

Authors Response to Referee 1

The authors acknowledge Referee1 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:

This manuscript by Kalogridis et al. describes direct BVOC concentration and flux measurements from a French oak tree forest. The BVOC measurements were carried out using the PTR-MS and disjunct eddy covariance (DEC) techniques during 2 weeks in June, 2012. The authors estimated fluxes of isoprene and some OVOCs, and reported a basal emission rate of isoprene using the G93 algorithm. For OVOCs, particularly they found within-canopy MVK+MACR production by isoprene was weak in this forest environment and they observed direct emission of methanol. Overall, this manuscript provides a valuable and useful data set for BVOC/OVOC flux and atmospheric chemistry community and could contribute to a better understanding the atmosphere-ecosystem interaction. However, I think that this manuscript still has to be improved and to be thoroughly discussed in the DEC flux data analysis with their measurement method before it can be published. One concern for this manuscript is that the authors poorly described the flux uncertainty and error, and this may cause a significant underestimate or overestimate in flux calculation. To be specific, the time of one cycle in PTR-MS VOC measurements was set to 4.6 s for 11 mass to charge ratios including primary ions, and this is not fast enough to fully capture small size of eddies. This might be problematic, because the authors estimated 30-60 s range of the vertical turbulent travel time scale during daytime, this time scale is comparable or non-negligible to the measurement cycle time applied. So, it is important to demonstrate whether or not the small size of eddies at the O3HP site is significant in the BVOC/OVOC DEC flux measurements. Moreover, when sampling the air was pumped through a half inch Teflon tube with 64 L/min to keep turbulent flow inside the tube. This is a big flow rate and may disturb the air motion within the detection region of 3-D sonic anemometer since the inlet was located close to the sensor. This should be also discussed.

As both referees pointed out in the original manuscript the quality assessment of the DEC flux data was not comprehensively discussed. This has been taken into account and in the revised paper, we have:

- Corrected the measured fluxes from high frequency losses

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

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

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 ($\approx 0.5 h_c$, 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 $\approx 7/8$. Over the whole measurement period, the attenuation correction ranged from 1.1% to 23%, with a mean value of 13%.”

- Estimated the error due to the disjunct sampling (~2%)

Added in the main text: “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”

- Provided more details about the results of the routine tests used for filtering purpose (see A15).
 - Discuss the disturbance from the air motion within the detection region of 3-D sonic
- More details are given in the answers to the specific comments.

Specific comments:

- 1. P876, L 20-21: Please include what method was used for measuring LAI, or add a reference that describes how LAI is determined.**

A1: As suggested by the reviewer, we include the above points in the revised manuscript:

“The single-sided mean leaf area index (LAI) was measured in August 2010 as part of the O₃HP monitoring activity with a plant canopy analyzer (LAI-2000, Li-Cor, Lincoln, NE, USA), and was found to be 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 above points in the revised manuscript:

“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/>) using the model developed by 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.

- 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

- 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”

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: We include the following in the revised manuscript. (p.8, l. 225-229)

“The internal gas canister provided by Ionimed contained a mixture of 17 VOCs. The species used for the calibration were methanol (contributing to m/z 33), acetaldehyde (m/z 45), acetone (m/z 59), isoprene (m/z 69), crotonaldehyde (m/z 71), 2-butanone (m/z 73), benzene (m/z 79) toluene (m/z 93) and α -pinene (m/z 137)”.

- **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 k_i ($\text{cm}^3 \text{s}^{-1}$) and sensitivities. Also, the k_i 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. The following sentence is included in Table 1 and in section 2.4.2 Calibration and volume mixing ratios (VMR) calculations

“As methylvinylketone (MVK) and methacrolein (MACR) were not included in the gas standard, it was assumed that the sensitivity for the sum of MVK+MACR is the same as the sensitivity of their structural isomer crotonaldehyde”

- 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).

“As the background counts of m/z 137 could not be measured from the scan mode, they were derived from the calibrations, when the instrument was zeroed with catalytically converted air. The dwell time on each mass was 2s during the calibration (instead of 500 ms during ambient measurements), thus, the background at m/z 137 might have been slightly underestimated. “

- 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 following sentence is included in section 2.4.3

“Isoprene for example, can fragment in the PTR-MS instrument and yield m/z 41[...]. During this study, the fragmentation of isoprene in the PTR-MS instrument was small: more than 80% remained on the parent ion (m/z 69). Considering, that m/z 69 to m/z 41 ratio is constant (for a fixed E/N value), then quantification of isoprene based on m/z 69 should not be affected by fragmentation.”

