

Answer to reviewer 1 comments

Reviewer 1 comments (<https://doi.org/10.5194/acp-2020-1328-RC1>)

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.

We thank the reviewer for this comment. We have tried to improve the readability of the manuscript by reorganising the sections (as also suggested by the reviewer 2). In particular, we have reorganised the section on calibration to include a species-specific calibration. We have also shorten the results section on mixing ratios and the discussion session on fluxes. We have still left the eddy-covariance fluxes calculation details in the supplementary, as the manuscript is already long and especially the material and method section.

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.

Thanks for the suggestion. We have shortened a bit this part.

- 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.

Thanks for this sound remark. We indeed used the kinetic approach, and are fully aware of its limitations, although at the time of the experiment we did not have the capability to do a better calibration. Following the reviewer suggestion, we have:

- (1) Modified the material and method section "2.2.5 Calibration procedures" which clarifies the calibration procedure. We have further added detailed part on the uncertainties computation for mixing ratios (with added material in the supplementary section). We have now included a calibration factor for each known compound based on a one-of calibration performed at the start of the experiment and calibration data from the work of Koss et al. (2018).**
- (2) The discussion on the uncertainties in the calibration and how these may affect the conclusions of the work has been strengthen.**

- 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.

Following the reviewer suggestion, we have moved Figures 4a, 4b that were only briefly used section 3.1 to supplementary material, while leaving Figure 5 that provides the most important parameters for fluxes.

- 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.

We thank the reviewer for this remark and suggestion. We homogenised the notations in the text and figures according to the suggestion.

- 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.

Thanks for suggestion. We have tried to improve the readability by change the caption to "The x-axis shows the week number in the year (black), the week number in the experiment (green), the starting date of the week (orange), and the hour of day (blue)."

- 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).

Considering the previous remark on the length and readability of the manuscript, we agree that these figures could be moved to the supplementary material, while keeping the text in the manuscript. This will help keeping the focus on the VOC fluxes and on the analysis of advected compounds from the nearby farm (in section 4.4).

- 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.

This is a sound remark.

- First of all, we should indeed stress that, yes the site is very close to high traffic roads especially close on the north-west (right at the edge of the field), but also on the east, and west and to a lesser extent on the south. This was discussed at length in Vuolo et al. (2017) about possible advection fluxes on NO_x (section 3.5). The road on the north had a traffic load of 5000 to 15000 vehicles per day as a 2010 counts (Statistiques du département des Yvelines pour 2010), and the traffic has increased since then, especially on the east.
- Second, we should may be recall that deposition and emission are not related in the same way to the flux footprint. Indeed, assuming there is no bi-directionality in the flux for the sake of simplicity here, a deposition flux (F) can be expressed as the product of a deposition velocity (V_a) with a

concentration (C): $F = V_d * C$. Hence the peaks in deposition fluxes results from either both peaks in V_d or C. We can assume in a first order approach that V_d over a crop follows the same pattern as the friction velocity u^* , and will hence peak around noon in our site (Loubet et al., 2012; Vuolo et al., 2017). Hence, when we observe a peak in a deposition flux F around 5 pm it is most likely that this is due to variations C. To explain it in a different way, the deposition velocity is driven by the surface characteristics, and hence depends on the flux footprint, while the concentration depends on the concentration footprint, which is much larger than the flux footprint. Moreover, we should also bear in mind that concentration footprint concepts can be substituted by a concept of “air mass”. At our site, we have clear evidence that the “air mass” changes when the wind is coming from the Parisian area (although Paris is at ~30 km away on the east). We usually observe an increase in NO_x pollution when air is coming from the east (see Supp. Mat. Figures S2, in Vuolo et al. 2017). This is also, what we observed in this study for NO showing a clear increase from the east (Figure S12 reproduced below). In conclusion, it is very likely that some traffic emitted VOC concentrations follow a traffic-like pattern, which, if the compounds are deposited will drive the deposition flux pattern.

For the compounds advected from the farm, the same reasoning holds.

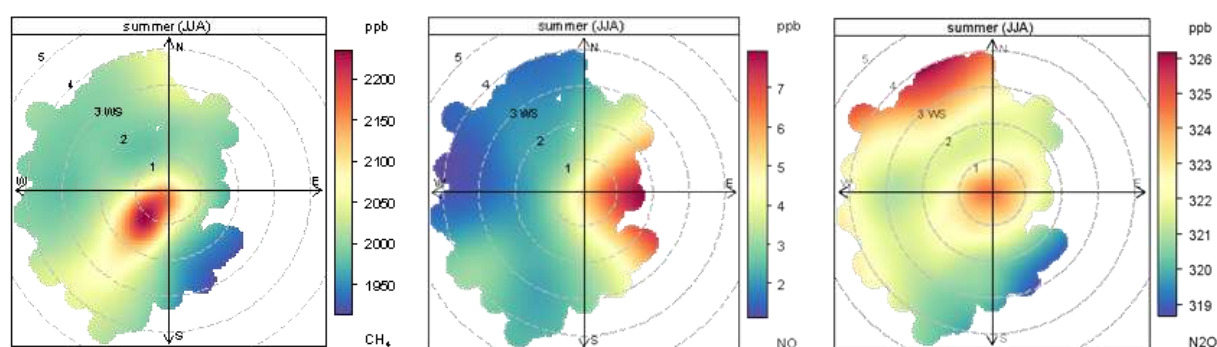


Figure S12. Pollution roses for CH₄, NO and N₂O.

