Comment on amt-2021-117

Anonymous Referee #1

Referee comment on "First eddy covariance flux measurements of semi-volatile organic compounds with the PTR3-TOF-MS" by Lukas Fischer et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2021-117-RC1, 2021

General comments

"First Eddy Covariance Flux Measurements of Semi Volatile Organic Compounds with the PTR3-TOF-MS" highlights the utility of the PTR3-TOF-MS in eddy covariance studies to observe the forest-atmosphere exchange of terpenes and sesquiterpene oxidation products with the implication of extending this application to other molecules. It adds many useful contributions to the current state of BVOC flux literature including an inlet design for limiting attenuation of low volatility compounds, direct flux measurements of compounds in low abundance like sesquiterpenes and diterpenes, the first eddy covariance measurements of diterpenes, and a novel analysis using direct measurements of oxidized products and precursors to obtain speciated flux. This paper should be accepted after mostly minor revisions listed below. These revisions primarily concern clarifications in experimental setup and in flux quality control and assessment that will ultimately aid someone new to eddy covariance that wants to do a flux measurement with their PTR3. I have a less minor set of comments on the authors' treatment in calculating the B-caryophyllene oxidation product (BCYO3) and want to know why they only consider reactions from the canopy top to the sensor rather than through the whole canopy.

Specific comments

Line 70: Please list the reference for this 8% value.

Line 100-101: How far away was the IRGA from the PTRMS? It is not mentioned how long the instrument bypass is where both the PTRMS and IRGA are sampling. Further, it is not specifically mentioned if the IRGA is in the same trailer as the PTRMS. These points should be clarified.

Line 103: What drift tube pressure was used in this study? This would be a helpful value.

Line 107: Please state the recent you use m/z 100.

Line 117-118: what were the other masses used in the mass calibration? Mentioning this would help show the points of calibration for your mass range and provide a starting point for others.

Lines 119-121: You should add a line about what the gap is. Is it that nitrate and iodide can detect OVOC at have high sensitivities that PTR previously could not, but those methods can't detect hydrocarbons?

Line 200: How often were field calibrations using the cylinders performed? I understand that the humidity correction is at 10 Hz but it's not mentioned how often calibration curves are ran. It's helpful for other readers to get an idea for what frequency of calibration works well for a PTR3 eddy covariance study.

Further, is there a notable difference at this height in calculated flux if you apply a 1 Hz humidity correction as compared to the 10 Hz one? It would be helpful to show the difference and the utility in this N2H+ method.

Line 208: is this correlation made by averaging the N2H+ data down to 1 Hz? Can you present the correlation coefficient for N2H+ against humidity compared to that of H3O+(H2O)? Since the latter is more frequently used, showing the better correlation can help strengthen your finding.

Line 221-222: Does "treated similar to acetonitrile" mean you used the same calibration factor as acetonitrile for the remaining compounds? If so, you should just say that.

Line 224: Since you are mentioning the effects of water you should include what the effect of fluctuations in air density from water vapor fluctuations air as in the WPL correction from Webb, et al. 1980. I assume it would have a small effect since your measured mixing ratios are small, but it would be helpful to just mention this as requiring consideration for flux measurements and the net effect:

Webb, E. K., Pearman, G. I., & Leuning, R. (1980). Correction of flux measurements for density effects due to heat and water vapour transfer. Quarterly Journal of the Royal Meteorological Society, 106, 85–100. https://doi.org/10.1002/qj.49710644707

Line 274: This site is not composed of broadleaf trees so this sentence does not read as relevant to the study as written. I understand this is meant to generally say that this instrument is useful in measuring an abundant NMHC but it might be more helpful for the point of this study to just merge the first few sentences of this paragraph and remove the broadleaf statement. If you do want to keep it then you should mention if you expect high isoprene emissions from the scots pine at your site or know where the isoprene comes from.

Line 281-282: Was this determined using measured fluxes and a calculation of a dilution rate and reaction rate from estimated OH? Or is this just a suggestion as to why this is happening? Would the authors be able to show that at relevant OH and dilution the source and sink are close? Or perhaps this has been shown in previous studies at this site?

