The authors would like to thank the two anonymous reviewers for their helpful comments and suggestions. All comments are addressed below. Comments are included in italics and author responses are in plain text.

Reviewer #1

1 – The statement about observed hydrolysis rate in the abstract does not match your discussion and last figure, which suggests a dependence of hydrolysis on RH. I think this rate should be reported cautiously and I would avoid stating a cutoff for hydrolysis given the lack of reproducibility in your measurements near 22%.

We have clarified and expanded the discussion of the non-linear dependence of hydrolysis on RH in the abstract of the revised abstract. The relevant excerpt now reads:

"The particle-phase ON hydrolysis rate consistent with observed ON decay exhibited a nonlinear dependence on relative humidity (RH): During experiments conducted at an average RH ranging between 20 and 60%, an ON hydrolysis rate of 2 day^{-1} was observed; no significant ON hydrolysis was observed at RH lower than 20%. During experiments when the highest observed RH exceeded the deliquescence RH of the ammonium sulfate seed aerosol, the particle-phase ON hydrolysis rate was as high as 8 day^{-1} and more variable."

We note that we are not the first to report an abrupt increase in nitrate loss rate with increasing RH. Liu et al. (2012) reported a loss rate of 0 up to ~18% RH but saw a consistent loss rate of 4 day^{-1} at 40% RH and above.

2 – P. 20635, re: wall loss correction: How would this correction be affected if wall loss rates depend on RH (likely) or are different for different chemical species?

As part of the applied wall loss correction the organic PM in each experiment was normalized to the ammonium sulfate from the same experiment. This correction assumes that the concentrations of ammonium sulfate PM only change due to wall loss and that the wall loss rates of organic PM is equal to the wall loss rate of ammonium sulfate (i.e. that the organics and ammonium sulfate form an internal mixture). A main advantage of this correction method is that variation of wall losses between experiments is accounted for; therefore differences in wall losses with RH are accounted for using this correction.

3 – P. 20636, obtaining mixing ratio of aerosol nitrate: Please flesh out explanation of this. Did you take mass loading of each NO and NO2 separately and use those fragments' MW's to convert to mixing ratios, which you then summed? Doesn't the AMS calibration assume that both NO and NO2 come from NO3 functional groups and therefore the MW to use to do the conversion would be that of the NO2 fragment, since it is assumed the O-N bond breaks and one of the O's would be detected amont the organic fragments? Please clarify what you did and be sure that the assumptions are correction – this *could give big errors in the mixing ratios and consequently change the partitioning coefficients substantially!*

This has been corrected. The reviewer is correct that each NO+ and NO_2+ fragment measured in the ACSM originates from an NO_3 functional group so the MW of 62 g/mol should be used to convert mass concentrations to mixing ratios. The resulting changes to partitioning coefficient are now discussed in further detail in the manuscript:

“the mass concentration of nitrate measured by the ACSM was converted to mixing ratio (ppb) using the molecular weight of the nitrate functional group (62 g/mol)”

An updated Figure 4 (partitioning coefficient) and discussion of the results has been included below.

“These results indicate that under typical ambient conditions (< 40 μg/m^3 of OA) 5-10% of organic nitrates formed from the photo-oxidation of α-pinene under high NOx conditions are expected to partition to the particle phase. This is significantly lower than the organic nitrate partitioning calculated by Rollins et al. (2013) for organic nitrates measured in Bakersfield, CA during the CalNex campaign in 2010 as shown in Fig. 4. The difference could be attributed to differences in precursor molecules and levels of oxidation. Studies have shown that high NO_x conditions can shift photochemical oxidation products of terpenes towards higher volatility compounds (Wildt et al. 2014). Rollins et al. determined using the SPARC model (Hilal et al., 2003) that precursor molecules (a mix of C5-C15 VOCs) would need two stages of oxidative chemistry beyond the initial oxidation of the VOC to reach the point when 19-28% would partition to the particle phase for a C_{OA} of 3 μg/m^3. This suggests that the ON formed in our experiments have undergone fewer than three generations of oxidation as they are more volatile than the ON measured in Bakersfield during CalNex 2010. It should also be noted that the thermal dissociation-laser induced fluorescence (TD-LIF), used by Rollins et al. 2013, has been shown in a recent study to measure PM ON a factor of two higher than the AMS (Ayres et al., 2015). While the reasons for this difference are unknown, it would result in an increased partition coefficient compared to the one calculated from the AMS (or ACSM) and explain part of the observed difference.”

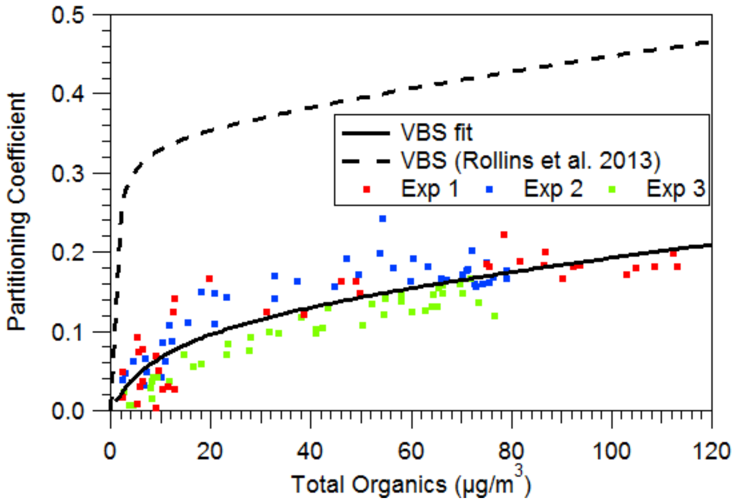

Figure 4 – Volatility basis set fit from this work shown with data from Expts 1, 2, and 3 and the VBS fit from Rollins et al. (2013)

4 – Ibid. I have serious reservations about the accuracy of the determination of gas-phase organonitrates from mass balance. This assumes there are no other Ncontaining species, such as HONO or NO3 and N2O5, which could certainly form in your experiments. Photolysis of these may be fast, but so might the production rate. You could include these in your model to show their expected concentrations and then determine whether they could be a source of error to your N balance. At least in the supplemental material, please show one of your time series of the partitioning coefficient.

