

Answers to reviewer 2 comments

Reviewer 2 comments (<https://doi.org/10.5194/acp-2020-1328-RC2>)

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.

We thank the reviewer for his comments. We agree that the manuscript still needed clarification in the compound assignment. This has been now performed making better use of the fragment analysis, and also of the literature on PTR-TOF-MS calibrations as explained in our answers to reviewer 1.

Abstract:

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

Thanks for the sound suggestion. We also added the location and plant stages with the following sentence: “The study took place near Paris over a 5 weeks period starting the 3rd June 2016 spanning crop maturity and senescence.”

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.

This is a very sound comment, which needs clarification. We have reprocessed a spectral analysis of this peak over some key hours for this compound. We also used the knowledge of the fragment and isotopes to get a more robust estimate and we are now convinced that this is actually an oxygenated compound (C₆H₄O, possibly furan), with a very small 0.5 ppm mass error. Other compounds have been reanalysed in a similar manner and Table S2, and figures have all been corrected accordingly.

Methods:

Please explicitly state the number of days the experiment lasted.

This has been included: 46 days

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).

Thanks for the suggestion. We changed the date format in the text.

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

Thanks for the suggestion. We have changed Figure 3 to include these. It shows like this now:

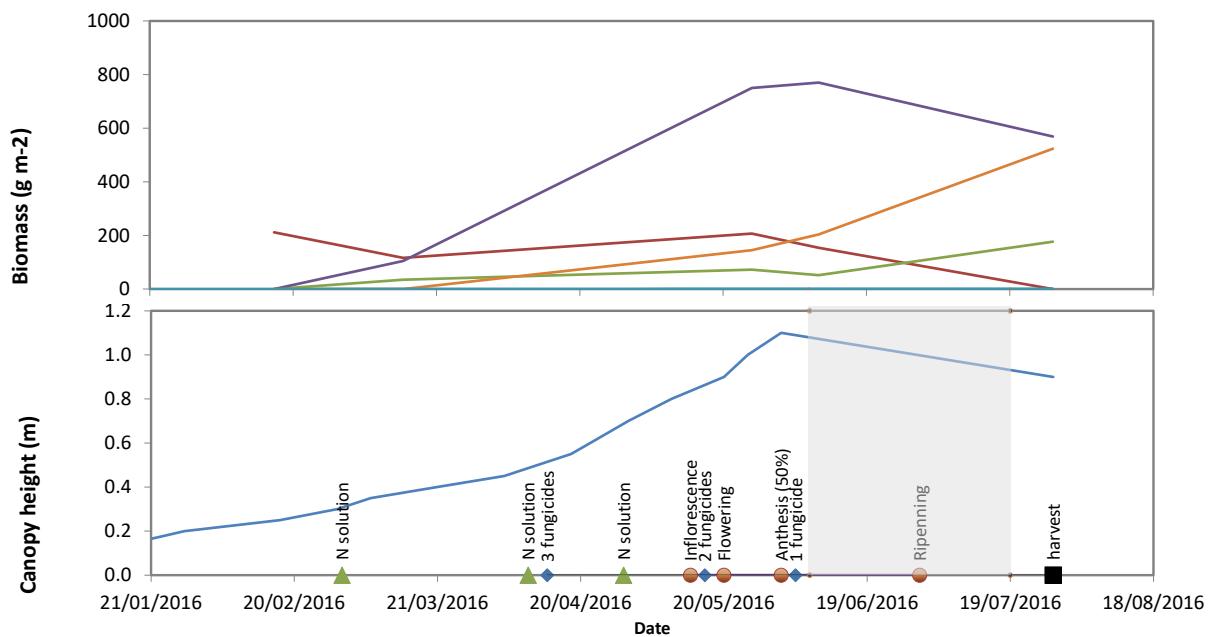


Figure 1. Top: evolution of the above ground biomass of different plant compartments. Bottom: crop height, crop developmental stages and farmer activity. The experimental period is highlighted in grey shading.

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.

The Reynolds number for the sampling line was set to 6120, so well above the critical value of 2000-3000, to ensure a turbulent regime to avoid high frequency losses. The Reynolds number value was added in the text. The crop heights h was below 1 m and the mast height was at 2.7 m, which gives a mast height above the displacement height d ($\sim 0.7h$) larger than 2 m. This is within the standard eddy-covariance measurement heights for low ecosystem heights such as crops. Rebmann et al. (2018) recommended a measurement height between 1.6 and 6 times the canopy height, which corresponds to our setup. 3 m might have been better of course, but we also wanted to minimise the risk that the footprint goes out of the field, especially for south and east wind directions, given the specific setup with a 30 m line as shown in Figure 2 and 3.

This 2.7 m height tower does not make the footprint calculation difficult as again this is a standard height for crops and the FIDES footprint model (Carozzi et al., 2013; Loubet et al., 2018) and others (Wilson et al., 2012) have been applied extensively for these heights?

