pag.22334 line 6: This sentence needs a reference. This is up to you, but one suggestion would be Williams et al., 2004. Organic Trace Gases in the Atmosphere: An Overview. DOI: 10.1071/EN04057. And Hallquist et al., 2009 The formation, properties and impact of secondary organic aerosol: current and emerging issues. DOI: 10.5194/acp-9-5155-2009.

Page22335 line 7: This is the first time you say MBO, state what it is and then remove 2-methyl 3-buten-2-ol from page 22336 line 21.

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Page 22335 line 12: add reference Bourtsoukidis et al., 2012. "Ozone stress as a driving force of sesquiterpene emissions: a suggested parameterisation". DOI: 10.5194/bg-9-4337-2012. And Jardine et al, 2011. "Within-canopy sesquiterpene ozonolysis in Amazonia". DOI: 10.1029/2011JD016243.

Page 22337 line 8: Put a dot after SVTAG)

Page 22337 line 13: Could you expand more on what is meant by fast GC?

Page 22337 line 17: It is easier to say the total height 5.2m above ground.

Page 22343 line 24: For clarification, please mention here the three SQT standards.

In page 22344 line 2 please mention if the total SQT204 you mention refers to the SVTAG-AMS measurements or the PTR-TOF-MS.

Page 22344 line 14: The study by Jardine et al, 2011, provides a vertical profile of SQTs, please add reference.

Page 22346 line 13: add some values for comparison.

Page 22346 line 28 you use acetonitrile data that comes from the PTR-TOF-MS I suppose. Please mention it.

Page 22347 line 2. You refer to the temporal variations of the diterpenoids. Please mention it.

Page 22347 line 6: add sesquiterpenes next to sesquiterpenoids.

Page 22348 line 11: Please tell what UCM means.

Page 22352 line 6: Please add Trajectory 1 and 4 to Figure 8.

Page 22352 line 17: The sentence needs a reference.

Page 22352 line 21: Give correlation coefficient for factor 1 and acetonitrile.

Page 22354 line 20: Add Trajectory 2 and 5 after periods.

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Page 22355 line 7: Exchange difference by differences.

Page 22355 line 24: You have always reported 1 decimal place for the correlations coefficient, keep it the same.

Supplement

S11: tell what the dots represent.

References:

- Williams et al., 2004. Organic Trace Gases in the Atmosphere: An Overview. DOI: 10.1071/EN04057.

- Hallquist et al., 2009 The formation, properties and impact of secondary organic aerosol: current and emerging issues. DOI: 10.5194/acp-9-5155-2009.

- Bourtsoukidis et al., 2012. “Ozone stress as a driving force of sesquiterpene emissions: a suggested parameterisation”. DOI: 10.5194/bg-9-4337-2012.

- Jardine et al, 2011. “Within-canopy sesquiterpene ozonolysis in Amazonia”. DOI: 10.1029/2011JD016243.

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