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.

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-NOx and high-NOx 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-NOx 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 NOx but not high NOx 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 > C7 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 NOx conditions?

Under low RH, the particle geometric mean was comparable between the high NO_x (~230 nm) and low NO_x (~215 nm) experiments at the time of collection; this was not the case under high RH. Under high NO_x conditions, the particle size remained constant across the various RHs. In contrast, under low NO_x 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 NOx and RH conditions in the figure captions just as a reminder since high-NOx and a range of RH are discussed in the manuscript

The figure captions were updated.

Effect of Relative Humidity on the Composition of Secondary Organic Aerosol from Oxidation of Toluene

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Abstract. The effect of relative humidity (RH) on the chemical composition of secondary organic aerosol (SOA) formed from low-NO_x toluene oxidation in the absence of seed particles was investigated. SOA samples were prepared in an aerosol smog chamber at <2% RH and 75% RH, collected on Teflon filters and analyzed with nanospray desorption electrospray ionization high-resolution mass spectrometry (nano-DESI-HRMS). Measurements revealed a significant reduction in the fraction of oligomers present in the SOA generated at 75% RH compared to SOA generated under dry conditions. In a separate set of experiments, the particle mass concentrations were measured with a Scanning Mobility Particle Sizer (SMPS) at RHs ranging from <2% to 90%. It was found that the particle mass loading decreased by nearly an order of magnitude when RH increased from <2% to 75-90% for low-NO_x toluene SOA. The volatility distributions of the SOA compounds, estimated from the distribution of molecular formulas using the “molecular corridor” approach, confirmed that low-NO_x toluene SOA became more volatile on average under high RH conditions. In contrast, the effect of RH on SOA mass loading was found to be much smaller for high-NO_x toluene SOA. The observed increase in the oligomer fraction and particle mass loading under dry conditions were attributed to enhancement of condensation reactions, which produce water and oligomers from smaller compounds in low-NO_x toluene SOA. ~~under dry conditions.~~ The reduction in the fraction of oligomeric compounds under humid conditions is predicted to partly counteract the previously observed enhancement in the toluene SOA yield driven by the aerosol liquid water chemistry in deliquesced inorganic seed particles.

1 Introduction

Secondary organic aerosol (SOA) is an important component of atmospheric particulate matter. It is formed in the atmosphere via oxidation of volatile organic compounds (VOCs) by common atmospheric oxidants such as O_3, OH, and NO_3 (Seinfeld and Pandis, 2016). The SOA formation mechanisms depend in a complex way on physical environmental parameters such as solar irradiance, temperature, and relative humidity (RH). They also depend on the type of oxidant, concentration of VOC precursors, which govern RO_2 concentrations, and NO_x levels, which determine the fate of the RO_2 radicals. The RH controls the amount of available water in the system, and therefore affects processes in which water acts as a reactant, product, or solvent in several ways. Firstly, gaseous water can directly participate in the VOC oxidation reactions. For example, it is well known to react with carbonyl oxide intermediates in ozonolysis of alkenes (Finlayson-Pitts and Pitts Jr, 2000). Additionally, aerosol liquid water (ALW) present in hygroscopic particles can lead to hydrolysis of organic compounds and other particle-phase reactions involving or catalyzed by water (Ervens et al., 2011). ~~Aerosol liquid water~~ALW also has a strong effect on acidity of particles and, therefore, affects acid-catalyzed processes occurring in particles (Jang et al., 2002). Furthermore, water can act as a plasticizer for SOA particles making them less viscous, thus affecting the rate of their growth (Renbaum-Wolff et al., 2013; Perraud et al., 2012; Shiraiwa and Seinfeld, 2012). Under supersaturated conditions, aqueous chemistry occurring in cloud and fog droplets promotes conversion of small water-soluble molecules into non-volatile products that would not form in the absence of liquid water (Herrmann et al., 2015). Finally, ~~water also promotes photodegradation of~~ dissolved SOA compounds may undergo more efficient photodegradation in water (Bateman et al., 2011; Nguyen et al., 2012; Romonosky et al., 2015; Romonosky et al., 2017; Zhao et al., 2017) compared to dry particles (Kourtchev et al., 2015).

Chemical composition is an important characteristic of SOA because it may determine~~s~~ the climate and health relevant properties of particles. The effect of RH on the chemical composition of particles~~SOA~~ has been studied for several types of biogenic SOA (Nguyen et al., 2011; Zhang et al., 2011; Riva et al., 2016; Harvey et al., 2016). For example, Nguyen et al. (2011) examined high-NO$_x$ isoprene SOA formed under high and low RH conditions and found that the high RH samples contained fewer oligomers than the low RH samples. Zhang et al. (2011) investigated the effect of RH on the composition of high-NO$_x$ isoprene SOA and found that oligoesters present in the SOA were suppressed at higher RH, while the formation of organosulfates was enhanced. Riva et al. (2016) studied the effect of RH on SOA made from oxidized isoprene hydroxy hydroperoxide (ISOPOOH) and found that increasing RH led to an increase in abundance of some oligomers while decreasing the abundance of other oligomers. Harvey et al. (2016) investigated the effect of RH on 3-hydroxypropanal ozonolysis SOA and found that increasing RH resulted in a decrease in SOA yield and a decrease in oligomerization.

