

We thank the reviewers for their comments. We have modified the text in response to these comments below. Specifically, we have clarified the differences in reaction conditions regarding the “RO₂+NO₃ dominant” and “RO₂+RO₂ dominant” reactions, as well as amended the discussion of Fig. 9 in the revised manuscript to better reflect the differences in the two reaction conditions. In the revised manuscript, we also make minor adjustments to our VBS fitting in order to include $C^* = 0.1 \mu\text{g}/\text{m}^3$ and represent these fits on a mass basis for their direct implementation in aerosol models. All changes made are minor and do not affect the conclusions of the manuscript.

Response to Referee 1 (Referees’ comments are italicized)

- 1. First paragraph of intro: suggest a slight rewording - leading with BVOCs being a major source of SOA does not make the observation of “modern” carbon a discrepancy – it resolves it – maybe instead of “However, . . .”, “This resolves the apparent contradiction that ambient organic aerosols . . .”?*

Author response: As requested, we have changed the sentence in the revised manuscript from:

Page 2681 Line 6: “However, there exists a contradiction that ambient organic aerosol (even in urban areas) is predominately “modern”, indicating a biogenic origin (Lewis et al., 2004; Schichtel et al., 2008; Marley et al., 2009) but often correlates with anthropogenic tracers (de Gouw et al., 2005; Weber et al., 2007).”

To:

“While this is supported by the observation that ambient organic aerosol is predominantly “modern” and therefore biogenic in origin (Lewis et al., 2004; Schichtel et al., 2008; Marley et al., 2009), there exists an apparent contradiction because ambient organic aerosol is well-correlated with anthropogenic tracers (de Gouw et al., 2005; Weber et al., 2007).”

- 2. P. 2686 line 4 & SI material about HCHO required: How well do you know the amount of HCHO present at the beginning of the HO₂+RO₂ experiments? Are you able to constrain it by any measurement (HCHO, production rate of any products?), or is it determined by the volume of solution injected?*

Author response: We estimated the concentration of HCHO in the chamber at the beginning of the “RO₂+HO₂ dominant” experiments from the volume of the HCHO solution injected into the glass bulb and from the assumption that all the HCHO injected into the glass bulb volatilized and is introduced into the chamber. While we did not measure the HCHO to constrain the uncertainty in its concentration, we expect the uncertainty to be small as the loss of HCHO (volatile compound) during the injection process is expected to be small.

- 3. P. 2686 line 8-9: I suggest modeling the oxidation of β -pinene in both conditions to both demonstrate clearly this dominance of NO₃ in the HO₂ conditions, and show the difference in rate and how it affects the timing of aerosol yield calculations. I see you have O₃ measurements – you could use these to constrain this model experimentally?*

Author response: As requested, we have provided the modeled oxidation of β -pinene under “ RO_2+NO_3 dominant” conditions in the supplementary material. The kinetic model predicts that $> 99\%$ of the β -pinene reacts with NO_3 instead of ozone. The model for the “ RO_2+NO_3 dominant” reaction indicates a rapid reaction time (~ 1 min) for β -pinene within the chamber.

Similarly, we attempted to model the oxidation of β -pinene under “ RO_2+HO_2 dominant” conditions. Unfortunately, the model does not converge with the inclusion of HCHO in the model but does converge when HCHO is not included. When HCHO is not included, the model shows that majority ($> 99\%$) of the β -pinene reacts with NO_3 rather than ozone. We calculate the ratio of HCHO: β -pinene needed to promote RO_2+HO_2 reaction, details of which are in the SI. The appropriate amount of HCHO (based on the calculated HCHO: β -pinene ratio needed) is injected in the “ RO_2+HO_2 ” dominate experiments. The added HCHO can also react with nitrate radicals. However, since the β -pinene+ NO_3 reaction is 13 faster than HCHO+ NO_3 the presence of HCHO does not affect the availability of NO_3 for β -pinene oxidation. Ultimately, most β -pinene ($>99\%$) still reacts with NO_3 .

The amount of time to reach peak growth in our experiments is longer than the modeled oxidation of β -pinene under “ RO_2+NO_3 dominant” conditions. Although complete β -pinene oxidation is expected to occur within minutes, the amount of time to reach peak growth experimentally (also addressed in comment #7) is 10-15 minutes in all reaction conditions except for the “ RO_2+HO_2 dominant” experiments under high humidity (which took 30 min). One possible reason for this discrepancy is that due to the fast reaction rates, most of the β -pinene has reacted before the chamber is well mixed, which will result in a lapse between aerosol formation and its measurement by the HR-ToF-AMS and SMPS. The timescales at which products condense onto seed particles are also not known. Due to these experimental constraints, we are unable to directly correlate the rates in our kinetic model to our measured rates of aerosol growth and the time it takes to reach aerosol peak growth.

We change Figure 9 to show the dominance of the BVOC+ NO_3 reaction and amend the caption to:

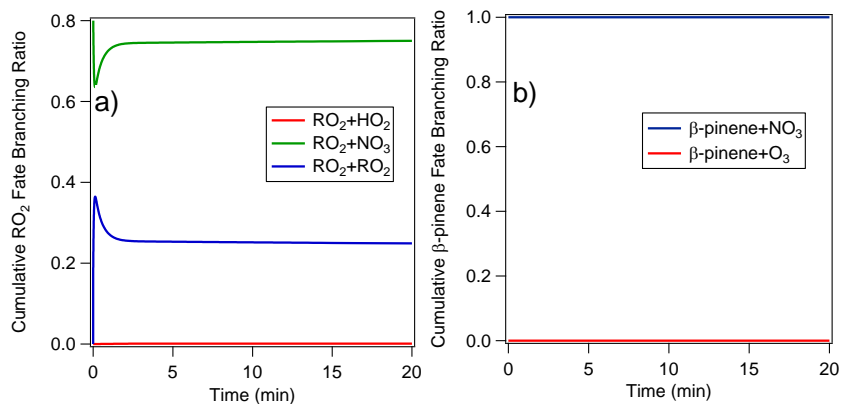


Figure S9: a) The RO₂ branching ratio and b) β-pinene fate for a typical “RO₂+NO₃” dominant experiment (Experiment 5 in Table 1 of the main text). The branching ratios are determined from the reactions in the Master Chemical Mechanism (MCM v 3.2). The plots show the cumulative amount of products formed from each possible reaction.

4. p. 2687 line 15-16: *Can you put an uncertainty estimate on the initial [HC] based on the volume measurement accuracy?*

Author response: Table 1 shows the uncertainties of the initial [HC] based on the volume measurement accuracy.

5. P. 2690 line 21-22: *The reference for wall losses refers to measurements made in a different chamber. If such data are already published for this chamber, could refer to that, else perhaps include the size-dependent wall loss rates measured for this chamber in the supplemental?*

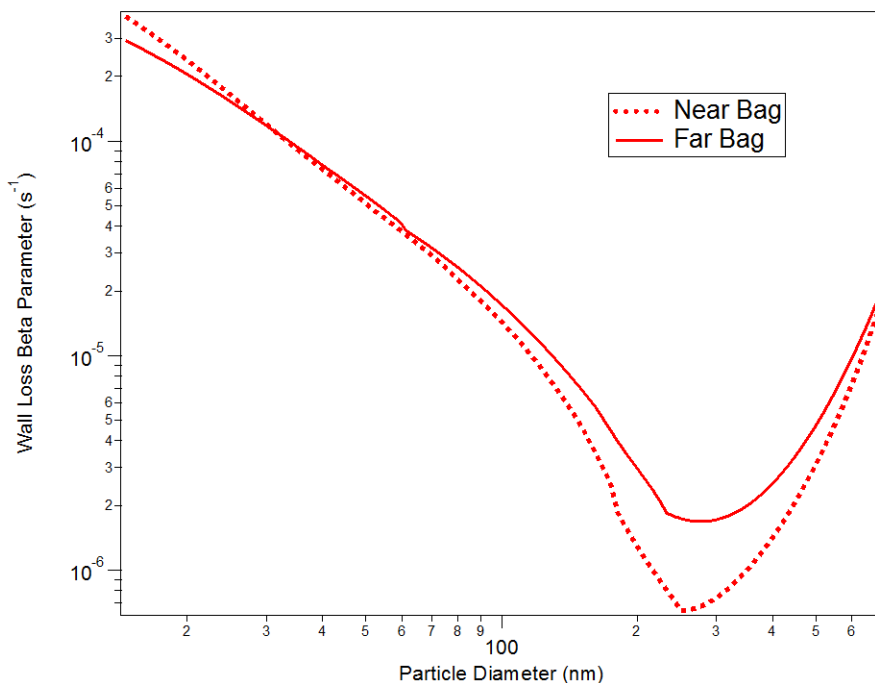
Author response: The original text referenced Keywood et al. (2004) only for the methodology for correcting for particle wall loss. To clarify any confusion regarding the size-dependence wall loss rates used for our experiments, we have changed the text from:

Page 2690 Line 21: “All SOA growth data are corrected for particle wall loss by applying size-dependent wall loss coefficients determined from wall loss experiments (Keywood et al., 2004).”

To:

“All SOA growth data are corrected for particle wall loss by applying size-dependent wall loss coefficients determined from wall loss experiments at GTEC following the methodology described in Keywood et al. (2004).”

The wall-loss coefficients for this chamber have not been published. As requested, we have added a figure showing the size-dependent wall loss rates measured in this chamber to the supplementary information:



“Figure S10: Size-dependent particle wall loss rates, β , calculated for both chambers at GTEC. Wall loss rates are determined by wall loss experiments performed using ammonium sulfate seed particles atomized from an 8 mM solution and measuring their decays over time. The first-order decay coefficients were measured for each particle size bin over the course of the wall-loss experiment.”

6. *Ibid* line 26: suggest “aerosol mass concentration produced (ΔMo)”

Author response: We have made the suggested modification.

7. *Ibid* line 29: Can you add some text about at what time the SMPS aerosol volume was taken for the mass yields – fixed time after injection? Or peak in volume? If the latter, how different was the lag time between starting reactions & aerosol peak for each type of experiment? Perhaps label the time of $\Delta(Mo)$ on Figure 2.

Author response: The SMPS aerosol volume used to calculate the aerosol mass yields in each experiment is the peak SMPS aerosol volume (averaged over 30 min). We have stated on page 2689, lines 24-26 that “Peak aerosol growth is typically observed within 10-15 minutes for all reaction conditions except in humid (RH= 50%, 70%) “RO₂+HO₂ dominant” experiments, where aerosol reaches peak growth in about 30 minutes.” As Fig. 2 already contains a huge amount of information, we feel that adding the time of $\Delta(Mo)$ will make the figure harder to understand.