We did not report the footprint in this introductory section but rather used a flux footprint model to compute the footprint and reported it as a result in section 3.1 (Figure4): “The flux footprint from the main field was mostly above 0.8 (median 0.86, interquartile 0.76 - 0.91) but showed some consistent periods with a lower footprint (down to 0.4) when the wind was blowing from the south. The periods with a footprint lower than 0.6 occupied 13% of the time.”

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?

This is a very sound comment, which was very consistent to reviewer 1 major comment. We have modified our approach to account for variations in k . Please see reviewer 1 section detailed answers to this key point.

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.

We were able to calculate the flux for 85% of the time. We did not do any gap filling on the VOC fluxes, as this would require a well-validated VOC flux model. It was furthermore not the primary objective of this study to provide time integrated VOC fluxes, but rather to provide high quality VOC fluxes for modelling purpose. We have reported this in the method section.

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.

The reason for the missing ribbons in the last week is that during this last week, there was only one day of measurement, hence leading to no estimate of the interquartile. We have mentioned this in the Figure legends when appropriate (Figure 6 and 7 of revised manuscript)

The second comment was also made by reviewer 1. All chemical species formula and names have been added to the figures when appropriate.

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.

Thanks for this very sound comment indeed. The VOC names in the text have been thoroughly checked and aligned to Table S2 that has been also completely checked, to answer previous comments from both reviewers regarding VOC identification.

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?

This comment feeds into the other comments on fragments and compound identification. We have reviewed our methodology and have accounted for these fragments now.

The authors present a measurement of formaldehyde, which shows a high humidity dependence in PTR due to 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.

Formaldehyde was indeed shown to depend much on humidity. We however do not have specific measurements with this instrument to allow evaluating and correcting for humidity effects on formaldehyde. When we plot the mixing ratio (MR, ppb) and the flux ($\text{nmol m}^{-2} \text{s}^{-1}$) of formaldehyde against the vapour pressure p_{vap} (kPa), we do not observe any clear trend (see figure below). However, this does not exclude that there might be an influence of water vapour on formaldehyde measurement. We have followed the reviewer suggestion not to report the formaldehyde fluxes and mixing ratios in Tables.

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?

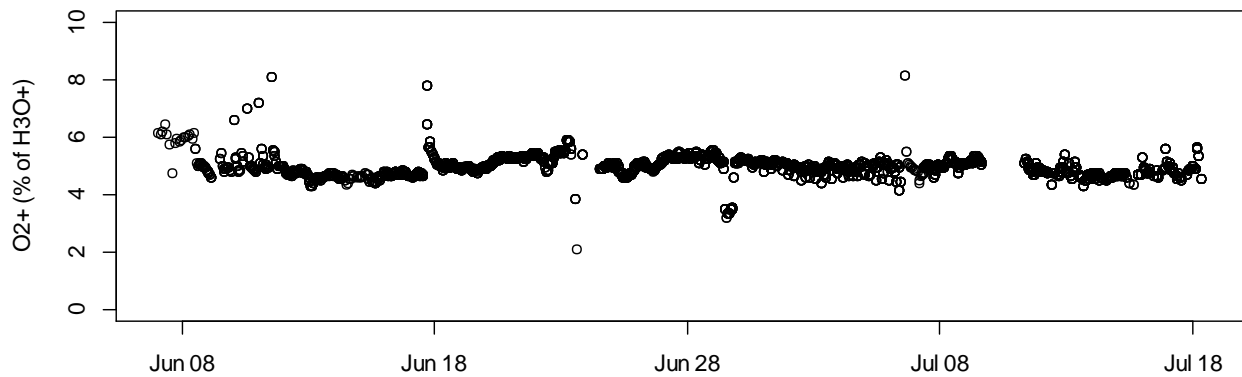
This is not plausible as the field is at 600 m from the farm (Figure 1). Moreover, the animals are mostly in buildings where the faeces are collected and stored for field applications. Cows go outside the farm but in an even further location on the west and south. Finally, the topography would not allow runoff to the field.

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.

Thanks for the comment. Indeed, there should be a minus sign in the second column for monoterpenes but also for isoprene. To clarify we have deleted the tilde in the table and the percentiles, which were only given for Bachy et al. and not compared to this study. We only kept the mean \pm standard error and the [min – max] ranges.

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

Yes, this is the hypothesis we made here. Yes, the O₂⁺ levels were pretty stable at around 5%. See figure below that has been added in the SI, and shows the percentage of O₂⁺ to H₃O⁺ measured



Lines 621-637: This is very good analysis.

Thanks for this kind comment.

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?

This is an interesting comment. Squalene is indeed a metabolite present in all plants playing a key role in the cell membrane properties (Lozano-Grande et al., 2018). It is also produced by wheat, and present in the grain, though in small quantities ($\sim 4 \mu\text{g g}^{-1}$) (Konopka et al., 2017). It is mostly present in grains that contains lipids and amaranth is by far the plant containing the largest quantities (8% of its oil). In crops it is most present in soybean maize and sunflower oils (Lozano-Grande et al., 2018). The observed trend in 5-OPA mixing ratio would be compatible with the growth of maize in the surrounding sites (maize most intense growth occurs end of June-July).

