

The authors would like to thank the Referees for their careful reviews and helpful comments to our manuscript. We have prepared responses to each of the concerns and questions, which are listed below. We address Reviewer #2 comments (C1943-C1947) first and Reviewer #1 comments (C2043-C2046) second. The referees' comments are in italics, followed by the authors' responses. Specific changes to the manuscript text are shown in bold type.

Response to Referee #2:

While I find the laboratory work and modeling to be of sufficient quality to merit publication, I am hesitant to sign off on this manuscript for publication in Atmospheric Measurement Techniques for several reasons. The majority of the analysis, conclusions, as well as validations of the results rely on approximations that when compounded could potentially result in significant over/under approximations of the gas and particle phase concentrations.

We understand the reviewer's concern. Traditionally, quadrupole-based chemical ionization mass spectrometer studies have focused on the measurement and quantification of a relatively small number of known molecules. However, in this work we are focusing on measuring approximately 50-120 molecules at a time (the approximate number of ions measured in α -pinene and naphthalene oxidation experiments performed in this work) and this requires a fundamentally different approach in order to be practical. We revised the text in an attempt to clarify our goals with the methodology applied in this manuscript:

P6389, L27: We note that the HR-ToF-CIMS spectra contain many different mass-to-charge ions – on the order of 100 or more unknown ions. Since calibration of each individual measured species may not be feasible due to unknown identity or unavailability of standards, we adopt a simplifying approach in which the measured species are quantified using an average calibration value for organic acids. Acetate-ionization may have an advantage in this respect since it is primarily selective for acids. While this assumption can lead to larger errors for any given individual species, it allows for a practical way of calculating average (ensemble) properties and mass concentrations for the large number of organic ions in the HR-ToF-CIMS spectra.

It is wildly unjustified in both previous as well as this current publication to apply a constant sensitivity factor across the entire observable mass range. Variation in ionization efficiencies aside, the formation of an acetate cluster ion, as the primary mechanism of ionization, occurs with a dramatically different efficiency than proton abstraction reactions.

In traditional quadrupole CIMS applications (e.g. Crounse et al. (2006), Veres et al. (2008)), the determination of explicit compound-dependent calibration factors for a handful of compounds is more feasible. However, the explicit calibration of the HR-ToF-CIMS response to ~100 or more molecules, many of which are unknown and/or commercially unavailable (as is the case here) is impractical. In the discussions paper, we applied the HR-ToF-CIMS calibration factor for formic acid to all ions that were detected. After consideration of the reviewer's comments, we agree that there is no compelling reason to justify the use of formic acid over other compounds aside from the fact that it is easier to calibrate with (which is non-trivial). In an attempt to improve this aspect of the manuscript, we did an extensive literature search of all available acetate-CIMS

calibration factors using acetate reagent ion chemistry. Using literature data from Veres et al. (2010), Yatavelli et al. (2012), and Aljawhary et al. (2013), and normalizing to the formic acid sensitivity to each instrument from these studies, we have applied an average relative acetate-CIMS sensitivity of 1.3 ± 0.8 to the measured 5.5 ± 0.9 Hz ppt⁻¹ sensitivity of formic acid. Thus, to all acid signals (except formic), we apply a total sensitivity of 7.1 ± 4.6 Hz ppt⁻¹. A table (shown below) will be added to the supplemental material listing the relevant literature data. Values in the text will be revised to reflect the calibration factor. In addition, the $\pm 1\sigma$ uncertainties inherent in this average calibration factor will be incorporated and discussed throughout the results and discussion section to more accurately reflect the underlying uncertainty in the application of a constant average calibration factor. With these uncertainties combined with those from the SIMPOL.1 group additivity method described later, errors in yields in the α -pinene system range from about 10 – 27%.

Organic Acid	Relative Sensitivity to Formic Acid	Reference
succinic acid	2.20119	Aljawhary et al. (2013)
malonic acid	2.09693	Aljawhary et al. (2013)
glyoxylic acid	1.861	Aljawhary et al. (2013)
oxalic acid	1.24072	Aljawhary et al. (2013)
pyruvic acid	1.39841	Aljawhary et al. (2013)
tartaric acid	0.892451	Aljawhary et al. (2013)
citric acid	0.53865	Aljawhary et al. (2013)
pinonic acid	1.76795	Aljawhary et al. (2013)
pyruvic acid	1.45291	Veres et al. (2010)
glycolic acid	1.79056	Veres et al. (2010)
methacrylic acid	0.233644	Veres et al. (2010)
acrylic acid	0.695613	Veres et al. (2010)
propionic acid	0.0348808	Veres et al. (2010)
palmitic acid	0.54	Yatavelli et al. (2012)
azelaic acid	0.88	Yatavelli et al. (2012)
tricarballic acid	2.6	Yatavelli et al. (2012)

Response Table 1: Relative Sensitivities of various organic acids and their corresponding references. Since pyruvic acid appears twice, the average is used in the determination of the average relative acetate-CIMS sensitivity.

