

## Anonymous Referee #1

(1) This manuscript describes an instrument configuration used to measure the volatility dependent composition and CCN activity of an aerosol. The experimental approach was used to measure a well-characterized inorganic aerosol and a well-studied secondary organic aerosol produced from ozonolysis of alpha-pinene. The measurements are useful and the description would be of interest for some readers of this journal. But while there is nothing wrong with the manuscript, it describes a rather straightforward configuration of components used by many researchers and, thus, is not especially novel. To me, the preliminary results are the most interesting element of the manuscript. But I wonder whether it would make more sense to present them in a separate paper focused on the interpretation of the data and not the experimental technique. Nevertheless, the manuscript could be suitable for publication after the points below are addressed. The text is easily understood but would benefit from additional editing.

We thank the referee for the helpful comments and suggestions. While we do agree that the experimental setup combines techniques that have been used in the past, we are proposing a new way to analyze the corresponding data and then synthesize them following the 2D-VBS framework. Our hope is that the same experimental method combined with the new analysis technique will provide valuable insights into these properties and their relationships. We do agree that the first results are quite interesting and this is the reason that we prefer to combine the presentation of the experimental technique, the data analysis method, and the results of this pilot study to demonstrate the utility of the proposed approach.

(2) The observation that O:C and hygroscopicity decreased for the least volatile particles is certainly interesting. The authors provide a plausible explanation for the unexpected pattern. But further explanation of the experimental technique is required. Specifically, the time required for the full measurement sequence and the order of the TD temperatures should be provided. The rationale for this is that it seems possible that the aerosol continued to evolve during the measurements such that what is sampled when the TD is set at 100 C differs from that when it is at 150 C.

We have added the requested details about the experimental technique. In short, the aerosol is passed through the TD for 7-10 SMPS scans (16-23 minutes). Then, the aerosol is sent through the by-pass line until the TD is at the next set point (usually 7-10 SMPS scans). Once the TD is at the desired new temperature, aerosol is sent through the TD for the same number of SMPS scans and this process is repeated until measurements in all TD temperatures have been performed. Depending on the number of temperature set points, a full sequence can take anywhere from 2.5-3.5 hours. In our experiments the temperature has been increasing during the TD scan. The potential evolution of the SOA during these measurements can be checked by comparing the AMS spectra to the original one in the beginning of the scan. The measurements can also be repeated by performing a second TD scan and collecting a second thermogram. In our experiment the change of the SOA spectra during the experiment was minimal (less than 5 degrees) in all cases. This information has been added to the revised paper.

(3) Page 6, line 22: Rather than just stating that the loss rate was determined it should be reported. A large correction for a high loss rate could significantly increase uncertainty in the measured MFR.

This is a good point. We have included the corresponding information about the TD loss rate constant as a function of temperature and particle size in the Supplement.

#### Minor points

(4) Page 2, line 19: “. . .is reasonable CCN material using supersaturated conditions” should be re-worded.

We have removed “using supersaturated conditions” from this sentence to avoid confusion. In the following sentence we added that all of the studies cited there performed measurements in supersaturated conditions.

(5) Page 4, line 23: Why “proposed”?

We included the word proposed because we are proposing a method to measure and relate these three properties. To avoid confusion, we have removed this word.

(6) Page 5, line 11: What is a “large response”?

We have removed this relative term and rewrote the sentence to state that we aligned the size distributions using the minimum that occurs between the DMA upscan and downscan.

(7) Page 5, line 13: If this level of detail about the analysis of the data is going to be provided then the approach to inverting the SMPS-CPC and SMPS-CCNC distributions should be included.

We have rewritten this section to include more detail regarding the inversion technique and included a reference to the study that developed this method.

(8) Page 6, line 21: Use metric or change in to inch or to in. to clarify.

Done.

(9) Page 7, line 11: “. . .behave as non-volatile” should be re-worded.

We have rewritten this sentence.

(10) Page 7, line 12: Replace “extremely” with something like “very”.

Done.

(11) Page 7, line 16: This final sentence repeats what was already explained.

We have removed this sentence to avoid repetition.

(12) Page 8, line 24: I appreciate what you are trying to explain here, but as written the first and second parts of the sentence seem contradictory.

We have removed the beginning of this sentence and added the rest to the end of the previous sentence to avoid repetition and confusion.

(13) Page 9, line 18: “. . .conventional thinking, which assumes” should be re-worded.

Done.

(14) Page 9, line 24: Change to something like “Similar to the pattern observed with the activation diameter. . .”

We have made the recommended change.

## Anonymous Referee #2

(1) In this submission, the author combines several established aerosol instruments to measure hygroscopicity, volatility, and oxygen to carbon ratio simultaneously. A new inversion technique to handle the output from the instruments is used. This technique assigns hygroscopicity, and oxygen to carbon ratio to each volatility bin in  $\log_{10}(C^*)$  space. This requires several assumptions, and no support for the legitimacy of the assumptions are made, however, to do so would be difficult and likely beyond the scope of the submission. There appears to be enough information to reproduce the experiment as well as the inversion routine.

The conclusion is original and adds to the discussion of oxygen-to-carbon ratio and hygroscopicity as a function of volatility bin. Several studies in this area contradict one another and sometimes theory. The paper's conclusion offers a possibility for previous results to be complimentary, but would require a shift in the proposed theory.

The author submits the results of 4 experimental conditions, and the paper uses a single experiment as an example. The results of other experiments appear to generally corroborate the author's conclusions and are located in the supplemental material. All experiments are used to test the noise and limitations of the proposed analysis method.

Several comments are listed below. In addition to those comments, a rewrite of the abstract should also be entertained as the first sentences are long and confusing. The main body of the document is clear and mostly precise. No large rewrites are deemed necessary, and I have no major objections.

We appreciate the positive assessment of our work by the referee. We have rewritten the abstract shortening the initial sentences. Detailed responses to the comments can be found below.

(2) Page 1 line 28: Acute not proper for all 3 cites. Miller is a long term study, Dockery is for acute aerosol episodes (not acute mortality), but Brooks seems appropriate.

We have removed the two citations following the suggestion of the referee.

(3) Page 2 line 12: Soften statement. Authors studying cancer causing aerosols may disagree with the "three of the most important properties of organic aerosol."

We rewrote this sentence to state that these properties are important for the OA lifetime.

(4) Page 2 line 14-15: Hygroscopicity is the measure of a volume of water associated with a unit volume of solute. This is a bit more precise than "ability to absorb water." Hygroscopicity is not a measure of a particles ability to form cloud droplets.

We have revised this sentence to better define hygroscopicity.

(5) Page 3 line 7-8: Massoli et al doesn't seem to make those conclusions. The Massoli paper cites Good et al 2010 and Petters et al 2009 which do make the proposed explanations.

We have added these two citations and removed the Massoli et al. citation to better reflect the proposed explanations.

(6) Page 3 line 18-19: Insert comma before “and.”

Done.

(7) Page 3 line 26-29: These two sentences can be combined to reduce repetitive nature.

We have combined the two sentences.

(8) Page 5 line 14: Please specify which diffusivity. Mass diffusivity describes the movement of the mass, while thermal diffusivity describes the movement of energy.

The CCNC exploits water’s higher mass diffusivity than heat’s thermal diffusivity in air. We have revised the manuscript to make this clear.

(9) Page 5 line 15: Replace “its” with a proper noun to avoid confusion.

Done.

(10) Page 5 line 15: replace “a” with “an”

Done.

(11) Page 6 line 10: Confused by the word “adding.” Does the author mean that we look up the activation diameter on the  $\log(S_c)$ - $\log(D_d)$  plot? A few more words may be necessary.

We have revised this sentence describing how we estimated  $\kappa$  from the activation diameters. We plotted the activation diameters at their measured supersaturations on the  $\log(S_c)$ - $\log(D_d)$  plot and then  $\kappa$ ’s were estimated by which line of constant  $\kappa$  on this plot fit the activation diameters.

(12) Page 6 line 14: “higher sensitivity” may not be necessary. If used, should specify that the author desired a higher sensitivity to signal and not mass-to-charge.

We have removed “higher sensitivity” to avoid confusion.

(13) Page 8 line 5-7: The thermogram (Figure 2a) displays the evaporation of Ammonium Sulfate below 150 C, but page 7 line 28 says Ammonium Sulfate is involatile below 150 C. In my experience, the thermogram is correct.

The evaporation of ammonium sulfate particles in a TD expressed as mass fraction remaining depends not only on the TD temperature but also on particle size and residence time of the aerosol in the TD. We have changed the temperature in the manuscript to “100°C” to cover all these cases and to be consistent with Figure 2.

(14) Page 8 line 10-12: Which theory? Köhler theory or previous observations. Appears Ammonium Sulfate is still stable at 100°C, but disassociates at higher temperatures. Is the hygroscopicity of disassociated Ammonium Sulfate the same as pure Ammonium Sulfate? What about when including impurities? Are these in the “theory?”

The activation diameters through the BP and the TD at 50 and 100°C are compared to Köhler theory assuming pure ammonium sulfate aerosol. We have added “Köhler” before theory to make this clearer. Disassociated ammonium sulfate will have the same hygroscopicity because the ammonium and sulfate ions will interact with water similarly. When aerosols have impurities the overall  $\kappa$  will be higher or lower depending on the  $\kappa$ 's of the impurities due to the mixing rule.

(15) Page 9 line 23-25: Some may contend that 0.39 is oxidized, especially when compared to alpha-pinene. A comparison may be better.

We have rephrased this sentence. We now compare the O:C ratio through the BP to the O:C ratio through the TD at 125°C in order to show that the least volatile material is less oxidized than the overall SOA.

(16) Page 11 line 18-19. In order to use equation 4, you must also assume density is constant between all volatility bins.

We now state this assumption in the corresponding discussion.

## Fred Brechtel

### General comments:

(1) A more appropriate title would be: A technique for the measurement of organic aerosol cloud nucleating potential, oxidation level, and volatility distributions. Hygroscopicity is more generally connected with measurements made below 100% RH using an HTDMA or some similar tool.

We can see the point, but one could also argue exactly the opposite: measurements of CCN properties are better for the quantification of the hygroscopicity of a compound given the non-ideal solution effects often dominating behavior below 100% RH. Given that it is clear that the hygroscopic parameter  $\kappa$  estimated in this method is  $\kappa_{\text{CCN}}$  we would prefer to keep the same title. To avoid any confusion we clarify now both in the Abstract and the Conclusions that the hygroscopicity is based on CCN activity.

(2) Why limit the method to only organic aerosol?

The method can be easily applied to inorganic or mixed aerosol populations. However, given that the volatility and hygroscopicity of the major inorganic aerosol components in the atmosphere is well understood, the organic aerosol is the primary focus of this work.

(3) Please add a short discussion in the introduction section of the application of the technique to unknown composition ambient aerosol.

We have added the corresponding paragraph.

(4) Techniques where multiple aerosol properties are determined simultaneously can be made much stronger by adding size resolution – e.g. by pre-selecting a time sequence of monodisperse particles with a DMA upstream of the various instruments, more easily interpretable data would likely result. This very likely, in part, explains the largely inconclusive previous studies as noted on page 4 line 15-20. Although beyond the scope of this work, I highly recommend the authors consider modifying their setup so a DMA is positioned upstream of the thermodenuder/bypass so all instruments sample the exact same monodisperse aerosol after having undergone the exact same thermal (or no) pre-treatment. This configuration will also help eliminate the ambiguity in the data comparison between aerodynamic diameter measured by the AMS and the electrical mobility diameter measured by the DMA and delivered to the CCN and CPC. Admittedly, the time resolution of the measurement will be sacrificed, but the much easier to interpret data and interesting size-dependent results that would be produced could be very exciting.

