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.

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 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.

In this study, we investigated the influence of the several factor (such as light or ozone) on the emissions of BVOCs from the considered litter. We are presenting a set of chamber runs under those changing experimental conditions, which is quite standard for this kind of

experiments (as it can easily be seen in this special issue). A number of preliminary runs have been performed, using small quantities of samples, to set the best conditions for our investigation. We agree with this reviewer that multiplying the experimental runs under varying conditions is required to improve the accuracy of the data obtained. While our strategy is quite common for chamber runs, we faced here another difficulty, which is related the samples investigated.

Obviously, the rapeseed litter is seasonal, and is 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 the senescence process. The same litter is reused for all the measurements throughout the experimentation to study the behaviour of the VOCs emitted over time. Replicate experiments are difficult to be performed in this case since other samples will have a different degree of senescence and 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 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 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 a SMPS failure, only one replica by condition was available.

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.

Well, we do need to disagree somehow with this reviewer here, and turn this comment into a request of providing more insights into the gas phase chemistry of emitted BVOCs. We however fully realize that our study does not cover all aspects the chemical transformations occurring in or on the litter, in the gaseous and particulate phases. It rather aims at uncovering the above-mentioned influences of light or ozone on the emissions pattern, with a focus on SOA. We do need to stress that models, such as a Gecko, would not be able to address the complex heterogeneous (on the litter), multiphase (in the particles) and gaseous homogeneous chemistries. Going into more details on all those aspects certainly goes far beyond one single study. This work provides more qualitative insights into a subfield of atmospheric chemistry where data are sparse. The format and content of this submission therefore match nicely the selected manuscript type i.e., a measurement report. Such type concerns new results from measurements of atmospheric properties and processes from field and laboratory experiments, with conclusions of more limited scope than in research articles.

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.

Rapeseed (Brassica napus) was chosen in this study as model plant species due to its wide geographic distribution and its importance as a crop. Rapeseed is grown for the production of animal feed, edible vegetable oils, and biodiesel. Rapeseed was the third-leading source of vegetable oil in the world in 2000, after soybean and palm oil. It is the world's second-leading source of protein meal after soybean. France is ranked at the fifth producer worldwide for this specific crop (Fischer et al., 2014).

The development cycle of rapeseed is divided into 3 phases: 1) vegetative; 2) reproductive and 3) maturation. For the vegetative phase, rapeseed is sown in August. This phase starts with an epigeous germination during the month of September. From September to December the rapeseed stem will grow from 10 to 20 cm and about 20 leaves forming a rosette. The reproduction phase, starts after the winter i.e., between February and March. It is at this time that the rape goes up. We observe then the beginning of the elongation. Flowering lasts between 4 and 6 weeks and the maturation phase is when the siliques are formed (in June). In July, they are ready for the harvest. It is in this period that we collected the rapeseed litter.

Rapeseed residues are often left on the field. The incorporation of crop residues into agricultural soils improves soil structure, reduces bulk density, reduces evaporation, and decreases erosion. Rapeseed in this rotation contributes improving the organic matter content of the soil. Organic matter, which is essential to fertility, contributes to the supply of nitrogen, to the improvement of structural stability (less sensitivity to soil compaction and erosion), and to the increase in the storage capacity of water and mineral elements (i.e., improvement of the cation exchange capacity) (Tiefenbacher et al., 2021). Therefore, the litter associated to Rapeseed is an important aspect of that process.

The volume of straw produced varies between 0.6 and 2.4 tons of dry matter per hectare. This estimate takes into account the important losses of material that occur during mowing operations and it corresponds to the volume of harvestable straw per hectare. Only half of the total volume produced is harvested, the rest is left in the field to return to the soil (FranceAgriMer, L'Observatoire National des Ressources en Biomasse (ONRB) :Evaluation des ressources disponibles en France ; 2016).

As consequence, bearing in mind the general importance of Rapeseed as a major crop, and the associated important litter, the new knowledge gained by our study comes with some regional importance that can indeed only be fully addressed by some mesoscale modelling. However, such modelling is currently quite difficult due to our limited knowledge. Therefore, we judged our investigations worthy to be published as measurement report.

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.

We checked these data. They do correspond to a rural location where the sampled were collected.

Data from the Airparif network (© 2021 Airparif, https://www.airparif.asso.fr/) reported an average concentration of ozone in this rural area, North-West to Paris, area of 60 µg/m^3, corresponding to 30 ppb, for the year 2020. The maximum ozone concentration, in the same area, reached 216 µg/m^3, corresponding to 108 ppb of ozone. Furthermore, 27 days with a concentration higher than 60 ppb were observed in 2020, and the peak ozone concentration was reached in June. All these data are reported in the "2020 annual report" of the Airparif network as a free data source.

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.

