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. The revised manuscript (with changes shown) has been included at the end this document.

Note that sections "Gas-Particle Partitioning of Organic Nitrates" and "Hydrolysis of Organic Nitrates" were switched to improve the manuscript readability. Figure numbers have changed and these changes are pointed to in this response document. Changes to figure numbers are as follows:

Fig. 3 → Fig. 4

Fig. 4 → Fig. 5

Fig. 5 → Fig. 3

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 manuscript. The relevant excerpt now reads:

"Particle-phase ON hydrolysis rates consistent with observed ON decay exhibited a nonlinear dependence on relative humidity (RH): An ON decay rate of 2 day^{-1} was observed when the RH ranged between 20 and 60%, and no significant ON decay was observed at RH lower than 20%. In experiments when the highest observed RH exceeded the deliquescence RH of the ammonium sulfate seed aerosol, the particle-phase ON decay rate was as high as 7 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 5 (partitioning coefficient, previously Fig. 4) and discussion of the results has been included below. The Rollins et al. VBS fit has been removed from Fig. 5 as it was only relevant below 10 $\mu g/m^3$ (the concentrations measured in the 2010 CalNex field campaign).

"As seen in Fig. 5 these results indicate that under typical ambient conditions (< 40 $\mu g/m^3$ 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. In those measurements >30% partitioning of ON was observed at organic aerosol concentrations of 10 $\mu g/m^3$. 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 $\mu g\ m^{-3}$. This may suggest 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."

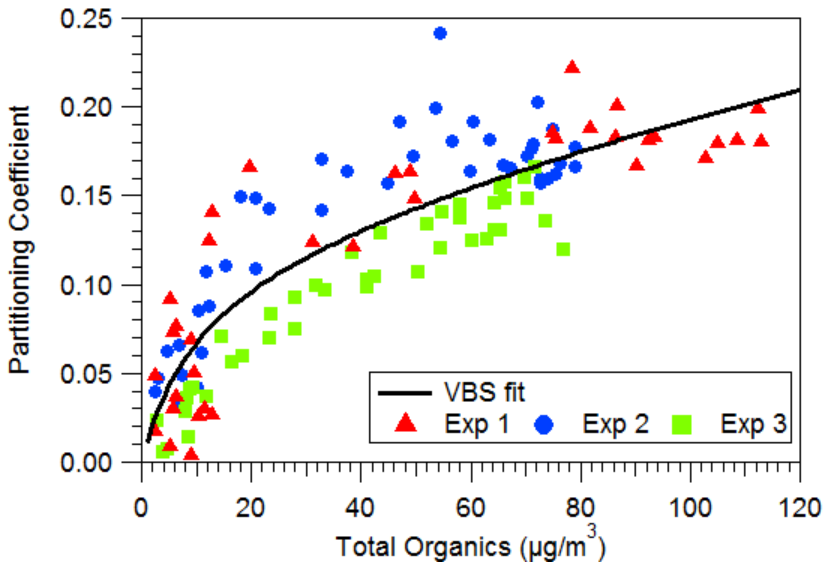

Figure 5 – Volatility basis set fit from this work shown with data from Expts. 1, 2, and 3.

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 S2 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 S2 shows that, based on the Statewide Air Pollution Research Center (SAPRC) model (http://www.engr.ucr.edu/~carter/SAPRC/), the concentrations of other forms of reactive nitrogen are orders of magnitude lower than the concentrations of these five forms."

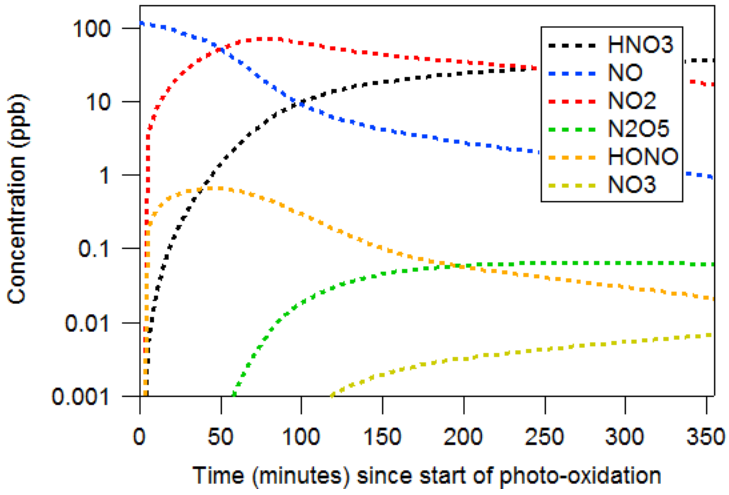

Figure S2 – SAPRC results from Expt. 7 showing significant nitrogen compounds

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 suggests 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 higher portion is tertiary ON functional groups."

"Similar VOC precursors such as α-pinene and β-pinene can form different fractions of primary/secondary and tertiary 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 carbon-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:

"All PM nitrate (measured by the ACSM as NO^+ and NO_2^+ fragments) was assumed to be organic because no inorganic nitrate was introduced in these controlled experiments. Nitric acid is formed in the gas phase as well as in the particle phase through hydrolysis, but it is assumed that nitric acid concentrations are negligible in the particle phase due to its high vapor pressure (Fry et al., 2009). A Henry's Law calculation suggests that the total amount of aqueous HNO_3 in particles is 3 orders of magnitude lower than that in the gas phase."

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 also decreased in some experiments, but their loss rate was lower and more variable than that of nitrate. 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 – slightly 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:

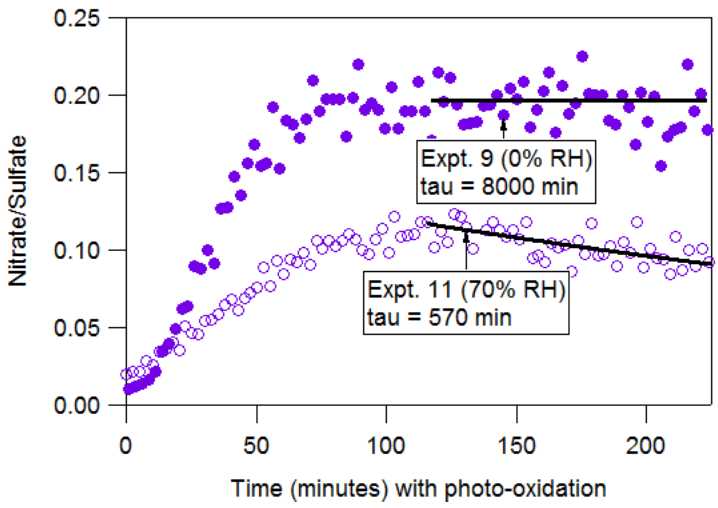

Figure S4 – Exponential decay for a low RH (Expt. 9) and high RH (Expt. 11) conditions

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. 3 (previously Fig 5):

"Experiments conducted at an average RH of 67% or higher can exhibit a significantly higher decay rate, probably due to effects of being near the deliquescence relative humidity of the ammonium sulfate seed 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. For these experiments the RH was above 80% (the deliquescence RH, DRH, of $(NH_4)_2SO_4$ for several minutes, potentially resulting in aqueous aerosol. Experiment 11 also reached a relative humidity above deliquescence, yet it shows a lower nitrate loss rate than Expts. 10 and 12. The ratio of organics and nitrates to sulfate (seed) particles was much lower in Expt. 11 compared to Expts. 10 and 12, but whether and why this would result in a different nitrate loss rate is currently unclear. The relative humidity in Expt. 4 did not reach the DRH of $(NH_4)_2SO_4$. Future work should focus on the fate of ON at higher (> 60%) relative humidity. The generally higher nitrate loss rate at higher RH makes hydrolysis of particulate nitrate functional groups the most plausible explanation for the observed decay."

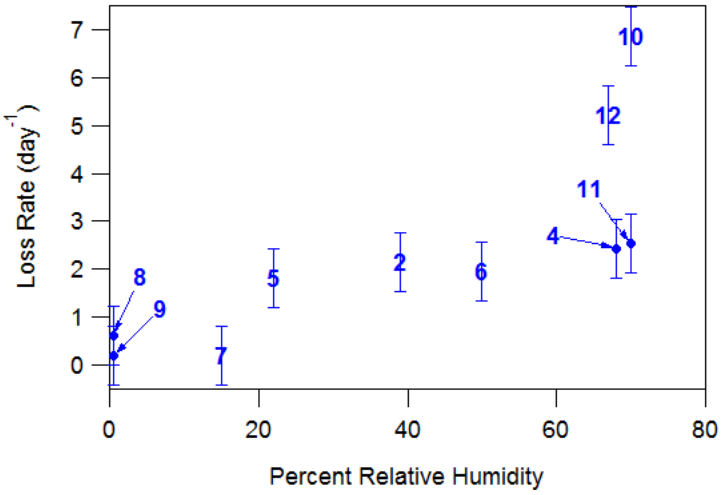

Figure 3. The organic nitrate loss rate as a function of relative humidity.

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) instrument used by Rollins et al. (2013) has been shown in a recent study to measure PM ON a factor of two higher than the ON measured by aerosol mass spectrometers (Ayres et al., 2015) which utilize similar measurement and detection techniques as the ACSM used in this work. While the reasons for this difference are unknown it would result in a higher partitioning 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 5 (previously Fig. 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 VBS fit for Rollins et al. 2013 has been removed as their data were mainly relevant below 10 μg/m^3) 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)"

"As seen in Fig. 5 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. In those measurements >30% partitioning of ON was observed at organic aerosol concentrations of 10 μg/m^3. 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 may suggest 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."

