We thank the reviewers for their time and insightful comments. Below are our responses to the comments. Reviewers' comments are italicized and the responses are underlined. When available, modified parts in the revised manuscript are presented in red. At the end, we have also included a list of minor modifications made in the revised manuscript.

Responses to Reviewer 1:

1. *Line 221: The supposition that autooxidation is occurring deserves more support. For example, the statement concerning "a few hydroxy radical reaction reactions" should be expanded into a formal kinetic argument concerning the low probability of multiple OH-initiated oxidation steps.*

In the revised manuscript, we compared the characteristic time of OH oxidation reaction derived from the lifetime of α-pinene with the peak time of $C_{10}H_{17}NO_{\geq 6}$ in FIGAERO-CIMS, which supports that these compounds are likely formed via one OH oxidation reaction. With one OH oxidation reaction, $C_{10}H_{17}NO_{\geq 6}$ is likely an autoxidation product (Xu et al., 2019; Berndt et al., 2016; Pye et al., 2019).

"This observation is consistent with the autoxidation mechanism, in which highly oxidized molecules are formed in a short time scale (Ehn et al., 2014; Crounse et al., 2013; Jokinen et al., 2015). Based on FIGAERO-HR-ToF-I-CIMS data (Fig. S1), $C_{10}H_{17}NO_{\geq 6}$ peak at 75 min. This is comparable to the lifetime of α-pinene at 53 min in the same experiment, which is related to characteristic time of OH oxidation. This suggests that the aforementioned ON are likely formed via one OH oxidation reaction, which is consistent with the autoxidation scheme to generate $C_{10}H_{17}NO_{\geq 6}$ proposed in prior studies (Berndt et al., 2016; Xu et al., 2019; Pye et al., 2019). It is important to note that…"

2. *Line 228: Again, the actual kinetic argument should be explicitly given. I assume that, combined with a typical RO2 + NO rate constant and 10 ppb NO, the predicted RO2 + NO pseudo first order rate constant is a "a few per second."*

We have included the typical rate constant of RO_2+NO in the revised manuscript.

"… that the autoxidation rate constant for the α-pinene+OH· system could be up to a few per second, which is comparable to the NO level of ~10 ppb, assuming a typical RO_2+NO reaction rate constant of 1×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Orlando and Tyndall, 2012)."

3. *Line 348: Although this paragraph is making an appropriate detailed argument about the difference between the two proxies, I think it is important to point out very simply to the reader that the reason why the proxy NO3-(org)/Org works better is because the common atmospheric chamber problem of wall loss effectively gets cancelled out with this proxy method.*

We have expanded the discussion in the revised manuscript. Precisely, the argument that the use of proxy $NO_{3,Org}$/Org cancels out the vapor wall loss effect may not be entirely valid because organic vapors get lost to the Teflon surface at a varying rate as a function of saturation mass concentration (Zhang et al., 2015). For the sake of simplicity, we assume in this study that the vapor wall loss rate of organics and organic nitrates is the same. This assumption is likely reasonable based on the thermal desorption profiles of CHO and CHON at the peak SOA growth that we have added in the revised SI (Fig. S5).

"For example, Huang et al. (2018) observe that the decay of isoprene hydroxyl nitrate depends on the reactor humidity. While SO_4 is practically non-volatile in the experimental condition of this study, both ON and non-nitrated organics could have some fractions of semi-volatile species whose vapors are subject to wall loss. Assuming a uniform loss rate of ON and non-nitrated organic vapors to the reactor walls, the effect of vapor wall loss could be effectively cancelled out in $NO_{3,Org}/Org$, but not in $NO_{3,Org}/SO_4$. This assumption is likely reasonable because the vapor wall loss rate is a function of saturation mass concentration (Zhang et al., 2015) and the average saturation mass concentrations of bulk ON and non-nitrated organic aerosol are similar based on the thermal desorption profiles in FIGAERO-HR-ToF-I-CIMS (Fig. S5). Therefore, $NO_{3,Org}/Org$ is a better proxy to infer hydrolysis of $_pON$ than others."

4. *Line 381: It is quite clear from previous work that iodide CIMS sensitivity varies greatly for moderately oxygenated organics. Therefore, it is also quite likely that these species are underestimated in the present work.*

We certainly believe that sensitivity varies greatly among moderately oxygenated organic species due to iodide CIMS selectivity. However, the focus in the concerned paragraph starting at line 369 in the original manuscript is β-pinene+NO_3· SOA that is comprised of less oxidized organic species instead of moderately oxygenated organics. Therefore, in the original manuscript at Lines 380-382, we included a sentence to describe the underestimating nature of our FIGAERO-HR-ToF-I-CIMS data.

5. *Line 385: This really supports the appropriateness of the "reconstructive" kinetics shown in Figure 3b and should be explicitly pointed out.*

We have made the suggested modification in the revised manuscript.

"As illustrated in Fig. 4, the time series of $_pON/OA$ stabilizes fairly quickly in most of the experiments, regardless of RH and/or the phase state of seed aerosol, supporting the appropriateness of the reconstructive approach shown in Fig. 3b."

6. *Line 397: It should be added that bulk studies also found that these reactions did not require low pH to be fast.*

We have made the suggested modification in the revised manuscript.

"Particle acidity is found to enhance hydrolysis rate of α-pinene hydroxy nitrate (Rindelaub et al., 2016), though no clear difference is observed here between experiments with AS and SA+MS seed particles (i.e., Exp. 5 and 2). It is worth noting that aqueous AS particles are not neutral but slightly acidic due to partitioning of ammonium to the gas phase once the particles enter the chamber (Gao et al., 2004). In Gao et al. (2004), the reported pH of aqueous AS particles is 4.6 and we expect a similar pH in our study. In Rindelaub et al. (2016), the reported hydrolysis lifetime is short at 1.3 h at pH of 4.0. On the other hand, previous studies have shown that isoprene-derived hydroxyl nitrates do not require low pH to undergo fast hydrolysis (Darer et al., 2011; Hu et al., 2011).Thus, $_pON$ formed from…"

7. *Line 219 (Figure S1): I think there must be something wrong with the symbols (or legend) here, as I don't understand what is actually being plotted. For example, does any green series correspond to any H17 compound and not just O8H17 (green squares)?*

Yes, all the combinations of $C_{10}H_{13,15,17}NO_{5-8}$ are plotted in Fig. S1 for consistency. To clarify, we have modified the legend of Fig. S1. We have also modified the figure caption as follows.

"FIGAERO-HR-ToF-I-CIMS time-series data of select organic nitrate aerosol. All combinations of $C_{10}H_{13,15,17}NO_{5-8}$ with different oxygen and nitrogen numbers are shown here. Different symbols correspond to compounds with different oxygen numbers, while different colors correspond to compounds with different nitrogen numbers. Shown are the data from Exp. 3 (α-pinene+OH·), though very similar trends are observed for β-pinene+OH· from Exp. 6."

8. *Line 236: Replace "subtraction" with "abstraction"*

We have made the suggested modification in the revised manuscript.

9. *Line 278 and beyond: Nitrate, sulfate, and ammonium ions must be indicated by their proper chemical formulas, NO3-, SO42-, and NH4+, respectively, rather than the shorthand NO3, SO4, and NH4 used in the manuscript. This is potentially particularly confusing as neutral NO3 radical reactions are important formation routes for organonitrates.*

It is a common practice to use NO_3, SO_4, and NH_4 to refer to aerosol nitrate, sulfate, and ammonium for AMS data (Jimenez et al., 2003; Allan et al., 2004; Canagaratna et al., 2007). This is because NO_3, SO_4, and NH_4 measured by AMS are not necessarily all from ions (i.e., NO_3^-, SO_4^{2-}, and NH_4^+) but can also come from covalently-bonded species, such as $R-ONO_2$, $R-OSO_3H$, and $R-NH_2$. For this reason, the use of NO_3^-, SO_4^{2-}, and NH_4^+ in our manuscript would not be appropriate, where we expect a substantial contribution of ON to NO_3 signal. In the original manuscript, we had explicitly written out "nitrate radical" (rather than formula) throughout the manuscript in order to avoid the confusion. To further clarify this, we have decided to replace "nitrate radical" with NO_3· (with a dot to denote a radical), such that readers do not get confused between NO_3 (aerosol nitrate) and NO_3· (nitrate radical). To be consistent, other radicals, such as hydroxyl radical written as OH·, now carry · in the revised manuscript.

10. *Line 298: This sentence is confusing. I suggest ": : :on hydrolysis on pON that partitions to the aerosol due to condensation rather than dissolution."*

    Line 314: This sentence is confusing. I suggest ": : : is a reaction in which liquid water is a reactant, it is : : :"

    Line 349: Typo: replace "rector" with "reactor"

    Line 355: Typo: replace "technique" with "techniques"

    Line 360: Isn't this a mass concentration? This should be clarified.

Line 394: Add "a" between "in" and "prior"

Line 395: Add "here" between "observed" and "between"

Line 401: Add "method" after "solution"

Line 445: Replace "several" with "a few"

We have made the suggested modifications in the revised manuscript.

Responses to Reviewer 2:

1. *Page 6, line 133: Please elaborate. What "negligible impact" on the results concerning hydrolysis was there?*

Regarding the injection order, we do not observe clear difference in pON/OA time-series data between Exp. 8 and 10 (both red filled circles), in which only difference is the injection order of precursor VOC and oxidant (Fig. 4c). Regarding the branching ratio of $RO_2\cdot$, as shown in Figure 4c, no clear difference in pON/OA time-series data is observed between $RO_2\cdot+NO_3\cdot$-dominant (filled circle) and $RO_2\cdot+HO_2\cdot$-dominant cases (cross) under low RH, dry AS and high RH, wet AS. We interpret these results as neither injection order nor RO_2 branching ratio in the case of α-pinene+$NO_3\cdot$ affects the susceptibility of pON against hydrolysis.

2. *Page 10, line 233: This is likely the case for beta-pinene + NO3, but alpha-pinene+ NO3 leads to very low ON yields (preferably forming volatile pinonaldehyde) and low SOA yields as discussed in Fry et al. (2014) as well as for -terpinene + NO3 as discussed in Slade et al. (2017). Favorability of nitrated to non-nitrated organics following NO3 oxidation vs. OH oxidation in the presence of NO will depend on the degree of branching on the carbon of the C-ONO2 bond. As stated, it is a bit oversimplified, please revise accordingly.*

   Concerning my second comment, it would be helpful if the authors included a discussion on the difference in the degree of nitration between the beta-pinene and alphapinene systems under the "nighttime" scenario when oxidized by NO3. The current discussion focuses more on differences between OH and NO3 oxidation and very little on differences between the precursor VOCs. The authors do say on page 9, lines 195-197 that a more distinct difference is observed between different oxidation conditions than between different precursor VOCs, but I would expect, based on previous literature, that substantial differences in CHO and CHNO fractions would exist between alpha and beta-pinene owing to the positions of their double bonds. Please elaborate.

Indeed, the total organic nitrate yield in $NO_3\cdot$ oxidation of α-pinene and γ-terpinene is low, compared to $NO_3\cdot$ oxidation of other monoterpenes. However, the corresponding section (i.e., Section 3.1) is focused on the chemical composition of particles rather than the total products in both gas and particle phases. Nevertheless, we have modified the corresponding paragraphs to clarify that our observation of a high abundance of ON is not in a direct contradiction to previously reported low ON yield, if low-volatility species contributing to SOA is composed of ON.

"This observation is consistent with a direct addition of a nitrate functional group to a double bond (Wayne et al., 1991; Ng et al., 2017), whereas the formation of ON in OH· oxidation condition is a minor channel of $RO_2\cdot+NO$ reaction (Perring et al., 2013). Although this is generally true for many monoterpenes, the organic nitrate yield in α-pinene+$NO_3\cdot$ has been known to be low (Fry et al., 2014) due to loss of a nitrate functional group followed by alkoxy radical bond scission (Kurten et al., 2017). Fry et al. (2014) observe no SOA formation in the same system, though another study has reported the formation of non-negligible SOA mass even at a relatively low initial concentration of α-pinene (Nah et al., 2016). Since the particle-phase compounds represent <10% of overall α-pinene+$NO_3\cdot$ products by mass, it is not necessarily inconsistent to observe a higher abundance of ON than non-nitrated organics in the particle phase if low-volatility compounds mainly consist of ON. Moreover, the contribution…"

3. *Page 10, line 236: I don't quite understand this statement. Both OH and NO3 can abstract hydrogens, but ultimately it depends on the degree of saturation, or? OH and NO3 preferably add to carbon-carbon double bonds over hydrogen abstraction. Please rephrase.*

We have made the suggested modification in the revised manuscript.

 "Moreover, the contribution from species containing $C_{<10}$ is minimal in the NO$_3\cdot$ oxidation condition. Once NO$_3\cdot$ attacks a double bond in the initial oxidation reaction of α-pinene and β-pinene, the reaction products no longer contain any double bond. Unlike OH$\cdot$, hydrogen abstraction reaction by NO$_3\cdot$ is slower by orders of magnitude (Atkinson and Arey, 2003). Therefore, multi-generation oxidation is unlikely to occur within the timescale of experiments (Wayne et al., 1991; Ng et al., 2017). This means that once the precursor VOC undergoes functionalization upon the initial NO$_3\cdot$ oxidation, it is not likely to experience fragmentation during the experiment."

