

### Overall comments:

The study by Harb et al. investigates the formation of secondary organic aerosol (SOA) from oxidation of  $\alpha$ - and  $\beta$ -phellandrene by nitrate radicals ( $\text{NO}_3$ ). This oxidation pathway denotes an important oxidation and SOA formation pathway during nighttime. The experiments are carried out in the laboratory and a suite of instruments is deployed to characterize both particle and gas phase during their experiments. The authors find relatively high SOA yields for both precursors studied and considerable fraction of condensed phase organic nitrates. Reaction mechanisms are proposed and cross reactions of  $\text{RO}_2$  radicals ( $\text{RO}_2 + \text{RO}_2$ ) are found to be a dominant for the conditions of their laboratory experiments. Overall, I find this study to be an important contribution to the literature of SOA formation by  $\text{NO}_3$  oxidation, which compared to oxidation of VOCs by OH or  $\text{O}_3$  is understudied.

The manuscript is very well written and structured, allowing the reader to follow the analysis of the experimental results and the interpretation thereof. I therefore recommend publication of this manuscript, after the authors have addressed the few specific comments that I list below.

We would like to sincerely thank the reviewer for the time spent reviewing our manuscript and for the thoughtful comments provided. We appreciate the positive feedback on the study and the structure of the manuscript. We have carefully considered all of the reviewer's comments and suggestions and have made revisions accordingly.

### Specific comments:

**L100-104:** More quantitative information should be added to the emission strength of  $\alpha$ - and  $\beta$ -phellandrene. Knowing the area covered by the stated Eucalyptus species is good to know, but I am curious how much vapors get emitted into the atmosphere of a given VOC type. How does this compare to other major SOA precursors such as  $\alpha$ -pinene? What is the global atmospheric relevance of the systems studied? Please extend the discussion in the manuscript

The paragraph has been modified following the reviewer's recommendation (L100-111): *"Among all emitted monoterpenes,  $\alpha$ -phellandrene has been identified as a major component in extracts and emissions from numerous Eucalyptus species (Li, Madden, and Potts 1995; Maghsoodlou et al. 2015; Maleknia, Bell, and Adams 2009; Pavlova et al. 2015; He, Murray, and Lyons 2000), which are the most widely planted hardwood forest trees on the global scale (>20 million ha) (Myburg et al. 2014). It can account for up to 21% of the monoterpene emission rate in some Eucalyptus species (He, Murray, and Lyons 2000). To our knowledge, while no global annual emission data are available for  $\alpha$ -phellandrene, it is listed among the most frequently emitted monoterpenes in the EMEP/EEA air pollutant inventory Guidebook (2023).  $\beta$ -phellandrene is a major contributor to emissions from coniferous trees, such as Scots pine and Norway spruce (Hao et al. 2009; Janson 1992; Joutsensaari et al. 2015; Ylisirniö et al. 2020; Yassaa et al. 2012). Yassaa et al. (2012) showed that it can constitute approximately 27 % of the total isoprenoid emissions from Scots pine and 15 % of the monoterpene emissions from Norway spruce.  $\beta$ -phellandrene is also considered as one of the major emitted monoterpenes, with a global annual total emission estimated at  $1.5 \text{ Tg yr}^{-1}$  (A. B. Guenther et al. 2012b; "EMEP/EEA Air Pollutant Emission Inventory Guidebook" 2023)."*

**L117:** It is not obvious to me how the low level of electrostatic charges on the chamber wall leads to longer aerosol lifetime in the chamber? I assume this is due to reduced diffusional loss? Please extend the discussion and provide appropriate references.

Electrostatic charges contribute to attracting the aerosol particles, which are charged, to the chamber walls. This has been shown in several papers (Wang et al., 2018; Charan et al, 2018). In particular, Charan et al. (2018) studied the charge effect on the rate of particle wall deposition, estimating both the eddy-diffusion coefficient and the average magnitude of the electric field within their chamber. These electrostatic effects were shown to be important in Teflon chambers, thus affecting the aerosol lifetimes. They are shown to be smaller in stainless steel reactors. More information can be found in the book entitled “A practical Guide to atmospheric simulation chambers” (<https://doi.org/10.1007/978-3-031-22277-1>) (Doussin et al., 2023). This reference has been added in the manuscript (L126).