To clarify this, we have changed the sentence:

Page 2690 Line 28: “For all experiments, aerosol mass concentration is obtained from the SMPS aerosol volume concentration and the calculated aerosol density.”

To:

“For all experiments, aerosol mass concentration is obtained from the SMPS aerosol volume concentration (averaged over 30 min at peak growth) and the calculated aerosol density.”

8. P. 2691 line 5: *Is it your view that these dry/humid conditions numbers are significantly different from one another?*

Author response: We think that the densities from the dry and humid experiments are not significantly different from one another (within 5% of each other). Prior to the experiments, we did not know how similar/different they would be. Thus we performed nucleation experiments under different conditions to determine the density at those specific conditions.

9. P. 2692 line 5: *“which make up about 11% of the total organics signal” – wording is slightly confusing – are NO⁺ and NO₂⁺ part of the organics signal (sounds like it with this phrasing) or is their magnitude equal to 11% of the organics signal (what I think you mean)*

Author response: To clarify this, we have changed the sentence

Page 2692, Line 3: **“A key feature of the mass spectrum is the high intensity of the nitrate ions at NO⁺ and NO₂⁺, which make up about 11% of the total organics signal.”**

To:

“A key feature of the mass spectrum is the high intensity of the nitrate ions at NO⁺ and NO₂⁺, which make up about 11% of the combined organic and nitrate signals.”

10. *Ibid around line 10: General question: why would the NO⁺:NO₂⁺ ratio be different for different oxidant regimes if the apparent product composition is largely identical? Or are these not really significantly different?*

Author response: At this time, it is not clear what causes the difference in the NO⁺:NO₂⁺ ratio in the different oxidation regimes (on average, 6.5 for “RO₂+NO₃ dominant” experiments and 8.6 for “RO₂+HO₂ dominant” experiments). It is possible that while the aerosol yields and product composition are similar in the different oxidation regimes, the relative concentrations of the particle phase organic nitrates may be different, resulting in the difference in the NO⁺:NO₂⁺ ratios. For example, the *m/z* 358 is higher in the “RO₂+HO₂ dominant” experiments, which we believe may be due to increased production of ROOH in the “RO₂+HO₂ dominant” experiments. It is also possible that the functional groups surrounding the nitrate group may affect the NO⁺:NO₂⁺ ratio. Additionally, it is possible that the products formed in the two reaction conditions are different but having similar volatility, thus resulting in similar mass yields but different NO⁺:NO₂⁺ ratios for the two oxidant regimes.

11. *Ibid line 19-21: I don't think this generalization really follows from the previous sentence, since these are 2 specific terpenes, and these fragments could be highly structure dependent.*

Author response: We agree that with the reviewer that the abundance of the $C_5H_7^+$ and $C_7H_7^+$ fragments may be highly dependent on the structure of the SOA components. However, as stated in the original text, the AMS mass spectra of the SOA formed from the oxidation (photooxidation, nitrate radical oxidation, ozonolysis) of BVOCs such as isoprene and α -pinene, does not exhibit large intensities at $C_5H_7^+$ and $C_7H_7^+$ (Ng et al., 2008; Chhabra et al., 2010). We suggest that these fragments may be important for monoterpene chemistry based on our observations but more study on the AMS fragmentation pattern for SOA formed by a larger suite of terpenes is needed. As such, we have revised the manuscript to be more circumspect in our explanation on the use of $C_5H_7^+$ and $C_7H_7^+$ fragments as indicators for monoterpene SOA oxidation, and have changed the sentence:

Page 2692, Line 17: “These ions have also been observed in SOA formed from the ozonolysis of β -caryophyllene (Chen et al., 2014). Therefore, m/z 67 ($C_5H_7^+$) and m/z 91 ($C_7H_7^+$) could potentially serve as useful indicators for SOA formed from monoterpene/sesquiterpene oxidations in ambient aerosol mass spectra.”

To:

“These ions make up a larger fraction of the HR-ToF-AMS signal for SOA formed from the ozonolysis of β -caryophyllene (Chen et al., 2014) when compared to other biogenic SOA. Therefore, m/z 67 ($C_5H_7^+$) and m/z 91 ($C_7H_7^+$) could potentially serve as useful indicators for SOA formed from monoterpene/sesquiterpene oxidations in ambient aerosol mass spectra. However, more studies of SOA formed from the oxidation of biogenic VOCs are necessary to apportion ambient OA based on these fragments.”

12. P. 2694, line 24-25: *the product of reaction 9 in the scheme shown is not a dihydroxynitrate.*

Author response: The reviewer is correct. The product should be “cyclic ether hydroxynitrate” instead. This has been corrected.

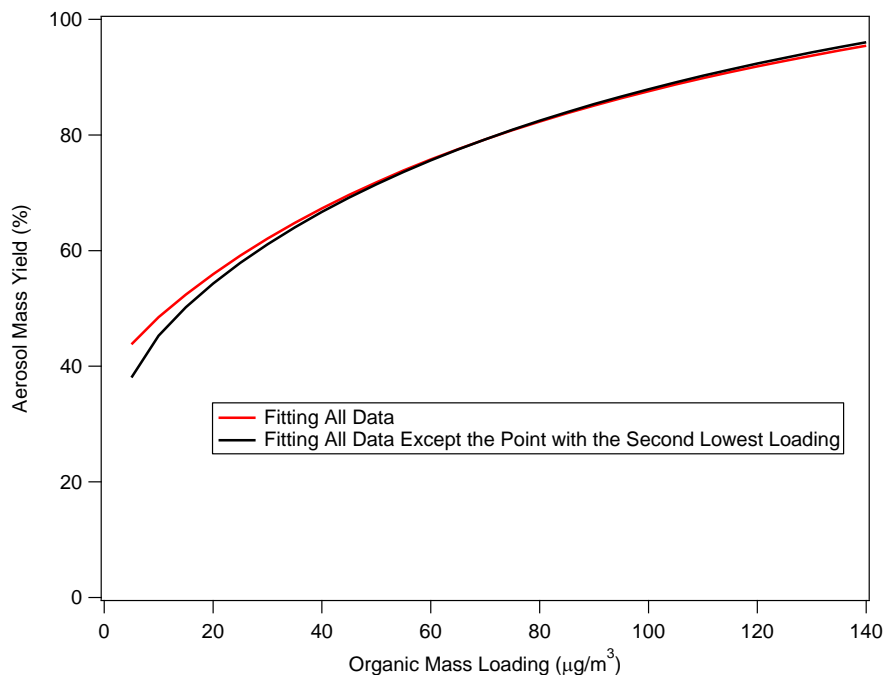
13. P. 2695 line 22: *“1.5h shift” should read “1,5-H shift”*

Author response: This has been corrected.

14. P. 2699 2nd paragraph: *general question about yield fitting: How do you interpret that the coefficient at 10 $\mu\text{g}/\text{m}^3$ is exactly zero? Did you do any sensitivity tests e.g. with a bigger basis set, or removing a point, to check how robust this fit is?*

Author response: The coefficients for the VBS represent the best mathematical fit to all of our data. The coefficient at 10 $\mu\text{g}/\text{m}^3$ is representative of that fit. The point we would like to emphasize in this discussion is not the exact coefficients used but rather the overall trend of the volatility fit. Specifically, the VBS fit to our data indicates that the β -pinene+ NO_3 SOA system is composed of both low-volatility and high-volatility products.

As suggested by the reviewer, we checked the robustness of the fit by removing a data point. By removing the second lowest point in the yield curve on Fig. 3 and re-fitting the data, the new yield curve shown below is very similar to our original yield curve, with a difference only about 10% at the lowest mass loading. Therefore, the original yield curve is robust and is not biased by the second lowest point during fitting.



We would like to make some revisions to the VBS fits presented in the original text. In the original manuscript, a molar basis was used for the VBS fitting using an average molecular weight of 230 amu but this was not specifically stated in the original text. In the revised manuscript, we change the fits to a mass basis. In addition, we would also like to correct the data in Griffin et al. (1999) to adjust for the deviations in temperature from 25 °C and change the basis set from $C^* = \{1,10,100,1000\}$ to $C^* = \{0.1, 1, 10, 100\}$. This will allow for a direct comparison of our VBS fits with the fit parameters currently used in aerosol models (e.g. Pye et al (2010)). This adjustment will be clearly stated in the revised manuscript. After making these adjustments, Table 3 has been changed from:

	Saturation Vapor Pressure, C^* ($\mu\text{g}/\text{m}^3$)			
	1	10	100	1000
β -pinene+NO ₃ (this study)	0.272	0.000	0.437	0.291
Griffin et al. (1999)	0.000	0.117	0.785	0

To:

	Saturation Vapor Pressure, C^* ($\mu\text{g}/\text{m}^3$)			
	0.1	1	10	100
β -pinene+NO ₃ (this study)	0.373	0.033	0.000	0.941
Griffin et al. (1999)	0.000	0.000	0.301	1.204

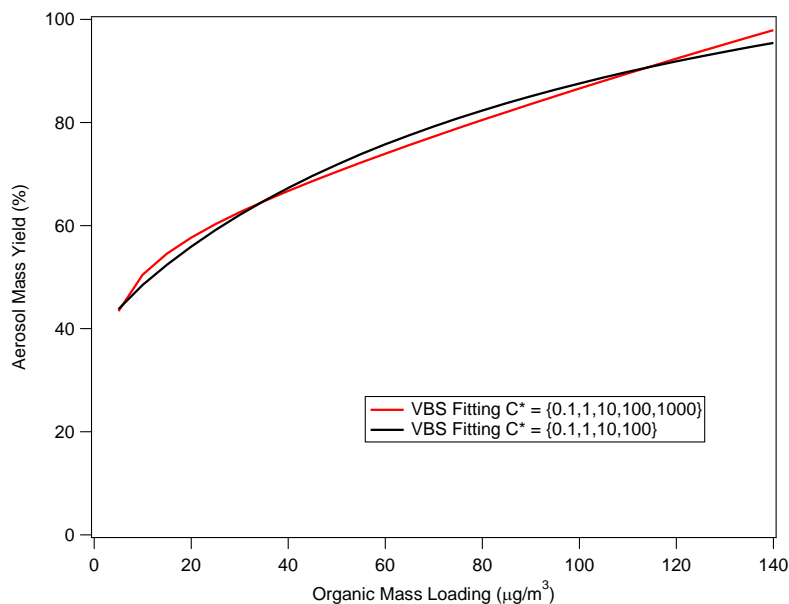
We have also changed:

Page 2699, Line 8: “The fit coefficients for the volatility basis set are shown in Table 3 for the aerosol yields of β -pinene+NO₃ from this study and that of Griffin et al. (1999)”

To:

“The fit coefficients for the volatility basis set are shown in Table 3 for the aerosol yields of β -pinene+NO₃ from this study and that of Griffin et al. (1999). It is noted that the data from Griffin et al. (1999) have been adjusted to a temperature of 25 °C and a density of 1.41 g cm⁻³”

To further test the robustness of our fit and confirm that the fit is not biased due to the basis set chosen, we can also expand the basis set to $C^* = \{0.1, 1, 10, 100, 1000\}$. Expanding the basis set to $C^* = \{0.1, 1, 10, 100, 1000\}$ gives a different set of parameters with a fit shown in the figure below. The curves deviate by a maximum of 4% in the range of the mass loadings measured in all experiments. While the fitting parameters have changed, the overall fit is robust.



