Response to reviewers for D. C. Draper, et al., "A comparison of secondary organic aerosol (SOA) yields and composition from ozonolysis of monoterpenes at varying concentrations of NO2." 2015.

We greatly appreciate the thorough and thoughtful feedback provided by both reviewers on this manuscript. A number of significant changes have been made to the revised manuscript in response to suggestions, which we believe to have substantially improved interpretation of this study. Presented below are specific comments by each reviewer (italicized) and our responses to each (indented and non-italicized).

Comments from referee #1

Draper et al. present results from laboratory experiments investigating the effect of varying NO2 concentrations on ozonolysis (and subsequent SOA formation) of four different biogenic terpenoids: alpha-pinene, beta-pinene, delta-3-carene, and limonene. These are the first reported results on this topic for a range of different monoterpenes rather than using alpha-pinene alone as a "model compound". The results demonstrate different effects for different monoterpenes and thus highlight the importance of this research related to biogenic SOA formation via nitrate radical chemistry. Authors also demonstrate the effects of nitrate chemistry on resulting SOA composition, and postulate that the higher molecular weight compounds that emerge in the high NO2 scenarios point to oligomerization as a key mechanism for SOA production from reactions with nitrate radical. Furthermore, the lack of high molecular weight compounds in alpha-pinene/NO2 experiments could explain the low SOA yields observed here and previously from the alpha-pinene/NO2 system. The results are well within the scope of ACP and constitute a valuable contribution to the existing literature on biogenic SOA production by filling in important gaps related to biogenic SOA production from nitrate radical chemistry. Overall the paper is very well-written and organized in a logical manner. Particular strengths of this paper are presented in results from Section 3.1 that compare aerosol formation trends under different experimental scenarios and results from Section 3.5 that compare SOA composition between the different experimental scenarios. There are some major weaknesses in Sections 3.2-3.4 that are discussed in detail in the comments below. Specifically, all results and discussion related to the SOA yield comparisons will need to be significantly revised before final publication in ACP.

General Comments

SOA Yields
As stated in the title of this manuscript, comparing "SOA yields" between different experimental scenarios was a major objective of this research. However, it is quite clear that the experimental set-up and design were not optimized to make comparisons of SOA yields between the experiments. I have listed the major concerns with regard to the SOA yield calculation/discussion with associated explanations below.

1) Yield is calculated as the amount of organic aerosol mass produced from the mass *of VOC reacted. Consequently, accurately measuring the mass of VOC reacted is crucial for calculating SOA yields. The authors used a GC-FID to measure monoterpene concentrations at the outlet of the Reed Environmental Chamber (REC), but did not directly and continuously measure the monoterpene concentration at the inlet (Figure 2; P. 14928 L. 27-29; P. 14929 L. 1-4; P. 14931 L. 2-5). While it is true that the initial VOC concentration was measured from the source flask before and after each experiment (P. 14928 L. 27-29), the authors also state that the "Source concentrations were somewhat variable over time" (P. 14929 L. 2). The authors dealt with this issue by modeling the initial VOC concentration based on the measured change in oxidant concentrations, which obviously introduces additional uncertainties to SOA yield calculations that could have been avoided with a simple modification to the set-up. Why was the GC-FID only sampling from the REC outlet and not from both the inlet and outlet? Sampling from the inlet and outlet is a commonly used approach for flow-through SOA chamber experiments with a variable VOC source (i.e. Joutsensaari et al., 2015; Mentel et al., 2009; VanReken et al., 2006). This approach allows one to calculate reacted VOCs in the chamber from the difference between measurements of the inlet and outlet concentrations. The authors do not provide suitable justification for why this approach was not used. On P. 14928, L. 27-28, authors state, "Since experiments were initiated by introducing BVOC into an oxidant-rich chamber, online measurement of the reaction of the BVOC was not possible", but this is an unsatisfactory defense because this would in no way prohibit VOC monitoring at the inlet and outlet with a simple valve-switching system.*

The experimental setup proposed by the reviewer would have indeed been much better suited to characterize reacted VOC, and we hope to implement that for future experiments on this chamber. At the time these measurements were made, the flow system on the chamber was not optimized to sample in that configuration. All reported GC measurements were done using an external dilution of the output of the source flask itself, which is then fed into the chamber inlet – Figure 2 erroneously showed the GC-FID sampling from the outlet and has been corrected in the revised manuscript.

At the time this manuscript was submitted to ACPD, we had not been able to pinpoint the source of uncertainty leading to such substantial scatter in the data, but we were encouraged by the linear correlation of GC-measured and modeled [VOC], so we showed this in a figure (S.4 in original manuscript). The scatter in that correlation prompted us to use our model to constrain reacted [VOC] instead and keep the GC data only to broadly validate the modeled values.

The reviewer's comments prompted deeper inquiry into the source of the scatter on this instrument, and following discussions with colleagues outside of this study as well as additional tests on the instrument, it is our belief that the integrated peak areas observed from the gas trap sampling configuration do not accurately correspond to the peak areas observed from our liquid injection calibration curve. Additional measurements of both the liquid monoterpenes and the gas-phase output of the source flask using an offline GC-MS convince us that our reagents were not contaminated. However, tests of the GC-FID sampling from the same source flask through the instrument's gas trap module set to different desorption temperatures showed multiple peaks that didn't show up in the liquid injection sampling mode, and each trap desorption temperature showed a different distribution of peaks with the total signal intensity varying substantially, indicating that chemistry and inefficient desorption was occurring on the trap itself, thereby providing inaccurate and uncorrectable data that should not be used.

This gas trap module will need to be more thoroughly characterized for future use, and we regret including data from this instrument in this manuscript. All references to this instrument will be removed from the revised manuscript, and we will solely rely on the model to constrain VOC.

2) In the absence of VOC measurements at the inlet and outlet, the modeling approach utilized here could provide a less-than-ideal, but reasonable, alternative. For example, no yields were presented for the highest NO2 experiments because of difficulties modeling the initial VOC under these conditions (P. 14932 L. 9-11). This highlights the fact that using this modeling approach to calculate the yields is not the best approach for an experiment with the objective to compare SOA yields.

We appreciate that the reviewer agrees that our modeling approach was a reasonable alternative to calculate reacted VOC. We agree that this study was not optimized to rigorously calculate yields to be used by the community at face value, and one of our tasks as we revise this manuscript is to make that point even more clear – to start, we have changed the title to "A **qualitative** comparison of secondary organic aerosol (SOA) yields and composition from ozonolysis of monoterpenes at varying concentrations of NO_2."

One of the main objectives of this study was to be able to connect observed differences in the evolution of particle size distributions originating from different monoterpenes (observed in this and other studies, e.g. Fry et al., 2014; Hallquist, et al., 1999) to compositional differences in those aerosol populations. Yields are a convenient way to numerically make such comparisons of aerosol distributions. Even if our absolute yields have uncertainty associated with them, comparison of relative yields is useful to highlight these differences between experiments in this study.

