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Reply on RC1

Letizia Abis et al.

Author 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.,
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This paper presents the emission of biogenic volatile organic compounds (BVOC) from rapeseed leaves litter under three different experimental conditions i.e. under UV light irradiation, in presence of ozone, and under simultaneous exposure to ozone and UV light irradiation. The experiments were carried out in a simulation chamber containing leaves litter collected nearby Paris in north of France.

The most emitted compound was methanol followed by acetaldehyde, acetoin and acetone in O₃ and UV-O₃ conditions. Surprisingly, isoprene was the 30th most emitted compound only in the experiment without presence of O₃. The BVOC emission influenced the secondary organic aerosol (SOA) formation process. In the presence of both UV light and O₃ the SOA formation was 9 and 52 higher than only UV light or ozone.

To my opinion this manuscript can be of broad interest for the atmospheric chemistry community, and it can be published in ACP. I have few comments that can possibly improve the quality of the manuscript prior to be published.

We would like to thank this reviewer for his/her insightful and helpful comments. They have helped us to improve our manuscript. Hereafter, please find our answers.

Main comments:

- In the "Experimental procedure" it is not clear how many experiments were performed (it is ambiguous for the blank experiments and missing for the experiments themselves). The authors should clearly state upon how many replicates are based their conclusions and provide a table for various initial conditions and main results.

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. Replicate experiments are difficult to be performed in this case since other samples would 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 nine 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., O₃, 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. Therefore, the BVOC data are the average of these replicas. However, due to a SMPS failure, only one replica by condition was available.

Table 1 below summarizes the different experimental runs performed in this study. For each selected conditions, blank experiments were made for 3 days under the same conditions and subtracted from the following experiments.

Table 1. List of experiments performed (each repeated twice), according to sample weight and surface covered

	Experimental conditions	Colza weight	Surface covered	Days of VOC detection	Days of SOA detection	Blank conditions
UV light	7h per day of irradiation with UV	Initial weight: 85 g, Weight after 6 days 52 g	Initial surface covered: 0.64 m ² Surface covered after 6 days: 0.45 m ²	6	1	3 days averaged with 7h per day of irradiation with UV
Ozone	Initial concentration of ozone injected in the chamber: 80 ppbv	Initial weight: 80 g, Weight after 6 days 49 g	Initial surface covered: 0.64 m ² Surface covered after 6 days: 0.45 m ²	6	1	3 days averaged with an initial concentration of ozone injected in the chamber of 80 ppbv
UV light and ozone	Initial concentration of ozone injected in the chamber: 80 ppbv, 7h per	Initial weight: 80,7 g, Weight after 6 days 47 g	Initial surface covered: 0.64 m ² Surface covered	6	1	3 days averaged with an initial concentration of ozone injected in

day of
irradiation
with UV

after 6 days:
0.45 m²

the chamber
of 80 ppbv
and 7h per
day of
irradiation
with UV

- Sometimes, the analysis are oversimplified. Some key measurements are not given, and the literature survey is not wide enough.

We added new data our measurements such as temperature, relative humidity, and pressure inside the chamber. Also, we expanded the literature survey on Rapeseed and associated VOC emissions, which now reads as:

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 the fifth producer worldwide of this specific crop (Fischer et al., 2014).

The development cycle of rapeseed is divided into 3 phases: 1) the vegetative; 2) the reproduction and 3) the 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).

The experimental section was also revised, in order to include more information.

- The authors should have tried to better define the behaviour of the chamber walls toward the air/light system. This is a valuable exercise which is required for most of the chamber application. There is no information about the estimated water quantity adsorbed on the Teflon wall or about the VOCs adsorbed on the wall.

The dynamic chamber used in this study was made fluorinated ethylene propylene film, FEP. This material is inert and is widely used in the literature in the analysis of BVOC from vegetation (Peron et al., 2021; Timkovsky et al., 2014). This measurement report did not aim at providing a full characterization of the chamber, but rather to provide new insights on the emissions from Rapeseed litter. This chamber have been already documented in the literature (Alpert et al., 2017; Bernard et al., 2016). But obviously, this reviewer is correct, wall effects are always important, and previous research has shown that time scales for organic monoacids to equilibrate with Teflon chamber walls occurs on the order of minutes (Krechmer, et al., 2016). Therefore, experimental time scales here allowed for equilibrium adsorption-desorption conditions. However, the chamber was run in a dynamic (i.e., flow) mode where the chamber was continuously flushed with an airflow to compensate the air withdrawn by the various analysers connected to it. Such conditions limited, while not removing them, the impact of wall losses and lead to fast response times of the chamber due to external stimuli (light, ozone, etc.). In addition, at the end of each experiment, the chamber was scrubbed using ethanol, then rinsed with water and dried thoroughly before each experiment. Under such conditions and by monitoring the blank levels of VOCs, we can state that the wall conditions were constant and maintained at a low level.

- Is the temperature constant during the chamber experiments?

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 O₃ only. We now added figures showing the temperature variations for all three experimental conditions in Appendix - A.

Minor comments

- As the wall material seems to have a significant importance, please provide the precise reference of the material: producer, ref number, and product name.

The chamber is made of fluorinated ethylene propylene film, FEP, obtained from Katco UK (Dupont FEP, 100µm thick).

- As the Teflon foil (FEP) is new and used just before the preliminary experiments how the blank experiments were distributed during the campaign? If, they were evenly distributed among experiments, did you notice any evolution of the wall chemical behaviour?

The blank was recorded during three days before each experiment. At the end of each experiment, the chamber, has been cleaned up with ethanol and flushed with an air flow of 60L/min to avoid any background effect from the previous experiment. We can say, looking at the evolution of the VOC concentration of the blank, that if any evolution of the chemical behaviour happened was negligible. The chamber is made of fluorinated ethylene propylene film, FEP, obtained from Katco UK (DuPont FEP, 100µm thick).

- Adsorbed organics on the chamber wall can also come from the foil production process.

As stated above, the background level of VOC was monitored through the various blank measurements and the chamber regularly cleaned (see above). Under such conditions, the impact of walls was maintained at a low level.

The section "Atmospheric Implications" and "Conclusion" can be combined as they are both very short or strengthen the "Atmospheric Implications" with some examples.

We agree with this reviewer, we merged both sections.

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