Figure S3 has been added which shows a time series of all N containing compounds formed in these experiments according to the SAPRC model. The time series shows that concentrations of HONO, NO_3 and N_2O_5 are orders of magnitude lower than the 5 compounds included in the mass balance. The error associated with ignoring HONO, NO_3 and N_2O_5 in the mass balance is therefore low and within the uncertainty of our experiments. A brief discussion of this has been added to the manuscript:

"Figure S3 shows that based on the SAPRC model that other forms of oxidized nitrogen are orders of magnitude lower than concentrations of these 5 forms"

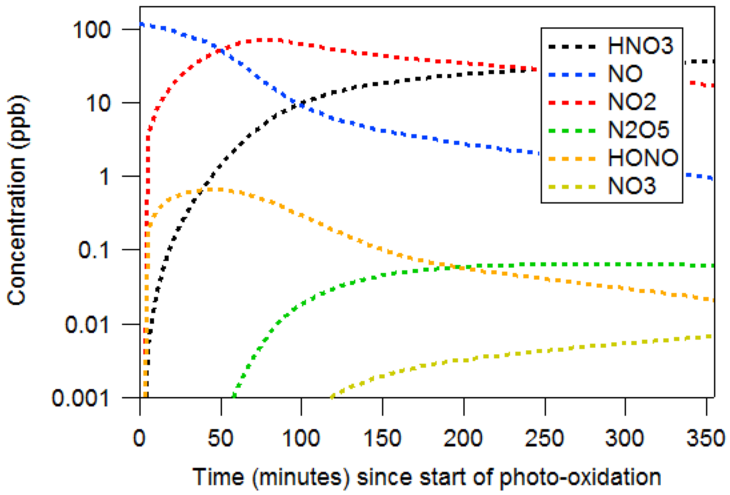

Figure S3 – SAPRC results showing significant nitrogen compounds

5 – P. 20637, discussion of hydrolysis rate: From Darer et al, it appears that tertiary nitrates should have rapid hydrolysis rate constants and primary should be quite slow. Boyd et al ACPD 2015 have used this to estimate in the case of NO3 + β-pinene, what fraction of the NO3 radical additions occur at which end of the double bond. This might be worth discussing here. Do you assume that all of your nitrate is tertiary and compare to the literature based on that? Is there any literature basis for a faster rate than the one you assume in your assessment of whether the gas/aerosol partitioning could be affected by hydrolysis? My sense was that these rates are not well known. You conclude hydrolysis can't affect partitioning – is this because the assumed hydrolysis rate was slow relative to the timescale of these experiments? Given the uncertainties in hydrolysis rates, you could flip this analysis around and ask instead, how fast does *the hydrolysis have to be to change the partitioning coefficient by X%? Perhaps in addition to what you have here. This would give future researchers a quick comparison point – if they determine a faster rate, this provides a quick assessment of whether that rate is partitioning-relevant.*

The difference between 10% of ON hydrolysis observed by Boyd et al. 2015 and this study is an important one as it shows the potential differences between ON formed from NO_3 (Boyd) and ON formed from OH + NO (this study). There are also differences in how β-pinene and α-pinene are oxidized. More discussion of this has been added to the revised manuscript. :

"Boyd et al. (2015) measured a lifetime of 3-4.5 hours for 10% of ON formed from NO_3 oxidation of β-pinene, with a much longer lifetime for the remaining 90%. This suggested that 10% of the ON functional groups were tertiary with the rest being primary or secondary as those have been shown to hydrolyze much slower in the bulk phase (Darer et al., 2011; Hu et al., 2011). Our results do not suggest that the hydrolysis is limited to 10% of ON, consistent with a higher fraction of tertiary ON. We do not observe a change in the ON hydrolysis rate, potentially partly because of the long lifetime (12 hours) of ON measured in this study. This higher fraction of tertiary ON shows that the split between primary/secondary and tertiary ON functional groups can be different for ON formed from different mechanisms and precursors."

"Similar VOC precursors such as α-pinene and β-pinene can form different types of ON. When NO_3 reacts and bonds with the terminal double bond of β-pinene, an alkyl radical is formed in either a primary or tertiary position (opposite of the nitrate bond). The tertiary alkyl radical is more stable, so primary organic nitrates are expected to be more abundant. The double bond in α-pinene is not terminal, so the NO_3 reaction produces either a secondary or tertiary ON and alkyl radical. NO_3 typically bonds with the less substituted carbon of a double bond so that a more highly substituted alkyl radical is formed. The reverse is true for OH+NO chemistry. In this case NO reacts with the peroxy-radical to form the nitrate group. The peroxy-radical, a product of O_2 and an alkyl radical, is likely to be on a more substituted carbon as this would have been the more stable alkyl radical. Thus, more highly substituted ON are expected from OH + NOx than from NO_3 chemistry. This has important implications for attempts to model ON and the resulting NO_x recycling."