15. P. 2702 line 18-19, refers to SI figure S9: my reading of figure S9 is not that RO₂+RO₂ reaction “are not significant” – in fact a substantial fraction appears to go via these cross-reactions

Author response: While the reviewer is correct in pointing out that there are some RO_2+RO_2 cross reactions, the majority (~70%) of the RO_2 radicals react with the NO_3 radical based on our modeling results. While it is impossible to completely eliminate RO_2 cross reactions, the experimental conditions were designed to minimize the RO_2+RO_2 reaction pathway and ensure that majority of the RO_2 radicals react with NO_3 radicals in the “ RO_2+NO_3 dominant” experiments. We determine that the “ RO_2+HO_2 dominant” experiments also minimize the RO_2+RO_2 pathway based on the concentrations of HCHO injected as discussed in the SI.

16. P. 2704 line 3: *what does “relative reactivity for both reaction channels” mean? In general, this figure (Fig. 9) and its interpretation were confusing. You seem to be asserting that the trend is the same across both oxidant conditions, but if the bars are correctly labeled (on the righthand panel the dry and humid are switched), the similarity in trend is not apparent.*

Author response: In our discussion of Fig. 9, the comparison we are referring to is only between the two bars for RO_2+NO_3 and between the two bars for RO_2+HO_2 , and not between the NO_3 panel and the HO_2 panel. To clarify this, we have added the following discussion before the sentence:

Page 2704 Line 4: “The relative reactivity for both reaction channels is similar within one standard deviation for all humidity conditions studied, indicating that each condition may have a similar product distribution.”

“By comparing the amounts (areas) of the 235 and 270 nm absorbing species, the effect of humidity on the two branching pathways (RO_2+HO_2 and RO_2+NO_3) can be assessed. How much $-\text{ONO}_2$, $-\text{C}=\text{O}$, ROOR and ROOH is produced under each humidity level determines the relative reactivity between the humid vs. dry conditions of each branching pathway.”

Additionally we have added the following after the sentence:

Page 2704 Line 4: “The relative reactivity for both reaction channels is similar within one standard deviation for all humidity conditions studied, indicating that each condition may have a similar product distribution.”

“A comparison between the $\text{RO}_2 + \text{HO}_2$ and $\text{RO}_2 + \text{NO}_3$ pathways cannot be made in this manner because the NO_3 concentrations were different. The seemingly smaller areas for species produced in the HO_2 panel could simply be due to a larger amount of non-nitrated organic matter being produced that absorbs at the normalization wavelength.”

17. *Furthermore, line 6: this molecular assignment is wrong/inconsistent. The formula you have listed would have $m/z = 245$, not 244, and the reaction you refer to (R22) you have elsewhere (bottom of 2695) described as producing a carboxylic acid, not a hydroperoxide. This should be clarified in the figure as well, by making the functional group unambiguous. This UHPLC portion of the evidence is most difficult to understand and I suggest reworking the discussion of this data. If you stick with the reasoning about R22 being an alternate pathway to a different, high- NO_3 product, it would be useful to have that competing pathway also indicated on the mechanism scheme.*

Author response: The MW and m/z are correct as written and have not been changed. Reaction R22 does form a carboxylic acid. The product (MW = 245 amu) formed from the R21 and R22 reactions can also be formed from R19 and R20. The reaction combination R19 and R20 can occur in both the “RO₂+NO₃ dominant” and “RO₂+HO₂ dominant” experiments while the reaction combination of R21 and R22 is expected to be prevalent in “RO₂+HO₂ dominant” experiments. We therefore expect an enhancement of the product with MW = 245 amu in the “RO₂+HO₂ dominant” experiments.

To clarify this, we have changed the text:

Page 2704 Line 5: “One slight difference is the enhancement in the production of C₁₀H₁₅NO₆ (m/z 244, an ROOH species) in the “RO₂+HO₂ dominant” experiments, which increases by 2 and 7 times under dry and humid conditions, respectively, relative to the “RO₂+NO₃ dominant” experiments.”

To:

“One slight difference is the enhancement in the production of C₁₀H₁₅NO₆ (m/z 244, a RCOOH species) in the “RO₂+HO₂ dominant” experiments, which increases by 2 and 7 times under dry and humid conditions, respectively, relative to the “RO₂+NO₃ dominant” experiments.”

We have also changed the sentence:

Page 2704 Line 10: “This can be explained by an increase in reaction R22 in Fig. 8.”

To:

“This can be explained by an enhancement of the reaction sequence R21 + R22 in Fig. 8, which is enhanced at high HO₂ radical concentrations.”

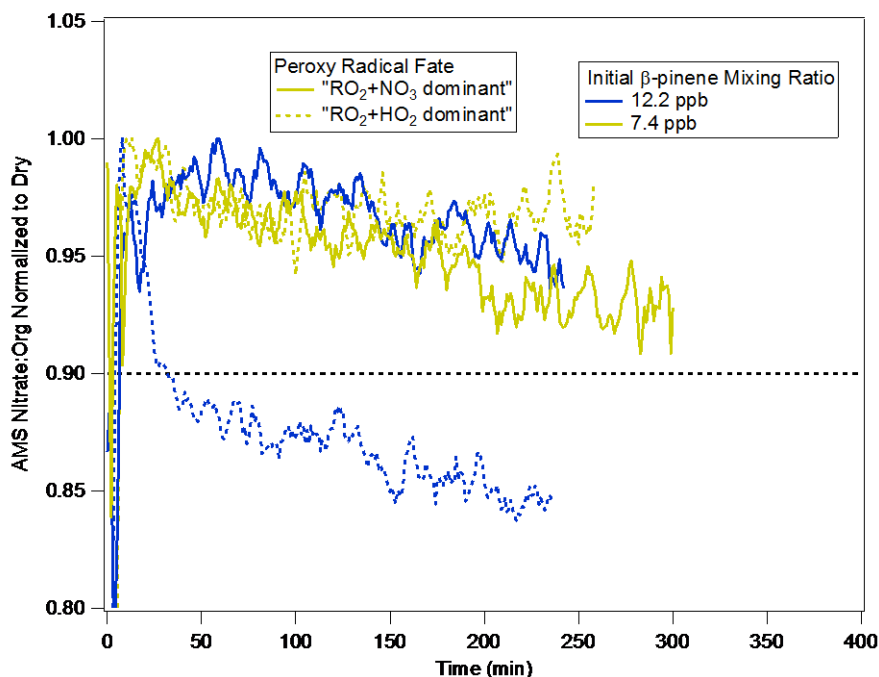
18. P. 2706 line 10 “carbons, the upper-bound molar organic nitrate”

Author response: This has been corrected.

19. P. 2707 lines 17-19: *Could there not be some RO₂+NO₃ vs RO₂+HO₂ difference in organic nitrate hydrolysis rate because subsequent reactions render some products more likely to “keep” the nitrate moiety intact where others might jettison the NO₂? Did you compare different oxidant fates and see no difference?*

Author response: As suggested by the reviewer, we compared the nitrate hydrolysis rates in the “RO₂+HO₂ dominant” and “RO₂+NO₃ dominant” reaction conditions. We compare the experiments where (NH₄)₂SO₄ + H₂SO₄ seed were used, since we only run the “RO₂+HO₂ dominant” experiments with this type of seed. When using (NH₄)₂SO₄ + H₂SO₄ seed, we expect the rates of hydrolysis to be faster than those experiments using (NH₄)₂SO₄ seed (Rindelaub et

al., 2015). It is therefore difficult to determine the extent of hydrolysis for experiments with $(\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{SO}_4$ seed because the hydrolysis of tertiary organic nitrates may occur so quickly that a portion of the organic nitrates hydrolyze before peak aerosol growth. Even though much of the tertiary organic nitrates could hydrolyze quickly, it is still clear from the graph that under all conditions, a small fraction of the organic nitrate species hydrolyze over the span of several hours. We do note that one of the experiments (12.2 ppb, “ $\text{RO}_2 + \text{HO}_2$ dominant”) may have a slightly slower rate of hydrolysis. In this case, the hydrolysis may have been slow enough that the organic nitrates do not hydrolyze appreciably prior to peak growth. Therefore, the peak value that we normalize the data by may have been higher for this experiment compared to other conditions.



In order to emphasize that the fraction of tertiary nitrates to total nitrates may have some variation in each experiment, we change:

Page 2707, Line 12: “As the oxidation products typically contain only one nitrate group (Fig. 8), we infer that 90% of the organic nitrates formed from the β -pinene+ NO_3 reaction are primary nitrates.”

To:

“As the oxidation products typically contain only one nitrate group (Fig. 8), we infer that, within experimental error, approximately 90% of the organic nitrates formed from the β -pinene+ NO_3 reaction are primary nitrates.”

20. *Ibid line 28: Suggest to replace “nitrate radical chemistry” with “nitrate + β -pinene” because many terpenes have internal double bonds, this feature of producing few tertiary nitrates is unique to β -pinene and shouldn't overgeneralized*

Author response: We expect the majority of terpenes to produce primary or secondary organic nitrates from nitrate radical oxidation. The list of terpenes commonly emitted by vegetation shown by Guenther et al. (2012), while not an exhaustive list, demonstrates that the commonly emitted terpenes typically have at least one double bond containing either a primary or secondary carbon; the exception is tricyclene which does not have a double bond. Upon reaction of the nitrate radical with the least substituted carbon (Wayne et al., 1991), these terpenes will form organic nitrates with nitrate functional groups present on either the primary or secondary carbon. Darer et al. (2011) have shown that primary and secondary organic nitrates have slow hydrolysis rates.

