This measurement report describes a study of BVOC emissions and SOA production from leaf litter of rapeseed, an important crop in some countries. The influence of uv light and ozone, both separately and together, was investigated. The topic fits well with the scope of ACP and there are few studies available on this topic. The manuscript is well organized but is difficult to read because it needs a thorough editing for English grammar.

We would like to thank this reviewer for his/her insightful and helpful comments. They helped us to significantly improve our manuscript. We also do apologies for the poor English in the initial submission. The revised version will be thoroughly edited for English grammar. Hereafter, please find our point-to-point answer to the comments raised.

The main issues that should be addressed before publication are:

1. There are a lot of unknown compounds and tentatively identified compounds, as is expected with having only PTR-MS measurements. The study would be improved by including a few measurements of rapeseed litter with complementary techniques, such as GCMS, to identify some of these compounds.

Obviously, the rapeseed litter is seasonal, and our group did not had access to GC-MS instrumentations during the experiments. It would therefore be quite difficult to run this additional analysis. However, we do need to stress that performing VOC analysis only by means of a PTR-MS approach is quite standard in the field of atmospheric sciences. We nevertheless increased the number of tentatively identified compounds using the PTR-Viewer tool.

Does the uv light or ozone change the BVOC emission? Measurements of the emission rates in the absence of uv light and ozone should be reported.

We thank this reviewer for his/her valuable comment. The emission factors of BVOC from litter have been already reported in the literature (Bigg, 2004; Derendorp et al., 2011; Faiola et al., 2014; Gonzaga Gomez et al., 2019; Greenberg et al., 2012; J et al., 2020). The purpose of this article was to point out if there is any contribution of biogenic VOC from litter to SOA formation. For this reason, we focused our experiments on the impact of light and ozone. Below, we show the evolution of the summed VOC concentration in the dark and without ozone. It can be seen that it only changes slightly at levels reduced compared to other conditions. This will be stressed in our revised version.

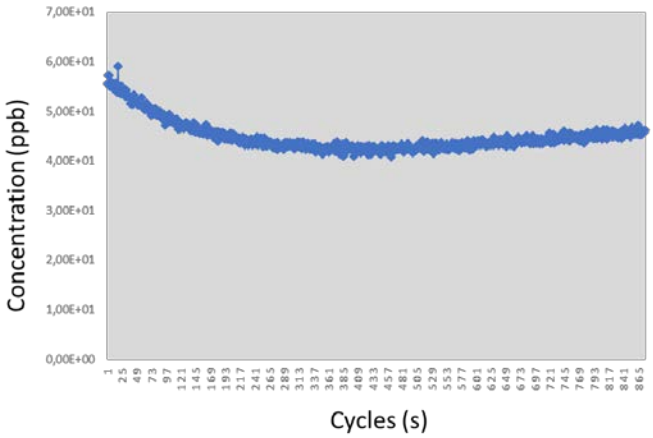

Figure 1. summed concentration of the VOC detected in the dark without ozone.

2. How repeatable are these measurements? Biological systems tend to have a lot of variability. Either replicate experiments should be performed or some evidence should be provided to show that the it is expected that results would be similar if the experiment were repeated.

The number of samples available was limited due to its collection procedure. On the day of the collection, the rapeseed litter used for the measurements was made of leaves at the beginning of senescence process. Replicate experiments are difficult to be performed in this case since other samples will have a different degree of senescence and therefore difficult to compare with the first set of experiments. The evolution of the litter over time is accompanied by a change in the colour of the leaves from green to yellow to brown. This is due to a degradation of the metabolism leading to the death of the cells and the degradation of the chlorophyll. To repeat the experimentation, we would need to renew the litter samples the following year.

Nevertheless, we had obviously to define an experimental plan to address the scientific questions underlying to this work. Such a procedure increases the reproducibility of the starting material for each runs performed here (in total 9 runs). We initially performed a preliminary study (not included in our manuscript) where the BVOC emission and SOA formation from rapeseed litter was investigated in the presence of both UV light and ozone (100 ppb). This preliminary testing showed the potential formation of SOA in the presence of light and ozone (see Figure 2 below). This testing showed some reproducibility (with some inherent variability when working with biological samples). We then decided to perform further experiments under complementary conditions (i.e., O_3, UV light, or both), to see the impact of each parameter on the BVOC emission and SOA formation. For each condition, the experiments were repeated 2 times. So, the BVOC data are the average of these replicas. However, due to SMPS failure, only one replica by condition was available.