On the topic of hydrolysis affecting partitioning: The 12 hour lifetime we measured for ON in PM at mid-level RH was used to find the maximum deviation in partition coefficient in Expt. 2. This was the only experiment used to calculate partitioning which had high enough RH to be significantly affected by hydrolysis. When the partition coefficient in this experiment was 0.2, the maximum seen in the data used in calculation of the VBS, if hydrolysis had not occurred the partition coefficient would increase from 0.2 to 0.23. This is the maximum effect that hydrolysis could have on the partitioning coefficient, with lower effects earlier in the experiment and no significant effects on the low RH experiments.

6 – P. 20639, interpreting the <0 values: You mention the possibility of HNO3 contributing to aerosol nitrate. A calculation using Henry's law coefficient for HNO3 will allow you to determine whether this could be happening.

The negative values were not anymore present after correcting the calculation of particulate nitrate as detailed in the response to comment 3. However a Henry's Law calculation shows that total particulate HNO_3 is 3 orders of magnitude lower than the total amount of HNO_3 in the gas phase under the conditions of these experiments. This detail has been added to the revised manuscript:

"Measuring the disappearance of nitrate with the ACSM assumes that HNO_3 formed through hydrolysis volatilizes, consistent with its high vapor pressure (Fry et al., 2009). A Henry's Law calculation shows that the total amount of aqueous HNO_3 in particles is 3 orders of magnitude lower than that in the gas phase. HNO_3 can also stick to the walls of the Teflon chamber but this would not affect the calculation as this would be included in the total amount of HNO_3 predicted by the SAPRC model."

7 – P. 20640, interpreting temperature ramps: Were these only done during the early states of oxidation, while the partitioning species would be the less oxidized and thus more semi-volatile? Or did you try this at different delay times to investigate the effect of increasing oxidation on (presumably) decreasing volatility?

These temperature changes were conducted at the end of the experiment, primarily to confirm that organic nitrate species are semi-volatile.

8 – P. 20642 bottom, discussion of observation of decrease in both organics and nitrate: why should PM organics also decrease? Hydrolysis producing HNO3 would certainly be expected to volatilize the nitrate, but mightn't the organic left behind be expected to stay in the condensed phase? Can you learn anything from the relative rates of loss of organic vs NO3?

PM organics did not decrease as significantly or consistently as PM nitrate and the discussion in the manuscript has been modified to more accurately describe this:

"Concentrations of wall-loss corrected PM nitrate (normalized to SO_4) were observed to decrease towards the end of most experiments … PM organics decreased as well in some cases – though not as significantly or as consistently. Based on the work by Chuang et al. (2015) the addition of a nitrate functional group decreases volatility of a compound by 2.5 orders of magnitude – more than the resulting alcohol group from hydrolysis. Thus, the organic compound resulting from ON is more volatile than the original organic nitrate, and as a result could partition to the gas phase, resulting in a decrease in PM organics."

9 – Ibid, + around p. 20643 line 1-3: please explain how you obtained these hydrolysis rates- just the decay rate of NO3 aerosol? Or normalized to SO4?

An exponential was fit to NO_3 normalized to SO_4. This has been clarified in the manuscript and in addition a new figure (S4) has been added to the SI to illustrate calculation of the hydrolysis rate:

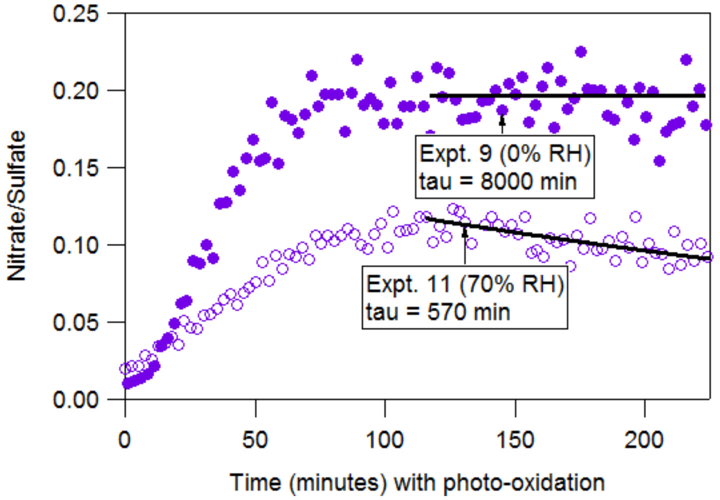

Figure S4 – Exponential decay for a low RH (Expt. 9) and high RH (Expt. 11) conditions

10 – Table 1: Looking at the hydrolysis rates here for RH = 22, 15, and the two 70's, I am not convinced of the reproducibility at a given RH. This either just means the rates are not known that well, or that RH is not the determining factor. Either way, I think this suggests a retreat from Fig. 5, which implies that there is a correlation between RH and NO3 loss rate.

An additional experiment was conducted at high (67%) RH and the results warranted additional discussion and an update to Fig. 5:

"Experiments conducted at an average RH of 67% or higher can exhibit a significantly higher decay rate, most likely due to effects of being near the deliquescence relative humidity for that particular aerosol. In experiments 10 and 12, which have decay rates well above 2 day^{-1}, the chamber was initially cooled to 20 °C before the UV lights were turned on. Once the UV lights were activated the temperature then increased to 25 °C and the RH settled at the values indicated in Table 1. So for these experiments the RH was above 80% (the deliquescence point of $(NH_4)_2SO_4$) for several minutes, potentially resulting in aqueous aerosol. Experiment 11 also reached a relative humidity above deliquescence, yet it does not show this increased nitrate loss rate. The ratio of organics and nitrates to sulfate (seed) particles was much lower in experiment 11 compared to experiments 10 and 12. Thus, the conditions of experiment 11 differed significantly from the conditions of experiment 10 and 12, but why this would result in different hydrolysis is currently unclear. Future work should focus on the fate of ON at higher (> 60%) relative humidity. The results presented here suggest that the ON formed from α-pinene photo-oxidation hydrolyze at a rate of approximately 2 day^{-1} at RH 20-60%, do not hydrolyze at an observable rate below an RH of 20%, and hydrolyze at a rate as high as 8 day^{-1} at higher RH."