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 find a maximum in the covariance function”* Added in the revised manuscript.

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: Added in the revised manuscript.

“The lower limit of friction velocity was set to 0.15 m s^{-1} , a threshold commonly used in eddy covariance routine tests (Misztal et al., 2011, Langford et al., 2010)”.

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: These information were added in the revised manuscript, in the main text and in Table 3.

Main text: *“In the current study, 30% of isoprene, 29% of methanol and 60% of MVK+MACR datapoints were rejected. Of the data that passed the quality assessment, more than 80% were ranked as high quality. More statistics about these tests are presented in Table 3”*

Table 3.

	Isoprene	Methanol	MVK+MACR
Failure percentage among flux datapoints			
<i>Quality Tests:</i>			
$u^* < 0.15 \text{ m s}^{-1}$	18%	19%	20%
$F < \text{LOD}$	11%	10%	37%
$\Delta s > 60\%$	1%	0%	3%
Data that passed the quality assessment:			
High quality Stationary data	94%	93%	81%
$\Delta s < 30\%$			
Low quality Stationary data	6%	7%	19%
$30\% < \Delta s < 60\%$			

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

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

“Relatively high ozone concentrations, typical of regions with strong photochemical activity such as the Mediterranean Basin, have been registered, with daily maximum ranging between 40-76 ppb.”

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.

Site	Method	Daytime Fluxes [$\text{mg m}^{-2} \text{h}^{-1}$]			Daytime VMR [ppbv]	Season	Reference
		Mean (Median)	Std conditions*	Max			
Mediterranean	Haute Provence, France downy oaks	DEC	2.77 (2.39)	7.43	9.85	2.09 (2.10) (max. 4.97)	Spring 2013 This study
	Haute-Provence, France downy oaks	DEC	-	-	10.08	-	Summer 2010 (Baghi et al., 2012)
	Western Italy, macchia ecosystem	DEC	(0.10/0.16/0.32)**	0.43	0.29	(0.16/0.25/0.17)** (max. 0.60)	Spring 2007 (Davison et al., 2009b)
Tropical	Malaysia borneo oil plantation	DEC	9.71 (8.45)	7.80	28.94	13.10 (13.80) (max.21.40)	Spring 2008 (Misztal et al., 2011)
	Malaysia Rainforest	DEC	0.93 (0.46)	1.60	3.7	1.30 (1.00) (max. 3.40)	Spring-summer 2008 (Langford et al., 2010)
	Central Amazon mature lowland	REA	2.38±1.8	-	6.12	3.40±1.8 (3.2) (max. 6.60)	Summer 2001 (Kuhn et al., 2007)
	La Selva, Costa Rica oil tree	DEC	1.35	1.72	2.90	1.66 (max. 3.00)	Spring 2003 (Karl et al., 2004)
	Tabajos, Brazil terra firme	EC	-	2.40	2.00	- (max. 4.00)	Spring 2000 (Rinne et al., 2002)
	Temperate	Central Massachusetts, mixed canopy	DEC	4.40	3.70-17.20	-13.50	- (max. >10.00)
Germany mixed deciduous: beech, oak		DEC	3.38	2.88	10.8	- (max. 4.00)	Summer 2003 (Spirig et al., 2005)
Eastern Belgium mixed coniferous species		DEC	-	2.01-3.28	7.06	- (max. <1.50)	Summer 2009 Laffineur et al., 2011

16. P888, L 14-15: Jardine et al. (2012) have found direct MVK and MACR emissions from some plants. Did you observe any signature of MVK and/or MACR emission from the branch enclosure experiments at the O₃HP 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 will be 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 α -pinene was representing $80\pm 13\%$ of the total monoterpenes at the site. Limonene was the second most abundant monoterpene ($15\pm 9\%$), 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 algorithm for the light + temperature dependent emission species and historical records of T & 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 O₃HP 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 authors discussed 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 error range of up-scaled BER to confirm if the range includes the BER by DEC? Also, as mentioned 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 up-scaled BER of $18\pm 5 \text{ mg m}^{-2} \text{ h}^{-1}$. (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 $7.43 \text{ mg m}^{-2} \text{ h}^{-1}$. (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 point 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 "*Error bars show \pm standard deviation of the covariance for t_{lag} far away from the true lag (+150-180 s)*".

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

Author's response: Information added to the caption.