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

Anonymous Referee #4

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Schallhart et al. present interesting measurements of VOC concentrations and fluxes from a mixed forest dominated by oak and hornbeam trees in the Po Valley. The number of direct measurements of VOCs above biogenic sources using PTR-ToF is very small so the results of BVOC emission and in particular less known BVOC/VOC deposition could be extremely valuable. Another interesting aspect of the study is that it is located in a region strongly emitting biogenic VOC close to anthropogenic influences (often high NOx) so should enable investigations of the atmospheric chemical interactions between BVOCs during polluted vs unpolluted/less polluted times. The context of pollution is brought up only to say that the conversion of MVK+MAC is unexpected. It would be very interesting to see also the anthropogenic ions such as aromatics which

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hopefully were not excluded from the analysis.

The paper makes a good impression initially, before it becomes clear that it is overly focused on specific nuances in flux filtering methodology which can be interesting but only for a relatively small subset of ACP readers. Specifically, large part of the paper is spent on arguing about which technicalities of flux quantitation in PTR-ToF systems are better, “objective” or “labour intensive”, yet basic information about flux criteria and quality are missing. I found this very distracting from the otherwise potentially interesting science which unfortunately seems to be only ancillary. The title is so inconsistent with the content. The content is more technical than scientific, thus it would be strongly suggested that the paper is sent for discussion in AMTD or if it is intended for ACP it should be refocused on the science and implications from observed BVOC fluxes, which in the current version seem largely fragmentary and adjunct. Even though the PTR-ToF is used, only a few selected species are reported and even basic details such as mass range, the list of detected ions, etc. are not reported or clear.

I have numerous concerns mostly about the presentation of the flux analysis which is either not explained at all or presented in a particularly confusing way. I have strong reservations about misinterpretation of the published literature and confusing method comparison. Hopefully, the authors can significantly improve the paper in terms of clarity and consistency of the methods and in particular they should focus on a coherent and structured science story to make this manuscript relevant for the majority of the ACP audience.

General

1) After reading Park et al., 2013a whose approaches are used and compared in this paper, I agree more with Park et al. that their comprehensive flux approach makes more sense in that it treats the mass spectra fully with clearly defined criteria. In Schallhart et al. it is completely unclear how fluxes were processed, how quality of the flux was assessed, what corrections were applied and if they were derived for

each ion consistently (e.g. lag time, stationarity, u* criteria). Park et al. approach is a significant advancement for PTR-ToF flux processing because it does not disregard ions other than the internal ions. The selective approach is defended in this manuscript but it seems like a return to the old school of quadrupole systems when one was forced to preselect the ions to keep the flux quality high. Because ToF systems measure the whole mass range instantaneously, selecting the ions no longer makes sense. I think this is clearly a step backward relative to what in principle should be possible from these comprehensive PTR-ToF datastets which allow for non-disjunct flux of the entire mass spectrum, so one would expect to see clear fluxes for many more masses than presented in this paper even at standard sensitivities.

2) The drastic exclusion of ions without any reason is surprising also because one would expect many interesting ions above the standard flux detection limit (e.g. Spirig et al., 2005). It is unclear why 10-sigma threshold is used instead of the 3-sigma threshold. It makes the impression that this was done to justify not reporting the full results. The companion paper (Acton et al.) shows that similar results are possible with just the quadrupole PTR-MS, so why invest in much more expensive PTR-ToF only to ignore its broader capabilities?

3) I fully agree with the clear evaluation by Reviewer 3 who has already explained the issues with misinterpretation of selective vs full approach. While I do not want to repeat the similar comments, I would also like to see more clarification and transparency of the flux methodology presented in such a way that the comparison between the selective and full flux approaches is fully transparent and based on solid criteria, as well as accounting for differences between the studies (ecosystem, season, temperature, climate).