4. *There is no mention of pH-dependent (i.e., acid-catalyzed) hydrolysis and the formation of organic sulfates (Liggio and Li, 2008;Rindelaub et al., 2016;Rindelaub et al., 2015). This is likely an important process affecting pON concentrations and the NO3,Org/SO4 ratio. Could you estimate what fraction of SO4 is organic?*

Regarding pH-dependent hydrolysis rate, in the original manuscript, we had briefly discussed previous studies on dependence of the hydrolysis rate on acidity (lines 394-397 of original manuscript). In response to comment #6 from Reviewer 1, we have made the suggested modification in the revised manuscript.

"Particle acidity is found to enhance hydrolysis rate of α-pinene hydroxy nitrate (Rindelaub et al., 2016), though no clear difference is observed here between experiments with AS and SA+MS seed particles (i.e., Exp. 5 and 2). It is worth noting that aqueous AS particles are not neutral but slightly acidic due to partitioning of ammonium to the gas phase once the particles enter the chamber (Gao et al., 2004). In Gao et al. (2014), the reported pH of aqueous AS particles is 4.6 and we expect a similar pH in our study. In Rindelaub et al. (2016), the reported hydrolysis lifetime is short at 1.3 h at pH of 4.0. On the other hand, previous studies have shown that isoprene-derived hydroxyl nitrates do not require low pH to undergo fast hydrolysis (Darer et al., 2011; Hu et al., 2011).Thus, $_p$ON formed from…"

Indeed, the formation of organic sulfate has been reported in past studies. However, the extent to which organic sulfate is formed will not affect our interpretation of the time-series data of NO$_{3,Org}$/SO$_4$ ratio (Fig. 3). In AMS, the majority of organic sulfate (>96%) is detected as organic ($C_xH_yO_z^+$) and sulfate ($H_xSO_y^+$) fragments rather than organosulfur fragments ($C_xH_yO_zS^+$) (Chen et al., 2019). Thus, the conversion of inorganic to organic sulfates hardly affects the absolute value of SO$_4$ measured by AMS.

5. *Page 14, line 330: The difference between the changes in NO3,Orgˇn/SO4 due to aerosol water content and reactor humidity alone is not clear. Doesn't the reactor humidity affect aerosol water content and subsequently pON hydrolysis? Please clarify how "reactor humidity alone" and not water content affects NO3,Orgˇn/SO4.*

Previous chamber studies (Liu et al., 2012; Boyd et al., 2015; Rindelaub et al., 2016) have investigated hydrolysis of pON by comparing results from low RH experiment (<10%) with those from high RH experiment (>40%). The issue of this approach is that chamber RH does not only affect aerosol water content but also absolute water vapor pressures (gas-phase chemistry) as well as other factors impacted by

RH, such as loss rates of organic vapors to chamber walls, as discussed in the response to comment #3 from Reviewer 1. In this study, we performed an experiment with high reactor RH but with effloresced seed aerosols to isolate the effects stemming from differences in water vapor pressures or vapor wall loss, to which we refer as "reactor humidity alone." As shown in Fig. 3, it is evident that the decay behavior of $NO_{3,Org}/SO_4$ from high RH experiments with effloresced (Exp. 4) and deliquesced seed aerosols (Exp. 5) is very similar, suggesting that changes in the time evolution of $NO_{3,Org}/SO_4$ between low and high RH experiments do not stem from changes in the aerosol water content but rather from changes in other factors impacted by RH, such as vapor wall loss.

6. *Figure 3b: The y-axis label is confusing "Exp.4/Exp.3", are you dividing results from Exp.4 by Exp.3? Please modify.*

Yes, each proxy in Exp. 4 is divided by that in Exp. 3 to express a relative decay between high and low RH experiments. We have modified the y-axis label of Fig. 3b and have added a sentence in the caption to clarify the y-axis.

"Figure 3. (a) Time-series data of $NO_{3,Org}/SO_4$ from Exp. 3-5 (α-pinene+OH·) and the exponential fits with corresponding characteristic times. (b) $NO_{3,Org}/Org$, $NO_{3,Org}/SO_4$, reconstructed $NO_{3,Org}/Org$ based on the decay rate of $NO_{3,Org}/SO_4$. Each proxy in Exp. 4 is divided by that in Exp. 3 to determine the relative decay between high and low RH experiments."

7. *Page 14, discussion on volatility: another interpretation of the NO3,Org/Org and NO3,Org/SO4 decay curves is the organosulfate products that possibly form are sufficiently low volatility that they remain in the aerosol phase, but a fraction of the hydrolyzed ON that is not organosulfate is sufficiently volatile that it repartitions to the gas phase.*

We have included a sentence indicating the possibility of the formation of organic sulfate as a way to generate sufficiently low volatile organics in the revised manuscript.

"This is because the organic moiety of hydrolysis product is generally considered to have a substituted alcohol group (Boschan et al., 1955) and to have a relatively similar vapor pressure to the ON compound and shall remain in the particle phase (Pankow and Asher, 2008). Similar to this is the formation of organic sulfate from hydrolysis of $_pON$ (Liggio and Li, 2006, 2008; Surratt et al., 2008), which has sufficiently low volatility to remain in the particle phase as with alcohol-substituted products. However, the measured…"

8. *Page 17, lines 394-395: If no difference in pON hydrolysis is observed between AS and SA+MS seed experiments, might it be that HNO3 in the particles sufficiently decreases aerosol pH that both "neutral" AS seed experiments and "acidic" SA+MS seed experiments are essentially the same pH? Aerosol pH measurements, e.g., with pH paper as in Craig et al. (2018), or predictions via AIM or ISORROPIA would help with interpretation but may be beyond the scope of this study.*

This is an interesting perspective on the effect of partitioned HNO_3. First, aqueous AS seed particles are not "neutral" but is already acidic due to partitioning of ammonium to the gas phase once the particles entered the chamber (Gao et al., 2004), as mentioned in the response to comment #6 from Reviewer 1. Second, while HNO_3 could potentially lower aerosol pH down to ~1-2 (Guo et al., 2016), it is not likely

reach the same level of pH as SA+MS seed particles (Gao et al., 2004). A more comprehensive study on pH-dependence on the hydrolysis rate as well as hydrolyzable fraction of organic nitrate under different pH conditions will be required.

9. *Page 17, line 415: Please include citation. Presumably, the authors refer to greater uptake of N2O5 at higher relative humidity due to changes in particle viscosity? A good example would be Grzinic et al. (2015).*

We have included the suggested citation in the revised manuscript.

"The reduction of NO_3/Org in Fig. S5 (~30 %) is greater than in Boyd et al. (2015) (10 %), which could be because (1) the amount of N_2O_5, a source of inorganic nitrate, used in our study is slightly larger and (2) RH in our study is higher by 10-20 %, which may have allowed greater uptake of N_2O_5 to produce inorganic nitrate due to changes in aerosol viscosity (Grzinic et al., 2015)."

Additional modifications:

- Typo correction

    - Line 181:   Ccondensation → Condensation

    - Line 213:   are → is

    - Line 437:   pahse → phase

    - Line 60 in SI: $C_{<9\ p}ON$ → $C_{\leq9\ p}ON$

- Figures and tables

    - RH reflecting the exact measurement values has been updated in Table 1.

    - A sentence has been added in the caption of Fig. 5 to clarify the use of different font sizes in the figure.

    - Label and unit on y-axis in Fig. 6 have been added.

- Clarification

    - The sentence describing the use of the unity collection efficiency for the AMS data has been added.

    - The sentence describing the use of uniform sensitivity among detected species in FIGAERO-HR-ToF-I-CIMS has been added.

    - Eq. 1 has been updated to include another form to express pON/OA.

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1 **Chemical Composition and Hydrolysis of Organic Nitrate Aerosol Formed from Hydroxyl and**

2 **Nitrate Radical Oxidation of α-pinene and β-pinene**

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14 Aerosol, chemical composition, hydrolysis, monoterpenes, organic nitrate, hydroxyl and nitrate radical

15 oxidation

16

Abstract

Atmospheric organic nitrate (ON) is thought to play a crucial role in the formation potential of ozone and aerosol, which are the leading air pollutants of concern across the world. Limited fundamental knowledge and understanding of the life cycles of ON currently hinders the ability to quantitatively assess its impacts on the formation of these pollutants. Although hydrolysis is currently considered as an important loss mechanism of ON based on prior field measurement studies, this process for atmospherically relevant ON has not been well constrained by fundamental laboratory studies. In this comprehensive study, we investigated the chemical composition and hydrolysis process of particulate ON ($_p$ON) formed from the oxidation of α-pinene and β-pinene by hydroxyl (OH·) and nitrate radicals (NO$_3$·). For $_p$ON that undergoes hydrolysis, the hydrolysis lifetime is determined to be no more than 30 min for all systems explored. This is significantly shorter than those reported in previous chamber studies (i.e., 3-6 h) but is consistent with the reported lifetime from bulk solution measurement studies (i.e., 0.02-8.8 h). The discrepancy appears to stem from the choice of proxy used to estimate the hydrolysis lifetime. The measured hydrolyzable fractions of $_p$ON (F_H) in the α-pinene+OH·, β-pinene+OH·, α-pinene+NO$_3$·, and β-pinene+NO$_3$· systems are 23-32, 27-34, 9-17, and 9-15 %, respectively. While a very low F_H for the NO$_3$· nitrate radical oxidation system is expected based on prior studies, F_H for the hydroxyl radicalOH· oxidation system is surprisingly lower than predicted in past studies. Overall, the hydrolysis lifetime as well as F_H obtained in this study serve as experimentally constrained parameters that are required in regional and global chemical transport models to accurately evaluate the impacts of ON on nitrogen budget and formation of ozone and aerosol.

1. Introduction

The oxidation of biogenic volatile organic compounds (BVOC) by ozone (O_3), hydroxyl radicals (OH·) and nitrate radicals (NO$_3$·) is a major source of secondary organic aerosol (SOA) globally (Kanakidou et al., 2005; Goldstein and Galbally, 2007; Spracklen et al., 2011). Many studies have pointed to the synergistic effects of anthropogenic emissions on biogenic SOA formation in the atmosphere (Weber et al., 2007; Carlton et al., 2010; Hoyle et al., 2011; Shilling et al., 2013; Xu et al., 2015a; Shrivastava et al., 2019). The oxidation of BVOC in environments with anthropogenic NO_x emissions is an important mechanism for coupled biogenic-anthropogenic interactions. In the presence of NO_x, the oxidation of BVOC can lead to the formation of organic nitrate (ON), a large component of reactive oxidized nitrogen. Results from ambient field measurements have revealed the ubiquitous presence of particulate ON ($_p$ON), where it contributes to a large fraction of submicron organic aerosol at different sites worldwide (Fry et al., 2013; Xu et al., 2015b; Liu et al., 2012a; Rollins et al., 2012; Rollins et al., 2013; Lee et al., 2016; Kiendler-Scharr et al., 2016; Ng et al., 2017). These findings highlights the importance to understand the formation and fates of ON to accurately evaluate its roles in NO_x recycling, O_3, and SOA formation.

Monoterpenes ($C_{10}H_{16}$) is a major class of BVOC, with annual emissions of 157-177 Tg C yr^{-1} (Guenther et al., 2012). Laboratory studies have demonstrated that the NO$_3$· nitrate radical oxidation of monoterpenes leads to a substantial formation of ON and SOA, with ON yields up to ~70% (Wangberg et al., 1997; Berndt and Boge, 1997; Griffin et al., 1999; Hallquist et al., 1999; Spittler et al., 2006; Fry et al., 2009; Fry et al., 2014; Boyd et al., 2015; Nah et al., 2016; Boyd et al., 2017; Slade et al., 2017; Claflin and Ziemann, 2018). For photooxidation of monoterpenes in the presence of NO_x, ON yields as high as 26% have been reported for α-pinene (Noziere et al., 1999; Aschmann et al., 2002; Rindelaub et al., 2015). Monoterpene emissions do not depend strongly on light and typically continue at night, making them important ON and SOA precursors at any times of the day (daytime and nighttime) and throughout the year (different seasons). It has been shown that monoterpene-derived ON is prevalent in areas where there are substantial biogenic-anthropogenic interactions and oxidation of monoterpenes contributes to a large

62   fraction of SOA observed in the Southeastern U.S. (Xu et al., 2015a; Xu et al., 2015b; Lee et al., 2016;

63   Zhang et al., 2018; Xu et al., 2018a).

64   One of the largest uncertainties in our understanding of monoterpene ON chemistry is the extent to

65   which ON act as a permanent sink versus temporary reservoir of NO_x (Takeuchi and Ng, 2018). This would

66   depend on the fates of ON as they can either retain or release NO_x upon further reactions. Once formed,

67   gas-phase ON can undergo photolysis or ~~hydroxyl radical~~OH· oxidation to release NO_x or partition into the

68   particle phase. $_pON$ in turn can undergo further chemistry to release NO_x or hydrolyze in the particle phase

69   to form nitric acid (HNO_3). Further, ON and HNO_3 can be removed via dry and wet deposition. One

70   important reaction of ON in the particle phase is hydrolysis in the presence of aerosol water, which is a

71   mechanism for NO_x loss (Day et al., 2010; Russell et al., 2011). Studies with bulk solutions showed that

72   particle-phase hydrolysis of tertiary nitrate is fast with a lifetime of minutes, while primary and secondary

73   nitrate is stable (Darer et al., 2011; Hu et al., 2011). However, the hydrolysis of $_pON$ in aerosol water is

74   largely unconstrained. Results from field and modeling studies suggested a $_pON$ lifetime of a few hours

75   (Pye et al., 2015; Lee et al., 2016; Fisher et al., 2016; Zare et al., 2018). A few recent laboratory chamber

76   studies elicited a complex picture where $_pON$ formed from photochemical oxidation and NO_3· ~~nitrate radical~~

77   oxidation of monoterpenes appear to experience different magnitudes of hydrolysis (Boyd et al., 2015;

78   Rindelaub et al., 2015; Bean and Hildebrandt Ruiz, 2016; Boyd et al., 2017), likely due to the difference in

79   the relative amount of primary, secondary, and tertiary nitrate in these oxidation systems. Overall, there are

80   very limited studies on the further evolutions of ON produced from the oxidation of monoterpenes.