The effect of RH on ~~anthropogenic SOA, including~~ SOA formed from monoaromatic compounds such as benzene, toluene, m-xylene, and 1,3,5-trimethylbenzene (TMB) has been studied as well.~~, however m~~ Most of these studies focused on the effect of RH on the SOA yield (Edney et al., 2000; Zhou et al., 2011; Cocker III et al., 2001; Kamens et al., 2011; Cao and Jang, 2010; Faust et al., 2017; Liu et al., 2017; Jia et al., 2017) and not chemical composition of SOA particles. The comparison between different experiments is complicated by the fact that some experiments are done in presence of hygroscopic seed particles, where ALW may be playing a role, others are done with seed particle containing strong acids, which favor acid catalyzed chemistry, and others use no seed particles. For toluene SOA produced in presence of hygroscopic seed particles, the yield is generally found to be larger under high RH conditions (Zhou et al., 2011; Kamens et al., 2011; Faust et al., 2017; Liu et al., 2017; Jia et al., 2017) because additional organic compounds are produced by aqueous photochemistry small highly soluble compounds, such as glyoxal, partitioned in ALW. However, ~~For instance,~~ Cao ~~et al.~~ and Jang (2010) ~~investigated the effect of RH on the yield of SOA made from toluene under both high and low-NO$_x$ conditions and~~ observed a negative correlation between RH and SOA yield for low-NO$_x$ experiments, i.e., lower RH resulted in higher SOA yields. ~~They also~~

~~found no significant RH dependence under high-NO_x conditions (Cao and Jang, 2010). However, White et al. (2014) investigated the effect of RH on composition of toluene SOA produced under high-NO_x conditions, and unlike Cao et al. (2010) observed slightly higher toluene SOA yields at elevated RH as well as higher yields of photooxidation products (White et al., 2014).~~

In the experiments done without seed particles, the acid catalysis and chemistry occurring in ALW do not contribute to the particle growth. However, this does not rule out a possibility that RH may affect the SOA chemical composition and yield by other mechanisms mentioned above. Indeed, White et al. (2014) investigated the effect of RH on composition of toluene SOA produced under high-NO_x conditions without seed particles and observed higher toluene SOA yields at elevated RH as well as higher yields of photooxidation products. In this work, we studied the composition of low-NO_x toluene SOA formed under dry and humid conditions in the absence of seed particles. We ~~have confirmed the results from Cao et al. (2010) that there is a~~observed a significant negative correlation between RH and low-NO_x SOA from toluene SOA mass loading and ~~observed~~ a strong RH dependence on SOA molecular composition. We attribute this effect to the more extensive oligomerization of SOA compounds driven by condensation reactions under dry conditions. The reduction in the fraction of oligomeric compounds under humid conditions is predicted to partly counteract the previously observed enhancement in the toluene SOA yield driven by the ALW chemistry in deliquesced inorganic seed particles.~~These findings have important implications for toluene SOA concentrations in dry, urban areas, especially in areas where regulations aim to reduce NO_x emissions in the future.~~

2 Materials and Methods

SOA was generated by photooxidation of toluene ~~under low-NO_x conditions~~ in a 5 m^3 smog chamber surrounded by a bank of UV-B lights. Before each experiment, the chamber was humidified to the desired RH by flowing purified air (typical VOC mixing ratios below 1 ppb) through a Nafion humidifier (PermaPure). The temperature (±1 °C) and RH (±2% RH) inside the chamber were monitored with a Vaisala HMT330 probe. No seed aerosol was used. Hydrogen peroxide (H_2O_2) was introduced to the chamber by injecting a measured volume of aqueous H_2O_2 (30 wt%) into a bulb where it was evaporated and carried into the chamber by a flow of purified air over a period of 30 minutes. The majority of the experiments were done under low-NO_x conditions with concentrations of NO and NO_2 being below the 1 ppb detection limit of the NO_y analyzer (Thermo Scientific 42i-Y). In the high-NO_x experiments, gaseous NO (1000 ppm in N_2) was added to achieve a total NO concentration of 300 ppb~~ (for the low-NO_x experiments this step was skipped)~~. ~~Next, t~~Toluene (Fisher Scientific, ACS grade) was introduced into the chamber ~~in a similar manner,~~ by evaporating a measured volume of liquid toluene into a stream of air over a period of five minutes, which resulted in a toluene mixing ratio of 1000 ppb. Following the addition of gaseous reactants into the chamber, the UV lamps were turned on, photolyzing the H_2O_2 and resulting in a steady-state OH concentration of 1×10^6 molec·cm^{-3} (determined in a separate experiment). These high concentrations were chosen in order to produce a sufficient amount of SOA to collect for offline analysis. Throughout each experiment, particle concentrations were monitored with a Scanning Mobility Particle Sizer (SMPS Model 3080, TSI Inc.). We used an effective SOA particle density of 1.4 g cm^{-3} for converting the SMPS measurements into particle mass concentration (Sato et al., 2007; Ng et al., 2007). The concertation of toluene in the chamber was tracked with a proton-transfer reaction time of flight mass spectrometer (PTR-ToF-MS). The observed decrease in the toluene concentration (typically ~40%) was the same under low and high RH conditions.