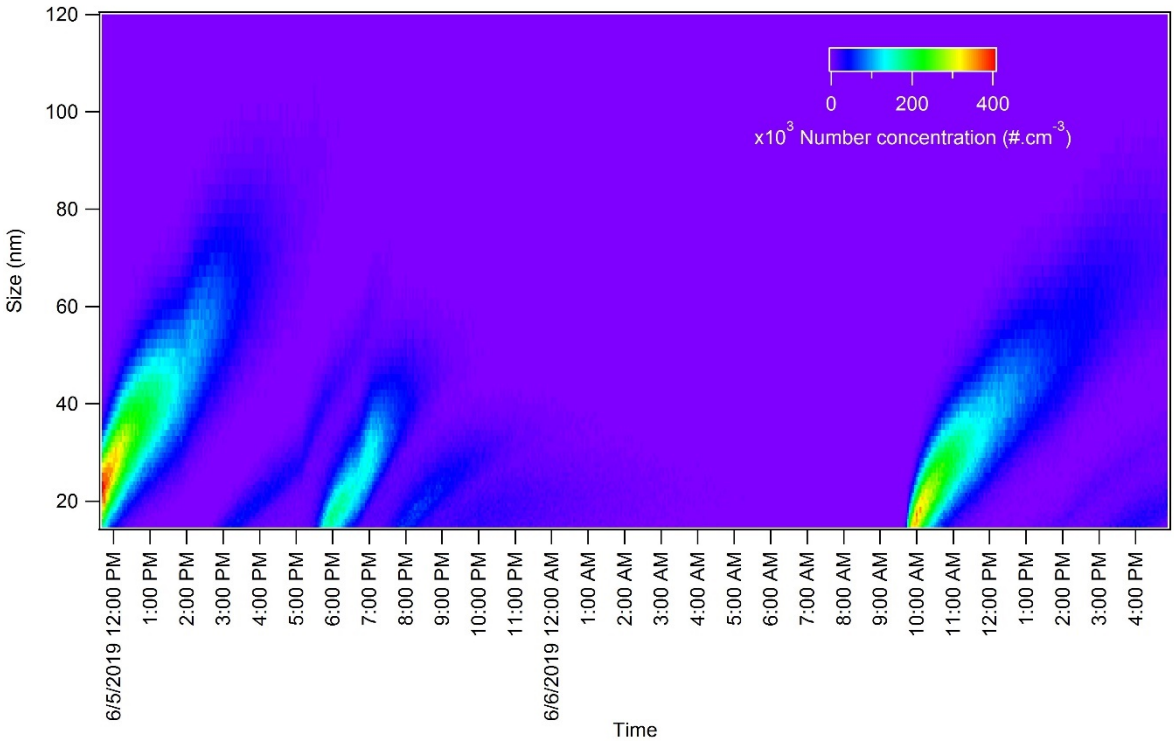

Figure 2. Temporal evolution of particle number and size distribution, ordinate represents the electrical mobility diameter (nm) and the color scale the particle number concentration. Particle formation for the first day of measurement under UV light irradiation and ozone injection combined.

Some other experiments (not shown here) performed in a small simulation chamber (30 L) were performed on the same litter samples (6 samples of soil + litter). Each sample was placed in an aluminium tray of 52.7 x 32.6 x 8 cm, and they were kept in a chamber at 15°C. In these experiments, only the VOCs were measured every 7 days during a 30-day period. The results are in line with the results shown in this study.

3. The authors state that emissions from rapeseed leaf litter may have been underestimated (Line 327) but they don't say what the current estimates are. Current estimates should be presented and compared with these results. It is also suggested that SOA formation from leaf litter might be important (Line 332) but there is no indication of how the SOA formation they observed compares with other sources. There should be some comparison with the SOA formation that is currently known or at least predicted in models.

New information about the current literature estimations of the corresponding BVOC emissions will be added, as follows.

Greenberg et al., (2012) detected a methanol flux of 1.3 μg m^{-2} h^{-1} from litter corresponding to 0.4 % of the total emission above the canopy, estimated to be 300 μg m^{-2} h^{-1}. In this study, the methanol flux from leaf litter ranged from 4.6 to 28.4 μg m^{-2} h^{-1} depending on the experimental conditions. Hence, our results suggest that the contribution to the total above canopy methanol emissions of the rapeseed litter could range from 2 to 10%.