Consider the following thought experiment considering an unknown composition ambient aerosol. As configured, the AMS samples the polydisperse particle distribution after a certain temperature exposure in the TD. Any number of originally differently sized particles could contribute to the AMS response at a single aerodynamic diameter depending on the volatility

distribution of the input aerosol to the TD. In fact, if some of the input aerosol to the TD were soot (or some other non-volatile species) coated with volatile SOA, the AMS may not detect the non-volatile core left after treatment in the TD. The scanning DMA and CCN systems would detect the presence of the non-volatile core, but there would likely not be a corresponding signal in the AMS. How would these results be interpreted? This situation is one where selecting monodisperse aerosol upstream of the TD would greatly facilitate interpretation of the measurement results.

This is an excellent suggestion. Adding size resolution measurements can enhance our results significantly. As with any experimental setup, there are trade-offs. By adding size resolution, we will lose time resolution, but use of both modes of operation is certainly possible in laboratory experiments that can be repeated. Additional challenges may include the characterization of the resulting low aerosol concentrations by the AMS. However, this approach could provide significant advantages in the interpretation of the results for ambient measurements. We will try to explore this idea in future work.

(5) Most volatility studies assume that material volatile at or below the thermodenuder temperature set-point is evaporated to the gas phase. However, it seems that chemical reactions stimulated by the high temperature environment may also change the composition and oxidation state of the particles within the TD. Can you comment on the likelihood of this?

There is always a possibility that chemical reactions can occur in the TD and this is one of the main weaknesses of this approach. In this study, however, the likelihood of chemical reactions occurring is relatively small because the temperature in the TD never rises above 125°C. This is a relatively low value compared to most TD studies. A second test is based on the relatively small changes of the particulate phase composition (based on AMS measurements) as the temperature is increasing. However, none of these tests is conclusive. A detailed characterization of the composition of the remaining organic phase is required to quantify the contribution of reactions to the observed changes. This important point has been added to the Conclusions of the paper.

(6) Another general question worth asking is: what is the relevance of volatility studies to the atmospheric aerosol since they are never exposed to most of the temperatures used in TD studies?

The major advantage of the volatility studies based on TDs is that they provide insights about the less volatile organic components. These are usually in the particulate phase at room temperature, but they may evaporate partially at higher atmospheric temperatures or when diluted significantly. The least volatile secondary components, when created by gas-to-particle conversion processes are important for the formation and growth of new particles in the atmosphere. Finally, the evolution of the volatility distribution of the organic aerosol can provide an indirect way to gain insights about the very difficult to measure chemical composition and evolution of these thousands of components. This discussion has been added to the introduction of the paper.



(7) Finally, it is not very clear to me why volatility would necessarily be well connected to hygroscopicity.

This is an excellent point. It has been assumed that the bridge connecting these two properties is the oxidation level. It has also been proposed that the link may be so strong that knowledge of the oxidation level may be sufficient to determine both properties. Our work here, among others, suggests that this is not so straightforward and these linkages are quite complex and may be even non-monotonic.

More detailed comments:

(8) Page 2, line 10: suggest adding that the gases can produce new particles AND condense on pre-existing particles.

Done.

(9) Page 2, line 29: please clarify what ‘this SOA system’ refers to.

It refers to the  $\alpha$ -pinene ozonolysis SOA system. We have changed this in the manuscript.

(10) Page 3, line 34: is ‘MFR’ defined somewhere?

We have added a definition for MFR the first time it appears.

(11) Page 4, line 4: suggest “. . .that the hygroscopicity of organic aerosol generally increases with . . .”

Done.

(12) Page 5, line 5: were flow mixers employed upstream of the two sample flow splits to ensure the AMS/DMA and CPC/CCN received the same aerosol populations?

We did not use flow mixers. The streams were split using a normal T union. We have clarified this in the manuscript.

(13) Page 6, line 20: please explain how ‘mass fraction remaining’ in the TD is determined using SMPS measurements. How is the density measured to convert the mobility volume distribution to a mass distribution?

To calculate the MFR, we divided the TD mass at each SMPS measurement by an interpolated BP mass using the BP measurements before and after the TD measurements. We used a constant density of  $1.4 \text{ g cm}^{-3}$  for  $\alpha$ -pinene ozonolysis SOA according to the recommendation of Kostenidou et al. (2007). We have updated the manuscript to include this information.

(14) Page 7, line 4: it is worth mentioning here the shorter residence time you expect at your maximum TD operating temperature.

We have added this point.

**(15)** Page 7, line 4: please comment on the expected range in residence time within the TD. For the low flow rate and large tube diameter, do you expect laminar flow conditions? If so, wouldn't particles traveling near the centerline experience a residence time roughly half those near the walls? If this is the case, how would this impact your results?

We do expect laminar conditions with a Reynolds number around 10, which would mean that particles traveling near the walls have longer residence times than those near the centerline. The effect of the simplifying assumption of an average residence time has been considered by Cappa (2010). The change in MFR when the more detailed fluid dynamics model was used was a few percent. So its effect on the results of the present study in which the volatility is characterized using logarithmically spaced bins is small.

**(16)** Page 9, line 1: please explain what  $C^*$  means.

$C^*$  is the effective saturation concentration used in the 1D-VBS. We have added an explanation and the corresponding reference in the manuscript.

**(17)** Page 9, line 15: I am confused by the statement that using the 1D-VBS allows for comparison of different TD studies regardless of TD operating conditions. If the physical residence time in a TD is too short to allow complete volatilization, or if the temperature time history within a TD is not represented by the temperature set-point of the study, how would a model allow successful intercomparisons of different TD study results?

As stated in the introduction, thermograms are heavily influenced by several factors (OA concentration, particle size, residence time, etc.) and TD studies use different experimental conditions. This can result in quite different thermograms for the same aerosol even when the same TD is used. So use of a model simulating the aerosol evaporation inside the TD can help “translate” the measurements to the same basis, the aerosol volatility distribution. The 1D-VBS is a good framework for this analysis, but of course other descriptions of the aerosol volatility distributions are possible. We have rewritten this section to make it clearer as to why we recommend using a model to generate volatility distributions to compare between studies.

**(18)** Page 10, line 2: please add the supersaturation value set in the CCN instrument after activation diameter.

Done.

**(19)** Page 10, line 6: 155 +/- 1 nm? This level of uncertainty or standard deviation in the measured activation diameter is a little hard to believe, you are reporting a size variation of only +/-0.06%. If you were to scan monodisperse 155 nm diameter PSL calibration particles 50 times and calculate the variation in the measured peak size, my guess is you would see higher intrinsic measurement uncertainty than 0.06%.

This is a valid point and it is probably a coincidence for these data points. The standard deviation of the various activation measurements was a few nanometers. To avoid misleading the readers about the overall variability of our measurements, we do not show in the main text the variability in this specific case, which is a lot less than the average. The variability of all the measurements is shown in the corresponding figures.

(20) Page 10, line 10: or that chemical changes to the particles that occurred within the TD rendered the particles less CCN active. . .?

We have added this to the manuscript.

(21) Page 10, line 15: You make a very good point here that trying to generalize relationships between volatility, hygroscopicity/cloud activity and oxidation level is over simplifying the situation. However, it would be extremely useful if such relationships could be developed, perhaps by dividing organic species into certain families or structures with key similarities. Any comments?

This could be very helpful in determining useful relationships for families of organic compounds. There are many different ways to divide the species, but one that is widely used is to group them using PMF. It has been shown that these groups (M-OOA, L-OOA, HOA, etc.) exhibit different properties and we could group them this way. For this specific work, since the OA is from one source, this method is not that useful. We hope to be able to develop such relationships applying the approach suggested here in more complex systems including of course ambient OA.

(22) Page 11, line 10: can you comment briefly on how you would extend this analytical approach to unknown composition ambient aerosol? E.g. mixtures of insoluble material, soluble inorganics and soluble SOA?

Our intention is to develop the method enough, so that it can be applied to ambient aerosol. However, we believe that the availability of real-time automatic instrumentation for the measurement of the size-composition distribution of the sub-micrometer ambient aerosol will allow us to work with known chemical composition (with the exception of the organic compounds). The analysis could use the known hygroscopic properties of the inorganic aerosol components and focus on the properties of the organics. There are a number of challenges including the determination of the size distribution of the refractory aerosol components that are not measured by the AMS (though the SP-AMS or the SP2 can help with black carbon), issues related to the mixing state of ambient particles, etc. Techniques like the Positive Matrix Factorization (PMF) could help to split the OA into a few components and then determine their corresponding properties. We have included a few lines in the manuscript on how the method would be applied to ambient aerosol.

(23) Page 11, end of page: missing period.

Added.

(24) Page 13: in performing the sensitivity analysis – did you systematically eliminate each one of the 18 equations and run 17 studies? Or did you just run one study after picking a single equation to eliminate? How would your sensitivity results change if you ‘randomly’ added + or – one standard deviation to the experimental data used to constrain the equations? What if you added one standard deviation to all of your data?

We have rewritten the beginning of the sensitivity analysis section to provide more clarity on how we performed this test. We systematically removed each one of the 18 equations and solved the resulting system 18 times. A more detailed uncertainty analysis would involve selections of values from the corresponding distributions of the various parameters, repeating the calculation, and estimating the distribution of the values of the resulting parameters. Perturbing one parameter at a time is a cheap way to do that. Selecting extreme values for all parameters may lead to an overestimation of the uncertainty (this combination is quite unlikely). We believe that our sensitivity analysis approach is adequate for its purpose, which is to identify if one of the measurements is dominating the answer of the problem.

(25) Page 13, line 17: suggests

Corrected.

(26) Page 14, line 2: if the method has difficulty with low concentrations, does this impact its usefulness for studies of the ambient aerosol?

The “low” is used in a relative not an absolute sense here. We now clarify in the revised paper that the mass fraction of a volatility bin must be greater than 0.1 to allow the accurate estimation of the bin’s properties based on a single experiment. When multiple experiments are combined together, the method is able to accurately estimate the bins’ properties as long as there was enough material (more than 10%) from that bin in at least one experiment.

(27) Page 14, it would be helpful if you rewrote the paragraph starting at line 6 so it was easier to understand.

We have rewritten this paragraph to help make it clearer to the reader.

# A technique for the measurement of organic aerosol hygroscopicity, oxidation level, and volatility distributions

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**Abstract.** Hygroscopicity, oxidation level, and volatility are three crucial properties of organic pollutants ~~are three crucial properties that determine their fate in the atmosphere~~. This study assesses the feasibility of a novel measurement and analysis technique to determine these properties of organic aerosol components at the same time and ~~to~~ establish their relationship. The proposed experimental setup utilizes a cloud condensation nuclei (CCN) counter to quantify hygroscopic activity, an aerosol mass spectrometer to measure the oxidation level, and a thermodenuder to evaluate the volatility. The setup was first tested with secondary organic aerosol (SOA) formed from the ozonolysis of  $\alpha$ -pinene. The results of the first experiments indicated that, for this system, the less volatile SOA contained species that had on average lower O:C ratios and hygroscopicities. In this SOA system, both low and high volatility components can have comparable oxidation levels and hygroscopicities. The method developed here can be used to provide valuable insights about the relationships among organic aerosol hygroscopicity, oxidation level, and volatility.