It is striking here to see that 4-OPA emissions increased during senescence, which is also the grain-filling period where metabolites are transferred in the plant to the grain.

During weeks 26-28, 4-OPA mixing ratio (MR, ppb) was strongly correlated to the ozone concentration (O_3 , ppb), while the deposition velocity is primarily correlated to u^* (Ustar, m s^{-1}), as shown in the figure below. The latter is expected from turbulent transfer theory. However, before senescence, the field did not show any peculiar deposition of 4-OPA. The link between 4mixing ratio and ozone concentration seem to suggest that 4-OPA at the field site resulted from an ozonation process. However, we measured a deposition and not an emission processes over wheat, indicating that the source elsewhere.

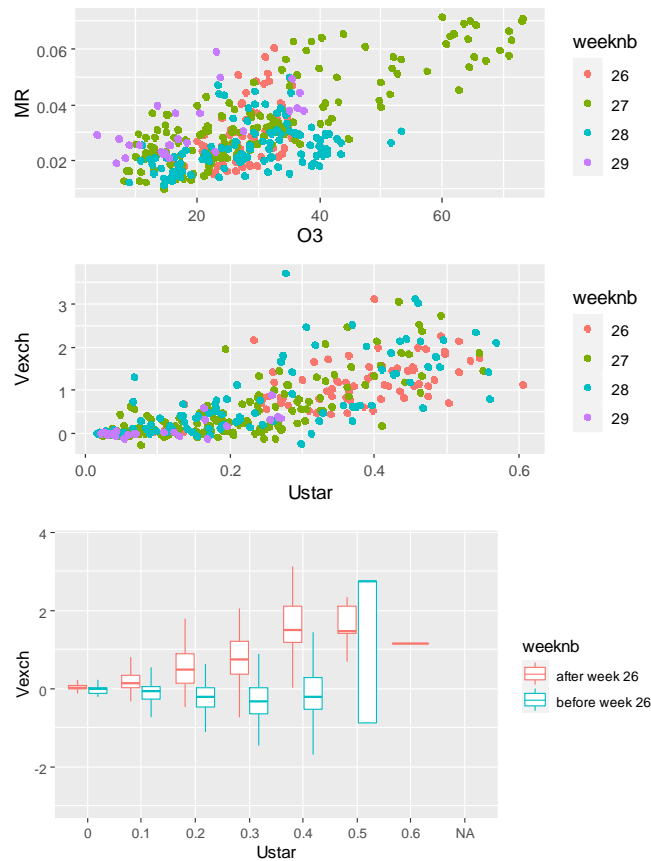


Figure. 4-OPA (m/z 101.060) mixing ratio (MR, ppb) as a function of ozone concentration (O3, ppb), and deposition velocity (Vexch) as a function of u^* (Ustar, $m s^{-1}$). A boxplot shows the difference in deposition velocity before and after senescence.

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

Thanks for this suggestion. We have done so.

Minor issues:

Line 29: “outmost”?

Changed to “high”

Line 95: “the field is at around...” remove “at”

Changed to “The field is around 450 m downwind from the farm buildings...”

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?

No we are referring to volatilisation. We clarified to “The site that is part of a dairy farm receives a lot of nitrogen as mineral or organic matter, which leads to large ammonia volatilisation to the atmosphere...”

Equation 1: Are there units for this constant?

This constant has indeed some units ($\text{L mbar}^2 \text{V}^{-1} \text{s}^{-1} \text{mol}^{-1} \text{K}^{-2}$). When multiplied by $\frac{U_{\text{drift}} T_{\text{drift}}^2}{k p_{\text{drift}}^2}$ is has units of (L L^{-1}) which is equivalent to mol mol^{-1} .

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

Yes of course! Thanks for spotting this mistranslation from the French name “loi des gaz parfaits”. It has been corrected.

Line 288: “7 NL per min” I’m unfamiliar with “NL”

NL stands for Litre inn standard conditions. It has been explained in the manuscript.

Line 387: “Region” to “region”

Done

Line 467-68: please rephrase

We rephrased the last two sentences to “We showed that the bias is however small and negligible when integrated over time (Figure S2 and S3). Nevertheless, we recommend to calculate the covariances using raw cps and normalise them by the primary ion H_3O^+ afterwards, to avoid this minimal though proven bias. This is important especially in conditions with very strong fluxes since $\overline{w' cps'_{\text{H}_3\text{O}^+}}$ may increase under such conditions.”

Line 564: extra “.”

Indeed, there was a missing part in this sentence. It has been rephrased as “. Bachy et al. (2020) found acetone to behave very similarly to acetaldehyde...”

Line 673: “leaves” to “leaf”

Changed

Line 682: “under brackets” to “in brackets”

Changed

Line 792: “less” to “fewer”

Changed

References cited in the answers

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