Furthermore, the treatment of cluster ions in this work is likely inappropriate, and nearly impossible (as the research was done) to quantify the errors associated with the cluster ion correction applied here.

In the discussions paper, we note that the voltages in the first quadrupole of the HR-ToF-CIMS were adjusted to minimize clustering as evidenced by the 5 to 1 ratio of m/z 119 to m/z 59. In that context we applied the following treatment of cluster ions:

1. We first define that a non-clustered base ion has a molecular formula i , and when the acetate mass is added, its formula is $i + \text{C}_2\text{H}_4\text{O}_2$ at the clustered mass.
2. The signal at the clustered mass is equal to the sum of the adduct ion signal and non-adduct ion signal at the same mass.

3. We assume that across all experiments of a given precursor, the ratio of clustered mass to non-cluster mass is constant and is no more than the ratio of signal at m/z 119 to signal at m/z 59, or 0.2.
4. Thus across all experiments of a given precursor, the minimum ratio of cluster:base ion or 0.2, whichever is smaller, is used to approximate the clustering ion signal.
5. To correct for clustering, the calculated cluster ion signal is added back to the base ion signal and subtracted from the cluster.

The reviewer claims this procedure is inappropriate in our application, but we respectfully disagree. We acknowledge that our method may introduce significant error for individual molecules because the kinetics of cluster ion formation are compound specific. However, our method is intended to provide an average correction for the ~100 ions detected with the HR-ToF-CIMS, which is a fundamentally different application than conventional quadrupole-CIMS measurements. We have revised the text as follows in an attempt to clarify this point:

P6394, L22-26: To correct for clustering, the estimated value of I_i' calculated from Eq. (2) is added back to I_i and subtracted from $I_{i+C_2H_4O_2}$. The effect of this correction on bulk composition values is minimal, on the order of a couple percent. The true clustering correction (and associated uncertainty) is likely significantly larger for individual molecules due to compound-specific acetate proton transfer reaction rates that are not known. Figures S1 and S2 in the Supplement illustrate how much signal in example spectra is estimated to be from clustering and redistributed to base ion signals.

I acknowledge that the authors are open about the assumptions made in this work; however, regard any mass loading, yields, or quantitative data reported here as mere speculation. Agreement is in many cases is somewhat misleading considering that the results are in many examples justified by comparison to other published works using similar flawed methods. This is a problem that is becoming systemic with TOF-CIMS measurements, and one that is continuing to be addressed by statements such as “We ignore such non-linearity here but note that they should be studied in the future.”

We respectfully disagree with the reviewer’s dismissal of previous ToF-CIMS measurements as “flawed”. Previous studies, including the acetate CIMS studies described here and a study by Ehn et al. (2014), routinely use a constant calibration factor. Ehn et al. (2014) applied a perfluoroheptanoic acid calibration factor to the quantification of extremely low volatility organic compounds (EL-VOC) using nitrate reagent ion chemistry. It is true that that this represents a fundamentally different approach from explicit, compound-specific calibration factors that have been used in traditional quadrupole-CIMS studies, but in our opinion it is unfair to dismiss this approach out of hand. Our analysis of the entire ToF-CIMS spectrum requires a different approach that is practical for use across hundreds of individual ions.

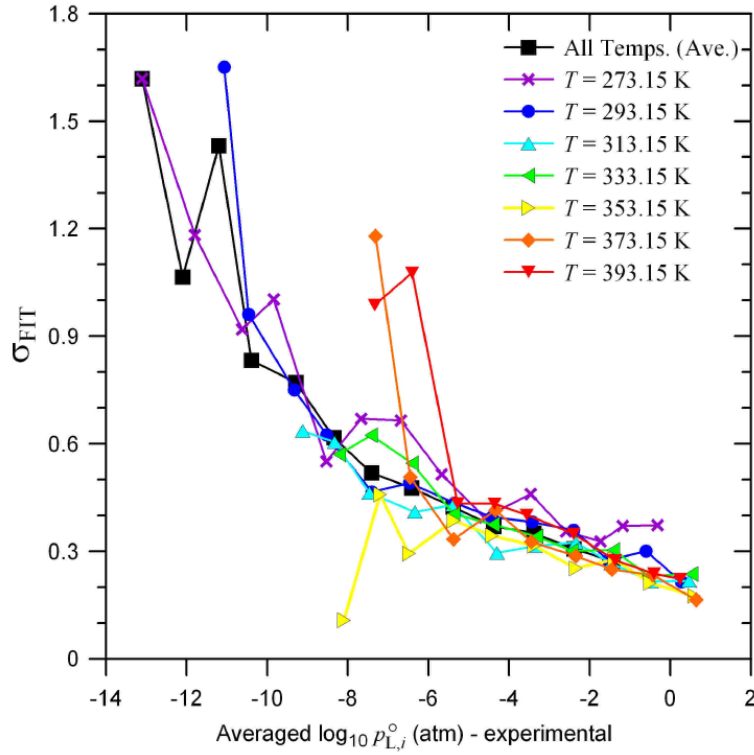
The last sentence in this comment raised by the reviewer: “This is a problem that is becoming systemic with TOF-CIMS measurements, and one that is continuing to be addressed by statements such as ‘We ignore such non-linearity here but note that they should be studied in the future’ is taken out of context. On P6404, L12-L18, we stated:

