Overall comment:
This work examined the composition and volatility changes of SOA formed from NO3 oxidation of three biogenic VOCs upon UV photolysis. This study used two state-of-the-art SOA molecular analysis instruments, FIGAERO-CIMS and EESI-TOF to examine the SOA composition change before and after photolysis. The authors also compared a few methods that were used to estimate SOA bulk volatility. The SOA compositions were shown to be very interesting that the oligomer fractions were extremely high (higher than ever reported for SOA systems) for all the three biogenic VOCs. The comparisons of bulk volatility estimates lead to a conclusion that SOA that largely contain nitrate groups are highly uncertain. Overall, the manuscript was well written, and the experiments and analyses were carefully carried out. However, there are some major concerns regarding the interpretation of the instruments and chemistry in the NO3 oxidation. These concerns should be addressed before the manuscript can be published in ACP.

Major comments:
1. Line 134 – 139. The determination of negligible fragmentation fractions due to thermal desorption is unclear. For a certain m/z or fitted chemical formula, FIGAERO-CIMS can usually produce an overall thermogram with a broad peak or peaks, each of which can be integrated by a number of individual species' thermogram peaks (Schobesberger et al., 2018, ACP). Deconvoluting the individual peaks might involve large uncertainties. When there is more than one broad peaks, it is apparent that the later broad peak is from thermal decomposition of a much lower volatility compound such as dimers (e.g., Figure S2a). But thermal decomposition peaks can also be hidden under the same broad peak, especially when the parent compound and the fragmentation compound have more close volatilities. For example, assuming a compound with formula CxHyOzN undergo thermal decomposition (dehydration) and produces CxHy-2Oz-1N, the decomposition product could be difficult to separate from original CxHy-2Oz-1N in the broad thermogram peak. The two steps described in the supporting information may not be able to identify such thermal decomposition. Therefore, the percentage ranges provided in Line 134 – 135 are likely the lower estimate of the thermally labile species in these SOA.

2. This is a related questions regarding thermal decomposition. In NO3 + biogenic VOC oxidation systems, it is likely common to have PAN species from RO2 + NO2 (NO2 as a byproduct from N2O5 decomposition). PAN species are very thermally labile and produce RO2 + NO2. This may happen even under moderate heating temperatures. Do the authors have a clue to what extent this chemistry has happened in FIGAERO-CIMS? This class of species was not mentioned throughout the manuscript.

3. Line 177. The authors clarified how particle mass concentration was corrected for wall loss and coagulation. But it is unclear how the ion signals from FIGAERO-CIMS and EESI-TOF were corrected, especially for coagulation. Can the detail be elaborated?

4. The reported oligomer fractions are very high in this work. In fact, I have not seen any studies reporting such high fractions of oligomers and wonder what could have caused these results. For the a-pinene + NO3 system, Nah et al. (2016 ES&T) found that the majority of the SOA was made by monomers. The discrepancy could be due to two different conditions:

(i) Nah et al. used much lower VOC (~ 10 ppb) vs. 100 ppb in this work; and
(ii) Nah et al. had RO2 + HO2 as the dominant condition vs. RO2+RO2 in this work;
But even these differences are responsible for the large oligomer fractions reported in this work, how is it possible that monomer products from RO2 + RO2 did not partition and form SOA? The SOA mass loadings were still > 10 ug/m3. Some discussion or explanation should be provided.

5. Line 304 and 310. Can you elaborate why CHO compounds were more prominent in EESI-TOF and what "degradation pathways" were referred to? In principle, the FIGAERO-CIMS requires heating and should be more likely to decompose CHON compounds than the EESI-TOF.

6. Can the authors show the changes of particle-phase N2O5 and HNO3 signals (FIGAERO-CIMS) under the various conditions? Since N2O5 is likely in excess and the experiments were carried out under humid conditions, it is interesting to see how N2O5 uptake might have affected the chemistry. In fact, the chemical compositions shown in Figure 2 have many peaks with 3-4 N in the formulas. Could they have to do with particle-phase chemistry related to N2O5 uptake, rather than just gas-phase oxidation?

7. SOA volatility. The authors compared a number of methods to estimate SOA volatilities and the results are very different. The authors concluded that the molecular formula derived parameterization is highly uncertain, especially for the compounds with multiple nitrate groups. Can the authors break down the comparison by #N? For example, how different are the methods for species with 0-4 nitrogen atoms? Also, dimers with multiple N atoms were found to have similar Tmax as monomers. Could this be real or some unrecognized artifact in FIGAERO-CIMS? If this were true, it somewhat contradicts the earlier discussions regarding evaporation of SOA after photolysis.

Minor comments:

1. Line 91. Change "outside" to "out".

2. Line 407 – 408. Some evidence to support this statement should be added.