The reviewer highlights a good example of why this model isn't optimal to calculate yields, given the fact that we are unable to constrain the BVOC concentration for the highest NO_2 experiments. This is indeed an

> unfortunate characteristic that arises from the fact that the model is constrained using the observed O_3 decay, whereas these high NO_2 experiments react nearly all of the BVOC by NO_3, leaving the O_3 decay nearly unaffected. We have added this explanation to the manuscript in Section 3.2 as well as the following statement: "Since this study was optimized to study aerosol size distributions and composition, the apparent low yields arising from the high NO_2 experiments are beyond our scope of analysis whether or not ΔHC is well-constrained."

A brief discussion of the model uncertainties was provided on P. 14931 L. 11-22. A much more detailed discussion of the model uncertainties including comparisons with measurements is presented in the supplement on pages 4-6 (section entitled "BVOC measurement and characterization of uncertainties"). If one of the major objectives of this work is to discuss SOA yields then this information should be included in the main body of the text rather than the supplement because it has significant implications for interpreting the SOA yield results. For example, on page 5 of the supplement the authors state that the estimated yields presented in the manuscript in Table 3 "would be lower limits to the true yields" based on their measurement/model comparison. This is important information that should not be tucked away in the supplement.

> We have significantly revised section 3.2 pertaining to aerosol yields, as will be further discussed in response to this reviewer's 3rd comment.
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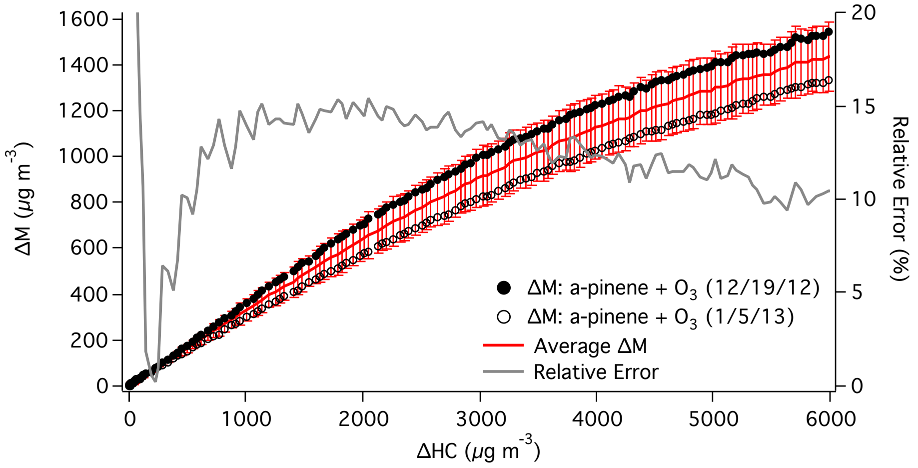
> One of the major corrections made related to how yield uncertainties were determined. The uncertainty in ΔHC is still determined by the range of $k_{RO2+RO2}$ as discussed in the original manuscript. Additionally, error bars on ΔM were calculated and discussed in the main body of the text as follows: "Uncertainty in ΔM was estimated using replicate measurements of α-pinene + O_3 (Expts 1 & 2 in Table 2) as described in detail in the supplemental information. The two ΔM time series were interpolated onto the same ΔHC trace, and time series of the average and standard deviation of ΔM were calculated. The error was slightly variable with ΔHC, as shown in Figure S.7 (and reproduced below), so we conservatively chose the highest stable value – 15% relative error – to use as the ΔM precision estimate."



We have re-written all of section 3.2 to highlight all of the known sources of uncertainty in these calculations. We have replaced Figure 4 with a Yield vs. ΔM plot (below) and removed the yields table completely. We feel that this plot highlights comparisons of mass-dependent yields between each experiment while removing the table de-emphasizes the numerical values of yields and keeps focus on the relative trends as was our original intent. In addition to the uncertainty range on ΔHC based on RO_2+RO_2 rate constants used in this yield calculation, we calculated uncertainty on ΔM based on two replicate measurements of the α-pinene + O_3 experiment. We conservatively took the maximum relative error observed in this time series (15%) and propagated that with ΔHC's uncertainty to find the uncertainty associated with the yields. This method of error analysis highlights the fact that our measurements had high enough precision to make robust relative comparisons.

Having removed the GC-FID data, we no longer have estimates on whether yields may be an over- or under-estimate, so that text has been removed from the manuscript.

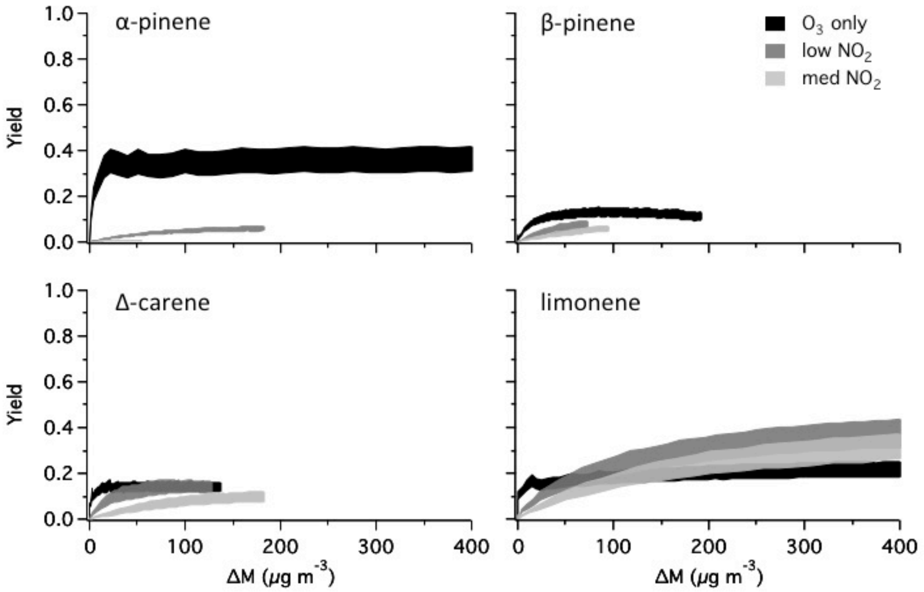


Figure 4. Yield vs ΔM for each experiment. ΔM is corrected for wall losses (described in supplemental information). Uncertainty ranges on yields arise from a constant 15% relative error on ΔM calculated based on two replicate experiments, propagated with modeled ΔHC values using the range of 10^{-15} cm^3 molec^{-1} s^{-1} to 10^{-12} cm^3 molec^{-1} s^{-1} for $k_{RO2+RO2}$ for the low and medium NO_2 experiments for each monoterpene. O_3-only experiments do not have an analogous ΔHC uncertainty range since all O_3 was assumed to react with the monoterpene directly, so uncertainty range on these traces is based exclusively on ΔM.