While the reviewer is correct in pointing out that many terpenes have internal double bonds, these terpenes typically have internal double bonds that contain a tertiary and secondary carbon. We still expect such terpenes to produce mainly secondary organic nitrates since the nitrate radical will add predominantly to the secondary carbon (to produce a secondary organic nitrate) because it is the least substituted carbon (Wayne et al., 1991).

To clarify this point in the revised manuscript, we have changed:

Page 2708 Line 1: “As primary and tertiary organic nitrates have drastically different hydrolysis rates, it is imperative that their relative contribution be accurately represented in models when determining the fate of ambient organic nitrates.”

To:

“While we directly demonstrate this to be true in the case of β -pinene+NO₃ system, this can also be applied to commonly emitted terpenes, including those with internal double bonds. From the list of terpenes in Guenther et al. (2012), all unsaturated terpenes have at least one double bond with a secondary or primary carbon. For example, α -pinene contains an internal double bond connecting a tertiary carbon to a secondary carbon. The nitrate radical is more likely to attack the less substituted carbon (i.e., the secondary carbon) and form a secondary organic nitrate. As primary/secondary and tertiary organic nitrates have drastically different hydrolysis rates, it is imperative that their relative contribution be accurately represented in models when determining the fate of ambient organic nitrates.”

21. *Same comment @ p. 2708 lines 16-19: this is only true where terminal double bonds dominate – so, where dominated by β -pinene.*

Author response: We refer the reviewer to the response to comment #20. As explained above, most commonly emitted terpenes with internal double bonds have one secondary carbon and one tertiary carbon. In the nitrate radical reaction of such terpenes, the nitrate radical will add predominantly to the less substituted carbon of the internal double bond (Wayne et al., 1991),

which in this case is the secondary carbon, to form a secondary organic nitrate. The resulting secondary organic nitrate will have slow hydrolysis lifetimes (Darer et al., 2011).

22. *P. 2711 line 6: inversely? Does this mean this partitioning coefficient is wall/gas, not gas/wall? Clarify.*

Author response: The partitioning coefficient we refer to in the original text is to the gas-wall partitioning coefficient. The original text meant to explain that if a particular compound (Compound A) has a lower vapor pressure than another (Compound B), it is expected that Compound A is more likely to partition to the chamber walls than compound B.

To clarify this, we have changed the sentence:

Page 2711 Line 6: “Additionally, the gas-wall partitioning coefficient has also been shown to correlate inversely with the vapor pressure for each compound (Yeh and Ziemann, 2014), where highly oxidized species typically have lower vapor pressures (Pankow and Asher, 2008).”

To:

“Additionally, the gas-wall partitioning coefficient for a specific compound has also been shown to increase with decreasing vapor pressure (Yeh and Ziemann, 2014), with highly oxidized species typically having lower vapor pressures than less oxidized species (Pankow and Asher, 2008).”

23. *Ibid, line 10: this phrase is unclear: “causing these compounds to re-partition back to the gas phase to re-establish equilibrium.” The oxidized molecules partition to the walls more quickly, only to partition back faster?*

Author response: The original text meant to explain that compounds that are lost quickly to the walls are also expected to evaporate quickly from the particle phase in order to maintain particle-gas equilibrium.

To clarify this, we have changed the text from:

Page 2711 Line 8: “If vapor-phase wall loss is the driving factor for the decrease in organics in this study, it would be expected that oxidized compounds would decrease more rapidly, causing these compounds to re-partition back to the gas phase to re-establish equilibrium”

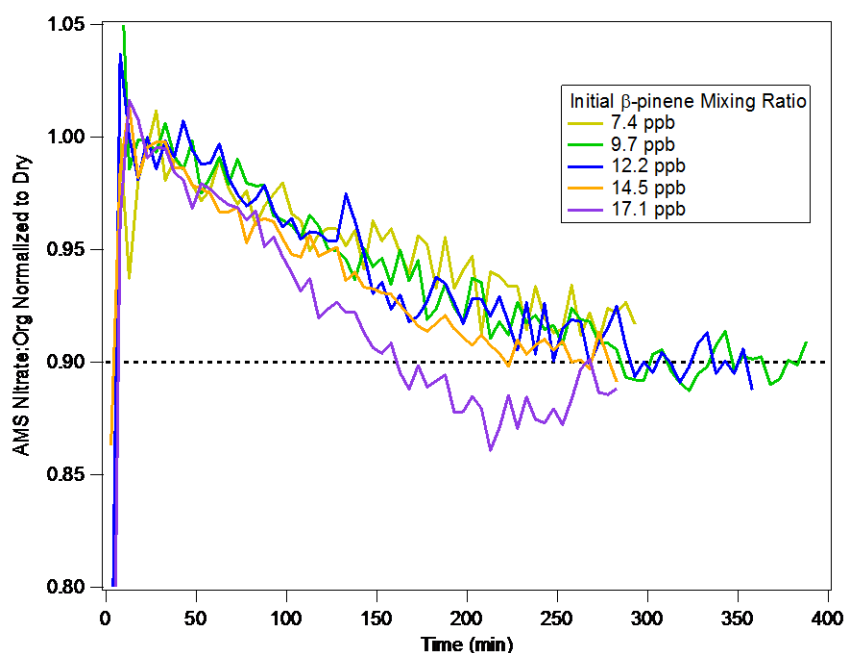
To:

“If vapor-phase wall loss is the driving factor for the decrease of organics in this study, it would be expected that oxidized compounds would be lost to the walls more rapidly. Subsequently, these highly oxidized compounds would re-partition back to the gas phase in order to re-establish particle-gas equilibrium.”

24. Table 1: the range of $\Delta(\text{HC})$ here doesn't seem to match Fig. 7, where the range of initial β -pinene concentrations is 9-21 ppb, which would be 50-117 $\mu\text{g m}^{-3}$. Also, I suggest using the same units throughout. If the times after chemistry initiation at which yields were evaluated is vastly different for different conditions, maybe include that time in this table?

Author response: The concentrations listed in Table 1 of the original manuscript are the nominal β -pinene concentrations based on a 10 m^3 chamber used for the experiments presented in this paper and so the concentrations are different from those presented in Table 1. These numbers were therefore inaccurate and have been corrected for a chamber volume of 12 m^3 .

We also agree with the reviewer that the same units should have been used throughout the manuscript. As requested by the reviewer, in order to stay consistent with the values shown in Table 1, we have added a column in Table 1 to report the mixing ratio of β -pinene in ppb to be consistent with Figure 7. The updated figure and table are shown below:



Experiment	RH (%)	Condition	Seed	ΔHC^c (ppb)	ΔHC^c ($\mu\text{g}/\text{m}^3$)	ΔM_o^d ($\mu\text{g}/\text{m}^3$)	Mass Yield (%)
1	< 2	RO_2+NO_3	AS ^a	2.5 ± 0.2	13.8 ± 1.3	5.3 ± 0.41	38.3 ± 5.5
2	< 2	RO_2+NO_3	AS	2.5 ± 0.2	13.8 ± 1.3	5.4 ± 0.15	38.7 ± 4.0
3	< 2	RO_2+NO_3	AS	7.4 ± 0.7	41.5 ± 3.9	25.3 ± 0.54	61.0 ± 6.0
4	< 2	RO_2+NO_3	AS	9.9 ± 0.9	55.4 ± 5.2	-- ^e	--
5	< 2	RO_2+NO_3	AS	12.4 ± 1.2	69.2 ± 6.5	--	--
6	< 2	RO_2+NO_3	AS	12.4 ± 1.2	69.2 ± 6.5	44.9 ± 0.73	64.9 ± 6.3
7	< 2	RO_2+NO_3	AS	14.9 ± 1.4	83.0 ± 7.8	--	--
8	< 2	RO_2+NO_3	AS	17.4 ± 1.6	96.9 ± 9.1	--	--
9	< 2	RO_2+NO_3	AS	24.8 ± 2.4	138.4 ± 13.1	134.6 ± 1.51	97.2 ± 9.3
10	< 2	RO_2+NO_3	AS	24.8 ± 2.4	138.4 ± 13.1	114.7 ± 2.51	82.9 ± 8.2
11	51	RO_2+NO_3	AS	2.4 ± 0.2	13.2 ± 1.2	7.3 ± 0.57	55.4 ± 8.2

12	50	RO ₂ +NO ₃	AS	2.4±0.2	13.2±1.2	6.8±0.36	51.7±6.3
13	49	RO ₂ +NO ₃	AS	7.1±0.7	39.6±3.7	23.0±0.65	57.9±6.0
14	49	RO ₂ +NO ₃	AS	9.5±0.9	52.8±5.0	34.2±0.89	64.8±6.6
15	51	RO ₂ +NO ₃	AS	9.5±0.9	52.8±5.0	33.1±0.56	62.5±6.1
16	50	RO ₂ +NO ₃	AS	11.9±1.1	66.1±6.2	43.5±0.60	65.9±6.4
17	50	RO ₂ +NO ₃	AS	11.9±1.1	66.1±6.2	42.2±0.98	63.9±6.4
18	51	RO ₂ +NO ₃	AS	14.2±1.3	79.3±7.5	60.7±0.83	76.6±7.4
19	51	RO ₂ +NO ₃	AS	16.6±1.6	92.5±8.7	68.4±1.26	73.9±7.2
20	71	RO ₂ +NO ₃	AS	11.9±1.1	66.1±6.2	50.5±1.32	76.4±7.8
21	70	RO ₂ +NO ₃	AS	11.9±1.1	66.1±6.2	50.0±0.44	75.7±7.2
22	72	RO ₂ +NO ₃	AS	23.7±2.2	132.1±12.5	125.5±1.35	95.0±9.0
23	68	RO ₂ +NO ₃	AS	23.7±2.2	132.1±12.5	132.9±1.33	100.6±9.5
24	51	RO ₂ +NO ₃	AS+SA ^b	7.1±0.7	39.6±3.7	25.5±0.69	64.4±6.6
25	50	RO ₂ +NO ₃	AS+SA	11.9±1.1	66.1±6.2	46.4±1.10	70.4±6.8
26	51	RO ₂ +NO ₃	AS+SA	16.6±1.6	92.5±8.7	74.4±1.23	80.5±7.7
27	< 3	RO ₂ +HO ₂	AS	7.4±0.7	41.5±3.9	27.0 ±0.54	64.9±6.4
28	< 3	RO ₂ +HO ₂	AS	7.4±0.7	41.5±3.9	22.9±0.71	55.0±5.8
29	< 3	RO ₂ +HO ₂	AS	12.4±1.2	69.2±6.5	49.3±0.97	71.2±7.1
30	< 3	RO ₂ +HO ₂	AS	12.4±1.2	69.2±6.5	36.1±1.17	52.2±5.6
31	< 2	RO ₂ +HO ₂	AS	17.4±1.6	96.9±9.1	71.2±2.32	73.4±7.8
32	< 3	RO ₂ +HO ₂	AS	37.3±3.5	207.6±19.6	216.1±1.96	104.1±9.9
33	49	RO ₂ +HO ₂	AS	35.6±3.4	198.2±18.7	147.8±1.42	74.6±7.1
34	69	RO ₂ +HO ₂	AS+SA	2.4±0.2	13.2±1.2	5.1±0.59	38.5±8.1
35	69	RO ₂ +HO ₂	AS+SA	4.7±0.4	26.4±2.5	16.1±1.14	61.0±9.0
36	66	RO ₂ +HO ₂	AS+SA	7.1±0.7	39.6±3.7	30.3±0.71	76.4±7.8
37	66	RO ₂ +HO ₂	AS+SA	11.9±1.1	66.1±6.2	47.7±1.77	72.1±8.1
38	< 1	RO ₂ +NO ₃	None	12.4±1.2	69.2±6.5	42.3±0.46	61.1±5.8
39	50	RO ₂ +NO ₃	None	11.9±1.1	66.1±6.2	44.3±0.34	67.0±6.4
40	<2	RO ₂ +HO ₂	None	12.4±1.2	69.2±6.5	18.7±0.51	27.0±2.8
41	66	RO ₂ +HO ₂	None	11.9±1.1	66.1±6.2	28.5±0.60	43.1±4.2
42	50	RO ₂ +HO ₂	None	11.9±1.1	66.1±6.2	18.4±0.34	27.8±2.7
43	<2	RO ₂ +HO ₂	AS*	12.4±1.2	69.2±6.5	33.6±0.79	48.5±4.9
44	68	RO ₂ +HO ₂	AS+SA*	11.9±1.1	66.1±6.2	46.6±0.86	70.6±7.0
45	66	RO ₂ +HO ₂	AS+SA*	11.9±1.1	66.1±6.2	44.5±0.87	67.3±6.7

