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Atmospheric Chemistry and Physics
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# *Interactive comment on* "Concentrations and fluxes of isoprene and oxygenated VOCs at a French Mediterranean oak forest" *by* C. Kalogridis et al.

**Anonymous Referee #1**

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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 $\sim$ 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.

Specific Comments:

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

- P876, L 24: Add the footprint analysis information at the site or a reference for it.

- P877, L 2: Specify the dates for the intensive measurement period instead stating ‘about two weeks’.

- P878, L 8-13: As mentioned above, discuss or justify that the air sampling by high flow rate did not interfere the wind measurement by 3-D sonic anemometer. Also, what Reynolds number in the tube was maintained with this setup?

- P879, L 7: Do you have any specific reason why you limited the m/z range up to 93 in scan mode?

- P879, L 14: You performed the calibration only twice throughout the intensive campaign period. How were the sensitivities changed between two calibrations?

- 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 calibration. 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?)? Did you use MACR+MVK mixture or only one of them for m/z 71?

- P879, L 26-28: As listed in Table 1, the detection limit of m/z 137 is 0.04 ppbv. However, the background of m/z 137 was not measured based on the mass range in scan mode. Clarify how you took into account this. In addition, what is the time scale of detection limit (e.g. 0.5s, 1s, 1min, 5min, etc. . .)?

- P880, L 6-8: Please give the range of monoterpene mixing ratios rather than stating just ‘low’.

- 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.

- 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?

- 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.

- 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.

- P884, L 4-6: How many data points were used for this intercomparison?

- 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.

- 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.

- P887, L 23-28: With very stable condition of the air and accumulation of the compounds within the canopy, the storage term becomes a very important parameter. Have you considered this factor in the flux calculation including other compounds such as isoprene and methanol?

- 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?

- 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/z 81, 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?

- 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?

- 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.

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

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.

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).

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.

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

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?

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.

Fig. 9: Please show the error bars.

## References

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), Atmos. Chem. Phys., 6, 3181-3210, 2006.

Jardine, K. J., Monson, R. K., Abrell, L., Saleska, S. R., Arneth, A., Jardine, A., Ishida, F. Y., Yañez Serrano, A. M., Artaxo, P., Karl, T., Fares, S., Goldstein, A., Loreto, F., and Huxman, T.: Within-plant isoprene oxidation confirmed by direct emissions of oxidation products methyl vinyl ketone and methacrolein, Global Change Biol, 18, 973-984, doi: 10.1111/j.1365-2486.2011.02610.x, 2012.

Tani, A., Hayward, S., and Hewitta, C. N.: Measurement of monoterpenes and related compounds by proton transfer reaction-mass spectrometry (PTR-MS), Int J Mass Spectrom, 223, 561-578, 2003.

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