SOA samples were collected onto Teflon filters for offline analysis by nano-DESI-HRMS. The filters were sealed and frozen immediately after the sample collection to avoid decomposition of less stable compounds, as observed for example by Krapf et al. (2017). The SOA filter samples were brought to room temperature and immediately analyzed in both positive and negative ion modes using an LTQ-Orbitrap mass spectrometer (Thermo Corp.) with a resolving power of 10^5 at *m/z* 400 equipped with a custom-built nano-DESI source (Roach et al., 2010a, b). The advantage of nano-DESI is in minimizing the time in which the sample is exposed to the solvent, thus minimizing solvolysis reactions. Mass spectra of the solvent~~s~~ and blank filters were recorded as controls. Mass spectra of ~~related~~ the samples with highest signal-to-noise ratio were clustered together, and the *m/z* axis was calibrated internally with respect to known SOA products. The solvent and impurity peaks were discarded. The peaks were assigned formulas, $C_cH_hO_oN_nNa_{0-1}^+$ or $C_cH_hO_oN_n^-$, constrained by valence rules and elemental ratios (c,h,o,n refer to the number of corresponding atoms in the ion) (Kind and Fiehn, 2007). The resulting ion formulas were converted into formulas of the corresponding neutral species. All data reported below refers to the formula and molecular weights of the neutral species.

3 Results and Discussion

The ~~raw~~ mass spectra of a low RH sample (<2% RH) and a high RH sample (75% RH) are shown in Figure 1, plotted as a function of the molecular weight of the neutral compound. The mass spectra obtained in the positive and negative ion modes represent the SOA compounds ionizable in these modes, and are not expected to be identical (Walser et al., 2008). The low-NO_x mass spectrum shown in Figure 1 is qualitatively similar to the low-NO_x mass spectrum of toluene SOA discussed in a previous study which was prepared in a different smog chamber but analyzed by the same nano-DESI instrument (Lin et al., 2015).

As shown in Figure 1, the increase in RH resulted in a visible reduction in the overall peak abundance for both ion modes, due to the fact that the high RH sample had a much lower particle mass during the SOA generation (see below), and thus there was less material on the substrate. There was also a reduction in the number of observed peaks. For example, the positive mode mass spectrum in Figure 1 contains 665 peaks at low RH but only 285 peaks at high RH; the corresponding peak numbers are 276 and 90 for the negative ion mode. Despite this reduction in peak abundance and number, the major observed ~~SOA compounds~~peaks in the mass spectra remained the same. Table 1 lists five most abundant peaks for both the low and high RH samples observed in positive and negative modes. The fact that the major peaks are ~~so~~ similar between the low and high RH samples suggests that the major products are produced by a similar mechanism that is not too sensitive to RH. It is of course still possible that the distribution of different structural isomers within each peak could be affected by humidity but the nano-DESI method used here would blind to this effect because it cannot separate isobaric species.

While the major oxidation products were similar at low and high RH, the less abundant products were much more strongly affected by RH. Specifically, the abundances of some high-molecular weight compounds were visibly reduced at high RH (Figure 1), suggesting that either the gas-phase oligomer formation is suppressed by water vapor or particle-phase oligomer formation is suppressed by ALW. (An alternative explanation is that oligomers hydrolyze after partitioning into the particle but the amount of ALW in the particles might be too small so sustain efficient hydrolysis). To better quantify this effect, Figure 2 shows the combined peak abundances as a function of the number of carbon atoms in each molecule. Monomer compounds containing n_C=7 carbon atoms and dimer compounds ~~containing~~ with n_C=14 ~~carbon atoms~~ clearly dominate the distribution. In fact, the combined abundance of dimers (n_C=14) represents the highest peak in the distribution in the positive ion mode. Many ~~other~~ larger compounds with n_C ~~carbon numbers~~ up to 32 also appear in the mass spectrum, and these minor compounds are the ones that are the most affected by RH.

When comparing the low RH sample to the high RH sample, there is a significant decrease in combined peak abundance for molecules with $n_C>$~~more than~~ 7 carbons under high RH conditions (except for the n_C=14 dimers). ~~This suggests that the abundance of dimers and trimers decreases with increasing RH.~~ Because these higher molecular weight oligomers tend to have lower volatility (Li et al., 2016), they play an important role in the formation and growth of aerosol particles. With the lower fraction of oligomers produced under high RH conditions, the population of the oxidation products becomes more volatile on average, which should result in a lower SOA yield ~~such as those reported by Cao et al. (2010)~~.

To better illustrate the possible effect of RH on the yield of condensable oxidation products, the volatility distributions were estimated for the low-NO_x toluene SOA compounds using the "molecular corridor" approach (Li et al., 2016; Shiraiwa et al., 2014). This parameterization was developed specifically for atmospheric organic compounds containing oxygen, nitrogen, and sulfur (Li et al., 2016), and it makes it possible to estimate the pure compound vapor pressure, C_0, from the elemental composition derived from high-resolution mass spectra (Lin et al., 2016; Romonosky et al., 2017). C_0 is related to the more commonly used effective saturation mass concentration, $C^* = \gamma \times C_0$, where γ is the activity coefficient (Pankow, 1994). C_0 becomes equal to C^* under the assumption of an ideal thermodynamic mixing. The C_0 values were calculated for each compound observed in the positive and negative ion mode mass spectra. The values were binned as commonly done in the volatility basis set (VBS) (Donahue et al., 2006) in equally spaced bins of base-10 logarithm of C_0. The contribution of each compound to its volatility bin was taken to be proportional to its relative abundance in the mass spectrum. Because of the correlation between the ESI detection sensitivity and molecular weight (Nguyen et al., 2013), the mass fraction of the detected SOA compound is approximately~~can be taken to be~~ proportional to its peak abundance. This is a considerable approximation because even for a series of carboxylic acids the ESI detection sensitivities can vary by several orders of magnitude within the same sample (Bateman et al., 2012). However, t~~T~~his ~~is an~~ approximation~~, but it~~ may still be ~~suitable~~ useful for comparing distributions for the same types of SOA produced and analyzed under the same experimental conditions (Romonosky et al., 2017).

