

General comments

Buyse et al. describe BVOC exchanges from a rapeseed crop in a temperate environment, measured at the ecosystem scale. From these, they derive standard emission factors and compare them with those currently used in the MEGANv2.1 model. The dataset spans two months, covering the maturity and senescence phases of the crop, and thus partially highlights the impact of phenology on exchanges. They also estimate OH reactivity levels, showing the importance of quantifying monoterpenes and isoprene, which are weakly emitted but contribute significantly to total OH reactivity. They also identify episodes of unusual deposition for compounds typically considered as emitted species and attempt to determine their causes.

The manuscript is well written (except for the remarks below), relies on a solid methodology and state-of-the-art instrumentation, and the results are well illustrated. It should enable the community to incorporate these findings to update emission factors for this crop. The data analysis is rather conventional and entirely phenomenological, with originality mainly stemming from the detailed investigation of a crop of regional and global importance whose BVOC exchanges remain poorly characterized. Overall, this work offers useful and timely information for updating rapeseed emission factors and understanding BVOC dynamics. The availability of data and code on an INRAE repository is a strong positive aspect, promoting transparency and reproducibility. Nonetheless, I recommend major revisions to address the points raised in the following comments.

My main concern relates to the analysis of periods influenced by the advection of large amounts of certain compounds:

My understanding of your manuscript is as follows: under northeasterly winds, high concentrations of monoterpenes and siloxanes are advected to the tower. These induce atmospheric chemistry leading to the destruction of these monoterpenes and siloxanes, as well as isoprene, below the EC measurement height, resulting in strong negative fluxes (deposition). To support this hypothesis, you derive a reaction rate from the differences in concentrations measured simultaneously using a short sampling line (EC) and a longer one (profile). You assume that there are no wall effects and no influence of radiation, and therefore that these reaction rates are representative of what occurs in ambient air during daytime. If I have understood your reasoning correctly, could you discuss the plausibility of this hypothesis (which seems rather bold to me) and its implications (given the very short implied lifetimes: substantial destruction already during transport from the adjacent field to the tower, destruction also within the 3.6 m EC inlet, which reactions would affect isoprene in terms of deposition, and why is it not similarly destroyed in the profile inlet)? Could you also estimate the implied local sink and compare it with the deposition fluxes measured by EC? If I have misunderstood your argument, then I believe this entire section should be rewritten. In any case, I find it confusing, with repetitions and a thread that is difficult to follow.

Furthermore, once this non-purely local effect has been identified, why not filter it out from the entire dataset using quantitative criteria, for example based on wind direction and/or concentration characteristics? Instead, the dataset is divided somewhat arbitrarily into periods affected or not by this phenomenon.

In summary, the analysis of these deposition events appears underdeveloped and insufficiently justified. In its current form, my recommendation would be to simply filter out these episodes using criteria described in the Methods section and possibly move their (improved) description to the supplementary materials.

If this section is to be retained in the main text, could you also more clearly discuss the usefulness of studying these deposition events, beyond the need to identify and filter them when isolating purely local ecosystem processes?

We agree with the reviewer's comments that the periods with unexpectedly large deposition fluxes were under-developed and insufficiently justified. We have analyzed these events in more detail (see the supplementary section at the end of this document, which will be inserted in supplementary material), considering the suggested plausibility criteria. This led us to conclude that the derived chemical reaction rates for siloxanes are rather implausible, with the current understanding of the situation. These episodes would therefore need further investigation to fully understand the observations. We therefore followed both recommendations of reviewer's to filter out these episodes and focus the paper on the standard emission factors. This will also answer the comments from both reviewers to revise the manuscript structure in order to ease the readability.

Here are our answers to the different questions raised on this topic by reviewer #2:

1/ Concerning the suggested use of a criterion described in the Methods section to filter out these episodes and possibly move their (improved) description to the supplementary materials. When analyzing our dataset, we looked for more objective criteria to filter out these periods, including instrument failures (which we did not observe during these episodes) and a simple filter based on wind direction and concentration levels. The combination of (i) wind direction and (ii) the difference in BVOC concentrations between the EC inlet and the 3m-profile inlet helped clarifying the sub-periods during which a few selected compounds (isoprene, monoterpenes and its potential fragments, and siloxanes) were seen to deposit outside usual ranges for these compounds, potentially suggesting advection episodes. We therefore filtered out the data for the whole dataset during these episodes, following this methodology: *"Differences in concentration levels between the EC and profile sampling lines were determined and combined with the observation of wind direction data. This allowed us to identify and filter out two episodes occurring over 9-10 May, 2017 and 23-30 May, 2017, characterized by north and north-eastern winds (0 to 105 °N) and very large (above 100%) concentration level differences, during which monoterpenes and its potential fragments, and siloxanes exhibited very large and*

unusual deposition fluxes. Practically, the period occurring over 9-10 May was characterized by 78 % of hourly data coming from North and North-East direction, conjugated with large concentration level differences between EC and profile 3-m height sampling lines for monoterpenes (64% of hourly values above 100% difference over these two days) and siloxanes (between 70 and 100% of hourly values above 100% difference over these two days). The period occurring over 23-29 May was characterized by about 50% of hourly data coming from North and North-East direction conjugated with large concentration level differences between EC and profile 3-m height sampling lines for monoterpenes (42% of hourly values above 100% difference over these 7 days) and siloxanes (between 64 and 92 % of hourly values above 100% difference over these two days)."

