

Review of Li et al.

Andrew Lambe (Referee)

Referee comment on "Isothermal evaporation of α -pinene secondary organic aerosol particles formed under low NO_x and high NO_x conditions" by Zijun Li et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-285-RC2>, 2022

Li et al. measured the humidity-dependent evaporation rate of SOA particles generated from the photooxidation of alpha-pinene in the presence and absence of added NO_x . Detailed chemical composition and volatility information was obtained using a FIGAERO-CIMS, and positive matrix factorization was applied to identify volatility-resolved classes of oxidation products, including organic nitrates. This study is an extension of similar/previous work performed by the Kuopio research group. I would support eventual publication after consideration of my comments below.

- The authors examine correlations between VFR in the residence time chamber and FIGAERO-CIMS characteristic thermal desorption temperature (T_{50}). Ultimately, only the FIGAERO-CIMS thermograms were used to infer the SOA volatility distributions. These SOA volatility distributions can likewise be derived from the evapograms and compared/contrasted with thermogram-derived volatility distributions, as has been done previously by this group (Tikkanen et al, 2020). In my opinion, a similar analysis should be done here. While adding NO_x to generate organic nitrates is certainly a novel component of this study, a significant portion of the results was dedicated to the analysis of the isothermal evaporation of alpha-pinene SOA under low- NO_x conditions, which has already been published in various forms (e.g. Buchholz et al, 2019; Li et al., 2021). Comparing C^* distributions obtained via evapograms and thermograms is a logical addition to this paper that will increase its impact by investigating the utility of evapograms as inputs to chemistry and climate models.
- **L88:** This is not an accurate description of the N_2O -based photochemistry that occurs in the OFR254- $i\text{N}_2\text{O}$ mode because N_2O does not photolyze significantly at 254 nm. Rather, NO and NO_2 are generated from the reaction: $\text{N}_2\text{O} + \text{O}(^1\text{D}) \rightarrow 2\text{NO}$ and $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$. In OFR185- $i\text{N}_2\text{O}$, however, note that N_2O photolysis at $\lambda = 185$ nm can generate NO via $\text{N}_2\text{O} + h\nu_{185} \rightarrow \text{N}_2 + \text{O}(^1\text{D})$ followed by $\text{N}_2\text{O} + \text{O}(^1\text{D}) \rightarrow 2\text{NO}$.
- **L90:** The OH exposure should be in units of molecules cm^{-3} s, not molecules cm^{-3} .
- **L90-L92:** NO_3 radicals are also generated using the OFR254- $i\text{N}_2\text{O}$ method ($\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$). Please add the appropriate NO_3 -based reactions that are listed in Palm et al. (2017) or Lambe et al. (2020) to the photochemical box model that was (presumably) used here. Then, calculate the NO_3 exposure values over the range of OFR254- $i\text{N}_2\text{O}$ conditions that were studied, and report the fractional oxidative loss of α -pinene to OH, O_3 , and NO_3 . For example, the fractional loss of α -pinene due to reaction with OH would be: $f_{\alpha\text{Pinene_OH}} = k_{\text{OH}} * \text{OH}_{\text{exp}} / (k_{\text{OH}} * \text{OH}_{\text{exp}} + k_{\text{O}_3} * \text{O}_{3\text{exp}} +$

$k_{\text{NO}_3} * \text{NO}_{3\text{exp}}$). Was IN_2O_5^- observed in the gas-phase iodide-CIMS spectra that were obtained for "fresh" samples?