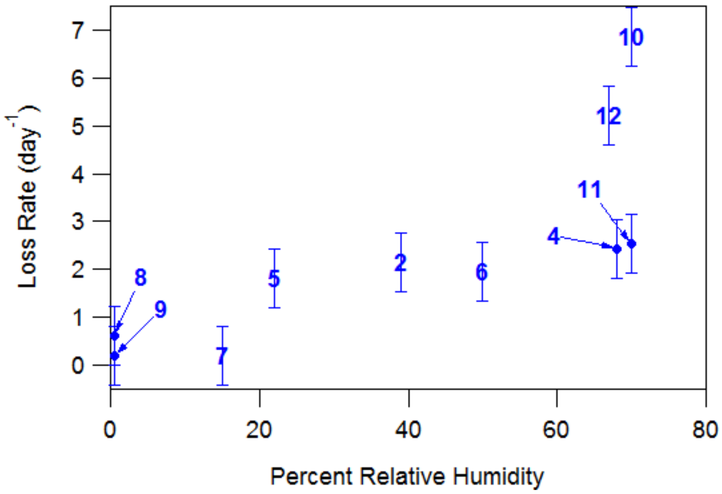

Figure 5. The organic nitrate loss rate as a function of relative humidity.

11 – Figure 2 is puzzling to me. Why don't the intermittent green traces match their previous trend? You interpret this as meaning that the more oxidized species are monotonically increasing, but that is not apparent here; they appear to have decreased around 200 minutes. This requires more explanation/interpretation.

We have since learned that there are start-up effects when the reagent ion is switched in the CIMS. The sensitivity slowly adjusts to a steady state value over the first ~20 minutes after start-up. Despite these issues with short-term trends the long-term trends are still useful. This has been clarified in the revised manuscript:

"In short time periods after switching reagent ions the sensitivity of the HR-ToF-CIMS slowly adjusts to a steady state value. Minor changes during these short time periods should be taken with caution but the overall trends over the 4.5 hour experiment are useful in viewing oxidation trends."

12 – Figure 3: the re-increase of the particle phase signals after cooling that you mention in the text isn't super clear to me here – clearer is the gas phase loss. Maybe this suggests that the re-condensing species are mostly partitioning to the walls? Could discuss in terms of relative SA of particles vs. walls.

It is true that in this cooling phase many compounds are likely lost to the walls as these are the coolest location of the chamber during active cooling. The primary purpose of this figure is to show that organic nitrates are semi-volatile, as shown by their evaporation upon heating. The temperature data is not used in a quantitative way in calculating partitioning. More discussion has been added to the revised manuscript:

"Other processes may influence particle and gas concentrations of organic compounds. Continuing reactions with O_3 and nitrate radicals (since O_3 and NO_2 are both present) limit the ability to stop all chemical activity. This is seen in the gas phase compounds, some of which appear to be changing in concentration after the UV lights are off. Despite this a clear change is seen in all compounds with a temperature increase. During the cooling phase (beginning at t = 320 minutes) the particle phase organic and nitrate concentrations do not return to the original levels. It is likely that some organic compounds are lost to the walls of the Teflon chamber, especially since they reach the coldest temperatures during active cooling, and thus Org/SO_4 does not return to the values seen before temperature changes began. Despite these limitations it is clear that both the Org/SO_4 and ON^{aer}/SO_4 ratios decrease with heating, consistent with semi-volatile organics and organic nitrates."

13 – Figure 4 comparison: Is the Rollins et al VBS fit also based on mole fraction, not mass fraction? Could this matter here for the discrepancy?

Rollins et al also uses a mole basis as their measurements are done with thermal dissociation-laser induced fluorescence (TD-LIF), which converts all organic nitrates to NO_2 before detection. Thus, this is not expected to be related to the observed difference. There is a different way that the measurement method may contribute to differences, which has been noted in the revised manuscript:

"It should also be noted that the thermal dissociation-laser induced fluorescence (TD-LIF), used by Rollins et al. 2013, has been shown in a recent study to measure PM ON a factor of two higher than the AMS (Ayres et al., 2015). While the reasons for this difference are unknown, it would result in an increased partition coefficient compared to the one calculated from the AMS (or ACSM) and explain part of the observed difference."

14 – Suggest to omit Figure 5. I'm not convinced RH is the driving factor here.

While RH may not be the only factor affecting the observed nitrate loss rate, our data do suggest that the RH affects hydrolysis in a non-linear way, as further discussed in our response to comments 1 and 10. Previous work (Liu et al., 2012; Boyd et al., 2015) has also found that ON hydrolysis proceeds under humid conditions but not under low RH. Other measured factors such as precursor concentration, OH levels and organic aerosol levels were analyzed for correlation with nitrate loss rate and no consistent trend was found.

15 – Supplemental Fig. S2: O3 goes up quite a bit over your experiments – could this compete with OH for your α-pinene? Or react with NO2 and affect N balance (this is where I started wondering about whether N2O5 could be another part of the N balance story). Is NO2+O3 in your SAPRC model?

The two major pathways of ON formation are OH+NO or direct oxidation by NO_3. Ozone and NO_2 can react to form NO_3 but this is quickly photolyzed and does not compete in ON formation in these experiments. Ozone formation in these experiments is roughly proportional to OH concentrations, and thus H_2O_2 concentrations. Thus, experimental conditions had similar ratios of these oxidants. The lifetime of α-pinene is similar at the OH or O_3 levels in these experiments. Regardless, the interest of these experiments is the organic nitrates formed in the oxidation of α-pinene through NO reacting with the peroxy-radical. Some of the ozone is expected to react with α-pinene, but the ozonolysis of α-pinene is not expected to result directly in ON, which is the focus of this work.