—

For instance, Greenberg et al., (2012) reported a VOC flux for leaf litter under the canopy of 0.3 µg m^{-2} h^{-1}, corresponding to the 0.2% of the total above canopy acetaldehyde emissions, while in this study the emission flux ranged from 1.97 ± 0.01 µg m^{-2} h^{-1} for the UV_O_3 condition to 26.7 ± 0.2 µg m^{-2} h^{-1} for the UV condition. The total above canopy acetaldehyde emissions reported by Greenberg et al., (2012) were 200 µg m^{-2} h^{-1}. As for methanol, our study suggest a higher contribution to the total above canopy acetaldehyde emissions from leaf litter ranging from 2 to 13 %.

—

Acetone ($C_3H_6OH^+$, 59.049 m/z). This compound was largely emitted from litter under UV irradiation. The average contribution of acetone was 13% under UV light, 1.64 % when influenced by both UV and ozone and 2 % when the litter was exposed to ozone only. Acetone has been reported as one of the most emitted compounds by plants and litter (Gonzaga Gomez et al., 2019; Greenberg et al., 2012). Greenberg et al., (2012) reported an average flux of 0.3 µg m^{-2} h^{-1} between 11:00 and 17:00. In this study, the emissions of acetone were 10 times higher under UV irradiation. Based on (Greenberg et al., 2012), the current estimates of litter contribution to the above canopy acetone emissions is 0.1 %. However, the flux reported in table 2 suggest that the litter contribution to acetone emission, in the absence of ozone, could be as large as 6 %.

For the SOA production estimation, we wrote a full paragraph comparing the SOA detected from our study and the SOA detected in previous works also resumed in Table 3. Please find it here:

Table 1. Comparison of the SOA formation from leaves litter samples reported in this study and the literature.

Sample type	Sampling period	Measured particles range (nm)	Type of chamber	Experimental conditions	Maximum peak of aerosol formation (μm^3 cm^{-3})	Total Aerosol volume concentration (μm^3 cm^{-3})	Volume Contribution of particles < 20 nm	Ref.
Mix of: Pinus ponderosa, Pseudotsuga menziesii Pinus monticola, Larix occidentalis litter and soil	May-June 2012	20-730	atmospheric chamber (7.7 m^3)	130 ppb of O_3 in dry conditions	0.97-5.43	-	-	(Faiola et al., 2014)
Mix of: Pinus ponderosa, Pseudotsuga menziesii Pinus monticola, Larix occidentalis litter and soil	May-June 2012	20-730	atmospheric chamber (7.7 m^3)	Reproducing raining event 130 ppb of O_3	0.29-2.55	-	-	(Faiola et al., 2014)
Brassica napus litter	June 2019	2.5-79.1	Multiphase simulation chamber (2m^3)	60-80 ppb of O_3	0.2	15.1	38%	This study
Brassica napus litter	June 2019	2.5-79.1	Multiphase simulation chamber (2m^3)	Only UV light	0.8	85.4	24%	This study
Brassica napus litter	June 2019	2.5-79.1	Multiphase simulation chamber (2m^3)	60-80 ppb of O_3 and UV light	7.6	787.8	24%	This study

4. One of the interesting findings is the relatively high contribution of various organic acids but this is not discussed in the text. The current limited discussion on organic acids should be expanded.

We now added a new paragraph to the discussion to stress this aspect more.

Acetic acid ($C_2H_4O_2$, 61.03 m/z) and formic acid (CH_2O_2 47.02 m/z). Organic acids such as acetic and formic acid are mostly emitted from living plants (Kesselmeier and Staudt, 1999), and by the foliage of trees and crops with a flux of 35 µg m^{-2} h^{-1} (Paulot et al., 2011). Viros et al., (2021) detected acetic and formic acid also from senescent litter, with a flux of 0.05 and 0.98 µg m^{-2} hr^{-1}, respectively. In this study, the emission rates of the two organic acids ranged from 0.76 to 64.28 µg m^{-2} h^{-1} for acetic acid, and from 0.23 to 9.12 µg m^{-2} h^{-1} for formic acid. Mozaffar et al., (2018) described that the acetic acid emissions were affected by temperature, as they recorded lower emissions in the early morning than during the late afternoon. This could explain the higher emissions of acetic acid observed in our study where the temperature reached 30 °C, higher than the conditions encountered by Viros et al., (2021) i.e., 22 °C. Mozaffar et al., (2018) while analysing BVOCs from senescent maize leaf litter, reported an acetic acid contribution to the total BVOC emission of up to 26 %. Similar results were obtained in our study, where under UV light conditions, the contribution of the acetic acid reached 20% of the total VOC emissions.

5. The measurement technique appears reasonable, but the description is lacking and needs more details such as standards, accuracy and precision, etc.

The analytical procedure used during this study is standard, and we add to our main text some additional details as follows.