Figure 3 shows the resulting distribution of the SOA compounds by the volatility. Under typical ambient conditions, compounds with C_0 above ~10 µg m^{-3}, i.e., the ones falling above the log(C_0) =1 bin, should exist primarily in the gaseous phase. Some of these more volatile compounds were detected in the negative ion mode. They may correspond to carboxylic acids that adsorbed to the filter during sampling. Less volatile compounds were preferentially observed in the positive ion mode. In both positive and negative ion modes, the compounds falling in the lower volatility bins were visibly suppressed at high RH. For example, 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.

In order to investigate whether the decrease in oligomers affects the SOA mass loading, we have done additional experiments in which the particle mass concentration was tracked with SMPS at different RH. The SMPS data were corrected for particle wall loss effects assuming an effective first-order rate constant for the loss of mass concentration of 9.3×10^{-4} min^{-1} measured in a separate experiment (the rate constant was assumed to be independent of particle size). ~~Most of the~~The SMPS experiments were performed under both low-NO_x and high-NO_x conditions. ~~However, in order to compare our results to the results of Cao et al. (2010), we did additional experiments under high-NO_x conditions.~~ A summary of these experiments is presented in Table 2. Representative examples of the wall loss corrected particle mass concentration as a function of photooxidation reaction time are shown in Figure 4 for both the low-NO_x and the high-NO_x toluene SOA systems.

Under high-NO_x conditions, there was a small difference in the maximum mass concentration achieved under <2%, 40%, and 75% RH (less than a factor of 2), but under low-NO_x conditions the difference was substantially larger. For the low-NO_x system, the wall loss corrected particle mass concentration decreased by a factor of 8 over the range of RHs studied. The effect was reproducible as essentially the same mass concentration was observed in experiments repeated on different days under the same initial conditions.

Combining the measured particle mass concentrations with the toluene concentrations measurements from PTR-ToF-MS makes it possible to estimate the apparent SOA yields, which are listed in the last column of Table 2. Under high-NO_x conditions, the yield decreased from ~27% and ~19% as RH increased from <2% to 77%. Under low-NO_x conditions, the yields dropped from 15% to 2% for the same change in RH. We note the previously reported SOA yield from toluene formed in presence of ammonium sulfate seed aerosol displayed the opposite trend, with the yield being higher (~30%) under low-NO_x conditions and lower under high-NO_x conditions (~19 %) (Ng et al., 2007). Hildebrandt et al. (2009) noted that the yields in the toluene SOA system are highly sensitive to the oxidation conditions, including the type of UV lights used in photooxidation and the seed aerosol concentration. Furthermore, the wall loss effects are especially prominent in the toluene SOA system (Zhang et al., 2014). We attribute the difference in absolute values of yields between our experiments and experiments by Ng et al. (2007) to the difference in the experimental design.

The differences between the low and high RH systems cannot be explained by hygroscopic growth of particles at elevated RH. Throughout the experiment, the SMPS sampled air directly from the chamber. Each experiment lasted many hours, which allowed the sheath flow in the SMPS to approach the RH of the chamber air. Therefore, the particles sized by the SMPS contained some ~~aerosol liquid water~~ ALW and would appear larger than their dry size. If the organic mass in particles did not change at different RH levels, we would have observed an *increase* as opposed to a decrease in the measured particle mass concentration. With a typical hygroscopic growth factor (the ratio of particle diameters in the humidified and dry air) for SOA of 1.1 at 85% RH (Varutbangkul et al., 2006), the increase in the apparent mass concentration would have been by a factor of about 1.3. Instead, the mass concentration decreased by almost a factor of 8 at higher RHs. The strong dependence of the low-NO_x toluene SOA mass loading on RH is therefore not an artifact of the SMPS measurements. ~~It is also consistent with results of Cao et al. (2010), who observed a negative correlation between RH and low-NO_x toluene SOA yield, but no correlation between RH and high-NO_x toluene SOA yield.~~

We cannot rule out the possibility that the mass loading of SOA was affected by the enhanced wall loss of more water soluble compounds under high RH conditions. Indeed, the chamber wall effects are expected to be stronger for the slowly reacting toluene compared to monoterpenes that are oxidized much faster (Pierce et al., 2008). Furthermore, in the absence of seed particles, the toluene SOA aerosol growth takes longer making the wall loss effects larger (Kroll et al., 2007; Zhang et al., 2014). It is conceivable that the products of low-NO_x oxidation of toluene are more soluble than the products of high-NO_x oxidation of toluene. This would result a stronger effect of RH on the mass loading of low-NO_x SOA. Distinguishing the wall-loss effects from the effect of water on the distribution of oligomers would require more careful chamber measurement of SOA yields over a broad range of concentrations and in the presence of seed aerosol (to suppress the wall loss effects).

A possible chemical explanation for the observed RH effect is that there are chemical reactions in the system that directly involve water and change the chemical composition of the particles thereby affecting their growth rate. Previous studies have shown that RH can affect the composition and potential yield of SOA by altering the fraction of low-volatility oligomers in SOA. Increased RH could suppress oligomerization occurring by condensation reactions (i.e., reactions that produce water as a product) by shifting the reaction equilibrium toward the products as discussed in Nguyen et al. (2011). Conversely, increased RH could promote hydrolysis of oligomers after they are produced in the gas-phase and partition into wet particles. As we pointed out above, the latter mechanism is less likely due to the low ALW content of the organic particles.

