Reviewer #1

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.

The following was added in Section 2.4 as a clarification:

"All mass concentrations are reported in nanograms per cubic meter of air sampled at standard conditions (298K, 1 atm), abbreviated as ng sm-3. Sesquiterpenes are also reported in pptv for comparison with PTR-TOF-MS data, by multiplying the mass concentration in ng m-3 by 204/24.45."

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.

In the last paragraph in the introduction, we have added the following sentence: "Here we present hourly and bihourly speciated measurements of S/IVOCs and their tentative identifications to achieve this objective."

Methodology

You do not mention what is the real canopy height. Do so please.

We have added to the Experimental Methods: "The average canopy height is 16 m."

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 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.

Most of the compounds observed were predominantly in the gas phase, but many of them are also found in the particle phase. We also agree with the reviewer that the description of

AMS in the previous draft was confusing. In the revised manuscript, we refer to the combined instrument capable of simultaneous bulk and speciated measurements as SV-TAG-AMS, the component for speciated organic analysis as SV-TAG (which is the focus of this paper) and the HR-ToF-AMS component for bulk particle analysis as AMS_{TAG}. AMS_{TAG} organic and sulfate mass concentrations were compared to those measured by a separate collocated standalone HR-ToF-AMS (referred to as AMS_{STD}). We have made changes to the Experimental Methods and supplementary material.

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. . .?

We have revised the description of the blanks to the following:

"Observed compounds are distinguished from cell desorption artifacts using periodic zero air blanks (passing ambient air through a charcoal filter into collection cell for 90 min) and cell blanks (desorbing a cell with no sample collection). Zero air blanks were conducted once every 2 days, and cell blanks were conducted once every day at different hours of the day."

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.

We have added the following to the description of PMF in Section 2.5:

The PMF model assumes a linear mixing model, where the observed concentrations of multiple species are a time-varying linear combination of contributions from multiple independent sources with constant composition profiles (Paatero and Tapper, 1994):

$$x_{ij} = \sum_{p} g_{ip} f_{pj} + e_{ij}$$

where x_{ij} is the observed concentration of species i at time j, g_{ip} is the contribution of species i to factor p, f_{pj} is the mass concentration of factor p at time j and e_{ij} is the residual error. Each factor p is interpreted to be a group of covarying compounds that originate from the same source or undergo similar transformation processes. The model is solved by minimizing the residual e_{ij} weighted by the measurement precision σ_{ij}:

$$Q = \sum_{i} \quad \sum_{j} \left(\frac{e_{ij}}{\sigma_{ij}} \right)^2$$

The objective function Q is minimized using the PMF2 algorithm operated in the PMF2.exe program (Paatero, 2007), and the results are interpreted using the PMF Evaluation Tool (PET) Panel (Ulbrich et al., 2009).

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.

We have modified the description of the PTR-TOF-MS to clarify inlet locations and cite publication on current deployment:

"Measurements of selected gas phase species by SV-TAG were qualitatively compared to those by proton-transfer reaction time-of-flight mass spectrometry (PTR-TOF-MS). Details of the instrument and its deployment at BEACHON-RoMBAS are described in a recent publication (Kaser et al., 2013). The PTR-TOF-MS inlet was at a height of 1 m above ground, and approximately 25 m away from the SV-TAG inlet horizontally in an area with an uneven distribution of trees. In brief, the PTR-TOF-MS measures a wide variety of VOCs using hydronium ions H_3O^+ as reagent ions (Graus et al., 2010). In this work, the PTR-TOF-MS measurements at the 1 m inlet were used for comparison. Owing to the difference in sampling methods and inlet locations, only qualitative comparisons were made for reactive compounds such as sesquiterpenes."

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.

We have added the following sentence to that paragraph:

"It should be noted that sesquiterpene emissions have a positive dependence on temperature (Duhl et al., 2008), but daytime oxidation and boundary dynamics lead to higher observed concentrations at night (Bouvier-Brown et al., 2009a)."

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?

We refer the reviewer (and readers) to Park et al. (2014) and Jardine et al. (2011) for the strong vertical gradients and spatial variability of different biogenic compounds. Sesquiterpenes are especially highly variable in space and time because of their high reactivity. Therefore we believe that it is conceivable that the different inlet locations may contribute to the discrepancy between the two measurements. We also believe that because of the relatively longer sampling time (90 min for SV-TAG, ~seconds for PTR-TOF-MS), adsorbed sesquiterpenes may undergo limited revolatilization and/or reaction during sampling of O_3-laden ambient air; therefore the quantified sesquiterpene is likely an underestimate of actual concentrations. We also agree with the reviewers that some SQT204 may be more volatile than longifolene and not reliably captured and analyzed by SV-TAG. We have added the following sentence to the 3rd paragraph in Section 3.1:

"There may also be some SQT204 more volatile than longifolene that are not reliably captured by the focusing trap, leading to underestimation of total SQT204 concentrations by SV-TAG."