- 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?

We are terribly sorry to have forgotten to include this file in the supplement. It is now included in the revised supplement.

- 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?

We were also surprised to find this behaviour for methanol fluxes. However, Gonzaga et al. (2021) also found this (Atm. Env. Accepted with minor revisions) in 2017 at the same site but with a different technique:

a chamber method, and by Bachy et al. (2020) with a similar technique. This suggests indeed that demethylation of pectin is still efficient during aging and senescence of plant tissues as shown by Michele et al. (1995), but also that another mechanism increases methanol fluxes. This may be due to a pronounced degradation of cellular constituents at the end of chlorosis that may promote methanol production and its release through higher leaf porosity chlorosis (Keskitalo et al., 2005; Woo et al., 2019). Increased methanol emissions have been reported above cut grasslands (Seco et al., 2007), which may suggest a similar process as during wheat senescence to occur in grasslands.

- 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.)

We thank the reviewer for the suggestion of shortening this section. We however disagree with the comment that there is not much benefit in this section. Indeed, we consider that we bring new results and new ideas in this section by comparing our results to the literature. As a first example, the previous comment shows that our results suggest a new methanol production process during plant senescence. Then, m/z 93.037 is for the first time reported to be emitted at that magnitude by an ecosystem. For acetaldehyde, our results suggest a new acetaldehyde emission route from crops through oxidation of organic matter by ozone that would be especially important during senescence. Regarding DMS, although our results confirm previous emission magnitudes, the discussion points towards a possible source from moist soil that we find important to mention here. For monoterpenes, the discussion on the ion fragment suggested a dominating MT I in our study (3-carene). Similarly, to m/z 93.037, phenols are first reported as being emitted by plants or soil. Regarding VOC deposition, there are little references reporting deposition over crops and the discussion allowed positioning this study with respect to the existing literature.

To conclude, we have hence shortened this section as suggested by the reviewer, but kept it as a separate discussion where new results have been highlighted.

- 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.

We have simplified the text to get rid of this term in most sections except in when strictly necessary (m/z 93.037). A thorough and careful assessment of species identification was indeed performed based on the literature and the lab experience.

- 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.

Farm is not in the flux footprint but in the concentration footprint for sure (see answer to the previous comment on traffic). As already explained, since $F = V_d * C$, if the concentration C is influenced by the farm then the flux F is also influenced by the farm. In addition, indeed, our data show clearly that the farm influences the concentration of methane (Figure S12 reproduced above), and some VOCs (Figure 10 reproduced below). In these figures, it is clear that the methane and $C_{10}H_{14}$ show enhanced concentrations

when the wind is blowing from the farm. Since the farm is the largest methane source in the surrounding, we can conclude that $C_{10}H_{14}$ is also coming from the farm. We have clarified this in the manuscript.

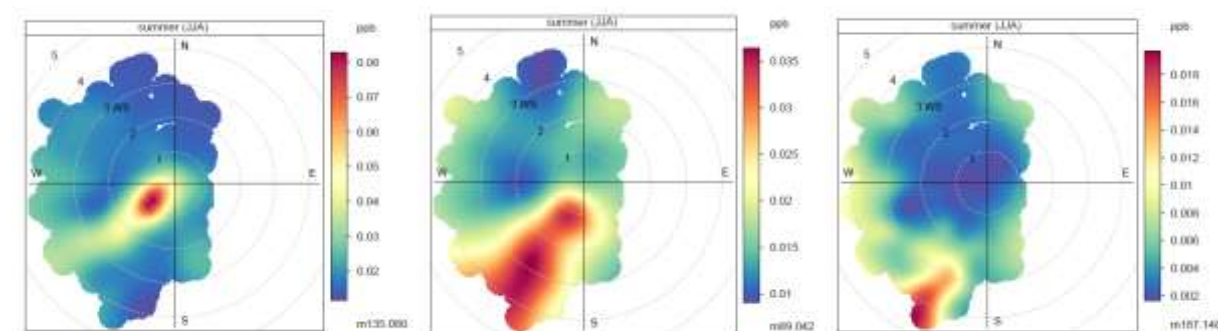


Figure 10. Three typical wind rose of compounds identified as coming from the farm. Colours show the mixing ratios, and plots are binned by averaged wind direction and wind speeds. Left: constantly emitting source (example $C_{10}H_{14}$). Middle: source emitting with a daily pattern (example of $C_4H_8O_2$). Right: secondary photo-produced compound (example m/z 187.148, possibly $C_{11}H_{22}O_2$)

- 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?