We provide the excel file "Sub-periods_selection criteria.xlsx" as a complement to this answer and will provide it as supplementary material in the revised version of the manuscript, for more transparency.

Other periods with North and North-eastern winds were observed in June 2017, but as the differences in concentration levels between EC and profile lines for monoterpenes were not as high as in the May period, it was decided to keep all data in the dataset for the June period.

2/ Concerning the unclear explanations of these unusual observations of sub-periods 3 and 4: Discuss the plausibility of this hypothesis (which seems rather bold to me) and its implications (given the very short implied lifetimes: substantial destruction already during transport from the adjacent field to the tower, destruction also within the 3.6 m EC inlet, which reactions would affect isoprene in terms of deposition, and why is it not similarly destroyed in the profile inlet. Estimate the implied local sink and compare it with the deposition fluxes measured by EC.

We have analyzed these events and their plausibility in more detail. The siloxane concentrations as measured by the EC sampling line was more than 5 orders of magnitude higher than the one measured with the profile sampling line, which is implausible. The very high chemical reaction rate is also not compatible with local advection events. The explanation for these events is therefore unclear, and we think it is safer to exclude these periods from the data analyzed in this manuscript, according to the criteria and data analysis explained above.

I also question the usefulness of presenting fluxes derived from the flux-gradient method. Since you have access to a more direct and accurate method (eddy covariance), why include less reliable flux estimates for the same periods? What is their added value? Moreover, they are not actually used in the paper.

We acknowledge that the EC method is more accurate and could be sufficient. The main purpose of presenting the results of both methods in the paper was to help the

interpretation of observations of episodes with large deposition fluxes. Since this section has now been withdrawn, there is indeed no need to include it in the manuscript. The comparison between concentrations measured by the EC and profile sampling lines will appear in the supplementary material, though, as they are used as a quality control criterion and used to filter out some of the data as explained in the previous paragraphs.

Specific comments

L94: more precise coordinates would allow locating the field on google earth (actually it's far off).

Thanks for spotting this. The coordinates were corrected (48.8442 N, 1.9519 E).

L157-164: The sentence is unclear and appears to be missing a verb in its second part ("*...and for methanol by comparing...*"). Please reformulate for clarity. In addition, more methodological detail is needed. (i) It is not explained how the comparison with the PTR-HR-MS instrument was used to derive a calibration factor for methanol (e.g., why only for methanol and was a regression between co-located measurements performed?). (ii) How does this methanol calibration factor compare with the one obtained from the "one-off" calibration and with the toluene strategy? (iii) Please clarify when this "one-off calibration" was performed, and whether the instrumental conditions (in particular the settings and toluene sensitivity) were identical to those during the May-June measurement period. These details are important to assess the robustness and representativeness of the calibration.

The sentence was reformulated in the manuscript. The requested methodological details have also been added and they are given below:

- (i) We calibrated only the methanol against the PTR-HR-MS run by the LSCE team because during the one-off calibration, which lasted 28 min, we suspected that the equilibrating time was not sufficiently long to allow for the methanol mixing ratio to reach a plateau in our setup. Indeed, as a polar molecule methanol requires much longer time to equilibrate with the tubes and the flowmeter, as we noticed in later experiments with the same setup. Indeed we found that 4 hours were necessary.

In practice, the calibration factor for methanol was derived by linear regression between the mixing ratio measured with the PTR-TOF-MS from the INRAE team and the PTR-HR-MS instrument from the LSCE team over a period of 2 days when the two instruments were sampling at the same location and height. The Figure 1 here below shows the mixing ratio of the two instruments and the corrected methanol mixing ratio over this two-day

period. The calibration was done by using a linear regression between the mixing ratio from LSCE and INRAE with no constrain on the offset, leading to a decrease of the sensitivity by a factor of 1.72. The uncertainty on the regression was included in the sensitivity standard error for methanol (Table SX).