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 methodology.

We have added the following sentence to Experimental Methods:

"For each compound, its ionization efficiency (and hence, calibration factor) is assumed to be same as that of the assigned surrogate standard. Mass concentration of each compound is obtained by multiplying the observed signal (normalized by signal of the internal standard) by the calibration factor obtained during calibrations."

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.

The SQT202 were discovered after the SV-TAG and AMS were decoupled for the field campaign. Therefore it was no longer available for calibration. We believe that while the absolute response could vary from one TOF-MS to another, we have made our best attempt to correct for this variability by using the same model of TOF-MS, and using the relative response to an internal standard. The post-campaign calibration for SQT202 was performed in a similar Tofwerk time of flight mass spectrometer. As in all calibration procedures in this work, we normalize the responses to that of an internal standard (hexadecane-d34) to correct for instrumental variability.

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.

We have added the following sentence to expand on the discussion of resin acid:

"They contain three fused six-membered rings with an isopropyl group, which is the same backbone as abietic acid and isopimaric acid. These acids are the primary components of wood resin, and are used as a chemical defense against insect and pathogenic fungi and bacteria (Dewick, 1997)."

In page 22347 line 18 you mention that longicamphenylone is more likely to be a primary product. Please expand why do you think so.

Since the correlation coefficients are weak, we cannot definitively conclude the primary nature of longicamphenylone observations. Therefore we have revised the discussion to:

"Many of these compounds are found in essential oils or plant extracts and were identified based on matching to essential oil mass spectral database (Adams, 2007). At the same time, longicamphenylone may also be a reaction product of longifolene and ozone (Isaacman et al., 2011b). Based on correlation of time series alone, the relative contributions of primary and secondary sources cannot be definitively identified. Manoyl oxide has also been previously observed in the Finnish coniferous forest (Anttila et al., 2005)."

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.

We have revised the sentence to the following:

"Similarly, MBO and isoprene emissions are strongly dependent on sunlight and temperature, and, as a result, their concentrations are typically higher during the day, despite the deeper boundary layer. As a result, there is no positive correlation with factor 1 signal ($r = -0.18$)."

In page 22355 line 27 you mention developed areas, do you mean areas with cleaner air? Please specify.

We have revised the sentence to the following:

"The back trajectory of an air mass arriving when factor 3 is strong suggests a mix of rural air (carrying long-lived biogenic compounds) with air from more developed areas to the east (with anthropogenic pollutants). "

Figures and Tables

Figure 1: add diagram after schematic

We opt not to include a diagram since the schematic has shown the operating principles and this is a custom version of TAG-AMS for analyzing semi-volatile organic compounds. Future TAG-AMS will have different configurations.

Figure 3: if you identify SQT204 and SQT202 why not identify the rest.

The parentheses indicate the abbreviations (SQT204 and SQT202) used in the main text. For the other compounds, no abbreviations are used.

Figure 4: In the diel profile are these averages? And the error bards, standard deviations?

We have added the following to the figure captions:

"The markers represent the mean concentration and the error bars represent one standard deviation."

Figure 6: please expand on description.

We have expanded the figure captions:

Factor profile of 3-factor solution using PMF. Factor 1 contains many biogenic terpenoids, while Factor 2 is mainly comprised of anthropogenic pollutants such as PAHs and PACs. Factor 3 may represent a mixed source of anthropogenic and biogenic compounds.

Figure 7: same as figure 6. In addition, mention what do dots and line represent.

We have added the following to the figure captions:

"For each factor, the grey markers represent factor signals for the entire sampling period (grouped by hour of day); the dark line and markers represent diel averages, and the error bars represent one standard deviation. The wind profiles are average factor signals grouped by average wind directions."

Page 22336 line 22: This sentence needs a reference.

We have added a reference to Ortega et al. 2014.

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, prop- erties and impact of secondary organic aerosol: current and emerging issues. DOI: 10.5194/acp-9-5155-2009.

Added as noted.

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.

Corrected as noted.

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.

Added as noted

Page 22337 line 8: Put a dot after SVTAG)

Corrected as noted.

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

Owing to the ability of on-column heating, there is no need for an oven for controlling column temperature and the thermal mass is significantly reduced. As a result, the heating ramp rates can be significantly greater than conventional GC ovens. However, for this campaign, we did not take advantage of increased ramp rates to improve sampling frequency, because we needed long sampling times for sufficient sample loadings. However, we expect that this feature can be exploited in more polluted areas for better time resolution. Since this feature was not a focus of this deployment, we have revised the description to "(2) GC system with on-column heating".