The PTR-TOF-MS has a mass resolution of 4500 m/Δm. A calibration gas standard (TO-14A Aromatic Mix, Restek Corporation, Bellefonte, USA) containing XX VOCs at a concentration of 100 ± 10 ppb in nitrogen was used to calibrate and regularly assess the instrument performance, including mass resolution, mass accuracy, sensitivity, and relative mass-dependent transmission efficiency. The sensitivity of these compounds ranged between 15 and 70 cps/ppb depending on the actual mass. However, since it was not possible to calculate the exact sensitivity for all the detected compounds, we assumed that the proton reaction constant was always equal to 2×10^{-9} cm^3 s^{-1} (Cappellin et al., 2011; Kalalian et al., 2020) and thus the average sensitivity of 30 cps/ppb was applied for all the compounds.

Specific points:

Table 1: It would be useful to report the “per mass” emission in addition to the reported per area emission (or at least provide the specific leaf area so readers can do this calculation) to enable comparisons with literature values.

The emissions were reported here per area, as this is the standard units used for these measurements in the literature. However, we have also provided the mass information for the sample investigated in the caption of table 1 (not to overload the table with information).

Also, this information is available in in the material and method sections:

Once acclimatized, leaves have been weighted and spread on to cover the whole surface of a FEP (fluorinated ethylene propylene) film (with a surface of 0.64 m^2) (**Figure 1a**). After 6 days of measurement, the surface covered by the rapeseed litter has been estimated to be 0.45 m^2 (**Figure 1b**).

And

The initial weight of rapeseed in the chamber ranged from 75 to 80 g. After 6 days of measurement, the weight decreased by 29-32 %.

Line 25: The authors note that VOCs are either “anthropogenic, related to human activities, or biogenic” and then go on to label emissions from rapeseed as biogenic. But since rapeseed is a crop grown by humans, shouldn’t this be considered anthropogenic?

This comment is a valuable one, and should certainly initiate some discussions on how to qualify agriculture. In the present work, we simply stick to the wording commonly used in this subfield of research and qualified VOC emissions from plant, leaves or litter as biogenic. (Mozaffar et al., 2018)

Line 199: Define the Shannon index.

A definition of the Shannon index is now added in the material and method section, please find it here:

Finally, the calculation of the Shannon index was performed. The Shannon index is a quantitative measure reflecting how many different VOC were emitted from each sample. It was calculated with the diversity function of the vegan package (version 2.4-3) in the R software (version 3.2.3). The diversity index was calculated as $H = \sum_{VOC} E_{VOC} \log(E_{VOC})$, where the sum is over all VOCs recorded in the mass table.

Line 292: The authors state that “mature leaves are known to emit less isoprene than young leaves”. The referenced papers report the opposite (mature leaves emit more than young leaves) as do other studies. In any case, it should be noted that this isoprene emission from rapeseed leaf litter is not likely to be the same process as

from living plants (whether they are mature or young) but is likely from bacteria or other non-enzymatic production of isoprene.

The paragraph has been rephrased and corrected as follows:

Isoprene ($C_5H_8H^+$, 69.07 m/z). In this study, isoprene was the 30th most emitted compounds only in the experiment without O_3. Its average contribution in the UV light experiment was 1% with a flux rate of 3.00±0.03 µg m^{-2} h^{-1} or 0.02 µg g^{-1} h^{-1} which is almost 20 times lower than the emissions reported by Morrison et al., (2016), where the maximum detected flux of isoprene from rapeseed was 0.35 µg g^{-1} h^{-1}. This difference is probably due to the different samples, indeed Morrison et al., (2016) investigated branches, while here only the emissions from senescent leaves were considered. However, the flux rate of isoprene reported by this study is in line with those reported by Gonzaga Gomez et al. (2019) i.e., 0.035 µg g^{-1} h^{-1}. Isoprene can also be emitted from microorganisms such as bacteria and fungi. Isoprene is an intermediate product of the mevalonate pathway, which lead to the production of essential organic compounds within the microorganisms cells (Hess et al., 2013). Isoprene is therefore a metabolite directly related to the presence of microorganisms in soil and plants (Hess et al., 2013)

Line 309-310. This sentence is confusing, and the meaning is not clear.

This sentence has been removed following the recommendation of reviewer #2.

