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Atmospheric Chemistry and Physics
Discussions

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

Anonymous Referee #2

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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:

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?

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.

3. Sect.2.2 consider changing the section title to include "GC cartridge"

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?

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

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

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

8. P.878 L.21 replace colons for example with "is"

9. 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? Did this configuration not suffer high frequency losses? Can you calculate the disjunct error for this set-up?

10. P.879 L.22 Sensitive should be "sensitivities"

11. 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).

12. 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 to insert "easily" after "cannot". Consider replacing isomeric with isobaric.

13. 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 $\sim$25% of the sensitivity at m/z 69 (e.g. Karl et al., 2012). If the signal at m/z 87 was MBO approx. half of isoprene signal could be affected. However, it is possible that you observed something else on m/z 87, so a GC confirmation would be useful. Did you check the cartridges? Unfortunately MBO can dehydrate in the GC so it is not a perfect confirmation, but perhaps you identified a different compound which would be contributing to m/z 87 (e.g. pentanones) and which does not fragment on m/z 69?

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.

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

Sect. 2.5 16. 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 each 25 min period? Add precision to the following sentence 15 s±XX s. Sect. 2.7 17. See comment # . If MBO was dehydrating in the GC, the good agreement could be for the wrong 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. Sect. 3.2.1 18. 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.

Sect. 3.2.2 19. 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. Sect. 3.2.3 20. 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?

Sect. 3.2.4

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 separate glycol aldehyde and acetic acid at m/z 61? Because you report the correlation of m/z 75, this makes sense for hydroxyacetone to correlate with glycol aldehyde, but why

would you expect acetic acid to correlate with hydroxyacetone? Sect. 4.2. "Isoprene oxidation within the canopy" 22. This section should be significantly rewritten including the discussion of recent evidence on isoprene oxidation (Liu et al., 2013) which reported the yields of MVK+MACR formation in hydroperoxyl pathway approx. 10 times lower than in the NO pathway This reviewer is uncomfortable with some of the speculations drawn 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? However, it is nice that the authors refer to the low NOx oxidation at the end of this section: "From the several field and chamber studies 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.

Sect. 5. Conclusions 23. 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 needs 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+MACR oxidation 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.

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.

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

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 $\sim$ 3 ncps/ppb, but it could be even less given the high E/N ratio you were using.

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?

28. 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. The Western Italy example has 3 values which are not explained.

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.

30. Fig. 1 What is the purpose of showing the vertical lines?

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

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

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

34. Fig. 5. Would it be interesting to show also the incanopy data on the same graph?

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])

36. Fig. 7. Second panel is overemphasizing night time when isoprene was low. Consider splitting the y-axis.

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.

Supplementary information.

38. Section S1.2 use correct units for drift tube pressure, not volts. What is “standar pression”? 39. Fig S3. This is a nice figure showing an impressive agreement of latent heat fluxes. I am just curious, why on June 14th the PTR seems to overestimate the latent heat fluxes if you showed in Fig. S1 that the water vapor concentration was rather underestimated by the PTR-MS on the same day? 40. Fig. S5. Show units on x axis

References:

Clarke, J. U.: Evaluation of censored data methods to allow statistical comparisons among very small samples with below detection limit observations, Environmental Science & Technology, 32, 177-183, 1998. Karl, T., Hansel, A., Cappellin, L., Kaser, L., Herdlinger-Blatt, I., and Jud, W.: Selective measurements of isoprene and 2-methyl-3-buten-2-ol based on NO+ ionization mass spectrometry, Atmos. Chem. Phys., 12, 11877-11884, doi:10.5194/acp-12-11877-2012, 2012. Liu, Y. J., Herdlinger-Blatt, I., McKinney, K. A., and Martin, S. T.: Production of methyl vinyl ketone and methacrolein via the hydroperoxyl pathway of isoprene oxidation, Atmos. Chem. Phys., 13, 5715-5730, doi:10.5194/acp-13-5715-2013, 2013. Misztal, P. K., Heal, M. R., Nemitz, E., and Cape, J. N.: Development of PTR-MS selectivity for structural isomers: Monoterpenes as a case study, International Journal of Mass Spectrometry, 310, 10-19, DOI 10.1016/j.ijms.2011.11.001, 2012. Tani, A., Hayward, S., and Hewitt, C. N.: Measurement of monoterpenes and related compounds by proton transfer reaction-mass spectrometry (PTR-MS), International Journal of Mass Spectrometry, 223, 561-578, 2003.

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