“Implicit in the calculation of the CIMS yield curves shown in Fig. 7 is the assumption that the total (sum of gas and particle phases) distribution of acids generated is only a function of OH exposure and is independent of the amount of hydrocarbon injected. In reality, variations in the amount of injected aerosol precursor can introduce non-linearity in the formation of product species, for example, through competition for oxidants or bimolecular reactions of radical products. **We ignore such non-linearities here but note that they should be studied in the future.**”

When placed in the context of the rest of the discussion, we hope this clarifies to the reader (and reviewer) that this text is specifically describing radical-radical chemistry that might be occurring in the PAM flow reactor but has nothing to do with reagent ion chemistry in the CIMS.

In my opinion, in order to be considered for publication this work requires a more detailed discussion on the magnitude of the errors from using the many approximations used as well as quantification of the errors associated with all mass yields and other numerical figures reported within this work. Without a thorough treatment of the errors in this analysis, the reader is unable to easily understand the accuracy of the values and subsequent discussion, which in turn makes this study of little use as a model for understanding real atmospheric oxidation. If in fact the authors are comfortable with the methods and results reported, then they should be able to place more finite bounds on the reported numbers.

We agree with the reviewer that a more detailed discussion of errors is necessary. In attempt to address this concern raised by the reviewer we quantify the errors arising from the CIMS measurement organic acids and errors from the SIMPOL vapor pressure estimation. Errors from CIMS measurements include random measurement error in spectra, error in the formic acid sensitivity (5.5 ± 0.9 Hz ppt⁻¹, as noted earlier), and uncertainty in the relative sensitivity of organic acids (1.3 ± 0.8 , as noted earlier), all of which are combined and propagated using standard rules of error propagation. Estimation of the uncertainty in estimated vapor pressures using the SIMPOL method is less trivial, so its derivation has been added to the supplemental material. We derive a correlation of uncertainty as a function of vapor pressure derived from Figure 12 of Pankow and Asher (2008), reproduced here as Response Figure 1.

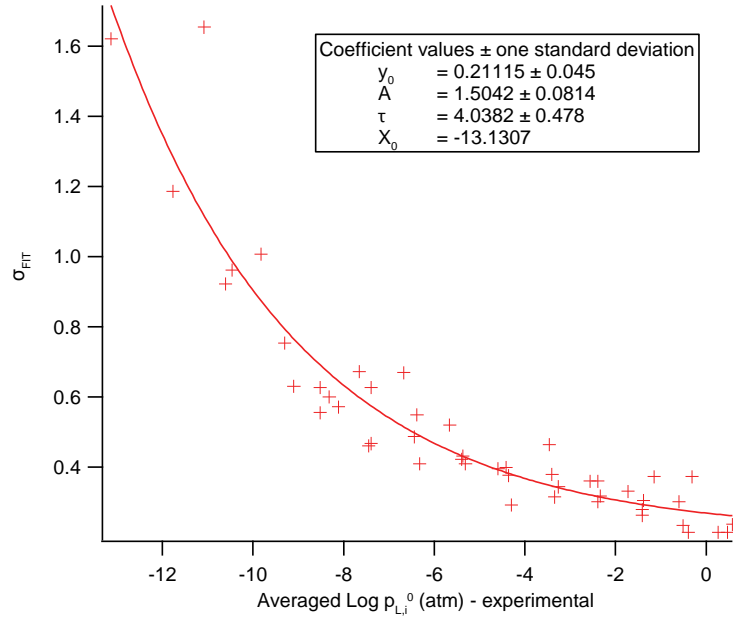


Response Figure 1: Figure 12 reproduced from Pankow and Asher (2008) illustrating decadal binned averages of σ_{FIT} as a function of the log of experimental vapor pressure

The parameter σ_{FIT} represents the average of the absolute deviations between the logarithm of predicted and experimental pressures, decadal binned according to the log of the experimental vapor pressure:

$$\sigma_{FIT} = \frac{1}{N} \sum_{i=1}^{N_C} \sum_{j=1}^{N_{T,i}} \left| \log_{10} \left(p_{L,i}^0(T_{j,i})_p \right) - \log_{10} \left(p_{L,i}^0(T_{j,i})_E \right) \right|$$