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

The total height is 4m above ground. Since the height above top of trailer is irrelevant, that information has been removed.

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

We have added the 3 SQT standards as noted.

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

We have revised the sentence to:

"The median concentration of total SQT204 measured by SV-TAG is 6.5 ng sm-3, or 0.7 pptv."

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

Added as noted.

Page 22346 line 13: add some values for comparison.

The sentence has been revised to:

The total concentration of SQT202 (1-23 ng sm^{-3}) is comparable to that of SQT204 (0-19 ng sm^{-3})

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

To clarify measurement technique, the sentence has been revised to:

However, the observed concentrations did not correlate with PTR-TOF-MS measurements of acetonitrile, a frequently used biomass burning tracer (Holzinger et al., 1999; de Gouw and Warneke, 2007).

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

We have revised the sentence to:

"Temporal variations in concentrations of diterpenoids were consistent from one day to another, with concentrations peaking at night and decreasing during the day."

Page 22347 line 6: add sesquiterpenes next to sesquiterpenoids.

Since sesquiterpenoids do not include sesquiterpenes, we now refer to SQT204 and SQT202 as sesquiterpenes. The only sesquiterpenoid we observe is longicamphenylone. We have updated our description to include only sesquiterpenes in our discussion.

Page 22348 line 11: Please tell what UCM means.

The UCM refers to the unresolved complex mixture. The definition of the abbreviation is added to the sentence:

"This group of hydrocarbons, commonly known as the unresolved complex mixture (UCM) is comprised of a large number of branched and cyclic hydrocarbon isomers (Chan et al., 2013)."

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

Added as noted.

Page 22352 line 17: The sentence needs a reference.

We have added a reference to Ortega et al. (2014).

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

Added as noted.

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

Added as noted.

Page 22355 line 7: Exchange difference by differences.

Corrected as noted.

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

We will be consistent with other reported correlation coefficient of 2 decimals places. For tetradecenoic acid we report r of 0.60.

Supplement

S11: tell what the dots represent.

We have added the following clarification to S11:

"The grey markers represent the concentrations of the different species Aug 19 and Aug 31 grouped by hour of day. The red markers represent the diel averages and the error bars are the standard deviation for each hour of the day."

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 emis- sions: a suggested parameterisation". DOI: 10.5194/bg-9-4337-2012.

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

Reviewer #2

Everyone trying to measure emissions of extremely reactive compounds or their low-volatility reaction products know how hard it is in practice. Especially SQT's (as SQT204) are known to be "impossible" to measure since they will react with ozone, OH or NO3 before you get them

even close to your detector. Also the information of reaction rates (k) of SQT with oxidants in the literature is limited and full of some very contradictory k-values are determined and published so far because of the difficulties with high SQT reactivity (e. g. Bonn and Moortgat 2003, Winterhalter et al., 2009, Shu & Atkinson 1995, Richters et al., 2015 an so on). What made you choose/believe one of these reaction rate coefficient?

We agree with the reviewer that SQT reaction rates are highly uncertain (to ~1 orders of magnitude. Our conclusions about OH and O3 reactivities are therefore valid only to one order of magnitude. Since it was difficult to decide which rate constant to use, we opt to use an intermediate value. Based on these assumptions, we can conclude that OH reactivities are still dominated by monoterpenes in the forest (using an upper limit of SQT – OH of 1 x 10-10 cm3 molec-1 s-1, the collision limit), while O3 reactivities are likely comparable between monoterpenes and SQT. This clarification has been added to the supplementary material S14:

"We stress that the rate constants for SQT in the literature span a wide range (1 to 2 orders of magnitude). Since it was difficult to decide which rate constant to use, we opt to use an intermediate value for the calculations here. Based on these assumptions, we can conclude that OH reactivities are still dominated by monoterpenes in the forest (even with an upper limit of SQT + OH of 1×10^{-10} cm^3 $molec^{-1}$ s^{-1}, the collision limit), while O_3 reactivities are likely comparable between monoterpenes and SQT. "

SQT also have a tendency to condense after oxidised in the air. I think your introduction is very positive in that sense. Maybe you could highlight the fact a little that what you just measured is really difficult in practice.

We have modified the following sentence to describe the analytical challenges associated with SQT in the third paragraph of the introduction:
"These properties of sesquiterpenes (low concentrations, high reactivity, line losses) present significant analytical challenges, but measurements of these reactive, less volatile compounds are essential for understanding their sources and chemistry."