Responses to Reviewer #2

1 – Page 20636, line 21. The authors noted that the NO and NO2 fragments were converted to ppb using the molecular weight of these fragments. I do not think this is correct. The NO and NO2 mass concentrations are nitrate (-ONO2) equivalent mass, so to convert them into molar basis, the molecular weight of –ONO2 should be used. If the authors indeed calculated the mixing ratios incorrectly, it would change the partitioning coefficients and affect the conclusions of the manuscript.

The manuscript has been corrected and Figure 4 has been adjusted. Additional discussion has been added about the partitioning and differences between this and the previous work by Rollins et al. 2013. The manuscript has been updated (as previously discussed in response to Reviewer 1, #3):

"the mass concentration of nitrate measured by the ACSM was converted to mixing ratio (ppb) using the molecular weight of the nitrate functional group (62 g/mol)"

"These results indicate that under typical ambient conditions (< 40 μg/m^3 of OA) 5-10% of organic nitrates formed from the photo-oxidation of α-pinene under high NOx conditions are expected to partition to the particle phase. This is significantly lower than the organic nitrate partitioning calculated by Rollins et al. (2013) for organic nitrates measured in Bakersfield, CA during the CalNex campaign in 2010 as shown in Fig. 4. The difference could be attributed to differences in precursor molecules and levels of oxidation. Studies have shown that high NO_x conditions can shift photochemical oxidation products of terpenes towards higher volatility compounds (Wildt et al. 2014). Rollins et al. determined using the SPARC model (Hilal et al., 2003) that precursor molecules (a mix of C5-C15 VOCs) would need two stages of oxidative chemistry beyond the initial oxidation of the VOC to reach the point when 19-28% would partition to the particle phase for a C_{OA} of 3 μg/m^3. This suggests that the ON formed in our experiments have undergone fewer than three generations of oxidation as they are more volatile than the ON measured in Bakersfield during CalNex 2010. It should also be noted that the thermal dissociation-laser induced fluorescence (TD-LIF), used by Rollins et al. 2013, has been shown in a recent study to measure PM ON a factor of two higher than the AMS (Ayres et al., 2015). While the reasons for this difference are unknown, it would result in an increased partition coefficient compared to the one calculated from the AMS (or ACSM) and explain part of the observed difference."

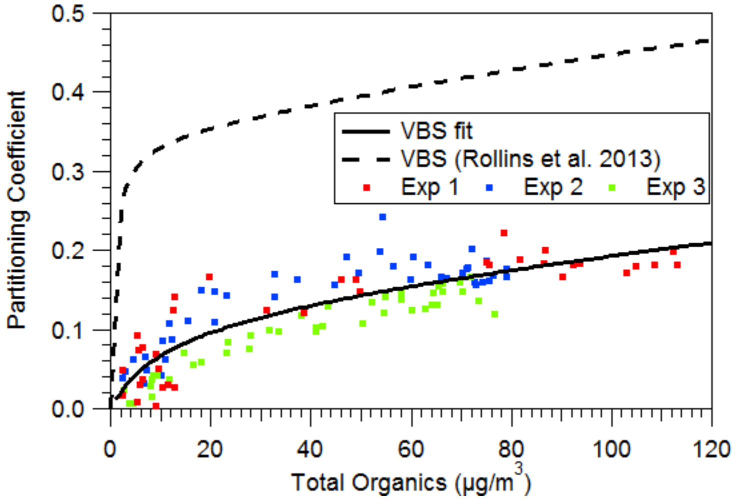

Figure 4 – Volatility basis set fit from this work shown with data from Expts 1, 2, and 3 and the VBS fit from Rollins et al. (2013)

2 – Page 20637, section 2.2. The calculation of partitioning coefficient is subjected to many uncertainties, which should be discussed in detail and the authors should evaluate how such uncertainties might affect the conclusions of the manuscript.

a. It is assumed that only five major forms of oxidized nitrogen are present. As this assumption forms the basis of the subsequent analysis, the authors need to justify this assumption. Other nitrogen-containing species can be formed in their experiments, e.g., NO3, N2O5, HO2NO2 (especially H2O2 is used as OH precursor, which would lead to formation of a large amount of HO2), HONO, etc. These species could be photolyzed or react with OH, but the authors need to provide justifications that all other nitrogen-containing species are negligible. If not, how would this affect the calculation of partitioning coefficient?

Please reference the response to Reviewer 1, comment #4. Other species which contain reactive nitrogen have been added to a new figure (S3) which shows that concentrations are several orders of magnitude lower than the five major forms.

b. It is noted that the H2O2 concentration used in the model was adjusted until the modeled NO, NO2, and O3 matched experimental data. Firstly, why is the H2O2 concentration not an input? Based on the experimental description, the concentration of H2O2 should be known (e.g., can be calculated from the injected H2O2 volume and chamber volume). Secondly, as seen in Table 1, the modeled H2O2 has a large variation. Is this expected? i.e., did the authors inject different amounts of H2O2 into the chamber in different experiments? If so, what are the H2O2 concentrations injected (this info needs to be in include in the table)?