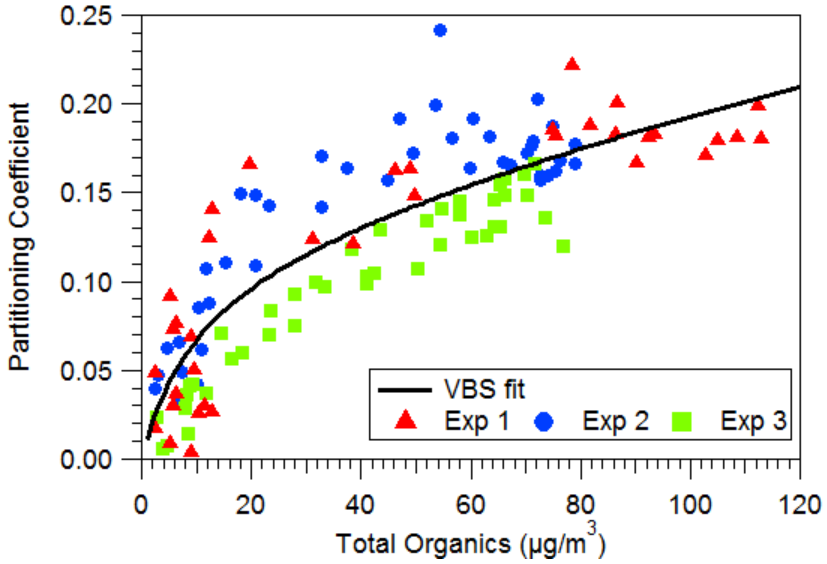

Figure 5 – Volatility basis set fit from this work shown with data from Expts. 1, 2, and 3.

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 (S2) 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.

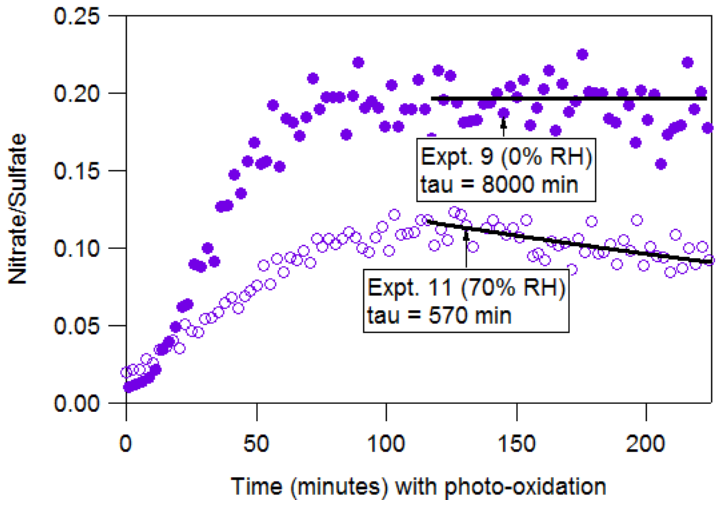

Figure S4 – Exponential decay for a low RH (Expt. 9) and high RH (Expt. 11) conditions

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. 3 (previously Fig. 5):

"Experiments conducted at an average RH of 67% or higher can exhibit a significantly higher decay rate, probably due to effects of being near the deliquescence relative humidity of the ammonium sulfate seed 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. For these experiments the RH was above 80% (the deliquescence RH, DRH, of $(NH_4)_2SO_4$ for several minutes, potentially resulting in aqueous aerosol. Experiment 11 also reached a relative humidity above deliquescence, yet it shows a lower nitrate loss rate than Expts. 10 and 12. The ratio of organics and nitrates to sulfate (seed) particles

was much lower in Expt. 11 compared to Expts. 10 and 12, but whether and why this would result in a different nitrate loss rate is currently unclear. The relative humidity in Expt. 4 did not reach the DRH of $(NH_4)_2SO_4$. Future work should focus on the fate of ON at higher (> 60%) relative humidity. The generally higher nitrate loss rate at higher RH makes hydrolysis of particulate nitrate functional groups the most plausible explanation for the observed decay."

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:

"No direct observation of hydrolysis (conversion of the $-ONO_2$ group to an –OH group) has been made in this or previous work. The estimated hydrolysis lifetime of 12 hours (loss rate of 2 day^{-1}) for particulate organic nitrates is similar to hydrolysis rates suggested by other studies under humid conditions. Liu et al. (2012) observed a trend similar to that shown in Fig. 3 in chamber experiments in which ON were formed from 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 minutes and 16 hours depending 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 suggests 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 higher portion is tertiary ON functional groups."

References

Ayres, B. R., Allen, H. M., Draper, D. C., Brown, S. S., Wild, R. J., Jimenez, J. L., Day, D. a., Campuzano-Jost, P., Hu, W., de Gouw, J., Koss, a., Cohen, R. C., Duffey, K. C., Romer, P., Baumann, K., Edgerton, E., Takahama, S., Thornton, J. a., Lee, B. H., Lopez-Hilfiker, F. D., Mohr, C., Goldstein, a. H., Olson, K. and Fry, J. L.: Organic nitrate aerosol formation via NOx + BVOC in the Southeastern US, Atmos. Chem. Phys. Discuss., 15(12), 16235–16272, doi:10.5194/acpd-15-16235-2015, 2015.

Boyd, C. M., Sanchez, J., Xu, L., Eugene, a. J., Nah, T., Tuet, W. Y., Guzman, M. I. and Ng, N. L.: Secondary organic aerosol formation from the β-pinene+NO3 system: effect of humidity and peroxy radical fate, Atmos. Chem. Phys., 15(13), 7497–7522, doi:10.5194/acp-15-7497-2015, 2015.

Chuang, W. K. and Donahue, N. M.: A two-dimensional volatility basis set – Part 3: Prognostic modeling and NOx dependence, Atmos. Chem. Phys. Discuss., 15(12), 17283–17316, doi:10.5194/acpd-15-17283-2015, 2015.

Hilal, S., Karickhoff, S. and Carreira, L.: Prediction of the vapor pressure boiling point, heat of vaporization and diffusion coefficient of organic compounds, QSAR Comb. Sci., 22(6), 565–574, doi:10.1002/qsar.200330812, 2003.

Liu, S., Shilling, J. E., Song, C., Hiranuma, N., Zaveri, R. a. and Russell, L. M.: Hydrolysis of Organonitrate Functional Groups in Aerosol Particles, Aerosol Sci. Technol., 46(12), 1359–1369, doi:10.1080/02786826.2012.716175, 2012.

Rindelaub, J. D., McAvey, K. M. and Shepson, P. B.: The photochemical production of organic nitrates from α-pinene and loss via acid-dependent particle phase hydrolysis, Atmos. Environ., 100, 193–201, doi:10.1016/j.atmosenv.2014.11.010, 2015.

Rollins, a. W., Pusede, S., Wooldridge, P., Min, K.-E., Gentner, D. R., Goldstein, a. H., Liu, S., Day, D. a., Russell, L. M., Rubitschun, C. L., Surratt, J. D. and Cohen, R. C.: Gas/particle partitioning of total alkyl nitrates observed with TD-LIF in Bakersfield, J. Geophys. Res. Atmos., 118(12), 6651–6662, doi:10.1002/jgrd.50522, 2013.

Wildt, J., Mentel, T. F., Kiendler-Scharr, a., Hoffmann, T., Andres, S., Ehn, M., Kleist, E., Müsgen, P., Rohrer, F., Rudich, Y., Springer, M., Tillmann, R. and Wahner, a.: Suppression of new particle formation from monoterpene oxidation by NOx, Atmos. Chem. Phys., 14(6), 2789–2804, doi:10.5194/acp-14-2789-2014, 2014.

Other Major Changes in Revised Manuscript

In Fig. 2 every 20 data points were averaged for the revised manuscript.

In Table 1 the significant figures were decreased on many values.

~~Hydrolysis and~~ Gas-particle Partitioning and Hydrolysis of Organic Nitrates Formed from the Oxidation of α-Pinene in Environmental Chamber Experiments

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Abstract

Gas-particle partitioning and hydrolysis of organic nitrates (ON) influences their role as sinks and sources of NO_x and their effects on the formation of tropospheric ozone and organic aerosol (OA). ~~Organic~~In this work organic nitrates were formed from the photo-oxidation of α-pinene in environmental chamber experiments under ~~varying~~different conditions. ~~A hydrolysis~~Particle-phase ON hydrolysis rates consistent with observed ON decay exhibited a nonlinear dependence on relative humidity (RH): An ON decay rate of 2 day^{-1} was ~~found for particle-phase ONs at a relative humidity of 22% or higher;~~observed when the RH ranged between 20 and 60%, and no significant ON ~~hydrolysis~~decay was observed at RH lower ~~relative humidity~~than 20%. In experiments when the highest observed RH exceeded the deliquescence RH of the ammonium sulfate seed aerosol, the particle-phase ON decay rate was as high as 7 day^{-1} and more variable. The ON gas-particle partitioning is dependent on total OA concentration and temperature, consistent with absorptive partitioning theory. In a volatility basis set the ON partitioning is consistent with mass fractions of [0 0.~~19~~11 0.~~29~~03 0.~~52~~86] at saturations mass concentrations (C*) of [1 10 100 1000] µg m^{-3}.