To investigate ~~this possibility~~ the mechanism, we examined the frequency of occurrence of mass differences between the peaks in the high resolution mass spectra. Table 3 lists the most common mass differences in all four mass spectra. The most frequently observed mass difference in the low-RH sample was C_2H_2O, and its frequency of occurrence dropped in the high-RH sample. It is possible that C_2H_2O results from oligomerization chemistry of glycolaldehyde ($C_2H_4O_2$), which can react by aldol condensation mechanism with compounds containing a carbonyl group (Scheme 1). Glycolaldehyde has been observed previously in oxidation of toluene (White et al., 2014; Yu et al., 1997), likely as an oxidation product of methylglyoxal. The difference corresponding to H_2O was not amongst the most common, however, it became more probable in the high RH sample, consistent with hydration reactions. Anhydrides, commonly found in toluene SOA (Bloss et al., 2005; Forstner et al., 1997; Sato et al., 2007), may undergo hydrolysis, which adds an H_2O unit to the formula.

We additionally tested whether oligomeric compounds occurring in low-RH toluene SOA can be produced by either simple addition or condensation of monomer compounds occurring in high-RH toluene SOA. If simple addition is responsible for the oligomerization, we would expect to see peaks in the low RH mass spectrum with molecular weights equal to the sum of two peaks from the high RH mass spectrum. If condensation is responsible for the oligomerization, we would expect to see peaks in the low RH mass spectrum with molecular weights equal to the sum of two peaks from the high RH mass spectrum minus the mass of water (the same relationship would hold in reverse for oligomers undergoing hydrolysis in the particle). In positive ion mode, the fraction of peaks that could be matched by the addition reactions was 69%, while the fraction of peaks matched by the condensation reactions was 83%. These numbers were 62% and 69%, respectively, for negative ion mode. This suggests that condensation reactions (that remove water) are more likely to be responsible for the enhanced oligomer formation under dry conditions. This conclusion is similar to the one reached in the study of the effect of RH on oligomerization in high-NO_x isoprene SOA (Nguyen et al., 2011).

4 Conclusions

This study has demonstrated that the composition of low-NO_x toluene SOA depends on the RH under which it is produced in smog chamber experiments without seed particles. Oligomers produced by condensation reactions were observed in higher concentrations in the mass spectra of toluene SOA produced under low RH, and were suppressed under high RH conditions. Additionally, the mass loading of low-NO_x toluene SOA was reduced under high RH conditions. ~~This is consistent with the results of Cao et al. (2010) who also reported a negative correlation between RH and toluene SOA yield. This correlation was much weaker for high-NO_x toluene SOA in this study and was not observed by Cao et al. (2010).~~ The plausible reason for the suppression of SOA mass loading at high RH is the change in the SOA chemical composition that favors lower-molecular weight, more volatile compounds. The reduction of dimers and trimers in the high RH samples suggests that low volatility oligomers are not forming in toluene SOA under low-NO_x conditions, which means particle growth is suppressed and mass loading is reduced.

In previous studies of the effect of RH on SOA yield from toluene in the presence of hygroscopic seed (Zhou et al., 2011; Kamens et al., 2011; Faust et al., 2017; Liu et al., 2017; Jia et al., 2017) and opposite affect was observed with the SOA yield increasing at high RH. This was attributed to the to aqueous partitioning and aquebsequent reactions in ALW of smaller photooxidation products, such as glyoxal (Faust et al., 2017). Our results suggest that the increase in the SOA yield due to the ALW-supported chemistry is at least partly counteracted by the lower yield of oligomers under high RH conditions. While it is not straighforward to compare experiments done with and without seed aerosol in different smog chembers, the ALW-supported chemistry ehnacement of the yield appears to be a more important effect.

~~These results have potential impacts in the urban atmospheric environment where toluene is commonly present alongside NO_x because both are emitted by anthropogenic sources. Under high-NO_x conditions, the total amount of toluene SOA will not depend strongly on atmospheric RH. However, these results suggest that if NO_x in urban areas is significantly reduced, the total amount of toluene SOA would be similarly suppressed under normal atmospheric conditions (~50% RH), even if toluene emissions stay the same. This may be relevant in cities like Los Angeles, which plan to significantly reduce NO_x emissions in the atmosphere.~~

~~Additionally, there are many locations that become dry under certain meteorological conditions. For example, during California's Santa Ana winds, the RH regularly decreases below 10%. Under such dry atmospheric conditions in a low-NO_x environment, the yield of toluene SOA would no longer be suppressed. This change would result in a "burst" of toluene SOA, changing the overall concentration of SOA in the area.~~

It is ~~also~~ conceivable that the effect of RH on the SOA yield is a common feature of all low-NO_x aromatic SOA, all of which should contain aldehyde compounds capable of oligomerization by condensation reactions. If this is the case, the production of SOA from naturally emitted aromatic compounds (indole, benzyl acetate, benzaldehyde, etc.), which exist in low-NO_x environments, would be strongly modulated by the ambient relative humidity. This definitively warrants further investigation.