## 1 Introduction

Anthropogenic activities, such as fuel combustion, as well as biogenic sources, such as emissions from vegetation, can introduce particles and particle precursors into the atmosphere. These airborne particles have been identified as a factor contributing to cardiovascular and respiratory diseases (Pope, 2000; van Eeden et al., 2005) and an increased risk for acute morbidity and mortality (Dockery, 2001; Miller et al., 2007; Brook et al., 2010). In addition, atmospheric aerosols influence the Earth's radiation balance directly by scattering and absorbing

solar radiation and indirectly by serving as cloud condensation nuclei (CCN). Despite their major role in the Earth's energy balance, their net effect on climate is one of the major uncertainties in the climate change problem (IPCC, 2013).

In most areas, organic compounds represent anywhere from 20–90 % of the submicron aerosol mass (Murphy et al., 2006; Zhang et al., 2007). Organic aerosol (OA) is traditionally classified either as primary (POA) or secondary (SOA). POA refers to organic compounds that are emitted to the atmosphere directly in the particulate phase. SOA refers to particulate matter produced by gas-to-particle conversion processes. In general, intermediate volatility, semi-volatile, and volatile organic compounds undergo oxidation in the atmosphere and form products that can produce new particles and condense on pre-existing particles.

Three of the most important properties ~~regarding~~ OA lifetime in the atmosphere are hygroscopicity, oxidation level, and volatility. Hygroscopicity, often ~~quantified~~~~expressed~~ by the hygroscopicity parameter,  $\kappa$  (Petters and Kreidenweis, 2007), is ~~at the~~ a measure of ~~the how a volume of water associateds with a unit volume of solute~~~~particle's ability to absorb water and form cloud droplets~~. Oxidation level often provides an indication of the age of the OA in the atmosphere. It is expressed as the oxygen to carbon (O:C) ratio or, more accurately, the average carbon oxidation state (OS<sub>C</sub>). Volatility determines the partitioning of organic compounds between the gas and particle phases. The one-dimensional volatility basis set (1D-VBS, Donahue et al., 2006) has been proposed as a framework for the description of the evolution of the OA volatility distribution using logarithmically spaced bins.

Several studies have shown that SOA from the ozonolysis of  ~~$\alpha$~~ -pinene is reasonable CCN material ~~using supersaturated conditions~~ (VanReken et al., 2005; Huff Hartz et al., 2005; Prenni et al., 2007; King et al., 2007; Engelhart et al., 2008; King et al., 2009; Wex et al., 2009; Massoli et al., 2010; Kuwata et al., 2011; Frosch et al., 2011). These studies all reported similar  $\kappa$  values based on ~~CCN supersaturated~~ measurements at supersaturated conditions, ranging from 0.07–0.15. Huff-Hartz et al. (2005) found that SOA produced from monoterpenes was more hygroscopic than SOA from sesquiterpenes. Both King et al. (2007) and Kuwata et al. (2011) observed that the CCN behavior of  $\alpha$ -pinene ozonolysis~~this SOA-system~~ was dependent on the OA mass concentration. Frosch et al. (2011) found that  $\kappa$  for  ~~$\alpha$~~ -pinene ozonolysis SOA increases with chemical aging.

Hygroscopic properties of  $\alpha$ -pinene ozonolysis SOA have also been studied using subsaturated conditions (Prenni et al., 2007; Wex et al., 2009; Poulain et al., 2010; Massoli et al., 2010; Tritscher et al., 2011). These studies determined a hygroscopic growth factor (HGF) to estimate  $\kappa$ , reporting values from 0.01–0.08. Massoli et al. (2010) used both a hygroscopic tandem differential mobility analyzer (H-TDMA) and a CCN counter while studying SOA from the ozonolysis of  $\alpha$ -pinene and found that the  $\kappa$  at subsaturated conditions (estimated from HGF measurements) was 20–50 % lower than that based on CCN measurements at supersaturated conditions. A number of explanations have been proposed for this behaviour including increasing dissolution of SOA components at supersaturated conditions, surface tension effects, etc. (Petters et al., 2009; Good et al., 2010; Petters et al., 2009)(Massoli et al., 2010).

The oxidation level of  $\alpha$ -pinene ozonolysis SOA has mainly been studied through the use of high resolution mass spectrometry (Bahreini et al., 2005; Alfarra et al., 2006; Song et al., 2007; Shilling et al., 2009; Huffman et al., 2009; Poulain et al., 2010; Massoli et al., 2010; Kuwata et al., 2011; Tritscher et al., 2011; Frosch et al., 2011). These studies reported O:C ratios from around 0.3–to 1. The higher O:C ratios were determined by Massoli et al. (2010) for extended periods of chemical aging; most of the average O:C ratios ranged from 0.3 to 0.5. The use of the O:C ratio can allow for easier classification of OA into different classes using the two-dimensional volatility basis set (2D-VBS, Donahue et al., 2011). Poulain et al. (2010) observed that the most oxygenated compounds were less volatile than the less oxygenated ones, and Kuwata et al. (2011) found that the O:C ratio for  $\alpha$ -pinene ozonolysis SOA depended on the mass concentration.

In addition to hygroscopicity and oxidation level, there have been a number of studies focusing on the volatility of SOA from the ozonolysis of  $\alpha$ -pinene with either a thermodenuder (TD) (An et al., 2007; Kostenidou et al., 2009; Huffman et al., 2009; Poulain et al., 2010; Lee et al., 2011; Cappa and Wilson, 2011; Kuwata et al., 2011) or a volatility tandem differential mobility analyzer (V-TDMA) (Stanier et al., 2007; Jonsson et al., 2007; Tritscher et al., 2011). The difficulty in comparing these volatility studies stems from the different experimental setups used. Different heating methods (TD, V-TDMA, etc.), residence times in heating sections, and temperatures make it challenging to determine a common thread. For example, Poulain et al. (2010) observed nearly all of the SOA evaporated at 200°C at a residence time of 9 s in the

heating section of a TD, but Lee et al. (2011) reported that most of the SOA evaporated at around 90°C for a residence time of 16 s. The use of the 1D-VBS (Donahue et al., 2006) can help overcome this obstacle, making it easier to compare volatility distributions rather than thermograms, which express ~~plot~~ the mass fraction remaining (MFR) as a function of temperature values ~~and~~ which are influenced by several different experimental factors (particle size, residence time in heating section, OA concentration, etc.) (Cappa, 2010; Riipinen et al., 2010; Kuwata et al., 2011). Furthermore, the evolution of OA's volatility distribution can provide an indirect way to gain insights about the very difficult to measure chemical composition and evolution of these compounds (Donahue et al., 2011).

Several studies have attempted to relate two of the three properties, but few have attempted to relate all three. Jimenez et al. (2009) proposed that the hygroscopicity of OA generally increases with the oxidation level expressed by the O:C ratio and that there is also an inverse relationship between the O:C ratio and volatility. Tritscher et al. (2011) used a volatility and hygroscopicity tandem differential mobility analyzer (V/H-TDMA) and an Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, hereafter AMS) during the chemical aging of  $\alpha$ -pinene SOA and found that volatility decreased while hygroscopicity and the O:C ratio remained fairly constant. Cerully et al. (2015) used a TD followed by a CCN counter, a scanning mobility particle sizer (SMPS), and an AMS in parallel and observed small changes in hygroscopicity for ambient OA components with dramatically different volatilities and concluded that the more volatile compounds were more hygroscopic than the remaining material. Several other studies (Poulain et al., 2010; Kuwata et al., 2011; Hong et al., 2014; Hildebrandt Ruiz et al., 2015) have investigated the effects of environmental parameters on one or all of these properties. However, these results are often inconclusive or even contradictory and the links among these three properties are yet to be elucidated.

A theoretical framework (Nakao, 2017)(Nakao, 2017) has attempted to relate these three properties using the 2D-VBS framework (Donahue et al., 2011). The approach utilized correlations between the O:C ratio, volatility, and hygroscopicity to predict lines of constant  $\kappa$  in the 2D-VBS. The study concluded that relatively volatile OA components with a low O:C ratio can have the same hygroscopicity as OA with lower volatility and a higher O:C ratio.

One major obstacle pertaining to an experimentally-determined relationship between these three properties for ambient aerosols is the often unknown or uncertain composition. The



AMS can quantify the concentrations of the non-refractory inorganic aerosol components as well as the total organic aerosol concentration, with further separation of the OA into components provided by techniques like is successful at breaking ambient aerosol into inorganic and organic species and further identification of the OA can be made using positive matrix factorization (PMF). However, the analysis of the combined measurements of all three properties remains challenging. more work is needed to develop a method that can characterize ambient aerosols and generate concrete relationships between hygroscopicity, oxidation level, and volatility.

The purpose of this work is the development of a method for the synchronous measurement of OA hygroscopicity, oxidation level, and volatility. In the next section, we describe the proposed technique that utilizes a suite of aerosol instrumentation to measure these properties. Then, the method is tested with  $\alpha$ -pinene ozonolysis SOA. This SOA system has been studied extensively so it can be a useful first test for the proposed experimental approach. Our objective is not to perform a comprehensive study of the properties of this SOA (which depend on SOA levels, relative humidity, etc.), but rather to use it as a pilot study. Finally, a data analysis technique is developed to interpret and synthesize the corresponding measurements.

## 2 Methodology

### 2.1 Instrument setup

A schematic of the proposed experimental setup can be seen in Fig. 1. Particles are sampled through either a TD or a by-pass (BP) line via two three-way valves and then the sample stream is split using a T union between an AMS and a differential mobility analyzer (DMA, TSI, model 3081). The stream from the DMA is split again with a T union between a condensation particle counter (CPC, TSI, model 3010/72) and a CCN counter (CCNC, Droplet Measurement Technologies). In this study, the AMS used a flow rate of  $0.1 \text{ L min}^{-1}$  while the CPC and the CCNC used  $0.3$  and  $0.5 \text{ L min}^{-1}$  respectively. The sheath flow in the DMA was set to  $8 \text{ L min}^{-1}$  to allow for a 10:1 sheath to aerosol flow ratio as the particles were classified. The upscan of the DMA was set to 120 s and the downscan was set to 15 s.

In a typical experiment, once particles are ready for sampling, they pass through the TD at the first temperature set point for 15-25 min 7-10 SMPS scans (16-23 min). Then, the particles are sent through the BP as the temperature of the TD increases to the next temperature (another

~~15-25 min usually 7–10 SMPS scans~~). Once the TD reaches the next set point, the particles are directed through the TD for the same ~~sampling period amount of SMPS scans~~ and this process is repeated until ~~measurements at all desired temperatures set points have been obtained measured~~. Total sampling time for 4–5 temperature set points is around 2.5–3.5 hr. Set points for the TD start at the lowest temperature and always increase.

## 2.2 Hygroscopicity

Hygroscopicity measurements were made with a CCNC, which generates supersaturations by exploiting water's higher mass diffusivity than heat's thermal diffusivity in air (Roberts and Nenes, 2005). The CCNC's fast response time allows it to be coupled to an SMPS, a technique called Scanning Mobility CCN Analysis (SMCA, Moore et al., 2010). In our experiments, polydisperse aerosol was charged with a Po-210 neutralizer and then entered a DMA where the particles were classified by their electrical mobility and counted by a CPC and the CCNC as the DMA voltage was scanned. Particle number concentrations (CN) and size distributions were obtained from the SMPS using the AIM software. CCN concentrations and size distributions were obtained following the technique described in Moore et al. (2010). The SMPS and CCNC size distributions were aligned by matching the minimum in concentration that occurs during the transition between the DMA upscan and downscan, since it is short and generates a large response in both the CPC and CCNC, was used to align both instruments' responses. An activation curve was produced by inverting the time series to generate number and CCN size distributions and dividing the CCN concentration by the total particle concentration (CN concentration) at each size. The activation diameter was calculated by fitting the activation curve to a sigmoidal function:

(1)

where  $CCN/CN$  is the fraction of activated particles,  $B$  and  $c$  describe the asymptote and slope of the sigmoid respectively,  $D_d$  is the dry diameter, and  $D_{p50}$  is the diameter at which 50 % of the particles activate for a symmetric size distribution; this corresponds to the activation diameter.