We thank the reviewer for the comment. We revised this sentence; it now reads as:

In this way, leaves reached room temperature (20 °C), which corresponds to the average temperature in the north of France during summertime.

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.

The weight loss was dominated by water. This will be stressed in the revision version.

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?

We thank the reviewer for the comment, we added this information in the revised experimental section, which now reads as:

The absolute irradiance within the chamber has been already reported by (Alpert et al., 2017). Light produced from the UV fluorescent tubes had wavelengths between 300 to 400 nm. Alpert et al., (2017) also reported that measurements for $\lambda < 300$ nm yielded detection limit values on the order of 10^{-3} W m^{-2} nm^{-1}, and thus total light output below 300 nm is negligible. The full spectrum is shown in **Fig. A1** for completeness. In comparison, the solar spectrum at the Earth's surface is shown derived using the online Quick Tropospheric Ultraviolet and Visible (TUV) calculator for a solar zenith angle of 0° (available at http://cprm.acom.ucar.edu/Models/ TUV/Interactive_TUV/).

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.

We agree with this reviewer that this is an overstatement. It was therefore removed.

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.

The temperature raised from 26 to 31 C during the experiment with UV lights switched on. The temperature was however constant for the dark experiments with ozone only. We now added figures showing the temperature variations for all three experimental conditions in Appendix - A.

We thank the reviewer for this valuable addition to our paper, we calculated the correlation between the temperature value and the BVOC emissions. We added a new graph to our paper substituting Figure 7 (following reviewer 2 suggestion). In this figure, we selected the 8 most correlated compound with the temperature (Spearman coefficient > 0.8).

We also added the following discussion to these results:

4.3 Temperature effect on the BVOC emissions

Higher temperatures increase chemical reaction rates, cellular diffusion rates, and vapor pressure of the VOCs, as a consequence BVOC emission rates are dependent on temperature. In this study, we identified 8 VOC emitted from rapeseed litter which are highly correlated with temperature. Among the most correlated ones, we identified methanol and MEK, in agreement with previous reports investigating such temperature dependence from rapeseed plants (Gonzaga Gomez et al., 2019). Harley et al., (2007) detected methanol emissions from 6 different plant species. Their results reported a correlation between its emission, temperature of the leaves, and stomatal conductance. The mechanisms behind this behavior have been explained by Niinemets and Reichstein, (2003). Methanol is produced within the cell walls, and it diffuses in the liquid phase following the diffusion gradient until it reaches the surface of the cell walls. Then, methanol diffuses in the gas phase into the substomatal cavity and is released as VOC in the ambient air through the stomata. In our study, stomata lock-open as a consequence of cellular death (Prats et al., 2006) and the increased temperature accelerated the diffusion process releasing methanol as the most emitted compound from rapeseed leaf litter.

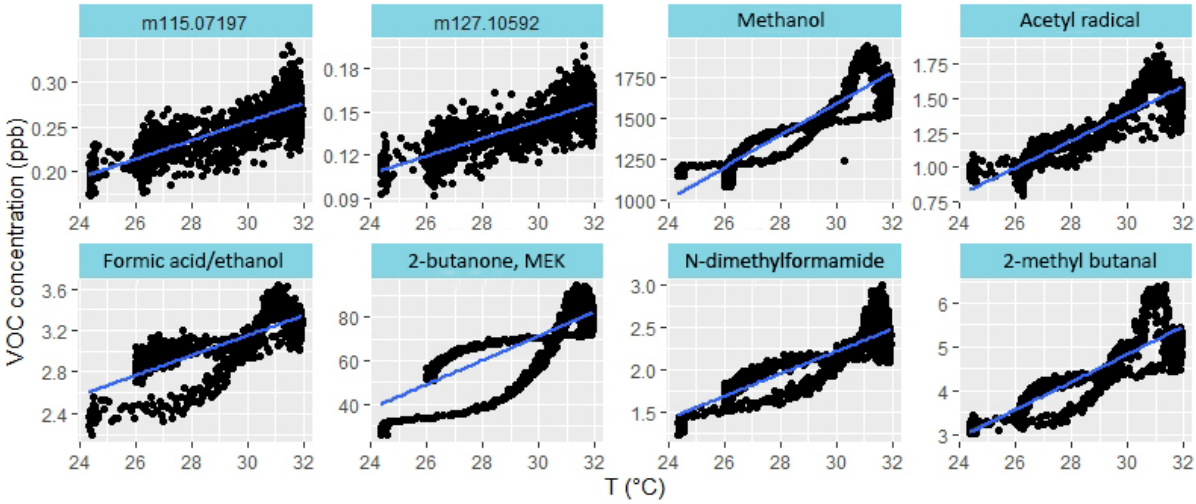


Figure 7. Correlation between VOC mixing ratios and temperature under the UV_O3 condition. The 8 most correlated VOC are shown(Pearson correlation coefficients > 0.8).

