EGUsphere, referee comment RC2
https://doi.org/10.5194/egusphere-2022-1015-RC2, 2022

Comment on egusphere-2022-1015

Anonymous Referee #2

Referee comment on "Observations of biogenic volatile organic compounds over a mixed temperate forest during the summer to autumn transition" by Michael P. Vermeuel et al., EGUsphere, https://doi.org/10.5194/egusphere-2022-1015-RC2, 2022

The manuscript describes an interesting study that measured BVOC concentrations and fluxes above a mixed coniferous/deciduous forest. One unique aspect was using a GC system to speciate monoterpenes and other BVOCs with the PT-TOF-MS. Another interesting point was considering BVOC emission during leaf senescence. The methodology is sound and well described in the manuscript.

I have a number of specific comments that need to be addressed. Most are minor, but there are several major items that need to be addressed. First, the measurements show an interesting enhancement of ecosystem-level emissions of monoterpenes after leaf senescence. But the authors go too far with the data they have collected and present too much speculation as results. I provide a number of detailed comments on this concern below. Next, the inclusion of the DMS data, while again interesting, makes the paper too long and does not have a strong enough scientific connection to the rest of the material. The paper will be improved by removing this information and perhaps it can be included in another publication.

Lines 138-139: give the inner diameter of the tubing.
Line 159: “these values” is a bit confusing. Instead, state explicitly “the calibration factors”.
Lines 175-176: there is no trouble with water vapor at this temperature?
Lines 181-182: was there a backflush to remove heavier HCs from the column during the 10-min runs?
Line 235 & SI lines 44-54: when computing the lag time for each 30-min period, was there still a clear max at night?
Line 248/Eq 3a: Shouldn’t gamma sub P only be applied to the LDF term? Also, give a bit more detail. This equation seems to be the leaf-level Guenther 1995, not the canopy emission model MEGAN, Guenther 2012. Are you accounting for leaf area, etc?
Lines 318-320: Also, could be changes in the intensity of vertical mixing, which in turn could be influenced by changes in the structure of the canopy due to leaf loss. Should add this and discuss.
Lines 352-353: This is a really big correction. You need to do an assessment of the error it

introduces into your isoprene measurements. I haven't seen this correction in other PTM-MS papers. Do you have any references? Can you quantify how much was from the Na2SO3 trap?
Line 420: remove "physical." These also could be biological and/or chemical factors. Also, switch all units, especially for Fig. 4, to the mass-based flux units which are the convention in the field. All the literature you site is in mass/(area x time) units: be consistent with the existing literature.
Lines 423-425: you haven't discussed any footprint analysis. Since this statement is inconclusive, simply remove it.
Line 441: insert "presumed" before cessation, since you did not actually measure this, but are inferring it from leaf senescence.
Line 443-446: Note that having a flux observed at mass 69 that behaves like isoprene does not mean you have successfully corrected the concentration at mass 69 with your correction. Even if there is still a significant offset in 69 due to another interference, if that offset is not correlated with the vertical wind speed, it will not contributed to the flux. Look back at your original Eq. 1. In theory, you could not apply the correction, and you would get the same flux, again as long as the interference is not correlated with w. Note this isn't exactly true, since some of the corrections you apply might be influenced by the absolute concentration of mass 69.
Line 449: "an" not "and".
Line 491: This is panel 6b, not 6c, which is isoprene.
Lines 490-492: while I agree this is good agreement between the two methods, why is the real-time data lower? Since the GC method only considers three compounds, shouldn't it be the lower value? Also, an inefficiencies with the trap would lead to the GC data being lower.
Line 494-524: I understand that many issues arise in field work, and often it is necessary to perform post-field experiment corrections and laboratory tests to recover data that was compromised by unexpected processes. But given the magnitude of the correction (1/3 during the day) for isoprene and the large variation in Figure 6d, the error bars on the isoprene concentration should be over 50%. (Note that you refer to 6b on line 521, but like above on line 491, that appears to be swapped and should be 6c.) While r2 is over 0.7, I don't consider that very good to start with and also much of that fit is driven by one high point. At lower isoprene concentrations (< 0.4 ppbv), there is only a poor correlation, visually. Fortunately, as discussed above, you can have isoprene concentration errors that do not influence your flux calculation. But, you need to conduct a more rigorous error analysis for the isoprene concentrations, and give error ranges whenever the concentrations are presented. This includes visually in graphs.
Lines 528-532: I'd put my $ on factor #4. No need to respond to this comment.
Lines 617-620: need more detail about the regression. You refer to Equation 3, but you have equations 3a and 3b in the text. Maybe your regression is only for temperature, while Equation 3a has light? I think maybe that's the case, but you need to be more explicit here. It's also confusing, since you have an exponential fit in Fig. 8a but also mention the loss factor rho. But note that the loss factor, if it's a simple exponential fit, won't affect the beta term.
Line 622: assuming air temperature is necessary but problematic. The reference Still et al 2022 is very good, but in parenthesis include "deg C" [using actual degree sign!] since the units matter with this ratio.
Lines 638-655: there is a _lot_ of existing literature about in-canopy oxidation which you are ignoring. Here is one citation: https://acp.copernicus.org/articles/12/8829/2012/. But you need to incorporate a state-of-the-art understanding into your discussion.
Lines 663-669: you need more detail on how this was accomplished. See comments above where I have experienced confusion about references to Eq. 3.
Table 2: why have both the slope and the ratio of the fluxes? This information is largely redundant, unless you have a specific reason to explore it.
Lines 701-702: while this might be true and is interesting, it is out of the scope of the current paper and the statement should be removed.

Lines 716-802: This section is very speculative and is stretching the data you collected too far. You are making too many qualitative assumptions and pronouncements. This section is also very long and needs to be more focused on the data you have and the conclusions you can draw from it directly. You can speculate about one or two hypotheses in your discussion, but this section ranges too far from the data you have collected.
Section 4.2.1: First, see my comment about the in-canopy oxidation literature. Second, you would need an error analysis to give ranges on your estimates.
Section 4.2.2: You don't have enough data to rule this out. Specifically:
Lines 752-753: I don't think canopy scale SQT measurements are of high enough quality to support this contention.
Lines 753-755: you don't present any measurement data about the state of the soils. You are introducing qualitative, and perhaps observational, data into your discussion.
Lines 756-760: you need to be much more cautious in your conclusions.
Lines 764-766: From what I see, the Mozaffar reference discusses hydrophilic compounds. Please clarify.
Lines 788-790: again, very speculative. I would be very, very surprised if there was a genotypic variation. The emissions of methanol in particular are fundamental to plant biochemistry.
Lines 791-802: and again, very speculative. It is very difficult to understand leaf biochemical processes from whole-stand flux measurements.
Lines 823-850: see my summative comments, but while this is very interesting, it feels jammed into the current manuscript.
Lines 861-866: your study did not demonstrate any of these mechanisms. Your study _did_ demonstrate that MT emissions were enhanced during senescence. You then speculate about mechanisms to explain this enhancement, but you cannot say your study demonstrated anything about these mechanisms.