Authors Response to Referee 1 and 2

The authors acknowledge the referees for their contribution in improving the study.
The authors have compiled the responses as follows. Reviews are in Bold. Author responses are numbered with [A0, A1, A2 …]. Italics and quotations are used for the information added in the revised manuscript.

A.General comments:
In regard to the comments of both referees, significant changes have been made concerning;

- The data quality control:
  - measured fluxes were corrected from high frequency losses (l.365-374)
  - the error due to the disjunct sampling was also estimated (l.375-381)
  - more details were provided about the routine tests used for filtering purpose (l.360-364 and Table 3)

- More details about the calibration of monoterpenes have been added, and interferences at m/z 71 are discussed.

B. Specific Comments

Authors Response to Referee 1: p1-p5, Referee 2 : p6-p12.

Authors Response to Referee 1

1. **P876, L 20-21: Please include what method was used for measuring LAI, or add areference that describes how LAI is determined.**
   A1: As suggested by the reviewer, we include the above points in the revised manuscript l.143:
   "The average single-sided leaf area index (LAI) measured (LAI-2000, Li-Cor, Lincoln, NE, USA) in August 2010 is 2.4"

2. **Add the footprint analysis information at the site or a reference of it.**
   A2: We thank the reviewer for this suggestion. We include the following sentence in the revised manuscript (l.144):
   "The flux footprint at the site was estimated to vary between 60 m and 120 m for respectively low and strong wind conditions. The calculation of the footprint was computed online (http://www.footprint.kljun.net/) based on Kljun et al. (2004)"

3. **P877, L 2: Specify the dates for the intensive measurement period instead stating'about two weeks'.**
   A3: The dates are specified in the revised manuscript

4. **What Reynolds number in the tube was maintained with this setup??**
   A4: Reynolds number: 9440. We include this information in the revised manuscript. l.185

5. **P879, L.7:Why you limited the m/z range up to 93 in scan mode:**
   A5: Prior to the beginning of the campaign, on the 17th of May 2012, we scanned during 5h30 (09h30-14h50) a wider range of masses (m/z 21- m/z 206) in order to see which masses showed a significant signal. Above m/z 93 the only significant signal was at m/z 137. As the scan mode lasted for only 5 minutes, we decided to reduce the number of compounds

measured in order to have at least 5 datapoints per cycle for each mass. Therefore, we chose to limit the *m/z* range up to 93 in scan mode, and to include m/z 137 in flux mode.
This information is added in the manuscript. l.205, l.219

6. **P879, L.14. P879, L 14: You performed the calibration only twice throughout the intensive campaign period. How were the sensitivities changed between two calibrations?**
A6.1 In order to answer to this question, we include the above points in the revised manuscript.
"The differences in sensitivities from the two PTR-MS calibrations were below 5% for the compounds most discussed in the paper (methanol, acetaldehyde, acetone, isoprene and MVK +MACR). Higher differences of 9.36%, 12.51% and 20.19% were observed for benzene, toluene and monoterpenes respectively" l.249

P879. L18-19. How were all the gas standards prepared? Was it a gas mixture in the cylinder or something else? List all the standard gas species that were used for the calibrations.
A6.2: This information is now included in the revised manuscript. (p.8, l. 225-229)

- **Also, the compounds in Table 1 are not clear. For example, what monoterpene species was used for m/z 137. (you did not include m/z 81 for monoterpene calibration?).**
A6.3: The following sentence is included in section 2.4.2 ,(p.8, l 236-238)
"The sensitivity of α-pinene was used for the sum of total monoterpenes. Sum of monoterpenes have been commonly quantified based on both molecular ion (m/z 137) and fragment ions (m/z 81). In this study, total monoterpenes were only calibrated against m/z 137. As considerable monoterpene fragmentation is expected for an E/N ratio of 132 Td, the abundance of the molecular ion (m/z 137) is expected to decline in favor of the fragment ions (dominant at m/z 81). Also, as fragmentation patterns are dependent on the different monoterpenes species present, the sensitivity of m/z 137 can slightly change if the monoterpenes composition is variable (Misztal et al. 2013). Nevertheless, additional measurements performed with cartridges have shown that α-pinene was the dominant terpene (80±13%) and therefore calculated sensitivity of total monoterpene from m/z 137 is justified (see supplement)."