Line 292-293: I am a little confused about the importance of the start of the growing season on isoprene emissions and it should be clarified. Is this sentence implying that there is extra leaf mass from new needles during the growing season that contributes to isoprene emissions or is there an initiated biochemical pathway that solely happens during the growing season that is not temperature dependent? Are you saying that deciduous leaf area increases from the generation of new springtime leaves? Is there enough deciduous leaf area in this site? Or is it just mentioning it got warmer earlier?

Line 331-332: Is the "known temperature dependence" taken from the fit of the data in Rinne et al. (2007)? Or do you normalize using a Beta factor of 0.09 /K and then assume a same basal emission rate across studies and seasons? It should be mentioned where this is taken.

Line 318-320: Is the aforementioned monoterpene source the sawmill that is a source for a lot of signal enhancement? The strong downward flux on 05/08 is very interesting. Do you have any ideas on what would be causing a monoterpene deposition? There probably are not any soil processes strong enough to drive this, right? Horizontal inhomogeneities would not contribute to an error in turbulent vertical flux since your vertical flux would then just be from the average of whatever monoterpene is sampled. Could you have outsourced, very reactive monoterpenes that are horizontally transported then are chemically lost below the sensor when vertically processed within your footprint? Or is it just that canopy MT is much lower below the sensor than the outsourced MT plume at the sensor and you are just seeing eddy diffusivity? There should be a some hypothesis as to why this is happening since this is an anomaly.

Figure 4: What is the frequency of data used in these histograms? 10 Hz data from a 30-minute period?

Also are you able to report concentrations of monoterpenes and isoprene in humidty-

corrected pptv and does the figure look any different when you do that? Monoterpene concentrations in pptv are not presented anywhere in this manuscript. Does the time series look odd because of the horizontal imhomogeneities discussed? It should be mentioned why a time series of monoterpene concentrations is not presented since it would have been helpful to get an idea of the impact of these downward fluxes as well as to infer relative chemical and dilution lifetimes as you do for isoprene. It would also have been helpful to show the relative concentrations of isoprene and monoterpene just from a terpene abundance and sourcing point of view. I understand the purpose of this paper is not to provide a full characterization of the site but to show the utility of the method for eddy covariance. However, a more direct statement of why a monoterpene concentration time series or even listed averaged monoterpene concentrations in the text are not reported should be made.

Line 365: One of the highest sesquiterpene rates at this site? From Scots Pine? In general? Please specify.

Line 376: Is $F_{BCYO3,tower}$ a calculated or directly measured value at the tower? If it is calculated then this is not clear.

Line 381-382: Is this yield from the lab study dependent on reaction time? Would there be a further correction of yield applied in the Line 375 equation based on residence time?

Line 383: Should remind that $H = 15$ m. You should also present your ranges in u_* since they are applied in the residence time calculation in Figure 5.

Further, why are you only considering the reaction time from the canopy top to the sensor and not from within the canopy to the sensor (as in Fulgham, et al. 2019 and Vermeuel et al. 2021)? It is likely that a sizeable fraction of your BCARYO3 was made within the canopy. I believe in the cited text (Karl, et al. 2018) the authors use the distance traveled from the injection site which is where the compound emanates from (in their case a point source). Daytime parcel residence times can be in the range of minutes (Fuentes, et al. 2015) under high turbulence conditions (above canopy $u_* = 0.65$ m/s) when emanating from the understory which is commonly where sesquiterpenes originate from. Zhou, et al. (2013) showed through a 1D vertical model at the SMEAR II site a that 70% of SQT reacts within the canopy and only ~29% escapes from the canopy. Are you only considering the reaction of that 29%?

Fulgham, S. R., Brophy, P., Link, M., Ortega, J., Pollack, I., & Farmer, D. K. (2019). Seasonal Flux Measurements over a Colorado Pine Forest Demonstrate a Persistent Source of Organic Acids. ACS Earth and Space Chemistry, 3(9), 2017–2032. research-article. https://doi.org/10.1021/acsearthspacechem.9b00182

Vermeuel, M. P., Cleary, P. A., Desai, A. R., & Bertram, T. H. (2021). Simultaneous Measurements of O3 and HCOOH vertical fluxes indicate rapid in-canopy terpene chemistry enhances O3 removal over mixed temperate forests. Geophys. Res. Lett. https://doi.org/10.1029/2020GL090996