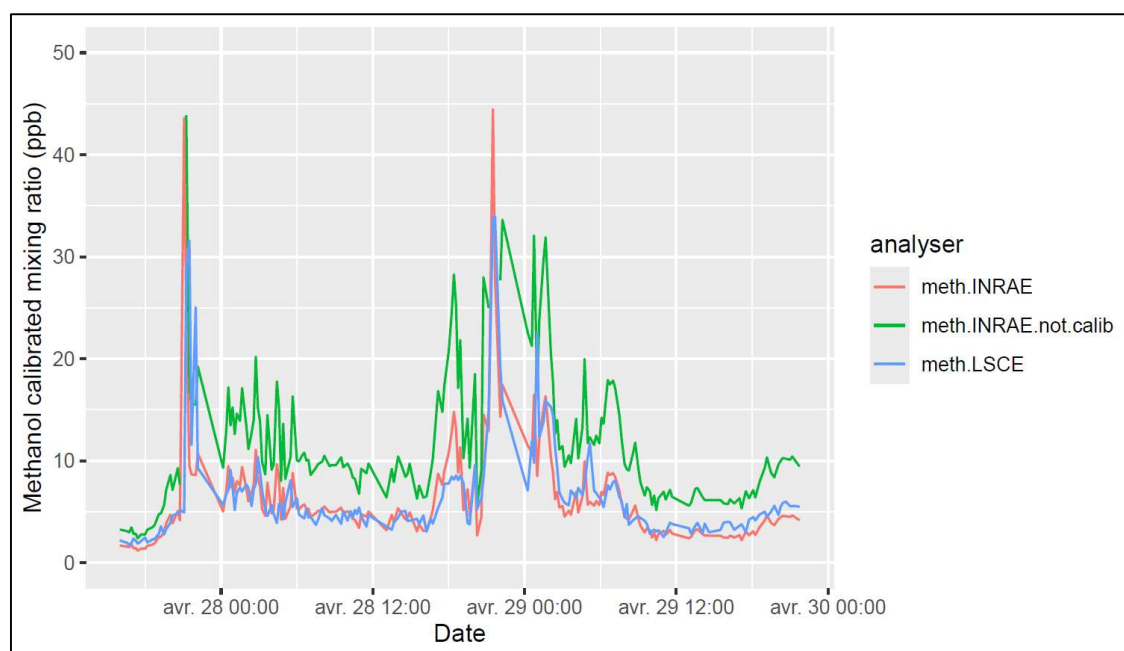


Figure 1 Comparison of methanol mixing ratio measured by the calibrated PTR-HR-MS from the LSCE team (meth.LSCE), by the PTRQI-TOF-MS from the INRAE team as obtained with the calibration procedure (meth.INRAE.not.calib), and after post-calibration against the LSCE PTRMS (meth.INRAE).

- (ii) Figure 1 above shows how the one-off calibration compares with Toluene strategy. Indeed, the green line shows the Toluene strategy calibration without adjustment and the red line show the one adjusted.
- (iii) The one-off calibration was performed on 10/05/2017, the same day as one of the calibrations for which the Toluene was derived. The instrumental conditions were similar during the one-off calibration and the rest of the experimental campaign. The sensitivity of Toluene changed from 2.1 to 2.37 between 1 may and end of June and increased afterwards to 3.46. We therefore selected periods with constant settings and stable sensitivity for Toluene.

L169: Was 2 minutes sufficiently long to stabilize the background concentrations?

We acknowledge that waiting for more than two minutes would have provided more robust background concentrations. This is why we decided to use a single background concentration for the whole experimental period. After checking that during the whole experimental period the background mixing ratios were quite stable, we decided to use the 0.001 quantile of the background concentrations over that period as the

background concentration. We should further point out that a background mixing ratio bias has no impact on the eddy-covariance flux since it is based on a mixing ratio difference. Therefore, the emission factors are not sensitive to the background mixing ratio computation. This is however not the case when computing the deposition velocity V_d of depositing compounds, since V_d is the ratio of the flux by the mixing ratio.

L178-179: no detectable dependance of the timelag on relative humidity for any compound? Why was it tested only on a selection of BVOCs?

The time lags were calculated for 8 different compounds (6 BVOC, NH_3 and CO_2) over the experiment: acetone, methanol, acetic acid, $\text{C}_6\text{H}_5\text{O}$, isoprene and formaldehyde. The reason for selecting only a specific set of compounds is that these BVOC presented larger fluxes, which made the time lag determination more robust.

Figure 2 here below presents the density functions of time lag values obtained during the experiment for the 6 BVOC listed above.