25. Fig. 3: Looks to me like the second-lowest point drives the shape of the yield curve – maybe check fit parameters without that point to see if robust. Also, you refer to x axis error bars which are not present in the plot.

Author response: The x-axis error bars for these experiments are included in the graph in the original manuscript. The size of each individual data point is larger than the stated uncertainties for the x-axis and cannot be seen in the closed triangles.

In terms of fitting the data without the second lowest mass loading, as we discussed in response to comment #14, this does not affect yield curve and thus our fitting is robust.

26. *Fig. 4 same missing x axis error bars. Why not include the unseeded yields on here too (currently in Figure S8)? This would make the comparison easier, rather than eyeballing data vs. the seeded fit line in the supplemental. If this makes the plot too busy, I retract the comment, just thought it would ease comparison.*

Author response: We refer the reviewer to the response to comment #25 regarding the x-axis error bars in Figure 4.

In the original manuscript, the unseeded yields for all experimental conditions are shown on Fig. S8. Moving the unseeded yields for the “RO₂+NO₃ dominant” and “RO₂+HO₂ dominant” from Fig. S8 to Fig. 3 and Fig. 4, respectively, puts too much information on the figures that we think would be distracting to the reader.

27. *Fig. 7: add into the caption that these data are all for the RO2+NO3 experiments.*

Author response: As requested, we have revised the caption of Fig. 7 from:

“Figure 7: The AMS Nitrate:Org ratio of humid (RH = 50%) experiments normalized to the corresponding dry experiments with same initial β-pinene mixing ratio, five-minute averaged. This ratio is referred to as (Nitrate:Org)_{norm} in the main text. For comparison purpose, all data are normalized to the highest (Nitrate:Org)_{norm} ratio.”

To:

“Figure 7: The AMS Nitrate:Org ratio of humid (RH = 50%) experiments normalized to the corresponding dry experiments with same initial β-pinene mixing ratio, five-minute averaged, for “RO₂+NO₃ dominant” experiments. This ratio is referred to as (Nitrate:Org)_{norm} in the main text. For comparison purpose, all data are normalized to the highest (Nitrate:Org)_{norm} ratio.”

28. *See comment 16 above about Figure 9 confusion. If you keep this plot, I suggest adding to the caption to state that 235 nm corresponds to ROOR & ROOH and 270 nm to C=O and nitrate functional groups.*

Author response: To clarify this, we have changed the caption of Fig. 9 from:

“Figure 9: Ratio of the total areas integrated under UV-visible chromatograms collected at (gray bars) 235nm and (teal bars) 270nm relative to 205nm for experiments dominated by (left-hand side panel) RO₂+NO₃ reaction and (right-hand side panel) RO₂+HO₂ reaction under both humid and dry conditions.”

To:

“Figure 9: Ratio of the total areas integrated under UV-visible chromatograms collected at 235 nm (gray bars, ROOR and ROOH) and 270 nm (teal bars, -C=O and -ONO₂) relative to 205 nm for experiments dominated by RO₂+NO₃ reaction (left-hand side panel) and RO₂+HO₂ reaction (right-hand side panel) under both humid and dry conditions.”

29. *Figure 10: Was this spectrum selected because agreement was better than RO₂+NO₃ conditions? Or because more likely to be atmospherically relevant? Would it look any different? I suggest omitting “Fraction of” in the annotation. “Signal x3” is clear.*

Author response: The mass spectrum shown in Fig. 10 was chosen because it is more likely to be atmospherically relevant, specifically for the SOAS campaign where the RO₂+HO₂ reaction pathways are believed to be dominant under high humidity and the aerosol are highly acidic. This is explained in the original manuscript, which stated that at SOAS, the predicted liquid water content is high while the predicted aerosol pH is in the acidic region. (Cerully et al., 2014;Guo et al., 2014).

As requested, we have removed the words “Fraction of” in the annotation.

SI: Suggest modeling the HO₂+RO₂ experiments as well as RO₂+NO₃ – since you are producing HO₂ simultaneous to NO₃+VOC reactions this is slightly more complex – so it would be better to model these conditions using MCM rather than just determining the ratio of HCHO to bpin. I suggest creating an analogous plot to S9 showing dominant fate for both RO₂ fate cases.

Author response: As we discussed in our response to comment #3, our model did not converge when we included HCHO in the simulations. Although it is possible that some HO₂ radicals could be produced from the NO₃+VOC reactions, Fig. S9 does show that these reactions do not produce an appreciable concentration of HO₂ radicals under “RO₂+NO₃ dominant” experiments as evidenced by the low RO₂+HO₂ reaction modeled in this scenario. Furthermore, HO₂ radicals produced by the NO₃+VOC reaction would only increase the RO₂+HO₂ reactions in “RO₂+HO₂ dominant” results, but we already suggest this to be the major pathway without this additional HO₂.

Response to Referee 2-Major Comments (Referees’ comments are italicized)

1. The authors present significant detail in terms of the identification of gas-phase organic nitrates in the system and some information on particle-phase composition such as the fact that 45-74% of the aerosol is likely organic nitrates. The information provided in the form of an Odum 2-product or VBS fit allows for an easy, but incremental, update to existing monoterpene+NO₃ SOA pathways in models. As organic nitrates are being increasingly recognized for their importance in recycling or removing NO_x from the atmosphere, contributing to nitrogen deposition in sensitive ecosystems, etc. they are being included in greater detail in models. Given the significant contribution of organic nitrates to aerosol, can modeling of monoterpene+NO₃ aerosol be further advanced to allow for a greater consistency between gas and aerosol-phase mechanisms? With aerosol yields on the order of 27 to 104%, adding an Odum 2-product SOA

yield on top of a gas-phase mechanism could lead to substantial double counting. Is there a later generation product (such as an organic nitrate) or rate limiting step beyond the initial monoterpene+NO₃ that models could base SOA formation on?

Author response: We agree that coupling the gas-phase mechanism with the Odum's two product model can lead to double counting and both methods should not be used simultaneously. However, the Odum's two product yield can provide a needed restraint for gas-phase mechanisms that predict aerosol yield based on the partitioning of products from each generation. Partitioning and abundance of each generation product can be adjusted to match the yield curve, so it is imperative that the yield curve accurately predict SOA yield at all atmospherically relevant aerosol concentrations.

If there are later generation products, Fig. 2 shows that the particle volume, HR-ToF-AMS organics, and several gas phase species measured by CIMS reach a maximum at around 15 minutes into the onset of reaction. As this is on a time scale similar to that of the mixing time of the chamber, determination of any intermediate compounds that are formed after initial β -pinene reaction and before the final products is difficult. There is evidence of later-generation products through hydrolysis. Our study showed that only a minority (10%) of the particulate organic nitrates hydrolyze (Fig. 7).

The hydrolysis of organic nitrates formed by most BVOC+NO₃ reactions are likely primary/secondary nitrates (see our response to comment #20 by Reviewer 1). Organic nitrates formed by the photooxidation of terpenes under high NO_x conditions, however, are more likely to form tertiary nitrates that hydrolyze in the span of hours (Darer et al. 2011). To accurately model the ambient hydrolysis of organic nitrates, it is important to consider the relative contributions of organic nitrates formed from nitrate radical chemistry and photooxidation. The hydrolysis of organic nitrates can produce HNO₃. On the other hand, organic nitrates that do not hydrolyze, can potentially be photolyzed or oxidized by OH radicals to release NO_x back into the atmosphere (Suarez-Bertoa et al., 2012) or lost by dry or wet deposition. Therefore, it is essential to determine the appropriate branching ratio of primary/secondary vs tertiary organic nitrates in order to accurately model global and regional NO_x cycles.

2. Can the laboratory AMS spectra be tied more quantitatively to the field LO-OOA? The critical link seems to focus on m/z 67 and 91. Given that those peaks are only a portion of the spectrum, how to you attribute the majority of the spectrum to monoterpene+NO₃ reactions?

Author response: We believe that the LO-OOA factor identified from the SOAS AMS data has a large contribution from monoterpene+NO₃ chemistry, specifically β -pinene+NO₃, based on the following three pieces of evidence. First, Xu et al. (2015) showed that the LO-OOA factor peaks at night, which indicates that LO-OOA is primarily formed by nighttime chemistry, where nitrate radical oxidation is likely dominant. Second, LO-OOA has a strong correlation with the estimated organic nitrate concentration, which makes up a significant fraction of SOA formed by monoterpene+NO₃ chemistry (Spittler et al., 2006; Fry et al., 2009; Perring et al., 2009; Rollins et al., 2009; Kwan et al., 2012; Fry et al., 2014). Third, Xu et al. (2015) showed high nocturnal monoterpene emissions at SOAS, a substantial fraction of which is made up of β -pinene. This

suggests that the particle phase products formed from the β -pinene+NO₃ reaction contribute a significant fraction to the nighttime SOA at SOAS.

