Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC1
https://doi.org/10.5194/acp-2020-1328-RC1, 2021
© Author(s) 2021. This work is distributed under
the Creative Commons Attribution 4.0 License.

Comment on acp-2020-1328

Anonymous Referee #1

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-RC1, 2021

This manuscript presents eddy covariance flux measurements of VOCs over a wheat field in Europe with a PTR-Qi-TOF-MS. It identified several most emitted and deposited VOCs for a crop field, and presented their fluxes. The paper is a bit hard to follow. But studies for reactive species over croplands are rare. I still consider the paper provides valuable data to the community. The error characterization of eddy-covariance flux calculation is potentially helpful though they are mostly presented in the supplement. I have the following concerns and suggestions:

Main concerns:

- Abstract: consider shortening it by cutting those introductions (1/3 of the current abstract) and highlight results.

- Sections 2.2.4 and 2.2.5 for Kinetic concentration and calibration: If I understand correctly, this study calibrated 5 VOCs, and the rest VOCs were estimated using the kinetic approach (Eqn. 1). This is a critical component of the paper, but unfortunately, it is confusing and lacks key details and discussions on measurement uncertainty. The kinetic approach using the same rate constant for all VOCs is subject to large uncertainties (maybe as high as +/-200% or more). Uncertainty and how that affects conclusions of the work should be discussed. What is the uncertainty for calibrated VOCs? How frequent was the calibration (what is 'several time' as mentioned)? How do these calibrations compare to each other? How do their calibration factors compare to if using the kinetic approach? This should give some range of error estimates, at least for these selected VOCs.

- Many figures in the texts are either not discussed or only very briefly discussed. Consider removing some of them as the manuscript is very long, and key messages would get lost with so much information blended in without actual contribution to the discussion.

- The figures and texts keep changing between using exact mass and species names. It needs to be consistent to improve the readability of the paper. I suggest using species names with exact masses in brackets if the mass is considered important.

- Time series figures are interesting, but it took a while to figure out what they are and how to interpret them. I'd suggest either improving the presentation or captions to explain them.

- Section 3.2 VOC mixing ratio: it doesn't add much value, and the time series figure 6 is misleading to some extent (see above).

- Figure 9: the deposition fluxes peaked around 5pm local time, which was explained as corresponding to afternoon rush hour. How is that possible since these are flux measurements which reflect a very small footprint given the height of the tower. Are there any traffics within the footprint? Further discussion on the footprint is needed. Later it presents the influence of the farm, and that should also be tied to the footprint discussion.

- Table S2: I cannot find this table in the supplement. It states, 'See file Loubet-COV3ER-wheat-2016-EC-Supp.Mat-VF.', but this table of VOC tentative identification is not available. Is the 'Loubet-COV3ER-wheat-2016-EC-synthesis-fluxes-VF' what you referred to?

- Section 4.2: Methanol. It is interesting that the study found that its emission increases towards senescence. Several studies have reported that methanol emission peaks when leaves are young during the early growing season, i.e., in the US (Karl et al., 2003; Hu et al., 2011), northern mid-latitude ecosystems (Wells et al., 2012), in MEGAN emission model (Guenther et al., 2012). Does this study suggest different mechanisms for crops/wheat to emit methanol compared to other ecosystems?

- Sections 4.2 and 4.3. Most of this section read like a literature review, and there is not much new knowledge added from what we already know about biogenic VOC emissions. I'd consider shortening them or likely merging with the previous sections when discussing their mixing ratio/flux results (Sections 3.3, 3.4, and 3.5.)

- Species 'tentatively attributed to': This term is overused in the paper. Sure, some compound identifications are tentative, but many others are certainly based on literature and the correlation analysis. A thorough and careful assessment of species identification is needed to address what is tentatively attributed.

- Section 4.4: influence by the farm. Would the farm affect the flux measurements? Does the flux footprint cover the farm? It should be easy to quantify that influence since footprint analysis is already done.

- Correlation analysis is helpful to identify possible fragmentation. The paper provides the results for two electric fields E/N 130 and 150. Do those excluded species show similar patterns under different E/N fields? Or do they fragmentation patterns change, at least for some masses?

- There are many typos, minor grammatical errors, citation errors. Thorough proofreading could help.

Specific comments:

- Line 125: What is the purpose of the 16-way sulfinert coated valve?

- Line 144: What is teflonised pump? Explain it?

- Section 2.2.1: what is the mass resolving power of this instrument? It'd be important for species identification.

- Line 158: Lower the electric field to diminish cluster formation and fragmentation. Even 129 Td, there'd be lots of fragmentation. I'd reword it.

- Line 206: Why 'a single calibration factor for all VOC using toluene'? I thought you performed calibrations for 5 VOCs, no?

- Line 354 and Figure 5: the flux footprint is presented as unitless. It needs to define what the footprint is and how to interpret it.

- Line 798: The sentence does not seem to be complete after 'New developments in this field would be helpful'?

Reference:

Karl, T., Guenther, A., Spirig, C., Hansel, A., and Fall, R. (2003), Seasonal variation of biogenic VOC emissions above a mixed hardwood forest in northern Michigan, Geophys. Res. Lett., 30, 2186, doi:10.1029/2003GL018432, 23.

Hu, L., Millet, D. B., Mohr, M. J., Wells, K. C., Griffis, T. J., and Helmig, D.: Sources and seasonality of atmospheric methanol based on tall tower measurements in the US Upper Midwest, Atmos. Chem. Phys., 11, 11145–11156, https://doi.org/10.5194/acp-11-11145-2011, 2011.

Wells, K. C., Millet, D. B., Hu, L., Cady-Pereira, K. E., Xiao, Y., Shephard, M. W., Clerbaux, C. L., Clarisse, L., Coheur, P.-F., Apel, E. C., de Gouw, J., Warneke, C., Singh, H. B., Goldstein, A. H., and Sive, B. C.: Tropospheric methanol observations from space: retrieval evaluation and constraints on the seasonality of biogenic emissions, Atmos. Chem. Phys., 12, 5897–5912, https://doi.org/10.5194/acp-12-5897-2012, 2012.

Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, Geosci. Model Dev., 5, 1471–1492, https://doi.org/10.5194/gmd-5-1471-2012, 2012.