To estimate σ_{FIT} as a function of vapor pressure, data from Response Figure 1 from temperatures 273.15K to 333.15 were extracted and fitted with an exponential function (σ_{CORR}) as shown in Response Figure 2,



Response Figure 2: Exponential correlation between σ_{FIT} and average log of vapor pressure binned to the nearest integer.

where:

$$\sigma_{CORR} = y_0 + Ae^{\left(\frac{-(p_{L,i}^0 - x_0)}{\tau}\right)}$$

The average absolute deviation from the mean is less than or equal to the standard deviation, and for a normal distribution the ratio of the mean absolute deviation to the standard deviation is $\sqrt{2/\pi}$ (Geary, 1935). Thus, to provide a more conservative estimate of the error, we divide σ_{CORR} by $\sqrt{2/\pi}$:

$$\sigma_{SIM} = \frac{y_0 + Ae^{\left(\frac{-(p_{L,i}^0 - x_0)}{\tau}\right)}}{\sqrt{2/\pi}}$$

where σ_{SIM} represents the uncertainty in SIMPOL vapor pressure (in log(atm)) used in our analysis. σ_{SIM} is propagated through the analysis and from which uncertainties in c^* and ξ_i are calculated using standard error propagation rules. Because $\log_{10}(p_{L,i}^0)$ and $\log_{10}(c_i^*)$ differ by a constant,

$$\sigma_{\log_{10} c_i^*} = \sigma_{SIM}$$

Thus:

$$\sigma_{c^*} = |10^{\log_{10} c^*}| \sigma_{\log_{10} c_i^*} (\ln 10)$$

and

$$\sigma_{\xi_i} = \frac{\sigma_{c^*}}{C_{OA} \left(1 + \frac{c_i^*}{C_{OA}}\right)^2}$$

P6397, L20: Technically, c^* is the product of the saturation concentration of the pure sub-cooled liquid, c^0 , and its activity coefficient in solution, but the activity coefficient is assumed to be unity. Derivation of the estimation in uncertainty in SIMPOL vapor pressure prediction is detailed in the supplemental material.

p6392, line 6-7: Am I right in understanding that the OH oxidation experiments were performed with 5 ppm of ozone and the ozone experiments we performed using only 1 ppm more? I find this to odd as that would mean the ozone exposure in both scenarios is very similar. Would this not allow a large amount of ozonolysis products to be observed during the OH experiments?

The referee is correct in noticing that ozone concentrations are similar in ozonolysis and photooxidation experiments. However, OH reactions were much faster than O_3 reactions over the range of OH exposures that were studied, suggesting that to first order the spectra are dominated by products formed from OH reactions. To illustrate this, consider the gas-phase oxidation lifetime of α -pinene with respect to O_3 and OH, defined as τ_{O_3} and τ_{OH} in the equations below:

$$\tau_{O_3} = 1/(k_{OH} \times [O_3])$$

$$\tau_{OH} = 1/(k_{OH} \times [OH])$$

In α -pinene + ozone experiments, τ_{O_3} is approximately 78 sec assuming $k_{O_3} = 8.7 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Seinfeld and Pandis, 2006). Over the range of OH exposures that were used (1.2×10^{11} to $9.7 \times 10^{11} \text{ molec cm}^{-3} \text{ s}$) τ_{OH} in α -pinene + OH experiments ranges from about 2 sec to 15 sec assuming an average residence time of 100 sec in the flow reactor and assuming $k_{OH} = 5.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Seinfeld and Pandis, 2006). Thus, α -pinene + OH reactions were approximately 5 to 39 times faster than α -pinene + O_3 reactions. Likewise, naphthalene + OH reactions were approximately 700 to 5700 times faster than naphthalene + O_3 reactions assuming $k_{OH} = 2.59 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_{O_3} = 3 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Aschmann, 1986).

We have added this detail to the experimental setup section:

p6392, L13: Although ozone concentrations were similar between ozonolysis and photooxidation experiments, OH concentrations were high enough that α -pinene + OH ($k_{OH} = 5.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) reactions are 5 to 40 times faster than ozonolysis reactions ($k_{O_3} = 8.7 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), and naphthalene + OH ($k_{OH} = 2.59 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) reactions are 700 to 5700 times faster than ozonolysis ($k_{O_3} = 3 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) reactions (Atkinson and Aschmann, 1986; Seinfeld and Pandis, 2006). These calculations suggest that photooxidation products measured with the CIMS are mostly from OH reactions, although we cannot completely rule out minor contributions from O_3 reactions particularly at the lowest OH exposures that were used.

p6392, line 11: Please be more specific as to what mass was used to monitor DCOOH. At unit mass resolution the authors should consider the contribution of other species to the ion at m/z 46. Any production of OH with trace amounts of NO will likely result in HONO, which also will be detected at m/z 46. Under certain conditions with the acetate ion CIMS, NO₂ is also detected at m/z 46 with relatively good efficiency depending on ionizer conditions. One would also expect some contribution of any HO₂NO₂ that may be formed in the chamber. If in fact you did use unit mass resolution to monitor this ion have you considered the following? How may production of any of these species effect you calculation of OH exposure? Have you modulated the DCOOH during an experiment to test if any other interference were present on this ion?