While we cannot exclusively rule out the contributions of various chemical reactions (BVOCs, oxidants), the above evidences suggested that LO-OOA has significant contributions from the β -pinene+NO₃ reaction. This is subsequently validated by similarities in the LO-OOA factor and the mass spectrum β -pinene+NO₃ via the C₅H₇⁺ (m/z 67) and C₇H₇⁺ (m/z 91) fragments. The similarities in AMS mass spectra are often not determined by the absolute abundance of each peaks, but the overall mass spectra signature (the relative intensities of the peaks).

Response to Referee 2-Minor Comments (Referees' comments are italicized)

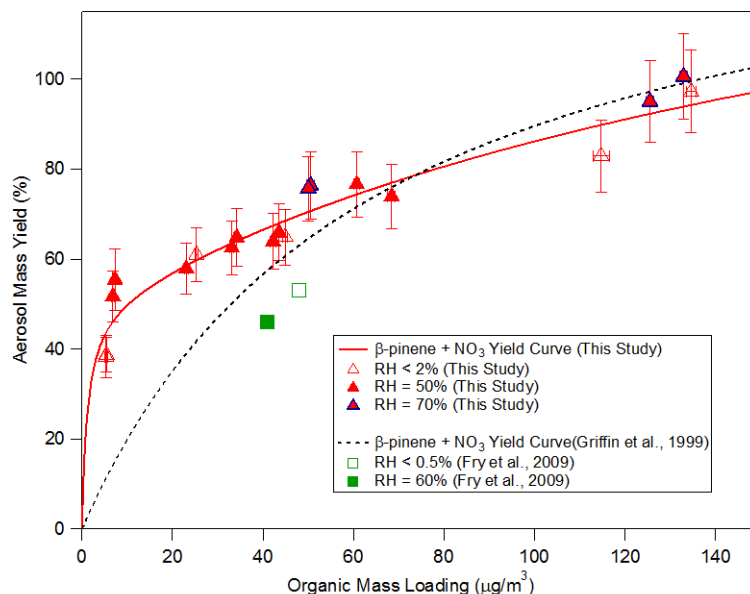
1. Is beta-pinene likely a good surrogate for all monoterpene+NO₃ SOA formation behavior in the southeast US? How likely is the abundance of species like alpha-pinene likely to bring down the overall monoterpene+NO₃ effective yield?

Author response: We believe that the β -pinene+NO₃ chemistry produces a large portion of the SOA formed by the monoterpene+NO₃ chemistry. Xu et al. (2015) previously reported that the α -pinene and β -pinene concentrations are higher than those of other monoterpenes by a factor of 5. In addition, Fry et al. (2014) and Spittler et al. (2006) have previously shown that the SOA mass yield from the α -pinene+NO₃ reaction is very low and does not contribute much to the SOA in the Southeast US. Therefore, we propose that the majority of the SOA produced by monoterpene+NO₃ chemistry could be attributed to the β -pinene+NO₃ reaction.

The abundance of species like α -pinene likely lowers the overall monoterpene+NO₃ effective yield, and models may over-predict aerosol yields from monoterpene+NO₃ chemistry if only the β -pinene+NO₃ reaction is considered. Therefore, we recommend that aerosol models implement subgroups for monoterpene+NO₃ aerosol mass yields instead of lumping all monoterpene+NO₃ yields into a single category.

2. Page 2691, in adjusting the yield curve for density other than 1, both the yield and loading should be multiplied by the density shifting the entire curve up and to the right. It's not clear if both the loading and Y values were adjusted or just the Y.

Author response: The reviewer is correct, only the yields were shifted by the density in the original manuscript. We have corrected this error in the revised manuscript and the density is now accounted for in both the yields and mass loadings in the revised figure. In addition to correcting the mass loading by density, we also corrected the data presented by Griffin et al. (1999) to account for the different temperatures used in their experiments. Using an enthalpy of vaporization of 42 kJ/mol and an average temperature of 306K used in Griffin et al. (1999), we adjusted the one-product fit parameter, K, for 298K using the Clausius-Claperyon equation (Chung and Seinfeld, 2002). After correcting for the density and temperature, the yield curve from Griffin et al. (1999) compares to our data as shown in the figure below.



In addition, Table 2 in the original manuscript showed data previously presented by Griffin et al. (1999) without density or temperature corrections. In the revised manuscript, we have changed the parameters in Table 2 to reflect the adjustments based on density and temperature.

Table 2: Fit parameters for two-product model proposed by Odum et al. (1996)

	α_1	K_1	α_2	K_2
β-pinene+NO₃ (this study)	1.187	0.004546	0.496	0.880
Griffin et al. (1999)	1.464	0.0158		

Due to these changes, the following modifications have been made to the text:

Page 2691 Line 22: “As Griffin et al. (1999) assumed an aerosol density of 1.0 g cm^{-3} , the yield curve from Griffin et al. (1999) shown in Fig. 3 has been multiplied by the density calculated in this study for “RO₂+NO₃ dominant” experiments under dry conditions (i.e. 1.41 g cm^{-3}).”

To:

As Griffin et al. (1999) assumed an aerosol density of 1.0 g cm^{-3} , the experimental data from Griffin et al. (1999) shown in Fig. 3 have been multiplied by the density calculated in this study for “RO₂+NO₃ dominant” experiments under dry conditions (i.e. 1.41 g cm^{-3}).

After this sentence:

Page 2691 Line 25: “The data shown in Fig. 3 from Fry et al. (2009) have also incorporated a particle density of 1.6 g cm^{-3} calculated in their study.”

We add:

“In addition to correcting for density, the yield curve partitioning coefficient, K, from Griffin et al. (1999) has been adjusted from 306K to 298K using an enthalpy of vaporization of 42 kJ mol⁻¹ (Chung and Seinfeld, 2002).”

We also change:

Page 2698 Line 12: “The two-product yield curve in Griffin et al. (1999) was generated from chamber experiments with $\Delta M_o > 30 \mu\text{g m}^{-3}$ (range of $\Delta M_o = 30\text{--}470 \mu\text{g m}^{-3}$) and extrapolated down to lower loadings.”

To:

“The yield curve in Griffin et al. (1999) was generated from chamber experiments with $\Delta M_o > 45 \mu\text{g m}^{-3}$ (range of $\Delta M_o = 45\text{--}660 \mu\text{g m}^{-3}$) and extrapolated down to lower loadings.”

We also add the following reference to the list of references:

Chung, S. H., and Seinfeld, J. H.: Global distribution and climate forcing of carbonaceous aerosols, *Journal of Geophysical Research: Atmospheres*, 107, 4407, 10.1029/2001JD001397, 2002.

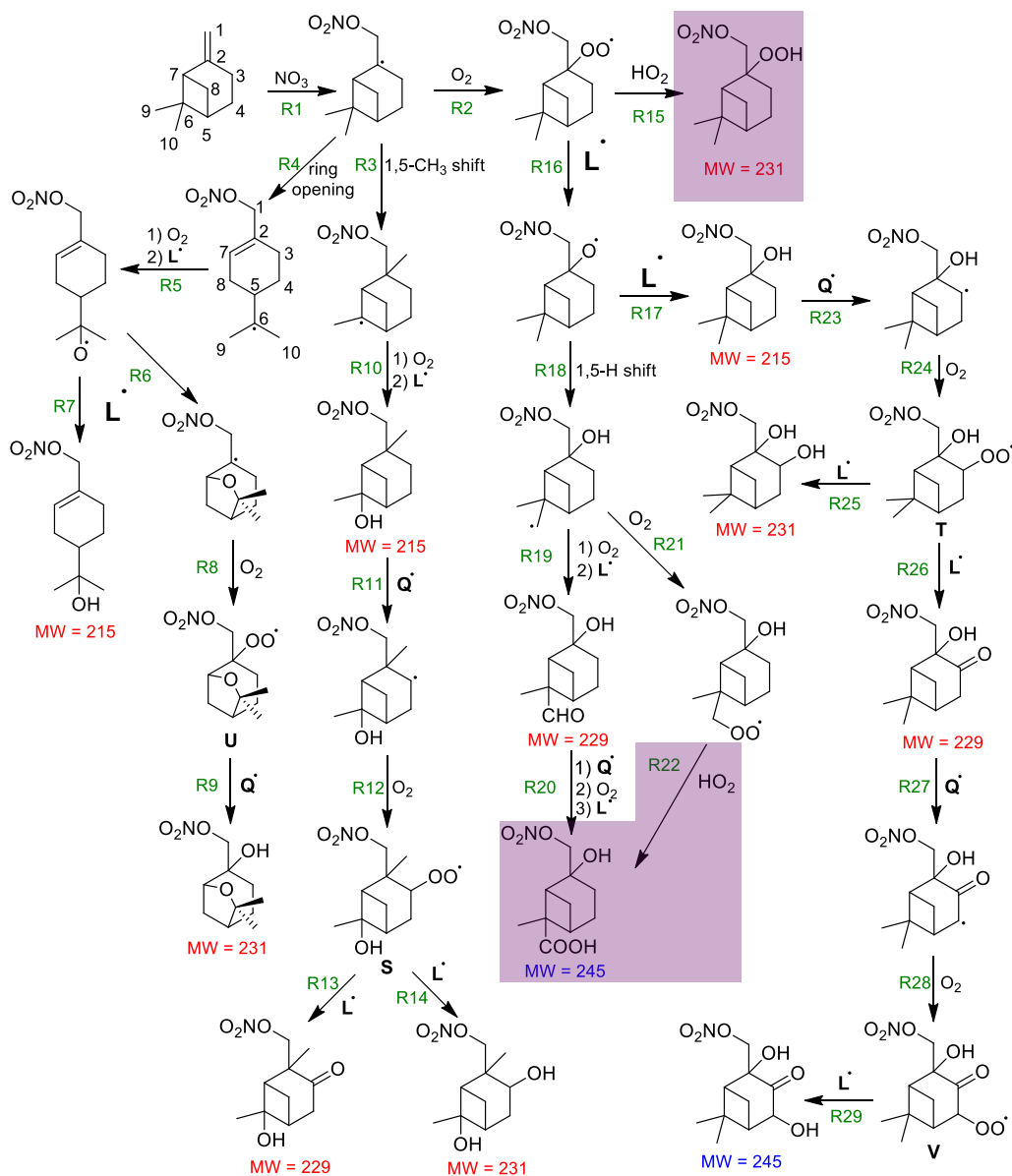
3. Figure 8: The description of “RO₂+HO₂” and “RO₂+NO₃” dominant regimes is used throughout the text. Is there a way to highlight how Figure 8 is different under those two regimes in a simple way? In terms of relative abundance of species or major reaction pathways?