81   Here, we present results from a laboratory chamber study on the chemical composition and

82   hydrolysis process of $_pON$ formed from oxidation of α-pinene and β-pinene by OH·~~hydroxyl~~ and

83   NO_3·~~nitrate radicals~~. Specifically, we report the hydrolysis lifetimes and the fraction of hydrolyzable $_pON$

84   formed in the systems examined in this study. This comprehensive chamber study on the hydrolysis of $_pON$

85   produced from various oxidation pathways of monoterpenes and peroxy radical (RO_2·) fates provides the

86   fundamental data to better constrain the role of hydrolysis in modulating $_pON$ concentrations and lifetimes

87 in the atmosphere, their potential as a NO$_x$ loss pathway, and their impacts on overall nitrogen budget, O$_3$

88 and SOA formation.

89

90 **2. Methods**

91 <u>2.1. Chamber experiment design and procedure</u>

92   A series of chamber experiments were performed in the Georgia Tech Environmental Chamber

93 facility (Boyd et al., 2015) housing two 12 m^3 Teflon reactors. Precursor volatile organic compounds (VOC)

94 were α-pinene (99 %, Sigma-Aldrich) and β-pinene (99 %, Sigma-Aldrich) and the oxidation conditions of

95 interest were OH·hydroxyl and NO$_3$· nitrate radical oxidation, which were represented as "daytime" and

96 "nighttime" experiments, respectively. Specifically, four different systems of VOC and oxidation

97 conditions were studied: α-pinene+OH·, β-pinene+OH·, α-pinene+NO$_3$·, and β-pinene+NO$_3$·. In order to

98 infer the hydrolysis process, experiments were performed under low RH (i.e., ~5 %) or high RH (i.e., ~50-

99 70 %) conditions and with effloresced or deliquesced seed particles for the same initial concentrations of

100 precursor VOC and oxidant precursors. Temperature in the reactors was kept at room temperature (22-

101 25°C). Experimental conditions are summarized in Table 1.

102   Prior to every experiment, the reactor was flushed with zero air (AADCO, 747-14) for at least a

103 day. A typical experiment began with the injection of seed aerosol into the reactor by atomizing dilute

104 ammonium sulfate (AS; 0.015 M) or sulfuric acid + magnesium sulfate (SA+MS; 0.01 + 0.005 M) aqueous

105 solution. The seed aerosol was either directly atomized into the reactor or passed through a dryer before

106 entering the reactor. The difference between efflorescence RH (~35 %) and deliquescence RH (~80 %) for

107 AS aerosol is fairly large (Seinfeld and Pandis, 2016). Taking advantage of this property, it is possible to

108 vary the amount of water in aerosol under the same RH in the reactor. Initial seed number and volume

109 concentrations upon atomization for 20 min were approximately 2 × 10^4 cm^{-3} and 2 × 10^{10} nm^3 cm^{-3},

110 respectively. A known amount of precursor VOC in the liquid form was transferred into a glass bulb, which

111 was then evaporated and carried into the reactor by flowing zero air at 5 L min^{-1} through the bulb. Although

112   the measurement of the precursor VOC concentration was not available for all experiments, the target and

113   measured concentrations in the experiments when the measurements were available were consistent.

114   For "daytime" experiments, an oxidant precursor (i.e., H_2O_2) was introduced to the reactor in the

115   same manner as VOC except that the glass bulb was gently heated by a heat gun to help evaporate faster.

116   During the injection of H_2O_2, a desired amount of NO was introduced into the reactor from a cylinder

117   containing 500 ppm NO (Matheson). For Exp. 3-5, 5 ppm NO at 5 L min^{-1} was continuously injected to the

118   reactor until the SOA growth ceased. For Exp. 1, 2, 6, and 7, 15 ppm NO at 5 L min^{-1} was injected for 5-

119   20 min several times until the SOA growth ceased. The NO concentration was usually on the order of tens

120   of ppb and always remained above a few ppb, making the bimolecular reaction with NO a favorable $RO_2\cdot$

121   reaction pathway. The experiment was initiated by turning on the irradiation of UV light approximately 20

122   min after the end of the last injection to ensure that particles and vapors were mixed well inside the reactor.

123   The procedure for "nighttime" experiments was the same until the end of the precursor VOC

124   injection. An oxidant precursor (i.e., N_2O_5) was pre-made in a flow tube by simultaneously injecting 500

125   ppm NO_2 (Matheson) at 0.4 L min^{-1} and ~250 ppm O_3 (Jelight 610) at 0.5 L min^{-1}. A simple kinetic box

126   model was used to adjust the concentration of O_3 and flow rates of both NO_2 and O_3 to maximize the

127   production of N_2O_5 and minimize the concentration of O_3, such that the VOC was dominantly oxidized by

128    $NO_3\cdot$ ~~nitrate radicals~~. Once N_2O_5 entered the reactor, it thermally decomposed to generate NO_2 and

129    $NO_3\cdot$ ~~nitrate radicals~~. VOC was usually depleted within the first 15 min of the experiment. For Exp. 8 and

130   14, the injection order of precursor VOC and oxidant precursor was switched such that the injection of

131   VOC marked the beginning of the experiment. For Exp. 12 and 13, 25 ppm formaldehyde was added to the

132   reactor to enhance the branching ratio of $RO_2\cdot$+$HO_2\cdot$ (Schwantes et al., 2015; Boyd et al., 2015) by injecting

133   an appropriate amount of formalin solution (37 % HCHO, Sigma-Aldrich) in the same manner as the

134   injection of H_2O_2. We do not discuss the details of the effect of the injection order nor the effects of the

135    $RO_2\cdot$ fate here as they had negligible impact on the results concerning hydrolysis.

136

137   2.2. Instrumentation and data analysis

138   A High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS; Aerodyne

139   Research Inc.) measured the concentrations of non-refractory organics (Org), sulfate (SO_4), nitrate (NO_3),

140   ammonium (NH_4), and chloride (Chl) (DeCarlo et al., 2006). The data were analyzed using PIKA v1.16I

141   and the unity collection efficiency was applied to all datasets. For the majority of nitrate-containing aerosol

142   regardless of the class (i.e., inorganic or organic), the nitrate moiety (i.e., $-NO_2$, $-ONO_2$, and $-O_2NO_2$) was

143   known to be thermally fragmented into NO^+ and NO_2^+ and was measured as NO_3 (Farmer et al., 2010). As

144   many past studies have demonstrated the feasibility to separate the contribution of inorganic ($NO_{3,Inorg}$) and

145   organic nitrate ($NO_{3,Org}$) to the measured NO_3 based on the ratio of NO^+ and NO_2^+ (Fry et al., 2009; Farmer

146   et al., 2010; Xu et al., 2015b; Kiendler-Scharr et al., 2016; Fry et al., 2018), we used Eq. (1) presented in

147   Farmer et al (2010) to obtain $NO_{3,Org}$. R_{AN} (i.e., NO^+/NO_2^+ from ammonium nitrate) was obtained from the

148   routine ionization efficiency calibration of HR-ToF-AMS using 300 nm ammonium nitrate particles. The

149   drawback of this method is that R_{ON} (i.e., NO^+/NO_2^+ from organic nitrate aerosol) could vary depending on

150   the chemical composition (Xu et al., 2015b). In addition, a non-negligible contribution of ammonium nitrate

151   could be expected in experiments with deliquesced seed aerosol owing to high solubility of HNO_3. Thus,

152   we obtained the R_{ON} measured in low RH experiments for each system of VOC and oxidation condition. In

153   order to account for changes in R_{AN} over time, R_{ON} was scaled accordingly assuming that the ratio of R_{ON}

154   to R_{AN} in the same system was constant (Fry et al., 2013). R_{AN}, R_{ON}, and R_{ON}/R_{AN} values obtained in this

155   study were consistent with previously reported values (Fry et al., 2009; Bruns et al., 2010; Boyd et al.,

156   2015; Nah et al., 2016) and are summarized in Table S1.

157   A Filter Inlet for Gases and AEROsols (FIGAERO) (Lopez-Hilfiker et al., 2014) coupled to a High

158   Resolution Time-of-Flight Iodide Chemical Ionization Mass Spectrometer (HR-ToF-I-CIMS; Aerodyne

159   Research Inc.) detected a suite of gaseous and particulate oxidized organic species as well as selected

160   inorganic species (Bertram et al., 2011; Lee et al., 2014). The operation of FIGAERO-HR-ToF-I-CIMS

161   was detailed in the previous studies (Nah et al., 2016; Sanchez et al., 2016). Reagent ions were generated

162   by flowing a mixture of CH_3I and dry ultra high purity (UHP) N_2 (Airgas) through a polonium-210 source

163   (NRD; Model P-2021). The instrument measured gaseous compounds by sampling air from the reactor at

164 ~1.7 L min^{-1} while collecting particles onto a Teflon filter. Upon completion of the collection period,

165 collected particles were desorbed by temperature-programmed dry UHP N$_2$ flow and subsequently analyzed

166 by HR-ToF-I-CIMS. Sensitivity could decrease if the amount of reagent ions were significantly depleted

167 and/or if the secondary chemistry in the ion-molecule reaction (IMR) chamber occurred at a significant

168 degree (Lee et al., 2014). To avoid changes in sensitivity among experiments, gas-phase sampling flow was

169 diluted with zero air immediately before the inlet such that the evaporation of aerosol was minimal. The

170 amount of aerosol collected on the filter was also adjusted by varying the sampling rate from 1 to 6 L min$^-$

171 ^{1} depending on the aerosol mass concentrations inside the reactor. Overall, the fraction of reagent ions to

172 the total ions was kept above 80 %. In addition, iodide ion chemistry has been known to be affected by the

173 water vapor pressure inside the IMR owing to the difference in thermodynamics between I$^-$ and IH$_2$O$^-$ to

174 analyte compounds (Lee et al., 2014). In order to minimize changes in the water vapor pressure inside the

175 IMR, a small continuous flow of humidified UHP N$_2$ (30-50 ccm) through a bubbler at a reduced pressure

176 was continuously added to the IMR directly. Therefore, while the instrument was not calibrated to report

177 the concentration of detected species, it was possible to quantitatively compare measured signal of each ion

178 among experiments because the instrument was operated under configurations that prevented undesired

179 changes in sensitivity. The data were analyzed using Tofware v2.5.11 and all the masses presented in this

180 study were I$^-$ adducts.

181   A Scanning Mobility Particle Sizer (SMPS) that consisted of a Differential Mobility Analyzer (TSI

182 3040) and a ~~Ccondensation~~ Condensation Particle Counter (TSI 3775) was operated under the low flow

183 mode with the sheath flow of 2 L min^{-1} to detect particles up to 1 μm in electrical mobility size. A Cavity

184 Attenuated Phase Shift spectroscopy (CAPS; Aerodyne Research Inc.) (Kebabian et al., 2005), an ultra-

185 sensitivity NO$_x$ analyzer (Teledyne M200EU), and an UV absorption O$_3$ analyzer (Teledyne T400)

186 measured NO$_2$, NO$_x$, and O$_3$, respectively. In selected experiments, a Gas Chromatograph coupled to Flame

187 Ionization Detector (GC-FID; Agilent) was used to make sure that a desired amount of a precursor VOC

188 was injected. Except CAPS, NO$_x$ analyzer, and O$_3$ analyzer, all instruments had their own dedicated

189 sampling line.