3) On P. 14931 L. 23-15, the authors state that the SOA yields were not constant in a given experiment and go on to say that the SOA yields they present in Table 3 are the "maximum yield observed during the course of the experiment". This is not a meaningful or appropriate approach to calculate and compare SOA yields between experiments using a flow-through chamber. A flow-through chamber will eventually reach a steady-state condition after a period of time dependent on the chamber residence time (an important number that was not provided anywhere in the manuscript). For flow-through chamber experiments, SOA yield should be calculated from the steady-state condition. This is in contrast to a batch chamber experiment where time-dependent SOA yields could be meaningful assuming only first-generation oxidation products contribute significantly to SOA growth (Ng et al., 2006). Based on the schematic in Figure 2, I estimated the residence time in the REC would have been approximately 90 minutes. Thus steady-state would likely not be reached until at least two (or possibly three) chamber lifetimesǎAˇT3 to 4.5 hours. The SOA yield results that were presented were calculated within the first two hours of introducing VOCs to the REC (P. 14931, L. 27) so it is evident that the chamber had not reached steady-state. This "maximum yield" is not a meaningful number for this experimental design. Furthermore, the yield presented in Table 3 is actually not always the "maximum yield", which immediately calls into question making any comparisons between the yields; authors state on P. 14931

L. 27-28 and P. 14932 L. 1-3, "In some cases, the aerosol growth rapidly exceeded the size range of the SEMS (20-800 nm). Aerosol data presented here is truncated as soon as the size distribution exceeds the range of the SEMS instrument and is represented as a lower limit to the maximum aerosol yield because all subsequent data will be an underestimation of mass." It is not clear from Table 3 which experiments exceeded the SEMS range and represent the "lower limit to the maximum aerosol yield". Was it just the beta-pinene experiments (this guess is based on Figure 3)? Regardless, none of these yield values were calculated from the steady-state condition in the chamber and an unidentified number of "some cases" were calculated at a different point than the others prohibiting any comparisons between them and other literature values.

> We thank the reviewer for calling attention to these points. Upon revisiting how to present our yield data, we discovered an error in which data had been plotted in the version of Figure 4 in the original manuscript. Versions of the ΔM and ΔHC traces that had not been interpolated onto the same time trace for a given experiment were erroneously plotted against each other instead of those traces with corresponding time steps. Correcting this mistake actually removed most of the unusual features of these yield curves and thus discussion of those unusual features has been removed from the revised manuscript. As seen in the updated version of Figure 4, shown above, most yield curves stabilize or slowly increase with increasing ΔM, and any evidence of *decreasing* yields over time (i.e. Δ-carene + O_3 and β-pinene + O_3) is very slight and may be attributable to chemical-dependent vapor or particle-phase wall losses that were not characterized in this study.
>
> In spite of the fact that the corrected yield curves now appear to stabilize quite rapidly, we recognize, as the reviewer points out, that these numbers were not taken from periods truly at steady state as should be done in a flow-through chamber aiming to rigorously measure yields. We have added the residence time (approximately 90 minutes) to the first paragraph of the Methods section as well as explicitly mentioned that experiments were all conducted without seed. The fact that experiments were unseeded prevented us from ever reaching a truly steady state distribution, even during experiments conducted for a period of time spanning several residence times. Without seed providing a constant size distribution for vapor products to condense onto, the observed particle distribution emerges as freshly nucleated particles and proceeds through a full growth curve until particles grow off the range of the SEMS, as seen in Figure S.6, and are eventually removed through the constant outflow of the chamber. This combination of growth and dilution leads toward an oscillatory behavior, meaning that a true steady state will never be achieved. All of the traces in Figure 4 track the time evolution of a single (first) growth event. Since we can calculate the amount of HC reacted and measure the aerosol mass formed at all times even prior to reaching to steady state, there should be no explicitly directional bias on the yield curves we present, and in fact we observe yields to stabilize far before the chamber has reached steady state. One potential difference between this experimental approach and seeded flow through chambers that do achieve a true

> steady state distribution is that here we cannot necessarily assume the aerosol distribution has reached equilibrium at each time step, and thus the influence of true equilibrium partitioning may be masked by other processes, such as kinetically limited growth. This fact may be one reason that absolute yield values observed in this study could differ from other studies.
>
> An additional paragraph has been added to section 3.2 highlighting factors from these experiments that likely differ from other yields studies and may contribute to the absolute yield values calculated in this study differing from other literature values. We include the discussion above about calculating yields prior to the chamber reaching steady state and how these yields may be kinetically driven rather than thermodynamically driven. Additional factors discussed include the fact that this study used a physically different chamber than others, which may have different mixing properties as well as uncharacterized vapor phase wall losses. Finally, and perhaps most importantly, this type of mixed oxidant chemical system has not been studied for three of the monoterpenes included in this study, so the chemistry itself, including radical fate, is not directly comparable to other systems in the literature.

4) In addition to the concerns raised above in comments, there are also some serious concerns about the authors' interpretation of the SOA yield data. On P. 14932 L. 4-5 the authors state, "With the mass yield effectively normalizing these mass yields across varying ΔHC […]" This statement displays a serious gap in understanding about factors affecting SOA yields. SOA yield is affected by a complex suite of variables including, but certainly not limited to, precursor concentration (Kang et al., 2011; Kroll et al., 2008; Pfaffenberger et al., 2013; Presto and Donahue, 2006), seed particle composition/loading (Ehn et al., 2014; Hamilton et al., 2011), and mass of absorbing organic aerosol material present in the chamber (Pankow, 1994; Odum et al., 1996). Presumably no seed was used in these experiments (because it was not stated anywhere in the manuscript) and perhaps the range of VOC concentrations used was not variable enough to have a major effect on yields (substantially higher concentrations can push equilibrium toward partitioning of higher volatility compounds to the condensed phase), but the mass of organic aerosol was clearly quite different between experiments (Figure 4). The authors recognize that this could be a factor on P. 14933 L. 10-11 "[…] which may simply be explained by having the lowest background aerosol mass and thus smaller absorptive partitioning contributions", but then they continue to make general comparisons between the different scenarios using the calculated SOA yields anyway. To present the SOA yields in more meaningful way, the mass of organic aerosol that was used to calculate the yields in Table 3 must be included in the table to be of any use for other researchers for making future comparisons with other SOA yield data. I would also recommend including the reacted hydrocarbon concentration and the initial hydrocarbon concentration as these numbers are also critical for interpreting the SOA yield data presented here. This would be valuable information to make available to the atmospheric chemistry community in general and could allow future comparisons of SOA yields from other experiments. However, to meaningfully compare SOA yields between different scenarios, SOA yield curves would need to be *generated under each condition. Comparing yields at different organic aerosol loadings is not appropriate. For example, the yield of alpha-pinene can vary anywhere from 1%-35% depending on the organic aerosol loading in the chamber (Donahue et al., 2012, Figure 2). Consequently, in contrast to the statement made by the authors, calculating the yield alone does not "normalize" the yield values for comparison with one another. Ideally, there would be repeated experiments within each scenario spanning a range of different organic aerosol mass concentrations (Yield vs. Organic Aerosol Mass). Then, these mass yield curves for each scenario could be compared with one another. With the data presented here, this is unfortunately not possible, but the authors should not compare the yields between experiments. Comparisons between the yields is erroneously interpreted throughout the manuscript (i.e. P. 14932 L.6-9; P.14933 L.20-28; P. 14936 L. 14-15; P. 14937 L. 11)*

> Yes, thank you. This was an oversight on our part and was phrased inaccurately. We recognize that mass yields depend on the organic mass already present and that the total aerosol mass varies substantially in this study. Our intention with all of the "yield" comparisons was really to highlight that latter point – that each of these oxidized organic systems, starting with no aerosol mass (organic or inorganic), were able to produce such vastly different number and mass concentrations compared to each other. Higher mass concentrations draw more volatile species into the particle-phase, but those higher mass concentrations came from a nearly identical system to those that resulted in low mass concentrations.
>
> As discussed previously, we are no longer incorporating a table presenting numerical yields since these studies were not optimized to make rigorous yield measurements meant to be compared to the literature. We also realize that our original assessment of yields was not rigorously appropriate to make direct intercomparisons within this study, but the yield curves presented in the new Figure 4 show the same trend as was originally reported and thus we feel confident now that these trends are sufficient to make the qualitative and relative yield comparisons that were the goal of this study. All references to numerical values of yields have been removed.