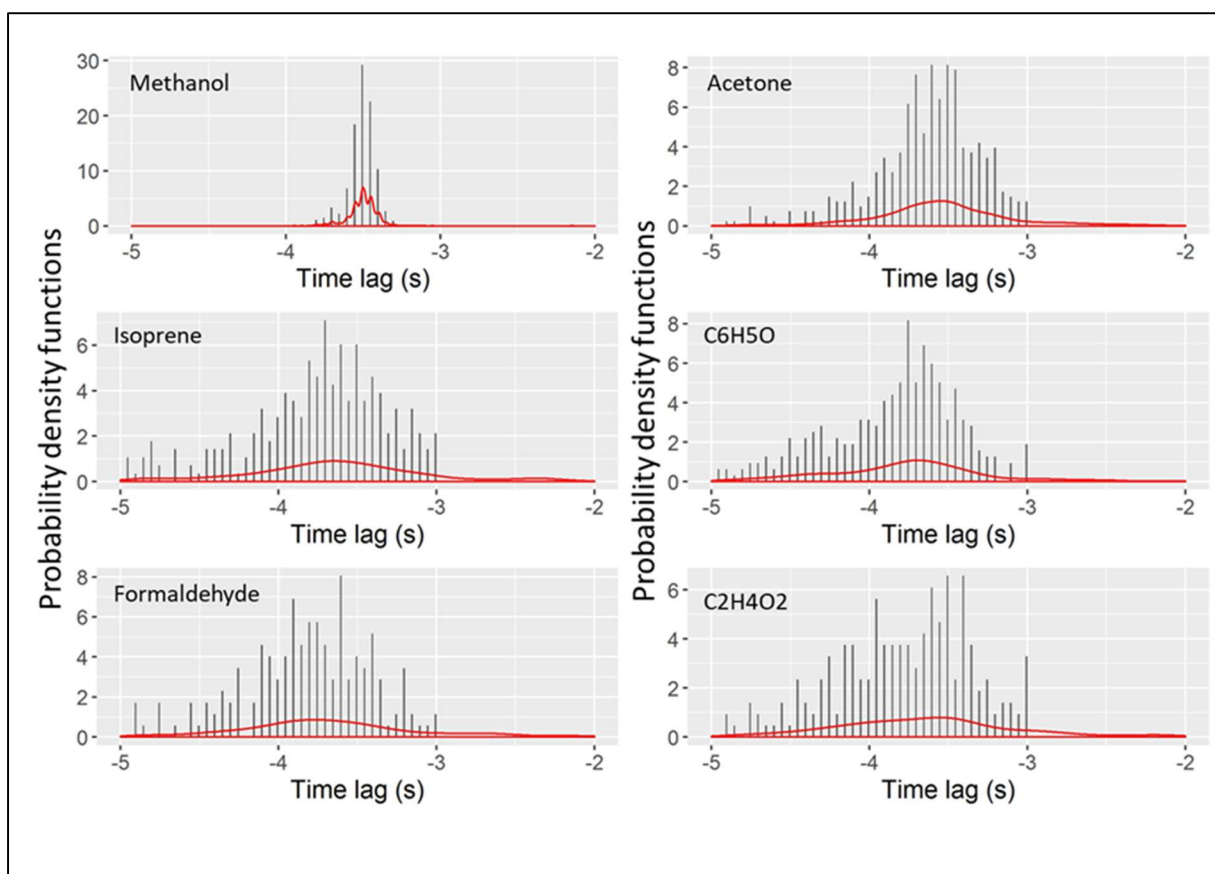


Figure 2 – Probability density functions for the 6 BVOC for which the time lag was determined: methanol (m/z 33.033), acetone (m/z 59.049), Isoprene (m/z 69.070), $\text{C}_6\text{H}_5\text{O}$ (m/z 93.065), formaldehyde (m/z 31.018), $\text{C}_2\text{H}_4\text{O}_2$ (m/z 61.048).

Figure 3 shows the absence of relationship between the observed time lags and the relative humidity, for the 6 above-mentioned BVOC compounds.