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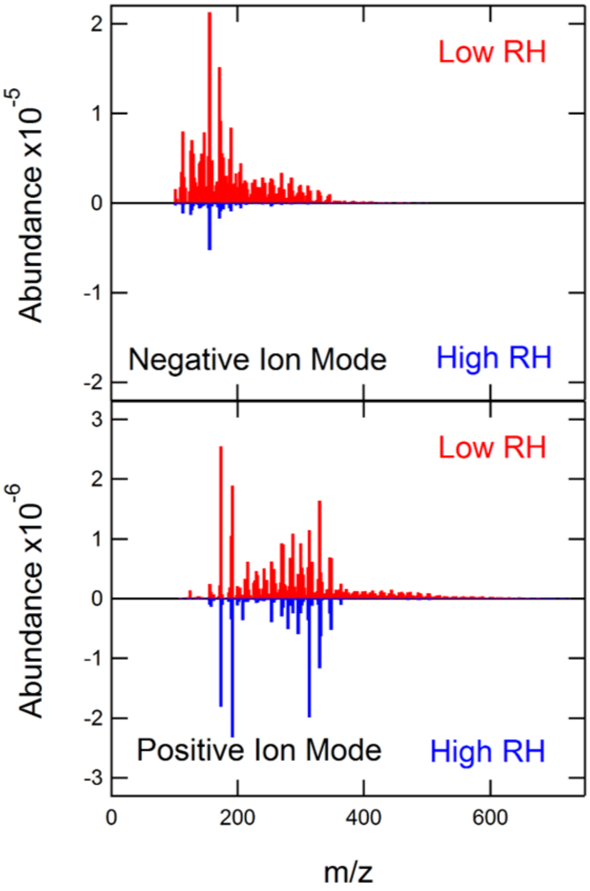


Figure 1: High-resolution mass spectra obtained in negative ion mode (top) and positive ion mode (bottom). The red upward-pointing mass spectra represent the low-NO$_x$ SOA sample made under low RH (<2%) and the blue inverted mass spectra represent the low-NO$_x$ SOA sample made under high RH (75%).

Table 1: Five most abundant compounds observed in the low and high RH low-NO_x toluene SOA samples. In negative ion mode, the same most abundant peaks were observed at the low and high RH. In positive ion mode, the most abundant species differed by one compound in the low and high RH experiments, hence the table contains 6 formulas.

Positive Ion Mode		**Normalized Peak Abundance**	
Nominal Mass	**Formula**	**Low RH**	**High RH**
174	$C_7H_{10}O_5$	1	1
192	$C_7H_{12}O_6$	0.74	0.86
330	$C_{14}H_{18}O_9$	0.64	0.78
314	$C_{14}H_{18}O_8$	0.45	0.50
288	$C_{12}H_{16}O_8$	0.43	0.11
332	$C_{14}H_{20}O_9$	0.17	0.27
Negative Ion Mode		**Normalized Peak Abundance**	
Nominal Mass	**Formula**	**Low RH**	**High RH**
156	$C_7H_8O_4$	1	1
172	$C_7H_8O_5$	0.71	0.86
174	$C_7H_{10}O_5$	0.43	0.78
190	$C_7H_{10}O_6$	0.40	0.50
114	$C_5H_6O_3$	0.38	0.27