- **Did you use MACR+MVK mixture or only one of them for m/z 71?**
A6.4: Unfortunately, MVK and MACR were not included in the gas standard we used for the calibration, whereas their structural isomer crotonaldehyde was. However, most aldehydes have similar proton transfer reaction rates *ki* (cm^3 s^{-1}) and sensitivities. Also, the *ki* rates of ketons are in similar range than those of aldehydes. Therefore, we preferred using crotonaldehyde as a proxy for MVK and MACR, instead of using the theoretical approach calculation.
Information included in Table 1 and in the main text *l.237-238* of the revised manuscript.

7. **P879 L 26-28. Background of m/z 137 was not measured based on the mass range in scan mode? Clarify how you took into account.In addition, what is the time scale of LOD (0.5 s, 1s, 1min, 5 min..).**
A7: The background of m/z 137 was derived from the two calibrations, when the instrument was zeroed with catalytically converted air for about 20 min. From the first calibration we derived a value at 0.34 ncps, and for the second one a value at 0.42 ncps. The mean of these two values has been used as the background value of m/z 137 during data process. For all masses in the range of m/z 21-93, the time scale of LOD was 0.5s. For m/z 137, the time scale was 10s.
This information is added in the text (p 9, l.255-259).

8. **Please give the range of MT mixing ratios rather than stating just 'low".**
   A8: values of mixing ratios in ppbv added

9. **P880, L 13-21: Shortly discuss that isoprene is also fragmented into m/z 41 if E/N ratio gets higher, though it should not be very significant. Probably, this fragmentation might explain the underestimation of PTR-MS than GC-FID. I think that the authors can simply look at the data in scan mode to check this**
   A9: We thank the reviewer for this suggestion. The discussion is included in section 2.4.3**,** l.277

10. **P882, L 15-18: How did you determine the lag time at night when the max covariance analysis did not give you a reliable value?**
    A10: "*The experimental mean time lag of each compound was used as the default value when we didn't found a maximum in the covariance function"* Added in the revised manuscript l.348.

11. P882, L 20: The selection of friction velocity criteria (0.15 m/s) for filtering the flux data needs to be discussed, or add a reference.
A11: Reference added in the revised manuscript l.351

12. **P882, L 23-28: Please indicate in Table 3 or mention in the text how much of data was fulfilled with each 30-60% (low quality) and 0-30% (good quality) of the stationarity test.**
    A12: The information was added in the revised manuscript, in the main text (l.360-364) and in Table 3.

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13. P884, L 4-6: How many data points were used for this intercomparison?
A13: As explained in the discussion paper, the GC-FID integrated air sample over 10 min every 30 min, and PTR-MS measurement were averaged over the 10 min sampling integration to give a single datapoint. As the intercalibration lasted 19 hours, 38 points were used for this intercomparison. This information is added in the manuscript. l.410

14. P886, L 8: Add a brief sentence that describes the ozone concentration level during the campaign since you discussed isoprene chemical degradation by ozone in the section 4.2.
A14: Added in the main text l.465-467

15. **P886, L 20-22: How was the isoprene mixing ratio range compared to other studies as discussed in the section 4.1 and shown in Table 4.**
    A15: In table 4, information about the mixing ratio range have been added.

16. **P888, L 14-15: Jardine et al. (2012) have found direct MVK and MACR emissionsfrom some plants. Did you observe any signature of MVK and/or MACR emission fromthe branch enclosure experiments at the O_3HP during CANOPEE?**
    A16: 98.7% of the carbon emitted by *Q.Pubescens* was found to be isoprene. The remaining 1.3% fraction, was represented by several BVOCs, among them MVK+MACR. More details are available in a companion paper studying BVOCs emissions from *Q.Pubescens* at the leaf level. The authors believe that this information should not be included in the finalized manuscript since the method and calculations are not presented here, but will be presented in details in the companion paper currently under review in ACPD (Genard et al., 2014).