In experiments 1, 2, and 3 (the experiments which were used to calculate partitioning) the H_2O_2 was injected by passing air through a solution of H_2O_2 and then into the chamber. Thus, the amount injected was not known and this had to be estimated by tuning the concentrations of NO, NO_2, and ozone in the SAPRC model. In the other experiments a measured liquid volume of H_2O_2 was heated as air was passed over it and into the chamber. The volume of H_2O_2 injected was varied between experiments but did not match the model results - the model matched data for NO, NO_2 and ozone at H_2O_2 levels lower than those injected. This could be because the injection method was not efficient, or it could be that the photolysis of H_2O_2 (which ultimately drives the concentrations of NO, NO_2 and ozone) is not accurately represented in the model. The absorption cross section of H_2O_2 only minimally intersects with the UV spectrum. Thus, small changes in the UV spectrum (or errors in measurements of the spectrum) could cause significant errors in estimated concentrations of [OH].

*c. If the H2O2 concentration indeed varies that much, it would seem very likely that the fraction of a-pinene reacting with OH vs. O3 also varies from experiment to experiment. Would different types of organic nitrates be formed in different experiments, depending on the reaction pathways? If so, how would this contribute to the calculation of the partitioning coefficient of organic nitrates as a whole***?**

As discussed in response to Reviewer 1, #15: The two major pathways of ON formation are OH+NO or direct oxidation by NO_3. Ozone and NO_2 can react to form NO_3 but this is quickly photolyzed and does not compete in ON formation in these experiments. Ozone formation in these experiments is roughly proportional to OH concentrations, and thus H_2O_2 concentrations. So experimental conditions had similar ratios of these oxidants. The lifetime of α-pinene is similar at the OH or O_3 levels in these experiments. Regardless, the interest of these experiments is the organic nitrates formed in the oxidation of α-pinene through NO reacting with the peroxy-radical. Some of the ozone is expected to react with α-pinene, but the ozonolysis of α-pinene is not expected to result directly in ON, which is the focus of this work.

d. Related to the previous comment – from Figure S2 it appears that the ozone concentration is quite high. Is the a-pinene concentration measured? If so, it should be included in Figure S2.

Measurements of α-pinene were not possible in these experiments because other peaks interfere with its measurement with the HR-ToF-CIMS; however, according to the model all the α-pinene has reacted well before the exponential is fit to the ON loss rate in the particle phase. As mentioned in the response to the comment above the lifetimes of α-pinene towards reaction with OH and O_3 were similar based on the end of experiment concentrations, but the slow build-up of ozone in the first hour means that the majority of α-pinene reacts first with ·OH.

e. This comment is not just relevant for the determination of the partitioning coefficient, but also relevant for the evaluation of organic nitrate hydrolysis. ACSM is a unit mass resolution instrument and cannot differentiate ions at the same mass. E.g., m/z 30 can be CH2O+ and NO+. Here, I guess the authors assume that all m/z 30 is from NO+. How did the authors justify this assumption? It has been shown that for organic nitrates formed from b-pinene+NO3 (Boyd et al., 2015), the organic CH2O+ fragment accounts for a fairly fraction of the total signal at m/z 30. If this applies for the current study, the particle-phase organic nitrate would be over-estimated, which would affect the calculated partition coefficient. It is possible that the organic interference at m/z 30 would depend on the particular system. However, the authors need to discuss what does this mean for their data analysis and conclusion.

The standard fragmentation table is used to calculate NO+ (Allan et al., 2004). Based on this table a portion of the m/z 30 signal is allocated to $(N_{15})_2$+ based on the measured N_2+. A portion is also allocated to organics, as the reviewer suggests; and the remainder is attributed to NO+. There is of course uncertainty associated with using the standard fragmentation table. We are currently planning future experiments in which we will measure organic nitrates using a high resolution time of flight aerosol mass spectrometer (HR-ToF-AMS). With data from the HR-ToF-AMS we will be able to evaluate the validity of this standard fragmentation table by comparing unit mass with high resolution data; in the meantime we are using the standard approach to separate nitrate mass used in unit mass resolution analysis. We do not own a HR-ToF-AMS (the planned experiments are with a borrowed instrument) and therefore do not have the high resolution data available for these experiments.

3. Page 20639. Figure 2. Are these the only organic nitrate species measured in the experiments? Please clearly state this in the manuscript.

The compounds shown in Figure 2 are a selected few of many which are observed with the CIMS. This has been clarified in the revised manuscript:

“Many compounds are identified with the CIMS and a select few of the most prominent compounds were chosen for Fig. 2”

4. Page 20640, discussion on gas-particle partitioning. The authors changed the chamber temperature to evaluate the reversibility of organic nitrate partitioning. The authors attributed all observations as a result of gas-particle partitioning, which I think is over-simplifying and not very convincing. I focus my comments on Figure 3 here.

a. First, what is the time series of a-pinene concentration? When the temperature perturbation occurred (~240 min), has all the a-pinene reacted? As seen from the figure, during the period between UV off and temperature increase, there is still an increase in org/SO4, which would seem to suggest a-pinene is still being reacted and SOA is still being formed? If a-pinene has not all been reacted away, can some of the trends we are seeing here a result of on-going reactions?

It is true that some chemistry appears to continue in both the gas and particle phases, although based on the model results the α-pinene has all reacted by this time. However, the primary purpose of this figure is to show that organic nitrates appear to volatilize when temperatures increase, suggesting that the organic nitrates are semi-volatile and their partitioning to the particle phase is reversible. Ozone and NO_2 are present in the chamber during this time, so nitrate radicals can be expected. Some chemistry may continue, but despite this a response in both the particle and gas phase to temperature increase is clearly observed. This has been clarified in the revised manuscript as noted in response to comment #12 from Reviewer 1.

b. The authors attributed the increase in gas-phase species as a result of evaporation of these species from the particle phase at higher temperatures. In the figure, during the warming period, all the particle signals decreased, however, some of the gas-phase signals reached a maximum first and then decreased, why? It seems that there is more than gas-partitioning going on here.