The method to determine ~~KK~~ follows the analysis done by Petters and Kreidenweis (2007) and will be explained briefly here. The defining equation is known as the ~~KK~~-Köhler equation:

(2)

where  $S$  is the saturation ratio,  $D$  is the wet particle diameter,  $D_d$  is the dry diameter,  $\sigma$  is the surface tension of the solution/air interface,  $M_w$  is the molecular weight of water,  $R$  is the universal gas constant,  $T$  is the temperature, and  $\rho_w$  is the density of water. For a selected  $D_d$  and  $\kappa$ , the critical supersaturation,  $S_c$ , can be computed from the maximum of Eq. (2). Then, lines of constant  $\kappa$  can be obtained by plotting  $\log(S_c)$  as a function of  $\log(D_d)$ . To estimate  $\kappa$ , by adding experimentally-determined activation diameters at different supersaturations were added to the  $\log(S_c)$ - $\log(D_d)$  plot and the  $\kappa$  was estimated by which isopleth fit the data, the corresponding  $\kappa$  can be estimated.

## 2.3 Oxygen content

An AMS was used to monitor the aerosol's composition. In our experiments, the AMS was operated in the higher-sensitivity V-mode (DeCarlo et al., 2006) and used an averaging time of one minute. The data were analyzed in Igor Pro 6.22A (Wavemetrics) using “Squirrel” version 1.56D for unit mass resolution analysis and “Pika” version 1.15D for high resolution analysis. The O:C ratios reported here were calculated using the Canagaratna et al. (2015) method.

## 2.4 Volatility

Volatility measurements were made with the TD and the SMPS. These instruments were used to generate thermograms (MFR as a function of TD temperature). To calculate the MFR, we divided the TD mass at each SMPS measurement by an interpolated BP mass using the BP measurements before and after the TD measurements. The MFR represents the fraction of particle mass that did not evaporate in the TD. The thermogram can be combined with a TD model (Riipinen et al., 2010), which describes the multicomponent OA evaporation to calculate the OA volatility distribution. The fitting algorithm has been described and evaluated by Karnezi et al. (2014). The 1D-VBS (Donahue et al., 2006) is used here, which discretizes the volatility distribution into logarithmically spaced bins based on an effective saturation concentration,  $C^*$ .

The TD used for this study consisted of two parts: a heating section and a cooling section. The heating section is 2 ft long and is surrounded by heating tape to control the temperature. The cooling section is also 2 ft long and contains activated carbon to avoid any recondensation while the aerosol returns to room temperature. Aerosol passes through the entire TD via 1.5 in. tubing. Therefore, after accounting for all of the flows after the TD, there will be laminar flow in the TD,

~~resulting in the a centerline residence time of 23 s at 298 K in the heating section was 23 s, but the residence time will be shorter for the higher temperatures used in this study. Residence times for particles near the walls of the TD will be roughly double that of the particles on the centerline.~~

As particles pass through the TD, some of the mass will evaporate, but some particles will also be lost to the walls. To characterize these losses, NaCl particles were generated and passed through the BP and TD alternately for several temperatures. By comparing the size distributions through the BP and TD, the particle losses were quantified as a function of temperature and particle size for the flowrate used in our experiments (Fig. S1). Particle losses increased with temperature in the TD, but were fairly low (< 25 % at 125°C) and roughly constant over the size range of interest in this study (50–250 nm).

## 2.5 Smog chamber setup

All experiments were conducted in the Carnegie Mellon University smog chamber, a 10 m<sup>3</sup> Teflon (Welch Fluorocarbons) reactor suspended in a temperature-controlled room (Pathak et al., 2007). Before each experiment, the chamber was flushed overnight with purified air under UV illumination (GE, model 10526 and 10244) to remove any potential contaminants. Purified air was generated by passing compressed air through a high-efficiency particulate air (HEPA) filter to remove any particles, an activated carbon filter to remove any vapors, and silica gel to maintain the relative humidity (RH) at less than 5 %.

## 3 System test with ammonium sulfate aerosol

To determine whether the proposed and rather complex setup of several instruments operating together in series and in parallel was operating properly, a 1 g L<sup>-1</sup> solution of ammonium sulfate was pumped through an atomizer (TSI, model 3075) at a constant rate of 90 mL h<sup>-1</sup> using a constant output syringe pump (Braintree Scientific, model BS-300). Before entering the chamber, the resulting droplets passed through a silica gel dryer to produce dry particles. Ammonium sulfate particles have traditionally been used in TD and CCN tests because they are easy to produce and ~~are~~ behave as relatively non-volatile at temperatures below approximately 105°C (Clarke, 1991; An et al., 2007). Furthermore, they are ~~very~~ extremely hygroscopic with well-known properties. Their CCN activity has been shown to be consistent

with Köhler theory (Cruz and Pandis, 1997). At different TD temperatures below 105°C, ammonium sulfate particles should behave the same hygroscopically as the particles passing through the BP. ~~Our system uses the CCNC to measure the fraction of particles that will activate and become cloud droplets as a function of particle size and water vapor supersaturation, resulting in an activation curve.~~

The thermogram for the ammonium sulfate particles is shown in Fig. 2a. No aerosol mass evaporated at 50 and 100°C, but nearly all of the mass evaporated at 150°C. The remaining material at 150°C also included impurities in the ammonium sulfate solution that do not evaporate at that temperature. The measured activation diameter for the BP, two TD temperatures (50 and 100°C), and Köhler theory from this experiment is shown in Fig. 2b. The activation diameters at all supersaturations through the BP and the TD agreed with Köhler theory, confirming that our system operates properly for at least this simple model system.

#### 4 Application to $\alpha$ -pinene ozonolysis SOA

The ~~proposed~~ experimental approach was then applied to SOA. For these experiments,  $\alpha$ -pinene (Sigma-Aldrich,  $\geq 99\%$ ) was injected into the chamber using a heated septum injector with purified air as carrier flow. Ozone was generated by an ozone generator (AZCO, model HTU-500ACPS) and injected into the chamber after the  $\alpha$ -pinene injection. Table 1 displays the different experimental conditions examined in this pilot study. The initial ozone concentration and RH remained almost the same in all experiments, but the initial  $\alpha$ -pinene concentration and water supersaturation in the CCNC were varied.

For Experiment 1, 100 ppb of  $\alpha$ -pinene were injected into the chamber immediately followed by around 500 ppb of ozone. After one hour of reaction time, the ozonolysis was practically complete and particles were sampled through the TD and BP alternatively for five temperatures (25, 50, 75, 100, and 125°C). The SOA mass concentration, measured with the SMPS assuming a density of  $1.4\text{ g cm}^{-3}$  (Kostenidou et al., 2007), increased immediately following the ozone injection and reached a maximum of around  $108\text{ }\mu\text{g m}^{-3}$ . The SOA then began decreasing due to particles being lost to the chamber walls.

To check that the SOA sampled at the beginning of the experiment was similar to the SOA sampled at the end of the experiment, we compared the corresponding AMS mass spectra

using the theta angle ( $\theta$ ) proposed by Kostenidou et al. (2009). The  $\theta$  angle between the mass spectra of the BP at the beginning of the experiment and the BP before passing through the TD at 125°C was 2.4°, indicating that the change of the SOA's spectra during the experiment was minimal. The same behaviour was observed in all other experiments in this study.

The thermogram, TD model prediction, and corresponding estimated volatility distribution, using the Karnezi et al. (2014) algorithm, for Experiment 1 are shown in Fig. 3. The TD model reproduced the MFR measurements well. For this experiment with OA around 100  $\mu\text{g m}^{-3}$ , over two-thirds of the SOA had an effective saturation concentration ( $C^*$ ) of 1 or 10  $\mu\text{g m}^{-3}$ , 20% had a  $C^* = 0.1 \mu\text{g m}^{-3}$ , and 10 % had a  $C^* = 0.01 \mu\text{g m}^{-3}$ . The  $C^* = 0.01 \mu\text{g m}^{-3}$  bin also includes compounds with even lower volatilities. An effective enthalpy of vaporization,  $\Delta H_{\text{vap}}$ , equal to 65  $\text{kJ mol}^{-1}$  was estimated assuming an accommodation coefficient equal to unity.

Our TD results are comparable to those in the literature for  $\alpha$ -pinene ozonolysis SOA. At 100°C, the MFR for the SOA in Experiment 1 was  $0.29 \pm 0.01$ . Huffman et al. (2009) and Poulain et al. (2010) reported a MFR of around 0.35 at 100°C, but their SOA levels were several times larger (4–6) and their residence times were about half of the one used in this study. Kuwata et al. (2011) observed a MFR of 0.50 at a TD temperature of 100°C for lower SOA levels (25–37  $\mu\text{g m}^{-3}$ ) and a significantly shorter residence time (0.4 s). This further reiterates the difficulty in comparing volatility studies using different experimental methods. Generating reproducible TD results requires the same TD operated at the same flow rate and temperatures, which is why our study uses the 1D-VBS, allowing for comparisons between studies, regardless of TD operating conditions.

In addition to volatility, the SOA's oxygen content was also measured. Figure 4 shows the average O:C ratio through the BP and TD at different temperatures for Experiment 1. The O:C ratio started around 0.49 and decreased at higher temperatures, ending at  $0.39 \pm 0.02$  while passing through the TD at 125°C. All of the O:C ratios at a TD temperature of 50°C and above were statistically lower than the O:C ratios through the BP and TD at 25°C (one-tailed  $t$ -test,  $p < 0.0001$ ). The final O:C ratio of 0.39 corresponds to 11 % of the least volatile SOA (Fig. 3a). When compared to an O:C ratio of 0.49 through the BP, an O:C ratio of 0.39 Through the TD at 125°C indicates that the least volatile material in these experiments contained components that were not very oxidized at least on average.

Our O:C ratios fall into the reported range of O:C ratios in the literature for  $\alpha$ -pinene ozonolysis SOA (Huffman et al., 2009; Massoli et al., 2010; Kuwata et al., 2011; Tritscher et al., 2011). Kuwata et al. (2011) observed that the O:C ratio dropped sometimes due to high TD temperatures, but argued that increases in the mass concentration were the main cause of the O:C ratio decreasing. Poulain et al. (2010) reported that the more oxygenated compounds were less volatile than the less oxygenated ones, which contradicts our results, but their conclusions were based on changing the RH at which the SOA was formed, which could impact the SOA's response to heat treatment.