17. **P888, L 18-20: Specify what monoterpene species was used for the calibration. The authors mentioned that the m/z 137 signal is more sensitive than m/z 81, however it is contradict statement with Table 1 showing the sensitivity of m/z 81 is much better. In**

addition, with 132 Td of E/N I expect that monoterpenes are highly fragmented into m/z81, so the signal at m/z 81 may be even higher (or almost similar level) than at m/z 137(Tani et al, 2002). Did you compare the signal intensity between m/z 137 in flux mode and m/z 81 in scan mode?

A17**:** The reviewer is right to point out that there was an error in the text. The signal at m/z 81 is more sensitive than signal at m/z 137 as indicated in the table, and the raw signal (cps) at m/z 81 (during scan mode) is slightly higher than raw signal at m/z 137 (flux mode).

As indicated in A6.3, α-pinene was used for the calibration. Additional analysis of cartridges by GC-MS (information added in the supplement) have shown that a-pinene was representing 80±13% of the total monoterpenes at the site. Limonene was the second most abundant monoterpene (15±9%), but its mixing ratios were very close to the detection limits, and always below 15 ppt. Considering the fact that we have calibrated m/z 137 against α-pinene, which was by far the dominant monoterpene, we don't expect to have significant changes in the sensitivity of m/z 137. This has also been confirmed from a comparison of the PTR-MS and GC-MS cartridges analysis measurements (added in the supplement)."

18. **P892, L 5-7: MEGAN model by Guenther et al. (2006) was updated from G93 algorithmfor the light + temperature dependent emission species and historical records ofT & PAR were considered. Have you tried this model with the DEC flux data?**

A18**:** As presented in the discussion paper, above-canopy fluxes were normalized to standard conditions using the G93 algorithm. This choice was made in knowledge of the results of the normalization of branch-level emission rates measured at the O_3HP during the CANOPEE campaign. Indeed, as presented in Genard et al. (2014), the G93 and the MEGAN parameterisation (Guenther et al., 2006) were tested at the branch-level. The results showed that MEGAN performed similarly to G93 when soil moisture was not considered in the model, whereas its performance was worse than G93 under water shortage and when soil moisture was taken into account. In regard to these observations, we preferred to use the much simpler G93 algorithm.

19. **P892, L 19-26: If isoprene is not significantly removed within the canopy as the authorsdiscussed throughout the section 4, it is not convincing that two fold discrepancy of isoprene basal emission rate (BER) between the up-scaled value by leaf-level measurement and the one derived from DEC flux measurement. Can you give an errorrange of up-scaled BER to confirm if the range includes the BER by DEC? Also, asmentioned in general comments, DEC flux measurement with 4.6 sec cycle time for isoprene may cause significant underestimation of isoprene fluxes by signal attenuation,and this might be a possible reason.**

A19:

- As suggested by the reviewers, we have estimated the error range of up-scaled BER, taking into account the error associated with the measurements of LAI and LMA. We find an upscaled BER of 18±5 mg m^{-2} h^{-1}.(value up-dated in the revised manuscript)
- Taking into account the high frequency loss for the DEC measurements, the new $F_{standard}$ calculated is slightly higher than before correction, with a value at 7.43 mg m^{-2} h^{-1}.(value up-dated in the revised manuscript).
- Even by taking into account the uncertainty ranges, there is still a significant difference between up-scaled BER measured at the branch-level and BER derived from DEC flux measurements. As discussed in the paper, we believe that the difference certainly arises :
    - from the effect of using an overestimated PAR
    - from the fact that the measurements from 7 different branches cannot be considered as statistically representative of the flux footprint area.