Ultimately, the results and discussion related to "SOA Yield" constitute the weakest parts of this manuscript. The yield data should still be included (with the additional information in Table 3 included as I suggested above), but the emphasis on comparing the SOA yields between the experimental scenarios needs to reduced. As a research community, we are already aware of the many factors that can affect SOA yields, and I think it is very important that we are more careful about how we present this type of data and how we use it to make comparisons between different chemical systems. I strongly suggest moving the emphasis of the paper away from a focus on SOA yields to focus more on the stronger sections/results. The data presented in Section 3.1, Figure 3 provides enough information to support authors' conclusions about nitrate effects on SOA production without making comparisons between yields that were calculated and interpreted in a potentially questionable manner. I would also recommend changing the title of the manuscript accordingly to be less focused on the SOA yield results.

We appreciate the reviewer's request to be cautious regarding adding questionable yield values to the SOA literature. We take a slightly different approach than that recommended by the reviewer to avoid this problem. It is our belief that the qualitative relative yield comparisons between experiments *in this study* are robust, given our experimental precision. Relative comparisons between yields come to nearly the same conclusion as the data presented in Section 3.1, but the yields include the additional factors of accounting for total mass and the actual amount of HC reacted in each experiment, thereby accounting for the effects of some of the variability between experimental conditions. We cannot say with certainty that the absolute values of yields are accurate according to rigorous standards of measuring yields, however, and therefore we discourage such absolute comparisons with other studies. As mentioned previously, we have changed the title of the manuscript to "A **qualitative** comparison of secondary organic aerosol (SOA) yields and composition from ozonolysis of monoterpenes at varying concentrations of NO_2." to enable us to continue using the valuable framework of mass yields to make comparisons while downplaying quantitative comparisons with the rest of SOA literature.

Section 3.4: Determination of dominant nighttime oxidant using NO2 to BVOC ratio This section did not use any of the experimental laboratory data and was disconnected from the rest of the paper. The implications of the quick calculations performed here were potentially very interesting and valuable. However, to constitute an entire section of the manuscript it needs to be integrated into the rest of the paper more smoothly. For example, it could potentially fit better after all the laboratory measurements have been presented, after Section 3.5. It could also be strengthened with some elaboration. For example, how variable was the NO2/BVOC ratio in the Fry et al., 2013 study? Authors calculate a crude NO2/BVOC ratio by stating the nighttime peak of the BVOC concentration and the nighttime peak of the NO2 concentration, but it is not stated anywhere that these two components peak at the same time during the night. Providing a range of the measured nighttime NO2/BVOC ratios would be more useful and convincing.

This section was included to highlight that differences in regional chemistry will impact the gas phase kinetics of the area and thus the SOA forming potential. We thank the reviewer for suggestions on how to strengthen the point and make it flow better with the rest of the paper. We have moved it to its own "Implications" section of the paper (Section 4) following the composition results and preceding the conclusion. Additionally, we have provided diurnally averaged calculations based on data from the BEACHON-RoMBAS campaign in addition to the SOAS campaign that took place in central Alabama in 2013 to show an example of how these ratios might vary regionally. The following figure has been added to the manuscript.

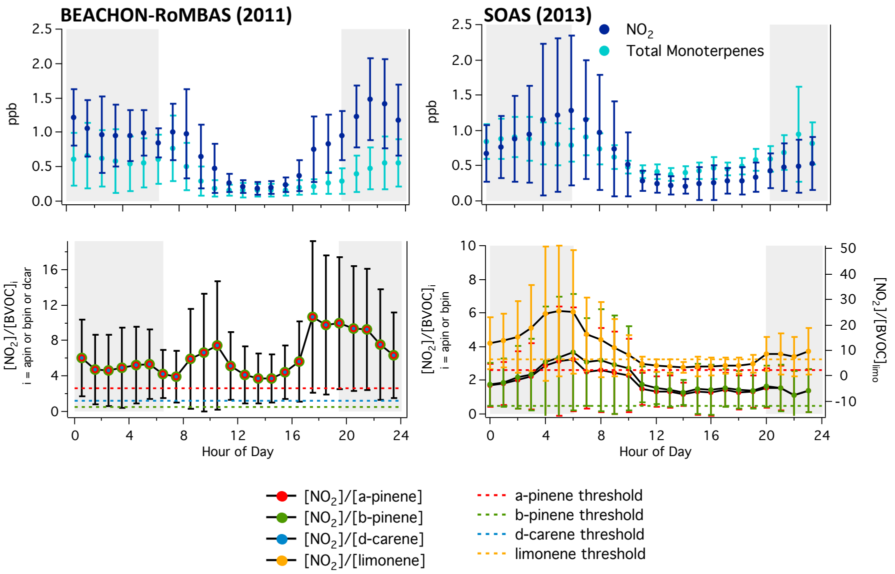


Figure 8. Diurnal average NO$_2$ and monoterpene concentrations (top panels) are shown for two field campaigns: BEACHON-RoMBAS 2011 (left panels) and SOAS 2013 (right panels) which both occurred at heavily biogenically influenced sites. The bottom panels show the diurnally averaged [NO$_2$]/[BVOC] values for the speciated monoterpenes used in this study. The speciated monoterpenes for BEACHON-RoMBAS are estimated as being 1:1:1 α-pinene:β-pinene:Δ-carene based on conversations with colleagues and unpublished gas chromatography measurements from that campaign. Shaded regions indicate nighttime hours.

Specific Comments

P. 14926 L. 24-26: "Ozonolysis of α-pinene has been previously observed to have high aerosol yields (Ng et al., 2006) but strikingly low (0-16%) SOA yields with NO3". A range of yields is provided for the nitrate radical yields, but ozonolysis yields are simply described as "high". Please provide a quantitative range for ozonolysis yields of alpha-pinene for better comparison with the range provided for nitrate radical.

> We have added the range 14-67% for α-pinene ozonolysis in that line citing Ng et al., 2006 and Hoffmann et al., 1997.

P. 14927 L. 23-24: how long did it take to reach steady-state? What was the residence time in the chamber? How does the ratio of O3/NO2 used in these experiments compare to ambient levels? What about absolute concentrations of O3 and NO2 compared to ambient levels?