1 Introduction

Organic nitrates (ON) play an important role in atmospheric chemistry as they can act as sinks and sources of NO_x ($NO + NO_2$) and thereby affect the formation of tropospheric ozone and organic aerosol. The sink reaction – addition of NO to a peroxy radical (R-O-O·) to form an organic nitrate (R-O-NO_2) – breaks the ·OH initiated oxidation cycle and reduces the formation of ozone (Seinfeld and Pandis, 2006). Most R-O-NO_2 molecules are semi-volatile and are therefore expected to partition between the gas and particle phases. They can be transported in either phase and can become a source of NO_x when they are photolyzed or oxidized, contributing to the regional nature of NO_x pollution. Attempts to implement organic nitrate decomposition reactions in a chemical transport model which did not account for gas-particle partitioning of organic nitrates resulted in over-prediction of NO_x and ozone concentrations (Yarwood et al., 2012), consistent with an over-estimate of the strength of organic nitrates as NO_x sources.

Recent studies have suggested that organic nitrates in the condensed phase may undergo hydrolysis, leading to the formation of HNO_3 (Day et al., 2010; Darer et al., 2011; Hu et al., 2011; Liu et al., 2012; Browne et al., 2013; Jacobs et al., 2014; Rindelaub et al., 2015). This is a more permanent sink for NO_x

and would decrease the regeneration of NO_x from organic nitrates. While these studies have found evidence for hydrolysis of aerosol-phase organic nitrates (ON^{aer}~~)~~), it is not clear at which rate ON hydrolysis occurs. Correctly modeling organic nitrates and ozone formation depends on knowledge of the ON partitioning ~~coefficient~~ and hydrolysis rate.

While ON hydrolysis in the bulk phase has been studied for decades (Baker and Easty, 1950; Baker and Easty, 1952; Boschan et al., 1955~~)~~), organic nitrate hydrolysis in atmospheric particles has only recently started to receive attention. Day et al. (2010) observed a decrease in particulate organic nitrates measured in coastal southern California under acidic conditions at high relative humidity and hypothesized hydrolysis as the cause. Browne et al. (2013) used ON hydrolysis to justify observations over the Boreal Forest of higher levels of HNO_3 despite higher production rates of organic nitrates. The chamber experiments (0 to >80% RH) performed by Liu et al. (2012) using trimethylbenzene (an anthropogenic volatile organic compound) and HONO as ~~a precursor~~oxidant were the first to measure the hydrolysis of condensed organic nitrates. Rindelaub et al. (2015) observed ON hydrolysis while measuring partitioning of α-pinene SOA but did not directly quantify it. Boyd et al. (2015) measured hydrolysis of ON formed from nitrate radical oxidation of β-pinene.

The partitioning of organic nitrates to the particle phase is important to determine their fate as only condensed organic nitrates are expected to hydrolyze appreciably to HNO_3. Absorptive partitioning theory (Pankow, 1994; Donahue et al., 2006, Rollins et al., 2013; Rindelaub et al., 2015) has been used to describe the gas-particle partitioning of organic nitrates. Rollins et al. (2013) used partitioning data from the 2010 CalNex Campaign to find a volatility basis set distribution for ON observed at ambient aerosol concentrations. Rindelaub et al. (2015) observed the partitioning of organic nitrates formed from the ·OH initiated oxidation of α-pinene at various levels of relative humidity. However, other work has suggested that the partitioning of organic nitrates to the particle phase is irreversible (Perraud et al., 2012). The goals of this work were to form organic nitrates in controlled environmental chamber experiments from the OH· initiated oxidation of α-pinene under high NO_x conditions and various relative humidity levels and:

1. Quantify the hydrolysis rate of organic nitrates.

2. Confirm that the gas-particle partitioning of organic nitrates is reversible and can therefore be modeled by absorptive partitioning theory

~~2~~3. Parameterize the gas-particle partitioning of organic nitrates

~~3. Quantify the hydrolysis rate of organic nitrates.~~

2 Methods

2. 1 Environmental Chamber Experiments

All experiments were performed in the Atmospheric Physicochemical Processes Laboratory Experiments (APPLE) chamber located at the University of Texas at Austin (UT-Austin). The APPLE chamber is a ~12

m^3 Teflon ® bag suspended inside of a temperature-controlled room. The walls of the room are lined with UV lights which can be used to induce photolysis reactions. The intensity of the UV lights has been characterized by the photolysis rate of NO_2, which was measured to be 0.4 min^{-1}, similar to ~~the expected~~ ambient NO_2 photolysis ~~rate~~rates (e.g. 0.46 min^{-1} at a zenith angle of 40°, Carter et al., 2005). Before each experiment the bag was flushed for at least 12 hours with clean air from an Aadco clean air generator (Model 737-14A) at a flow rate exceeding 100 liters per minute (LPM). Ammonium sulfate ($(NH_4)_2SO_4$) particles (Fisher Scientific, 99.5%) were injected both to monitor wall loss rates (Hildebrandt et al., 2009) as well as to act as seed particles onto which organic vapors can condense. Gas phase NO was injected directly into the chamber from a cylinder (Airgas, 9.94 PPM ±2%) and liquid-phase α-pinene (Sigma Aldrich, 98%) was injected to a glass bulb and subsequently evaporated into the chamber with a steady stream of mildly heated air. H_2O_2, which photolyzes to 2·OH, was used as ·OH radical source and was either injected by bubbling air through an aqueous H_2O_2 solution (Fisher Scientific, 30% weight) or by injecting H_2O_2 solution into a glass bulb and subsequently ~~evaporate~~evaporating it into the chamber with a steady stream of mildly heated air. Some experiments were performed under dry conditions (<5% relative humidity); in other experiments humidity was increased by passing air through clean water and then into the chamber. Experimental conditions and results are summarized in Table 1. Results are discussed in Sect. 3.

Reactions were allowed to proceed for at least 4 hours with continuous UV light. Experiments were run in a batch mode with no injections or dilution after the experiment was started; the bag volume of 12 m^3 allowed ample time for sampling. In some cases the temperature effects on gas-particle partitioning were observed by increasing temperature to 40 °C in the chamber after the UV lights had been turned off (see Sect. 3.2).

2.1.1 Instrumentation

The composition of PM_1 (particulate matter smaller than 1 micrometer in diameter) was measured using an Aerosol Chemical Speciation Monitor (ACSM) from Aerodyne Research Inc. (Ng et al., 2011). In the ACSM, particles are flash-vaporized on a heater at 600 °C, and the resulting gas molecules are ~~then~~ ionized using electron-impact ionization. This harsh ionization method results in fragmentation of most molecules. The molecular fragments, which are measured by a quadrupole mass spectrometer, are attributed to four categories—organics, nitrate, sulfate, and ammonium - using a fragmentation table (Allan et al., 2004). The instrument alternates between normal sampling and sampling through a particle filter, enabling subtraction of a gas-phase background. During this study the ACSM was operated at a time resolution (filter/sample cycle length) of approximately 90 seconds. The size distribution of particles was measured using a Scanning Electrical Mobility System (SEMS) from Brechtel Manufacturing, Inc. The SEMS uses a Differential Mobility Analyzer (DMA) to size-select particles based on their electric mobility, which are then counted by a Condensation Particle Counter (CPC). The DMA continuously cycled between the voltages which select particles ranging from 5 to 1000 nm, resulting in a time resolution of the particle size distribution of approximately 60 seconds.

Gas phase reaction products were monitored using a High-Resolution Time-of-Flight Chemical Ionization Mass Spectrometer (HR-ToF-CIMS) from Aerodyne Research, Inc.. The HR-ToF-CIMS uses softer chemical ionization which results in minimal fragmentation of parent molecules. Mass spectra are derived from measurements of the ions' time-of-flight as they are pulsed through a low pressure chamber in a "V" shape. Two chemical reagent ions were used—water clusters ($H_3O^+ \cdot (H_2O)_n$) and iodide-water clusters ($I^- \cdot (H_2O)_n$). Water cluster ionization is most sensitive towards detection of moderately oxidized hydrocarbons; the ability to ionize and thus sensitivity is based on the relative proton affinity between the water cluster and the parent molecule (Lindinger et al., 1998). This method was used to monitor α-pinene as well as early-generation oxidation products. Iodide-water cluster ionization is most sensitive towards detection of more highly oxidized hydrocarbons; this method was used to observe later-generation oxidation products as well as HNO_3 and H_2O_2. In the work presented here data from the HR-ToF-CIMS are only used qualitatively since, as it was later discovered, a partially clogged inlet may have interfered with instrument calibration and quantitative measurements.

Concentrations of NO and O_3 were measured using Teledyne chemiluminescence NO_x and absorption O_3 monitors (200E and 400E, respectively); concentrations of NO_2 were measured via an NO_2 monitor from Environnement (Model AS32M), which uses a Cavity Attenuated Phase Shift (CAPS) method to directly measure NO_2 (Kebabian et al., 2008). The advantage of this direct NO_2 measurement is that it does not rely on NO_2 conversion to NO and therefore does not suffer from interference by other oxidized nitrogen compounds such as HONO and organic nitrates (Winer et al., 1974).

2.1.2 Data Analysis

Data from the ACSM were analyzed in Igor Pro using the software package "ACSM Local," which includes a correction for relative ion transmission efficiency as well as changes in the flow rate throughout the experiment. The SEMS volume concentration was converted to mass using the densities 1.77 g/cm^3 for ammonium sulfate and 1.4 g/cm^3 for organics and organic nitrates (Ng et al., 2007). The time series of particle mass concentration (not corrected for wall losses) during Expt. 7 is shown in Fig. S1; other experiments exhibited similar time series.