20. **Table 1: Was m/z 87 calibrated by MBO gas standard? If not, this should move to the right column.**

A20**:** As the reviewer 2 pointed out, there is a probably an error in the identification of m/z 87 as MBO. Since no GC measurements enable us to identify with certitude signal at *m/z* 87 we have withdrawn MBO from Table 1.

21. **Table 2: For monoterpenes, I guess m/z 137 is representative for total monoterpenes mixing ratio since you calibrated by monoterpene standard. However, is m/z 81 also total monoterpenes or only considered by fragment ion counts? If it is the latter case,it would be not worthy to show.**
    A21**:** The authors agree with the reviewer comment. m/z 81 won't appear in the revised version of table 2, since the signal of m/z 81 is not shown/discussed in the paper.

22. **Table 3: Please add or replace the column to show the data that passed stationarity test in each range of 0-30% (good quality) and 30-60% (low quality).**

A22. Added. See answer A12.

23. **Table 4: I like this table and appreciate the authors for summarizing the isoprene fluxes from different studies. Also, I would suggest adding a column that indicates mean (or range of) mixing ratios from those studies if the data is available.**

A23**:** We added an extra column indicating the volume mixing ratios. See answer A15.

24. **Fig. 1: Is temperature data in May 2011 and May 2012 unavailable?**

Author's response**:** Yes, the data are not available for these days.

25. **Figs. 3 and 4: It would be better if these two figures are merged in one, so the reader can more easily compare each other compound. In addition, explain why some data points were missing but no missing point for m/z 79. Probably, it is due to different data usage from scan mode and flux mode?**

Author's response**:** The 2 figures are now merged in one. The graphical representation was hiding the missing points for m/z 79. This has been corrected.

26. **Fig. 6: If I understood well, one flux data point present a flux result in a 25min period.How did you get the standard deviation (error bar) for each data point? Is it the standard deviation of noise in certain lag time windows? If so, please add this information to the caption.**
    Author's response**:** the information is added to the caption

27. **Fig. 9: Please show the error bars.**

Author's response**:** Information added to the caption.

Authors Response to Referee 2

1. **The abstract seems to end abruptly. What is the "so what?" factor or take-home message from this study? What is the science behind the results?**
   A1: abstract modified

2. **P.874 L. 1-4. Please include more up to date references. How BVOC deposition impacts SOA? For example, see Goldstein and Galbally, 2007.**
   A2: Added in the text**.** l73-77*"*

3. **2.2 : Change the section title to include « GC cartridge ».**
   A3:The title is revised as follows, l.162:
   "*Monthly isoprene sampling on cartridges and GC-MS analysis"*

4. **P.877 L.8, were the adsorbent cartridges commercially packed? Mention how they were packed, how were they stored after sampling? Were the cartridges analyzed immediately after the sampling?**

A4: The revised text reads: l.164-170*"Air was collected onto cartridges using an autosampler (SASS, TERA Environnement, Croles, France).* ***Commercially packed*** *cartridges consisted of stainless-steel tubes filled with Tenax TA adsorbents. Once (or twice) a month, twelve cartridges collected air for 2 h with a volume of 700 mL. The air entering the cartridge was filtered in order to eliminate any particulate matter. Each sampling tube was* ***kept refrigerated at 4°C*** *and analysed at the laboratory* ***within a month****."*

5. **P.877 L.22. "a.g.l." is mentioned twice. Spell out the first occurrence.**

A5: We thank the reviewer for pointing out this omission.

6. **Section 2.4 6. P.878 L.11. 800 ml/min sounds like a very high inlet flow for the PTRMS. Typically lower flows are used (e.g. 200 ml/min). I am guessing it was the latesPTR-MS model? Give more details on the PTR-MS instrument (give serial number andyear) in the next section.**

A6: There appears to have been a typographical error. The inlet flow rate was **80** ml/min. This information is corrected in the manuscript and details on the PTR-MS instrument are included in the revised manuscript (serial number 10-HS02 079, 2010), l.192 and l.200

7. **P.878 L.16. "Online" can be unclear. Did you mean processed in the real time?**