The SOA's hygroscopic activity was also measured at the same time. The measured activation diameter as a function of temperature for Experiment 1 is shown in Fig. 5a. The activation diameter of all the SOA remained fairly constant around 140 nm (0.2 % supersaturation) during the experiment and as the temperature in the TD increased to 50°C. However, for even higher TD temperatures, the activation diameter increased, ending at 155  $\pm$  4 nm (0.2 % supersaturation) for the least volatile 11 % of the SOA. The activation diameters through the TD at temperatures of 75°C and greater were statistically larger than the activation diameter through either the BP or TD at 25°C (one-tailed *t*-test, *p* < 0.0001). This indicates that the least volatile components of the  $\alpha$ -pinene ozonolysis SOA also contained components that were not very hygroscopic ~~or that chemical changes to the particles that occurred within the TD rendered the particles less CCN active.~~ This is contradictory to [the hypothesis of Jimenez et al. \(2009\) conventional thinking](#), ~~which proposed~~ [assumes](#) that the least volatile material is usually the most processed and therefore the most hygroscopic ~~(Jimenez et al., 2009)~~. However, the least volatile material in all [our](#) experiments had consistently the lowest O:C ratio and highest activation diameter, indicating a more complex relationship between hygroscopicity, oxidation level, and volatility in this system. ~~There is however the possibility that chemical changes that occurred to the particles within the TD rendered them less CCN active.~~

The estimated  $\kappa$  parameters as a function of TD temperature in Experiment 1 can be seen in Fig. 5b. Similar to the [pattern observed with the](#) activation diameters, the  $\kappa$  through the TD at temperatures greater than or equal to 75°C were statistically lower than the  $\kappa$  through either the BP or TD at 25°C (one-tailed *t*-test, *p* < 0.0001), reiterating the notion that the least volatile SOA contained components that were less hygroscopic than the rest of the SOA. The  $\kappa$ 's obtained in all experiments were similar to observed values for  $\alpha$ -pinene ozonolysis SOA



in other CCNC studies (Engelhart et al., 2008; Massoli et al., 2010; Frosch et al., 2011) and the decrease in hygroscopicity after heat treatment has also been reported by Kuwata et al. (2011).

Detailed results for Experiments 2, 3, and 4 can be found in the supplement to this paper. They were all conducted with 50 ppb of  $\alpha$ -pinene and around 500 ppb of ozone, generating around  $40 \mu\text{g m}^{-3}$  of SOA. In general, the O:C ratios and  $\kappa$ 's were slightly higher than those in Experiment 1. However, as with Experiment 1, these experiments also resulted in statistically lower O:C ratios and  $\kappa$ 's through the TD at higher temperatures. The following section proposes and discusses a novel analysis method to further investigate this behavior.

## 5 Relating hygroscopicity and O:C with volatility

The above data can be used to estimate the SOA's hygroscopicity and oxidation level as a function of volatility. The compounds in a volatility bin,  $i$ , have an average O:C ratio,  $[\text{O:C}]_i$ , and hygroscopicity parameter,  $\kappa_i$ . The O:C ratio and  $\kappa$  distributions as a function of volatility can be determined utilizing the data obtained at each TD temperature by using the following equations:

$$(3)$$

$$(4)$$

where  $[\text{O:C}]_{TD}$  and  $\kappa_{TD}$  are the measured O:C ratio and  $\kappa$  at a TD temperature,  $x_{i,TD}$  is the SOA mass fraction in the  $i^{th}$  bin at the same temperature, and  $[\text{O:C}]_i$  and  $\kappa_i$  are the unknown O:C ratio and  $\kappa$  for the  $i^{th}$  bin. The mass fraction for each bin as a function of TD temperature is estimated by the TD model. An example for Experiment 1 is shown in Fig. 6. As expected, as the temperature in the TD increases, the more volatile components evaporate and the SOA is comprised of mostly low volatility compounds.

For a future extension of the approach to ambient aerosols with unknown compositions, nothing in the equations remain the same changes. But the OA components could must be separated into different groups using PMF with corresponding  $\kappa$ 's, O:C ratios, and volatility distributions. This is similar to how (Paciga et al., 2016) used PMF on ambient OA in Paris and generated volatility distributions for each factor.

Equation (3) assumes implicitly that the SOA in the various volatility bins has similar average number of carbon atoms per molecule and also similar average molecular weights. These



are clearly zeroth order approximations and introduce corresponding uncertainties in the estimated O:C ratio for each bin. Equation (4) is based on the work of Petters and Kreidenweis (2007) and assumes that the average density of the material in is constant between the various volatility bins is similar. These equations can be used to generate a system of equations for both the O:C ratios and  $\kappa$ 's that can be solved separately.

First we focus on how to determine the O:C ratio distribution as a function of volatility, but the process to determine the  $\kappa$  distribution is exactly the same. Each measurement at a specific ~~TDthermodenuder~~ temperature results ~~into~~ one equation of the form of Eq. (3) with unknowns ~~the~~ O:C ratios ~~for~~ the various volatility bins. For example, for Experiment 1, we used the average O:C ratios from Fig. 4 and the mass fractions from Fig. 6 at each TD temperature to generate 5 equations with 4 unknowns. The combination of the results of all experiments led to 18 equations (5 from Experiment 1, 4 from Experiment 2, etc.) with 4 unknown O:C ratios ( $[O:C]_{0.01}$ ,  $[O:C]_{0.1}$ , etc.). The optimum values of the O:C ratios were determined by minimizing the squared residual between the measured ( $[O:C]_{TD}$ ) and predicted () O:C ratios. Matlab's linear least squares solver, *lsqov*, was used for this task.

The results for the O:C ratio distribution can be seen in Fig. 7a. The  $C^* = 0.01 \mu\text{g m}^{-3}$  bin had the lowest O:C ratio, while the  $C^* = 1 \mu\text{g m}^{-3}$  bin had the highest values. The  $C^* = 0.1$  and  $10 \mu\text{g m}^{-3}$  bins had nearly identical O:C ratios. These results suggest that, for this system and the conditions examined, the relationship between the O:C ratio and effective volatility was not monotonic.

The hygroscopicity parameter  $\kappa$  distribution was determined in exactly the same way and the results are depicted in Fig. 7b. The O:C ratios and corresponding  $\kappa$ 's for each volatility bin were correlated extremely well ( $r^2 > 0.99$ , Fig. S143), which has been reported in numerous studies (Rickards et al., 2013). The SOA in the  $C^* = 1 \mu\text{g m}^{-3}$  bin had the highest hygroscopicity while the most and least volatile components had lower  $\kappa$  values.

In order to determine the robustness of our solution, we compared the predicted O:C ratios and  $\kappa$ 's at each TD temperature using the best fit values of the  $[O:C]_i$  and  $\kappa_i$  for each bin  $i$  to the measured values for every experiment. For the predicted values, we used the distributions in Fig. 7, multiplied them by their corresponding mass fractions, and summed the products up at each TD temperature. The predicted versus measured O:C ratios and  $\kappa$ 's can be seen in Figs. 8 and 9 respectively. The O:C ratio distribution appears to be a better predictor than the  $\kappa$

distribution because most of the predicted O:C ratios lie on the 1:1 line or very close to it, while the predicted  $\kappa$ 's were more scattered. However, essentially all of the predicted values were very close to the measured ones and the remaining values were within one standard deviation of the measured values.

Figure 7 presents results that could, at least in principle, connect different, or even contradicting, results from previous studies. For example, Jimenez et al. (2009) proposed that hygroscopicity and the O:C ratio increase as volatility decreases. However, Cerully et al. (2015) reported contradicting results that the more volatile components of ambient OA were more hygroscopic than the remaining material. The results presented here, albeit over a small range and only for  $\alpha$ -pinene ozonolysis SOA, provide a context in which both conclusions can be true. As the volatility decreased from a  $C^* = 10$  to  $1 \mu\text{g m}^{-3}$ , the O:C ratio and  $\kappa$  increased (i.e. supporting the results of Jimenez et al. (2009)), but the O:C ratio and  $\kappa$  of the more volatile  $C^* = 1 \mu\text{g m}^{-3}$  bin were higher than those of the  $C^* = 0.01$  and  $0.1 \mu\text{g m}^{-3}$  bins (i.e. supporting the results of Cerully et al. (2015)). Therefore, the approach described in this study can provide a more comprehensive method to determine the relationship between OA hygroscopicity, oxidation level, and volatility.

## 5.1 Sensitivity analysis

As a test, we optimized the system of equations again, but this time ~~we systematically~~ ~~we eliminated~~ ~~removed~~ one equation so that when we optimized the solution, we were only using 17 equations. After optimizing the system, we replaced the missing equation and removed another one. This test allowed us to determine if there was one measurement that significantly affected the results in Fig. 7. In all cases but one, the average values were nearly identical to the distributions from Fig. 7, demonstrating that one equation was not overly influencing the results. The only substantial deviation from Fig. 7 was observed for the  $C^* = 10 \mu\text{g m}^{-3}$  bin when the  $\kappa$  equation through the TD at  $25^\circ\text{C}$  for Experiment 1 was omitted. When the system was optimized without this equation, the  $\kappa$  for this bin decreased from 0.10 to 0.05. Since the mass fraction of the  $C^* = 10 \mu\text{g m}^{-3}$  bin for Experiment 1 was almost double the next highest mass fraction in any measurement, it holds significantly more information, and therefore, weight, in the optimization process and impacts the solution for this bin. However, even if the  $\kappa$  for this bin changed when the corresponding measurement was omitted, the change is consistent with the

large uncertainty bars for the  $\kappa$  of the  $C^* = 10 \mu\text{g m}^{-3}$  bin in Fig. 7. This exercise suggests that our results appear to be relatively robust.

As seen in Fig. 9, the  $\kappa$  distribution in Fig. 7 under predicts all of the measured  $\kappa$ 's from Experiment 2. In order to investigate the cause of this discrepancy, we used Eq. (4) to determine the  $\kappa$  distribution just for Experiment 2. Since this experiment only had 4 TD temperatures (Fig. S24), 4 equations could be written with 4 unknowns. However, when the system of equations was solved, the solution provided reasonable  $\kappa$ 's for the three lowest bins, but produced a  $\kappa = -0.15$  for the  $C^* = 10 \mu\text{g m}^{-3}$  bin. We hypothesized that the unreasonable value for the highest bin was due to the small mass fraction of the SOA in this bin at all temperatures (Fig. S54). At 25°C, only 4 % of the SOA had a  $C^* = 10 \mu\text{g m}^{-3}$  and those compounds completely evaporated as the temperature in the TD increased. Therefore, there was insufficient information to accurately estimate the properties of this bin for this experiment. To determine if this was true, we used Eq. (3) to solve for the O:C ratio distribution for Experiment 2. When we solved the system of equations, the solution again provided reasonable O:C ratios for the three lowest bins, but produced an O:C = 2.16 for the  $C^* = 10 \mu\text{g m}^{-3}$  bin. Since both solutions provided unreasonable values for the highest bin, we concluded that the method is unable to accurately estimate the properties of bins with very low concentrations (i.e.  $x_i < 0.1$ ). However, when experiments with different concentrations were combined, as we did with Experiments 1–4 above, the method is able to determine reasonable estimates for the bins' properties.

