

Response to Reviewer Comments

We gratefully thank the reviewers for the constructive comments and suggestions to improve our manuscript. Reviewer comments are reproduced below and their references to page and line numbers are for the *original* manuscript. Author responses are given in bold and the page and line numbers in our responses refer to the *revised* manuscript.

Reviewer 1

1. The referee questions the “similarity” of the size distributions for polydisperse samples a and d (Table S1 and Figure S1).

Author response: We recognize the confusion caused by our wording. What we meant to say, and have modified the text accordingly on p. 4 lines 22-23, is that fine tuning of the size distribution of the control aerosol was done in order to assure that we had a sufficient aerosol mass concentration at each of the mobility sizes of interest (35, 60, 85, 110 nm) to permit chemical analysis. Fine tuning was required because of the difficulty of generating particles at the smallest mobility diameter using our particular atomizer.

2. The referee asks about the definitions of entries in Table S3.

Author response: We have modified Table S2 to include a footnote for the “Unique Molecular Formulas” column saying that these values represent the average and standard deviation from five replicate samples. Each replicate gives slightly different results, which is why it is important to perform several replicates. (See p. 6 lines 3-5.) The difference among replicates arises mostly from formulas that have very low signal intensities. We also added a new column entitled “Common Molecular Formulas” that gives the number of common formulas observed in all five replicates for a given sample type – these are the formulas that are evaluated and discussed in the results and discussion. This will give the reader a better idea of repeatability of the experiment, and will show that most of the assigned formulas are indeed detected in all five replicates.

3. Referee comment concerning page 7 lines 8-10 and Figures 2a and 2b.

Author response: We modified the legend and caption of Figure 2 (p. 19) to clearly indicate the identities of the markers (NAMS, HRMS(+)) and HRMS(-)), for both size-selected and polydisperse aerosols. (By the way, the referee got the representations correct in their comment.)

4. Referee comment about page 9, lines 18-22, why is it “not surprising” that there is no composition dependence for negative ions in Fig. 6b?

Author response: On p. 19 lines 18-23, we expanded this discussion to explain our reasoning more thoroughly, while at the same time removing the “not surprising” phrase. Our group and others (e.g. Hall 2013, Tu 2016, Mutzel 2015) have noted in the past that molecular formulas obtained from negative ion spectra are generally more highly oxygenated/oxidized than those obtained from positive ion spectra. Highly oxygenated/oxidized formulas are suggestive of molecules that have very low volatilities. If essentially all of the monomers detected in negative ion spectra are nonvolatile, there will be no particle size dependence in their *relative* ability to be incorporated into particles – all of these molecules will condense with similar probability when striking the particle surface. In contrast, the next paragraph (p. 9 line 24 to p. 10 line 2) discusses positive ion monomers, which potentially have a very wide range of volatiles – some are nonvolatile, while others are semivolatile. The relative amounts of non- vs. semi- volatile monomers will change as a function of particle size for the reasons given in this paragraph.

5. Referee comment about Figure S2.

Author response: The caption to Figure S2 has been modified – this spectrum is for 60 nm size-selected particles.

6. Referee comment about Figure S3.

Author response: Labels displaying the specific mass loading have been added.

7. Typographical errors noted by referee:

Author response: All will be corrected as mentioned by the reviewer: p. 1 line 29, p. 3 line 11, p. 5 line 13-14, p. 6 line 1.

Reviewer: 2 (comments are listed by page number / line number in the original manuscript)

1/26: The reviewer suggests that we remove “small” from this sentence.

Author response: The wording change has been made (p. 1 line 28).

2/12: The reviewer suggests our use of “condensation” and “partitioning” in the manuscript is confusing.

Author response: The reviewer is correct that absorptive “partitioning” as described in Pankow (1994) is a process that describes the movement of all molecular species between the gas and particle phases, independent of where the molecules were initially formed (gas or particle phase) and whether the specific molecules involved are nonvolatile, semivolatile or volatile. However, the distinction we find important to make in this manuscript is the difference between nonvolatile molecules that are initially formed in the gas phase and then distribute between the two phases vs. nonvolatile molecules that are initially formed in the particle phase and then distribute between the two phases. In either case, most of the material resides in the particle phase at equilibrium. The origin is important to consider when assessing particle size dependent composition, since movement of nonvolatile molecules from the gas phase to the particle phase is governed by particle surface-limited kinetics, while formation of nonvolatile molecules directly in the particle phase is governed by particle volume-limited kinetics. For this reason, we use the term “condensation” to describe specifically the process whereby a supersaturated vapor of nonvolatile molecules is formed in the gas phase, with subsequent particle growth at the condensation rate. We have rewritten this paragraph to clarify our use of the terms and rationale for doing so (p. 2, lines 12-19), and have made a similar change to the abstract (p. 1 lines 8-13). These changes are consistent with wording elsewhere in the manuscript.

3/9: The reviewer would like a clarification of the origin of oligomers in the references we cite, since our text implies a gas phase origin for all of the studies cited in this paragraph.

Author response: The reviewer is correct to point out that oligomers in α -pinene SOA (Kidd, 2014) are thought to be produced directly in the particle phase rather than the gas phase. The particle size dependence in that particular study is complicated since the particle sizes examined were much larger than those in the other studies cited in this paragraph. The main point of most of the studies cited in this paragraph is that lower volatility species are

preferentially found in smaller particles as would be expected for a surface area driven process (i.e. nonvolatile molecule formation in the gas phase with subsequent movement to the particle phase). We rewrote this sentence accordingly (p. 3 line 9).

3/24: The reviewer suggests the addition of actual volume to surface area ratios for the particles studied.

Author response: The specific line in question was modified to emphasize surface to volume ratio (p. 3 lines 29-30). We note that the ratios are given for all samples in supporting information Table S1. Also see response to reviewer comment 10/16.

4/9: The reviewer asks why we didn't perform these experiments at e.g. 40% RH.

Author response: In our previous work (Tu, 2016), we found very little difference in the molecular composition of SOA from β -pinene ozonolysis that was generated with 35-70% RH vs. the conditions used in the current work. For this reason, we report this study at low RH. However, understanding how RH (as well as other experimental conditions) might quantitatively impact oligomer formation is an important topic for future study. We added text to discuss this on p. 4 lines 10-12.

7/20: The reviewer suggests modifying this paragraph to be more representative of the topic of this section (molecular composition of the particle phase) rather than the gas phase composition, which was not measured in this study.

Author response: We modified the text on p. 7 lines 20-22 to provide a reasonable transition to this section and put the discussion of gas phase products in context.

10/16: The reviewer suggests that our emphasis on mass loading for the polydisperse aerosols is misleading, since it is really the change in the particle size distribution that is driving the molecular changes we observe.

Author response: We understand the confusion that can result from our choice of wording. We modified the text in the last paragraph of p. 10 (especially lines 17-20 and 26-30) to make it clear: 1) that volume to surface area ratio scales with mass loading for the aerosol generation method we used, 2) that the range of volume to surface area ratios for the

polydisperse samples studied are similar to the monodisperse samples studied, and 3) we linked this result to a similar result from our group that was recently published (Wu and Johnston, 2017).