A7: The sentence is revised as follows:
"*Concentrations and fluxes of VOCs above the canopy were* ***processed in real-time*** *with a PTR-MS..."*

8. **P.878 L.21 replace colons for example with "is"**
   A8:replaced

9. **a. Why did the authors choose 0.5 s dwell time and not 0.1 or 0.2 s, given the PTR was high sensitivity which should not have been limited by the reaction time?**
   A9.1: At the beginning of the setup we made one test with a dwell time of 0.2 s and the instrument "noise" for some mass channels, such as m/z 137, was considerably increased. That is why we opted for 0.5s.

   b. Did this configuration not suffer high frequency losses?

A9.2. In regard to the comments of both referees, we have calculated the high frequency losses and have corrected the measured fluxes. Information on the calculations is added in the revised manuscript, in the main text, l.369-377

c. Can you calculate the disjunct error for this set-up?

A9.3 *l/378-385"Eventually, the error introduced by disjunct sampling was estimated by comparing sensible heat fluxes calculated from continuous data with sensible heat fluxes calculated from disjunct series. In order to simulate the disjunct sampling protocol on sensible heat data, a LabVIEW routine was used to average the wind and temperature data to match the sampling rate of the PTR-MS (2 Hz) and set the sampling interval to 4.6 s. The difference between EC and DEC heat fluxes was small, typically below 2%. Assuming similarity between the heat flux and our VOC flux, a 2% error was estimated and no additional corrections have been made on the VOC fluxes".*

d. P.879 L.22 Sensitive should be "sensitivities"
A9.4: corrected

10. You mention percentages of the data below the detection limit for individual masses, but it is unclear how these data were treated. Did you remove these periods or did you do gap-filling? There are statistical methods for reducing the bias from data below detection limits (e.g. Clarke, 1998).
A10: We did not remove any datapoints. We kept the points under the LOD in order not to bias the results towards larger/lower values. For further clarification, the revised text reads:
"Various techniques for statistical analysis of data below the detection limits have been developed and used. Most of these methods have advantages and disadvantages. A simple approach, commonly used, consists in replacing values below the LOD, with one-half their respective detection limits (Caudill et al., 2007; Clarke, 1998; Porteret al., 1988). However, this substitution method can result in bias, either high or low depending on the value substituted (Helsel and Hirsch, 1992). In this study, all the compounds were considered representative in their full dataset, and no datapoints have been removed or substituted."

11. P880 L10 "Standard PTR-MS instruments operate with a unit mass resolution and therefore cannot distinguish isomeric molecules." This is not entirely true, for example, for isomers which fragment differently. I suggest inserting "easily" after "cannot". Consider replacing isomeric with isobaric.
A11: Added/replaced

12. P880 L16-18 "Signal of MBO is also detected at the parent ion m/z 87. In this study, m/z 87 was about 5–10% of the signal at m/z 69 in daytime. " This is worrying, because the sensitivity to MBO at m/z 87 is typically _25% of the sensitivity at m/z 69 (e.g. Karlet al., 2012). If the signal at m/z 87 was MBO approx. half of isoprene signal couldbe affected. However, it is possible that you observed something else on m/z 87, so aGC confirmation would be useful. Did you check the cartridges? Unfortunately MBOcan dehydrate in the GC so it is not a perfect confirmation, but perhaps you identifieda different compound which would be contributing to m/z 87 (e.g. pentanones) and which does notfragment on m/z 69?
A12: We thank the reviewer for this input. In regard to this comments, we agree that the attribution of MBO to m/z 87 cannot be justified. Unfortunately during the analysis of cartridges we have not targeted compounds such as MBO or pentanone and we cannot attribute with

certainty m/z 87 to any of these compound. Still, we defend the fact that isoprene was not biased in a significant way from any interference, based:

- On current research on downy Oak at O_3HP using a PTR-MS-Tof that demonstrates that fragment 69 comes from isoprene and not from MBO.
- on the intercomparison made between the PTR-MS and **two** different chromatography systems:
    - As presented in the text, a good correlation was observed between the PTR-MS and an online GC-FID (R^2 = 0.92), with a difference of 10%, which is within the uncertainty range of both measurements.
    - An additional intercomparison took place between the PTR-MS and GC-MS measurements of cartridge samples (not presented in the manuscript). Both instruments agreed with a difference of 5-8%.