> The approximate 90 minute residence time has been added to the first paragraph of the methods section. At the end of this paragraph, we have also added: "While precursor concentrations used in this study are all quite high and thus absolute observed aerosol yields are likely not atmospherically relevant due to high mass loadings and unrealistic radical fates, the ratios of [O$_3$]:[NO$_2$] ranging from 1:0.5

> to 1:4 are somewhat reasonable depictions of ratios observable in the atmosphere from relatively cleaner sites (O_3 dominated) to heavily polluted sites (NO_2 dominated). Similarly [NO_2]:[BVOC] ranging from approximately 1:1 to 2:1 is not unreasonable for relatively clean to relatively polluted sites, making relative comparisons between these conditions informative to aerosol formation in the real atmosphere.

Section 2, Methods: Please describe the procedure used to clean the chamber between experiments. Were these experiments unseeded? Please make this clear. Also, recent research has shown that yields can be significantly impacted by seed concentrations (Ehn et al., 2014; McVay et al., 2014; Zhang et al., 2014a, 2014b). Please include a short discussion about implications of these findings for the yields presented in this paper.

> The following short paragraph detailing the chamber's cleaning procedure has been added to the end of the methods section: "Between each experiment, the chamber was cleaned for at least 24 hours by flushing with zero air and O_3 from the source used during experiments until particle concentrations were at or below their typical background level ($<1\ \mu g\ m^{-3}$) and NO_2 concentrations were below 5 ppb. Particle formation was never observed while O_3 and NO_2 were stabilizing for a new experiment, indicating that any traces of BVOC from the previous experiment had been sufficiently removed from the chamber."
>
> We recognize that seed concentrations could affect measured aerosol yields, but since these experiments were unseeded, we believe such a discussion would not aid in our comparison of yields measured in this study.

P. 14929 L. 2 "Source concentrations were somewhat variable over time". Please be more specific and provide a quantitative description of the variability.

> This variability was observed from GC measurements, and since the source of this instability was likely due to the instrument itself, this sentence has been removed entirely along with all other mentions of the GC.

P. 14931 L. 15: Please be more specific/quantitative about "reasonably well known" regarding the rate constant for RO2 + NO3. There should be a quantitative uncertainty associated with the rate constant.

> We have added to the revised manuscript and in the supplemental information a value for this rate constant with error bars reflective of the measurements in the Vaughan et al. 2006 study for C_2 to C_6 RO_2 radicals most likely to be proxies for the ones generated in our study. ($1.8\pm1.5\times10^{-12}\ cm^3\ molec^{-1}\ s^{-1}$) We use the rounded 2×10^{-12} value in the model and keep mention of this number in the text as well.

Comments from referee #2

The authors reported results from a series of laboratory chamber experiments to evaluate the effect of added NO2 (to ozonolysis experiments) on SOA formation, yields, and compositions for a series of BVOC. Experiments were conducted in a 400L flow through chamber. For a-pinene, the SOA mass appeared to decrease with increasing NO2, possibly a result of increasing reaction between a-pinene and NO3 radicals. The authors noted that b-pinene and carene retained similar mass yields with increasing NO2, while limonene generated more SOA with increasing NO2. Filter samplers were collected from these experiments, and higher molecular weight products were detected in experiments with more NO3 oxidation, suggesting the importance of oligomerization reactions.

The research topic would be of interest to the research community and is certainly worthy of investigating. Unfortunately, there is a mismatch between the experimental design and set up and the goals of this study, which is a critical weakness of the study. The experiments were conducted by introducing BVOC into the chamber after the oxidant concentrations stabilized. The BVOC concentration was not measured during the experiments. Instead, the BVOC concentration from the flask containing it was measured before and after the experiments, and compared to estimates from a model. The modeled BVOC was then used to calculate yields (Y = delMo/delHC). As shown in Figure S4, the uncertainties associated with [BVOC] are very large. The authors did not specify the uncertainties, but from Figure S4 it appears that the uncertainties can be as large as +/- 50% and even a factor of 4 for limonene. With a lack of direct measurements of [BVOC] and such large uncertainties in the estimated [BVOC], the authors cannot attribute their observed yield differences to the effects of added NO2 and subsequent NO3 chemistry. Further, when taking such uncertainties into account, except for the a-pinene reactions, the data shown in Figure 4 for differing amount of added NO2 are essentially the same within uncertainties. One cannot use the data from Figure 3 to draw any conclusions either. As the experiments have different NO2 and BVOC concentrations, one cannot attribute the difference in SOA growth in Figure 3 to NO2 only.

I have some serious concerns regarding the authors' interpretation of SOA yields. Many of the discussions reflect a lack of understanding of SOA yields. First and foremost, SOA yields should not be reported on their own, and be compared across different systems/experiments, without taking into account the corresponding delMo values. Even for the same BVOC reacting system, SOA yield is a function of delMo (Odum et al., 1996). Secondly, in performing chamber experiments in flow-through mode, one typically waits till the chamber achieves steady state and reports the yield (with the corresponding steady state delMo). However, here, it appears that the chamber did not reach steady state (base on info from the experimental schematic). With this, what do the "yields" reported in this study mean? It is some sort of time-dependent yield, but with the chamber not reaching state, the authors cannot simply compare these time-dependent yields between different experiments and make conclusions regarding the effects of added NO2.

Overall, the experimental design and setup in this study do not allow for an accurate assessment of the effects of NO2 concentration on SOA formation and yields. While the writing is clear, the data interpretation is questionable and the conclusions are not well justified. I do not think the manuscript is suitable for publication in ACP in its current form.

Specific comments.

1. Page 14929, line 1-5. The authors stated that the initial [VOC] was characterized directly from the flask using GC-FID before and after each experiment.

a. Why is the GC-FID measurement not performed during the experiment at chamber inlet/outlet? This would seem like the most logical way to greatly reduce the uncertainties in their yield calculations.

> We agree with the reviewer that this proposed setup would be a much better way to operate, and we intend to optimize flows enabling us to implement this setup for future studies. However, at the time of these experiments, flow conditions prevented accurate measurement from the chamber outlet, and a higher dilution flow was necessary to sample from the low VOC flow at all, which necessitated we sample from the high concentration source flask directly in order to measure high enough signal in the GC-FID following dilution.

b. Figure S4 shows the average GC-FID measurements of BVOC source concentrations plotted against the BVOC source concentration range predicted by kinetics modeling for each experiment. This figure needs to be discussed extensively in the main text. As seen in Figure S4, the uncertainty in the modeled BVOC concentration is easily as high as +/-50%, and even can be a factor of 4 for limonene. These are very large uncertainties. As SOA yield = delMo/delHC, the large uncertainties in [VOC] will directly translate to the uncertainties in yields, making it extremely difficult to compare the yields across different experiments and arrive at any concrete, well-supported conclusions.