190

3. Results and discussion

3.1. Chemical composition of secondary organic aerosol

Shown in Fig. 1 are the mass spectra of particle-phase species obtained from FIGAERO-HR-ToF-I-CIMS at peak SOA growth. Many of the major species detected in this study are previously reported using the same or different technique (Eddingsaas et al., 2012; Claflin and Ziemann, 2018; Boyd et al., 2015; Nah et al., 2016; Lee et al., 2016; Romonosky et al., 2017). Concerning the chemical composition of SOA from each system, a more distinct difference is observed between different oxidation conditions (i.e., $OH\cdot$ ~~hydroxyl~~ vs. $NO_3\cdot$ ~~nitrate radical~~ oxidation) than between different precursor VOC (i.e., α-pinene vs. β-pinene). This is expected as α-pinene and β-pinene have the same chemical formula and very similar structures while the oxidation condition is distinctively different (Kroll and Seinfeld, 2008; Ziemann and Atkinson, 2012).

For "daytime" experiments where $OH\cdot$ ~~hydroxyl radicals~~ are the dominant oxidants, the contribution of ON (i.e., $C_xH_yN_{1,2}O_z$) and non-nitrated organics (i.e., $C_xH_yO_z$) are comparable and their contributions are well spread out over a wide range of masses. A large contribution of $C_xH_yO_z$ is expected because the formation of ON is a minor pathway in $RO_2\cdot$+NO (Perring et al., 2013). In Eddingsaas et al. (2012), the major compounds reported in the α-pinene+$OH\cdot$ system include $C_8H_{12}O_{4\text{-}6}$ and $C_{10}H_{16}O_{4,6}$, which are also detected in our study. A suite of C_{10} ON from the chamber experiment of the α-pinene+$OH\cdot$ system are reported in Lee et al. (2016) with the chemical formula of $C_{10}H_{15,17,19}NO_{4\text{-}9}$. All of these masses are detected in this study, though we observe a considerable contribution of $C_{<10}$ ON (i.e., $C_7H_{9,11}NO_6$ and $C_9H_{13,15,17}NO_6$) as well as a small fraction of C_{10} dinitrate (i.e., $C_{10}H_{14,16}N_2O_{9,10}$) that has been rarely reported (Fig. 1a). This significant contribution from species containing $C_{<10}$ indicates the large contribution of fragmentation process that is a preferred pathway in high NO conditions (Kroll and Seinfeld, 2008; Ziemann and Atkinson, 2012; Perring et al., 2013). It is possible that these species with $C_{<10}$ are thermally decomposed products during the thermal desorption process (Stark et al., 2017). However, it is unlikely

215 that thermal decomposition plays a significant role for the SOA generated via OH· ~~hydroxyl radical~~

216 oxidation of monoterpenes because the desorption temperature for these compounds (i.e., peaking at ~50-

217 70 °C) ~~are~~ is much lower than the temperature at which decarboxylization or dehydration reactions (>120

218 °C) are expected to occur (Stark et al., 2017). SOA chemical composition of the β-pinene+OH· system is

219 similar to that of the α-pinene+OH· system but with a larger contribution of $C_xH_yO_z$.

220   Another interesting observation in the α-/β-pinene+OH· systems is that a selected class of

221 compounds (i.e., $C_{10}H_{13,15,17}NO_{5-8}$) with the same H/C exhibit the same ~~the~~ time evolutions regardless of

222 the number of oxygen (Fig. S1). This observation is consistent with the autoxidation mechanism, in which

223 highly oxidized molecules are formed in a short time scale (Ehn et al., 2014; Crounse et al., 2013; Jokinen

224 et al., 2015). Based on FIGAERO-HR-ToF-I-CIMS data (Fig. S1), $C_{10}H_{17}NO_{\geq6}$ peak at 75 min. This is

225 comparable to the lifetime of α-pinene at 53 min in the same experiment, which is related to characteristic

226 time of OH oxidation. This suggests that the aforementioned ON are likely formed via one OH oxidation

227 reaction, which is consistent with the autoxidation scheme to generate $C_{10}H_{17}NO_{\geq6}$ proposed in prior studies

228 (Berndt et al., 2016; Xu et al., 2019; Pye et al., 2019). ~~The detection of compounds with $O_{\geq7}$ also supports~~

229 ~~the presence of autoxidation process; otherwise it is extremely difficult to produce highly oxidized~~

230 ~~molecules in a timescale of a few hydroxyl radical oxidation reactions.~~ It is important to note that the

231 concentration of NO in our experiments has been mostly kept on the order of tens of ppb over the course

232 of the experiments by a continuous injection of dilute NO and, therefore, this result suggests that

233 autoxidation is not a negligible pathway of RO_2· fate even at a moderately high NO level in laboratory

234 experiments and in polluted ambient environments. Indeed, recent studies (Berndt et al., 2016; Xu et al.,

235 2019; Pye et al., 2019) suggest that the autoxidation rate constant for the α-pinene+OH· system could be

236 up to a few per second, which is comparable to the NO level of ~10 ppb, assuming a typical RO_2·+NO

237 reaction rate constant of 1×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Orlando and Tyndall, 2012). The autoxidation rate

238 constant as well as the role of NO in autoxidation based on this observation will be discussed in details in

239 a forthcoming publication.

240   In contrast, the signals of $C_xH_yN_{1-2}O_z$ are dominant in the $NO_3\cdot$ ~~nitrate radical~~ oxidation condition,

241 indicating that the production of ON is greatly favored over non-nitrated organics. This observation is

242 consistent with a direct addition of a nitrate functional group to a double bond (Wayne et al., 1991; Ng et

243 al., 2017), whereas the formation of ON in ~~the hydroxyl radical~~OH$\cdot$ oxidation condition is a minor channel

244 of $RO_2\cdot$+NO reaction (Perring et al., 2013). Although this is generally true for many monoterpenes, the

245 organic nitrate yield in α-pinene+$NO_3\cdot$ has been known to be low (Fry et al., 2014) due to loss of a nitrate

246 functional group followed by alkoxy radical bond scission (Kurten et al., 2017). Fry et al. (2014) observe

247 no SOA formation in the same system, though another study has reported the formation of non-negligible

248 SOA mass even at a relatively low initial concentration of α-pinene (Nah et al., 2016). Since the particle-

249 phase compounds represent <10% of overall α-pinene+$NO_3\cdot$ products by mass, it is not necessarily

250 inconsistent to observe a higher abundance of ON than non-nitrated organics in the particle phase if low-

251 volatility compounds mainly consist of ON.

252   Moreover, the contribution from species containing $C_{<10}$ is minimal in the $NO_3\cdot$ oxidation

253 condition. ~~This~~ Once $NO_3\cdot$ attacks a double bond in the initial oxidation reaction, the majority of the

254 reaction products no longer contain any double bond. ~~is because u~~Unlike ~~hydroxyl radical~~OH$\cdot$ ~~oxidation~~, a

255 hydrogen ~~subtraction~~ abstraction reaction by ~~a nitrate radical~~NO$_3\cdot$ is ~~less efficient~~slower by orders of

256 magnitude (Atkinson and Arey, 2003). ~~and, thus~~Therefore, multi-generation oxidation is unlikely to occur

257 within the timescale of experiments (Wayne et al., 1991; Ng et al., 2017). This means that once the precursor

258 VOC undergoes functionalization upon the initial $NO_3\cdot$ ~~nitrate radical~~ oxidation, it is not likely to

259 experience fragmentation during the experiment. Unlike "daytime" SOA, the distribution of masses is

260 dominated by a few signature ions, such as $C_{10}H_{15}NO_{5,6}$ and $C_{20}H_{32}N_2O_{8-10}$ (Fig. 1c and 1d). In Boyd et al.

261 (2015), Nah et al. (2016), and Lee et al. (2016), the major species reported in the α-/β-pinene+$NO_3\cdot$ systems

262 are monomeric nitrate aerosol (i.e., $C_{10}H_{13,15,17,19}NO_{4-10}$), while in this study a substantial contribution of

263 dimeric species (i.e., $C_{20}H_{32}N_2O_{8-11}$) is observed. The abundant presence of dimeric compounds has been

264 previously observed in some studies on $NO_3\cdot$ ~~nitrate radical~~ oxidation of α-/β-pinene (Romonosky et al.,

265   2017; Claflin and Ziemann, 2018) and particle-phase reactions to produce such dimers have been proposed

266   by Claflin and Ziemann (2018). Many of the reported species in Claflin and Ziemann (2018) except the

267   trimeric species (mass scan range not extended to trimeric species in our study) are observed in our study.

268   One major difference between Claflin and Ziemann (2018) and this study is the substantial presence of

269   monomeric nitrate aerosol (i.e., 30-60 % by signal) in this study. This difference may be attributed to the

270   difference in the amount of available monomeric blocks to form dimer species. Assuming reversible

271   dimerization process, the concentration of dimer species shall be proportional to the square of monomer

272   concentration, such that the monomer to dimer ratio increases in a quadratic manner as the available

273   monomer concentration decreases. Since the amount of SOA formed in Claflin and Ziemann (2018) is

274   approximately two orders of magnitude higher than that in this study, the concentration of monomers in the

275   particle-phase is higher, favoring a more efficient formation of dimeric species. Together, these results

276   suggest that the contribution of dimeric nitrate aerosol could vary greatly depending on the concentrations

277   of monomeric blocks at the specific time and location.

278   Previous field studies have reported the mass spectra of ambient C_{10} $_p$ON obtained by FIGAERO-

279   HR-ToF-I-CIMS in rural Alabama site during the Southern Oxidant and Aerosol Study (SOAS) (Lee et al.,

280   2016) and in rural forest in Germany (Zhang et al., 2018). A comparison of the ambient mass spectra with

281   those obtained in this study reveals that average ambient $_p$ON resembles "daytime" $_p$ON more than

282   "nighttime" $_p$ON (Fig. S2). $_p$ON from "daytime" experiments has a distribution of masses centered around

283    $C_{10}H_{13,15,17}NO_7$, which is consistent with the ambient measurement data. On the other hand, NO$_3$· ~~nitrate~~

284   ~~radical~~ oxidation does not seem to oxidize organic species enough that the distribution of masses is skewed

285   towards a less-oxidized region (i.e., $C_{10}H_{13,15,17}NO_{5-6}$). However, it is difficult to draw a quantitative

286   conclusion simply based on this comparison because O_3, another important oxidant at night, is not studied.

287   Moreover, an average lifetime of aerosol could extend up to a week and thus ambient aerosol is continuously

288   exposed to further oxidation while the experiments here are more applicable to freshly formed aerosol. In

289   addition, the use of C_{10} $_p$ON alone may not be a good representative of monoterpene-derived $_p$ON as 42-74

290   % of $_p$ON in this study contains fewer or more than 10 carbon (Table S2). Nonetheless, the chemical

291   composition of aerosol generated in this study is comparable to those in the atmosphere and, thus, the results

292   shall be directly applicable to relevant ambient conditions.

293

294   3.2. Hydrolysis of particulate organic nitrate

295   3.2.1. Proxy used to evaluate hydrolysis process

296   Various proxies using HR-ToF-AMS data have been used to infer ON hydrolysis in previous

297   studies. In Bean and Hildebrandt Ruiz (2016), NO_3 measured by an Aerosol Chemical Speciation Monitor

298   (ACSM, practically similar to how AMS operates and measures aerosol species) (Ng et al., 2011) is

299   normalized to SO_4 as a means to account for particle wall-loss and is fitted by an exponential function to

300   estimate the ON hydrolysis rate. On the other hand, Boyd et al. (2015) normalize NO_3 measured by HR-

301   ToF-AMS to Org and attribute the relative decay of NO_3/Org between humid (RH ~50 %) to dry (RH <5

302   %) conditions to hydrolysis. Other approaches include the SMPS-derived particle wall-loss correction of

303   NO_3 measured by HR-ToF-AMS followed by fitting its decay trend (Liu et al., 2012b) and the determination

304   of fraction of total (i.e., gas and particle) ON to the precursor VOC consumed as a function of RH using a

305   Fourier-Transform InfraRed spectroscopy (FTIR). Below, we systematically examine the use of different

306   proxies using HR-ToF-AMS data to infer hydrolysis and discuss how the corresponding results are

307   interpreted.

308   Figure 2 shows the time series of Org, NO_3, SO_4, and NH_4 measured by HR-TOF-AMS for α-

309   pinene+NO_3: system. There is a substantial difference in NO_3 for the same VOC system but under different

310   reactor RH and phase state of seed particles (Exp. 10 and 11), while Org and SO_4 concentrations are similar.

311   The spike in NO_3 in high RH wet seed experiment (Fig. 2b) is attributed to the uptake of N_2O_5 and/or

312   dissolution of HNO_3 into aqueous aerosol followed by neutralization with ammonia to produce ammonium

313   nitrate. This is consistent with the sharp increase in molar ratio of NH_4/SO_4 to higher than 2, which is the

314   theoretical value for AS particles. It is also possible that inorganic nitrate is generated via hydrolysis of

315   gaseous ON that is too volatile to condense but is soluble enough to dissolve in aqueous aerosol and, thus,

316   only appears in high RH experiments. Since we do not have a way to quantitatively differentiate the

13

317 contribution of the aforementioned sources, the focus of this study is on hydrolysis of $_p$ON that ~~is~~ partitions

318 to the aerosol due to condensation rather than dissolution.~~condensed driven by volatility.~~ However, further

319 study is required to investigate the hydrolysis of volatile yet soluble gaseous ON, and the approach must be

320 different from the comparison between low and high RH experiments to obtain meaningful results.

