

Interactive comment on “Particle Size Dependence of Biogenic Secondary Organic Aerosol Molecular Composition” by Peijun Tu and Murray V. Johnston

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Received and published: 12 April 2017

We thank the reviewer for insightful questions and comments that will significantly clarify and improve the manuscript. Reviewer comments (listed by page/line of the original manuscript and paraphrased by us) are given below along with our responses.

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

Author response: We will make the wording change as suggested.

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

C1

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 non-volatile, 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 non-volatile 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 movement to the particle phase. We will rewrite this paragraph to clarify our use of the terms and rationale for doing so, and we will make sure that wording elsewhere in the manuscript is consistent.

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

C2

phase with subsequent movement to the particle phase). We will reword this paragraph, being careful to maintain consistency with the nomenclature discussed in #2 above.

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

Author response: We will modify this paragraph to include the polydisperse samples studied along with a comparison of volume to surface area ratios for the monodisperse vs. polydisperse samples. We note that the values for all samples are given in supporting information Table S1.

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 will provide some explanatory text in the revised manuscript.

7/13: 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 will modify this paragraph accordingly. It is important, though, to discuss what is known about gas phase products at the beginning of this section, because the gas phase products provide context for understanding the particle phase measurements we discuss later in the section.

10/5: 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.

C3

Author response: We understand the confusion that can result from our choice of wording. We do specifically link the mass loading trends to the change in volume to surface area ratio, but this occurs near the end of the paragraph. Here and elsewhere (e.g. see #4 above), we will reword the text to make it clear that the key parameter for understanding molecular composition changes is particle volume to surface area ratio, not simply mass loading. We will also add a reference to and briefly discuss another study of ours that was recently published and addresses this same issue for polydisperse aerosol from a different chemical system (Wu and Johnston, *Environmental Science and Technology*, 2017, DOI: 10.1021/acs.est.7b00655).

Interactive comment on *Atmos. Chem. Phys. Discuss.*, doi:10.5194/acp-2017-53, 2017.

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