Response to Referee Comment 1 (RC1) on 'Effect of temperature on the formation of Highly-oxygenated Organic Molecules (HOM) from alpha-pinene ozonolysis" by Lauriane L. J. Quéléver et al.

"This study investigates the temperature effect on the formation of highly oxidized molecules (HOMs) from the a/b-pinene ozonolysis. The authors found that temperature plays a controlling role in the yields of HOMs: the molar yields dropped by around a factor of 50 when experiments were performed at 273 K, compared to 293 K. Interestingly, the distribution of HOMs molecules is not significantly affected by the temperature, that is, the formation rates of more oxidized HOMs did not decrease more than the less oxidized HOMs. A possible explanation, as the authors proposed, is that the rate limiting step forming these HOMs occurs before the products become oxygenated enough to be detected by the CIMS instrument used in this study. Overall the paper is well written and approaches an important aspect of atmospheric nucleation processes. Yet there seem to be various uncertainties in the quantitative representation of HOMs formation and comparison under different temperature scenarios, see detailed comments below."

We thank the reviewer for the positive feedback and will answer the comments point-by-point below:

Comment 1: **"Temperature plays a governing role in the SOA formation by affecting the vapor pressure of the condensing molecules. The vapor pressure of any given molecule may decrease by orders of magnitude as the temperature drops to certain degrees. As a result, the SOA yield from the oxidation of a given hydrocarbon like a-pinene at low temperature (e.g., -15 C) is expected to be significantly higher than at room temperature. This in turn provides more surface area to absorb more organic vapors from the gas phase to the particle phase. It is therefore not surprising that the observed gas-phase concentrations of HOMs are lower at low temperature. However, the authors did not take into account of this effect when drawing the conclusion that 'the HOMs molar yields dropped by around a factor of 50 when experiments were performed at 273 K compared to 293 K'. The vapor pressure and saturation concentration of each HOM molecule can be estimated based on the carbon and oxygen numbers (see 2D VBS paper as an example) in the molecule. With the measured total aerosol mass concentration, the authors should be able to estimate the fraction of each HOM molecule in the particle phase vs. gas phase at equilibrium at different temperatures. Or the authors can compare the calculated condensational sinks at different temperatures and evaluate the impact of changes in condensational sinks on the estimated molar yields of HOMs."**

Reply to Comment 1: The reviewer is correct that a decrease in temperature will decrease the vapor pressure of molecules, thereby forming more SOA. However, in our study, we accounted for this effect by explicitly including the condensation sink (CS) in our HOM yield estimation (see Eq. 2 and section 2.5.). Thus, the reported decrease of a factor ~50 in HOM yield between 20 and 0 degrees already accounts for the difference in CS between the two temperatures.

The condensation sink was calculated for each experiment based on aerosol size distribution measurements with a Scanning mobility particle sizer (SMPS). As an example, in the experiments with [α-pinene] = 50 ppb, 40 min after α-pinene injection, the calculated CS was 6.2 10^{-2} s^{-1} at 20 °C (12-Jan-2017), and 8.1 10^{-2} s^{-1} at 0 °C (16-Jan-2017). In other words, the CS increased ~30 %, while the HOM signals decreased by more than 98%, clearly indicating that the CS is not the main driver for the decreased HOM concentrations. A comparison of the evolution of condensation sinks for a few experiments performed at different conditions is shown below in Figure R1.

Comment 2: "The authors used a simplified expression for the HOMs molar yield (Eq 2). The authors assume that all HOMs molecules are first-generation oxidation products and the only source of HOMs is the apiene+O3 reaction. While this assumption seems reasonable for the monomers, it does not seem to work adequately for the dimers, as shown in Figure 5. In the expression of the condensational sinks, the authors stated that the loss rate on the wall is ~10-3 s-1. Many studies have shown that the loss rate of individual molecules depends on their molecular weight or vapor pressure. Is the value of ~10-3 s-1 representative of the loss rate of monomers or dimers? In the presence of relatively little number of particles at the beginning of low aerosol loading experiments, is the wall loss rate still much lower than the particle condensation rate? Same for the representation of condensation on particles, a single value for the case of C10H16O7 is applied to all HOMs molecules. Have the authors estimated the uncertainties associated with this simplified treatment?"