321 To evaluate the extent of $_p$ON hydrolysis, the contributions of inorganic nitrate (NO$_{3,Inorg}$) and

322 organic nitrate (NO$_{3,Org}$) to the measured NO$_3$ need to be calculated. Firstly, NO$_{3,Org}$ is estimated by

323 subtracting NO$_3$ associated with excess NH$_4$. Secondly, NO$_{3,Org}$ is derived from NO$^+$/NO$_2^+$ approach (Sect.

324 2.2.). Figure S3 shows the comparison of NO$_{3,Org}$ estimated by these two independent methods for the α-

325 pinene+NO$_3$: system. It is clear that NO$_{3,Org}$ from both methods are consistent and that there is a

326 considerable contribution of NO$_{3,Inorg}$ to NO$_3$ in the experiment. We note the contribution of NO$_{3,Inorg}$ to

327 NO$_3$ can vary depending on experimental conditions with a range from to 28 to 90 % for all experiments in

328 this study. Nevertheless, these results demonstrate that for laboratory experiments with high RH and wet

329 seeds, when using HR-ToF-AMS data to infer hydrolysis, it is important to separate the measured NO$_3$ into

330 NO$_{3,Inorg}$ and NO$_{3,Org}$.

331 Once NO$_3$ is separated into NO$_{3,Inorg}$ and NO$_{3,Org}$, we evaluate whether the normalization of NO$_{3,Org}$

332 to SO$_4$ and Org provides a consistent decay trend. Photooxidation of α-pinene (Exp. 3-5) is used as a case

333 system. As hydrolysis is a reaction ~~where~~ in which liquid water is ~~directly involved in~~a reactant, it is

334 expected that the rate of hydrolysis will change proportionally as a function of aerosol water content. Based

335 on the hygroscopicity parameter for AS (κ = 0.53) (Petters and Kreidenweis, 2007) and for ambient LO-

336 OOA (κ = 0.08) (Cerully et al., 2015) that has a substantial contribution from $_p$ON (Xu et al., 2015a),

337 estimated aerosol water contents at peak SOA growth in Exp. 3-5 are approximately 0, 1, and 26 µg m^3,

338 respectively. Figure S4 illustrates that AS seed particles are indeed effloresced in Exp. 4 (high RH, dry AS)

339 but not in Exp. 5 (high RH, wet AS). These mass concentrations of aerosol water translate to 0, 6, and 36

340 mol L^{-1}, respectively, under the assumption that SOA is miscible with liquid water. It is speculated that

341 SOA formed in Exp. 3-5 are miscible with water because (1) the measured O/C ratio in HR-ToF-AMS

342   (Canagaratna et al., 2015) is close to 0.7, which is near the lower end but above the liquid-liquid phase

343   separation condition (Song et al., 2012) and (2) there is evidence of aqueous-phase reactions which highly

344   depend on the availability of aerosol water, as discussed in Sect. 3.3. Thus, the decay rate of $NO_{3,Org}$

345   normalized to SO_4 and/or Org between Exp. 4 and Exp. 5 shall differ by a factor of 6 based on the molar

346   concentrations of aerosol water.

347   Figure 3a shows the mass ratio of $NO_{3,Org}/SO_4$ and the decay rate as a characteristic time in Exp. 3-

348   5. The characteristic times of Exp. 4 and 5 (4.4 vs. 4.0 h) do not differ regardless of the molar concentrations

349   of aerosol water, suggesting that the decreasing trend in $NO_{3,Org}/SO_4$ may not be due to changes in aerosol

350   water content and $_pON$ hydrolysis, but arise from the difference in the reactor humidity alone. A comparison

351   of $NO_{3,Org}/SO_4$ and $NO_{3,Org}/Org$ also reveals that these two proxies capture a different range of decay

352   mechanisms. Figure 3b shows the relative decay trend of $NO_{3,Org}/SO_4$ and $NO_{3,Org}/Org$ between Exp. 4 (high

353   RH) and Exp. 3 (low RH). If hydrolysis is a dominant decay mechanism of $_pON$, the trend of $NO_{3,Org}/Org$

354   would be identical to that of $NO_{3,Org}/SO_4$. This is because the organic moiety of hydrolysis product is

355   generally considered to have a substituted alcohol group (Boschan et al., 1955) and to have a relatively

356   similar vapor pressure and shall remain in the particle phase (Pankow and Asher, 2008). Similar to this is

357   the formation of organic sulfate from hydrolysis of $_pON$ (Liggio and Li, 2006, 2008; Surratt et al., 2008),

358   which has sufficiently low volatility to remain in the particle phase as with alcohol substituted products.

359   However, the measured decay trend of the two proxies is greatly different. It is possible that some organic

360   moiety of hydrolysis product could be significantly more volatile and repartition back to the gas phase

361   (Rindelaub et al., 2016; Bean and Hildebrandt Ruiz, 2016) and, thus, both organics and HNO_3 formed from

362   hydrolysis evaporate. In this case, not only $NO_{3,Org}$ but also some fraction of Org would decrease because

363   Org measured by HR-ToF-AMS includes the contribution from the organic part of $_pON$. This will lead to

364   the relatively smaller decrease in $NO_{3,Org}/Org$ compared to $NO_{3,Org}/SO_4$. We can reconstruct the decay rate

365   of $NO_{3,Org}/Org$ assuming 1) the decay rate of $NO_{3,Org}/SO_4$ is solely due to hydrolysis of $_pON$ and 2) the

366   maximum contribution of $_pON$ to OA is 35 % (see Fig. 4 and discussions below). The reconstructed decay

367   rate of $NO_{3,Org}/Org$ is shown in Fig. 3b. As observed in the figure, the decay rate of the reconstructed

15

368   NO$_{3,Org}$/Org is much larger than the measured NO$_{3,Org}$/Org. This suggests that hydrolysis is not the only loss

369   process reflected in the decreasing trend of NO$_{3,Org}$/SO$_4$, while NO$_{3,Org}$/Org is likely a better proxy that

370   isolates hydrolysis from other loss processes. The likely important loss process manifested in NO$_{3,Org}$/SO$_4$

371   is the loss of organic vapors to the walls of the ~~rector~~ reactor (Matsunaga and Ziemann, 2010; Krechmer et

372   al., 2016; Huang et al., 2018; Loza et al., 2010; Mcvay et al., 2014; Zhang et al., 2015; Zhang et al., 2014;

373   La et al., 2016). For example, Huang et al. (2018) observe that the decay of isoprene hydroxyl nitrate

374   depends on the reactor humidity. While SO$_4$ is practically non-volatile in the experimental condition of this

375   study, both ON and non-nitrated organics could have some fractions of semi-volatile species whose vapors

376   are subject to wall loss. Assuming a uniform loss rate of ON and non-nitrated organic vapors to the reactor

377   walls, the effect of vapor wall loss could be effectively cancelled out in NO$_{3,Org}$/Org, but not in NO$_{3,Org}$/SO$_4$.

378   This assumption is likely reasonable because the vapor wall loss rate is a function of saturation mass

379   concentration (Zhang et al., 2015) and the average saturation mass concentrations of bulk ON and non-

380   nitrated organic aerosol are similar based on the thermal desorption profiles in FIGAERO-HR-ToF-I-CIMS

381   (Fig. S5). Therefore, NO$_{3,Org}$/Org is a better proxy to infer hydrolysis of $_p$ON than others.

382

383   3.2.2. Hydrolysis lifetime of particulate organic nitrate

384   In order for the data to be easily comparable with those reported in models or using other

385   techniques, the use of general terms instead of the AMS specific terms (i.e., NO$_{3,Org}$ and Org) can be

386   convenient. We define $_p$ON as the total mass concentration of particulate organic nitrate (includes organics

387   part and nitrate part of the ON compounds) and OA as the total mass concentration of organic aerosol

388   (includes nitrate and non-nitrated organics). The inclusion of nitrate mass concentration in OA is important

389   as the contribution of nitrate functional groups to the total organic aerosol mass concentration is large. The

390   conversion method from NO$_{3,Org}$/Org into $_p$ON/OA is illustrated in Eq. (1).

$$\frac{_pON}{OA} = \left(\frac{NO_{3,Org}}{Org + NO_{3,Org}} \right) \times \left(\frac{MW_{pON}}{MW_{NO_3}} \right) = \left(\frac{\frac{NO_{3,Org}}{Org}}{1 + \frac{NO_{3,Org}}{Org}} \right) \times \left(\frac{MW_{pON}}{MW_{NO_3}} \right) \qquad (1)$$

391   MW_{pON} represents the average molecular weight of $_pON$ per nitrate functional group estimated from

392   FIGAERO-HR-ToF-I-CIMS data assuming a uniform sensitivity among detected species, and MW_{NO3}

393   indicates the molecular weight of nitrate (i.e., 62 g mol^{-1}). Since MW_{pON} does not significantly vary during

394   the course of experiments (i.e., relative standard deviation of <1.2 %), the average value is applied to each

395   experiment. The variability of MW_{pON} among different systems is also found to be small, ranging from 229

396   to 238 g mol^{-1} and, thus, an average MW_{pON} is used for experiments where FIGAERO-HR-ToF-I-CIMS

397   data are not available. Figure 4 shows the time-series data of $_pON$/OA for all the systems investigated in

398   this study.

399   For "nighttime" experiments, the relative ratio of $C_xH_yN_{1-2}O_z$ and $C_xH_yO_z$ obtained from

400   FIGAERO-HR-ToF-I-CIMS data in Fig. 1 does not appear to match well with $_pON$/OA from HR-ToF-

401   AMS data. For example, the signals are dominated by $C_xH_yN_{1-2}O_z$ in the β-pinene+NO$_3$· system, as shown

402   in Fig. 1d, while $_pON$/OA is at most 0.5, as shown in Fig. 4d. The discrepancy would be attributed to the

403   overestimation of Org (in particular, C_xH_y family) in HR-ToF-AMS and/or underestimation of $C_xH_yO_z$ in

404   FIGAERO-HR-ToF-I-CIMS. Relative ionization efficiency (RIE) of less-oxidized organic species in HR-

405   ToF-AMS is experimentally measured to be higher at least by a factor of 2 (Xu et al., 2018b). As previously

406   reported (Boyd et al., 2015), the HR-ToF-AMS mass spectrum of SOA formed from β-pinene+NO$_3$·

407   contains significant amounts of C_xH_y fragments, indicating the less-oxidized nature of SOA from β-

408   pinene+NO$_3$·. For example, if the true RIE of Org by β-pinene+NO$_3$· SOA were to be a factor of 2 higher

409   than the default RIE of Org (i.e., 1.4), the reported concentration of Org would have been overestimated by

410   a factor of 2, such that actual $_pON$/OA would have been higher than reported in Fig. 4d. On the other hand,

411   an iodide reagent ion is not quite selective to detect less oxidized species, which could overestimate the

412   contribution of $_pON$ to OA (Aljawhary et al., 2013). Nonetheless, this discrepancy between HR-ToF-AMS

413   and FIGAERO-HR-ToF-I-CIMS data, however, should not affect the results regarding the hydrolysis

414   lifetime and hydrolyzable fraction of $_pON$ presented later.

415   As illustrated in Fig. 4, the time series of $_pON$/OA stabilizes fairly quickly in most of the

416   experiments, regardless of RH and/or the phase state of seed aerosol, supporting the appropriateness of the

417 reconstructive approach shown in Fig. 3b. This suggests that the timescale of $_p$ON hydrolysis in the systems

418 studied is significantly shorter or longer than the timescale of our experiments. It is also evident from Fig.

419 4 that $_p$ON/OA in high RH experiments are always lower than that in low RH experiments. These two

420 observations imply that the rate of $_p$ON hydrolysis may be fast enough that the decay trend of $_p$ON compared

421 to OA is not visibly manifested, though a clear difference of $_p$ON/OA between low and high RH

422 experiments is exhibited as a result of fast hydrolysis. Since no sudden, drastic change in $_p$ON/OA is

423 observed except for a few initial data points, we conclude that the hydrolysis lifetime of hydrolyzable $_p$ON

424 for α-/β-pinene derived ON shall be no more than 30 min (i.e., 3 data points in Fig. 4). Particle acidity is

425 found to enhance ~~rate of hydrolysis in prior study~~hydrolysis rate of α-pinene hydroxy nitrate (Rindelaub et

426 al., 2016), though no clear difference is observed here between experiments with AS and SA+MS seed

427 particles (i.e., Exp. 5 and 2). It is worth noting that aqueous AS particles are not neutral but slightly acidic

428 due to partitioning of ammonium to the gas phase once the particles enter the chamber (Gao et al., 2004).

