

## Response to Reviewer 2

The Hinks et al. manuscript reports on differences in secondary organic aerosol (SOA) mass concentration and composition during high vs. low relative humidity (RH) chamber experiments. Toluene was oxidized under low-NO<sub>x</sub> and high-NO<sub>x</sub> and low (<2%) and high RH (up to 90%) conditions. Differences in mass concentration were evaluated using an SMPS; and differences in composition using nano-DESI-HRMS. While chamber experiments and SOA formation studies largely have been conducted under dry conditions, much recent attention has been given to the effects of water on particle formation and composition. Much of that effort has been focused on understanding the effects of RH on particle viscosity. There is much opportunity to advance the mechanistic understanding of SOA formation through compositional studies such as the one presented in the Hinks et al. manuscript. That said, while the methodology and results are presented clearly, the analysis and discussion could be more robust. There have been a large number of papers published on the photooxidation of toluene (and other aromatics) and subsequent SOA formation. The results of the experiments presented are not adequately placed in the context of what is already known about toluene SOA formation, including recent mechanistic studies looking at the role of aerosol liquid water on SOA formation from toluene. The results presented are new, and with some further analysis and discussion, this work could become a significant contribution to the field. This work is suitable for publication in ACP, following some strengthening of the analysis and discussion.

We felt it would be overwhelming to include all existing references on photooxidation of toluene and other aromatic compounds in this short paper. We included what we thought were the most relevant references for understanding the humidity effects. However, in response to this comment we added a few additional references, including previous toluene SOA studies and a few new papers on this topic that were submitted/published after our ACPD submission. We also made it clear in the summary section that our conclusions do not necessarily apply to conditions when hygroscopic seed particles are present, where aerosol liquid water (ALW) can also contribute to particle growth. We hope the current version gives better justice to previous studies of toluene SOA.

## Technical and Editorial Comments:

- 2.1** The abstract reports that the nano-DESI-HRMS analysis was performed on filters from the low (<2%) and high (75% only) experiments, and particle size analysis on a wider range of high RH (75-90%). This is not as clear in the manuscript itself. Are the nano-DESI-HRMS results from a single experiment? Or averaged over all of the 75% RH experiments? This should be made clearer in the text and in the figures/tables.

The SMPS measurements were performed for all experiments. However, only selected samples were analyzed by HRMS. Our previous experience with HRMS analysis of SOA has shown that the mass spectra of SOA collected under the same conditions are reproducible, and we normally pick the sample with the highest signal-to-noise ratio for the analysis. We clarified it in the revised paper.

- 2.2** p. 4, lines 1-4 (referencing Fig. 1/Table 1): The observation that there seems to be no mechanistic difference between high and low RH and only differences in the formation of oligomers is not completely satisfactory. For the positive ion mode, it is clear that the mass spectra are more similar (samples share the same “compounds”); it is not quite as clear that there is a reduction in peak abundance. For the negative ion mode, it is clearer that there is a reduction in peak abundance, but it is not as clear that there is similarity among the most abundant compounds. For both positive and negative mode there seems to be a reduction in peak diversity, with significant differences in the negative ion mode.

Can these differences be further probed to support the hypothesis or provide alternative hypotheses?

This is a good point. We added a statement that not only the peak intensity drops at high RH but also the observed peak number (referred here as “diversity”).

One could get a deeper understanding of the toluene SOA system with a more sophisticated analysis method that separated the compounds before HRMS analysis. For the nano-DESI based approach, which is not capable of separating isobaric species the description can only be qualitative. We added a note about it as well.

**2.3** There have been a number of mechanistic/product studies of toluene, and other aromatics, under high- and low-NO<sub>x</sub> conditions. Do those studies (e.g., observed gas-phase intermediates) combined with what is known about oligomerization pathways (e.g., as discussed on p.6) support the RH dependence under low NO<sub>x</sub> but not high NO<sub>x</sub> conditions? Citation of similar results in Cao et al. (2010) is not sufficient.