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.

Each bar represents the entire 24-h period including the dark phase. We redraw this figure following the suggestions of reviewer 2. Please find the new version below with a new caption:

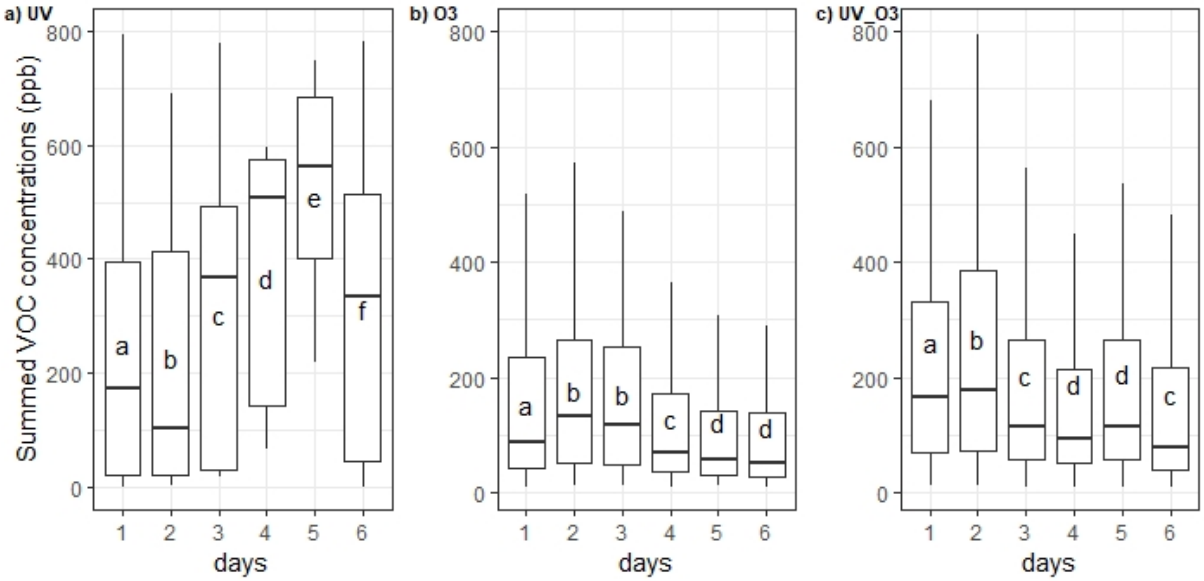


Figure 3: Summed VOC concentrations for each day (24-h period) incubation condition a) UV, b) O3 and c) UV_O3 Letters indicate the statistical difference obtained by the Tukey test.

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 measurement 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 datasets. 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.

We agree with the reviewer that the PCA needed some clarification. We modified the PCA as suggested by this reviewer by comparing discrete and independent datasets and thus comparing the 6 days for each condition. Each point now represents 1 day of measurement and so even they appear to be superposed for the condition O3 and UV_O3 we compared 6 days measurement for each condition. Please find the below of this revised treatment.:

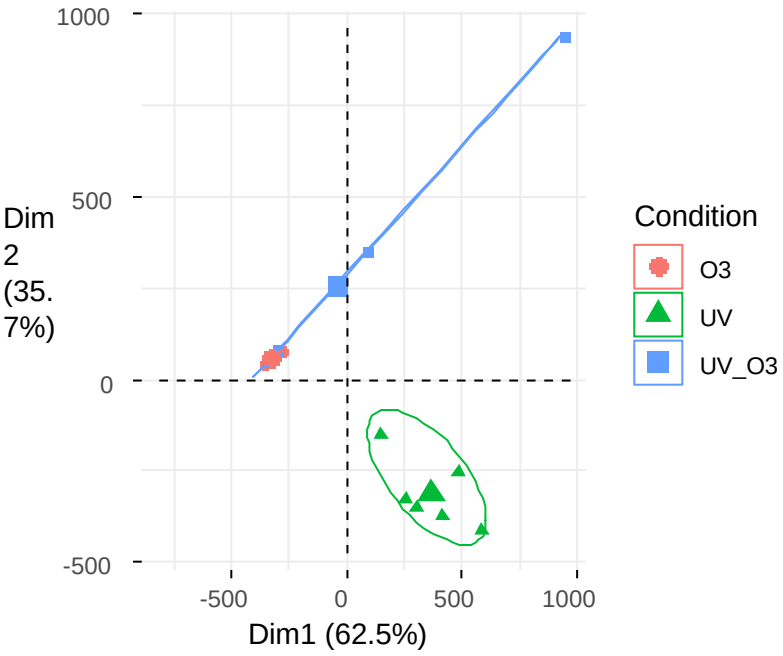


Figure 4: VOC profiles differences between UV light, UV_O_3, and O_3 conditions, each point represent 1 day of measurement. The percentage of the variance explained by the 2 first components is shown on each axis (Dim1 and Dim2