All PM nitrate (measured by the ACSM as NO^+ and NO_2^+ fragments) was assumed to be organic because no inorganic nitrate was introduced in these controlled experiments. Nitric acid is formed in the gas phase as well as in the particle phase through hydrolysis ~~as well as in the gas phase~~, but it is assumed that nitric acid concentrations are negligible in the particle phase due to its high vapor pressure (Fry et al., 2009). A Henry's Law calculation suggests that the total amount of aqueous HNO_3 in particles is 3 orders of magnitude lower than that in the gas phase.

The ACSM does not detect all sampled particles, primarily due to particle bounce at the vaporizer, resulting in a collection efficiency (CE) smaller than 1. Collection efficiency and wall losses were accounted for simultaneously by multiplying the ACSM concentrations of organics and organic nitrates by the mass concentration ratio $C_{SEMS}^{t=0}/C_{ACSM}^{seed}(t)$ as has been done in previous work (Hildebrandt et al., 2009). Here, $C_{SEMS}^{t=0}$ is the mass concentration of ammonium sulfate seed just before the UV lights are turned on and organic aerosol formation commences and C_{ACSM}^{seed} (t) is the time dependent mass

concentration of $(NH_4)_2SO_4$ measured by the ACSM throughout the experiment. This correction assumes that particles on the chamber walls participate in gas-particle partitioning as though they are still in suspension and that the suspended ammonium sulfate concentration changes only due to wall losses. It accounts for partitioning of organic vapors into wall-deposited particles (Hildebrandt et al., 2009) but does not account for losses of organic vapors onto the clean Teflon® walls (e.g. Matsunaga and Ziemann, 2010).

The ACSM standard fragmentation table was adjusted based on filter measurements taken in each experiment as described in the supplementary information. Data from the HR-ToF-CIMS were analyzed in Igor Pro (Wavemetrics) using Tofware, the software provided with the instrument. The data were first mass calibrated based on HR-ToF-CIMS reagent ions and other known ions. The baseline was subtracted and the average peak shape was found so it could be used for high resolution analysis, through which multiple ions can be identified at any given integer *m/z*. Ions up to *m/z* 300 were analyzed in high resolution mode. Only prominent ions were fit above *m/z* 200 because of the high number of possible ions at this high *m/z*. After ions were identified in the high resolution spectrum, the peaks were integrated to yield a time series of ions. Analyte ion concentrations were then normalized by the reagent ion concentrations – the sum of H_3O+, $H_3O+\bullet (H_2O)$ and $H_3O+\bullet (H_2O)_2$ for water cluster ionization and the sum of I- and $I-\bullet (H_2O)$ for iodide-cluster ionization. This correction accounts for changes in reagent ion concentrations and instrument sensitivity during and between experiments. Relative humidity can affect instrument sensitivity but this varied by less than 5% during each experiment.

The partitioning coefficient of a species is defined as the ratio of the species concentration in the particle phase to the total species concentration (gas and particle phase). For a single compound the partitioning coefficient is the same whether it is on a mass or mole basis. However, for a mix of compounds, such as those formed in ·OH-initiated oxidation, the mass and mole-basis partitioning coefficients will be different, with the coefficient expected higher on a mass basis since higher molecular weight compounds typically have lower vapor pressure. The partitioning coefficient in this work was calculated on a mole basis, in part because fragmentation in the ACSM makes it impossible to tell the original size and identity of ON molecules. This mole-basis partitioning coefficient is also more useful for most modeling efforts which group chemical species without knowledge of their exact molecular identity. The particle-phase ON concentration was quantified using data from the ACSM: the mass ~~concentrations~~concentration of ~~NO^+ and NO_2^+ fragments~~ nitrate measured by the ACSM ~~were~~was converted to mixing ~~ratios~~ratio (ppb) using the molecular ~~weights~~weight of the ~~fragments, and the sum of the PM NO^+ and NO_2^+ mixing ratios was used as the ON mixing ratio.~~nitrate functional group (62 g/mol). This assumes that the ON have only one nitrate functional group. Conversion of the ~~NO^+ and NO_2^+~~nitrate mass ~~concentrations~~concentration to mixing ~~ratios~~ratio avoids the need to assume an ON molecular weight (needed to estimated ON mass concentrations from ACSM) and is therefore deemed to be a more accurate measure of ON from the ACSM. Quantification of all gas phase ON species would necessitate calibration and identification of all ON species which is not feasible. Instead, a chamber box model and nitrogen balance was employed to estimate total gas-phase ON as described below.

2.2 Chamber Modeling and Partitioning Coefficient

In these experiments only five major forms of oxidized nitrogen are present in significant concentrations—NO, NO_2, HNO_3, ON^{gas} and ON^{aer} (gas and aerosol-phase organic nitrates, respectively). Figure S2 shows that, based on the Statewide Air Pollution Research Center (SAPRC) model (http://www.engr.ucr.edu/~carter/SAPRC/), the concentrations of other forms of reactive nitrogen are orders of magnitude lower than the concentrations of these five forms. Concentrations of NO and NO_2 were measured using gas-phase monitors, and ON^{aer} was measured using the ACSM. Concentrations of HNO_3 were approximated using the ~~Statewide Air Pollution Research Center (SAPRC) box model (http://www.engr.ucr.edu/~carter/SAPRC/). The~~SAPRC box model. The concentration of H_2O_2 cannot be estimated from the injection method used in these experiments. Therefore, the H_2O_2 concentration used in the model was adjusted until the modeled NO, NO_2, and O_3 concentrations closely matched those observed throughout each experiment as shown in Fig. ~~S2~~S3 for Expt. 7. The modeled HNO_3 concentration was then used with the measured NO, NO_2, and ON^{aer} to find the ON^{gas} based on a nitrogen mass balance ($ON^{gas} = NOx^{initial} - NO_2 - NO - ON^{aer} - HNO_3^{model}$). The partitioning coefficient ~~(ON^{aer} / ON^{aer} + ON^{gas})~~ was then calculated as a time series for each experiment.

SAPRC simulations were conducted with the reaction mechanism Carbon Bond 6 revision 2 (CB6r2), which includes organic nitrate hydrolysis through a rate estimated from a combination of the work of Liu et al. (2012) and Rollins et al. (2013) (Hildebrandt Ruiz and Yarwood, 2013). Experiments were modeled with and without organic nitrate hydrolysis to see the effect this has on the predicted ON partitioning coefficient. The overall effect of this process ~~in the model~~ was small~~: in 80% of the data points used (individual time points from each experiment) to find the volatility basis set (described below) the removal of the hydrolysis process in the model causes~~, with a maximum effect being a 5% decrease ~~in~~to the ~~calculated~~ partitioning coefficient ~~of less than 5%. The maximum decrease in partitioning coefficient (8.6%) due to removal of the modeled hydrolysis process~~ by removing the hydrolysis mechanism from the model. This corresponded to a 17% decrease in HNO_3 ~~of 27% at that particular time. This shows~~, which suggests that the partitioning coefficient estimated in this work is not very sensitive to changes in the modeled HNO_3 concentrations. For the results and analysis presented here the HNO_3 concentrations were taken from CB6r2 with the inclusion of the ON hydrolysis process for experiments above 20% RH and without the hydrolysis process for experiments below 20% RH.

According to absorptive partitioning theory (Pankow, 1994; Donahue et al., 2006), the gas-particle partitioning of an organic species depends on its vapor pressure and the concentration of organic material ~~already~~ in the ~~condensed~~particle phase. The fraction of a compound i in the particle phase (Y_i) is given by (Donahue et al., 2006):

$$Y_i = \left(1 + \frac{C_i^*}{C_{OA}}\right)^{-1} \quad (1)$$

where C_{OA} is the organic aerosol concentration and C_i^* is the saturation mass concentration of species i (the saturation vapor pressure converted to concentration units). In the volatility basis set (VBS, Donahue et al., 2006), organic species are lumped by C_i^* spaced logarithmically. This leads to an overall partitioning coefficient

$$Y_{tot} = \sum_{i=1}^{n} F_i \left(1 + \frac{C_i^*}{C_{OA}}\right)^{-1} \quad (2)$$

(Rollins et al., 2013), where F_i is the fraction of organic species in the volatility bin described by C_i^*. In this work we used measurements of C_{OA} and Y_{tot} to fit the F_i using a Matlab optimization routine. These VBS parameters can be used in models to represent the gas-particle partitioning of organic nitrates and account for changes in partitioning with temperature and C_{OA}.

3 Results and Discussion

A typical time series of compounds containing oxidized nitrogen is shown in Fig. 1 (Expt. 7). Initially the chamber contains only NO and a small amount of NO_2, in addition to α-pinene and inorganic seed aerosol. When the UV lights are activated at time = 0 the NO immediately begins to react with ·OH and other radicals to form NO_2 and additional NO_y compounds such as organic nitrates. ~~Concentrations of ON^{aer} and ON^{gas} from all experiments are summarized in Table 1.~~ Table 1 summarizes results from all experiments. Concentrations of O_3, ON^{aer}, PM organics, and ON^{gas} are averaged over approximately 20 minutes of the time when PM organics and nitrates peak in concentration. This averaging period was chosen so that experiments with different H_2O_2 concentrations could be compared even though they reach their maximum concentrations at different rates. Higher initial loading of NOx, α-pinene, and H_2O_2 resulted in higher concentrations of ozone and PM.

