Response to Reviewer 1

General comments

The authors describe a laboratory study on the atmospheric oxidation and secondary organic aerosol formation from toluene oxidation under different relative humidity conditions. Humidity dependence of the SOA composition is reported for low NOx conditions. The chemical composition of SOA collected on filter samples was analyzed by offline nano desorption electrospray ionization coupled to a high resolution mass spectrometer (nano-DESI-HRMS) in both polarity modes. The mass concentration of the formed SOA was monitored for a different set of chamber experiments using a scanning mobility particle sizer (SMPS). The authors report different chemical composition at different RH, and hypothesize that oligomerization by condensation reactions in the condensed phase can explain the observation of enhanced SOA yield at low humidity. In agreement with earlier studies they see no humidity dependence of toluene SOA formation under high NOx conditions.

The work addresses the relevant scientific question of anthropogenic SOA formation, and therefore contributes to build a better mechanistic understanding on urban SOA burden under different atmospheric conditions. Therefore the paper certainly lies within the scope of “Atmospheric Chemistry and Physics”. It contributes with new experimental results on the SOA composition from toluene. As the authors state, toluene SOA yield experiments have already been described by others, but the linkage between SOA mass and composition has been missing. The scientific method of the SOA chamber experiment is clearly described and the measured SOA mass is corrected for chamber wall-losses. The offline analysis of Teflon filters is based on the established tool nano-DESI-HRMS, which provides the elemental composition of the condensed phase oxidation products as a basis for the hypothesis of different oligomerization efficiencies under different RH conditions.

I therefore recommend the article to be published in ACP, after the following specific comments and technical corrections have been addressed.

Specific comments

1.1 p.1 l.28: SOA formation mechanisms not only depend on solar irradiance, temperature and RH, but also on VOC precursor mixtures that ultimately govern RO2 radical concentration and on NOx levels which can affect branching and termination of oxidation pathways.

Thank you for pointing this out. A note about the importance of RO2 concentrations and NOx levels has been added to the introduction.

1.2 p.2 l.9: Another more recent publication (Zhao et al., 2017) that addresses a photochemical aqueous phase sink of dimers from VOC oxidation should be added.

This reference has been included in the text, as well as a few other related references.

1.3 p.3 l.16: A commonly known risk in offline analysis is (positive and negative) artefact formation on the filter, especially when reactive species, such as organic hydroperoxides (ROOH), organic peroxides (ROOR), peroxyacids etc., are sampled. This implies that the measured composition not necessarily reflects the composition and state of the aerosol in the chamber. Krapf et al. (2017) have shown that a significant fraction of highly oxidized and thermodynamically unstable products of VOC ozonolysis can decompose on the scale of minutes to a few hours. This brings me to the question of how the authors evaluated the effect of filter artefacts? How long and under which conditions were the filters stored until analysis by nano-DESI-MS? Was the aerosol in the high RH experiments dried before being sampled on the filter? How and by which solvent were the filters extracted during nano-DESI-MS analysis?

This is a good point. In order to avoid decomposition of organic compounds, the filter was placed inside a vacuum sealed pouch and frozen immediately after the collection. It was then shipped in dry ice overnight to PNNL for HRMS analysis. The aerosol in the high RH experiments was not dried during the collection, and it is possible that the amount of decomposition occurring on the filter during collection was different in high vs. low RH experiments. We have not corrected for this filter artefact.

We should clarify that the filters were never extracted. The advantage of nano-DESI is that it dissolves the sample on the fly and analyzes it within seconds of exposure of the sample to the solvent. We have added a note about this to the last paragraph in the Materials and Methods section.

1.4 p.4 l.1: The authors use the term “SOA compounds” when discussing mass spectral patterns. How was the possibility of ion source cluster formation evaluated?

In our previous work we observed that weakly bound clusters do not survive the injection of ion into the Orbitrap. Therefore, we have not examined the possibility of contamination of the mass spectrum with cluster ions in this study. We have not made a change to the paper in response to this comment.

1.5 p.4 l.4: The fact that common major peaks were observed, suggests that these are the same products, however, the possibility exists that different isomers are formed. Whether this is the case can only be evaluated by a separation technique before mass spectrometry, and should be mentioned in this paragraph.

We agree with this assessment, and have included a note about this at the end of the second paragraph in the Results and Discussion section.