Author response: As requested, we have highlighted the reactions that are enhanced in the RO₂+HO₂ dominant pathway in Figure 8 (highlighted in purple). We believe that all the other reaction pathways shown in Figure 8 are possible under both the “RO₂+NO₃ dominant” and “RO₂+HO₂ dominant” pathways.

The Figure 8 caption is changed to read:

“Figure 8: Generation of gas-phase species with molecular weights (MW) of 215, 229, and 231 amu detected by CIMS (red font), aerosol species with MW=245 amu in filters analyzed by UHPLC-MS (blue font). Reaction numbers are given in green font and reaction with generic radical Q· (e.g. NO₃, RO₂, etc.) is used to symbolize any species abstracting hydrogen atoms. Reactions which can be accomplished by any of the radicals present (RO₂, HO₂, NO₃ etc.) are symbolized by reaction with generic radical L·. Reactions enhanced in the RO₂+HO₂ dominant pathway are highlighted in purple.”

The updated figure is shown below.



4. Page 2698 line 20-29, page 2699: Is all the data from Griffin et al. 1999 shown in figure 3 (just 2 points)? Discussing the mass loadings of those points more clearly demonstrates the shortcomings of previous work than discussing the previous Odum fit. Also note that on line 12 on page 2698, the Griffin fit is referred to as an Odum 2-product, while only one product was successfully fit in Table 2.

Author response: There are four data points presented in the study by Griffin et al. (1999). However only two of these data points have a mass loading below $216 \mu\text{g m}^{-3}$, the highest mass loading recorded in our study. These are the two data points shown in the original manuscript. After correcting the yield curve produced using Griffin et al. (1999) for temperature, only the yield curve will be shown because the Clausius-Clayperyon equation cannot be used to correct individual data points. The high mass loadings in the study by Griffin et al. (1999) lead to an

under prediction of aerosol yield at low loadings and we believe that these high mass loadings and the previous Odum fit are intertwined.

The reviewer is correct in pointing out that the Griffin fit should not be referred to as an Odum two-product fit since only one product was successfully fit in Table 2.

Therefore we have changed:

Page 2698 Line 12: “The two-product yield curve in Griffin et al. (1999) was generated from chamber experiments with $\Delta M_o > 30 \mu\text{g m}^{-3}$ (range of $\Delta M_o = 30\text{--}470 \mu\text{g m}^{-3}$) and extrapolated down to lower loadings.”

To:

“The yield curve in Griffin et al. (1999) was generated from chamber experiments with $\Delta M_o > 45 \mu\text{g m}^{-3}$ (range of $\Delta M_o = 45\text{--}660 \mu\text{g m}^{-3}$) and extrapolated down to lower loadings.”

The following are additional minor changes the authors would like to make to the text:

1) In the original manuscript, the ratio for $\text{NO}^+:\text{NO}_2^+$ was based on where the majority of the data clustered. We feel that it is more appropriate to report the full range and add to the discussion of the $\text{NO}^+:\text{NO}_2^+$ ratio in the revised manuscript

Page 2680 Line 9: “The ions at m/z 30 (NO^+) and m/z 46 (NO_2^+) contribute about 11% to the total organics signal in the typical aerosol mass spectrum, with $\text{NO}^+:\text{NO}_2^+$ ratio ranging from 6 to 9 in all experiments conducted.”

To:

The ions at m/z 30 (NO^+) and m/z 46 (NO_2^+) contribute about 11% to the total organics signal in the typical aerosol mass spectrum, with $\text{NO}^+:\text{NO}_2^+$ ratio ranging from 4.8 to 10.2 in all experiments conducted.

We also changed

Page 2692 Line 7: “The mass spectrum for the aerosol generated in the “ RO_2+HO_2 dominant” and “ RO_2+NO_3 dominant” experiments are similar, one notable difference being the $\text{NO}^+:\text{NO}_2^+$ ratio. While the $\text{NO}^+:\text{NO}_2^+$ ratio is typically 6-7.5 for “ RO_2+NO_3 dominant” experiments, it is typically 8-9 for “ RO_2+HO_2 dominant” experiments.”

To:

“The mass spectrum for the aerosol generated in the “ RO_2+HO_2 dominant” and “ RO_2+NO_3 dominant” experiments are similar. One notable difference between the “ RO_2+HO_2 dominant” and “ RO_2+NO_3 dominant” experiments is the $\text{NO}^+:\text{NO}_2^+$ ratio for

the organic nitrates (R-ON), which ranges from 4.8-10.2 for all experiments. While the $\text{NO}^+:\text{NO}_2^+$ ratio averages 6.5 for “ RO_2+NO_3 dominant” experiments, it averages 8.6 for “ RO_2+HO_2 dominant” experiments. Since the R-ON may depend on the instrument, we normalize the R-ON to the $\text{NO}^+:\text{NO}_2^+$ of ammonium nitrate (R-AN), which is expected to be a better metric (Farmer et al., 2010). In our study, multiple measurements of R-AN are obtained from the ionization efficiency (IE) calibrations and the average value is about 1.8 (range of 1.2-2.7). We calculate the average R-ON:R-AN ratio to be 3.2 for “ RO_2+NO_3 dominant” experiments and 4.8 for “ RO_2+HO_2 dominant” experiments.

Additionally, after the sentence:

Page 2705 Line 14: Previous studies (Fry et al., 2009; Bruns et al., 2010) on the β -pinene+ NO_3 reaction suggested that the $\text{NO}^+:\text{NO}_2^+$ ratio for β -pinene+ NO_3 SOA is on the order of 10:1, higher than the values determined in this study.

We add:

One explanation for the difference in R-ON between this study and previous literature is instrument bias. Different instruments may have different R-ON values. One way to circumvent this bias is to compare the R-ON:R-AN ratio. The averaged R-ON:R-AN for all experiments is 3.9, which is in agreement with values calculated by Fry et al. (2009) and Bruns et al. (2010) (range 3.7-4.2).

2) We change:

Page 2681 Line 21: “Results from previous field studies provided evidence of aerosol formation from nitrate radical oxidation of BVOCs during both daytime and nighttime (McLaren et al., 2004; Iinuma et al., 2007; Fuentes et al., 2007; Brown et al., 2009; Rastogi et al., 2011; Rollins et al., 2012; Brown et al., 2013; Rollins et al., 2013).

To:

“Results from previous field studies provided evidence of aerosol formation from nitrate radical oxidation of BVOCs during both daytime and nighttime (McLaren et al., 2004; Iinuma et al., 2007; Fuentes et al., 2007; Brown et al., 2009; Rastogi et al., 2011; Rollins et al., 2012; Brown et al., 2013; Rollins et al., 2013). Monoterpenes have also been found to make up as much as 28% non-methane organic carbon emissions from biomass burning in both field and laboratory studies (Akagi et al., 2013; Hatch et al., 2015; Stockwell et al., 2015). Fires from biomass burning are more likely to smolder at night and are therefore more likely to emit monoterpenes (Akagi et al., 2013).”

3) We find that we were using older rate constants to model the equilibrium partitioning of the N_2O_5 with NO_2 and NO_3 instead of the constants reported in Table S1. We have updated our model to include the rate constants from Saunders et al. (2003), as reported in Table S1. With this, the ratio of the amount of N_2O_5 injected to hydrocarbon injected is 6:1 (instead of 4:1) in the RO_2+NO_3 experiments. The change in the rate constants only slightly changes the branching

ratios of RO_2+NO_3 , RO_2+RO_2 , and RO_2+HO_2 and do not affect the dominant branching ratio in either the “ RO_2+NO_3 dominant” or “ RO_2+HO_2 dominant” experiments. The RO_2+NO_3 reaction still dominates the “ RO_2+NO_3 dominant” experiments and the RO_2+HO_2 reaction still dominates the “ RO_2+HO_2 dominant” experiments as stated in the text.

We change

Page 2687 Line 2: We aim for an initial N_2O_5 : β -pinene ratio of ~4:1.

To:

We aim for an initial N_2O_5 : β -pinene ratio of ~6:1.

4) In the study done by Hallquist et al. (1999), we refer to an experiment conducted at low mass loading. In the study by Hallquist et al. (1999), the experiment was performed at 7 ppb of β -pinene but, in error, this was reported as $7 \mu\text{g m}^{-3}$. To correct this, we change

Page 2699, Line 26: “There is a substantial difference between our β -pinene+ NO_3 SOA yield and that from Hallquist et al. (1999), which reported an aerosol mass yield of 10% for a mass loading of $7 \mu\text{g m}^{-3}$.”

To:

“There is a substantial difference between our β -pinene+ NO_3 SOA yield and that from Hallquist et al. (1999), which reported an aerosol mass yield of 10% for a mass loading of $4 \mu\text{g m}^{-3}$.”

5) In error, the sentences below reference the wrong reaction. Therefore, we change:

Page 2702 Line 22: “The reaction of RO_2+NO_3 produces an RO radical (Fig. 8, Reaction R2) which can undergo decomposition or isomerization (Orlando and Tyndall, 2012; Ziemann and Atkinson, 2012).”

To:

“The reaction of RO_2+NO_3 produces an RO radical (Fig. 8, Reaction R16) which can undergo decomposition or isomerization (Orlando and Tyndall, 2012; Ziemann and Atkinson, 2012).”

6) We change

Page 2710 Line 1: “Since the Org:Sulfate ratio decreases after SOA reaches peak growth (Fig. 6), it is likely that aerosol fragmentation is the dominant aging pathway of SOA.”

To:

“The use of Org:sulfate is a good proxy for aerosol aging when the organics only condense onto existing ammonium sulfate particles. A study by Loza et al. (2012) has demonstrated that in the case of rapid condensation of organic species, the time scale of condensation is less than the time scale of diffusion to existing seed particle. When in this “diffusion-limited growth” regime, the organic mass partially nucleates to form new particles. Since the nucleated particles are smaller than those particles in which ammonium sulfate acted as a seed for condensation, organics contained in these nucleated particles will be lost to the chamber walls more rapidly than the existing seed particles (Fig. S10). This could lead to an overall decrease in the Org:sulfate ratio. In our study, the Org:Sulfate ratio decreases after SOA reaches peak growth (Fig. 6). It is possible that this decrease is caused by wall loss of organic particles formed in the diffusion-limited growth regime. It is also possible that fragmentation of aerosol components is the dominant aging pathway, resulting in a decrease in the Org:Sulfate ratio.”