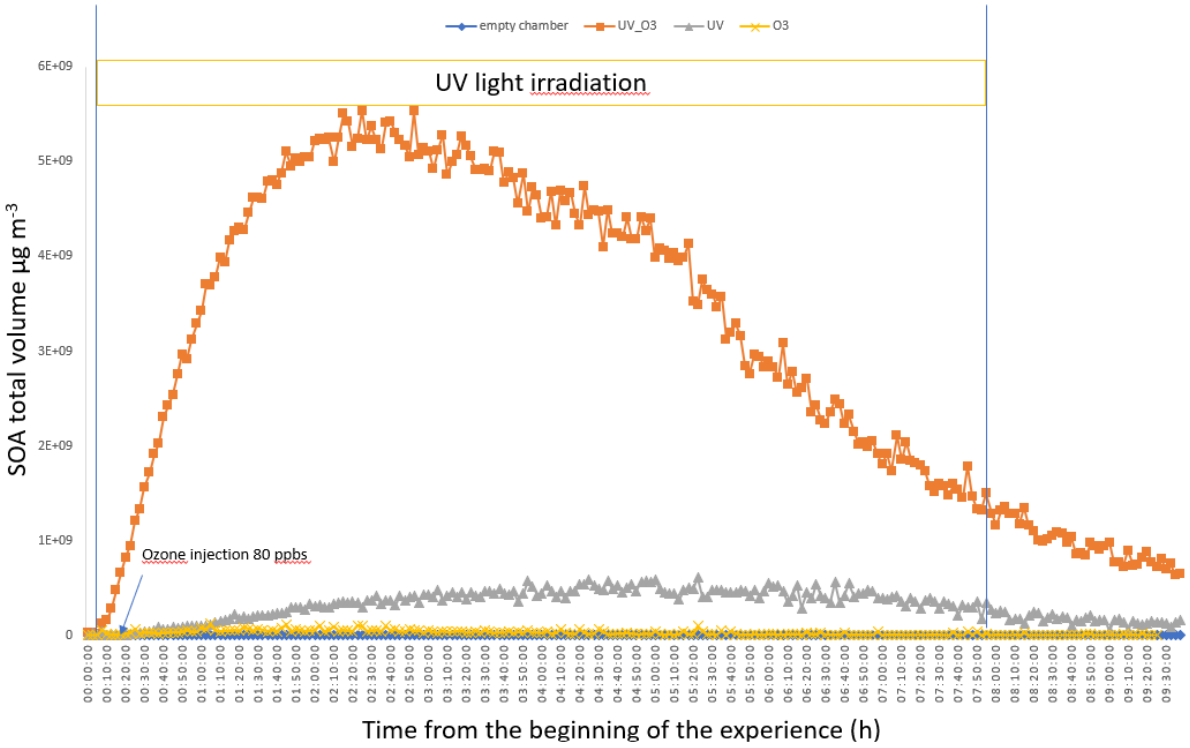
L. 201: how are you calculating any “statistical difference” with an N=1 representing each condition?

The statistical difference in this case refers to the number of days for each condition, and thus the number of samples is N=6.

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?

The particle decrease could be due to coagulation and dilution (due to the flow mode used here). In figure 7, showing SOA formation as a function of particles number concentration, we can indeed see a decrease of the particles number. Below, we report a similar variation using the particle volume, and obviously the same trend is observed. We mainly attribute this variation to a source strength, which is reducing with time, and to the dilution occurring in our chamber. In fact, the chamber was continuously flushed with an air flow to compensate the air withdrawn by the various analysers connected to it.



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.

We changed the Figure 7 by substituting it with the correlation between BVOC emissions and the temperature as reported above. We also agree with this reviewer that the correlation between the SOA and the number of particles does not necessarily mean that the VOC correlated are precursors of the SOA. Therefore, this section was removed.

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.

Comparing the measurements made here with the data of a monitoring station is far from being obvious, as we observed new particle formation events (i.e., characterized with low particle mass but high number concentration) and not the mass of PM1 (typically observed in such networks). Therefore, if we simply extrapolate our data to the regional conditions, it will show that these data have little to no significance when considering the particle mass, but a major one when it comes to number concentration. However, such extrapolation would not be scientifically sound, as only a mesoscale modelling approach would allow a proper assessment of the associated regional importance. However, this was clearly beyond the scope of this investigation, submitted as a measurement report.

Technical Comments

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

We thank the reviewer for the comment. We will follow that advice i.e.; a professional proofreading service will correct our English in the revised manuscript.

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