429 In Gao et al. (2004), the reported pH of aqueous AS particles is 4.6 and we expect a similar pH in our study.

430 In Rindelaub et al. (2016), the reported hydrolysis lifetime is short at 1.3 h at pH of 4.0. On the other hand,

431 previous studies have shown that isoprene-derived hydroxy nitrates do not require low pH to undergo fast

432 hydrolysis (Darer et al., 2011; Hu et al., 2011). Thus, $_p$ON formed from OH· ~~hydroxyl~~ and NO$_3$· ~~nitrate~~

433 ~~radical~~ oxidation of α-pinene and β-pinene may not require a low pH to undergo hydrolysis at a rate

434 comparable to the timescale of chamber experiments.

435 Comparing with the results from past chamber studies reporting a $_p$ON hydrolysis lifetime of 3 to

436 6 h (Liu et al., 2012b; Bean and Hildebrandt Ruiz, 2016; Boyd et al., 2015), our estimated hydrolysis

437 lifetime is substantially shorter, but is consistent with the range (i.e., 1 min to 8.8 h) reported in studies

438 using the bulk solution method (Darer et al., 2011; Hu et al., 2011; Jacobs et al., 2014; Rindelaub et al.,

439 2016) (Fig. 5). In Liu et al. (2012) and Bean and Hildebrandt Ruiz (2016), the hydrolysis lifetime is derived

440 from the decay rate of NO$_3$ corrected for the particle wall loss or normalized to SO$_4$. As demonstrated in

441 Sect. 3.2.1., this NO$_3$/-SO$_4$ decay rate is likely affected by other loss processes, such as vapor wall loss, and,

442 thus, is not a good proxy to estimate the hydrolysis lifetime. The apparent discrepancy does not stem from

443   the contradiction in the obtained data itself but rather in the data interpretation. Indeed, the lifetime

444   estimated based on the decay of $NO_{3,Org}/SO_4$ in our study is 4 h (Fig. 3a) that is consistent with 6 and 3 h

445   reported in Liu et al. (2012) and Bean and Hildebrandt Ruiz (2016). On the other hand, in Boyd et al. (2015)

446   the hydrolysis lifetime is estimated based on the decay rate of NO_3/Org. The discrepancy in the reported

447   hydrolysis lifetime here could be attributed to the fact that NO_3 is not separated into $NO_{3,Org}$ and $NO_{3,Inorg}$.

448   Figure ~~S5~~ S6 shows our data analyzed in the same manner as Boyd et al. (2015). The lifetime calculated

449   based on the decay is 2.2 h, which is close to the reported 3-4.5 h (Boyd et al., 2015). The reduction of

450   NO_3/Org in Fig. ~~S5~~ S6 (~30 %) is greater than in Boyd et al. (2015) (10 %), which could be because (1)

451   the amount of N_2O_5, a source of inorganic nitrate, used in our study is slightly larger and (2) RH in our

452   study is higher by 10-20 %, which may have allowed greater uptake of N_2O_5 to produce inorganic nitrate

453   due to changes in aerosol viscosity (Grzinic et al., 2015).

454   In previous bulk solution studies where the concentration of interested organic nitrate (in particular

455   hydroxyl nitrate) in aqueous solution rather than in aerosol water is monitored over time, it is unlikely that

456   the data interpretation is affected by other loss processes present in chamber experiments, such as vapor

457   wall-loss. It is also common to monitor the organic moiety of hydrolysis product (Darer et al., 2011), while

458   it is extremely difficult in chamber experiments where hundreds of organic species are present at the same

459   time, leading to the difficulty in accurately measuring the hydrolysis lifetime in chamber experiments.

460   Based on the comprehensive analysis we demonstrate above on evaluating $_pON$ hydrolysis in chamber

461   experiments, we recommend the use of the hydrolysis lifetime reported in this study, which is no more than

462   30 min, for $_pON$ formed from α-pinene and β-pinene.

463

464   3.2.3. Hydrolyzable fraction of particulate organic nitrate

465   The fraction of hydrolyzable $_pON$ (F_H) can be directly estimated from the difference in $_pON/OA$

466   between low and high RH experiments shown in Fig. 4. Although we show that hydrolysis is substantially

467   faster than the timescale of chamber experiments in our study, there still appears a clear difference in

468     $_pON/OA$ between high RH experiments but with a different phase state of seed aerosol (i.e., Exp. 4 and 5).

469　The difference mass spectra among Exp. 3-5 obtained from FIGAERO-HR-ToF-I-CIMS reveal that the

470　difference in $_p$ON/OA between Exp. 4 and 5 does not arise from the reduction in $_p$ON but from the increase

471　in non-nitrated organics (Fig. 6). The reason for this OA increase with the abundant presence of aerosol

472　water is speculated to be uptake and other aqueous-phase reactions than hydrolysis and is briefly discussed

473　in Sect. 3.3. Thus, the absolute difference in $_p$ON/OA between low RH, dry seed and high RH, dry seed

474　experiments best indicates F_H. Depending on the fate of the organic moiety of the hydrolysis product (i.e.,

475　stay in the particle phase or repartition back to the gas ~~pahse~~phase), F_H varies. Since we are unable to

476　determine the fate of hydrolysis product, an upper and lower limit of F_H are reported as a range of F_H. For

477　the α-pinene+OH· system, 23-32 % of $_p$ON formed undergoes hydrolysis within the timescale of the

478　experiments. For the other systems with no experiment under high RH with dry seed aerosol, the same level

479　of additional contribution from non-nitrated organics encountered in α-pinene+OH· system is assumed and

480　F_H is scaled accordingly. For the β-pinene+OH·, α-pinene+NO$_3$·, and β-pinene+NO$_3$· systems, 27-34, 9-

481　17, and 9-15 % of $_p$ON are found hydrolyzable within the timescale of the experiments. Table 2 summarizes

482　the hydrolysis lifetime and F_H in the systems explored in this study.

483　　　F_H has been only reported in ~~several~~ a few studies (Liu et al., 2012b; Boyd et al., 2015; Zare et al.,

484　2018). The determination of F_H is essential because the assumption that all $_p$ON hydrolyzes biases the

485　relative importance of hydrolysis among the loss mechanisms of $_p$ON and NO$_x$. Boyd et al. (2015) report

486　that F_H of $_p$ON formed via β-pinene+NO$_3$· is ~10 %, which is in a good agreement with our range of 9-15

487　%. From a perspective of predicted molecular structures of $_p$ON, <5 % of $_p$ON from β-pinene+NO$_3$· are

488　tertiary (Claflin and Ziemann, 2018) that is expected to undergo hydrolysis in minutes (Darer et al., 2011;

489　Hu et al., 2011). In our study, a considerable contribution of monomeric (C$_{10}$) $_p$ON is observed (Fig. 1d),

490　while dimeric (C$_{20}$) $_p$ON is dominant in Claflin and Ziemann (2018). This may indicate that monomeric

491　$_p$ON is more susceptible to hydrolysis such that F_H in this study is slightly higher than expected based on

492　the proposed molecular structures of $_p$ON in Claflin and Ziemann (2018).

493   F_H for α-/β-pinene+OH· systems are higher than those from α-/β-pinene+NO₃· systems. This trend

494   is consistent with the understanding that $_p$ON via OH· ~~hydroxyl radical~~ oxidation have a larger fraction of

495   tertiary nitrate groups, which are significantly more susceptible to hydrolysis (Darer et al., 2011; Hu et al.,

496   2011) than those formed via NO₃· ~~nitrate radical~~ oxidation (Ng et al., 2017). Although the relative trend of

497   F_H between α-/β-pinene+OH· and α-/β-pinene+NO₃· systems is consistent, the magnitude of F_H in the α-

498   /β-pinene+OH· system appears to be smaller than expected based on the tertiary nitrate fraction estimated

499   via the explicit gas-phase chemical mechanism (Browne et al., 2013; Zare et al., 2018). In previous studies,

500   F_H are estimated to be 62 and 92 % for α-/β-pinene+OH· systems, respectively. However, our results

501   indicate F_H is 23-32 and 27-34 % for the same systems (Fig. 5). The chemical mechanism used in Browne

502   et al. (2013) and Zare et al. (2018) are based on the Master Chemical Mechanism (MCM) that is well known

503   in the degradation chemistry of VOC in the gas phase (Jenkin et al., 1997; Saunders et al., 2003). However,

504   the same mechanism performs poorly in regards to the chemical composition of SOA (Faxon et al., 2018)

505   as well as the prediction of SOA formation (Ruggeri et al., 2016; Boyd et al., 2017) when equipped with

506   gas-particle partitioning modules based on the absorptive gas-particle partitioning theory (Pankow, 1994).

507   It is, therefore, reasonable to argue that the chemical composition of $_p$ON could greatly differ from that of

508   total ON predicted by the MCM. Thus, F_H reported in this study provides the fundamental experimental

509   constraints on $_p$ON hydrolysis, that can be used in regional and global models for elucidating potential

510   impacts of ON on nitrogen budget and formation of ozone and aerosol.

511

512   3.3 Signature of other aqueous-phase reactions than hydrolysis

513   As briefly discussed in the above section, the presence of elevated level of aerosol water seems to

514   have enhanced the contribution of small (i.e., $C_{<9}$) but more-oxidized organic species to SOA. As shown in

515   Fig. 5c, the enhancement is observed for a variety of non-nitrated organic aerosol including $C_4H_{6,8}O_3$,

516    $C_4H_4O_4$, $C_5H_6O_5$, $C_7H_{8,10}O_4$, and $C_8H_{8,10}O_{4,5}$, while $_p$ON overall neither increase nor decrease. $C_5H_6O_5$ has

517   been reported as a product of the aqueous-phase reaction of α-pinene derived compounds (Aljawhary et al.,

518   2016). Other compounds, such as $C_4H_4O_4$, $C_7H_{8,10}O_4$, and $C_8H_{10}O_5$, also appear to result from the aqueous

519   processing because compounds with similar chemical formulae but with slightly higher degrees of oxidation

520   (i.e., $C_4H_4O_5$, $C_7H_{10}O_5$, and $C_8H_{12}O_6$) are reported in Aljwhary et al. (2016). The reason for this less

521   oxidized nature of SOA in this study may be attributed to our experiments being performed in moderately

522   high NO conditions that promotes a higher contribution of a carbonyl group than a hydroperoxyl group,

523   which is preferred in low NO conditions. In Aljwhary et al. (2016), the starting compound is a product in

524   low NO conditions (pinonic acid, $C_{10}H_{16}O_3$). Thus, it is reasonable that products of the aqueous processing

525   in this study are slightly less oxidized than observed in Aljwhary et al. (2016).

526   The enhancement of non-nitrated organic aerosol in FIGAERO-HR-ToF-I-CIMS may be due to

527   aqueous processing of species in the particles in the presence of aerosol water. This can come from further

528   reactions of semi/low-volatile species in the particle phase, or reactive uptake of volatile (but highly water-

529   soluble) species into the aerosol followed by subsequent aqueous-phase reactions to form low-volatility

530   products (Ervens et al., 2011). A comparison of the average thermogram at peak SOA growth among Exp.

531   3-5 indicates a higher contribution of low-volatility compounds in Exp. 5 than in Exp, 3 and 4, as illustrated

532   by the bimodal peaks (Fig. S6S7). Given the same degree of gas-phase oxidation expected among Exp. 3-

533   5, these results show that that aqueous chemistry in wet aerosol contributes to the further formation of low-

534   volatility compounds. Overall, the highest average degree of oxidation (O/C = 0.77) is observed in high RH

535   wet aerosol experiment (Expt. 5). The effect of particle water on monoterpene SOA formation warrants

536   further studies.

537

538   3.4 Atmospheric implications

539   There is emerging evidence that monoterpene SOA greatly contribute to atmospheric aerosol in the

540   Southeastern U.S. (Zhang et al., 2018; Xu et al., 2018a). ON is no exception; a substantial fraction of $_p$ON

541   is considered to be from monoterpenes (Lee et al., 2016; Huang et al., 2019; Xu et al., 2015a). While C_{10}

542    $_p$ON measured in FIGAERO-HR-ToF-I-CIMS is a good tracer of monoterpene derived $_p$ON, we show that

543   a fair amount of α-/β-pinene $_p$ON is found as $C_{<10}$ or C_{20} depending on the oxidation condition. This implies

544   that the contribution of monoterpene derived $_p$ON could be substantially underestimated when only

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545   considering C_{10} $_p$ON. Fraction of $_p$ON with different number of carbon reported in this study (Table S2) is

546   a useful parameter to quantitatively determine the contribution of monoterpenes derived $_p$ON to total $_p$ON.

547   Many previous modeling studies using ambient measurement data as constraints report that the

548   lifetime of $_p$ON is likely several hours (Pye et al., 2015; Fisher et al., 2016; Lee et al., 2016; Zare et al.,

549   2018). Hydrolysis of $_p$ON is used as a dominant loss process with the lifetime of several hours to improve

550   the concentration of modeled OA (Pye et al., 2015) and to improve the concentrations of gaseous and

551   particulate ON (Fisher et al., 2016). If the ambient $_p$ON concentration is indeed governed by a loss process

552   with a few hours of lifetime, our results imply that the particle-phase hydrolysis may not be the only

553   dominant loss process because the hydrolysis lifetime reported in this study is significantly shorter. Other

554   potential but less-studied loss mechanisms of ON and $_p$ON include deposition (Nguyen et al., 2015),

555   photolysis (Muller et al., 2014), and aqueous photooxidation (Romonosky et al., 2017; Nah et al., 2016).