  Even though, anytime that a sample treatment involves heating, MBO can dehydrate, this intercomparison between 3 different instrument supports the fact that there are not significant interferences in isoprene measurements. As a matter of fact, the conversion of MBO into isoprene will strongly dependent on the operational conditions of instruments. Therefore, it seems very unlikely that the MBO fragmented in the same way on 3 different instruments to give results with such good agreement. Additionally, only slight conversion (less than 5%) of MBO dehydration is expected when Tenax cartridges are desorbed rapidly (Harley et al., 1998), which was the case during the GC-MS analysis.

As a conclusion we will remove any statement attributing m/z 87 to MBO in the revised manuscript, which is anyway not discussed in the results of the manuscript.

14. Regarding m/z 71 which you attribute to MVK+MACR – you should also mention potential inteferences from isoprene hydroperoxides (ISOPOOH) (Liu et al., 2013). This is particularly relevant for low-NOx conditions when ISOPOOH is abundant.

A14: We thank the reviewer for his input and add this precision in the revised manuscript l.307-313

15. P881 L14. How can fragmentation occur on the parent ion? Rephrase

A15: The sentence is revised as follows:

"Total monoterpenes are detected predominantly on the parent m/z 137 and the fragment m/z 81 ions"

16.Sect. 2.5. P882 L18"A maximum covariance typically occurred around 15 s." How was the very long cycle length of 4.6 s affecting the precision of the lag time in each25 min period? Add precision to the following sentence 15 sXX s.

A16: Precision added in the main text:l.349-353

"For isoprene, a maximum covariance typically occurred around 15.0± 0.6s. Based on isoprene results, MVK+MACR maximum covariance was search within a window between 14 and 16s. Due to its sticky nature, methanol showed slightly longer lag times with a mean value 16.2±1.4 s. The experimental mean time lag of each compound was used as the default value when we didn't found a maximum in the covariance function.

17. If MBO was dehydrating in the GC, the good agreement could be for thewrong reason, in particular because the signal at m/z 87 was high? To better defend the attribution of isoprene to m/z 69, the authors could consider searching chromatograms

for non-MBO compounds that could occur at m/z 87, or inject MBO to the GC to assess if and how much gets converted to isoprene.
A17: the reviewer is invited to refer to answer 13.

18. Sect. 3.2.1 P886 L19-20 "Maximum concentrations occurred in the afternoon, peaking between 2–5 ppbv and 2–16 ppbv at 10m and 2m heights, respectively". The range for 2m height is not consistent with the range mentioned in the conclusions.
A18: Corrected

19. Sect. 3.2.2 Again I strongly refer the authors to the ACP paper from Harvard group on MVK+MACR oxidation (Liu et al., 2013) which showed contrastingly different yields for MVK+MACR formation depending on the level of NOx. Because you show relatively low yields at a canopy scale it would be interesting to check if these yields differed when NOx changed. However, you should at least try to estimate the contribution from peroxides on m/z 71, which can be difficult if you have not cooled the line to trap ISOPOOH.
A19:
NO concentrations remained low during the field campaign. They featured a mean value of 20 ppt and 90% of the datapoints where below 60 ppt over the whole measurement period. Thus, the ratio MVK+MACR/Isoprene did not vary a lot from day to day during daytime, and presented a mean value of 0.13±0.05..
Eventually, as the reviewer pointed out, as we have not cooled the line to trap ISOPOOH, we cannot estimate the possible contribution from other isoprene oxidation products to m/z 71. However, as the ratio MVK+MACR/Isoprene is in the lower range that what has been measured in other ecosystems of the world we don't believe to have a significant overestimation for MVK+MACR.