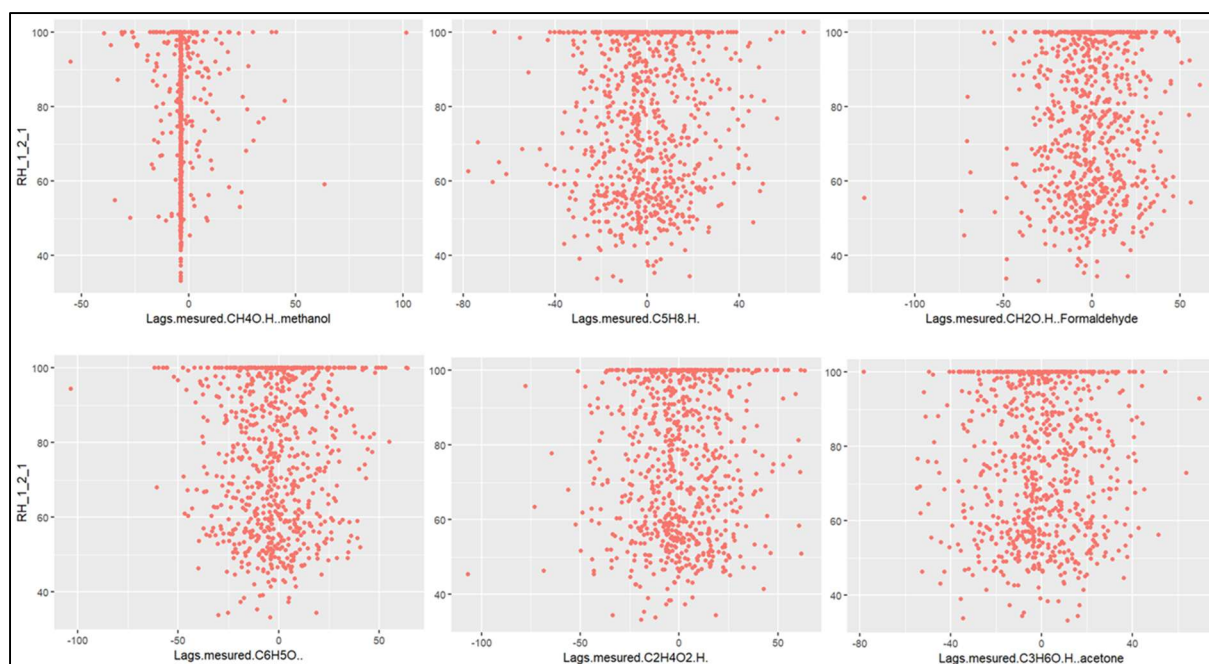


Figure 3 – Relationships between measured time lag values and air relative humidity (RH_1_2_1, in %) for the 6 investigated BVOC.

L180: Why is the standard deviation used here instead of the root mean square deviation (RMSD), as described in Langford et al. (2015; doi:10.5194/amt-8-4197-2015, Eq. 9 and associated discussion)?

We actually used the method of Spirig et al. (2005), not that of Langford et al. (2015), to determine random error in this manuscript. This is a very good comment that we will implement in future studies. We have, however, checked in a few cases that the two methods would have provided the same answer since the average of the cross-covariance function within the defined time window was much smaller than its standard deviation.

Technical corrections

These comments will be addressed directly in the revised version of the manuscript.

L18: “42 BVOC”. Should “BVOC” be pluralized (“BVOCs”) here, since it is used as a countable noun referring to multiple compounds? If so, please correct this throughout the manuscript where applicable.

L149: use a capital for si

L174: “denote time averages”

L194 : a closing parenthesis is missing

L207: add a coma: “...analogy, the ...”

Figure 3: The resolution should be improved, as the m/z values are difficult to read (slightly blurred).

L381: "exchanged fluxes", remove "exchanged"

L383: a closing parenthesis is missing

L412: "making it more difficult to detect it", delete the second it

Figure 3, 4 and 5: uniformizing the way to mention the sub-period would help (fig 4 with the top title is nice)

L527-530: consider rephrasing (show is used three times in the same sentence)

L569: "closer much" should be "much closer"

Detailed study of chemical reactions

1. Identification of potential fast gas-phase chemical reactions for BVOC at the site

Most of the time, the mixing ratios measured with the EC and 3m-profile inlets were in good agreement for most compounds. However, during some periods, the mixing ratios measured at the EC inlet were up to 15 times higher than those measured at the 3m-profile inlet. During these episodes, high mixing ratios of terpenes and siloxanes were observed. After thorough checking, we concluded that no instrumental failures (PTRMS malfunction, changes in flow rates, leaks, or water in the tube) could explain these differences. We therefore hypothesize that these differences may be due to chemical reactions in the gas phase occurring during transport through the tubes. Indeed, given the difference in inlet diameters, length and flow rates, the transport time in the EC line was $t_{EC} = 3.6$ s, while in the profile line it was $t_{profile} = 11.3$ s. Assuming a pseudo first-order reaction during the transport in the tube, for a compound i with non-limiting reactants we can write:

$$\frac{dC_{tube_i}}{dt} = -k_i C_{tube_i} \quad (S2)$$

where C_{tube_i} is the mixing ratio of compound i in the tubes, and k_i is the reaction constant of compound i . Eq. (S3) integrates to:

$$C_{tube_i}(t) = C_{tube_i}(tube\ entrance) \times \exp^{-k_i t} \quad (S3)$$

Where t is the transport time in the tube. Since the EC inlet and the 3m-profile inlet sample both the same air, they have therefore the same $C_{tube_i}(tube\ entrance)$, which equates the concentration in the atmosphere C_i at 3 m height. Further acknowledging that $C_{tube_i}(t_{EC})$ is the concentration measured by the instrument through the EC line and that $C_{tube_i}(t_{profile})$ is the concentration measured by the instrument through the profile line, eq. (S3) leads to the following two equations:

$$C_{i_{measEC}} = C_i \times \exp^{-k_i t_{EC}} \quad (S4)$$

$$C_{i_{measProfile}} = C_i \times \exp^{-k_i t_{profile}} \quad (S5)$$

Combining these equations leads to:

$$\frac{C_{i_{measEC}}}{C_{i_{measProfile}}} = \exp^{-k_i(t_{EC} - t_{profile})} \quad (S6)$$