When you mention SOA production, I think recent discovery/development in ELVOC (extremely-low-volatility-VOC) should be mentioned (e.g. Ehn et al., 2014). They could be the key of explaining missing SOA and the first models on the matter are already out (Jokinen et al., 2015). SQT concentrations may not always be so low as expected (like in Helmig et al., 1994), but they might be even close to MT concentrations (Tarvainen et al., 2005). This would make the measurements of SQT's and their oxidation products even more important at least locally and seasonally.

We have added references to ELVOCs in the introduction:

Recent evidence suggest that a group of extremely low-volatility organic compounds (ELVOCs) may be a significant contributor to SOA in forest atmospheres (Ehn et al., 2014; Jokinen et al., 2015).

In the section 2.2. Instrumentation, I (as a non expert user of this particular instrument) had hard time understanding how many instruments you actually use, when you measure gas and when particles (AMS is not the most common detector for gases I assume). Also you mention sample collection and GC analysis that have different time resolutions, which I did not understand why. Please clarify this section.

We refer to response to review 1 regarding clarification about the AMS analysis. We have also modified the description of sampling time and sequence in Section 2.2:
"The total time for filter desorption and GC analysis is 30 min. As a result, the total sample turnaround time (sample collection + filter desorption + GC analysis) is 60 min (hourly time resolution) for the first 3 days, and 120 min (bihourly time resolution) subsequently."

Calibrations and GC data: Did you detect any nitrogen containing compounds or are they not separated with this GC column you used? What is the relationship with c and RI? Is it only the fact that a longer carbon skeleton effects volatility?*

No nitrogen containing compounds were detected. It is likely organic nitrates decompose upon thermal desorption or at higher GC temperatures. The relationship between c* and retention index is determined using the vapor pressure of n-alkanes calculated by SIMPOL. Therefore the c* determined is the equivalent n-alkane saturation concentration with the same retention index. The volatility is affected by carbon skeleton but also by the polarity (and polarizability) of the compound. For example, tetradecenoic acid has a carbon skeleton of n-C14, but have vapor pressures equivalent to that of n-C17 (retention index of 1737) owing to the acidic functional group.

Throughout the manuscript: You claim that emissions are dependent on sunlight but I would think it is rather the temperature (and also seasonality) this also goes with MT's and isoprene but that isn't the only reason the latter are more abundant at day light hours (p. 22352, r~.15). Please correct this.

We agree with the reviewer, and have clarified this:

Section 3.1, 2nd paragraph: It should be noted that sesquiterpene emissions have a positive dependence on temperature (Duhl et al. 2008), but daytime oxidation and boundary dynamics lead to higher observed concentrations at night.

Section 5.1, 3rd paragraph: Similarly, MBO and isoprene emissions are strongly dependent on sunlight and temperature, and, as a result, their concentrations are typically higher during the day, despite the deeper boundary layer (Ortega et al., 2014)

Figures: Figures 4-7 figure captions seem truncated. Please provide information about the error bars (Fig 4 & 7). Since figures are usually the most read part of articles, I would use some time to clearly state what information is in them.

The figure captions have been expanded:

Fig. 4: (a) Time series of SQT204 concentration measured by PTR-TOF-MS and by TAG during measurement overlap. (b) Diurnal profile of SQT204 concentration during the entire measurement period of TAG (19–25 August) and PTR-TOF-MS (20 July – 25 August). The markers represent the mean concentration and the error bars represent one standard deviation. The general diurnal trends between the two instruments agree qualitatively, but are not expected to be quantitatively consistent owing to different sampling locations.

Fig. 5: Average volatility distribution of total hydrocarbons observed by SV-TAG. The whiskers represent the standard deviation of the measurements. The volatility distribution was calculated using fitting of high resolution mass spectrometry data, and the vapor pressures are estimated from retention times of n-alkanes.

Fig 6: Factor profile of 3-factor solution using PMF. Factor 1 contains many biogenic terpenoids, while Factor 2 is mainly comprised of anthropogenic pollutants such as PAHs and PACs. Factor 3 may represent a mixed source of anthropogenic and biogenic compounds.

Fig. 7: PMF factor wind and diurnal profiles. For each factor, the grey markers represent factor signals for the entire sampling period (grouped by hour of day); the dark line and markers represent diel averages, and the error bars represent one standard deviation. The wind profiles are average factor signals grouped by average wind directions. Factor 1 is strongest during the night and during transport from forests to the west and south of the field site, consistent with local biogenic emissions. Factor 2 appears to be strongest during the day, and likely originates from a temperature-dependent volatilization process (see Fig S12). It may also represent compounds transported from developed areas to the east. Factor 3 appears to be have mixed sources.