~~In high RH experiments (Expts 4, 10 and 11) ON^{gas} concentrations calculated using this mass balance approach are very low and sometimes below zero. This could be caused by an overestimate of wall-loss corrected ON^{aer} concentrations at high relative humidity. The wall loss correction used here and in previous work (Hildebrandt et al., 2009) assumes that particles lost to the walls still participate in partitioning as though in suspension. This assumption may be poor if small amounts of water condense onto the walls of the chamber in high RH experiments. It is also possible that at high relative humidity HNO_3 partitions to the particle phase and is measured by the ACSM. In this case it would be double counted in the mass balance as both HNO_3 and as ON^{aer}, which would lower the estimates for ON^{gas}. Due to these issues with calculating the gas-phase ON concentrations in high RH experiments only low RH experiments are used for calculating the ON partitioning coefficient.~~

Figure 2 shows time series of ~~selected~~ molecular ions identified using the HR-ToF-CIMS using water cluster ("positive mode") and iodide-water cluster ("negative mode") ionization. Many compounds are identified with the CIMS and a select few of the most prominent compounds were chosen for Fig. 2. 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. The initial data collected in negative mode show that formation of organic nitrates begins immediately after oxidation has started. ~~The~~Later in the experiment the less-oxygenated compounds observed in positive mode begin to decrease while the more highly oxygenated compounds observed in negative mode continue to increase, consistent with oxidation and conversion of less- oxidized compounds to more highly- oxidized compounds continuing throughout the experiment. Highly- oxidized compounds which still contain ten

carbon atoms (as the precursor α-pinene) begin to decrease towards the end of the experiment while fragmented ~~compound~~compounds (containing less than ten carbon atoms) continue to increase, consistent with fragmentation of the carbon backbone during oxidation. Molecular weights of the gas-phase compounds identified here range from 221 to 279 g mol^{-1} and align well with the range of molecular weights estimated by Fry et al. (2009) for particle-phase organic nitrates formed from NO_3 oxidation of α-pinene (229±12 to 434±25 g mol^{-1}). Gas-phase organic nitrates identified here are therefore expected to be semi- volatile and to partition significantly to the particle phase.

3.~~2~~1 Hydrolysis of Organic Nitrates

Concentrations of wall-loss corrected (normalized to SO_4) PM ~~organics and~~ nitrate were observed to decrease ~~towards~~at the end of most experiments. ~~(The exception was experiment 1, in which concentrations continued to increase.)~~ These decreases of PM ~~organics and PM~~ nitrate are attributed to physical or chemical processes in the gas and aerosol phases, and an exponential decay was fit to the data to quantify the decay. ~~A correlation is observed between the rate of this decay for PM nitrate and the~~ The exception was experiments 1 and 3 during which production of SOA was slow (primarily due to lower initial H_2O_2 and α-pinene) and continued throughout the experiment, so a decay could not be observed. Examples of the decay for a humid and dry experiment are shown in Fig. S4. The decay rates for each experiment are reported in Table 1 and appear to depend on relative humidity as shown in Fig. ~~5. The details for each experiment are found in table 1. In~~ 3. When the ~~four experiments with~~RH ranged between 20 and 60%, an ~~RH at 15% or below there appears to be little or~~ ON decay rate of 2 day^{-1} was observed; no ~~disappearance of nitrate. However, for experiments with~~ significant ON decay was observed at RH ~~at 22% and~~ lower than 20%. Experiments conducted at an average RH of 67% or higher ~~the nitrate loss rate is approximately 2 day^{-1}. The one exception to this is Expt. 10 (RH = 70%), which exhibited~~can exhibit a significantly higher decay rate, ~~possibly~~probably due to effects of being near the deliquescence relative humidity ~~for that particular~~of the ammonium sulfate seed aerosol.

~~Measuring~~In experiments 10 and 12, which have decay rates well above 2 day^{-1}, the ~~disappearance of nitrate with~~chamber was initially cooled to 20 °C before the ~~ACSM assumes that HNO_3 formed through hydrolysis volatilizes, consistent with its high vapor pressure (Fry et al., 2009). If HNO_3 does not volatilize completely, this method~~ 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. For these experiments the RH was above 80% (the deliquescence RH, DRH, of $(NH_4)_2SO_4$ for several minutes, potentially resulting in aqueous aerosol. Experiment 11 also reached a relative humidity above deliquescence, yet it shows a lower nitrate loss rate than Expts. 10 and 12. The ratio of organics and nitrates to sulfate (seed) particles was much lower in Expt. 11 compared to Expts. 10 and 12, but whether and why this would result in ~~an underestimate of the ON hydrolysis~~a different nitrate loss rate is currently unclear. The relative humidity in Expt. 4 did not reach the DRH of $(NH_4)_2SO_4$. Future work should focus on the fate of ON at higher (> 60%) relative humidity. The generally higher nitrate loss rate at higher RH makes hydrolysis of particulate nitrate functional groups the most plausible explanation for the observed decay.

~~These results are consistent with other studies of the~~ PM organics also decreased in some experiments, but their loss rate was lower and more variable than that of nitrate. 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 – slightly more than the resulting alcohol group from hydrolysis. Thus, the organic ~~nitrate~~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.

No direct observation of hydrolysis ~~rate.~~(conversion of the -ONO_2 group to an –OH group) has been made in this or previous work. The estimated hydrolysis lifetime of 12 hours (loss rate of 2 day^{-1}) for particulate organic nitrates is similar to hydrolysis rates suggested by other studies under humid conditions. Liu et al. (2012) observed a trend similar to that shown in Fig. ~~5~~3 in chamber experiments in which ON were formed ~~through~~from 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 ~~and~~but a ~~loss rate~~lifetime of ~~4 day^{-1}~~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.~~minutes and 16 hours depending 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 suggests 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 higher portion is tertiary ON functional groups.

Similar VOC precursors such as α-pinene and β-pinene can form different fractions of primary/secondary and tertiary 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 carbon-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.

As Table 1 shows~~, we conducted~~ experiments were conducted at varying NO_x and α-pinene concentrations, relative humidity, and hydrogen peroxide (·OH radical source) levels, which resulted in different final concentrations of PM nitrate and total OA. Liu et al. (2012) suggested that a lower PM nitrate / OA ratio at higher RH could be due to ON hydrolysis. In these experiments, the correlation between the ratio of PM nitrate/total OA (measured when total OA was highest) and RH was very low (R^2 = 0.02). Thus, based on these experiments, differences in the observed final PM nitrate / OA ~~could be~~are due to experimental conditions other than relative humidity.

3.~~1~~2 Gas-particle Partitioning of Organic Nitrates

In order to test the reversibility of ON partitioning the temperature of the chamber was increased after OA had formed (and when the UV lights were off) in some experiments. Figure ~~3~~4 shows gas and particle-phase measurements taken from a representative experiment (Expt. 2). After the UV lights are

turned off there is a 60 minute period in which the temperature stabilizes around 15 °C. This is followed by ~90 minutes of heating to a final temperature of 45 °C. After this the chamber is quickly cooled back to 15 °C. Figure ~~3b~~4b shows a time series of the Org/SO_4 and ON^{aer}/SO_4 ratios measured by the ACSM. Sulfate has a low vapor pressure and does not evaporate significantly at the temperatures investigated; therefore changes in the ON^{aer}/SO_4 and Org/SO_4 ratios with chamber temperature can be attributed to partitioning of organic nitrates and other organic species between the gas and particle phases~~.~~ or wall losses of gas-phase species. As Fig. ~~3b~~4b shows, Org/SO_4 and ON^{aer}/SO_4 decreased with increasing temperature and increased with decreasing temperature, suggesting evaporation of species at higher temperatures and their re-partitioning to the particle phase at lower temperatures.

Figure ~~3b~~4c shows the effects of temperature on various compounds measured in the gas phase. Several organic compounds – with and without ON functional groups - increase with increasing temperature. This suggests that these compounds are present in both the gas and particle phases and evaporate at higher temperature resulting in increased gas phase concentrations. As temperature is increased the percent change in the concentration of gas-phase $C_{10}H_{16}O_2$ is less than the change in $C_{10}H_{16}O_4$ and the percent change in the concentration of gas-phase $C_{10}H_{15}NO_4$ is less than the change in $C_{10}H_{15}NO_6$. This is consistent with the more highly oxidized compounds having a lower vapor pressure and evaporating less. As the temperature is decreased back to 15 °C the concentrations return to the pre-heating trends, suggesting that re-condensation to the particle-phase has occurred. These observations, as well as the trends seen in particle-phase measurements are consistent with equilibrium partitioning and inconsistent with the irreversible partitioning of ON recently suggested by Perraud et al. (2012).

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.

Table 1 summarizes ~~results from all experiments. Each value in the table is an average~~the ON partitioning coefficient averaged over approximately 20 minutes ~~of the time~~from when PM organics and nitrates peak in concentration. ~~We chose to compare the data at the maximum so that~~ Partitioning data is not calculated for experiments above 60% RH. As discussed, these experiments ~~with different H_2O_2 concentrations could be compared even~~had higher and less consistent nitrate decay rates which may affect partitioning. In addition, the wall loss correction used here and in previous work (Hildebrandt et al., 2009) assumes that particles lost to the walls still participate in partitioning as though they ~~reach their maximum concentrations at different rates. Higher initial loading of NOx, α-pinene, and H_2O_2 results in higher ozone and PM concentrations. The average partitioning coefficient of ON for this time period in each experiment is also shown; a more detailed analysis~~were still in suspension. This

assumption may be poor if small amounts of ~~ON partitioning follows. As mentioned above gas-phase ON could not be estimated reliably for~~water condense onto the walls of the chamber in these high RH experiments~~, and therefore Table 1 only shows partitioning coefficients for low RH experiments~~.