Which, when we take the log leads to:

$$\ln\left(\frac{C_{i_{measEC}}}{C_{i_{measProfile}}}\right) = -k_i(t_{EC} - t_{profile}) \quad (S7)$$

And hence:

$$k_i = \frac{\ln\left(\frac{C_{i_{measEC}}}{C_{i_{measProfile}}}\right)}{(t_{profile} - t_{EC})} \quad (S8)$$

Which gives the reaction rates of a compound i (k_i s⁻¹) in the tubes. With this equation, k_i was computed from the concentrations measured with the EC inlet $C_{i_{measEC}}$ and with the 3m-profile inlet $C_{i_{measProfile}}$, taking $t_{profile} - t_{EC} = 7.7$ s. We found reaction rates as in Figure 1.

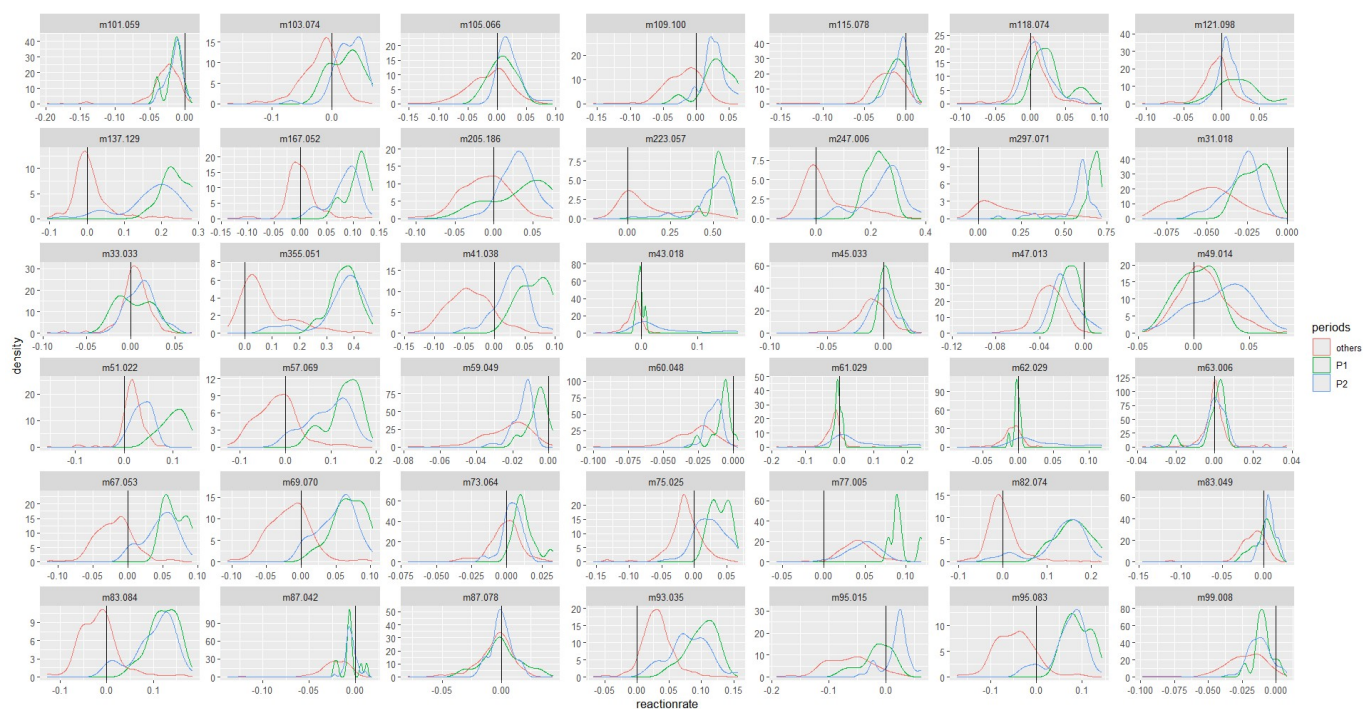


Figure 1. Reaction rate (s^{-1}) distribution for each compound over the whole course of the experiment and special events P1(9-10 May) and P2 (22-30 May) and wind direction from the north-west sector. Five compounds show clearly high reactivity rate from these periods and sectors (siloxanes, and 82.074, 95.083) and to a lesser extent also Monoterpenes 137.129 and 167.052.