Specific

4) Flux methodology is completely missing which is unacceptable in a flux-reporting paper. What is discussed in Sect. 3.1 is only a rough comparison of procedures

to identify "detectable" fluxes which is confusing. Table 1 showing the differences between the full approach (which is referred to as "automatic") and the selective approach (which is referred to as "manual") lacks the specificity expected in scientific papers. For example, a) first row: standard flux corrections: Classical (yes) Automated (yes). This is surprising. I can see that both approaches are based on classical foundations. It is unclear why suddenly the selective approach is more classical? b) Third row: Manual evaluation of CCFs (several 100s): Classical (yes) Automated (no). This seems incorrect. See Figure 3 in Park et al. (2013b). c) Fourth row: Average absolute CCFs: Classical (no) Automated (yes). This is misleading because as I understand the comprehensive approach uses average CCFs as additional information and not instead of the standard CCF. d) Filter results (fragments, isotopes, clusters): Classical (yes) Automated (no). This is again a major misinterpretation. See Park et al. (2013) SI "Sect. 2 Determination of m/z ratios exchanging with the ecosystem . . ." e) Work intensive: Classical (yes) Automated (no). This is a very subjective comparison. Each method is work intensive, in particular in the comprehensive methods there are more ions to go through the extensive quality control. Analysis of millions(?) of CCFs manually not only does not make sense and is a waste of time but is inappropriate due to potential pseudo peaks which need intelligent lag-time verification approaches, not just an arbitrary visual assessment. f) Maximum of found masses in literature: Classical (10-20) Automated (ca. 500). This is misleading, because there were only few reports of fluxes in the literature and the number might be dependent on other factors such as detection limits, m/z range, and the number of ions passed for the flux evaluation and then the ecosystem type or the amount of air pollution (other VOC sources) in the region.

Overall, Table 1 is extremely confusing and should either be deleted or expanded to contain the full account of like for like comparison.

5) The scientific conclusions can be different depending on which filtering approach is used (i.e. selective vs comprehensive). The reader is lost with the most important take home messages. This kind of debate on which method approach is better should be

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more appropriate for methodological journals (e.g. AMTD). Despite much effort spent on explaining the methods, the essential information related to flux quality criteria and justification of the controversial filtering (10 sigma, 10% cutoff) is missing. This justification is particularly important as the authors speculate on which approach (selective or full) is better or worse, and the reader is confused about what the real picture of the total ecosystem exchange in the Po Valley is. This is unfortunate, because the authors would be in a good position to give a more in-depth insight into the science.

6) Part of the community might have no idea what the automated, classical, manual, comprehensive method is and might be deterred from using novel approaches which seem to be misrepresented here. I think the authors might not realize that the automatic method should be fully consistent with conventional flux methods (all criteria including lag time and covariance assessment+verification should also be thoroughly included) and that it enables comprehensive treatment of entire TOF spectra. There are subtle differences which need to be compared more clearly.

7) The companion paper (Acton et al.) cites Park et al. 2013a approach for their reported PTRTOF fluxes so the recommendation from Schallhart et al paper for automated method with a mass filter is inconsistent and surprising. Table 2 with the flux mass ions looks like a selection of abundant and unabundant ions out of many more expected and misinforms the reader. Automated method with the compound filter is not a new method. Whether you include the fragments or not depends on whether you use transmission method or calibration method. If you use calibration method it would be better to sum up fragments and use the sum of the sensitivities of the fragments and the parent ion. What it seems is that the authors have calibrated a single ion for monoterpenes (m/z 137.123) assuming that the proportion of fragments is constant. This is actually not the case for different monoterpenes as well as in particular when instrumental conditions change. The standard contained a-pinene only, so the sum of fragments must be used in order to prevent an error in case monoterpenes other than a-pinene were present. In the PTR with quadrupole detector not summing up the frag-

ments could be justified by potential interference at m/z 81 from hexenal, but here the authors should be able to include and sum up all the relevant exact-mass ions (at least 81.07, 95.09 and 137.123 for total monoterpenes) and use the sum of their calibrated sensitivities. Using the compound filter does not make sense.

8) 27% of upward flux of MVK and MACR from photo-oxidation seems interesting but it assumes constant yield (which I understand was taken from MCM based on chamber studies). Do authors suggest that NO/HO2 does not vary diurnally at the Po Valley? There is nothing like "high NOx" and "low NOx" environment, and you need to be aware of the pathways changing diurnally. The value of 27% also does not seem reasonable if it was based on the analysis in Figure 7 which suggests that relatively small flux footprints are compared with much larger concentration footprints. Do the authors suggest that majority of MVK+MAC is directly emitted from plants and ignore the long-lived MVK+MAC from aged air mass which would be expected from isoprene oxidation? How did Isoprene/(MVK+MAC) ratio vary at the Po Valley site?

