Authors Response to Referee 2

The authors acknowledge Referee2 for his 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.

General comments:

**Kalogridis et al., present interesting results of VOC fluxes and concentrations from French oak forest with a considerable focus on isoprene and its oxidation products. Because there is a small number of VOC data reports from biogenic ecosystems in particular with respect to direct fluxes, the results from these type of studies can be extremely valuable and useful for improvement of estimates of biogenic emission models and for understanding the mechanisms of BVOC production, transport and chemistry. There is no doubt that authors have put a large effort on data processing and analysis of the presented results and that these topics are appropriate for publication in ACP. However, the paper has also a significant potential for improvement before potential publication. My general impression from reading this version of the paper is that different, sometimes remote, topics (transport, chemistry, in-canopy/above-canopy processes, "air chemical regime", benzene to toluene ratios, MVK+MACR/isoprene ratios,etc.) are discussed together without linking them with a consistent coherent thread. This interesting dataset could form a much more coherent story of novel science behind the results. I think, more emphasis should also be made on data quality control which could change the interpretation of the results, in particular, validation of the potential interferences in PTR-MS such as from MBO to m/z 69, peroxides to m/z 71,
glycol aldehyde to m/z 61, etc. I suggest the following comments should be addressed before publication:**

In regard to the comments of both referees, major changes have been made concerning;

- The data quality control:
  - measured fluxes were corrected from high frequency losses
  - the error due to the disjunct sampling was also estimated
  - more details were provided about the routine tests used for filtering purpose

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

- As suggested by Referee 2, Section 4.2 "*Isoprene oxidation within the canopy*" has be significantly rewritten including the discussion of recent evidence on isoprene oxidation, (Liu et al., 2013)

Specific comments:

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

"The CANOPEE project aims to better understand the biosphere-atmosphere exchanges of biogenic volatile organic compounds (BVOC) in the case of Mediterranean ecosystems and the impact of in-canopy processes on the atmospheric chemical composition above the canopy. Based on an intensive field campaign, the objective of our work was to determine the chemical composition of the air inside a canopy as well as the net fluxes of reactive species between the canopy and the boundary layer. Measurements were carried out during spring 2012 at the Oak Observatory of the Observatoire de Haute Provence (O_3HP) located in the southeast of France. The field site presents one dominant tree species, Quercus pubescens Willd., a typical Mediterranean species which features large isoprene emission rates. Mixing ratios of isoprene, its degradation products methylvinylketone (MVK) and methacrolein (MACR) and several other oxygenated VOC (OxVOC) were measured above the canopy using an online proton transfer reaction mass spectrometer (PTR-MS), and fluxes were calculated by the disjunct eddy covariance approach. The O_3HP site was found to be a very significant source of isoprene emissions, with daily maximum ambient concentrations ranging between 2-16 ppbv inside and 2-5 ppbv just above the top of the forest canopy. Significant isoprene fluxes were observed only during daytime, following diurnal cycles with midday net emission fluxes from the canopy ranging between 2.0-9.7 mg m^{-2} h^{1}. Net isoprene normalised flux (at 30 °C, 1000 µmol m^{-2} s^{-1}) was estimated at 7.4 mg m^{-2} h^{-1}. Evidence of direct emission of methanol was also found exhibiting maximum daytime fluxes ranging between 0.2-0.6 mg m^{-2} h^{-1}, whereas flux values for monoterpenes and others OxVOC such as acetone and acetaldehyde were below the detection limit. The MVK+MACR-to-isoprene ratio provided useful information on the oxidation of isoprene, and is in agreement with recent findings proposing weak production yields of MVK and MACR, in remote forest regions where the NOx concentrations are sufficiently low. In-canopy chemical oxidation of isoprene was found to be weak and did not seem to have a significant impact on isoprene concentrations and fluxes above the canopy."

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:

   *"These large uncertainties can be partly explained from the fact that current models use simplified SOA mechanisms that lump gaseous precursors and therefore loose information on the dry deposition removal of organic compounds which compete with the uptake of gases to the aerosol phase (**Goldstein and Galbally, 2007, Hodzic, 2013)**"*

3. **2.2 : Change the section title to include « GC cartridge ».**

   A3:The title is revised as follows:

   "*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:

*"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).