We used high-resolution analysis to determine that during the DCOO⁻ calibration, DCOO⁻ was the dominant ion at m/z 46. ONO⁻, while present in the spectra, had negligible signal. We have revised the manuscript as follows:

P6392, L11: measured in high resolution spectra as m/z = 46.00393, as deuterated formate ion DCOO⁻)

p6393, line 27: How exactly did you approximate that < 7% of even mass signal is due to organic ions? This merits a bit more discussion.

We came to that estimate by summing high resolution signal at nominally even mass to charge ratio that could not be explained by isotopic signal of nominally odd mass to charge ions or nitrogen containing inorganic ions such as NO₂⁻ and NO₃⁻. The latter, originating as contamination from tubing and the ionizer, dominated the signal at even massed ions. The manuscript has been revised as follows:

P6393, L27: Signals at nominally even mass-to-charges were dominated by NO₂⁻ and NO₃⁻, originating as contaminate signal from metal tubing and the ionizer. By summing high-resolution signals from even massed ions that are not inorganic or isotopes of odd massed ions, we estimate that less than 7% of the total signal at even masses is from organic ions.

p6394, line 24: While I can understand that the correction, as you have applied it, may only contribute a couple percent to the error on the bulk composition, this is not the actual error of this treatment of the ion clusters and is a misleading statement. Statements like this only serve to mislead the reader as to the true errors associated with a significant assumption such as this. It is essential to your quantitative analysis that you represent the true errors of involved in this work.

As was stated earlier, we agree that on an individual basis, the clustering correction could introduce significant error given that clustering kinetics are likely compound specific. However, we believe that on a bulk basis where ~100 mostly unknown ions are considered together, our correction is appropriate. Revisions to the manuscript making this point have been stated earlier.

p6395, line 3: How can you be certain that you are removing the proper background considering that you have no clean spectra of naphthalene? Is the Van Krevelen diagram not also affected by the contamination?

Because of the highly unsaturated nature of naphthalene, its oxidation products with relatively high carbon numbers tend to have low H/C values (≤ 1). In the Van Krevelen Diagram, these ions separate well from α -pinene products that have higher H/C values (≥ 1). However, small carbon number acids produced from both systems overlap on the Van Krevelen Diagram. That is why, to remove the contribution of small acids from α -pinene, a normalized α -pinene spectrum is first subtracted from the naphthalene. We are confident that this procedure corrects for most of α -pinene contamination in naphthalene spectra, however some additional uncertainty might be introduced into signals for smaller acids. We have revised the text as follows:

P6394, L27: CIMS spectra of oxidized organic vapors produced from naphthalene contained contaminant ion signals from α -pinene products. To remove ions overlapping both systems, an α -pinene spectrum corresponding to the nearest exposure and normalized to the $C_9H_{14}O_3^-$ ion was subtracted from the naphthalene spectra (possibly introducing some additional uncertainty in small acid signals). Subsequently, because of the highly unsaturated nature of naphthalene tracer products ($H/C \leq 1$), some ions could be exclusively attributed to α -pinene ($n_C \geq 6$ and $H/C > 1$, supported by the spectral separation in Van Krevelen space illustrated in Fig. 3) and were removed.

p6398, line 6: There is currently a lot of unknowns regarding the nearly ubiquitous production of these small acids from the oxidation of practically all organics in chamber studies, specifically I am thinking formic and acetic acid. Yet, the authors seemingly make this statement in a rather matter of fact manner. The mechanism for the formation of these acids is currently completely unknown and not an insignificant gap in available knowledge, considering the magnitude of secondary formation of small acids observed in the atmosphere via unknown processes. If the authors wish to make a statement like this, and other places throughout the paper, I believe a bit more justification is required. Perhaps the authors would like to comment on the oxidative fragmentation mechanism they believe is forming these small acids.

Unfortunately, we were unable to measure acetic acid because of the use of acetate as our reagent ion. We have revised the text as follows:

p6398, line 6: The prominence of these small acids in acetate-CIMS spectra has been previously observed by Yatavelli et al. (2012). Production of small acids in urban atmospheres has been correlated with photochemical activity Veres et al. (2011) and although their exact formation mechanism is unknown, it is likely they are generated from the oxidative fragmentation of the parent VOC and subsequent products.

