

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2021-135

Anonymous Referee #2

Referee comment on "Measurement report: Biogenic volatile organic compound emission profiles of rapeseed leaf litter and its secondary organic aerosol formation potential" by Letizia Abis et al., Atmos. Chem. Phys. Discuss.,
<https://doi.org/10.5194/acp-2021-135-RC2>, 2021

Review for Abis et al., "Measurement report: biogenic VOC emissions profiles of Rapeseed leaf litter and their SOA formation potential"

Review Summary

Abis et al present measurements of biogenic volatile organic compound (BVOC) emissions from rapeseed leaf litter. Leaves were collected in the field, transported to the lab, and placed in an FEP chamber where they were exposed to one of three conditions: 1) UV irradiance, 2) 80 ppb once-daily ozone injection, or 3) UV irradiance + 80 ppb once-daily ozone injection. UV lights were turned on and off to represent a 7 hour daytime light schedule. BVOC emissions were measured continuously with a PTR-MS for 6 days. In addition, an SMPS was used to monitor particle formation from oxidation of the BVOC emissions in the chamber. The paper highlights this as a potential significant source of secondary organic aerosol (SOA). The topic is interesting and worthy of investigation. However, the limited number of replicates of each condition preclude any ability to make meaningful comparisons. Furthermore, the analysis is described at a superficial level that reads as an early draft, but still requires additional data synthesis and interpretation before publication. I recommend rejection at this stage, but encourage the authors to increase their replicates (or at least better discuss the implications of their results within the context of their limited replicates) and to synthesize the data more thoroughly to complete the project. I provide some ideas for how to proceed with data analysis below.

General Comments

In general, there were a lot of grammatical errors that made the manuscript very difficult to read. I recommend sending it to an editing service. Some examples include: referring to "leaves litter" instead of the correct, "leaf litter" throughout the text; writing "biogenic volatile organic compounds emissions" instead of the correct, "biogenic volatile organic compound emissions"; capitalizing terms that are not proper nouns, such as "Volatile Organic Compounds"; L. 28 "Furthermore, the currently most accredited emission model for BVOC (MEGAN v2.1), estimates that 760 Tg C yr⁻¹ are emitted into troposphere"; L. 49 "This affect leaves litter"; "Samples collection" and "Samples preparation" instead of

the correct, "Sample collection" and "Sample preparation"; "leaves have been weighted" instead of the correct, "leaves have been weighed". These are just some examples. Not an exhaustive list. I also recommend using "were" or "was" instead of "have been" or "has been" throughout the methods section. It would make it much easier to read.

The number of replicates for each condition were not stated anywhere in the methods. Based on what is written (and what is missing), I assume there was only a single 6-day experiment conducted with leaf litter under each condition (UV, O3, UV_O3). This makes it impossible to compare between the different conditions because we have no information about the natural variability between different leaf litter samples under the same laboratory conditions. I highly recommend conducting more replicates to explore natural variability between samples under the same experimental conditions. If that is not possible, the authors could present this instead as a survey of the change over time in emissions and SOA formation from each condition, separately, BUT it is not appropriate to make comparisons between the conditions when N=1.

The analysis presented was preliminary. I highly recommend adding some additional simple box modeling to better interpret the chemistry occurring in the chamber. Models such as GECKO could provide a place to start. Furthermore, to make any statements about the potential regional impact of these results on SOA formation, the authors should provide more detailed estimates of how much SOA the leaf litter BVOCs could contribute and how this compares to typical ambient measurements. At the moment, the authors have not made a compelling case that this could actually be a significant source of SOA.

The authors do not provide proper context for using rapeseed leaf litter as an important system for studying this topic. Even if it is the third most commonly cultivated species in France, don't agricultural crops contribute to a minor fraction of total leaf litter in France? And how would agricultural land management practices influence the leaf litter? Do rapeseed leaves senesce every year? What time of year? If so, what do the farmers usually do with that litter? Do they just leave it on the ground for natural decomposition or do they manage it? For example, do they remove the litter once the leaves senesce from the branches? What implications does this have for regional impacts? This does not provide a compelling rationale to study rapeseed litter for this project and there is some missing information that would help us understand the broader context of these results.

Specific Comments

L. 48: 60 ppb rural background ozone seems REALLY high. Perhaps, double-check this number and better clarify what this means. Is this the annual average? A daytime average? A particular rural area that is affected by a nearby city? This is much higher than a typical background mixing ratio of tropospheric ozone.