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:

“BVOC fluxes were corrected from high-frequency losses using the following equation:

$$\begin{aligned} F_{non-attenuated} &= F_m * f_c \\ &= F_m * (1 + ((2\pi \times \tau \times n_m \times \bar{u})/(z - d))^{a}) \qquad (2) \end{aligned}$$

where F_m *is the measured flux,* $F_{non-attenuated}$ *is the non –attenuated flux, and* f_c *the correction factor (Horst, 1997; Davison et al., 2009b).* f_c *was calculated as a function of* τ*, the response time of the PTR-MS (here 0.5 s), z the measurement height (10 m), d the displacement height (⅔.*h_c*, where* h_c *is the canopy height , and* $\bar{u}$ *the average wind speed at the measurement height. For neutral and unstable stratification, the dimensionless frequency at the co-spectral maximum is* $n_m = 0.085$ *and* $= 7/8$*. Over the whole measurement period, the attenuation correction ranged from 1.1% to 23%, with a mean value of 13%”.*

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

A9.3 *“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 following paragraph:

"The isomers methylvinylketone (MVK) and metacrolein (MACR) were detected at the same mass-to-charge ratio, m/z = 71. Until recently, the $C_4H_7O^+$ *ions have been exclusively attributed to the sum of the former compounds (De Gouw and Warneke, 2007, Blake et al. 2009). New evidence suggests additional contribution from isoprene hydroperoxides fragments at the same m/z ratio as the product ions of MVK and MACR, especially for low-NOx conditions (Liu et al., 2013). As isoprene hydroperoxides are expected to have similar diurnal variability to MVK and MACR,it is particularly difficult to estimate the contribution of isoprene hydroperoxides to m/z 71.. Thus, we we have to keep in mind that the concentration attributed to MACR and MVK might be slightly overestimated."*

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:

"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. However, this low ratio is consistent with the ratio measured at low NOx conditions in the chamber experiment of Liu et al 2013 (Table1). This information is added and discussed in the section 4.2.

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, and in very good agreement with the results of Liu et al. 2013, 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: Added in the main text

"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)."

21. How do you know m/z 61 is acetic acid? How did you assess the losses in theline? 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:

"Signals at m/z 61 include mainly acetic acid and glycoaldehyde but can also suffer interferences from ethyl acetate fragments originated from industrial emissions (De Gouw and Warneke, 2007; Haase et al., 2012; Haase et al., 2012; Yuan et al., 2013)."

"For example, the good correlation between m/z 75 and m/z 61, suggests that these masses include important contributions from hydroxyacetone and glycoaldehyde, two second-generation products from isoprene. However, additional contributions from other compounds cannot be excluded."

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).

“*4.2 Isoprene oxidation within the canopy*

In the last few years, there has been a special interest for better understanding the isoprene chemistry, especially in sites such as the O_3HP, where the isoprene emissions are strong and the NOx levels are low (NO mean value ~25 ppt). As a matter of fact, inconsistencies between observations in rural sites and model estimates of the ratio of isoprene to its oxidation products have pointed out the uncertainties associated with the isoprene oxidation mechanism. Lately, a strong effort has been made through laboratory studies, to measure rate coefficients and product branching ratios yields (Paulot et al., 2009; Peeters et al., 2009; Silva et al., 2009; Peeters and Müller, 2010; Fuchs et al., 2013). In the following section, we investigate the isoprene oxidation and production of MVK and MACR at the O_3HP and discuss our results with regard to recent findings that suggest very low production yields of MVK and MACR yields under low NOx conditions (NO<70ppt) (Liu et al., 2013).

OH-oxidation of isoprene is initiated by the addition of the hydroxy radical to the double bonds of isoprene. The alkyl radical formed reacts with oxygen (O_2) to form alkyl peroxyl radicals (HOC5H8OO°), commonly called ISOPOO. ISOPOO radicals subsequently react whether with NO (Tuazon and Atkinson 1990), hydroxyperoxyl radicals HO_2 (Paulot et al., 2009), or organic peroxyl radicals RO_2 (Jenkin et al. 1998). Additional isomerization reactions of ISOPOO radicals have also been suggested in the recent literature (Peeters et al. 2009, da Silva et al.; 2010, Fuchs et al., 2013). At high NOx concentrations the dominant fate of ISOPOO is generally the reaction with NO. However, under low NOx conditions, reaction with HO_2 dominates and leads to lower MVK and MACR yields (Miyoshi et ak. 1994, Ruper and Becker 2000). Using atmospheric simulation chambers, Liu et al. (2013) found the lowest MVK and MACR yields that have ever been reported, with values of (3.8±1.3)% for MVK and (2.5±0.9)% for MACR, i.e more than 60% smaller than previous “low-NOx” experiments (Miyoshi et ak. 1994, Ruper and Becker 2000, Navarro et al., 2011), and about 10 times lower than via the NO pathway.