> We agree that the large degree of scatter in Figure S.4 is problematic. Prompted by both reviewers' comments, we investigated additional sources of uncertainty in the GC-FID measurements, and discovered that the gas trap sampling module on the GC-FID seems to initiate chemistry as well as non-linear desorption onto the column, resulting in tremendous instrumental uncertainty. As a result, we have decided to remove all references to data from this instrument in this manuscript and sincerely regret including it in the first place. Please refer to our response to Reviewer #1, General Comment #1 for a more detailed description of this decision.

c. What is the relative importance of RO2+RO2 in the experiments? With the very high mixing ratios of VOC used in these experiments, one would imagine RO2+RO2 would *dominate. Please comment on the atmospheric relevance of these experiments in this regard.*

> In the experiments that include NO_2, RO_2 fate is split between RO_2, NO_3, and NO_2. The relative contributions of each of these radical sinks vary with time in each experiment and also vary depending on the $k_{RO2+RO2}$ used in the model. Typically NO_2 and NO_3 sinks dominate at the beginning of experiments and are gradually replaced by RO_2. We mention in the supplemental information (kinetics modeling section) that these experiments are not expected to produce HO_2, "which is a significant deviation from the real atmosphere where nighttime HO_2 concentrations can be comparable to RO_2 concentrations (Wolfe et al., 2014; Andres-Hernandez et al. 2013)." We have also added a line in the first paragraph of the methods section regarding the atmospheric relevance (or lack thereof) of using such high precursor concentrations, which mentions unrealistic radical fates.

2. Page 14830, section 3.1. I think this section is misleading. One a first read, it looks like the authors are comparing the aerosol formation in each system systematically, as a function of NO2 added. This would be fine is everything in the system is maintain constant, except for the amount of NO2 added. However, this is not the case.

a. With the large uncertainties in [VOC] modeled, one can see from Table 1 that the [VOC] concentration can vary up to a factor of > 3 for the same VOC system. Therefore, the authors simply cannot discuss the trends in Figure 3 as a result of varying [NO2] on SOA formation (because there is a large variation in [VOC] as well). For instance, if one looks at the results for b-pinene in Table 2, the ozonolysis experiment has [VOC] = 370 ppb, while the low [NO2] experiment has [VOC] = 470 – 680 ppb. The authors argued that the addition of NO2 enhanced SOA formation. However, given the large uncertainties in [VOC], one can argue that the higher SOA formation in the low [NO2] experiment (as compared to the ozone-only) is a result of a larger amount of VOC reacted.

> We agree with the reviewer that these raw traces are not directly and systematically comparable due to non-trivial variations in initial [VOC]. It is our belief that we highlight this caveat appropriately in the text, and this is the main reason we felt compelled to calculate SOA yields in addition. We needed a framework under which aerosol formation trends could be more directly compared between experiments. Our rationale for keeping this section is twofold: 1) following (a now more rigorous) analysis of yields, we observe that comparisons in yields tell nearly the same story as the V_{tot} traces in Figure 3, suggesting that even though initial VOC concentrations were variable, they did not have a huge effect on our conclusions about relative yields. While yields from β-pinene and Δ-carene with the addition of NO_2 may not be enhanced relative to their ozonolysis yields, they still behave similarly to each other and qualitatively different from the other two monoterpenes. 2) We have no way of correcting N_{tot} for differing initial [VOC], but this is an interesting piece of data

elucidating the difference in aerosol formation mechanisms from different precursors. Again, the broad consistency of trends between Figure 3 and our new Figure 4 indicate that this N_{tot} data is interesting and useful to include even if there are caveats associated with it.

b. Are the "ozone-only" experiments truly ozone only? Is any OH scavenger added? This is not mentioned in the text so I assume no scavenger was added. Thus, in the ozone-only experiment, there can also be BVOC+OH reactions. If so, the different extent of BVOC+OH reactions in the "ozone-only" experiments and "NO2 added" experiments can also contribute to the difference in the observed SOA loadings and yield. Thus, this could also alter the interpretation of the trends observed and the conclusions of the manuscript. Please comment.

We did not include an OH scavenger in these studies and discuss this fact in section 3.3 when we discuss the contributions from individual oxidants. Modeled contributions from each oxidant, including OH, are included in Table 4 in the original manuscript (which is now Table 3 in the revised manuscript as the yields table has been removed). Distinct effects of O_3 and OH are not separable in this study, but we acknowledge and indicate in the text that both oxidants are likely present.

c. All the [VOC] data in Table 2 should include uncertainties.

The [VOC] data in Table 2 reflects uncertainty ranges constrained by our modeling approach, which used the range in $k_{RO2+RO2}$ values to provide an estimate of the magnitude of that uncertainty. O_3 experiments do not have an associated uncertainty range since RO_2+RO_2 was the only sink for RO_2, so changing this rate constant did not affect how much BVOC was reacted overall. Regarding the highest NO_2 experiments, the initial concentration of BVOC is constrained in the model using the observed O_3 decay following BVOC addition for each experiment. In the highest NO_2 experiments nearly all oxidation goes by way of NO_3, which means there is not a distinguishable O_3 decay to match. Having removed all mentions of the GC-FID data, the footnote on these values in Table 2 now reads, "[BVOC] estimated according to flow rate and temperature dependent vapor pressure within source flask." These estimates are not used in any subsequent analysis, since we do not calculate yields for these high NO_2 experiments.

3. Page 14932 and onwards, discussion of SOA yields.

a. These discussions reflect a lack of fundamental understand of SOA yields. SOA yield is a function of delMo (e.g., Pankow , 1994, Odum et al., 1996). The two product model governs that SOA yield will increase with delMo. In this regard, it is not meaningful to simply report SOA yields without providing the corresponding delMo data as well (Table 3, and page 14933, line 9, line 20, etc). One should never compare a "SOA yield" from one precursor to another (or from one experiment to another), without tak-

ing into the corresponding delMo values. (unless SOA yield is constant for all delMo values).

> We thank both reviewers for calling attention to our flawed treatment of yields in our original manuscript. We have substantially rewritten section 3.2 and replaced Figure 4 in the original manuscript with a plot highlighting Yield vs ΔM so now comparisons can be made across comparable ΔM values for each experiment, as suggested. A number of corrections have been made to this analysis and interpretation, and we request this reviewer reference our response to Reviewer #1 on General Comments #2, 3, and 4 for full details.

b. Page 14932, line 10. What are the "difficulties"? Do these reflect the uncertainties in the modeling framework? Please provide more information. Why were these "difficulties" only encountered for the high NO2 experiments?

> Please refer to our response to Reviewer #1, General Comment #2 as well as Reviewer #2, Specific Comment #2c for this explanation.

c. Page 14933, line 4. Is it possible that the "0 %" SOA yield from a-pinene is a result of the experimental deign and set up? (e.g., high a-pinene mixing ratio, higher contributions from RO2+RO2, mixing, etc?).

> Low to zero SOA yields from α-pinene + NO_3 have been observed in two studies with different experimental designs (Fry et al., 2014; Hallquist et al., 1999), with additional corroborating evidence from this study. These two studies also measured NO_3 yields from multiple monoterpenes. We have no reason to expect that experimental design would affect α-pinene experiments differently than the other monoterpenes studied (in the current study or the two mentioned monoterpene comparison studies in the literature), so whether or not the absolute 0% yield is an artifact of experimental design, it still shows extreme and systematic differences relative to other monoterpenes explored under comparable conditions.

d. Page 14933, line 16. The authors noted that in the b-pinene experiments, aerosol size distribution grew out of range of SEMS. Did the size distribution grow out of range in other experiments? What are the implications of this on data interpretation and conclusions of the manuscript? Does this mean that the delMo data reported for b-pinene are underestimated (and the authors did not know the extent to which the underestimation is?), which would also affect the SOA yields?