P6399, line 25: The formation of formic acid from α -pinene ozonolysis and photooxidation has been previously observed in several studies (Lee et al., 2006a; Lee et al., 2006b; Librando and Tringali, 2005; Orlando et al., 2000). We measured a formic acid molar yield from α -pinene ozonolysis of 10%, which is similar to the molar yield of 7.5% previously observed by Lee et al. (2006a). Given that our experiments were performed under low- NO_x conditions, it is possible that formic acid was formed via the reaction of formaldehyde with HO_2 (Su et al., 1979). Orlando et al. (2000) also proposed formic acid as a first generation product from terpene-OH reactions. Formation of glyoxylic acid and glycolic

acid from the gas-phase oxidation of α -pinene or naphthalene has not previously been reported. We note that glyoxal can be produced from the photooxidation of terpenes (Fu et al., 2008) and naphthalene (Nishino et al., 2009), and that glyoxal may be a source of glyoxylic and glycolic acid (Galloway et al., 2009; Lim et al., 2010). Similarly, methylglyoxal is also a product of terpene oxidation (Fu et al., 2008) and is a possible source of pyruvic acid (Lim et al., 2010).

p6403, line 10: I am under the impression that the measurements made here were in the gas phase, with particle phase ‘concentrations’ calculated using vapor pressures and partitioning theory. As such, there are no acetate-CIMS signals measured for particle phase species. Am I misunderstanding something here? Are we looking at volatilized particle contents or gas phase products? This should be better explained not only here but also much earlier in the paper.

Yes, acetate-CIMS measurements were taken of the combined gas and volatilized SOA products of oxidation experiments. We have made the following revisions.

P6392, L1: and was heated to 200°C. These conditions were chosen to maintain laminar flow and to minimize condensation of organic vapors within the tube. Thus, collected spectra represent the combined contribution of gas-phase and particle-phase organics.

P6392, L26: The VOC concentrations that were used resulted in particle mass loadings $\sim 7 \mu\text{g m}^{-3}$ (assuming SOA density of 1.4 g cm^{-3}), measured after the heated sample line, or approximately 3% of the total organic carbon.

P6401, L5: Spectra represented in Figures 2-4 are for organic acids in the combined gas and particle phases. To estimate their relative contributions in each phase, we first calculated effective...

Figure 2. The figure displays unit mass resolution however the ions identified are given as high mass resolution species. There need to be agreement here. Please change the mass spectra to high mass resolution or the masses to unit.

In the revised manuscript, we have changed the labels to unit mass resolution/

p6386, line 17: add comma after “yields”, delete “and” before O/C, and add comma after “O/C”. Fixed.

p6388, line 25: organics to organic Fixed

p6390, line 23: delete “or” Fixed

p6392, line 14: The unit molec cm-3 s, in my opinion should be expressed as moles s cm-3.

We have changed the units to **molec s cm-3**.

P6392, line 14: approximate and ~ express the same thing therefore “approximately ~” is redundant. Fixed

P6403, line 19: add comma after “yields” and a second comma after “study”. Fixed

P6403, line 20: should “approximately” be “corresponding”? Yes. Fixed

P6403, line 22: remove comma before “for 10 to 100” Fixed

P6403, line 23: add comma after “mass” Fixed

Table 1. Can you include errors on the VOC concentrations used?

We estimate an error of 38% in the naphthalene concentrations used based on the variability of literature vapor pressure values. Additionally we estimate a 20% error in the α -pinene concentrations. These errors will be included in the analysis

Table 2. From the figure description one has no idea why there is a column labeled “Constant (1.79)”. Variables corresponding to Equation 11 have been added and the caption has been revised

Figure 3. The smaller numbers in the figure space are near impossible to see. Please consider scaling up the lower end of the size scale to make these more observable.

We have oriented the panels vertically to expand the size of the figure on the page.

Supplemental Figure 3 and 4. These identities contained here and throughout the manuscript are in most cases best guesses as an identity based on previous literature and assumptions about the molecular formula. I think that this point needs to be stressed a bit more in the manuscript in order to be more transparent about the potential for misidentifications here.

We have edited the caption of Supp. Fig 3. to read: **Van Krevelen plot of tracer acids shown in Figure 3, Panel A. Tracers are numbered, corresponding to their proposed identities shown below. Tracers identified by Yu et al. (1999) are in black and tracers identified by Claeys et al. (2013) are in red.**

We have edited the caption of Supp. Fig 4. to read: **Van Krevelen plot of tracer acids shown in Figure 3, Panel A (Kautzman et al., 2009). Tracers are numbered, corresponding to their proposed identities shown below.**

P6399, L5: ...(Claeys et al., 2013); proposed identities are given in Fig. S3 in the Supplement.