Data from the lower-concentration experiments (Expts 1, 2, and 3) were fit to a volatility basis set as these experiments were conducted under conditions which are more atmospherically relevant ~~conditions~~. Experimental data were used after total PM organics (corrected for wall losses) had reached 2 μg m^{-3} to avoid effects of noise and model uncertainty at the beginning of the experiments when concentrations of both gas- and particle-phase organic nitrates were low. Outlying points (for example, when PM organics temporarily ~~jumped to~~rose above 2 μg~~/m³~~ m^{-3} but subsequent data suggested that condensation had not begun) were removed as well. Figure ~~4a~~5 shows the data used to find the volatility basis set along with the fit. The C^* values used for this were 1, 10, 100, and 1000 μg m^{-3}; the corresponding mass fractions (F_i ~~)=)~~ calculated to give the best fit for Eq. (2) (Sect. 2.2) are F_i = 0, 0.~~19~~11, 0.~~29~~03, and 0.~~52~~86.

~~The data from higher concentration experiments (Expts 5-9) is shown with the volatility basis set trace~~As seen in Fig. ~~4b. The data selected are those from the time period from when the NOx monitor reading of NO was first below 5 ppb to ten minutes after the peak of the corrected PM nitrate signal. The NO concentration of below 5 ppb was chosen to minimize any hysteresis effects of the NO monitor on the mass balance calculation of the partitioning coefficient (time delays in measurements were observed during calibrations of the Teledyne NO_x monitor). This was not needed for low concentration experiments because they were conducted with low H_2O_2 levels and slower resulting rates – minimizing the effects of hysteresis from the NOx monitor. Data were only used up to the time of 10 minutes after the peak of PM nitrate to minimize effects of uncertainty in the wall loss correction, which increase over the course of an experiment. There is good agreement between the data points from these experiments and the volatility basis set which was found from only the lower-concentration experiments.~~

~~These~~5 these results indicate that under typical ambient conditions (< 40 μg/m^3 of OA) 5-~~20% partitioning of ON is expected.~~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 ~~coefficient~~ calculated by ~~Rollings~~Rollins et al. (2013) for organic nitrates measured in Bakersfield, CA during the CalNex campaign in 2010~~ as shown in Fig. 4.~~. In those measurements >30% partitioning of ON was observed at organic aerosol concentrations of 10 μg/m^3. 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 ~~OH +~~ oxidation of the VOC to reach the point when ~~they~~19-28% would partition ~~at 19-28%~~ to the particle phase for a C_{OA} of 3 μg~~/m³. Our chamber data using α-pinene as a precursor appears to be~~ m^{-3}. This may suggest that the ON formed in our experiments have undergone fewer than three generations of oxidation as they are more volatile than ~~that~~the ON measured in Bakersfield during CalNex 2010. It should also be noted that the thermal dissociation-laser induced fluorescence (TD-LIF) instrument used by Rollins et al. (2013) has been shown in a recent study to

measure PM ON a factor of two higher than the ON measured by aerosol mass spectrometers (Ayres et al., 2015) which utilize similar measurement and detection techniques as the ACSM used in this work. While the reasons for this difference are unknown it would result in a higher partitioning coefficient compared to the one calculated from the AMS (or ACSM) and explain part of the observed difference.

4 Conclusions

~~We give evidence that organic~~ Organic nitrates formed during the oxidation of α-pinene ~~are hydrolyzed~~decay in the particle phase at a rate of 2 day^{-1} when RH is ~~22% or higher.~~between 20 and 60%, with no significant decay observed below an RH of 20%. During experiments when the highest observed RH exceeded the deliquescence RH of the ammonium sulfate seed aerosol, the particle-phase ON decay was as high as 7 day^{-1} and more variable. The dependence of observed decay rate on relative humidity suggests organic nitrate hydrolysis as the most plausible explanation. The gas-particle partitioning of ON determines their potential to hydrolyze. ~~We find that partitioning~~Partitioning of the ON is reversible and can be described by a volatility basis set ~~where the mass fractions at saturation mass concentrations of 1, 10, 100, and 1000 μg m^{-3} are 0, 0.190, 0.275, and 0.535, respectively~~.

The conversion of NOx to organic nitrates affects local ozone production. Partitioning and hydrolysis of organic nitrates affect regional concentrations of organic particulate matter and ozone. The organic nitrate partitioning coefficient and hydrolysis ~~rate~~rates from this work can be used to include these processes in chemical transport models and more accurately represent the effect of organic nitrates on concentrations of ozone and particulate matter.

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6 References

Allan, J. D., Delia, A. E., Coe, H., Bower, K. N., Alfarra, M. R., Jimenez, J. L., Middlebrook, A. M., Drewnick, F., Onasch, T. B., Canagaratna, M. R., Jayne, J. T. and Worsnop, D. R.: A generalised method for the extraction of chemically resolved mass spectra from Aerodyne aerosol mass spectrometer data, J. Aerosol Sci., 35(7), 909–922, doi:10.1016/j.jaerosci.2004.02.007, 2004.

Ayres, B. R., Allen, H. M., Draper, D. C., Brown, S. S., Wild, R. J., Jimenez, J. L., Day, D. A., Campuzano-Jost, P., Hu, W., de Gouw, J., Koss, A., Cohen, R. C., Duffey, K. C., Romer, P., Baumann, K., Edgerton, E., Takahama, S., Thornton, J. A., Lee, B. H., Lopez-Hilfiker, F. D., Mohr, C., Goldstein, A. H., Olson, K. and Fry, J. L.: Organic nitrate aerosol formation via NOx + BVOC in the Southeastern US, Atmos. Chem. Phys. Discuss., 15(12), 16235–16272, doi:10.5194/acpd-15-16235-2015, 2015.

Baker, J. and Easty, D.: Hydrolysis of Organic Nitrates, Nature, 166(4212), 156–156, doi:10.1038/166156a0, 1950.

Baker, J. and Easty, D.: Hydrolylic Decomposition of Esters of Nitric Acid .1. General Experimental Techniques - Alkaline Hydrolysis and Neutral Solvolysis of Methyl, Ethyl, Isopropyl, and Tert-Butyl Nitrates in Aqueous Alcohol, J. Chem. Soc., (APR), 1193–1207, doi:10.1039/jr9520001193, 1952.

Boschan, R., Merrow, R. T. and Van Dolah, R. W.: The Chemistry of Nitrate Esters, Chem. Rev., 55(3), 485–510, doi:10.1021/cr50003a001, 1955.

Boyd, C. M., Sanchez, J., Xu, L., Eugene, A. J., Nah, T., Tuet, W. Y., Guzman, M. I. and Ng, N. L.: Secondary organic aerosol formation from the β-pinene+NO3 system: effect of humidity and peroxy radical fate, Atmos. Chem. Phys., 15(13), 7497–7522, doi:10.5194/acp-15-7497-2015, 2015.

Browne, E. C., Min, K.-E., Wooldridge, P. J., Apel, E., Blake, D. R., Brune, W. H., Cantrell, C. A., Cubison, M. J., Diskin, G. S., Jimenez, J. L., Weinheimer, A. J., Wennberg, P. O., Wisthaler, A. and Cohen, R. C.: Observations of total $RONO_2$ over the boreal forest: NO_x sinks and HNO_3 sources, Atmos. Chem. Phys., 13(9), 4543–4562, doi:10.5194/acp-13-4543-2013, 2013.

Carter, W., Cockeriii, D., Fitz, D., Malkina, I., Bumiller, K., Sauer, C., Pisano, J., Bufalino, C. and Song, C.: A new environmental chamber for evaluation of gas-phase chemical mechanisms and secondary aerosol formation, Atmos. Environ., 39(40), 7768–7788, doi:10.1016/j.atmosenv.2005.08.040, 2005.

Chuang, W. K. and Donahue, N. M.: A two-dimensional volatility basis set – Part 3: Prognostic modeling and NOx dependence, Atmos. Chem. Phys. Discuss., 15(12), 17283–17316, doi:10.5194/acpd-15-17283-2015, 2015.

Darer, A. I., Cole-Filipiak, N. C., O'Connor, A. E. and Elrod, M. J.: Formation and stability of atmospherically relevant isoprene-derived organosulfates and organonitrates., Environ. Sci. Technol., 45(5), 1895–902, doi:10.1021/es103797z, 2011.

Day, D. A., Liu, S., Russell, L. M. and Ziemann, P. J.: Organonitrate group concentrations in submicron particles with high nitrate and organic fractions in coastal southern California, Atmos. Environ., 44(16), 1970–1979, doi:10.1016/j.atmosenv.2010.02.045, 2010.

Donahue, N. M., Robinson, A. L., Stanier, C. O. and Pandis, S. N.: Coupled partitioning, dilution, and chemical aging of semivolatile organics., Environ. Sci. Technol., 40(8), 2635–43, doi:10.1021/es052297c, 2006.

Fry, J. L., Rollins, A. W., Wooldridge, P. J., Brown, S. S., Fuchs, H. and Dub, W.: Organic nitrate and secondary organic aerosol yield from NO3 oxidation of β-pinene evaluated using a gas-phase kinetics / aerosol partitioning model, Atmos. Chem. Phys., 9(3), 1431–1449, 2009.