Reply to Comment 2: We estimate our wall loss rate to be on the order of 10^{-3} s^{-1} based on earlier studies, e.g. Ehn et al. (2014) who measured a value of ~10^{-2} s^{-1} for the wall loss rate of HOM in a 1.5 m^3 chamber with active mixing assisted by a fan. The AURA chamber is ~3 times larger than the chamber used in that study, and without mixing, and therefore the wall sinks for HOM much lower, likely even below 10^{-3} s^{-1}. This value can be compared to the typical CS values during the experiments, e.g. as shown in Figure R1, which are much larger. As also described in section 2.5, based on earlier work, HOM are expected to condense irreversibly onto walls and particles, whether monomers or dimers. Thus, the exact vapor pressures will not influence the loss rates of different HOM. However, the larger dimers will move more slowly, causing their loss rates to be slightly lower than the smaller monomers. The variety of HOM-products formed upon monoterpene ozonolysis includes compounds from 308 Th to 622 Th, with compounds containing 10 to 20 carbon atoms and 7 to 19 oxygens. Figure R2 shows an estimation of the net condensation sink for a few example molecules at 20 °C, with [α-pinene] = 50 ppb (12-Jan-2017). The difference between the smallest monomer and one of the largest dimers is on the order of 30%, which is close to the uncertainty of the CS calculation itself, as the exact structures of the HOM are not known. Hence, we concluded to use the representative value of one of the most abundant HOM for the analysis. We added a sentence to section 2.5 about the uncertainty of a few tens of percent that arises from this simplification. But we again emphasize that this uncertainty is marginal compared to the factor of 50 increase in HOM yield between the 20- and 0-degree experiments.

In Figure 5, which the reviewer refers to, we show the resolved molar yield based on Eq. 2 for each HOM molecule. At 20 °C and 0 °C, the method used showed good results and reliability (goodness of fit indicated by the color coding and sizing of the markers), while at -15 °C, the fits were poor due to the very low HOM signals. We interpret the reviewer's comment about our assumptions "not working adequately for the dimers" to concern the inset figure, where the fit for the dimer shows much more scatter. However, these inset plots merely show examples with $C_{10}H_{14}O_9$ and $C_{19}H_{28}O_{12}$

to better visualize a 'good fit' ($r^2 = 0.99$) and a 'bad fit' ($r^2 = 0.62$) at 20 °C. The quality of the fit is due to the much lower concentration of the dimer in this example, and is not a result of the molecule being a dimer to begin with. This can also be clearly seen from the color coding in Figure 5, where dark blue markers ($r^2 > 0.9$) are abundant also in the dimer range. This result is also in line with the current knowledge of the formation mechanism of these dimers from peroxy-radical cross reactions (e.g. Bianchi et al., 2019), i.e. also the dimers are first-generation oxidation products.

Finally, all our experiments were performed with practically zero initial particles at the beginning of the experiment. Therefore, it is clear that in the first minutes of each experiment, the assumption that CS dominates over the wall loss will not hold. However, at this stage the chamber is still not homogeneously mixed either, and we did not include data from the first 40 minutes in our calculations for the HOM yield. We note that this was not clearly stated in the manuscript and we have now added this information to section 3.4. in the text and in the legend of Figure 5. After these 40 minutes, the CS was always clearly higher than the wall loss rate. E.g., in the case of low VOC loadings (02-Dec-2016), the calculated CS was 1.2 10^{-2} s^{-1} after 40 min.

Comment 3: "It is well-known that HOMs are easily deposited on the chamber wall or the CIMS inlet. However, factors that likely impact the HOMs loss rate are still unclear. Have the authors performed any characterization experiments on the temperature effect on the wall loss rate? For experiments conducted at low temperature, e.g., -15 C, was the chamber air drawn directly to the CIMS inlet? Would the mixing of the chamber air with room temperature sheath air cause any turbulence inside of the inlet? Would any turbulence cause any unstable signals or intensive loss of HOMs?"

Reply to Comment 3: The optimal sampling with the CI-APi-TOF is indeed a challenge when the sample air temperature is different than room temperature, whether the sample is cold ambient air or from a cooled chamber, as in this study. We performed the measurements in a similar way for all temperatures in the chamber, as our larger concern was that sampling colder (i.e. denser) air into the mass spectrometer could alter the pressures, and therefore the performance, of the instrument. In order to assure the validity of our results, we carefully examined the pressures and reagent ion count (RIC) data as described in section 3.1 "Effect of the temperature on the CI-APi-TOF". For the two highest temperatures, the RIC remained the same, but at -15 °C the RIC is slightly lower by roughly 15%. This change is likely due purely to instrumental effects caused by sampling the colder air. However, this change was again minor when comparing to the dramatic changes seen in the HOM concentrations, indicating that changes inside the instrument were unlikely to be the cause for our results.

Concerning turbulence/mixing inside the CI inlet, it is possible that air of different temperatures could cause some additional mixing, but as the reagent ions are pushed electrostatically into the sample air in the beginning of the drift tube, added mixing (leading to losses of HOM) would also cause a similar loss of the reagent ions. This was not observed, and would still, to a certain extent, have been corrected for by the normalization of HOM signals to the RIC. Thus, our observations indicate that instrumental effects could only explain a small fraction of the changes we observed in the HOM yields. We added some more details of the sampling protocol to the manuscript in section 2.4.

Comment 4: **"It seems like experiments conducted at ~30 C are likely more representative of the intensive photochemistry of biogenic emissions at summertime, compared with the conditions in the current study, i.e., -15 C, 0 C, and 20 C."**

Reply to Comment 4: It would certainly be of interest in future work to map out a wider temperature range, with many more points than we were able to in this study. The probed range in this work does cover a large fraction of the expected temperatures in e.g. the boreal forest. We also note that we did not focus on photochemistry, but rather the ozonolysis of monoterpenes, which takes place also during nights.