Fuentes, J. D., Wang, D., Bowling, D. R., Potosnak, M., Monson, R. K., Goliff, W. S., & Stockwell, W. R. (2007). Biogenic hydrocarbon chemistry within and above a mixed deciduous forest. Journal of Atmospheric Chemistry, 56(2), 165–185. https://doi.org/10.1007/s10874-006-9048-4

Zhou, P., Ganzeveld, L., Taipale, D., Rannik, Ü., Rantala, P., Petteri Rissanen, M., et al. (2017). Boreal forest BVOC exchange: Emissions versus in-canopy sinks. Atmospheric Chemistry and Physics, 17(23), 14309–14332. https://doi.org/10.5194/acp-17-14309-2017

Line 383-384: It should be at least mentioned that surface layer scaling theory or any type of scaling is not always applicable, especially as you get nearer to the canopy surface and are within the roughness sublayer that is associated with multiple length scales. It is likely that non-local mixing frequently occurs, and the canopy undergoes sweeps and ejections of air parcels where the reaction time is harder to assume. This concept is explained further in Cilfton et al. (2020), Section 4.4. There the authors consider O_3 but the idea is the same:

Clifton, O. E., Fiore, A. M., Massman, W. J., Baublitz, C. B., Coyle, M., Emberson, L., et al. (2020). Dry Deposition of Ozone Over Land: Processes, Measurement, and Modeling. Reviews of Geophysics, 58(1). https://doi.org/10.1029/2019RG000670

Line 388-389: How were these percentages chosen for the upper and lower limits?

Further, if you were to pick another common sesquiterpene that you expect to see and factor that error into your k value in the equation on line 375, would it be beyond your listed range in error? Are there any other sesquiterpenes at all from Scots Pines you would expect to emit? You have the reference for speciated SQT dominated by beta-caryophyllene from a July study, but do you expect there may be a seasonal dependence in speciation since you measure in spring? You should mention that there should be no seasonal dependence, if so.

Is your $C_{15}H_{24}O_3$ in lab only detected from ozonolysis of beta caryophyllene and no other likely sesquiterpenes? Stating that would be further evidence that the dominant SQT is only B-caryophyllene.

Figure 5: Showing your SQT and SQT oxide flux at night seems misleading since you likely don't pass your flux filters at night and it is hard to generate turbulence. Further, it looks like all data is included for the bottom panel since you get reaction times greater than 50 s which would be the longest reaction time with your u_* of 0.3 m/s filter. It should be specified that you do not filter data in this figure, and you should present what the average and range in daytime reaction times are in the text as well as the average and range in daytime reacted BCARY. I believe panel B would be more helpful if it presented the daytime (~10-18 local time) averages rather than the whole day which includes nights of 100% of a small, more uncertain BCARY source reacting away. If you already do only include daytime averages then this should be specified.

Lines 410-412: If providing a survey of CIMS methods that can detect pure hydrocarbons at high sensitivity then you should mention benzene CIMS from Lavi, et al. 2018. They report very high sensitivities for terpenes although they might not be able to get down to the LoD of your PTR3.

Lavi, A., Vermeuel, M. P., Novak, G. A., & Bertram, T. H. (2018). The sensitivity of benzene cluster cation chemical ionization mass spectrometry to select biogenic terpenes. Atmospheric Measurement Techniques, 11(6), 3251–3262. https://doi.org/10.5194/amt-11-3251-2018

Lines 413-414: Are the two weeks of flux measurements just the length of the full study or was a portion chosen? Can you mention that this is just the whole study if the former?

Line 435-441: While these ogives do look nice, a visual assessment of a semilog plot is a little misleading for readers. The area you are highlighting and comparing to is halfway through your total area. The authors should calculate what they expect the error attributed from inlet dampening and sensor separation should be by calculating a transfer function using Massman et al. 1991 and Moore 1986. If it does not look too messy on the plot it would also be helpful to include the calculated transfer function. Based on your flow rate and wall length it should only help support your claim of no visible dampening. You could also show what the resulting transfer function is when comparing to wT. There should be a more quantitative description to support your statement of little to no attenuation.