Hilal, S., Karickhoff, S. and Carreira, L.: Prediction of the vapor pressure boiling point, heat of vaporization and diffusion coefficient of organic compounds, QSAR Comb. Sci., 22(6), 565–574, doi:10.1002/qsar.200330812, 2003.

Hildebrandt, L., Donahue, N. M. and Pandis, S. N.: High formation of secondary organic aerosol from the photo-oxidation of toluene, Atmos. Chem. Phys., 9(9), 2973–2986, 2009.

Hildebrandt Ruiz, L. and Yarwood, G.: Interactions between Organic Aerosol and NOy ~~: Influence on Oxidant Production.,~~ , Austin, 5 TX. Prepared for the Texas AQRP (Project 12-012), by the University of Texas at Austin, and ENVIRON International Corporation, Novato, CA, available at: http://aqrp.ceer.utexas.edu/ projectinfoFY12_13/12-012/12-012FinalReport.pdf, 2013.

Hildebrandt Ruiz, L., Paciga, A., Cerully, K., Nenes, A., Donahue, N. M. and Pandis, S. N.: Aging of Secondary Organic Aerosol from Small Aromatic VOCs: Changes in Chemical Composition, Mass Yield, Volatility and Hygroscopicity, Atmos. Chem. Phys. Discuss., 14, 31441–31481, 2014.

Hu, K. S., Darer, A. I. and Elrod, M. J.: Thermodynamics and kinetics of the hydrolysis of atmospherically relevant organonitrates and organosulfates, Atmos. Chem. Phys., 11(16), 8307–8320, doi:10.5194/acp-11-8307-2011, 2011.

Jacobs, M. I., Burke, W. J. and Elrod, M. J.: Kinetics of the reactions of isoprene-derived hydroxynitrates: gas phase epoxide formation and solution phase hydrolysis, Atmos. Chem. Phys., 14(17), 8933–8946, doi:10.5194/acp-14-8933-2014, 2014.

Kebabian, P. L., Wood, E. C., Herndon, S. C. and Freedman, A.: A practical alternative to chemiluminescence-based detection of nitrogen dioxide: Cavity attenuated phase shift spectroscopy, Environ. Sci. Technol., 42(16), 6040–6045, doi:10.1021/es703204j, 2008.

Lindinger, W., Hansel, A., Jordan, A. and Hansel, A.: Proton-transfer-reaction mass spectrometry (PTR – MS): on-line monitoring of volatile organic compounds at pptv levels, Chem. Soc. Rev., 27, 347–354, 1998.

Liu, S., Shilling, J. E., Song, C., Hiranuma, N., Zaveri, R. A. and Russell, L. M.: Hydrolysis of Organonitrate Functional Groups in Aerosol Particles, Aerosol Sci. Technol., 46(12), 1359–1369, doi:10.1080/02786826.2012.716175, 2012.

Matsunaga, A. and Ziemann, P. J.: Gas-Wall Partitioning of Organic Compounds in a Teflon Film Chamber and Potential Effects on Reaction Product and Aerosol Yield Measurements, Aerosol Sci. Technol., 44(10), 881–892, doi:10.1080/02786826.2010.501044, 2010.

Ng, N. L., Chhabra, P. S., Chan, A. W. H., Surratt, J. D., Kroll, J. H., Kwan, A. J., McCabe, D. C., Wennberg, P. O., Sorooshian, A., Murphy, S. M., Dalleska, N. F., Flagan, R. C. and Seinfeld, J. H.: Effect of NOx level on secondary organic aerosol (SOA) formation from the photooxidation of terpenes, Atmos. Chem. Phys. Discuss., 7(4), 10131–10177, doi:10.5194/acpd-7-10131-2007, 2007.

Ng, N. L., Herndon, S. C., Trimborn, A., Canagaratna, M. R., Croteau, P. L., Onasch, T. B., Sueper, D., Worsnop, D. R., Zhang, Q., Sun, Y. L. and Jayne, J. T.: An Aerosol Chemical Speciation Monitor (ACSM) for Routine Monitoring of the Composition and Mass Concentrations of Ambient Aerosol, Aerosol Sci. Technol., 45(7), 780–794, doi:10.1080/02786826.2011.560211, 2011.

Pankow, J. F.: An absorption model of gas/particle partitioning of organic compounds in the atmosphere, Atmos. Environ., 28(2), 185–188, doi:10.1016/1352-2310(94)90093-0, 1994.

Perraud, V., Bruns, E. a, Ezell, M. J., Johnson, S. N., Yu, Y., Alexander, M. L., Zelenyuk, A., Imre, D., Chang, W. L., Dabdub, D., Pankow, J. F. and Finlayson-Pitts, B. J.: Nonequilibrium atmospheric secondary organic aerosol formation and growth., Proc. Natl. Acad. Sci. U. S. A., 109(8), 2836–41, doi:10.1073/pnas.1119909109, 2012.

Perring, A. E., Bertram, T. H., Wooldridge, P. J., Fried, A., Heikes, B. G., Dibb, J., Crounse, J. D., Wennberg, P. O., Blake, N. J., Blake, D. R., Brune, W. H., Singh, H. B. and Cohen, R. C.: Airborne observations of total $RONO_2$: new constraints on the yield and lifetime of isoprene nitrates, Atmos. Chem. Phys., 9(4), 1451–1463, doi:10.5194/acp-9-1451-2009, 2009.

Rindelaub, J. D., McAvey, K. M. and Shepson, P. B.: The photochemical production of organic nitrates from α-pinene and loss via acid-dependent particle phase hydrolysis, Atmos. Environ., 100, 193–201, doi:10.1016/j.atmosenv.2014.11.010, 2015.

Rollins, A. W., Pusede, S., Wooldridge, P., Min, K.-E., Gentner, D. R., Goldstein, A. H., Liu, S., Day, D. A., Russell, L. M., Rubitschun, C. L., Surratt, J. D. and Cohen, R. C.: Gas/particle partitioning of total alkyl nitrates observed with TD-LIF in Bakersfield, J. Geophys. Res. Atmos., 118(12), 6651–6662, doi:10.1002/jgrd.50522, 2013.

Seinfeld, J. H. and Pandis, S. N.: Atmospheric Chemistry and Physics, 2nd ed., Wiley-Interscience, Hoboken, 2006.

Wildt, J., Mentel, T. F., Kiendler-Scharr, A., Hoffmann, T., Andres, S., Ehn, M., Kleist, E., Müsgen, P., Rohrer, F., Rudich, Y., Springer, M., Tillmann, R. and Wahner, A.: Suppression of new particle formation from monoterpene oxidation by NOx, Atmos. Chem. Phys., 14(6), 2789–2804, doi:10.5194/acp-14-2789-2014, 2014.

Winer, A. M., Peters, J. W., Smith, J. P. and Pitts, J. N.: Response of Commercial Chemiluminescent NO-NO, Analyzers to Other Nitrogen-Containing Compounds, Environ. Sci. Technol., 8(13), 1118–1121, doi:10.1021/es60098a004, 1973.

Table 1. Experimental conditions and summary of results.

Exp	initial α-pinene (ppb)	initial NO (ppb)	RH (%)	H_2O_2 conc in model (ppb)[a]	O_3 (ppb)[b]	ON^{aer} ($\mu g/m^3$)[b,c]	PM Org ($\mu g/m^3$)[b,c]	ON^{gas} (ppb)[b]	Part coeff[d]	Hyd. (day^{-1})
1	40	30	22	100	90	7	90	13	0.19	NA[e]
2	40	40	39	60	50	6	60	11	0.18	2.2
3	40	40	0	40	50	4	30	13	0.10	NA[e]
4	130	110	68	600	210	150	1700			2.4
5	130	130	22	900	330	70	780	57	0.33	1.8
6	130	120	50	500	240	40	460	47	0.26	1.9
7	130	120	15	200	210	50	510	34	0.38	0.2
8	80	80	0	1000	300	30	310	32	0.26	0.6
9	80	80	0	1500	330	20	270	28	0.25	0.2
10	50	50	70	600	180	20	220			6.9
11	40	40	70	200	70	10	70			2.5
12	50	50	67	500	170	170	2200			5.2

[a] H_2O_2 concentration for which SAPRC model most closely matched measurements of NO_x and O_3

[b] Measured and averaged over a 20 minutes period when PM organics peaked

[c] Corrected for wall-losses as described in Sect. 2.1.2

[d] Molar basis

[e] Experimental conditions resulted in aerosol growth throughout the experiment

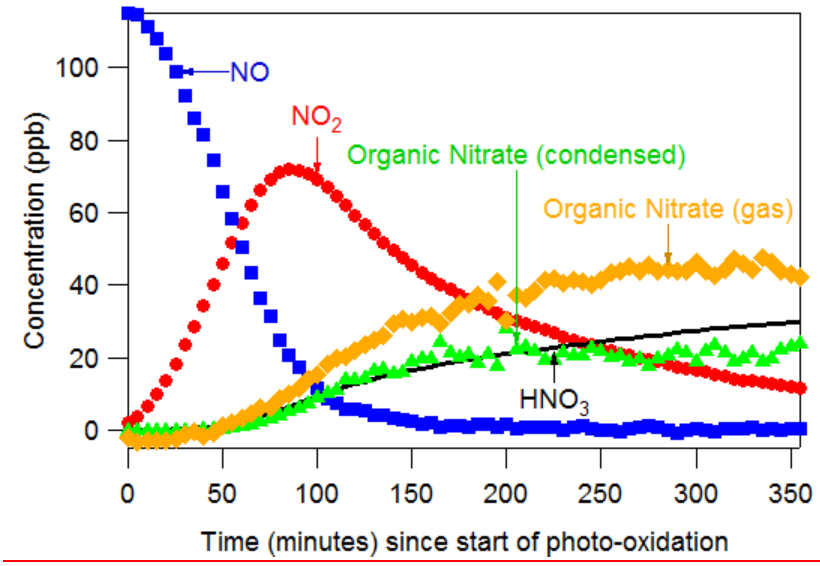

Figure 1 – ~~A time~~Time series of oxidized-nitrogen species in Expt. ~~7~~7. NO, NO_2, and ON^{aer} are measured directly. HNO_3 is modeled using SAPRC. ON^{gas} is calculated from a mass balance.