References

Bigg, E.K., 2004. Gas emissions from soil and leaf litter as a source of new particle formation. Atmospheric Research 70, 33–42. https://doi.org/10.1016/j.atmosres.2003.10.003

Cappellin, L., Biasioli, F., Granitto, P.M., Schuhfried, E., Soukoulis, C., Costa, F., Märk, T.D., Gasperi, F., 2011. On data analysis in PTR-TOF-MS: From raw spectra to data mining. Sensors and Actuators B: Chemical 155, 183–190. https://doi.org/10.1016/j.snb.2010.11.044

Derendorp, L., Holzinger, R., Röckmann, T., 2011. UV-induced emissions of C2 - C5 hydrocarbons from leaf litter. Environ. Chem. 8, 602. https://doi.org/10.1071/EN11024

Faiola, C.L., VanderSchelden, G.S., Wen, M., Elloy, F.C., Cobos, D.R., Watts, R.J., Jobson, B.T., VanReken, T.M., 2014. SOA Formation Potential. of Emissions from Soil and Leaf Litter. Environ. Sci. Technol. 48, 938–946. https://doi.org/10.1021/es4040045

Gonzaga gomez, L., Loubet, B., Lafouge, F., Ciuraru, R., Buysse, P., Durand, B., Gueudet, J.C., Fanucci, O., Fortineau, A., Zurfluh, O., Decuq, C., Kammer, J., Duprix, P., Bsaibes, S., Truong, F., Gros, V., Boissard, C., 2019. Comparative study of biogenic volatile organic compounds fluxes by wheat, maize and rapeseed with dynamic chambers over a short period in northern France. Atmospheric Environment 214, 16 p. https://doi.org/10.1016/j.atmosenv.2019.116855

Greenberg, J.P., Asensio, D., Turnipseed, A., Guenther, A.B., Karl, T., Gochis, D., 2012. Contribution of leaf and needle litter to whole ecosystem BVOC fluxes. Atmospheric Environment 59, 302–311. https://doi.org/10.1016/j.atmosenv.2012.04.038

Hess, B.M., Xue, J., Markillie, L.M., Taylor, R.C., Wiley, H.S., Ahring, B.K., Linggi, B., 2013. Coregulation of Terpenoid Pathway Genes and Prediction of Isoprene Production in Bacillus subtilis Using Transcriptomics. PLOS ONE 8, e66104. https://doi.org/10.1371/journal.pone.0066104

J, V., C, F., H, W., J, G., C, L., E, O., 2020. Litter of mediterranean species as a source of volatile organic compounds. Atmospheric Environment 242, 117815. https://doi.org/10.1016/j.atmosenv.2020.117815

Kalalian, C., Letizia, A., Depoorter, A., Lunardelli, B., Perrier, S., George, C., 2020. Influence of indoor chemistry on the emission of mVOCs from Aspergillus niger molds. Science of The Total Environment 741, 140148. https://doi.org/10.1016/j.scitotenv.2020.140148

Kesselmeier, J., Staudt, M., 1999. Biogenic Volatile Organic Compounds (VOC): An Overview on Emission, Physiology and Ecology. Journal of Atmospheric Chemistry 33, 23–88. https://doi.org/10.1023/A:1006127516791

Morrison, E.C., Drewer, J., Heal, M.R., 2016. A comparison of isoprene and monoterpene emission rates from the perennial bioenergy crops short-rotation coppice willow and Miscanthus and the annual arable crops wheat and oilseed rape. GCB Bioenergy 8, 211–225. https://doi.org/10.1111/gcbb.12257

Mozaffar, A., Schoon, N., Bachy, A., Digrado, A., Heinesch, B., Aubinet, M., Fauconnier, M.-L., Delaplace, P., du Jardin, P., Amelynck, C., 2018. Biogenic volatile organic compound emissions from senescent maize leaves and a comparison with other leaf developmental stages. Atmospheric Environment 176, 71–81. https://doi.org/10.1016/j.atmosenv.2017.12.020

Paulot, F., Wunch, D., Crounse, J.D., Toon, G.C., Millet, D.B., DeCarlo, P.F., Vigouroux, C., Deutscher, N.M., González Abad, G., Notholt, J., Warneke, T., Hannigan, J.W., Warneke, C., de Gouw, J.A., Dunlea, E.J., De Mazière, M., Griffith, D.W.T., Bernath, P., Jimenez, J.L., Wennberg, P.O., 2011. Importance of secondary sources in the atmospheric budgets of formic and acetic acids. Atmospheric Chemistry and Physics 11, 1989–2013. https://doi.org/10.5194/acp-11-1989-2011

Viros, J., Santonja, M., Temime-Roussel, B., Wortham, H., Fernandez, C., Ormeno, E., n.d. Volatilome of Aleppo Pine litter over decomposition process. Ecol. Evol. https://doi.org/10.1002/ece3.7533