Massman, W. J. (1991). The attenuation of concentration fluctuations in turbulent flow through a tube. Journal of Geophysical Research, 96(D8), 15269. https://doi.org/10.1029/91jd01514

Moore, C. J. (1986). Frequency Response Corrections for Eddy Correlation Systems. Boundary-Layer Meteorology, 37, 17–35.

Line 441-443: Were the present cospectra also made in the same way the presented ogives were determined? By taking an average of fluxes that passed quality control tests? Or is this a collection of a single, representative averaging period? If the latter, then you should show an average of more than one to be more representative of the study.

Figure 7: The purpose of the grey bar should be indicated in the caption well.

Section 4.6: Uncertainties are presented throughout the text in the respective sections of detected analytes so this section written as is may be repetitive and unnecessary unless the authors provide a quantitative summary of uncertainties for all presented compounds and/or want to explain in more detail their uncertainty method. Either way, the uncertainty method should be explained more at some point in the text (either when it is first introduced or in this uncertainty section) in the case that the reader does not want to go back and read all of Finkelstein and Simms (2001). This could be a few sentences and does not need to be a rewrite of the cited paper. Also, there are some compounds (monoterpenes, diterpenes) where the study uncertainty is not mentioned so they need to be mentioned at some point in the manuscript.

In addition, unless the uncertainties are calculated by using only the cross-covariance as in some of the methods of Langford et al. (2015), then Figure 8 does not seem to fit or at least there is no connection between cross-covariance and uncertainty as presented. It is an excellent figure that highlights the utility of the inlet but adds more to the previous section and should be included there instead and that whole section could become a "spectral analysis" section. The connection should be further explained if it is related to uncertainty.

Langford, B., Acton, W., Ammann, C., Valach, A., & Nemitz, E. (2015). Eddy-covariance data with low signal-to-noise ratio: Time-lag determination, uncertainties and limit of detection. Atmospheric Measurement Techniques, 8(10), 4197–4213. https://doi.org/10.5194/amt-8-4197-2015

Figure A2: Is the humidity data used on the y axis from the IRGA or the met station? Is the trace from the IRGA on the right time-corrected to match the N_2H^+ signal or are those just both raw data traces? These should both be acknowledged. This also brings me back to my earlier comment of what is the time delay between the air sampled reaching the PTR3 and the IRGA. You mention potential dampening and time delay, so I am assuming they are far from each other?

Further, is the N_2H^+ data on the right noisier solely due to a higher collection rate and averaging both down to 1 Hz makes them match better? Including the correlation coefficient of N_2H^+ and time-corrected water as I mentioned earlier will help show the utility of N_2H^+ as a water tracer.

Line 509: B-caryophyllene is consumed as in completely gone? Or is that the e-folding lifetime? Under how much ozone? This should be clarified. I mention this because it is a little misleading looking at Figure B1 and its caption would make you think that a function of time meant a function of reaction time. Also, the sesquiterpene is not completely consumed in the figure.

Figure 1B: There needs to be a little more clarification on what this figure is showing. You are sending a known amount of B-caryophyllene through an ozone-containing reactor at different reaction times which makes the step pattern? Or is the reaction time in the flow tube fixed and you are changing the ozone amount. If the latter, can you show the ozone on the right y axis of this figure?

Technical corrections

Line 33: "..growth is critical.."

Line 43: need to cite Millet et al., 2018 correctly here and for subsequent citations to this article

Figure 2: indicate the blue part is the blower

Line 168: I think the use of "cross-talk" is a little misleading since you're referring to the interference of adjacent peaks. I suggest replacing "cross-talk" with "interference".

Line 269-270: This sentence should be rewritten. One suggestion for how it could start: "A study that may serve as a better comparison was performed in…"

Line 278: suggestion: "…frequent calibrations across multiple studies"

Line 343: remove "were"

Line 404: "leaf level"

Figure 5: Bottom panel should have y axes and the y axis scale needs to include the whole

graph. Middle panel should be described in caption.

Line 483: I do not think you need the phrase "reserves in" in the section "…with the large reserves in flux signal to noise ratio…" or I do not understand what it means.

Figure A1: need to reformat the legend to be a more legible time and include what the lines mean. The fitted curve equations also should be presented more neatly as well as designate which curve they are the equation of.

Line 515: "losing" instead of "loosing"