P6399, L27: ...(depicted by gray square boxes, proposed identities given in Fig. S4 in the supplement)

Response to Referee #1:

The authors stated that exact quantification of the many organic acids is important, but requires a large number of standards. Chemical ionization relies on an ion-neutral chemical reaction to create the quasimolecular ion. The sensitivity is therefore a strong function of both the kinetics (rate constant) and the thermodynamics (free energy), which can vary greatly depending on molecular structure and functional group. Are there theoretical calculations that can be performed to provide some insights? The proton transfer reaction mass spectrometer (PTR-MS) is a very similar instrument, and in many cases, the sensitivity of unknown compounds can be calculated using the ion-molecule reaction rate. Is there literature on rate constants of proton abstraction by acetate ions? Currently formic acid is the only standard (measured by a different gas monitor), but many more are commercially available and can potentially be used for understanding the range of sensitivities. One should also mention that a convenient feature of this system is that only acids are involved, which reduces the variability in functional groups somewhat. It would be important to demonstrate that the range in calibration factors for a number of acids involved in atmospheric oxidation. The manuscript would be more convincing if one quantifies the range rather than just accepting that there is a range. The ability of this instrument to quantitatively measure a large number of oxygenated compounds will be a key success of this work.

Unfortunately, we are not aware of theoretical calculations or literature data available for rate constants of proton abstraction reactions by acetate ions. We have edited the last paragraph of P6389 to note the selectivity of acetate ionization to acids. We agree with the reviewer's comments that constraining the range of representative calibration factors is necessary. A similar point was raised by the other reviewer; our response to Reviewer #2 Comment #2, which is also relevant here, is copied below:

In traditional quadrupole CIMS applications (e.g. Crounse et al., 2006; Veres et al., 2008), the determination of explicit compound-dependent calibration factors for a handful of compounds is more feasible. However, the explicit calibration of the HR-ToF-CIMS response to ~100 or more molecules, many of which are unknown and/or commercially unavailable (as is the case here) is impractical. In the discussions paper, we applied the HR-ToF-CIMS calibration factor for formic acid to all ions that were detected. After consideration of the reviewer's comments, we agree that there is no compelling reason to justify the use of formic acid over other compounds aside from the fact that it is easier to calibrate with (which is non-trivial). In an attempt to improve this aspect of the manuscript, we did an extensive literature search of all available acetate-CIMS calibration factors using acetate reagent ion chemistry. Using literature data from Veres et al. (2010), Yatavelli et al. (2012), and Aljawhary et al. (2013), and normalizing to the formic acid sensitivity to each instrument from these studies, we have implemented an average relative acetate-CIMS sensitivity of 1.3 ± 0.8 to the measured 5.5 ± 0.9 Hz ppt⁻¹ sensitivity of formic acid. Thus, to all acid signals (except formic), we apply a total sensitivity of 7.1 ± 4.6 Hz ppt⁻¹. A table will be added to the supplemental material listing the relevant literature data. In addition, the $\pm 1\sigma$ uncertainties inherent in this average calibration factor will be incorporated throughout the results and discussion section to more accurately reflect the underlying uncertainty in the application of a constant average calibration factor.

The instrument comparison with the Aerodyne AMS, described in Section 3.4.2, is an important discussion to better understand and interpret the measurements. Incorporating a gas/particle inlet such as the MOVI would certainly be useful, but that may be beyond the scope of this work. At the very least, more comparisons with Yatavelli et al. (2013) would be useful.

We have revised the last paragraph of Section 3.4.2 to the following:

Figure 8 also shows average O/C and H/C ratios of ambient organic aerosols measured with an acetate-MOVI-HRToF-CIMS during the BEACHON-RoMBAS field campaign (Ortega et al., 2014; Yatavelli et al., 2014). The BEACHON-RoMBAS measurements were obtained in a ponderosa pine forest and thus were influenced by emissions of biogenic compounds such as α -pinene. CIMS elemental ratios of highly oxidized α -pinene products produced in the PAM reactor agree with ambient measurements within 10%. Interestingly, Yatavelli et al. (2014) were able to successfully model the partitioning of organic acids in bulk as alkanolic acids with excess oxygen in the form of hydroxyl groups, each lowering the vapor pressure by SIMPOL estimated factors. Our method uses the measured ion formulas to constrain the double bond equivalency and limit additional oxygen functional groups. These similarities suggest that the volatility estimation algorithm successfully captures atmospheric photochemistry of atmospherically relevant SOA precursors, and that our results can be used to interpret ambient measurements in different source regions.

In the conclusions, the authors mention many new ideas for better characterizing ionization chemistry in the instrument. Some of these can be implemented quite easily. For example it should be rather straightforward to use isotopically labeled acetic acid, which is commercially available and reasonably priced. It can be used offline to measure the extent of clustering when the ratio of m/z 59 to m/z 119 is 5:1.