1.6 p.4. l.7: The authors argue that oligomer formation (in the condensed phase) is **suppressed** under high RH condition. Have the authors considered that oligomerization (especially dimerization) can also occur in the gas phase by RO2-RO2 recombination? Once the dimers that are formed in the gas phase partition to the condensed phase, they might undergo more rapidly hydrolysis reactions under high RH conditions, which in the end would result in a similar observation.

The reviewer is correct in recognizing that we cannot distinguish between the two scenarios in which oligomer formation is suppressed by high RH or oligomers are destroyed more efficiency at high RH. We have added both possibilities in the text in the third paragraph in the Results and Discussion section. However, we pointed out that the amount of water in particles is too small and the possibility of hydrolysis is less likely than suppression of condensation.

1.7 p.4 l.27: ESI sensitivity is not only driven by mass but also by functionality, solvent composition, polarizability and by the tendency of the analyte to interact with other matrix components. Therefore it is highly questionable that peak abundance is proportional to the observed mass fraction. The strongest argument against the proposed simplified relationship between sensitivity and molecular weight is actually given in figure 1: If the sensitivity would only be a function of molecular weight, why is the monomer-to-dimer ratio different between the positive and negative mode? Furthermore, we observed that ESI sensitivity between two very similar commercially available standards (pinonic acid and camphoric acid) can be different by orders of magnitude. Therefore, the authors should argue here more carefully and consider that different ionization efficiency can introduce a significant bias.

We agree that the approach we take is rather approximate and provides at best a qualitative picture of the relative abundances. This is a drastic approximation because even for a series of carboxylic acids, the ESI detection sensitivities can vary by three orders of magnitude within the same sample (Bateman et al., 2012). However, we still see value in this approach for making relative comparisons for the same types of SOA samples. We have emphasized the approximate nature of this approach in the text and added the following reference:

Bateman, A.P., Laskin, J., Laskin, A., and Nizkorodov, S.A.: Applications of high-resolution electrospray ionization mass spectrometry to measurements of average oxygen to carbon ratios in secondary organic aerosols, Environ. Sci. Technol., 46, 8315-8324, http://dx.doi.org/10.1021/es3017254, 2012.

1.8 p.5, l.1: I agree that the signal in the lower volatility bin (Figure 3) is suppressed under high RH in the positive mode. However, for the negative mode this is not obvious. Did the authors try to normalize the figures on the base peak in the mass spectrum to present the relative changes more in detail?

We did not normalize the mass spectra. It was more important to see whether these species would be present in the gas or particle phase. See the last sentence in that paragraph copied below:

“the high RH to low RH ratio of the combined peak abundances for the compounds falling below $\log(C_0) = 1$ is 0.3 in the positive ion mode and 0.05 in the negative ion mode.”

1.9 p.6, l.22-24: Again: the authors should discuss the possibility of enhanced condensed phase hydrolysis reactions of dimers under high RH conditions. The enhanced viscosity of particles under low RH might suppress the rate of hydrolysis reactions.

We have included this possibility in last paragraph in the Results and Discussion section, and in other places in the text.

1.10 p.13, Figure 3: The volatility distribution in (a) looks as it is cut on the high volatility end. How many products appear in the bins log10(C0)>6? Can these products be summed up into one bin which contains all compounds of all bins with log10(C0)>6?

The plot was not cut at the high volatility end. What appears as a cut was likely an outcome of the mass spectrometer limitation – it could not observes ions below m/z 100.

Technical corrections

p.13, Figure 3: The figure caption contains (a) and (b) which is not shown in the figure. Also, the colour description in the caption is wrong: high RH should be “blue” and low RH “red”.

The figure caption was updated.

Literature

Krapf, M., El Haddad, I., Bruns, E. A., Molteni, U., Daellenbach, K. R., Prévôt, A. S. H., Baltensperger, U. and Dommen, J.: Labile Peroxides in Secondary Organic Aerosol, Chem, 1(4), 603–616, doi:10.1016/j.chempr.2016.09.007, 2017.

Zhao, R., Aljawhary, D., Lee, A. K. Y. and Abbatt, J. P. D.: Rapid Aqueous-Phase Photooxidation of Dimers in the α-Pinene Secondary Organic Aerosol, Environ. Sci. Technol. Lett., 4(6), 205–210, doi:10.1021/acs.estlett.7b00148, 2017.