It is absolutely correct that there have been a number of studies dealing with the identity of the toluene photooxidation products. Unfortunately, almost none of them examined the chemical nature of oligomeric compounds. There is a suggestion in Sato et al. (2007) that oligomers may represent hemiacetals. We re-wrote the discussion to cite more mechanistic papers.

**2.4** p. 4, lines 5-10 (referencing Fig. 2): While the formation of higher order oligomers is suppressed, it is interesting that the most abundant peak > C<sub>7</sub> in the positive ion mode spectra under high RH appears to be a dimer.

Indeed, this is an interesting observation. We added a sentence pointing it out but we do not have a good chemical explanation for it.

**2.5** p. 4, lines 31-34: The fraction of compound detected in the particle phase is discussed in terms of ambient organic aerosol (OA) levels, and an explanation is given for gas-phase adsorption artifacts. However, based on table 2 (and discussion in the manuscript) the experimental OA levels vary widely between the low and high RH experiments. The discussion of partitioning and artifacts needs to be expanded to reflect the range of experimentally observed OA levels. One question that arises is whether there are more artifacts with high RH than low RH and if so what may be the reason for that? There is little to no discussion of the role gas-phase chemistry plays in the observations. There is an underlying assumption that because the initial VOC and oxidant concentrations were the same between experiments that the reacted VOC concentrations were also the same. Are there measurements to support that assumption? While many things can

influence SOA yield, were the observed yields (if known) generally consistent with other published studies?

The only gas-phase measurement carried out during these experiments was measurements of the amount of toluene reacted. Over the course of an experiment, the PTR-ToF-MS signal for toluene at low RH and at 75% RH decreased to about 60% of its original signal, at both RH values. This suggests that the rate of consumption of toluene was similar under low and high RH conditions. We have added this info to the experimental section.

We could only estimate the yield values in this study and elected not to place them in the original submission. However, based on this comment we calculated the approximate SOA yields and included them in Table 2. We have included a comparison with previously reported yields.

## **2.6 Did the average particle size change between high and low NO<sub>x</sub> conditions?**

Under low RH, the particle geometric mean was comparable between the high NO<sub>x</sub> (~230 nm) and low NO<sub>x</sub> (~215 nm) experiments at the time of collection; this was not the case under high RH. Under high NO<sub>x</sub> conditions, the particle size remained constant across the various RHs. In contrast, under low NO<sub>x</sub> conditions, the particle geometric mean decreased as RH increased.

## **2.7 p. 5, lines 17-27: The authors mention the hygroscopicity of SOA here, but further discussion may be helpful. Is the amount of aerosol liquid water under high RH (75%) sufficient to prohibit/limit condensation reactions?**

Aerosol liquid water is not needed for the condensation reactions since it is a product. In fact, in organic synthesis, condensation reactions go better when a desiccant is added to the mixture to remove the water from it as it forms. In the aerosol experiments such as the ones described here dry air acts as the desiccant.

Since SOA is not too hygroscopic water would be present in particles in trace levels. Even under humidified conditions, it is probably not sufficient for hydrolysis reactions in the particle (we do mention it as a possibility because reviewer #1 insisted on including hydrolysis as a possible explanation).

**2.8** p. 7, lines 3-12: The extension of the experimental observations to atmospheric implications is not well supported and unnecessary. There are so many elements of experimental design that may affect the results and the extension to the ambient atmosphere; these include absence of seed aerosol (chemical and physical effects), absolute levels of precursors and particles, and relative levels of radicals. Further in the ambient atmosphere the gas-phase chemistry is controlled by more than a single VOC precursor, and the particle composition will affect the extent of aerosol liquid water.

We removed the two paragraphs discussing possible implications of the measurements. However, we kept the paragraph suggesting that RH dependence of SOA from other aromatic compounds should also be investigated. We also added a paragraph that compares the seeded and seedless experiments, and stated that the effect of the seed is likely stronger than the effect on the oligomers observed in this study.

**2.9** Figures: It is recommended to specify the NO<sub>x</sub> and RH conditions in the figure captions just as a reminder since high-NO<sub>x</sub> and a range of RH are discussed in the manuscript

The figure captions were updated.