**L215-219: In Section 2.3, I would appreciate it if the authors could be a bit more quantitative. E.g., What was the air flow rate over the crystals? Over which range was the temperature varied/adjusted? This information could easily be added to the text.**

We thank the reviewer for this suggestion. The optimal conditions for the cold bath temperature were between 203 K and 193 K, and for the flow rate over the N<sub>2</sub>O<sub>5</sub> crystals, between 0.5 and 3 L min<sup>-1</sup>. This missing information has now been added to the text in line 228 for clarity:

*“The rate of N<sub>2</sub>O<sub>5</sub> injection was optimized by varying the temperature of the cold bath (**between 203 K and 193 K**) and the air flow rate (**between 0.5 and 3 L min<sup>-1</sup>**) in order to allow a progressive and complete consumption of the monoterpene.”*

**L225: “organic nitrate yield” use the introduced acronym, i.e.: “ON yield”**

Thank you for pointing this out. The modification has been made.

Table 1:

**- Please add information about what the stated values and the range indicated by “±” means to the Table caption. How is this uncertainty calculated?**

Thank you for your comment. To address the request, we have updated the table caption by adding *Absolute uncertainties are indicated after “±”*.

All the uncertainties presented are absolute uncertainties (A.U.). The calculation of relative uncertainties (R.U.) is described in Section 2.4.

- For YONg (FTIR), see lines 234-236:

$$\begin{aligned} \text{Total R.U. on YONg (FTIR)} \\ = \text{R.U. on the slope} + \text{R.U. on the IBI of ONs} + \text{R.U. on the IBI of the BVOC} \end{aligned}$$

- For YONp (FTIR), see lines 238-239:

$$\begin{aligned} \text{Total R.U. on YONp (FTIR)} \\ = \text{R.U. in the spectra analysis} + \text{R.U. on the IBI of ONs} \\ + \text{R.U. on the IBI of the BVOC} \end{aligned}$$

- For YONp (ACSM), see lines 251-252: R.U. on YONp (ACSM) = 20 %
- For YSOA, see line 265-266: R.U. on YSOA = R.U. on the slope
- For YON(p+g) molar: Total R.U. ON YON(p+g) was calculated as the sum of the total R.U. on both YONp and YONg
- For YONp/YSOA : Total R.U. on YONp/YSOA was calculated as the sum of the total R.U. on both YONp and YSOA

**- Please decide if you want to report your SOA yields as percent values (see my comment below to Fig. 2).**

The modification has been made. All yields in Table 1 are now reported in % units

**L299-301:** “... allowing a good fit using only one class of products.” How can I see this from your Fig. 2? Is it possible to add a fit line (e.g., as dashed line) to your Fig. 2 where you only use the term for the first class of products of eq. (4)? To visualize this effect.

To address the reviewer’s suggestion, we have added a dashed fit line to Figure 2, representing a fit using only the first class of products from Eq. (4). As shown in the updated figure, the fit remains unaffected. This visualization helps to clarify the point made in lines 320-321: “... allowing a good fit using only one class of products.”

**L304:** Replace “Odum parameterization” with “eq. (4)”

The modification has been made. (L324)

Fig. 2:

- SOA yield is not given in units of %, as suggested by the y-axis. In general, I find it hard that you switch back and forth between yields given in percent vs. fractional values between Table 1, the Figures and the text. I would encourage you to choose e.g. %-values and consistently use these throughout.

We apologize for the confusion regarding the units of SOA yield in Figure 2. The y-axis in Figure 2 now corresponds to YSOA in % units. For consistency, all yields in Table 1 are also now reported in % units, as suggested.

- Left-side panel: The x-axis is cut, the upper limit should be “450”, not “45”.

Thank you for pointing this out. The modification has been made

- Change caption to read on L310: “... colors and Odum parameterization corresponds to the black solid curves (eq. 4).”

The modification has been made.

- Please use panel labels (a), (b), ... for this figure as you do in Fig. 1, for consistency.

The modification has been made

**L342-342:** “... the total ON concentration in the aerosol phase even though it is associated with large uncertainty due to assumptions made for the data treatment.” What are the assumptions and how large are these uncertainties? These uncertainties are not reflected in the values listed in Table 1 (at least the uncertainties listed there seem small to me), please clarify.

In fact, we are primarily referring to the  $\pm 20\%$  uncertainty mentioned in line 251, which arises from the choice of the  $R_{org}NO_3$  value.

**L347-348:** Please add uncertainties as e.g. “range from  $8 \pm xx$  to  $18 \pm xx$  %” and consider reporting yields in units of % also in Table 1. Also, according to your Table 1 (column Y\_ONp,ACSM) it appears that the smallest ON mass yield was 10% (06/02/2021), and not 8%.

Uncertainties have been added to Lines 367 and 368. Yields in Table 1 have also been updated by using % units. As mentioned in Lines 368-369, the reported range of ON mass yields in the aerosol phase includes data from both techniques (FTIR and ACSM). The value of 8% corresponds to the ON mass yield for the same experiment (now labeled as experiment 6) column YONp FTIR mass in Table 1.

**L350:** add “can reach up to approximately 50%.” (the largest yield value in Table 1 is 0.47)

This modification has been made (L371).