9) Table 2. CT ions are dependent on the optimization of NO+ and O2+, so the authors should report the percentage of NO+ and O2+ relative to H3O+. On what basis is it concluded that 67.05 must be isoprene fragment and not for example cyclopentadiene or other isomer? Did you compare the signals? I suggest to include the full mass list (concentrations and fluxes) of identified ions. How many ions did the ToF-Analyzer software detect? How many ions were selected for concentrations (manual selection)? How many ions were included in the flux evaluations? And finally how many ions passed any given filtering criteria or in other words which ions were filtered by which criteria?

10) Section 2.3.2 shows average sensitivities for the entire compound families. This seems inappropriate as has been pointed out in other reviews. It would make more sense to use compound-specific sensitivities or to convert sensitivities to proton transfer reaction rate coefficients for compound families and use the transmission equation which accounts for mass discrimination of each ion mass within the compound family.

11) Table 3. Deposition for m/z 61.028 (attributed to acetic acid) is shown. Was acetic acid calibrated on a standard or did you use the sensitivity for CxHxOz family (19.1 ncps/ppb, P.27635, L10)? Most acids including acetic acid dehydrate in PTR, so the sensitivity on the parent mass can be relatively small and is humidity dependent (e.g. Baasandorj et al., 2015). The sensitivity of 19.1 ncps/ppb seems by a factor of ∼2 higher than previously reported in the literature (Table 1 in Baasandorj et al., 2015). Nowhere in the text it is shown whether the fragment on m/z 43.018 was accounted for.

12) Figure 1. Can you show overlaid flux footprint on the map?

13) Figure 2. Could be moved to SI. Would it be possible to show the flow rates, temperatures of the lines if they were heated, and internal diameters of the lines.

14) Figure 3. Why are the response times different for the first and second water cluster? 26% of high frequency correction (P.27640 L5) seems like there were substantial losses in the system. It would be interesting to see how these losses vary with the flow rates, heating, dimensions of the tubing, data acquisition rate, and other factors.

15) Figure 6. It is unclear what this figure is supposed to teach the reader or at least it is not discussed sufficiently. The wind roses look quite random in pattern. It is unclear where the pollution sources are. It would be interesting to add an aromatics tracer such as benzene and/or C8, C9 aromatics, as well as NO.

16) Figure 7. Why to show isoprene concentration vs MVK+MACR flux, instead of flux vs flux and concentration vs concentraiton? The MVK+MACox.isop figure assumes constant yields from isoprene but the yields change during the day as the ratio of HO2/NO changes. The authors seem to treat the chemistry as black or white without the shades of grey. It would be more instructive to show the diurnal trends of isoprene/(MVK+MAC) concentration (and/or flux) ratio vs concentration (and/or flux).

17) Figure 8. Was isoprene filtered out from the 10 most abundant compounds? I do not see the C5H8+ ion in the figure.

18) Figure 9. The interruptions are not described in the figure. Was the night turbulence well developed to observe the night time fluxes (mostly deposition). Again, what were the filtering criteria (u*, stationarity performed for each ion?)?

19) P27644 L17-24 “Compared to the classical method, the automated method gives a fast and objective result, but the σnoise threshold can vary, as the standard deviation of the noise can be reduced by taking its absolute value. The reduction of the standard deviation takes place if the signal, which is used for the error calculation, is around zero and, therefore, varies between negative and positive values. If there is some offset, so that the signal is just positive or just negative inside the error areas, using absolute values does not influence the value of σnoise.” I do not understand this paragraph. Is it correct? Do you suggest that the standard deviation will be affected by where the mean value is? The standard deviation will depend on the CCF averaging (e.g. Taipale et al., 2010) if this has been done.

Technical: 20) P27633 L23 needs to provide SI units here and later in the text. Also provide inner diameters of the tubing not just ODs. 21) P27634 L1 PDFE acronym is undefined. 22) P27634 L6 what valve was used? Needs to provide material and brand. 23) P27634 L8 30 mL/min is taken by the drift-tube in most PTR instruments. What was the flow in the subsampling inlet line and what was the temperature?

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