> All data was truncated immediately before size distributions began to grow off the instrument, so the only implication is that faster-growing experiments have less data to compare to other experiments. For example in the revised version of Figure 4, the two NO_2 + β-pinene experiments were truncated before even 100 μg m^{-3} of aerosol mass had formed, making thorough inter-experimental comparisons at higher mass loadings difficult. We have added a sentence to section 3.2

> clarifying this point. "Aerosol data presented here is truncated as soon as the size distribution begins to exceed the range of the SEMS instrument resulting in these experiments "ending" at quite low mass loadings before the yield curves have flattened."

4. Figure 4 and related discussions. The data shown in Figure 4 demonstrate the main weakness of the manuscript.

a. The main goal of the study is to evaluate the effect of added NO2 on SOA formation and yields from various hydrocarbon precursors. As noted in the comments above, the uncertainties in [VOC] are very large (as large as +/- 50% and a factor of 4 for limonene). If one takes these uncertainties into account, for each precursor (perhaps except for a-pinene), all the delMo vs. delHC plots shown in Figure 4 would essentially be the same within uncertainties. Thus, one cannot arrive at any conclusion regarding the effect of added NO2 on SOA formation and yields. This is not to say such a study cannot be performed, but the experimental design and the uncertainties in [VOC] in this work is suitable to evaluate the effect of added NO2 on SOA formation and yields.

> As discussed in response to Reviewer #1, General Comment #2, many changes have been made to the analysis and interpretation of section 3.2. To summarize, in our revised manuscript, we use the two replicate α-pinene + O_3 experiments to generate an estimate of experimental precision on our chamber. We have added a paragraph to this section detailing ways in which our absolute yields may differ from other reported values, however, given our own measurement precision, we feel that comparisons between experiments in this study are robust.

b. When operating the chamber in steady state mode, one typically reports the yield at steady state. In this study, it appears that the chamber never reached steady state after BVOC was added, thus, the yields reported in this study are time-dependent yields. It is not clear what time-dependent yields in a flow-through chamber mean and how such data can be interpreted, as the results can be drastically affected by mixing, injection, etc. If one operates the chamber as a batch reactor, the time-dependent SOA yields can be similar or different from "final yields". Here, without performing a series of experiments over a range of initial [BVOC] (for each BVOC) and wait till steady state, it is difficult to compare yields from these experiments and make conclusions regarding the effect of added NO2.

> This point is discussed thoroughly in response to Reviewer #1, General Comment #3. A true steady state particle size distribution is not possible in these unseeded, flow through experiments, necessitating use of instantaneous yields to make yield comparisons at all. We expect physical experimental conditions such as mixing and injection to be comparable throughout all experiments in this study allowing intercomparison of measured yields within this study, however, the potentially unique mixing in this chamber provides a reason to avoid making comparisons of yields in this study to other literature values. We suggest that due to not being at

steady state, these yields may be reflective of kinetically-limited growth processes than true equilibrium partitioning.

c. If one still tries to calculate the time-dependent SOA yields from the data shown in Figure 4, another issue arises. Typically, SOA yield increases with reaction time, and may decrease towards the end of experiment due to particle wall loss being greater than SOA growth. However, the shape of the curves (convex shape) in Figure 4 indicates that in these experiments, the slope (and hence SOA yield) decrease with time. What caused such an atypical behavior? Please explain.

This strange behavior was due to a calculation error, as described in detail in response to Reviewer #1, General Comment #3. We are very grateful to both reviewers for such careful critique of our original yield data, which helped us to find this error. The new version of Figure 4 that is now plotting Yield vs ΔM, as mentioned previously, shows a very slight decrease in yield at increasing ΔM for only two experiments, which, as the reviewer points out, could be attributed to wall losses. All other yield curves either stabilize or slowly increase with increasing ΔM as would be expected.

5. Page 14934, comparing yields from the current study to prior studies.

a. When taking delMo into account, one can compare the SOA yields between different studies. The SOA yields from the "ozone-only" experiments appear to be quite different from those in Griffin et al, for a delMo = 200 ug/m3. Does this reflect the limitation of the yields reported in the current study (i.e., yields are not steady state yields)?

As mentioned previously, our goal was to make qualitative comparisons between experiments in this study, and we mention a large variety of factors, including use of a different chamber and calculating yields that are likely heavily influenced by kinetic growth factors, to caution that these yields are not rigorously measured (due to reliance on modeled VOC) and should not be compared at face value to other studies.

b. In line 2, the authors noted that the "relative yield" for each monoterpene follow the same trend as in Fry et al. (2014). This research group has published multiple studies reporting SOA yields from various BVOC with nitrate radicals. However, when comparing SOA yields at similar delMo values for the same BVOC, it appears that the SOA yields are quite different between the different studies from the same group, and that there are no detailed discussions regarding why they are different. This makes it difficult for the readers to interpret their results. Of course, there are many factors affecting SOA yields, but it's important to ensure the results are consistent with their own prior studies, or other studies in literature, if the experiments are performed under similar conditions. If any yield differences can be a result of differing experimental design and conditions that should be pointed out clearly and discussed as well. In this case, the authors mentioned that their results are consistent with the trends in Fry et al. (2014), where it appears to be a flow-through chamber study as well. Fry et al. (2014)

showed that the SOA yield for b-pinene at a delMo of 30 ug/m3 is 0.5. From Table 4 of the current study, the model predicted that a majority of the b-pinene in the med [NO2] experiment should react with NO3. However, if one converts the b-pinene med [NO2] data shown in Figure 4 of the current study into a yield curve, it would be very different than the one shown in Fry et al. (2014). This is just one example. I encourage the authors to carefully compare and discuss their findings with their prior results/other results in literature, and justify any differences observed.

> One difficulty with comparing SOA yields from NO_3 oxidation from this study to those from the literature is that this chemical system was quite different. The Fry et al., 2014 study was performed in a much larger chamber, had much lower mass loadings due to low precursor concentrations, and introduced NO_3 to the chamber through dissociation of N_2O_5 rather than including high concentrations of O_3 and NO_2 as was done in this study. Even if most of the BVOC reacted by way of NO_3, we cannot rule out contributions by O_3 and/or OH in our experiments, and the high concentrations of $[NO_2]$ present are suspected to significantly affect radical fates. Our original intention with this comparison was to highlight the relative trend (not absolute values) of yields in the two studies. The revised manuscript has further deemphasized putting any numbers on our yields from this study, and thus this discussion has been removed.

6. The composition data are quite interesting. There are several speculative chemical structures, could the authors provide some discussion (speculation) as how these large molecular weight compounds can be formed.

> We appreciate the reviewer's interest in the composition data. With just mass spectrometry data and thus just chemical formulae, we cannot actually say anything conclusively about the structure of these products. We highlighted a few speculative oligomer structures to point out that those formulae can correspond to compounds that clearly have building blocks of monoterpene monomers. However, many oligomerization mechanisms discussed in the literature can lead to products that would "make sense," so we cannot provide more detail regarding actual mechanisms.