L. 70: authors state "leaves reached room temperature, which corresponds to the average temperature in the north of France during summertime". Which is what temperature, approximately? The actual temperature itself should be stated here.

L. 81: authors state that the weight of the leaves decreased by 29-32% after the 6-day experiment. How much of this loss is just water? This should be mentioned. Otherwise, the implication here seems to be that this much mass of VOCs was released, which I suspect was actually a minor component of the loss of mass.

L. 90: it is fine to only show the detailed spectrum of the lamps in the SI, but some general information about the lamps should still be included in the main text. For example, what range of wavelengths does it emit? How does this compare with UV exposure in an ambient environment?

L. 97: authors state the multiphase simulation chamber "allowed the closest representation of the atmospheric conditions." This statement needs a lot more context. What does this mean, "closest representation to atmospheric conditions"? By what metric? By temperature, light, humidity? Are the UV lamps actually similar to the UV the leaves would experience in the field? Were the experiments seeded with polydisperse seed aerosol? If not, the surface area to volume ratio of this chamber could certainly lead to substantial wall loss of oxidized VOC vapors. This is also different from "atmospheric conditions". It is fine to be different from atmospheric conditions, but this statement should be qualified with the ways in which the chamber represents the natural environment well AND the ways in which the chamber likely does NOT represent the natural environment very well. This helps provide necessary context for interpreting the results.

L. 100: how much did turning on the light affect the chamber temperature? How much of the emissions could be explained by the known exponential relationship between temperature and saturation vapor pressure of the different compounds? The latter could be included in the analysis. Any eventual parameterization of these emissions (say included in a model such as MEGAN) would require these temperature-emission relationships, so this could actually be really useful information that could come from this experiment.

Figure 3: is each bar an average of the entire day? Just during light-on conditions? Or an entire 24-hour period? This is unclear. Also, the legend isn't necessary here. Each bar corresponds to the x-axis which already indicates the day. The day does not also need to be indicated with a different color. The different colors could be used to compare different treatments on the same graph (especially if more than one replicate was conducted for each condition), but it doesn't make sense to have the different colored bars in this context.

Figure 4: very unclear how the data was organized to conduct the PCA. Some conditions have way more data points than others. It also appears that the authors are using multiple points along the same time-series as independent datapoints for the PCA. This is not appropriate. Are the authors using each individual measurements at each measurement time-point from the PTR for the analysis? Or some smoothed (say 5-minute

averaging interval) measurement as an independent data point? A PCA should not be performed with time-series data in this manner. Two datapoints in a single time series are not independent data points in the context of the analysis being conducted here. PCA should be used to compare discrete, independent data-sets. Based on the methods, it looks like only one experiment was conducted for each condition and thus, you would only have one multivariate datapoint for each condition (3 total). "multivariate" referring to the entire VOC emission profile. At best, you might be able to argue for using the average emission profile from each day as a single multivariate data point. Ultimately, this needs better clarified, though.

L. 201: how are you calculating any "statistical difference" with an N=1 representing each condition?

L. 209: Authors state "the number of particles decreased" after the initial nucleation. However, the methods state there was a particle wall loss correction applied to the data. Shouldn't this have eliminated the observed decrease in particle number? If not, it seems like the particle wall loss correction was not adequate. How else would they be losing particles? Conditions in this chamber, and the particle size distribution described, likely wouldn't lead to substantial coagulation, correct?

Section 3.3: I think the authors intend to refer to Figure 7, not Figure 8. It is also very unclear why the analysis was conducted this way. What does a negative correlation between VOC mixing ratio and particle number really tell us? Is that information meaningful? Why conduct this analysis using particle number? It is well established that gas-particle partitioning increases with increasing SOA mass. How much of the differences in partitioning behavior could be explained by increased absorption due to increased mass? The relevance of this analysis is unclear. The correlation doesn't necessarily indicate the compounds that contributed to SOA production. Perhaps they were just the most reactive in the gas-phase. Some modeling approaches could be used here to better understand the chemistry occurring in the chamber. As is, this analysis is very preliminary. More synthesis is required to make this data meaningful.

Section 4.4: How does the mass of SOA generated here (and scaled to an ambient field environment) compare to typical measured PM? It looks like it would be a relatively minor source of aerosol based on the results shown, but a more convincing comparison could be made using some simple box modeling calculations.

Technical Comments

Too numerous for me to list here. I recommend sending to an editing service.