The reviewer makes an excellent point.

Both the title and the abstract should be rewritten to focus on the methodology. Currently, both are written in such a way that the new discoveries in gas phase composition of α -pinene and naphthalene oxidation products are the main contributions of the main contributions. Specifically, the first sentence after the overall introduction in the abstract is, “Here we examine gas-phase O₃ and OH oxidation products of α -pinene and naphthalene formed in the PAM flow reactor. . .”. Immediately after that, the authors report the OH oxidation exposures used and the consistencies with previous experiments. It would seem to me that focusing on the methodology to analyze soft ionization data would make a better manuscript for AMT, and α -pinene and naphthalene are used only as examples.

It seems to me that an AMT paper would be focused on exploring these ideas, while the current manuscript should be submitted to journals like Atmospheric Chemistry and Physics, Atmospheric Environment, Environmental Science and Technology, or other atmospheric chemistry journals. Again, I defer the decision about the scope of this paper to the editor.

We appreciate the reviewer's suggestions to make the manuscript more appropriate for AMT. We have changed the title to the following: **"Application of high-resolution time-of-flight chemical ionization mass spectrometry measurements to estimate volatility distributions of α -pinene and naphthalene oxidation products"**

We have also revised the abstract to the following:

Recent developments in high resolution, time-of-flight chemical ionization mass spectrometry (HR-ToF-CIMS) have made possible the direct detection of atmospheric organic compounds in real-time with high sensitivity and with little or no fragmentation, including low volatility, highly oxygenated organic vapors that are precursors to secondary organic aerosol formation. Here, using ion identified by high-resolution spectra from an HR-ToF-CIMS with acetate reagent ion chemistry we develop an algorithm to estimate the vapor pressures of measured organic acids. The algorithm uses identified ion formulas and calculated double bond equivalencies, information unavailable in quadrupole CIMS technology, as constraints for the number possible oxygen containing functional groups. The algorithm is tested with acetate-CIMS spectra of O_3 and OH oxidation products of α -pinene and naphthalene formed in a flow reactor with an Integrated OH exposures ranged from 1.2×10^{11} to 9.7×10^{11} molec s cm⁻³, corresponding to approximately 1.0 to 7.5 days of equivalent atmospheric oxidation. Measured gas-phase organic acids are similar to those previously observed in environmental chamber studies. For both precursors, we find that acetate-CIMS spectra capture both functionalization (oxygen addition) and fragmentation (carbon loss) as a function of OH exposure. The level of fragmentation is observed to increase with increased oxidation. The predicted condensed-phase SOA average acid yields and O/C and H/C ratios agree within uncertainties with previous chamber and flow reactor measurements and ambient CIMS results. While acetate reagent ion chemistry is used to selectively measure organic acids, in principle this method can be applied to additional reagent ion chemistries depending on the application.

The nC distribution in Fig. 4 is very interesting. One can observe the reaction chemistry through the nC distribution: naphthalene dissociates into mostly even carbon number products because of its molecular structure. Why would there be strong signals of C9 and C7 compounds? Acetate clustering does not explain these compounds, because it is a C2. Is it possible for larger compounds to dissociate in the ionization and mobility region (e.g. loss of CO2 or formaldehyde)?

The authors cannot find evidence to show possible dissociation of larger compounds in the IMR or CDC region of the acetate-CIMS. However, Kautzman et al., (2008) did identify C7 and C9 acids (as shown in supplemental figure 4), including benzoic acid and cinnamic acid, as naphthalene-OH products.

In both the abstract and the conclusions, the authors suggest that the method can be applied to other reagent ion chemistries. The authors should also mention that other reagent ion chemistries are potentially more useful and easier to analyze since some do not contain carbon atoms (such as iodide).

We have revised the manuscript as follows:

P6409 L7: Additionally, different reagent chemistries (e.g. $(\text{H}_2\text{O})_n\text{H}^+$, I^- , NO^{-3}) can and should be tested with our model to validate its effectiveness on different classes of compounds. For instance, iodide spectra may be more easily analyzed since its clusters do not contain carbon.

Page 6392 Line 1: The tubing was heated to 200C. Are there any concerns of decomposition of acids?

Yes, we do state that the differences in agreement between AMS elemental ratios and elemental ratios for modeled condensed phase acids may be due to decomposition of acids (see Page 6406, line 20. This is a concern for any method that will heat the condensed phase so that it may be sampled by the CIMS.

Page 6391 line 9: Presumably the authors mean α -pinene ozonolysis instead of isoprene
Yes, this has been corrected.

Page 6391 Line 12: It is unclear if the achieved resolution of 4000 is for the V- or W-mode.
No experiments were conducted in W-mode. This has been corrected.

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