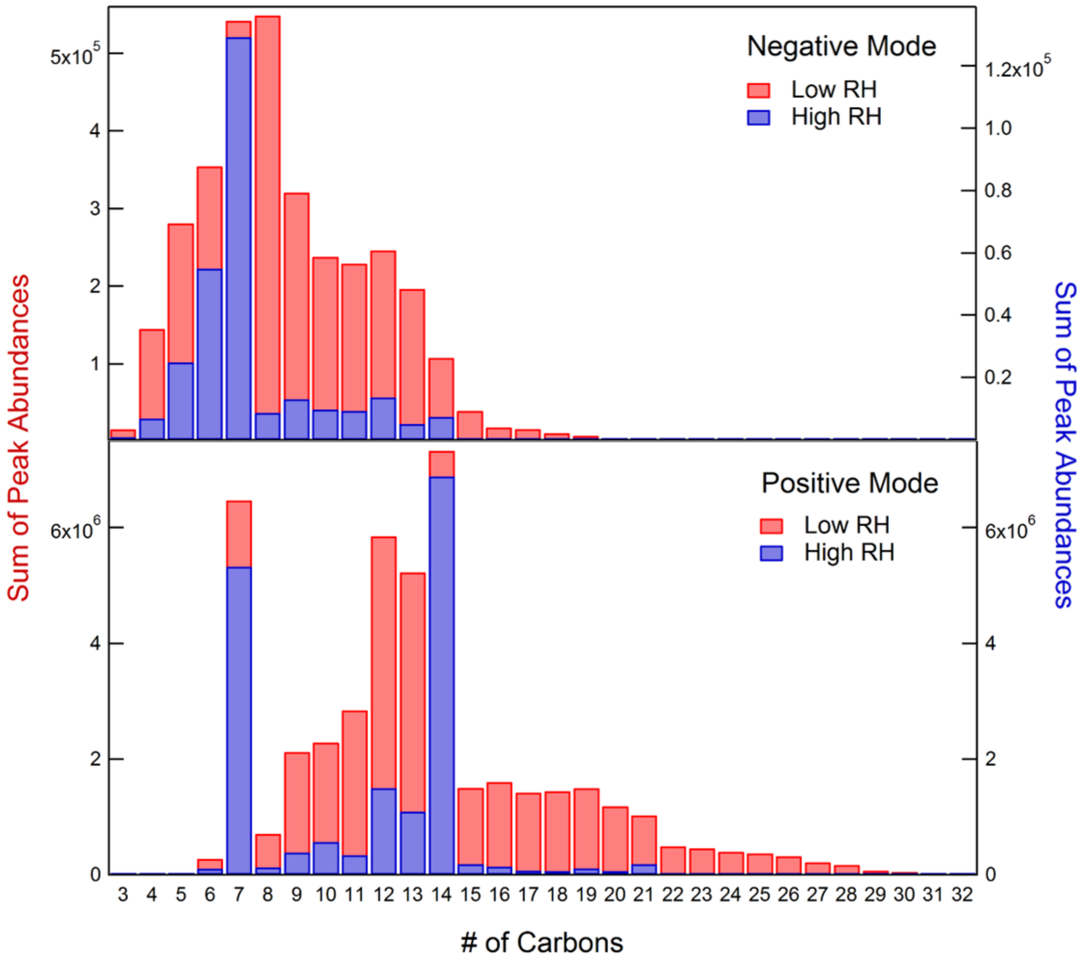


Figure 2: Combined abundance of all peaks as a function of number of carbon atoms in negative mode (top) and positive mode (bottom). The data for the low RH sample are shown in red and the data for the high RH sample are shown in blue. The samples were prepared under low-NO_x conditions.

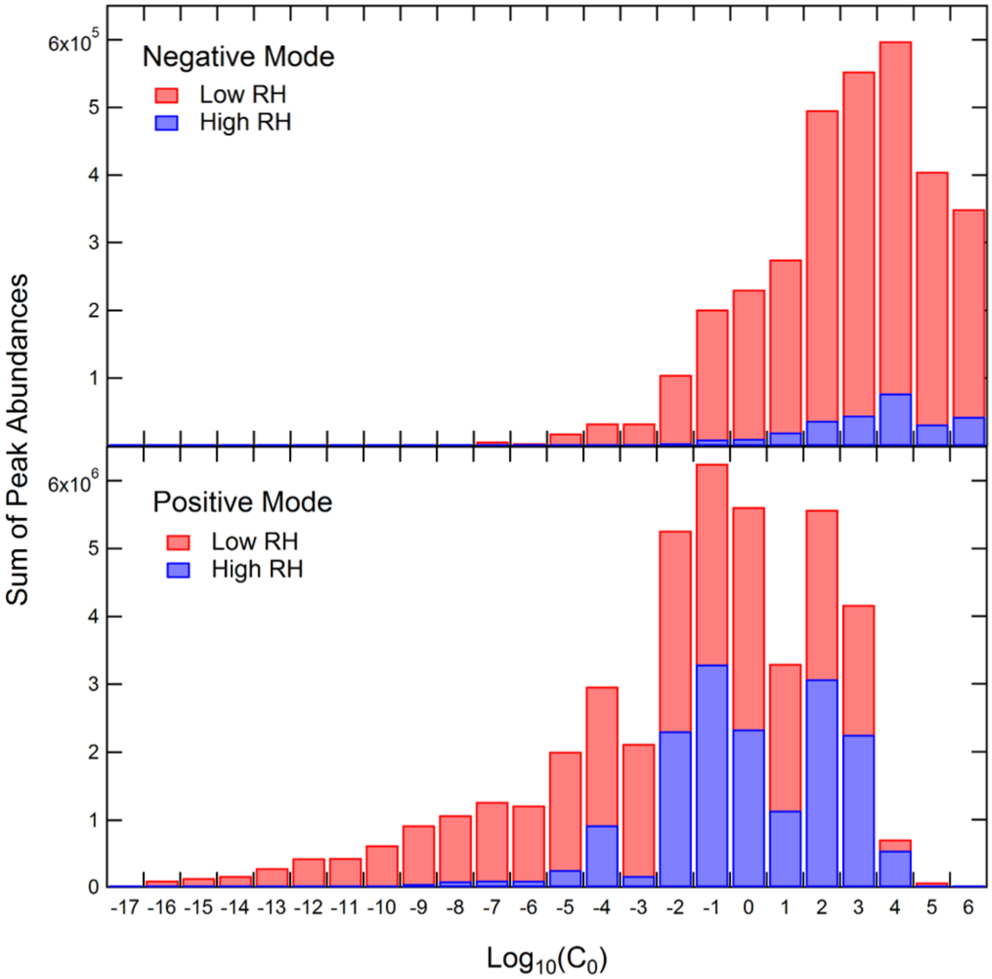


Figure 3. Estimated volatility distribution for the compounds observed in low-NO$_x$ SOA samples in the ~~positive (a) and~~ negative (top~~b~~) and positive (bottom) ion mode at high (~~red~~ blue bars) and low (~~blue~~ red bars) RH. The height of each bar is proportional to the total ESI abundance of compounds falling within the volatility bin.

Table 2: Summary of SMPS experiments. The uncertainties included in this table are based on ~~the~~ one standard deviation in the data for repeated experiments.