556   For instance, enhanced photolysis rate is observed for carbonyl nitrate derived from isoprene (Muller et al.,

557   2014), while no similar study is available for monoterpene derived ON in literature. Also, it has been

558   demonstrated that different monoterpene $_p$ON can have drastically different photochemical fates (Nah et

559   al., 2016). Taken together, results from this study highlight the importance to investigate other potential

560   loss processes of monoterpene derived $_p$ON.

561   Aside from the hydrolysis lifetime, many modeling studies assume F_H as unity (Pye et al., 2015;

562   Fisher et al., 2016; Lee et al., 2016). Even when F_H is considered, the value of F_H used in other studies is

563   still substantially higher than estimated in this study (Browne et al., 2013; Zare et al., 2018). The use of

564   higher F_H would result in overestimating the contribution of hydrolysis as a loss process of $_p$ON and NO_x.

565   While hydrolysis is considered as a permanent sink of NO_x, many other loss processes, such as further OH·

566   ~~hydroxyl radical~~ oxidation and photolysis, are considered as a temporary reservoir of NO_x. If the relative

567   importance of $_p$ON fates in models was not accurate, the role of ON in NO_x cycling and the formation

568   potential of ozone could have been inaccurately interpreted. Therefore, results from this study regarding

569   the hydrolysis lifetime and F_H serve as experimentally constrained parameters for chemical transport

570   models to accurately evaluate the role of ON in regards to nitrogen budget and the formation of ozone and

571   fine aerosol.
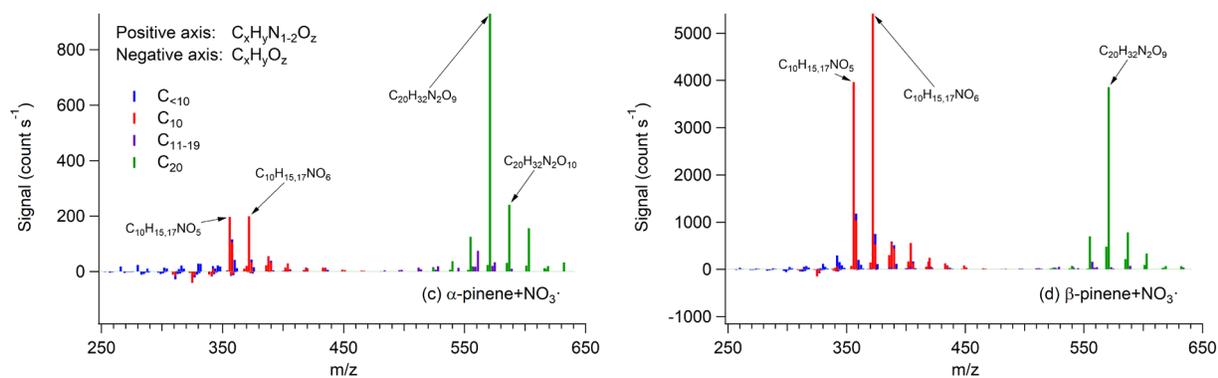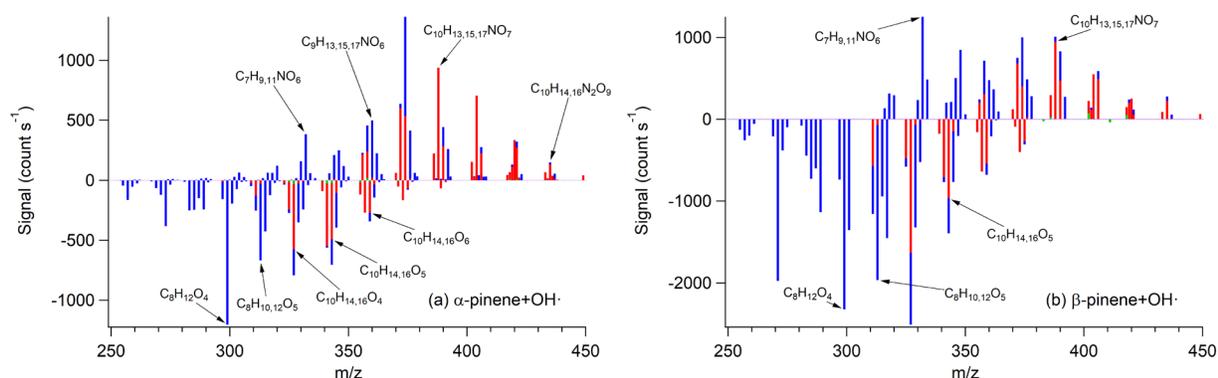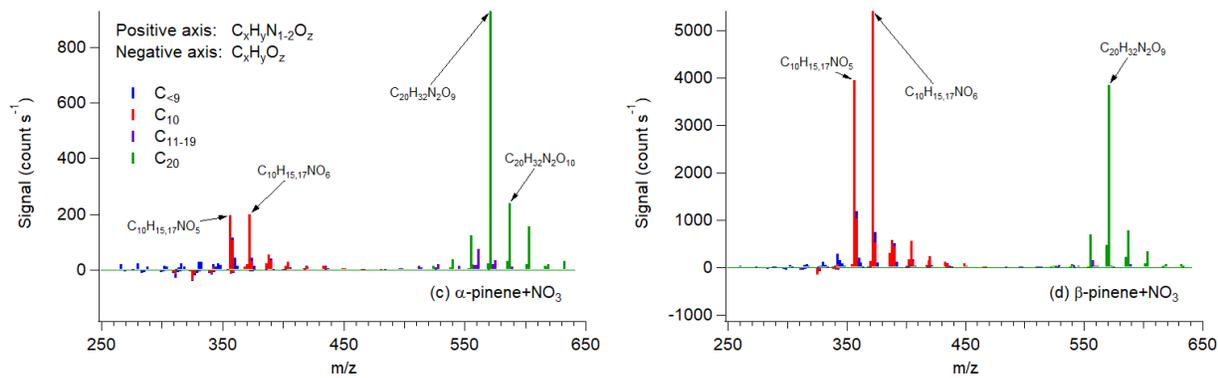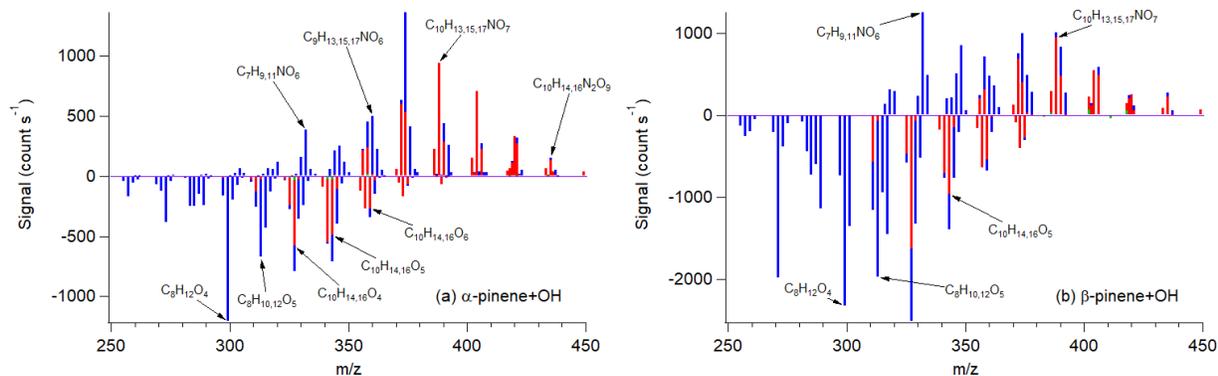
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573   **Author contribution**

574   M.T. designed and performed the research and analyzed the data with substantial inputs from N.L.N. M.T.

575   and N.L.N. wrote the manuscript.

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Figure 1. FIGAERO-HR-ToF-I-CIMS mass spectra of SOA in (a) α-pinene+OH· from Exp. 3, (b) β-

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586   pinene+OH· from Exp. 6, (c) α-pinene+NO$_3$· from Exp. 10, and (d) β-pinene+NO$_3$· from Exp. 14. Top

587   portion of each panel represents $C_xH_yN_{1-2}O_z$, whereas bottom represents $C_xH_yO_z$. Bars are colored by the

588   number of carbon as noted in the legend. Prominent masses are labeled with the corresponding chemical

589   formulae without an iodide ion.