Additional Figures (For referee comment reply only):

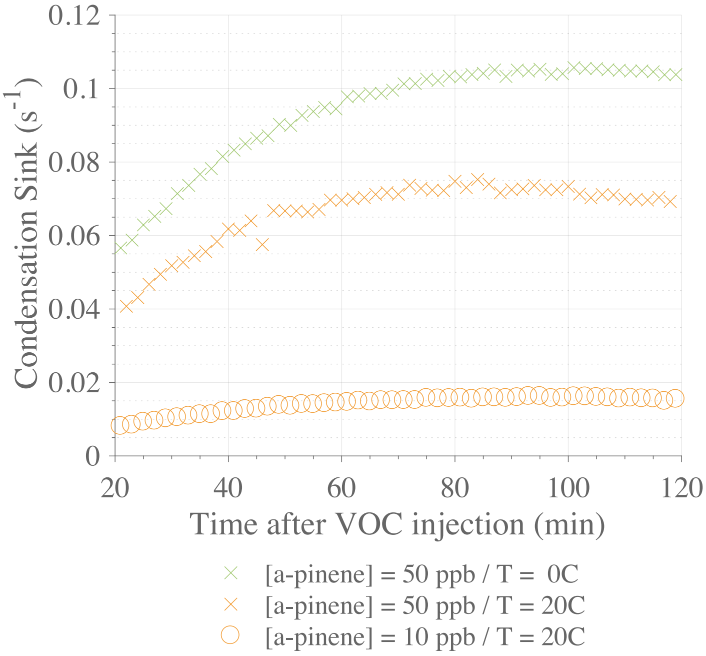

Figure R1: *Comparison of the Calculated condensation sinks over the ACCHA runs. Data shown from 20 min to 120 min after α-pinene injection for experiments performed at 50 ppb at 0 ℃ (16-Jan-2017) - green crosses, and 20 ℃ (12-Jan-2017) – red crosses, and at 10 ppb at 20 ℃ (12-Dec-2016) – red circles.*

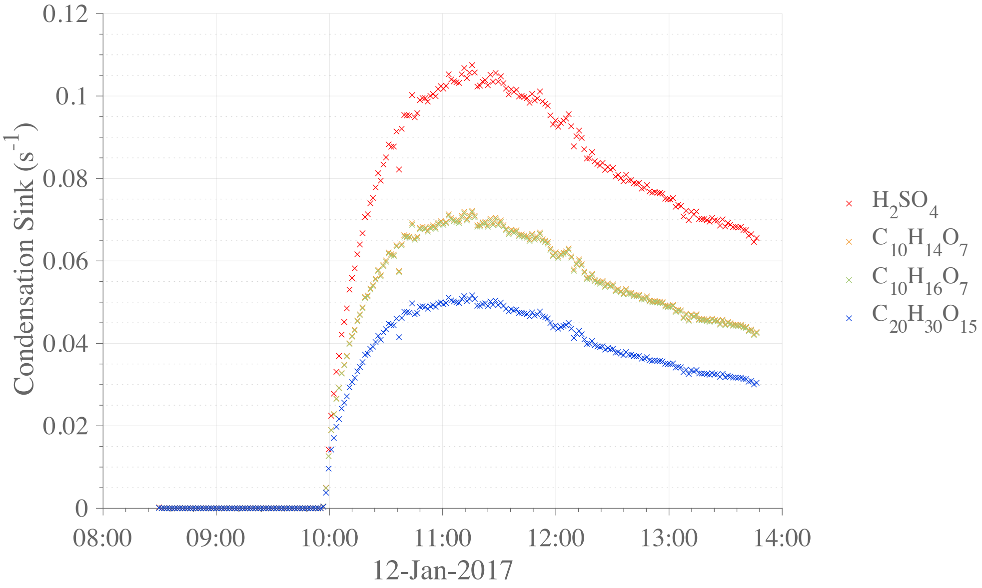

Figure R2: *Comparison of estimated condensation sinks for Sulfuric acid (red crosses),* $C_{10}H_{14}O_7$ *(orange crosses),* $C_{10}H_{16}O_7$ *(green crosses), and* $C_{20}H_{30}O_{15}$ *(blue crosses) during a high loading experiment (i.e. [α-pinene] = 50 ppb) at 20 ℃ (12-Jan-2017).*

References:

Bianchi, F., Kurtén, T., Riva, M., Mohr, C., Rissanen, M. P., Roldin, P., Berndt, T., Crounse, J. D., Wennberg, P. O., and Mentel, T. F.: Highly Oxygenated Organic Molecules (HOM) from Gas-Phase Autoxidation Involving Peroxy Radicals: A Key Contributor to Atmospheric Aerosol, Chemical Reviews, 2019.

Ehn, M., Thornton, J. A., Kleist, E., Sipilä, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., and Lee, B.: A large source of low-volatility secondary organic aerosol, Nature, 506, 476, 2014.