

## ***Interactive comment on “Characterization of total ecosystem scale biogenic VOC exchange at a Mediterranean oak-hornbeam forest” by S. Schallhart et al.***

**Anonymous Referee #3**

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This manuscript reports “total ecosystem scale biogenic VOC exchange at a Mediterranean oak-hornbeam forest”, measured by PTR-TOF-MS for a period of 22 days. A main focus of the manuscript is on methodology used for flux calculations and the determination of what constitutes a detectable flux.

The main strengths of the manuscript include a thorough description of methods used for flux calculation (both manual and automated data processing approaches), the observation of deposition of methanol due to dew (very interesting, although not a novel result), confirming evidence for the bidirectional exchange of MVK+MAC, and providing new information on fluxes observable by PTR-TOF-MS in an oak dominated system

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which serves as an important source of BVOCs in Mediterranean regions.

My main concern with the manuscript is that the authors report detectable fluxes for 12 compounds in the abstract, ignoring the extreme data filtering that lead to this small number, leaving the reader with an incorrect impression of how many compounds are really exchanging between the ecosystem and the atmosphere. A careful reading of the manuscript reveals that this is based on a  $10\sigma$  noise threshold, which is an extreme signal to noise filter for defining detectable fluxes. For most scientific measurements a threshold of  $3\sigma$  noise would be considered typical and appropriate. In the manuscript they report 42 masses contributed to the total VOC flux at a  $3\sigma$  noise threshold. If the manuscript is going to focus on reporting how many masses (or compounds) had detectable fluxes, a more complete description is needed of how many masses were observed to have detectable mixing ratios, and then how many masses were excluded by each of the criteria used to filter the data. Specifically: a) How many masses had mixing ratios that were determined to be above the “limit of detection (LOD =  $2\sigma$  zero, where  $\sigma$  zero is the standard deviation of the zero-air signal)?” What amount of time averaging was used to determine the LOD (should be very different for 0.1 sec, 1 sec, 60 sec, etc)? Reporting information on detection limits and absolute sensitivities, or at least primary ion count rates would be useful. For example, it is possible that detection limits were low due to low primary ion counts. It would also be useful for the reader to see averaged CCFs and absolute value CCFs for a couple of ions that cover the range 0-10 sigma. Adding a supplement with the sigma of ALL detected ions would be appropriate. Averaged background and ambient air signals could also be included to help the reader assess the LOD determination. b) How many of these detected masses were excluded from the flux calculations based on each criteria used to filter the data? - “stationarity criteria introduced by Foken and Wichura, (1996): every 30 min period was divided into six 5 min sub-periods and VOC fluxes were calculated from both 5 and 30 min intervals. If the values differed more than 30 %, the period was disregarded from further analysis.” - “For the calculation of the diurnal 30 min flux data, a trimmed mean function was used, which disregarded the lowest and highest 5 % of

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the data and then averages the remaining 90 % of the data." This exclusion criteria is particularly concerning because it might discard many species for which an otherwise detectable flux was present (e.g. a flux which only showed up in 5% of the data but was otherwise significant), and also might cause distortion of the data including the mean. Furthermore, 'outliers' should not be discarded unless there is a very clear technical reason. In the latter case there must be a smarter way to get rid of the unwanted data. More discussion on the nature of the outliers is needed. -Any other criteria used. c) What fraction of the masses determined to be above the LOD also had detectable fluxes (at the  $3\sigma$ noise threshold)?

Additional suggestions and concerns: 1) It would be interesting to specifically compare the number of "masses that are found to contribute to the total VOC flux: 42 ( $3\sigma$ noise), 35 ( $4\sigma$ noise), 28 ( $5\sigma$ noise), 24 ( $6\sigma$ noise), 23 ( $7\sigma$ noise), 22 ( $8\sigma$ noise), 20 ( $9\sigma$ noise), 19 ( $10\sigma$ noise)" to the results from Park et al. 2013 shown in their Figure 1. Park et al only found 4 ions with fluxes above  $10\sigma$ noise and these only accounted for 46% of the total net flux, 18 ions with fluxes above  $7\sigma$ noise accounting for 66% of total net flux, and 494 above  $3\sigma$ noise accounting for 97% of total net flux. Several major differences exist between the locations of these studies including: a) The current paper reports measurements for a location that is dominated by isoprene emissions with a total midday flux ( $10\sigma$ noise, including 19 masses) that is approximately 1 full order of magnitude larger than the orange orchard studied by Park et al ( $10\sigma$ noise, including 4 masses). Almost all of this difference in total flux magnitude between the sites is due to isoprene. b) The current paper reports "Figure 5 shows the diurnal variation of the net flux for the different approaches. The difference in the net flux between a  $3\sigma$ noise threshold and a  $10\sigma$ noise threshold is less than  $1.6 \text{ nmol m}^{-2} \text{ s}^{-1}$ ". The Park et al paper shows a Net Flux difference of approximately  $2 \text{ nmol m}^{-2} \text{ s}^{-1}$  between a  $3\sigma$ noise threshold and a  $10\sigma$ noise threshold.

Thus, there seems to be strong agreement between these studies in the quantitative difference of total ecosystem scale BVOC exchange using  $3$  vs  $10\sigma$ noise thresholds.

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The main difference in these studies is in the number of masses for which fluxes were "detected", and the dominance of isoprene emission in the total bVOC exchange of the oak forest versus the orange orchard. These similarities are not obvious from the text of the current manuscript which seems to suggest that Park et al overstates the number of masses for which flux is observable and the amount of total flux that is contributed by masses between the  $3$  vs  $10\sigma$ noise thresholds.

2) It would be good to see more in-depth discussion of the actual results and science. In the current manuscript the focus is mainly on flux calculation and data processing details which are interesting but might be more relevant for the AMT audience.

3) Similarly, the conclusions are very narrow, focused on the methods and not so much on the total ecosystem scale exchange that is expected based on the title.

4) PTR-TOF-MS (without SRI or variable E/N) cannot distinguish between methyl acetate (MA) and hydroxyacetone (HA) each at the same  $m/z$  75.0441 ( $\text{C}_3\text{H}_6\text{O}_2\text{H}^+$ ). It is likely that MA is incorrectly attributed because isoprene-dominated atmospheres should have high concentrations of HA. Therefore deposition of MA is less likely than HA deposition (Nguyen et al. 2015 showed clear deposition of HA).

5) Calculation of concentration of uncalibrated compounds was done using average sensitivities for families of compounds ( $\text{C}_x\text{H}_y$ , etc.) instead of using the transmission approach. This may be inaccurate if the detected families contain fragments (e.g. in  $\text{C}_x\text{H}_y$  propyl/isopropyl, in  $\text{C}_x\text{H}_y\text{O}_1$  dehydrated acid fragments, etc.). Therefore the total budget may be biased. Transmission is very important to consider because the authors used low mass compounds for an average family sensitivity and the transmission greatly increases with the mass scale (which they do not discuss).

6) The authors' double-counting argument does not make sense. If they use calibrated sensitivities for some of the compounds, they should remove the fragments and isotopes related to the parent mass. Alternatively, they should use proton reaction rate constants derived from the calibrations. Their text misleads the reader that the auto-

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mated approach is worse because it might lead to double counting while the selective approach is better because it relies on more accurate sensitivities. The selective approach inhibits scientific progress because it focuses on those compounds which are routinely in the standards while ignoring newly observed and low concentration compounds.

7) Typo on p27637, line 9: Park 2013 not 2014

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.

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