Review of "Characterization of total ecosystem scale biogenic VOC exchange at a Mediterranean oak-hornbeam forest," Schallhart et al. (2015)

Summary

This study presents a set of tower-based VOC flux observations acquired with PTR-TOF-MS in a mixed deciduous forest over a period of ~22 days. TOF-MS instruments measure a lot of ions, and special attention is given to method development and proper use of such a dataset. Several unique aspects of the dataset are explored in further detail, including flux divergence from in-canopy MVK/MACR production and methanol deposition to wet surfaces.

The data presented are new. The analysis generally follows previously-published procedures but does make an effort to compare several methods, which will be useful to the community. The English is OK but could be improved beyond the technical comments listed below. The paper is appropriate for publication in ACP after consideration of the following minor revisions.

General Comments

None.

Specific Comments

P27635, L15: "For compounds included in the standard, the calibration implicitly accounts for the fragmentation pattern." Based on the later discussion, this statement seems incorrect. If the fragments were "accounted for" in the calibration, then one would not have to filter them from the automated flux list.

P27637: Was any filtering done for wind sector to exclude time when the wind is coming through the tower? Vertical wind measurements are likely unreliable at these times.

P27639, L3: This equation does not appear to be correct. Assuming spectral similarity between c' and theta', the transfer function should be the ratio of the normalized cospectra, not the product. Thus, in the case where the spectra are identical $H_{wc}(f) = 1$ at all frequencies. This is also consistent with Eq. (10) in the limiting case tau = 0. Presumably the values in Fig. 3 were calculated with the correct equation since they range from 1 to 0.

P27639: A 26% upward correction seems substantial. Why is the instrument time constant so large? Does it really take so long to flush out the internal volume?

P27640: Please provide some metric of calculated OH values (midday mean, range, whatever works).

P27641, L16: The left-hand size should be called F_Q or something similar, as it is a flux and not a rate (and Q is used for the rates in Eq. 14-15). Also, might be worth mentioning/justifying that MVK+MACR chemical loss in the canopy does not affect flux, since it is not explicitly accounted for.

P27644, L1: " . . . as it is not possible to differentiate between deposition and other sinks terms . . . ". To the reviewer, this rationale supports *not* calling these fluxes deposition and emission, since the latter two terms refer to specific processes. Why not just call these downward and upward fluxes? This avoids confusing observation of a flux and attribution of its drivers.

P27643, L7: Most of the methods section discusses the distinction between two methods; however, here and in Table 2 there are three methods presented. If possible, Sect. 2.3.3 should be modified to more clearly set up what is presented here. Alternatively, it could still be presented as two methods, and the discussion of the results with the "compound filter" could come a little later.

P27644, L3: This is the first time the phrase "compound filter" appears (other than abstract), and it is presented without a proper definition. If possible, this could be defined in Sect. 2.3.3. Also, this may not be the best label, since "compound" simply means a combination of several things. Other terms might be considered, e.g. "redundant ion filter" "double-counting filter," etc.

P27644, L21: This paragraph is confusing. In section 2.3.3, no mention was made of calculating noise with absolute values. This would not be a correct procedure (since, as noted in the text, it alter the statistics) and thus does not warrant discussion. Perhaps these methods are still in development, but it seems that one could also the RMS error (P27638, L8), rather than the standard deviation, to define a cutoff value for the automated case. This would also account for any non-zero offsets in the CCF. All we are really talking about here is defining a flux detection limit and the signal/noise ratio where we say observed fluxes are "real."

P27647: It is not clear that Figure 7a is necessary. Suggest deleting it.

P27647, L28: Several other papers have also dealt with this topic, with varying results (Fares et al., 2015; Karl et al., 2009; Karl et al., 2010).

P27648, L4: "ISPOOH reacts readily with NO . . . " This is not true. What is true is that ISOPOOH is made through ISOPO2 + HO2, which is a low-NOx channel, so that its production is dependent on the fate of ISOPO2 radicals (which do react with NO). Please revise. Also, from a flux perspective, any such interference would likely give a downward flux contribution due to deposition of peroxides (Nguyen et al., 2015).

P27650, L1: not sure this logic makes sense. Why would low wind speeds imply a source outside the forest? Is it also possible that it is a ground source (e.g. rotting leaves), and fluxes are only observed when turbulence is sufficient to mix out the lowermost canopy?

P27650: How does the deposition lifetime compare with oxidation for methanol?

Table 3: Deposition velocities would also be helpful.

Technical Comments
P27627, L9: 65% by mixing ratio or by mass?

P27628, L22: delete hyphen.

P27629, L16: "measurements have inherently"

P27630, L19: "study of dew potentially causing methanol deposition in the morning."

P27634, L1: "PTFE" (I assume)

P27636, L13: "eddy covariance (EC) method. In EC,…"

P27638, L18: "method will bias"

P27636, L15: If the vertical wind measurement is instantaneous, and the time lag is caused by gas sampling and can vary from ion to ion, it makes more sense (to the reviewer) to present this equation with the lag time applied to c' rather than w'.

P27642, L24: delete "chapter"

P27645, L28: replace "influence" with "contribution"

P27646, L23: replace "rates" with "fluxes"

P27647, L6: replace "rates" with "fluxes"

P27647, L19: "25th and 75th percentiles"

P27649, L22: "night"

Table 3: In footnote "a", replace "do" with "to".

Figure 3 caption, second line: "measurements"

Figure 4 caption, third line: "abundant"

Figure 5: need better y-axis label: flux of what?

Figure 6: please describe what the % circles mean in the top panel.

References

Fares, S., Paoletti, E., Loreto, F., and Brilli, F.: Bidirectional Flux of Methyl Vinyl Ketone and Methacrolein in Trees with Different Isoprenoid Emission under Realistic Ambient Concentrations, Environ Sci Technol, 49, 7735-7742, doi: 10.1021/acs.est.5b00673, 2015.
Karl, T., Guenther, A., Turnipseed, A., Tyndall, G., Artaxo, P., and Martin, S.: Rapid formation of isoprene photo-oxidation products observed in Amazonia, Atmos. Chem. Phys., 9, 7753-7767, 2009.
Karl, T., Harley, P., Emmons, L., Thornton, B., Guenther, A., Basu, C., Turnipseed, A., and Jardine, K.: Efficient Atmospheric Cleansing of Oxidized Organic Trace Gases by Vegetation, Science, 330, 816 - 819, doi: 10.1126/science.1192534, 2010.

Nguyen, T. B., Crounse, J. D., Teng, A. P., St. Clair, J. M., Paulot, F., Wolfe, G. M., and Wennberg, P. O.: Rapid deposition of oxidized biogenic compounds to a temperate forest, P. Nat. Acad. Sci. USA, 112, E392-E401, doi: 10.1073/pnas.1418702112, 2015.