Initial RH	**# of Experiments**	**NO_x ppm**	**Toluene ppm**	**H_2O_2 ppm**	**SOA from SMPS $\mu g/m^3$**	**Wall Loss Corrected SOA $\mu g/m^3$**	**SOA Yield (%)**
Low-NO_x – High Toluene							
<2	4	-	1.0	2.0	180 ± 20	210 ± 20	15±2
20 ± 3	2	-	1.0	2.0	76 ± 4	87 ± 6	6.2±0.5
43	1	-	1.0	2.0	74	84	5.9
76 ± 1	4	-	1.0	2.0	27 ± 7	28 ± 7	2.0±0.5
89 ± 1	2	-	1.0	2.0	25 ± 8	26 ± 9	1.9±0.6
Low-NO_x – Lower Toluene							
<2	1	-	0.3	0.6	23	27	5.5
75	1	-	0.3	0.6	8	9	2.2
High-NO_x – High Toluene							
<2	1	0.3	1.0	2.0	330	390	27
43	1	0.3	1.0	2.0	210	260	18
77	1	0.3	1.0	2.0	230	270	19

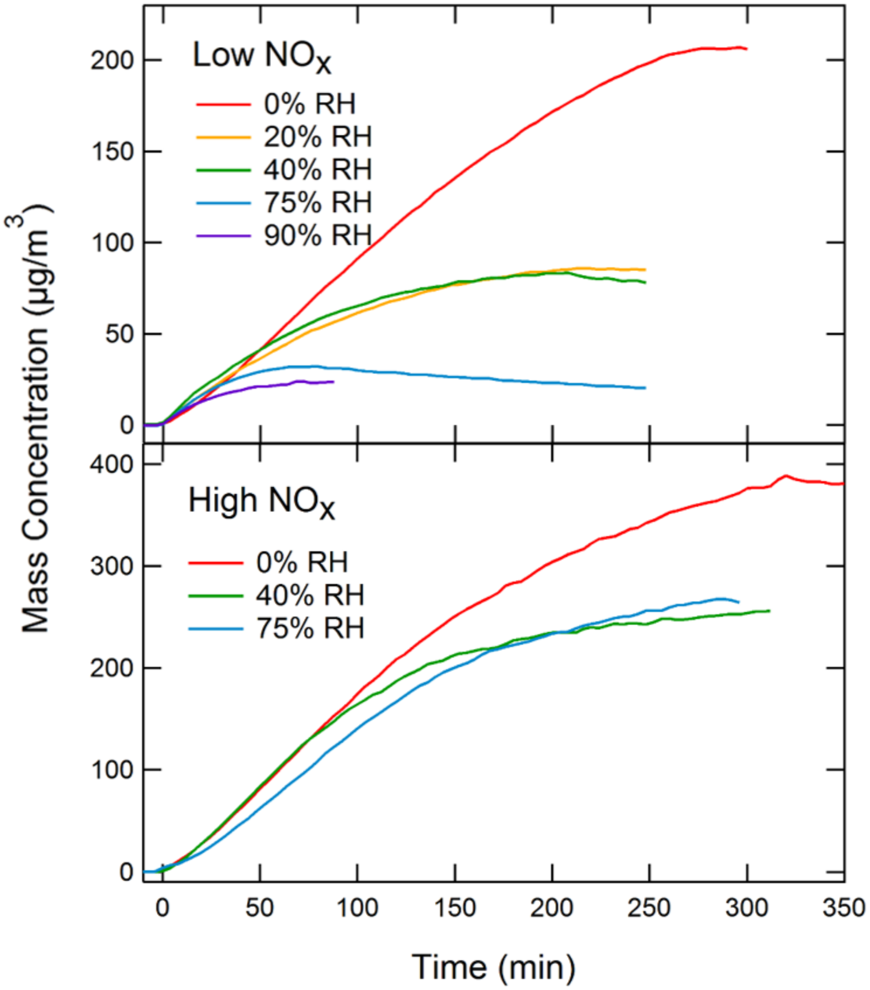
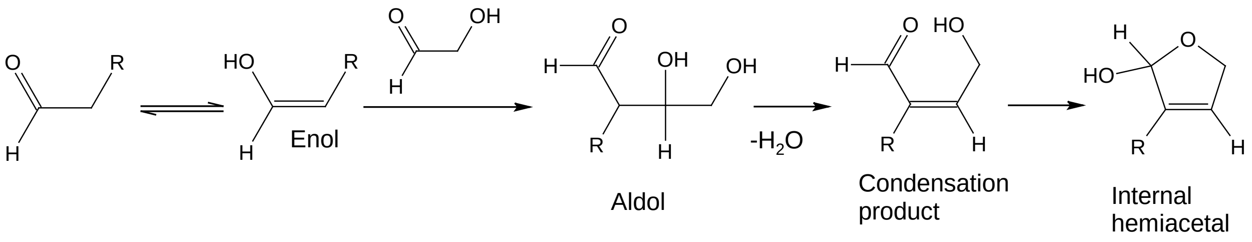


Figure 4: Examples of particle mass concentration measurements by SMPS (corrected for wall-loss) as a function of photooxidation time under low-NO$_x$ (top) and high-NO$_x$ (bottom) conditions.



Scheme 1: An aldol condensation reaction involving glycolaldehyde that results in an addition of C_2H_2O to the formula of the aldehyde co-reactant.

Table 3: Most common mass differences in the high resolution mass spectra of low-NO_x toluene SOA (in the order of decreasing frequency of occurrence).

Positive Ion Mode		Negative Ion Mode	
Low RH	**High RH**	**Low RH**	**High RH**
C_2H_2O	CH_2	C	O
CH_2O	O	C_2H_2O	CH_2O
C	CH_2O	O	C
CH_2	C_2H_2O	CH_2O	C_2H_2O
O	C	CH_2	CH_2
$C_3H_4O_2$	CO	CO	C_2H_2