20. Sect. 3.2.3 You should at least discuss the limitations from using only m/z 137. For example, the proportion between m/z 81 and m/z 137 is different for different monoterpenes (e.g. Misztal et al., 2013, Tani et al., 2003) because the different structures fragment slightly differently and thus the sensitivity to m/z 137 can be slightly different. The question is what monoterpene was in the gas standard? Was monoterpene composition variable or constant based on the GC measurements?
A20:This information is added in the main text. l.243-252

21. How do you know m/z 61 is acetic acid? How did you assess the losses in the line? Glycol aldehyde is a significant product from MVK oxidation. How did you separateglycol aldehyde and acetic acid at m/z 61? Because you report the correlation ofm/z 75, this makes sense for hydroxyacetone to correlate with glycol aldehyde, but why would you expect acetic acid to correlate with hydroxyacetone?
A21: The rewiever is right that there is no strong argument for attributing m/z 75 to hydroxyacetone and m/z 61 to acetic acid. As no GC measurements enable us to better distinguish between the different isomers, we have corrected our statement and better discuss all the possible contributions to each mass.
Added in the main text, l.304-307 and l.575-578

22. Sect. 4.2. "Isoprene oxidation within the canopy" This section should be significantly rewritten includingthe discussion of recent evidence on isoprene oxidation

(Liu et al., 2013) which reportedthe yields of MVK+MACR formation in hydroperoxyl pathway approx. 10 timeslower than in the NO pathway However, it is nice that the authors referto the low NOx oxidation at the end of this section: "From the several field and chamberstudies which examined the influence of nitrogen oxides on the OH-induced oxidation of isoprene it was found that low NOx isoprene oxidation leads to low yields of MVK and MACR (Ruppert and Heinz Becker, 2000; Pinho, 2005; Navarro et al., 2011)." This should be expanded to include the recent literature as earlier suggested. This reviewer is uncomfortable with some of the speculationsdrawn from this section, for example, P895 L3 "A first explanation to the low rate of isoprene oxidation inside the canopy is the fact that isoprene did not have the time to react with OH radicals from the moment of its release 5 by the vegetation and its arrival at the sampling inlet." Why would it have time above the canopy then if you showed the emission rather than deposition?

A22: We are grateful to the reviewer for suggesting us to read the paper of Liu et al; (2013). As suggested, the section 4.2 has been significantly rewritten and our results were compared to the recent findings of the literature. We have modified the discussion. Emission fluxes of MVK+MACR suggest indeed some production inside the canopy. However, the emission is very low. By comparing the isoprene chemical degradation time to the turbulence transport time inside the canopy we conclude that in-canopy chemistry is minor, even though there is some MVK+MACR produced).

"

23. Sect. 5. Conclusions. The conclusions look modest and could summarize better what is best from the authors' research. For example, what was so novel about the results that need to be mentioned as a take home message? The sentence "As expected, biogenic VOCs were found to be dominated by isoprene with daytime maxima ranging between 2–15 ppbv inside the forest and 2–5 ppbv just above the top of the canopy" sounds odd. Why do we need these studies if all is always as expected? Was there anything unexpected? How can we do a better job next time and is there anything new from the previous studies? What is new knowledge and science? The basal emission rate will definitely be useful for the models. The conclusion on weak MVK+MACRoxidation is weak because it does not consider the oxidation chemistry. I strongly suggest the authors to read the paper by Liu et al. and get familiarized with NO-pathway and hydroperoxyl pathway of isoprene oxidation. The yields of MVK and MACR are substantially different in these two pathways. The authors could make a better use of their NOx data for interpretation of MVK+MACR oxidation, but they also should make it clear that under low NOx the signal at m/z 71 can be significantly affected by isoprene hydroperoxides.

A23: The conclusion has been modified in order to take into account the rewiever comments:

24. Regarding the isoprene concentration ranges, it seems that the time periods used for in-canopy and above-canopy data ranges are not consistent (see Fig. 4). The last day (17 june) shows only inside canopy data which were characterized by much higher concentrations as before. Perhaps the range would have been also broader for the above-canopy isoprene concentrations if they had been available. Thus, you need to make sure that the data are consistent. Also from looking at figure 4, it looks like the top two points on June 17th were around 17 mg m-2 h-1.