- **L93:** Please provide a reference justifying the assumed SOA particle density of 1.5 g cm^{-3} .
- **L94, L97:** Is "ug/cm3" a typo (?) ($0.1 \text{ ug/cm}^3 = 10,000 \text{ ug/m}^3$)
- **L104:** "gas vapors" seems superfluous
- **L119:** Add space between "as" and "("
- **L162:** Please quantify "similar" in this context.
- **L183:** In the OFR254-i N_2O mode, NO is generated via $\text{N}_2\text{O} + \text{O}(^1\text{D})$ reactions, not N_2O photolysis – see comment #2
- **L251-L270:** This text should be moved to methods or the supplement
- **L286:** I disagree that a "negligible amount of HNO_3 [is] produced in the OFR" – while gas-phase I-CIMS spectra were not presented here, my guess is that IHNO_3^- (or NO_3^-) is probably the largest signal in spectra obtained under OFR254-i N_2O conditions as it is continuously generated via $\text{OH} + \text{NO}_2$. I suggest using the photochemical model to constrain $[\text{HNO}_3]$ that is obtained at the OFR254-i N_2O conditions that were used here, then compare to the HNO_3 concentrations that are necessary to initiate/catalyze heterogeneous reactions before concluding they are too slow to occur.
- **L446-L451:** It would be useful to add a brief discussion of the atmospheric implications of these results, especially in regards to the higher evaporation rate of $\text{C}_x\text{H}_y\text{O}_z\text{N}$ compounds (relative to $\text{C}_x\text{H}_y\text{O}_z$) that are formed from BVOC oxidation in the presence of NO_x and what this means for the SOA formation potential in (sub)urban regions compared to pristine conditions.
- **Figure 1** -"Volume Fraction Remaining" axis label is ambiguous - I know from reading the paper that this refers to the SOA VFR, but someone who just looks at the figure might not make this connection. "RTC" is not defined in the caption text, and it may not be obvious to the reader that "Residence Time" refers to the RTC residence time - please clarify this. The legend and/or caption needs to be clarified to indicate that "low- NO_x " and "high- NO_x " labels refer to the photochemical conditions in the OFR, rather than RTC conditions; and "RH" should be added to the "dry (<7%)" label
- **Figure 1:** I know what an evapogram is, but as far as I can tell this term is not formally defined in the manuscript.
- **Figure 1:** It would be useful to overlay a subset of "evapograms" from Buchholz et al. (2019) and/or Li et al. (2021) (or related studies). Alternatively, a table could be added to compare evaporation rates across these studies and others (e.g. Vaden et al.), perhaps by treating the SOA evaporation a first order process for comparison purposes.
- **Figure 2e:** Clarify that the x-axis label refers to **SOA** chemical composition.
- **Figure 2 caption, line 1:** Indicate that thermograms shown here and elsewhere were obtained from the FIGAERO-CIMS.
- **Figure 2 caption, line 2:** add "RH" or perhaps change to "low RH" to more closely parallel "high RH (80% RH)" conditions. or change "high RH" to "humid"
- **Figure 3:** Here again, and elsewhere in the text and other figures, I would note that the "low- NO_x " and "high- NO_x " labels refer to the OFR conditions rather than the RTC conditions, and note that the "desorption temperature" is associated with the FIGAERO-CIMS.
- **Figures 3 and 5:** With Fig 1 already in place to show how volatility information is extracted from thermograms, I think adding more thermograms in the main paper makes Figures 3 and 5 unnecessarily complex. I would instead show something more like Fig 1e here, i.e. a 4-panel figure plotting T_{50} for each of the factors, one panel each for low- NO_x /fresh, low- NO_x /RTC, high- NO_x fresh, high- NO_x Then add the factor thermograms to the supplement for the advanced reader.
- **Figures 4 and 5:** What does "normalized fraction" mean, and why is it negative for some species? I assume these figures are showing difference spectra that subtract "fresh" spectra from "RTC" spectra (?) but this should be clarified.
- **Figure 4:** It seems more accurate to refer to the "average m/z" rather than "average MW" because a) the FIGAERO-CIMS is not necessarily detecting all of the SOA mass

- and b) thermal decomposition of larger-MW products may bias low the calculated MW.
- **Figure 4:** I suggest adding the " T_{50} " (and/or C^*) value for each factor to the legend. Along with earlier Figure 3 comments, this addition to Figure 4 might allow the authors to move Figure 3 entirely to the supplement.
 - **Figure 6:** This figure would be easier to interpret if the signal fractions for F1-F5 in low- NO_x and high- NO_x OFR cases were presented as pie charts. Each pie chart could then just show the total "estimated mass concentration" for the low- and high- NO_x SOA above or below it.
 - **L251-L270 and Figure 6:** It's not clear to me why the summed gas + condensed phase signal is derived in the text and referred to in the figure when the separate gas/particle phase partitioning fractions are never discussed? Presenting and discussing the fraction of signal in gas and condensed phases as a function of C_{OA} seems like it would be a logical extension of the volatility information obtained from the FIGAERO thermograms.
 - **Figure 7:** Why are there only 3 symbols for F1 (no 'high RH RTC case') but 4 symbols for each of the other factors?
 - **Figure 7a:** Why not put SVOC, LVOC, ELVOC text labels at the top of the figure along with the colored bars (as was done with Fig 2)? Similarly, it might be useful to show C^* on a secondary axis parallel to T_{50} as was done earlier.
 - **Figure 7b:** What do the 'x' symbols represent in the top (F1) panel?
 - Can you come up with a brief name/description for each of the factors so that when information about F1-F5, etc. are presented in subsequent figures, it's easier to make a connection as to what they represent?
 - Repeatedly using the terms "non-nitrated" and "nitrated" is cumbersome – perhaps consider using " $\text{C}_x\text{H}_y\text{O}_z$ " and " $\text{C}_x\text{H}_y\text{O}_z\text{N}$ " descriptors instead (after defining them once).

References

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