7) We change

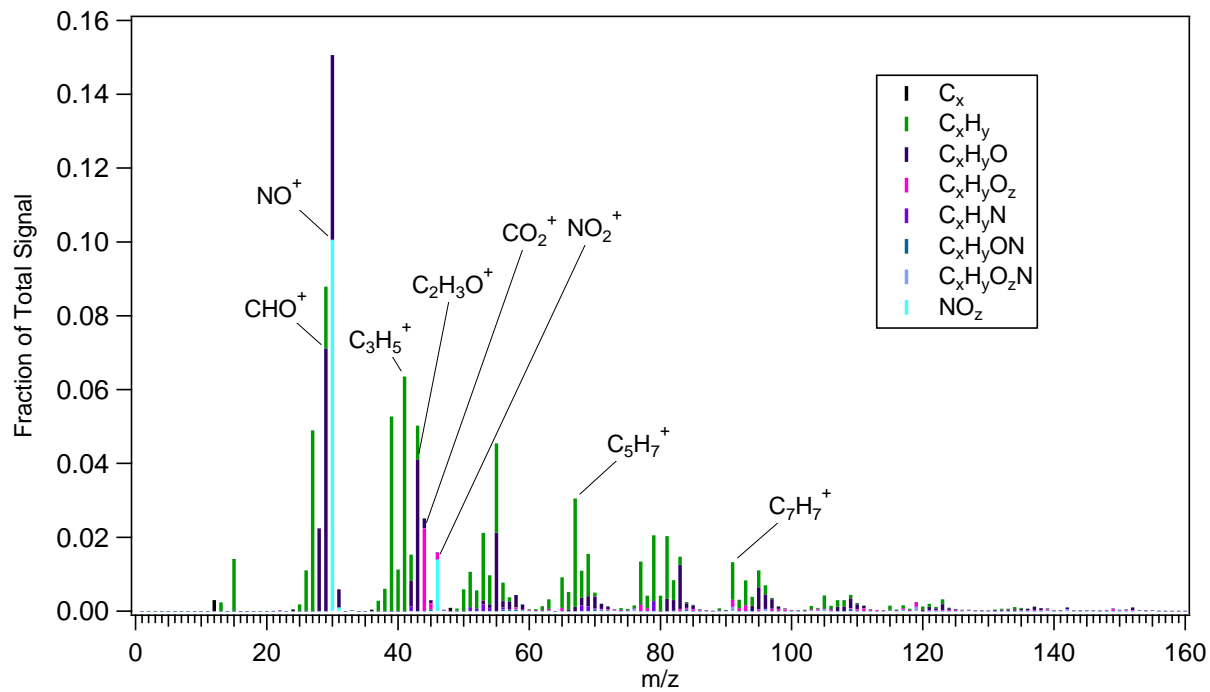
Page 2710 Line 4: “Fragmentation of SOA alone would cause all AMS organic families to either decrease or remain constant relative to sulfate.”

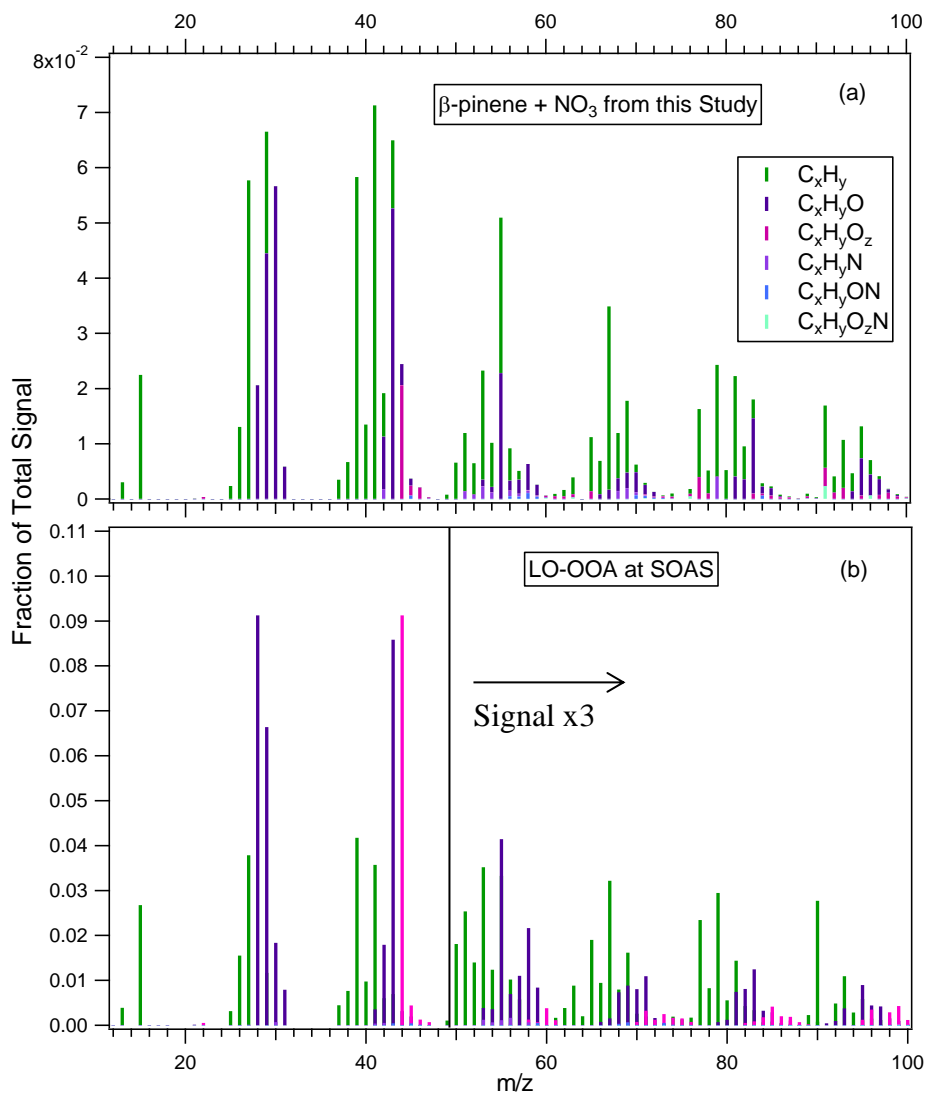
To:

“Rapid loss of organics due to particle wall loss or fragmentation of SOA would cause all AMS organic families to either decrease or remain constant relative to sulfate.”

8) Table 1: The experiments are renumbered to correct for the omission of the number “44”

9) In order to correct the absence of the CO^+ fragment in the mass spectra in Fig. 2 and Fig. 10, we change these figures to include the CO^+ fragment:





This resulted in some changes in the calculation of some of our numbers, specifically the ratio of the $\text{NO}^+ + \text{CH}_2\text{O}^+ / (\text{NO}_2^+ + \text{CH}_2\text{O}_2^+)$ ratio and $\text{C}_5\text{H}_7^+/\text{C}_7\text{H}_7^+$ ratios. We change

Page 2705 Line 18: Specifically, if we were to include the contribution of the organic CH_2O^+ fragment at m/z 30 (in addition to contribution from NO^+ and NO_2^+), the corresponding $\text{NO}^+:\text{NO}_2^+$ ratios would be higher, i.e., 10:1 for “ RO_2+NO_3 dominant” experiments and 13:1 for “ RO_2+HO_2 dominant” experiments.

To:

Specifically, if we were to include the contribution of the organic CH_2O^+ and CH_2O_2^+ fragments at m/z 30 and m/z 46 (in addition to contribution from NO^+ and NO_2^+), the corresponding $\text{NO}^+:\text{NO}_2^+$ ratios would be higher, i.e., 9:1 for “ RO_2+NO_3 dominant” experiments and 11:1 for “ RO_2+HO_2 dominant” experiments.

We also change:

Page 2713, Line 5: Most noticeable of these are m/z 67 ($C_5H_7^+$) and m/z 91 ($C_7H_7^+$) with a ratio of these two ions ($C_5H_7^+ : C_7H_7^+$) of about 2.9 (ranging from 2.5-3.5 in other experiments).

To:

Most noticeable of these are m/z 67 ($C_5H_7^+$) and m/z 91 ($C_7H_7^+$) with a ratio of these two ions ($C_5H_7^+ : C_7H_7^+$) of about 2.9 (ranging from 2.5-3.6 in other experiments).

The following references have also been added in the revised manuscript:

Akagi, S. K., Yokelson, R. J., Burling, I. R., Meinardi, S., Simpson, I., Blake, D. R., McMeeking, G. R., Sullivan, A., Lee, T., Kreidenweis, S., Urbanski, S., Reardon, J., Griffith, D. W. T., Johnson, T. J., and Weise, D. R.: Measurements of reactive trace gases and variable O₃ formation rates in some South Carolina biomass burning plumes, *Atmos. Chem. Phys.*, 13, 1141-1165, doi:10.5194/acp-13-1141-2013, 2013.

Hatch, L. E., Luo, W., Pankow, J. F., Yokelson, R. J., Stockwell, C. E., and Barsanti, K. C.: Identification and quantification of gaseous organic compounds emitted from biomass burning using two-dimensional gas chromatography-time-of-flight mass spectrometry, *Atmos. Chem. Phys.*, 15, 1865-1899, doi:10.5194/acp-15-1865-2015, 2015.

Loza, C. L., Chhabra, P. S., Yee, L. D., Craven, J. S., Flagan, R. C., and Seinfeld, J. H.: Chemical aging of m-xylene secondary organic aerosol: laboratory chamber study, *Atmos. Chem. Phys.*, 12, 151-167, doi:10.5194/acp-12-151-2012, 2012.

Stockwell, C. E., Veres, P. R., Williams, J., and Yokelson, R. J.: Characterization of biomass burning emissions from cooking fires, peat, crop residue, and other fuels with high-resolution proton-transfer-reaction time-of-flight mass spectrometry, *Atmos. Chem. Phys.*, 15, 845-865, doi:10.5194/acp-15-845-2015, 2015.

Xu, L., Suresh, S., Guo, H., Weber, R. J., and Ng, N. L.: Aerosol characterization over the southeastern United States using high resolution aerosol mass spectrometry: spatial and seasonal variation of aerosol composition, sources, and organic nitrates, *Atmos. Chem. Phys. Discuss.*, 15, 10479-10552, doi:10.5194/acpd-15-10479-2015, 2015a.