At the O_3HP, the twelve days of measurements featured a [MVK+MACR]-to-isoprene ratio of 0.13±0.05 during daytime (Fig. 8). We should keep in mind that this ratio could be lower if any interference occurred at m/z 71 from other oxidation products. Despite this possible overestimation, the [MVK+MACR]-to-isoprene ratio at the O_3HP is at the lower end of the range that has previously been observed in other ecosystems of the world, which usually fall between 0.3-0.75, depending also on the height measurement (Montzka et al., 1993; Biesenthal et al., 1998; Holzinger et al., 2002). Nevertheless, a few studies have shown ratios close to our estimates: a ratio of 0.12 has been reported in a rural forest of Michigan (Apel, 2002), and a ratio of 0.1 to 0.36 was obtained in a South-East Asian tropical rainforest (Langford et al., 2010). Our findings are also very similar to the results of Liu et al., (2013), which report a [MVK+MACR]-to-isoprene ratio at 0.13±0.02 and therefore support the low MVK and MACR yields proposed.

The low [MVK+MACR]-to-isoprene ratio is also in agreement with the fluxes of mass 71 (related to MACR and MVK and possible contribution from isoprene hydroperoxides) Fluxes of mass 71, showed a general trend of emission and thus, suggest a production throughout the forest canopy. However, the magnitude of these fluxes was very low: about 40% of the MVK+MACR fluxes were below the detection limit, and the data that passed all the quality assessment tests represented about 3% of the isoprene fluxes. Estimates of the isoprene that is converted to MVK+MACR below the flux measurement are usually in order of 5 to 15%, also depending on the measurement height (Stroud et al., 2005). Additionally to the poor NOx conditions, leading to low yields of MACR and MVK, minor chemical processing of isoprene is expected below the measurement height due to the canopy architecture of the O_3HP. The forest of the O_3HP is low (5 m height on average), well ventilated and therefore closely coupled to the boundary layer above. Thus, the turbulent transport time τ between ground surface and the measurement height was estimated to be around 30-60 s in daytime (See Supplementary Material for calculation details), i.e considerably faster than the isoprene chemical degradation estimated at about 4h against its oxidation by OH for typical summer daytime. Thus, isoprene rapidly reaches the atmosphere and do not have the time to react in a significant way with OH radicals from the moment of its release by the vegetation and its arrival at the sampling inlet. “

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:

"We have presented high resolution atmospheric measurements of concentrations and direct above-canopy fluxes of BVOCs for a Mediterranean Downy oak forest. High concentrations of isoprene have been observed, with daytime maxima ranging between 2-17 ppbv inside the forest and 2-5 ppbv above the top of the canopy. Isoprene concentrations showed a clear diurnal cycle with a daytime maximum and a minimum in the early morning and at night. Above the canopy, isoprene concentrations were about 40% lower than inside the canopy; this loss was attributed to physical processes such as mixing with isoprene-depleted air masses (or, conversely, the build-up of isoprene within the canopy). Isoprene fluxes at the O_3HP site were among the largest fluxes reported in the Mediterranean region, with mid-day maxima ranging between 2.0-9.7 mg m^{-2} h^{-1}. Based on these measurements, an isoprene basal emission rate of 7.43 mg m^{-2} h^{-1} is recommended for downy oaks in this region for biogenic emission models. OxVOCs were abundant at the site with mean daytime concentration of 2.48, 1.35 and 0.42 ppbv for methanol, acetone and acetaldehyde respectively. Of these compounds, only methanol exhibited significant fluxes, indicating a primary source inside the canopy. Methanol fluxes featured maxima daytime values ranging between 0.20-0.63 mg m^{-2} h^{-1}, i.e about 5 to 20 times lower than isoprene fluxes. No above-canopy fluxes of monoterpenes have been observed, and, as a result, ambient concentrations of monoterpenes were close to the detection limits. These observations are in agreement with branch-level measurements, who found that Q.pubescens was a strong emitter of isoprene and very weak emitter of monoterpenes (Genard et al. 2014). At the forest site of the O_3HP, where the isoprene emissions were high and the NOx levels low, a small [MVK+MACR]–to-isoprene ratio has been observed (mean daytime value of 0.13±0.05), supporting the recent findings of Liu et al. (2013) proposing very low production yields for MVK and MACR for the oxidation of isoprene peroxyl radicals via the HO_2 pathway. Up-ward fluxes of MACR and MVK indicated a production from isoprene throughout the forest canopy, but represented less than 3% of the isoprene flux. Additionally, no systematic deposition fluxes could be detected for either of the compounds investigated here. Therefore, we conclude that intra-canopy processes had a minor effect on above-canopy fluxes"

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 .

"A non-exhaustive overview of isoprene flux measurements in Mediterranean, tropical, and temperate ecosystems is presented in Table 4. Reported values are displayed as found in the reference papers and demonstrate a difficulty of intercomparison due to the multiple statistical ways of expressing a set of numbers (mean/median/range) used in every study. However, this table gives an idea of the orders of magnitude of isoprene emission rates at the canopy scale, and confirms that isoprene emissions from Mediterranean forests can be comparable or higher than those observed in other regions of the world dominated by isoprene-emitting vegetation."

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 coorect the language imperfections.