Chemistry may continue as gas and particle phase concentrations continue to change slightly without UV light. A potential explanation is that both ozone and nitrate reactions continue to age gas and particle phase compounds. As mentioned in the response to comment a. above the data still show clearly that the particle-phase concentrations respond to an increase in temperature, consistent with semi-volatile species evaporating at higher temperature.

c. At about ~320 min, the temperature decreased. The authors attributed the decrease in gas-phase signals to repartitioning of these species to the particle phase. However, the increase in the particle-phase concentration is not as substantial (much lower than pre-temperature ramp loading). Why?

When the chamber is cooled the area which will be cold quickest will be the chamber walls. It is not surprising that many gas phase compounds condense to the cold walls of the chamber instead of to particles. The key information in Figure 3 is that when warmed the organic nitrates evaporate from the particle phase. Temperature data (both heating and cooling) is not used in a quantitative way. This has been clarified in the revised manuscript.

d. What is the role of gas-phase wall loss in these observations? One can also argue that the change in gas-phase species (in Figure 3c) can be affected by gas-phase wall loss.

We agree, as mentioned in our responses to the above comments.

5. Page 20642 onward, I do not think that the authors can make any definite conclusions regarding organic nitrate hydrolysis based on their data.

a. Line 22. Why did the concentration in Expt 1 continue to increase? Please explain.

In this experiment lower concentrations of α-pinene and hydrogen peroxide delayed and limited the production of SOA. Thus, there was not enough time at the end of the experiment (when OA formation had ceased) to fit an exponential. The data from this experiment were still useful for partitioning calculations, but they were not used to find the nitrate loss rate. This explanation has been updated in the revised manuscript.

b. In determining the rate of decrease in particle-ON, I assume the chamber lights are off? (otherwise further photochemical reactions can affect gas and particle-phase composition).

The chamber lights were left on during that time period to avoid the formation of NO_3 radical (from NO_2 + O_3). While we agree that some further photochemical reactions may have been occurring, during that time period all α-pinene had reacted and the OA composition was not changing significantly (based on f44 signal in the ACSM). With high concentrations of O_3 and NO_2 in the chamber nitrate radicals would form in the dark – which can directly form organic nitrates if double bonds are still present in gas-phase compounds.

c. If the lights are off, are there nitrate radicals in the chamber, are there any further reactions induced by the nitrate radicals?

As indicated in our response to 5b above, the lights were left on so nitrate radicals were not expected to be present.

d. The authors need to show the decay (raw data) of the nitrates in the SI, and show clearly how the decay rate is determined. e. What does the "decay rate" mean for experiments with RH=0% (Expts 8 and 9)? Do the authors think that's also from hydrolysis? If so, where does particle water come from? The ammonium sulfate seeds should be solid for a chamber RH of 0%.

Figure S4 has been added to show how this was calculated for experiments – an exponential decay was fit to wall-loss corrected concentrations of organic nitrates and organics. As seen in this figure, even what appears to be a flat line can have a nonzero exponential decay due to scatter in the data. Thus, a fitted/calculated nitrate loss near zero does not necessarily imply hydrolysis was significant or that water was present in the particles.

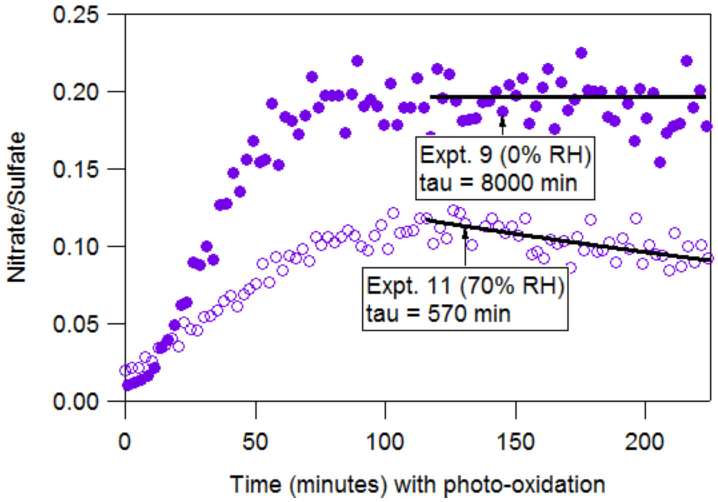

Figure S4 – Exponential decay for a low RH (Expt. 9) and high RH (Expt. 11) conditions

f. Overall, the authors attributed the decay in nitrates to hydrolysis. To do so, the authors must first justify that no other processes or reactions can contribute to the decay of the nitrates (e.g., comments b and c, etc)

While it is true that other factors can play a role in the decay of particulate nitrate, the correlation with relative humidity, which follows a similar trend to the work from Liu et al. (2012) is consistent with hydrolysis as the main factor in the observed decay of particulate nitrate. The very low nitrate loss rate at RH below 20% suggests that other factors are minimal in comparison with RH. Other measurements from experiments (organic aerosol concentration, ·OH levels, precursor concentrations) were analyzed for trends with nitrate loss rate but no trends were observed besides that with RH.

Ultimately, what we measure are losses of particle-phase organic nitrates. Based on previous work (Liu et al., 2012; Boyd et al., 2015; Rindelaub et al., 2015) the most likely explanation for these particle-phase losses is hydrolysis of the organic nitrates. Neither we nor the previous work observed hydrolysis directly (conversion of the -ONO_2 group to an –OH group). This has been clarified in the revised manuscript.

g. One way to evaluate hydrolysis rates would be to normalize the decay in nitrates in the humid experiments to those in dry experiments, similar to the analysis in Boyd et al. (2015). Have the authors look into this?