A24: On the 17th June, the PTR-MS was measuring inside the canopy (2 m a g.l) for an intercomparison with the GC-FID, that is the reason why just inside-canopy data are

presented. We agree with the rewiever, that we would expect to have also broader above-canopy isoprene concentrations, but these data are not available. The maximum value for inside-canopy isoprene data is corrected in the revised manuscript.

25. The conclusions could be further expanded to include main "take-home" messages.
A25: See A23

26. Table 1. The interpolated sensitivity value for MBO looks wrong. It would be about right for the combined MBO sensitivity from m/z 69 and 87, but you need to consider strong fragmentation of MBO. I would expect the sensitivity for MBO at m/z 87 _ 3ncps/ppb, but it could be even less given the high E/N ratio you were using.
A26: In regard of the reviewers comment, we are more aware that is not trustful to attribute m/z 87 at MBO. We are will therefore withdraw this compound from Table 1,

27. Also in Table 1 shown are separately the compounds for which there was a standard (left) and compounds derived from transmission (right). Why do you have monoterpenes in both groups?
A27: We agree with the reviewer that since monoterpenes have been calibrated just against m/z 137, there is no use on presenting the sensitivity calculated for m/z 81, thus, we have removed it from the revised table.

28.a Table 4. The mean flux column looks untidy. For example sometimes a range is given instead of the mean flux. In another case you compare mean with a median of other studies.
A28: We recognize that there is lack of harmonization in table 4. However, the values are displayed as found in the reference papers. The differences are inherent to the different statistical concepts (mean 24h/mean daytime/median) used in every study. We did our best to provide as much as possible normalized emissions rates (to standard light and temperature conditions), but this information was not always available. In the revised manuscript (**paragraph 4.1),** we will modify Table 4 and point out this lack of mathematical formalism in the main text . l.612-619

28.b The Western Italy example has 3 values which are not explained:
A28 The 3 values correspond to fluxes measured using the DEC method using three different proton transfer reaction mass spectrometers (PTR-MS). This information was added to the caption of the Table 4.

29. Also in Table 4, second row (Haute-Provence) the mean flux is shown as 5.4-10 mg m-2 h-1, while the max is shown as 10.1 mg m-2 h-1. In the first column the max value is shown to one significant digit while you show, 2, 3 and 4 significant digit for other studies.
A29 We thank the reviewer for pointing out this error. The values are corrected in the table 4.

31. Fig. 3 Can you also show the wind speed on the second panel?
A31 Added

32. Fig. 4. Can you change the colors/shades for inside and above canopy traces?
A32 Modified

Can you decrease the size of the marker so the markers are not so congested on the MT trace? Make m/z italic on the axis legend.
A32 Modified

33. It would be very interesting to see the panel for MVK+MAC separately for inside and above canopy.

A33:Unfortunately, there have not been simultaneous measurements for MVK and MACR inside and above canopy.

34. Fig. 5. Would it be interesting to show also the incanopy data on the same graph?
A34:In canopy data added**.**

35. Fig. 6. Please reduce the size of the marker for VOC fluxes. The legend occupies 1/3 of the horizontal space. Perhaps place it above or below the graph so that the fluxes can be stretched horizontally. Make smaller y-axis limits (e.g [-1.5 1.5])
A35: Modified

36. Fig. 7. Second panel is overemphasizing night time when isoprene was low. Consider splitting the y-axis.
A36: An extra panel with the ratio in daytime has been added

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37. There are numerous language imperfections (e.g. P.876 L.4, P876 L26, P877 L3-4). For example, "follow" is used excessively and not always correctly (e.g. P877, L9).It would be advised the native speaker (I can see at least one in the author list) refines the text.
A37. The text has been read again in order to correct the language imperfections.