Thanks for this sound question. Correlation results shown in the supplement data table S4b and Table S4c were used to find species that fragmented in both E/N fields. Overall, as expected, the fragmentation was much larger with E/N = 150 than in E/N = 130. E/N=150 also tend to give more C fragments, while E/N=130 lead to more H_2O clusters. Three examples are given in the table below that shows that the pattern are quite similar between the two E/N. We see that isoprene clearly fragmented to m/z 57 and m/z 41 in similar amounts for the two E/N. Similarly, monoterpenes fragmented to m/z 81 in similar amounts for the two E/N but fragments to m/z 125 only with E/N = 150. C_8H_{12} fragmented to a lot of m/z with E/N 150 but to only one significantly with E/N 130.

m / z	formula	m/z missing fragment	fragment missing formula	peak ratio @ E/N=150	Corr. coeff. @ E/N=150	peak ratio @ E/N=130	Corr. coeff. @ E/N=130	Ratio of peaks 150/130
137.132	$C_{10}H_{16}$							
125.132	C_9H_{16}	12.00	C	2.09	0.95	NA	NA	NA
81.070	C_6H_8	56.06	C_4H_8	2.71	0.95	2.47	0.98	1.10
69.070	C_5H_8							
57.070	C_4H_8	12.00	C	1.63	0.98	1.37	0.93	1.19
41.039	C_3H_4	28.03	C_2H_4	3.42	0.97	3.14	0.81	1.09
109.101	C_8H_{12}							
95.088	C_7H_{10}		CH_2	2.94	0.95	3.21	0.95	0.92
83.085	C_6H_{10}	26.02	C_2H_2	1.85	0.95	1.78	0.81	1.04
71.090	C_5H_{10}	38.01	C_3H_2	0.81	0.95	1.90	0.80	0.43
69.070	C_5H_8	40.03	C_3H_4	2.38	0.97	4.83	0.89	0.49
57.070	C_4H_8	52.03	C_4H_4	3.85	0.97	6.21	0.88	0.62
41.039	C_3H_4	68.06	C_5H_8	8.33	0.96	NA	NA	NA

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

Thanks for this comment. We have asked an English speaker to proofread the manuscript.

Specific comments

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

The Sulfinert valve was used for switching to calibrations as well as vertical profiles and chamber measurements that are not reported in this manuscript. We however think it is better to give this detail here for a complete understanding of the setup.

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

A teflonised pump is a pump which internal chamber is made of Teflon to avoid any interference. The reference has been added in the text for clarity sake.

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

This is a sound remark. The mass resolving power corresponded to a resolution (ratio of ion peak width at mid-height to peak value) of around 4500 during the experiment. This means that the instrument had a mass resolving power of ~ 0.007 m/z at m/z = 30 and ~ 0.03 m/z at m/z = 150. The last two sentences have been added in the manuscript.

- 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.

Thanks for the suggestion. We do agree. We changed the sentence to "The E/N ratio at the start of the experiment was rather high and was hence lowered down to 129 Td in the second half of the experiment to minimise cluster formation and fragmentation, although the latter cannot be avoid".

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

This has been changed completely, thanks to the useful reviewer comments. See answers to previous comments.

- 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.

The following explanation has been added in the manuscript: "The flux footprint $\varphi(x,y)$ of the measurement mast is the probability density that the measured flux F originates from the field point of coordinates (x,y) . The measured flux is then: $F = \int \varphi(x,y)f_0(x,y)dxdy$, where $f_0(x,y)$ is the surface flux at coordinates (x,y) . The flux footprint should be distinguished from concentration footprint $h(x,y)$ that relies the concentration measured at the mast C minus the background concentration C_{bgd} to the surface flux: $C - C_{bgd} = \int h(x,y)f_0(x,y)dxdy$. Assuming $f_0(x,y)$ is constant over the studied field, which is a reasonable assumption for a crop; the previous equations can be integrated to provide integrated footprints:

$$F = f_0 \times \int_{field} \varphi(x,y)dxdy = f_0 \times \phi_{field} \quad (7)$$

$$C - C_{bgd} = f_0 \times \int_{field} h(x,y) dx dy = f_0 \times H_{field} \quad (8)$$

Here $\emptyset_{field}$ has no units while H_{field} has units of a transfer resistance ($s\ m^{-1}$)."

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

Yes indeed. We replaced it by the following: "Further analysis of the high frequency losses using a PTR-TOF-MS is still required to better characterise these potential errors."

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