2. Effect of inlet reactions on the measured EC concentrations and fluxes

Once the reaction constant is known the concentration measured in each line can also be corrected to account for the amount of compound lost in the tube using eqns. (S4-S5):

$$C_i^{corr} = C_{i_{measEC}} \times \exp^{k_i t_{EC}} = C_{i_{measProfile}} \times \exp^{k_i t_{profile}} \quad (S9)$$

By construction, these two estimations of C_i^{corr} agree.

This correction on the concentration also affects the fluxes measured by EC or estimated from the profile. For the EC flux, if the reactant has a small flux, the correction to the EC flux is equal to $\exp^{k_i t_{EC}}$. If the reactant shows a flux the correction on the EC flux would be dependent on that flux. For the gradient flux estimated from the profile, if the reactant has no vertical concentration gradient, then the correction is equal to $\exp^{k_i t_{profile}}$. If the reactant shows a vertical concentration gradient, then the correction on the gradient flux would depend on that gradient.

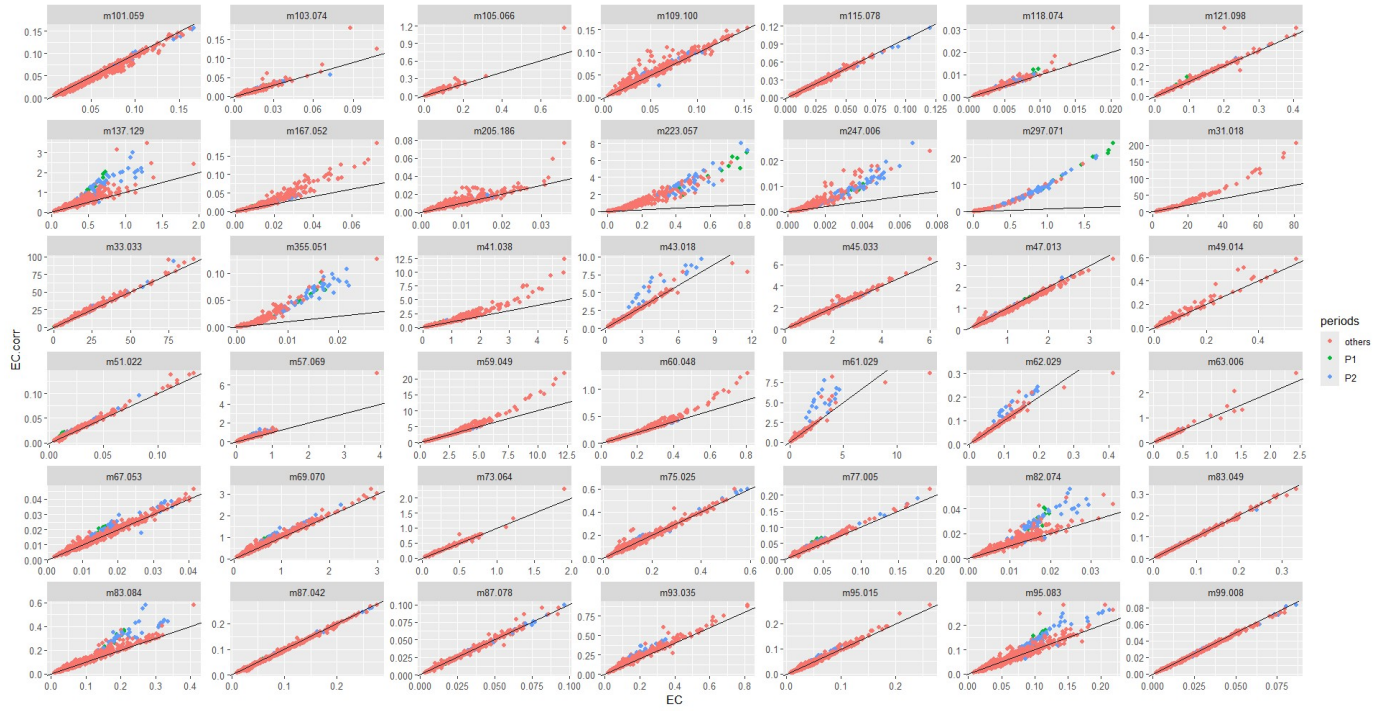


Figure 2. Corrected vs uncorrected concentrations at 3 m height, per periods. This shows that siloxanes do not respond differently during periods P1 and P2 but concentration were higher. So the air masses may not be different.