**L356: “plot reveals a non-zero slope at the origin”. It is unclear to me what you mean here?**

In Figure 3, the X-axis represents the amount of reacted MT, while the Y-axis represents the concentration of ONs formed. The slope at the origin is not zero indicating that ONs are produced immediately and proportionally as MT is consumed, consistent with the behavior of first-generation products. If ONs were secondary products, their formation would depend on intermediates or additional reaction steps. In such a scenario, the slope near the origin would approach zero, as no ONs would form until intermediates accumulated. The observed linear relationship, starting with a measurable slope at the origin, supports the conclusion that ONs are primary products.

The sentence has been rephrased in the manuscript to make it clear.

**L361: “to be less than 10%”. On L197 you claim less than 5%, please choose appropriately.**

The difference arises because the values refer to different aspects of the study. In Line 205, the "less than 5 %" refers to the particle wall loss, whereas in Line 383, the "less than 10 %" corresponds to the wall losses estimated for gas-phase organic nitrates.

**L450: Looking at your Fig. S2 it appears that some of the traces slope downwards. On L194 you state that your data is wall loss corrected, so I would have expected the traces in Fig. S2 to stay constant at a certain value, after the initial increase. Why is this not the case?**

The wall loss correction was applied to the particle phase, as mentioned in Lines 202-204, and no correction for wall loss was performed for the gas phase products. Wall losses for organic nitrates were estimated to be less than 10 % as previously mentioned. As indicated in Lines 294-295, the concentration of  $\text{N}_2\text{O}_5$  remains below the detection limit of the FTIR spectrometer until the BVOC is completely consumed. After this point, the  $\text{N}_2\text{O}_5$  concentration increases, reaches a maximum, and then decreases (Fig. 1.a). Since  $\text{N}_2\text{O}_5$  is the source of  $\text{NO}_3$ , we still have  $\text{N}_2\text{O}_5$  in the chamber after the oxidation of the BVOC. This could lead to further oxidation of these compounds and may explain the observed downward slope in some of the traces in Figure S2.

**L464: I cannot find any “Table 3”.**

We thank the reviewer for pointing this out. This was indeed a mistake, and the reference to "Table 3" has been corrected to "Table 2" in the text.

**L470: Please put comma in front of “which” (almost always)**

This modification has been made.

**L477: note correct formatting of parenthesis: “(e.g. Shen et al., 2021)”.**

This modification has been made (L504).

**L494: Delete “recent”**

This modification has been made.

**L508: “Remarkably, following the drop of the dimer signals to zero, the number of particles formed, and their total mass reached their peak values.” (and your statement on L518-519) Can you visualize this by adding traces for the particle mass concentration of e.g., your SMPS data to Fig. S2?**

In response to the reviewer’s suggestion, we have added the particle mass concentration, based on the SMPS data, to Figure S2.

**L527: Replace “which” by “that” (also on L546)**

This modification has been made (L567 and L547).

**L529: Would it be more appropriate to say “...also contribute to SOA formation and growth.”? Other-wise, how do you disentangle formation and growth from your experimental data?**

Thank you for pointing this out.

Based on our experimental data, we observe that the temporal profile of dimers shows a rapid increase once BVOC oxidation begins (Figure S2), followed by a rapid decrease in their signals, coinciding with an increase in particle size and number/mass concentration. Additionally, dimers are also detected in the particle phase. This suggests their participation in the formation and/or the growth of SOA but we agree with the reviewer that we cannot distinguish their contribution in both processes. The sentence has been modified accordingly by replacing “formation and growth” by “formation and/or growth”. The final sentence is *“this rapid decrease of dimers coincides with the particle formation, suggesting that HOMs dimers also contribute to SOA formation and/or growth”*.

**L573: “... constitutes of the SOA, ...” I feel it would be more appropriate to say “particle phase” here instead of SOA, at least this is how I understand your statement. Might be good to clarify your statement here.**

This modification has been made (L595).

In our experiment, SOA and the particulate phase are effectively the same, as no seed particles were used. Additionally, ACSM data confirmed that the particles consist predominantly of organic constituents.

## **References:**

- Charan, S.M., Kong, W., Flagan, R.C., Seinfeld, J.H., 2018. Effect of particle charge on aerosol dynamics in Teflon environmental chambers. *Aerosol Science and Technology* 52, 854–871. <https://doi.org/10.1080/02786826.2018.1474167>
- Doussin, J.-F., Fuchs, H., Kiendler-Scharr, A., Seakins, P., Wenger, J. (Eds.), 2023. *A Practical Guide to Atmospheric Simulation Chambers*. Springer Nature. <https://doi.org/10.1007/978-3-031-22277-1>