To address the uncertainty introduced by the low concentration of material in the  $C^* = 10 \mu\text{g m}^{-3}$  bin for Experiment 2, we ignored the  $C^* = 10 \mu\text{g m}^{-3}$  bin and removed the  $\kappa$  equation at 25°C. This approach implicitly assumes that the material in the  $C^* = 10 \mu\text{g m}^{-3}$  bin has evaporated at 50°C, which is reasonable because the mass fraction for the bin is less than 2 % at 50°C (Fig. S5). This resulted in three equations with three unknown  $\kappa$ 's. We solved the system of equations algebraically and using the measurements at TD temperatures greater than or equal to 50°C and the three lowest bins ( $C^* = 0.01, 0.1, \text{ and } 1 \mu\text{g m}^{-3}$ ). This approach implicitly assumes that the material in the  $C^* = 10 \mu\text{g m}^{-3}$  bin has evaporated at 50°C, which is reasonable because the mass fraction for the bin is less than 2 % at 50°C (Fig. S4). The results for the  $\kappa$  distribution can be seen in Fig. 10. When compared to the  $\kappa$  distribution in Fig. 7b, the  $\kappa$ 's for the  $C^* = 0.1$  and  $1 \mu\text{g m}^{-3}$  bins are the same within uncertainty (0.09 to 0.11 and 0.19 to 0.16

respectively), but the  $\kappa$  for the  $C^* = 0.01 \mu\text{g m}^{-3}$  bin is nearly twice that of the one in Fig 7b (0.14 to 0.08). This indicates that the SOA that had a  $C^* = 0.01 \mu\text{g m}^{-3}$  in Experiment 2 was more hygroscopic than indicated in Fig. 7b. To demonstrate this, we predicted the  $\kappa$ 's for Experiment 2 again. In order to do this, we used the  $\kappa$ 's for the three highest bins remained the same from Fig. 7b, but we used the  $\kappa$  for the  $C^* = 0.01 \mu\text{g m}^{-3}$  bin estimated in Fig. 10 instead of the one in Fig. 7b. The results can be seen in Fig. S145. With the larger  $\kappa$  for the  $C^* = 0.01 \mu\text{g m}^{-3}$  bin, the predicted  $\kappa$ 's were nearly identical to the measured ones. This demonstrates the variability that can occur from experiment to experiment, but the analysis method developed here can examine experiments separately to determine the cause of the variability.

## 6 Conclusions

This study evaluates the feasibility of a novel measurement and analysis technique to quantify OA's hygroscopicity, O:C ratio, and volatility distribution. The experimental approach used a CCNC to study hygroscopicity, an AMS to determine the O:C ratio, and a TD to evaluate volatility. The experimental setup was tested with SOA generated from the ozonolysis of  $\alpha$ -pinene. The results of these experiments revealed that the O:C ratio and  $\kappa$  decreased as the SOA passed through the TD at higher temperatures. This indicates that the lowest volatility material in this system contained components that had lower O:C ratios and  $\kappa_{\text{CCNC}}$ 's. However, a detailed characterization of the composition of the remaining compounds after the TD is required to quantify the contribution of chemical reactions to these observed changes.

An analysis technique to synthesize the data from this novel experimental setup was also developed. The results from this analysis confirmed that the SOA for this system had some low volatility material with a low O:C ratio and  $\kappa$ . It also showed that both low and high volatility compounds can have comparable oxidation levels and hygroscopicities.

This approach can be used to connect studies that were once thought to have contradicting results regarding the relationship between these three properties. Further chamber studies and ambient sampling are necessary in order to describe the relationship between OA hygroscopicity, oxidation level, and volatility for multiple SOA systems, but also for ambient OA. This study was able to analyze a small portion of the 2D-VBS framework space, but this method can be utilized to help identify the relationship across the entire OA volatility axis. This

approach also serves as an experimental branch to the theoretical framework proposed by Nakao (2017).

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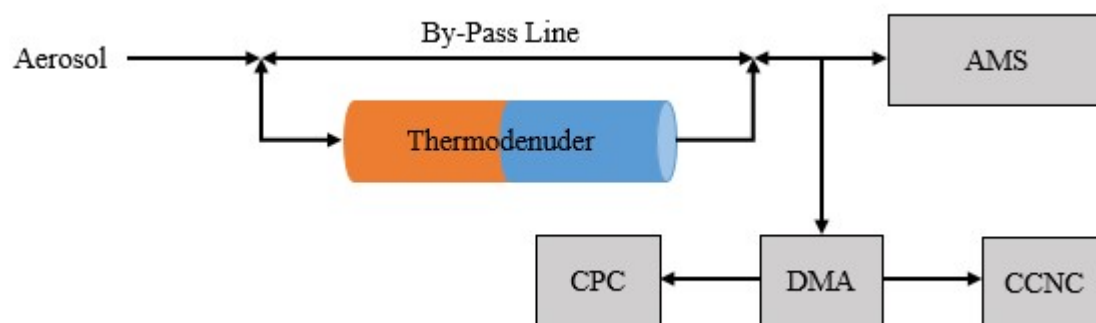
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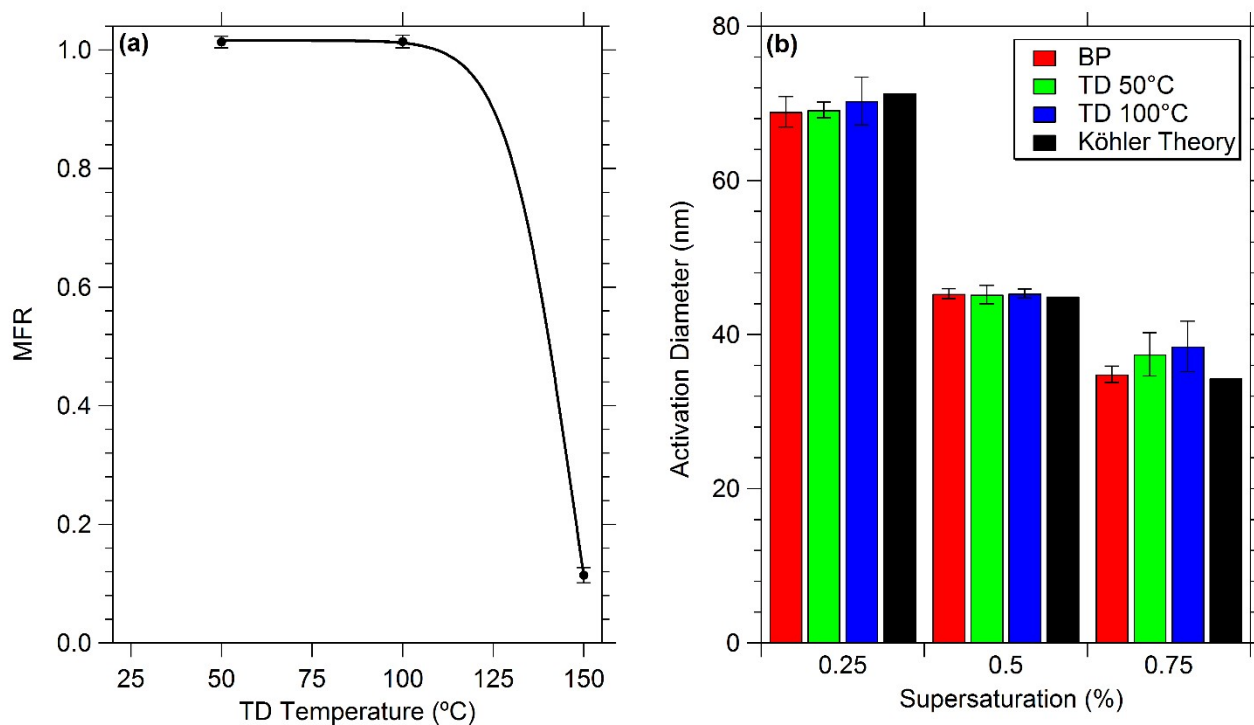
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<b>Table 1.</b> Description of experimental conditions used in this study.					
<b>Exp.</b>	<b><math>\alpha</math>-Pinene (ppb)</b>	<b>Ozone (ppb)</b>	<b>RH (%)</b>	<b>Supersaturation (%)<sup>a</sup></b>	<b>Max. OA (<math>\mu\text{g m}^{-3}</math>)</b>
1	100	~500	<15	0.20	108
2	50	~500	<15	0.30	35
3	50	~500	<15	0.25	39
4	50	~500	<15	0.27	46

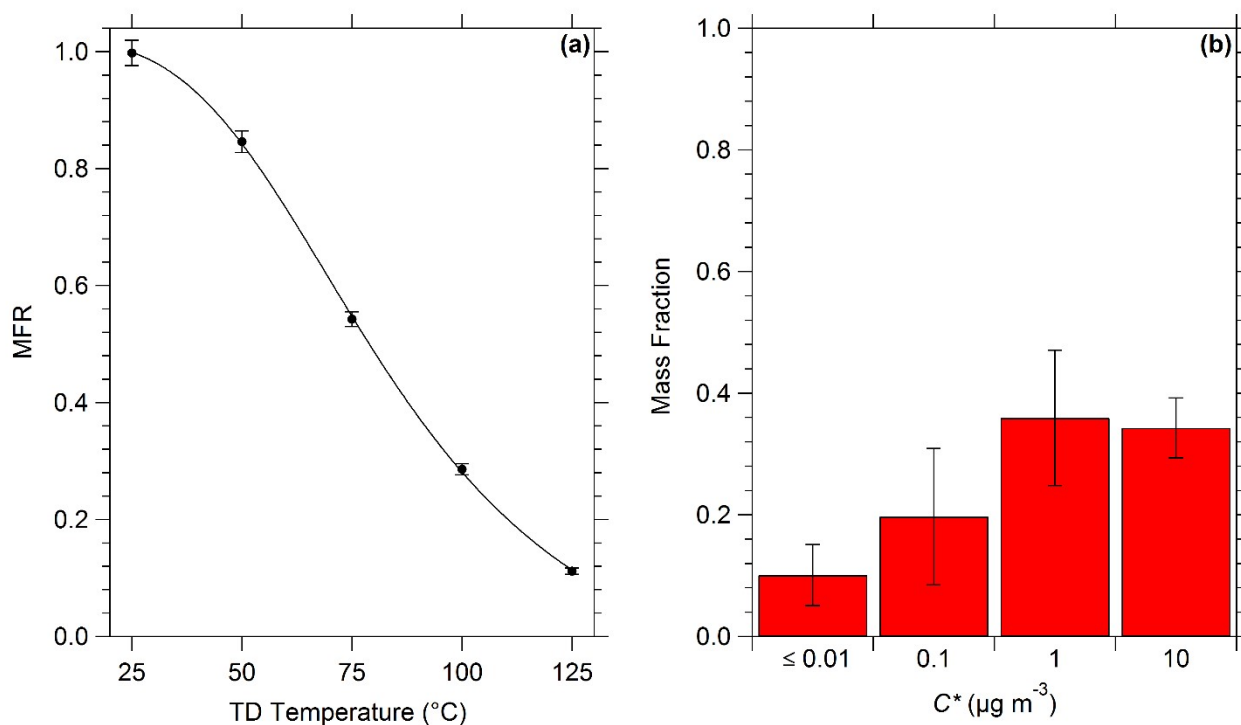
<sup>a</sup>CCNC supersaturation was held constant during experiments in order to allow sufficient time for an average activation diameter to be measured at each TD temperature.