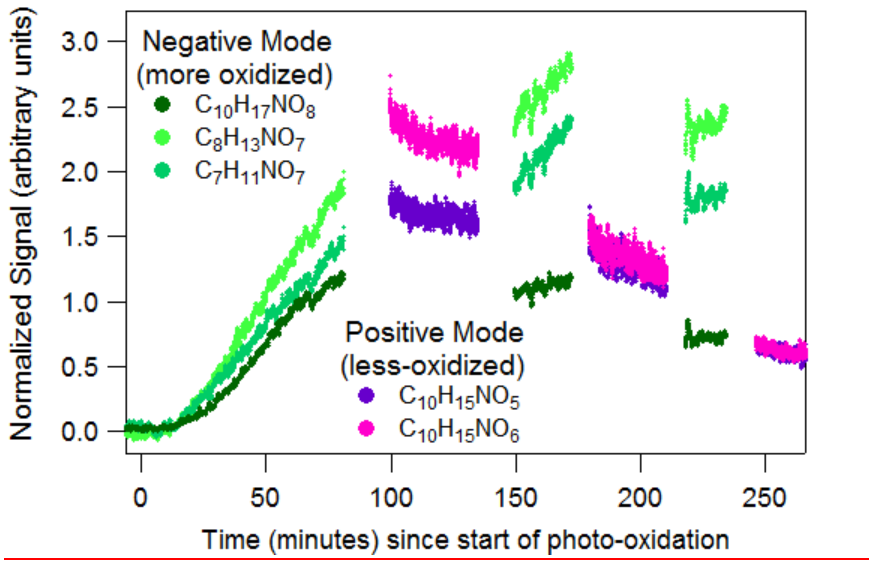

Figure 2 – Time series of selected organic nitrates identified by HR-ToF-CIMS (Expt. 10)

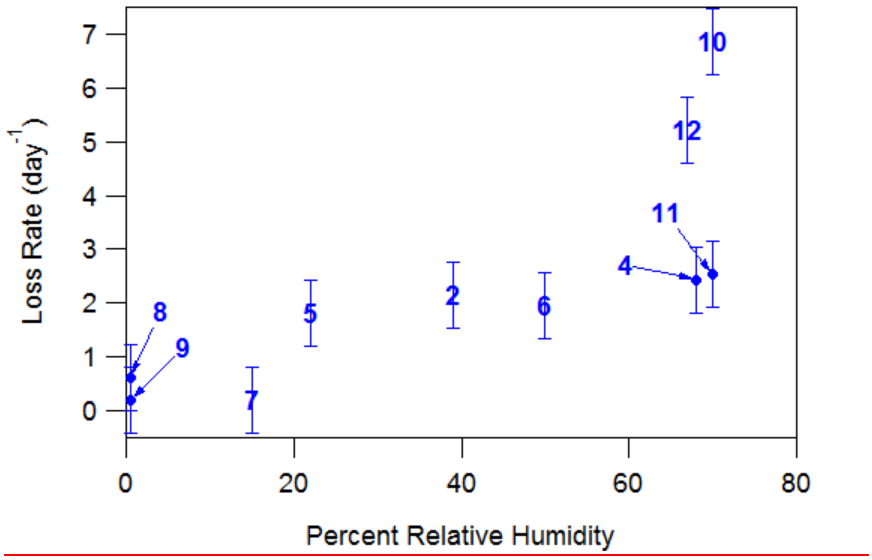

Figure ~~5~~3. The organic nitrate loss rate as a function of relative humidity for Expts. ~~2 11~~2, 4-12. Uncertainty (error bars) is estimated as 0.6 day^{-1}, the highest loss rate observed in experiments below 5% RH (Expt. 8).

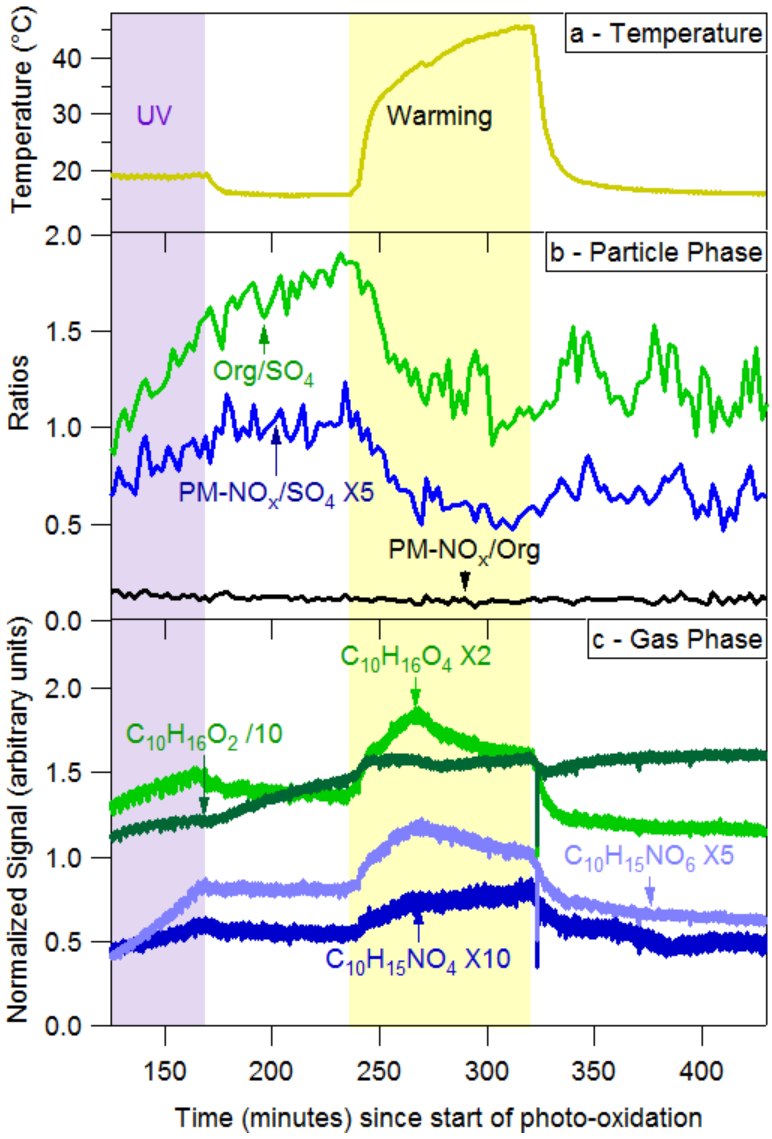

Figure ~~3~~4 – Temperature effects on gas-particle partitioning of organic nitrates (Expt. 2).

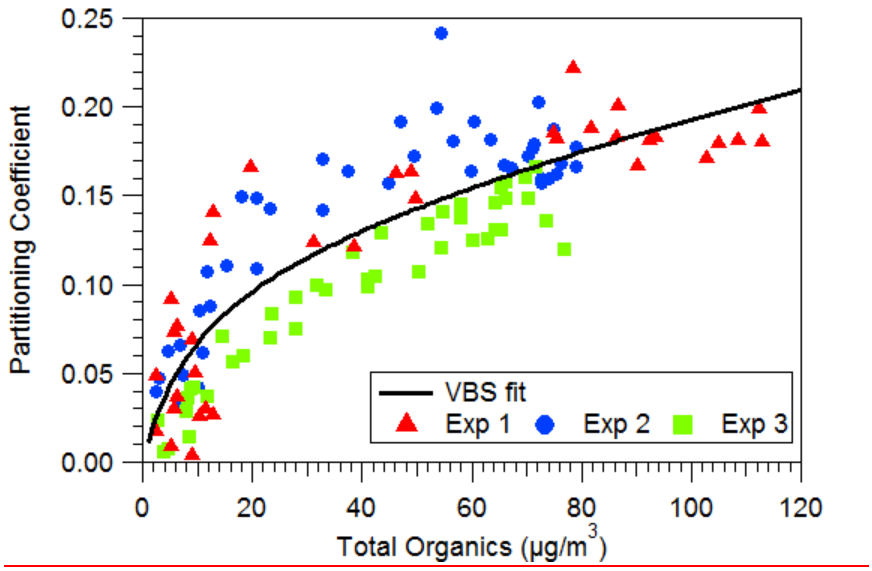

Figure ~~4~~5 – Volatility basis set fit from this work ~~shown a)~~ with data from Expts. 1, 2, and 3 ~~and the VBS fit from Rollins et al. (2013) and b) with data from Expts 1-3 and 5-9 (RH 0-50%).~~