Since the decay rate at 0% RH is approximately zero this would not change the results significantly. Figure S4 illustrates the difference between exponential decay at high and low RH.

h. What are the uncertainties of the data points shown in Figure 5? Is there supposed to be an increasing trend, or the authors think that the loss rate should be constant? Why? Either case, more justifications and discussions are needed.

Uncertainties from the ACSM collection efficiency (CE) are not expected to play a role unless CE were to change during the time that the exponential was fit, which is not likely. Wall loss effects are not expected to contribute to uncertainty significantly because the nitrate signal is normalized to sulfate. The uncertainty associated with using the standard fragmentation table (see comment 2e above) would only affect the results if any error introduced by the lack of high resolution data (i.e. the ratio of nitrate mass from high resolution data vs. nitrate mass from low resolution data), changes during the time of the experiment. These changes are expected to be minor during the relatively short time (~ 90 minutes) when the exponential is fit. Based on the variation of measured/fit nitrate loss rate at RH=0% some uncertainty exists. The difference between the measurements of nitrate loss rate at RH=0% (0.6 day^{-1}) has been added to the figure as an estimate of uncertainty.

i. The authors noted that Expt 10 is an exception, "possibly due to effects of being near the deliquescence relative humidity for that particulate aerosol". Firstly, do the authors mean the DRH for ammonium sulfate, or the organic + sulfate aerosol? The DRH for ammonium sulfate is ~80%, so at the experiment RH of 70%, the ammonium sulfate should be solid? Secondly, the experimental conditions in Expt 10 and Expt 11 are very similar, yet the loss rate is drastically different? Why? This goes back to the previous comment, what are the uncertainties of the decay rates?

As in response to Reviewer 1, comment #10: An additional experiment was conducted at high (67%) RH and the results warranted additional discussion and an update to Fig. 5:

"Experiments conducted at an average RH of 67% or higher can exhibit a significantly higher decay rate, most likely due to effects of being near the deliquescence relative humidity for that particular aerosol. In experiments 10 and 12, which have decay rates well above 2 day^{-1}, the chamber was initially cooled to 20 °C before the UV lights were turned on. Once the UV lights were activated the temperature then increased to 25 °C and the RH settled at the values indicated in Table 1. So for these experiments the RH was above 80% (the deliquescence point of $(NH_4)_2SO_4$) for several minutes, potentially resulting in aqueous aerosol. Experiment 11 also reached a relative humidity above deliquescence, yet it does not show this increased nitrate loss rate. The ratio of organics and nitrates to sulfate (seed) particles was much lower in experiment 11 compared to experiments 10 and 12. Thus, the conditions of experiment 11 differed significantly from the conditions of experiment 10 and 12, but why this would result in different hydrolysis is currently unclear. Future work should focus on the fate of ON at high (> 60% relative humidity). The results presented here suggest that the ON formed from α-pinene photo-oxidation hydrolyze at a rate of approximately 2 day^{-1} at RH 20-60%, do not hydrolyze at an observable rate below an RH of 20%, and hydrolyze at a rate as high as 8 day^{-1} at higher RH."

j. Page 20643, lines 9-15. The authors need to discuss how the hydrolysis rate determined in this study compared to those reported in recent literature. For instance, Rindelaub et al. (2015) studied the formation of organic nitrates from photooxidation of a-pinene (same as this study). While Rindelaub et al. (2015) did not report a hydrolysis rates for organic nitrates, their results suggested that organic nitrates formed from a-pinene+OH+NOx appear to hydrolyze fairly quickly, which is different from the current study? Please discuss. Furthermore, Boyd et al. (2015) reported that majority of the organic nitrates formed from b-pinene+NO3 are primary/secondary nitrates and are stable, while ~10% of the organic nitrates are tertiary and hydrolyze on the order of few hours. The hydrolysis rates determined in the current study is fairly slow, are the authors implying most of the organic nitrates formed are primary/secondary? (this would seem to contradict the results by Rindelaub et al. (2015)?)

The lifetime of particulate ON in this study (12 h) is similar to that measured in two previous studies – Liu et al. 2012 (6 h), Boyd et al. 2015 (3-4.5 h). This discussion has been added to the manuscript as discussed similarly in response to Reviewer 1, comment #5:

"This 12 hour lifetime (loss rate of 2 day^{-1}) for particulate organic nitrates is consistent with other studies. Liu et al. (2012) observed a trend similar to that shown in Fig. 5 in chamber experiments in which ON were formed through the oxidation of tri-methyl benzene using HONO as the ·OH and NO_x source. In those experiments, PM nitrate was found to have negligible loss rate below 20% RH but a lifetime of 6 hours at 40% RH and higher. Perring et al. (2009) estimated the lifetime of isoprene nitrates to be between 95 min and 16 hrs based on their branching ratio in isoprene ·OH oxidation.

Boyd et al. (2015) measured a lifetime of 3-4.5 hours for 10% of ON formed from NO_3 oxidation of β-pinene, with a much longer lifetime for the remaining 90%. This suggested that 10% of the ON functional groups were tertiary with the rest being primary or secondary as those have been shown to hydrolyze much slower in the bulk phase (Darer et al., 2011; Hu et al., 2011). In our results hydrolysis is not limited to 10% of ON, suggesting that a much higher portion is tertiary ON functional groups. This shows that hydrolysis proceeds at similar rates for ON formed through a different mechanism (·OH plus NO) though the split between primary/secondary and tertiary ON functional groups can be very different for ON formed from different mechanisms, even for similar VOC precursors such as α-pinene and β-pinene. This has important implications in attempts to model ON and the resulting NO_x recycling."

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