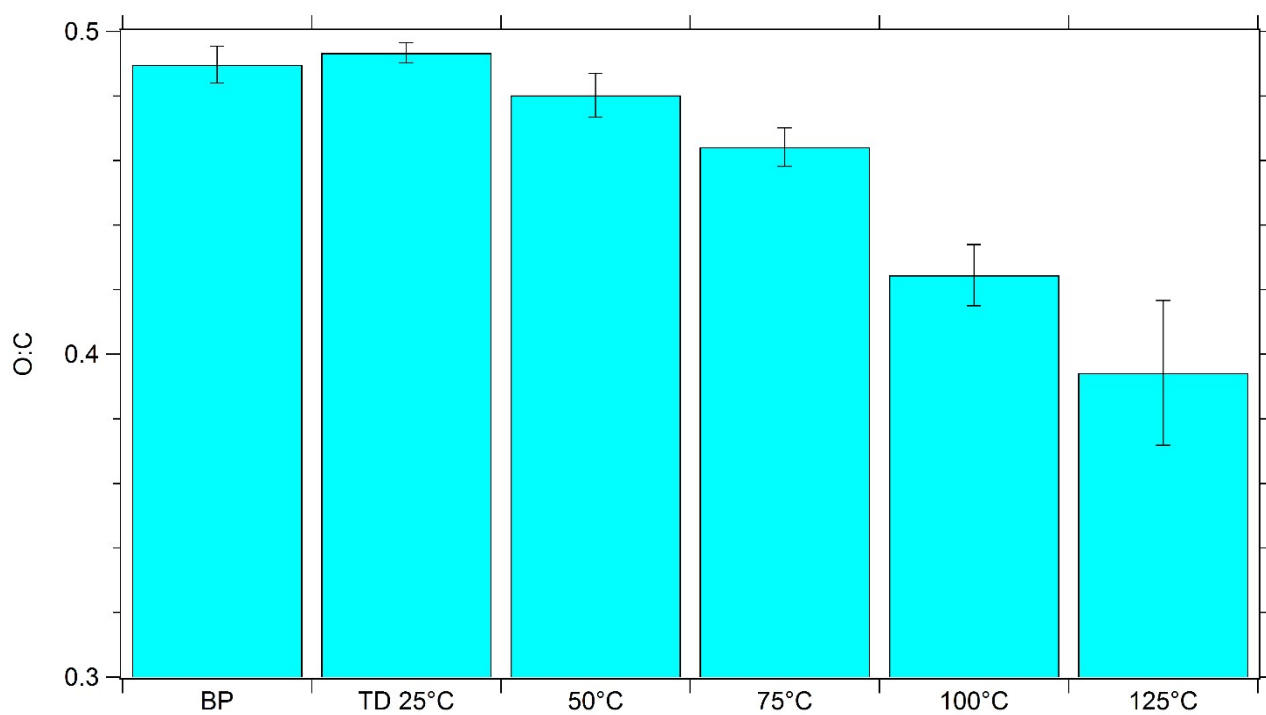
**Figure 1.** Schematic of the experimental setup for the hygroscopicity, oxidation level, and volatility measurements. The sampling technique employs a TD to measure volatility, an AMS to study the oxidation level, and a CCNC to determine hygroscopic activity.



**Figure 2.** (a) The thermogram for ammonium sulfate aerosol. (b) The calculated activation diameter at three CCNC supersaturations for the BP (red), two TD temperatures (green and blue), and Köhler theory (black) for ammonium sulfate aerosol. The error bars represent one standard deviation of the mean.

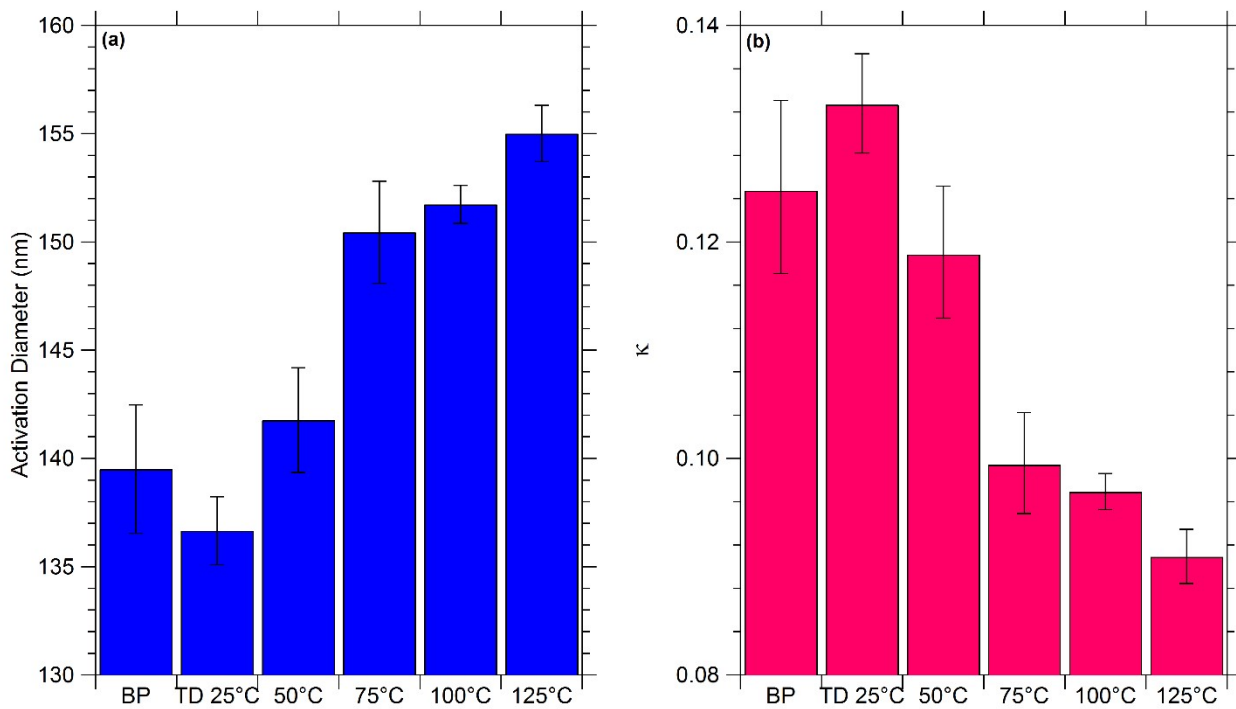


**Figure 3.** (a) Thermogram, corrected for losses in the TD, for Experiment 1 with the fit from the TD model (Riipinen et al., 2010; Karnezi et al., 2014). The error bars represent one standard deviation of the mean. (b) SOA volatility distribution for Experiment 1 using the 1D-VBS framework (Donahue et al., 2006). The error bars correspond to one standard deviation of the solution calculated by the model.

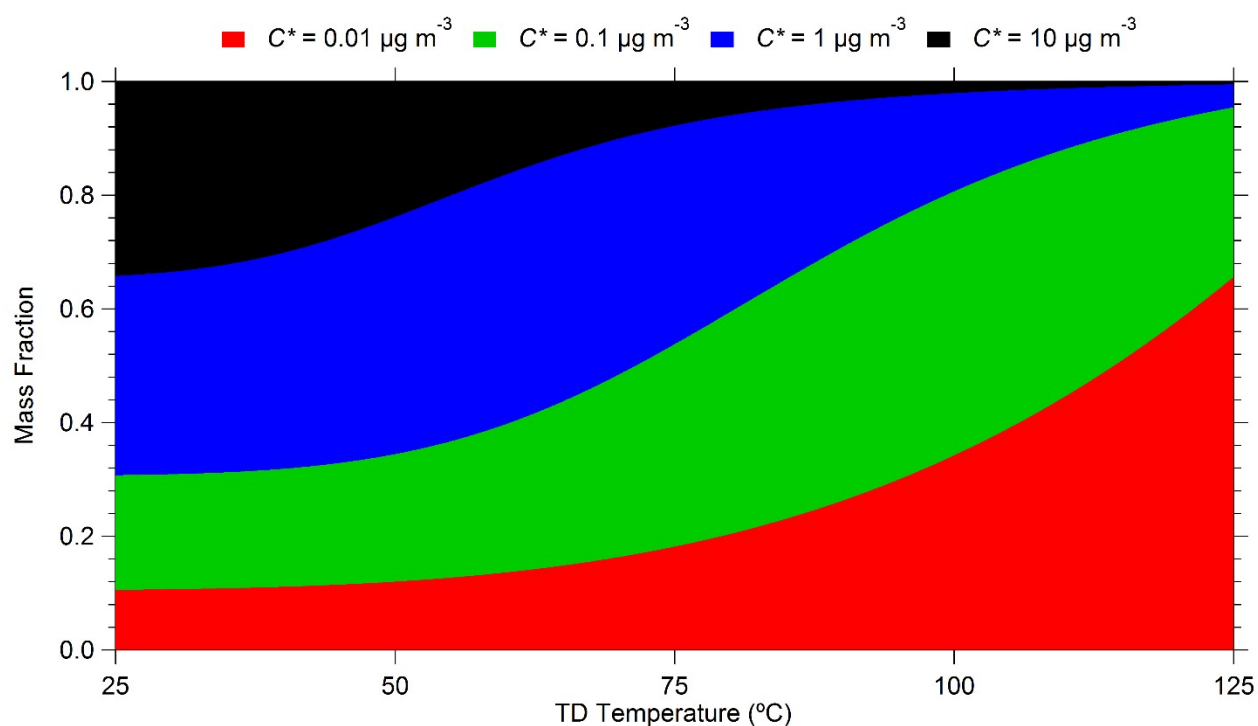


**Figure 4.** The average O:C ratio observed through the BP and several TD temperatures for Experiment 1. The error bars represent one standard deviation of the mean. The O:C ratios at a TD temperature of 50°C and greater were statistically smaller than the values at the BP and the TD at 25°C.

