

Atmos. Chem. Phys. Discuss., referee comment RC2
<https://doi.org/10.5194/acp-2020-1328-RC2>, 2021
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Comment on acp-2020-1328

Anonymous Referee #2

Referee comment on "Volatile organic compound fluxes over a winter wheat field by PTR-Qi-TOF-MS and eddy covariance" by Benjamin Loubet et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2020-1328-RC2>, 2021

The authors present multi-week measurements of hundreds of VOC fluxes over a wheat field. They discuss the technical aspects of their measurement well, making this work quite useful for further investigations. They highlight the highest positive and negative flux compounds, and do a good job expounding upon their significance. Overall, I consider this paper valuable to the community. I have some concerns, listed below. Most importantly, please ensure that the compound assignments are correct and match the very impressive SI. Secondly, while the authors go into significant technical detail, there are still areas to improve clarity, and ensure future studies can benefit from the techniques used in this work.

Abstract: please state the start date and duration of the study in the abstract.

Mass 93.037 or 93.033? In the abstract and at line 802 this mass is referred to as mass 93.037, not 93.033. This is quite important: if the measured mass was 93.037, it may be more appropriately identified as C₃H₉OS⁺, or 2-Methylmercaptoethanol as identified in the GLOVOCS database. Additionally, this would put the assigned formula of C₆H₅O⁺ some 38 ppm from the measured mass, an error much larger than one expects from the authors' instrument.

Methods: Please explicitly state the number of days the experiment lasted.

Also, for the sake of our backwards American counterparts, please consider using an unambiguous date format in the text, such as June 3rd 2016 rather than 03/06/2016 (although the latter is perfectly fine in figures and tables).

Would it be possible to add the events discussed in lines 101-111 to Figure 3?

Section 2.2.1: Can you provide the Reynolds number for the sampling line? Can you comment on the height of the tower, as it seems short relative to the height of the wheat. Does this make calculating a footprint difficult? Also please report the size of the footprint in this section.

Section 2.2.4: This section feels a bit rushed, and as this is an AMT paper it would be appropriate to walk the reader through these steps. Additionally, along with section 2.2.5 this would be a good place to discuss uncertainty in both mixing ratio and flux measurements. While many have used the default reaction rate constant to calculate transmission based mixing ratios, the method does have a substantial error stemming from the variability in rate constants. Regarding section 2.2.5, it seems the authors take the mixing ratio calculated in equation 1 and then correct it with a calibration factor derived from the instrument response to toluene. What exactly does this calibration correct for, and why are the mixing ratios calculated using the default reaction rate constant of 2.5×10^{-9} in need of correction, as they are already normalized to the primary ion signal, accounting for MCP and other changes?

In the methods section, please report the amount of time for which you were able to calculate fluxes. For times when you could not, did you do any gap-filling, and if so what was your method.

Results:

For figures 4, 5, 6, 7, 8, the standard deviation ribbons disappear in the final weeks of the plots. Why is this? Also, please add the assigned formula or compounds to the plots, not all of us know that m59.049 is acetone.

Line 366: "The most concentrated VOC at the site were methanol, acetone, C₆H₄O, propanoic acid, ketene, propyne, acetaldehyde, formaldehyde, and hydrazine acetate (Table S2)" This does not align with the data in table S2. For instance, hydrazine acetate is not listed. Please correct.

In line 485, the authors mention butene (m/z 57.070), but it does not appear in table S2. Please ensure that Table S2 and the main text are in agreement on both names, formulas, and masses. If a compound is discussed in the main text, I would like to see it included in S2. Additionally, have the authors considered that butanol will likely fragment onto the butene assigned ion?

The authors present a measurement of formaldehyde, which shows a high humidity dependence in PTR due to its having a similar proton affinity as water. Can the authors show some figures in the SI that show their formaldehyde measurement is not too influenced by water vapor concentration? Otherwise I would not report the value, as it is not too discussed and there are many other interesting findings.

Section 3.5: Very interesting!

Discussion:

Large emissions of MeOH have been seen from dairy operations. Could methanol be coming from runoff from the nearby animals?

Table 1: please explain the format of the flux better. I am a bit confused by the table note "Mean \pm se [5 – 95 percentiles] and max – min" and how it relates to the fluxes. Also, when using the tilde, "~", you seem to omit the negative sign, which could lead to confusion. For instance, the first flux column for monoterpenes is negative, but the second reads positive.

Is it possible that the signal at 68.06 is from O₂⁺ ionization of isoprene? If so were O₂⁺ levels stable?

Lines 621-637: This is very good analysis.

4-OPA is missing from Figure 10, please include it. 4-OPA is a known ozonolysis product of squalene a component of human skin oil, and sometimes cited as a tracer for skin oil ozonolysis. It is very interesting to see it emitted/deposited in a wheat field. Is it known if wheat produces squalene as well? Did the authors see a pattern with 4-OPA and ozone?

Figure 11: consider adding the direction of the farm to these plots.

Minor issues:

Line 29: "outmost"?

Line 95: "the field is at around..." remove "at"

Line 93: "The site that is part of a dairy farm receives a lot of nitrogen as mineral or organic matter, which leads to large ammonia emissions" Are you referring to manure and runoff?

Equation 1: are there units for this constant?

Line 223: While I like the idea of a perfect gas constant, I believe you mean "ideal"

Line 288: "7 NL per min" I'm unfamiliar with "NL"

Line 387: "Region" to "region"

Line 467-68: please rephrase

Line 564: extra "."

Line 673: "leaves" to "leaf"6

Line 682: "under brackets" to "in brackets"

Line 792: "less" to "fewer"