Figure 2 shows that the correction is small overall. We also observe in Figure 2 that, for the Siloxanes, the correction is large and increases with concentration, but does not differ between the advection episodes P1 and P2 and the rest of the campaign.

3. Estimation of the chemical sink at the tower and comparison with the EC flux

Another way to assess the plausibility of a local advection event of siloxanes and monoterpenes is to evaluate the chemical sink at the tower and compare it with the measured EC flux. The chemical sink of a compound i below the EC mast (3m height), was estimated with a rough approach assuming the reactant is non-limiting and has no vertical gradient, and further assuming a homogeneous stationary situation as:

$$F_{chemical\ sink} = -k \times V_{mol}^{air-1} \times C_i^{corr} \times z_{meas} \quad (S10)$$

Where z_{meas} is the measurement height, arising as the ratio of the reaction volume of a 1m² surface below the measurement height divided by the surface, to get a flux per m² surface.

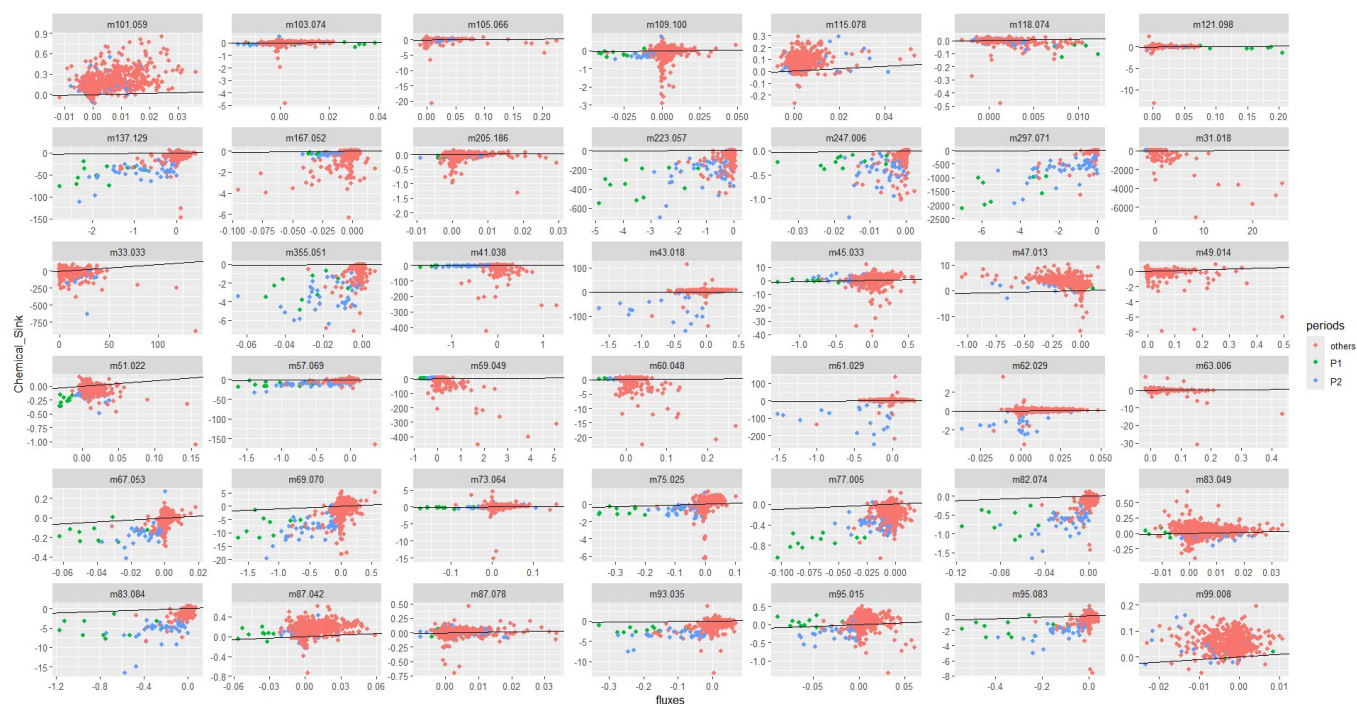


Figure 3. Chemical sink versus EC flux as a function of periods. For D3, D4 and m137, but also m31, m41, m59, and m61 in period 2.

Figure 3 shows that the rough estimate of the chemical sink is implausible for siloxanes and for m137, m31, m41, and m61. This suggests that the method used to determine the chemical reaction rate would need further evaluation to be used with confidence

Conclusions

In conclusion, the chemical reaction rates obtained for D3 and D4 are implausibly large, and we believe it is premature to present these data in this manuscript. We therefore think it is a safe idea to follow the reviewer's proposal to just filter out periods with unexplained differences between the EC inlets and profile concentrations at 3 m height. To that prospect, we have clarified the selection method.