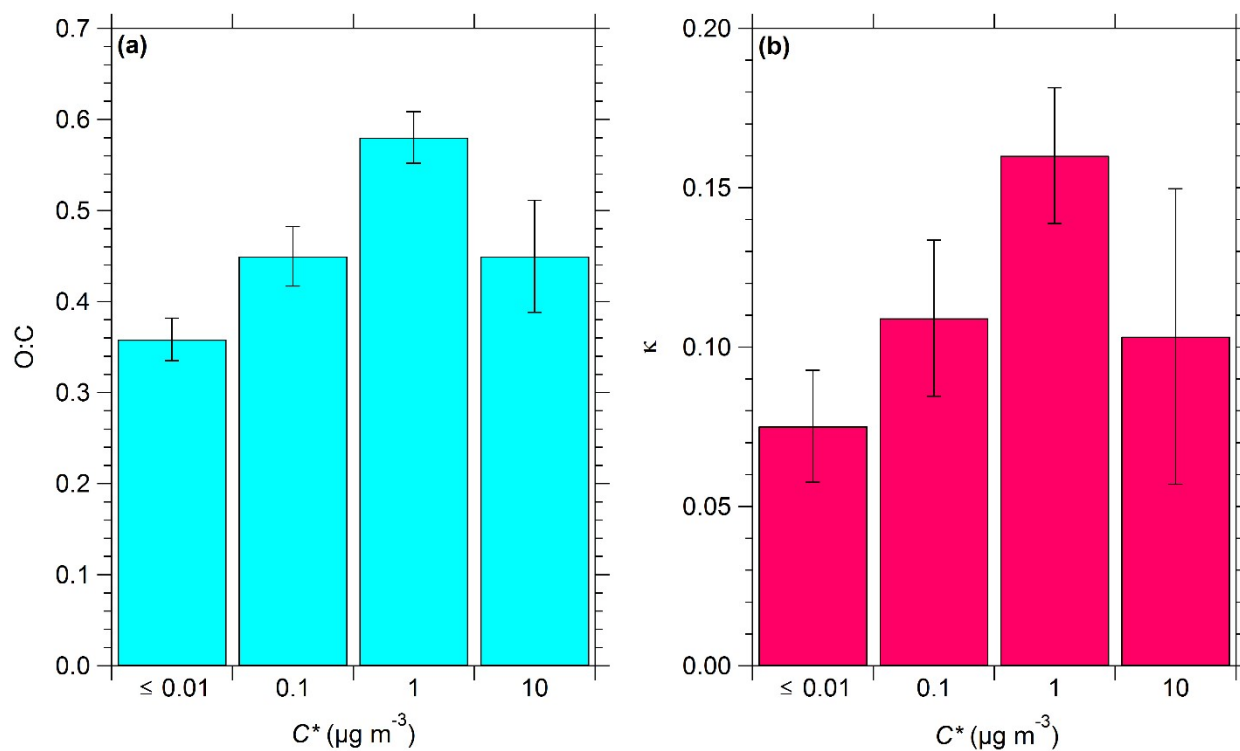




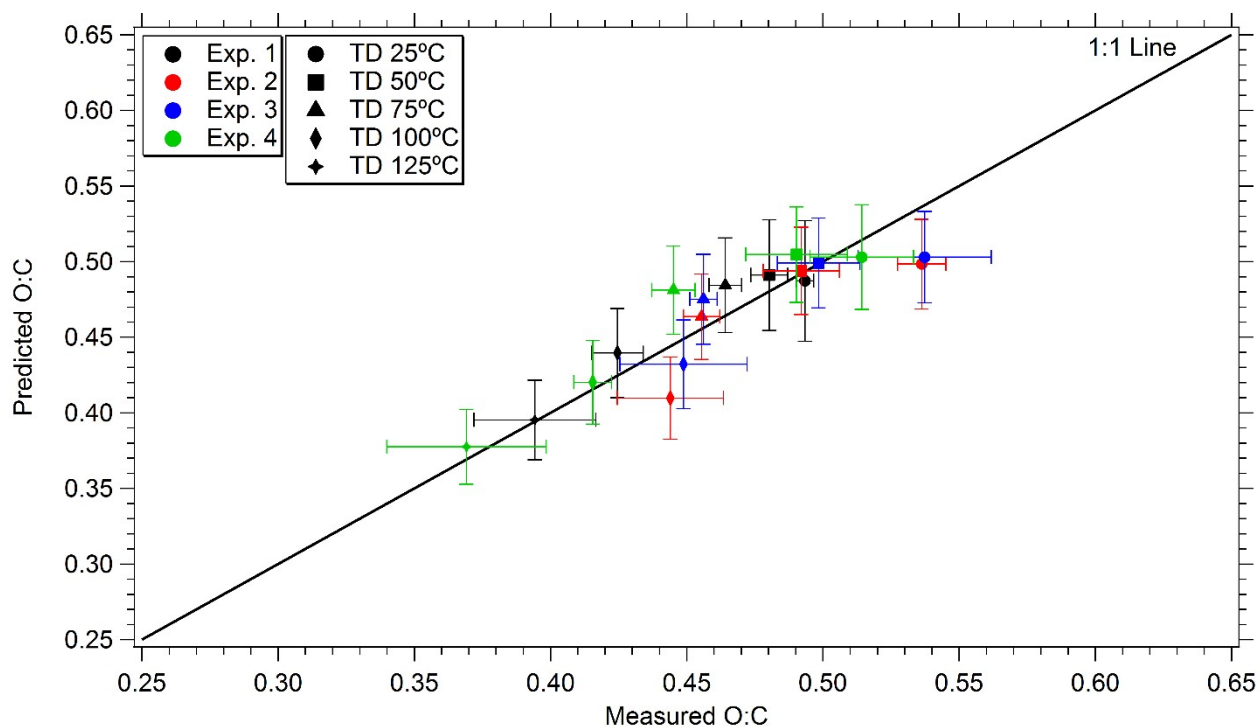
**Figure 5.** (a) The average activation diameter observed at 0.2 % supersaturation in the CCNC for Experiment 1. The error bars represent one standard deviation of the mean. (b) The estimated  $\kappa$  values for Experiment 1. The error bars were obtained by estimating the  $\kappa$  at  $\pm$  one standard deviation of the average activation diameter measured. The values at TD temperatures of 75°C and greater were statistically different from the values at the BP and the TD at 25°C.



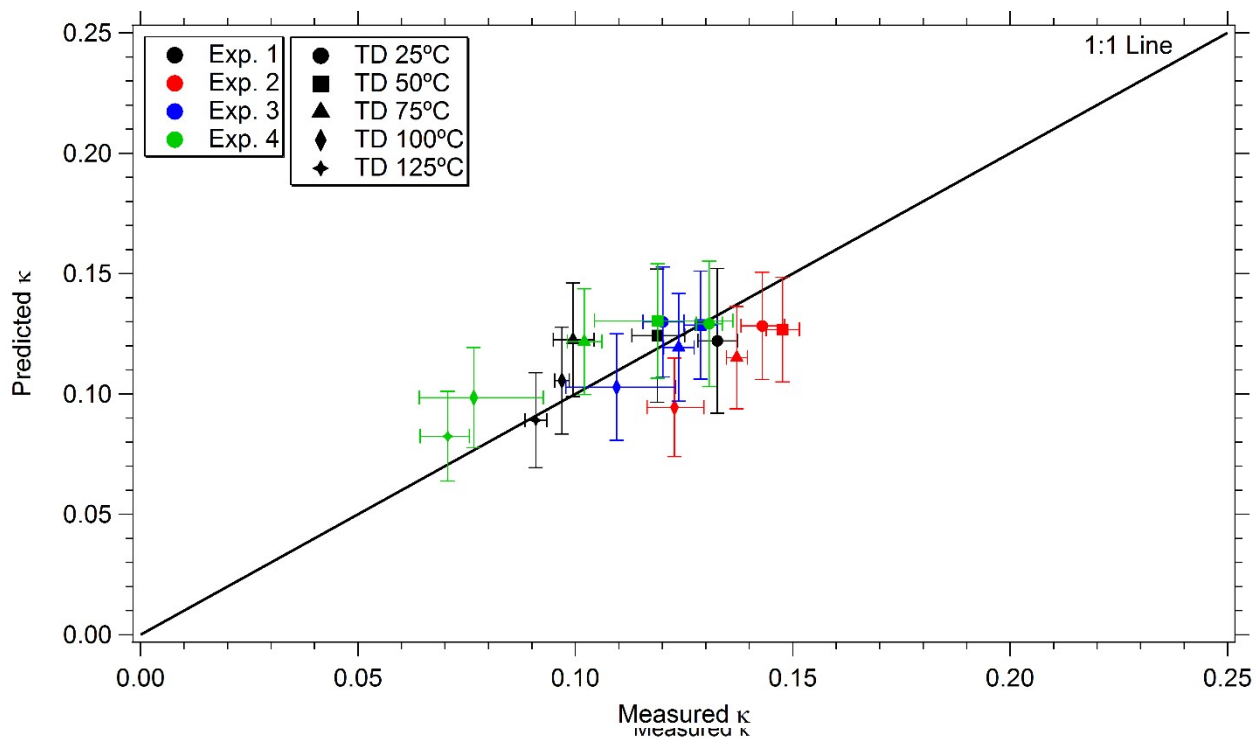
**Figure 6.** The estimated mass fractions for each volatility bin as a function of TD temperature for Experiment 1. Red represents the  $C^* = 0.01 \mu\text{g m}^{-3}$  bin, green the  $C^* = 0.1 \mu\text{g m}^{-3}$  bin, blue the  $C^* = 1 \mu\text{g m}^{-3}$  bin, and black the  $C^* = 10 \mu\text{g m}^{-3}$  bin.



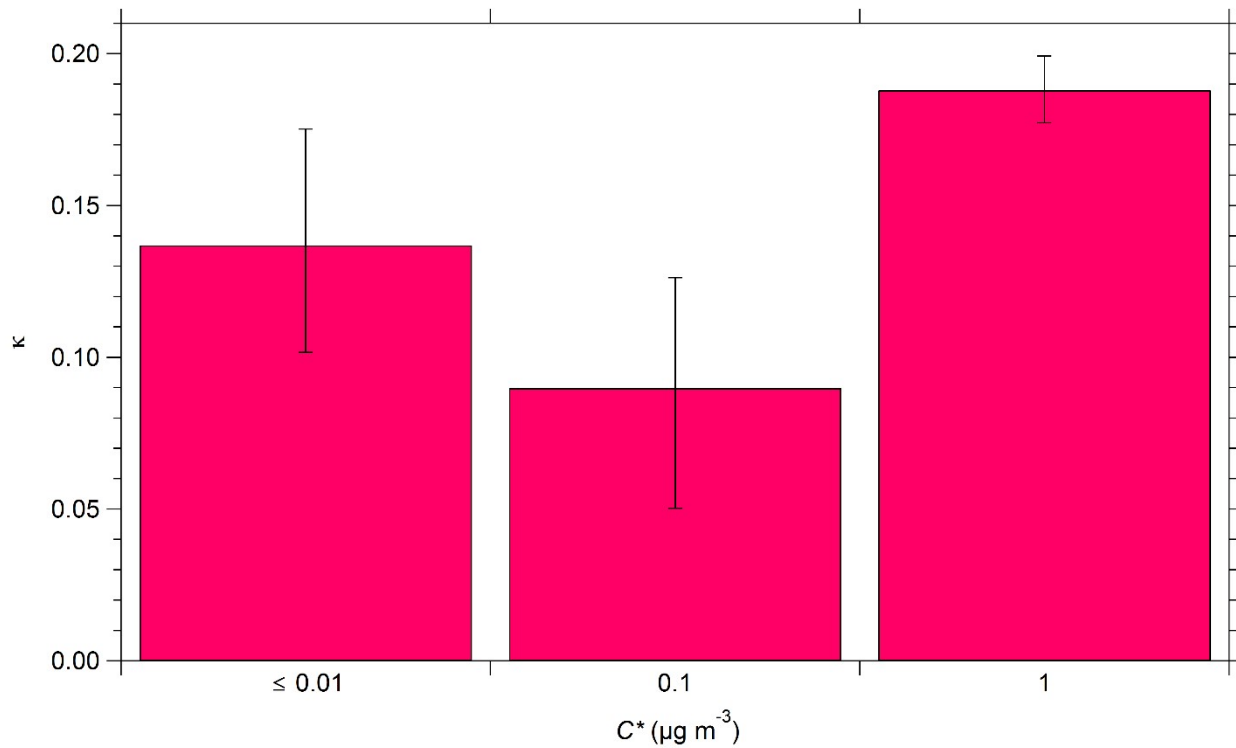
**Figure 7.** The (a) O:C ratio and (b)  $\kappa$  distributions for the volatility bins characterized in this study for  $\alpha$ -pinene ozonolysis SOA. The error bars represent one standard deviation of the mean obtained from the least squares solver.



**Figure 8.** The predicted versus measured O:C ratios for all TD temperatures in all of the experiments. The color indicates the experiment number and the symbol indicates the TD temperature. The error bars for the predicted O:C ratios were obtained by predicting the O:C ratios using the O:C ratio distribution at  $\pm$  one standard deviation in Fig. 7a.



**Figure 9.** The predicted versus measured  $\kappa$ 's for all TD temperatures in all of the experiments. The color indicates the experiment number and the symbol indicates the TD temperature. The error bars for the predicted  $\kappa$ 's were obtained by predicting the  $\kappa$ 's using the  $\kappa$  distribution at  $\pm$  one standard deviation in Fig. 7b.



**Figure 10.** The  $\kappa$ -distribution that resulted from solving Eq. (4) for TD temperatures greater than 50°C and the three lowest bins for Experiment 2. The error bars represent one standard deviation obtained by solving the equations at +/- one standard deviation of the measured  $\kappa$ .