Additional corrections from authors

> In addition to responses to specific comments and questions from reviewers, the authors wish to highlight one other significant change made to the revised manuscript. Yield calculations and discussions in Section 3.2 were significantly rewritten, requiring much of the discussion and calculations in Section 3.3 to be rewritten as well. Since this study is focusing heavily on relative yields between experiments and discouraging comparisons to absolute yield measurements in the literature that were far more rigorously measured, we no longer try to calculate yields from individual oxidants and instead focus on qualitative indications of whether or not reaction with NO_3 could be explanatory of observed yield

differences with different oxidant conditions. Additionally, the calculation error made in the original manuscript regarding properly matched timing of all traces results in a slight change in Figure 5.

The new version of Figure 5 (below), shows that β-pinene still produces aerosol when only oxidized by NO_3, but now there is a time lag before any aerosol is produced. To explain this time lag, we calculate the ratio of RO_2+NO_2 products relative to all RO_2 products formed (i.e. the sum of RO_2+RO_2, RO_2+NO_3, and RO_2+NO_2) from the model, and plot this time series on top of the oxidant contribution figures. There is a local minimum observed in this ratio at early times in each experiment that, in most cases, corresponds quite well to the timing of aerosol mass starting to form, although, notably, **not for α-pinene**. Therefore, we attribute this initial aerosol suppression to rapid formation of volatile peroxynitrates, and aerosol is only able to form once RO_2+NO_3 and RO_2+RO_2 begin to compete as RO_2 sinks. The combined observations that the timing of peroxynitrate domination cannot explain the timing of SOA formation for α-pinene and that α-pinene is not observed to make any aerosol during periods dominated by NO_3 oxidation (as was the argument in the original manuscript), whereas the opposite is true for all other monoterpenes studied, brings us to the same conclusion as the original manuscript. Observed aerosol suppression with NO_2 in the α-pinene system is likely caused by reaction with NO_3 that leads to 0% aerosol yields, and differences in yields for other monoterpenes in the different oxidant regimes can likely, at least in part, be attributed to different aerosol yields from NO_3 relative to O_3.

The following figure will replace Figure 5 in the original manuscript. This figure reflects the corrected change in timing and also includes the ratio of RO_2+NO_2 products on it to highlight this explanation for the timing.

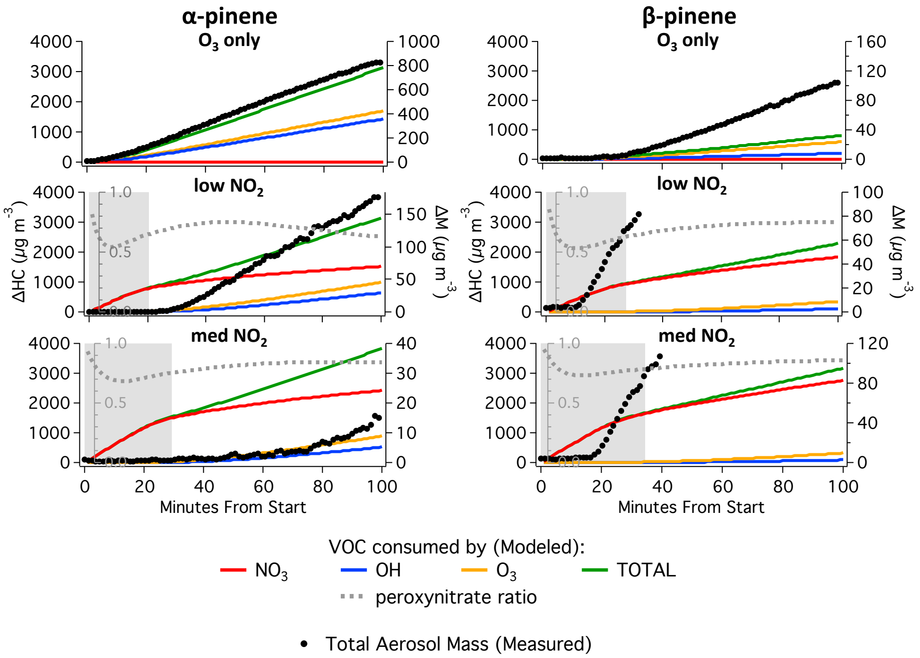
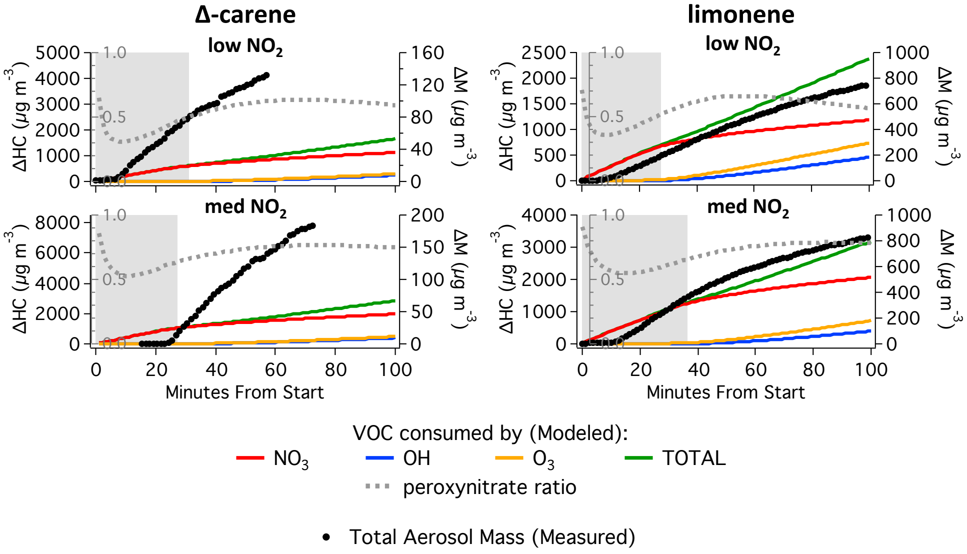


Figure 5. Time series of wall loss corrected aerosol mass (right axis) and VOC consumed by each oxidant (left axis) for α-pinene and β-pinene at zero ("O_3-only"), low, and medium NO_2 concentrations, highlighting how much aerosol is produced at times dominated by NO_3-oxidation (shaded regions). ΔHC values shown are the lower limits calculated using the lowest RO_2+RO_2 rate constant (10^{-15} cm^3 $molec^{-1}$ s^{-1}), which gives the low limit on how much NO_3 reacts with VOC directly. Dashed grey traces (inner left grey axis) represent the ratio of RO_2+NO_2 products that are present in the chamber (instantaneous concentration) relative to the sum of the instantaneous concentrations of RO_2+RO_2, RO_2+NO_3, and RO_2+NO_2 products. This ratio is a representation of the time dependence of peroxynitrate formation in the chamber.

A figure (shown below) highlighting this same data for the Δ-carene and limonene experiments influenced by NO_2 has been added to the supplemental information as well, with a similar figure caption, to make the comparison complete.



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