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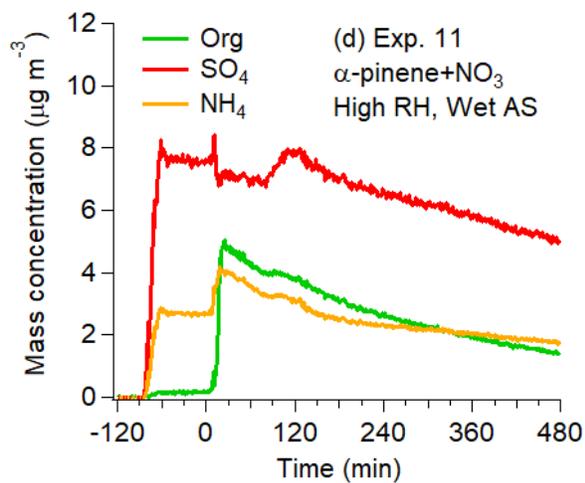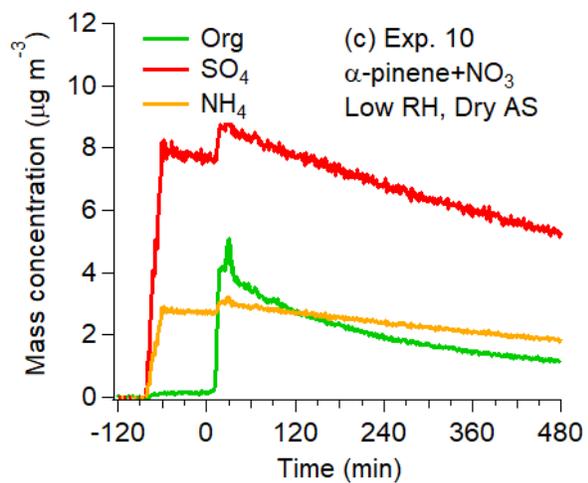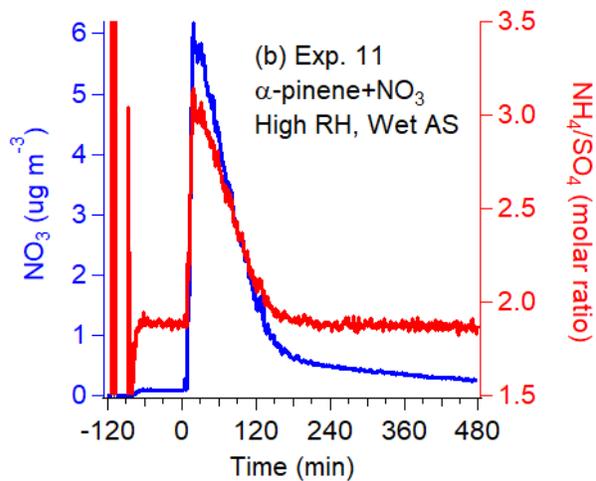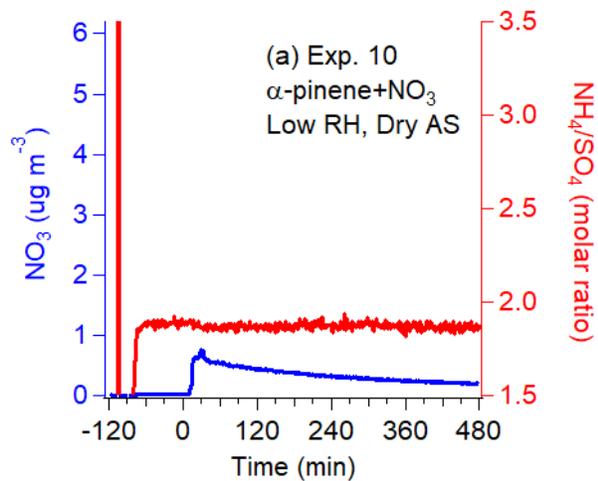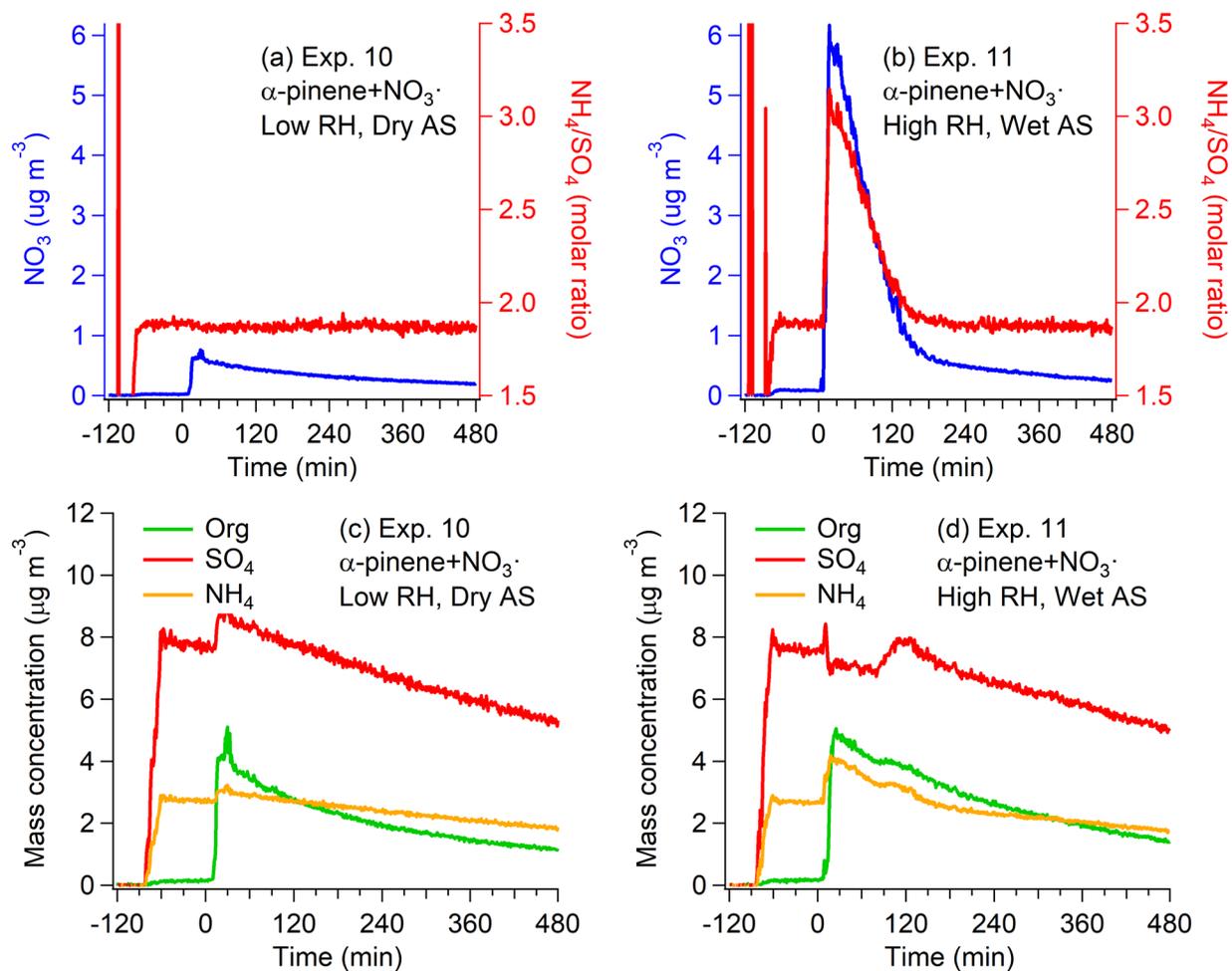
Figure 2. (a, b) NO_3 concentration and the molar ratio of NH_4 to SO_4 and (c, d) concentrations of Org, SO_4, and NH_4 measured by HR-ToF-AMS. Data presented in Panels (a) and (c) are from Exp. 10 (low RH, dry AS), while those in Panels (b) and (d) are from Exp. 11 (high RH, wet AS). These two experiments are essentially the same except for RH and phase state of seed aerosol.
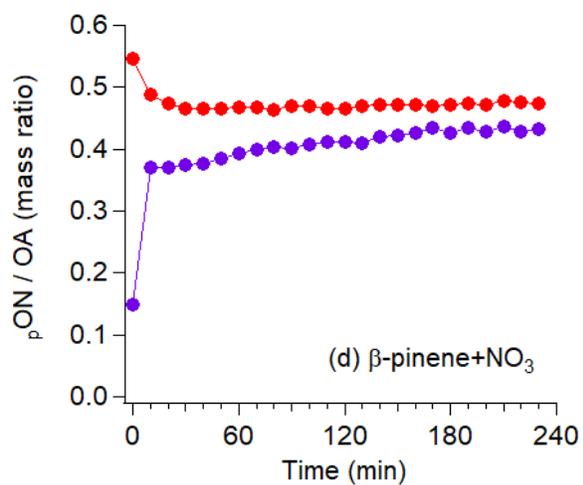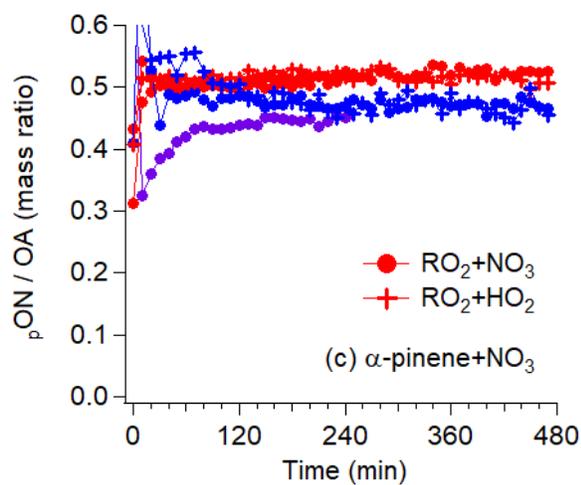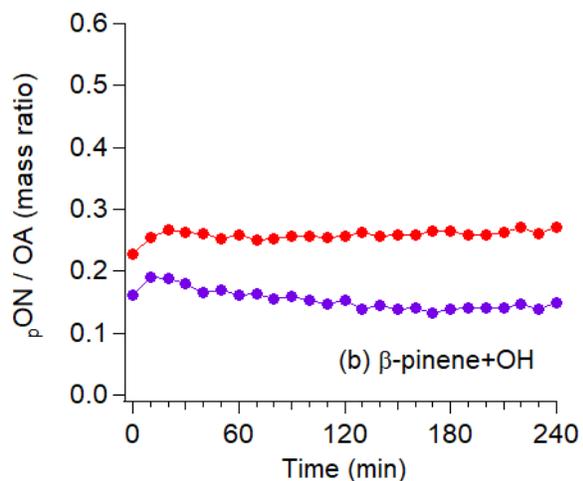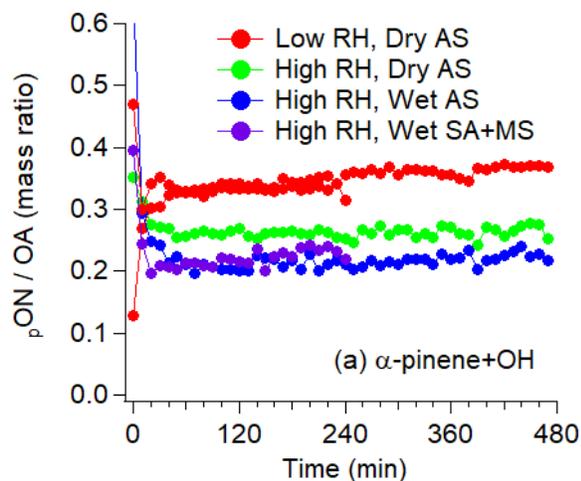
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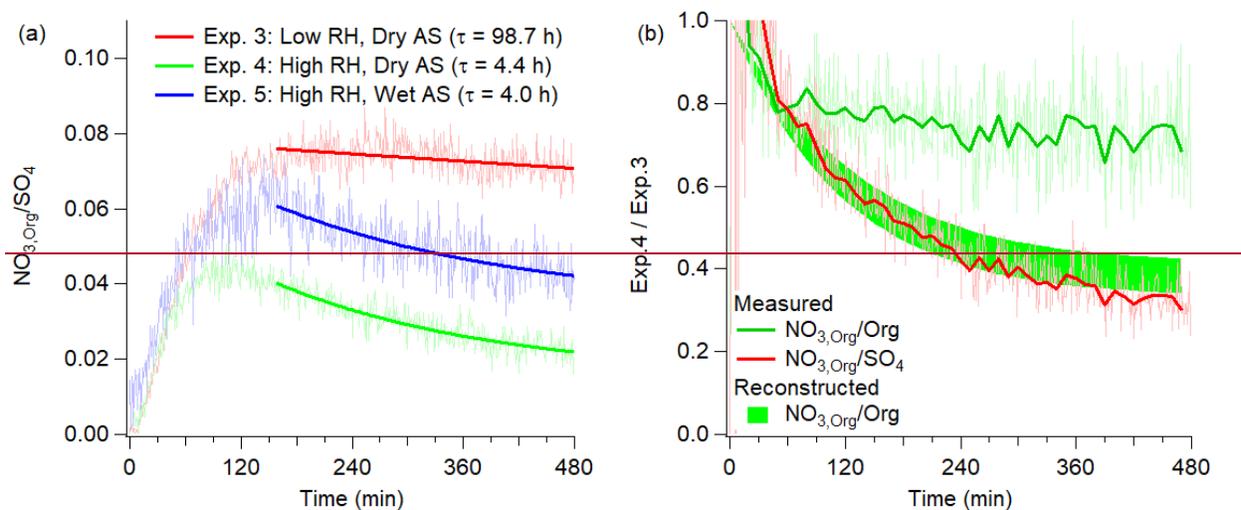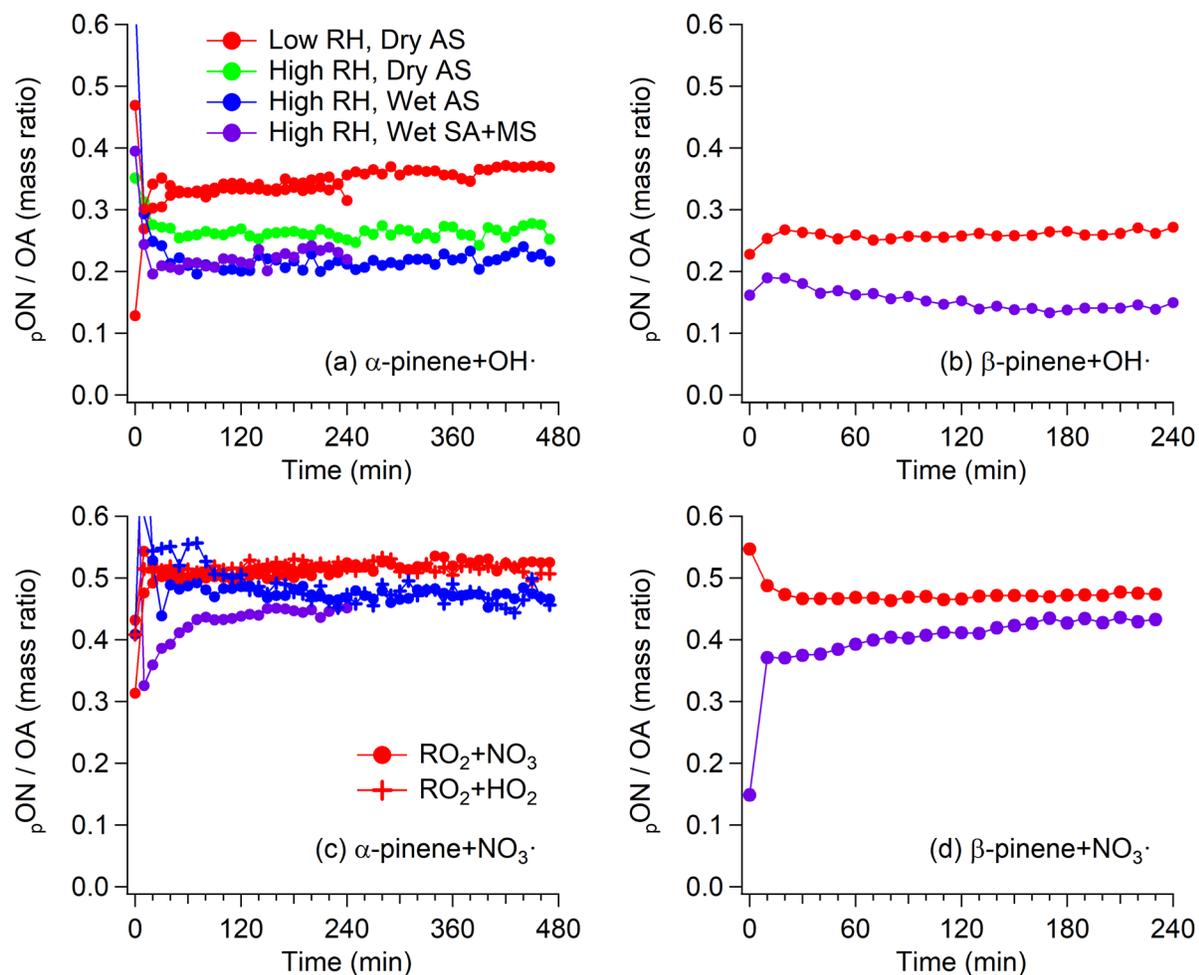

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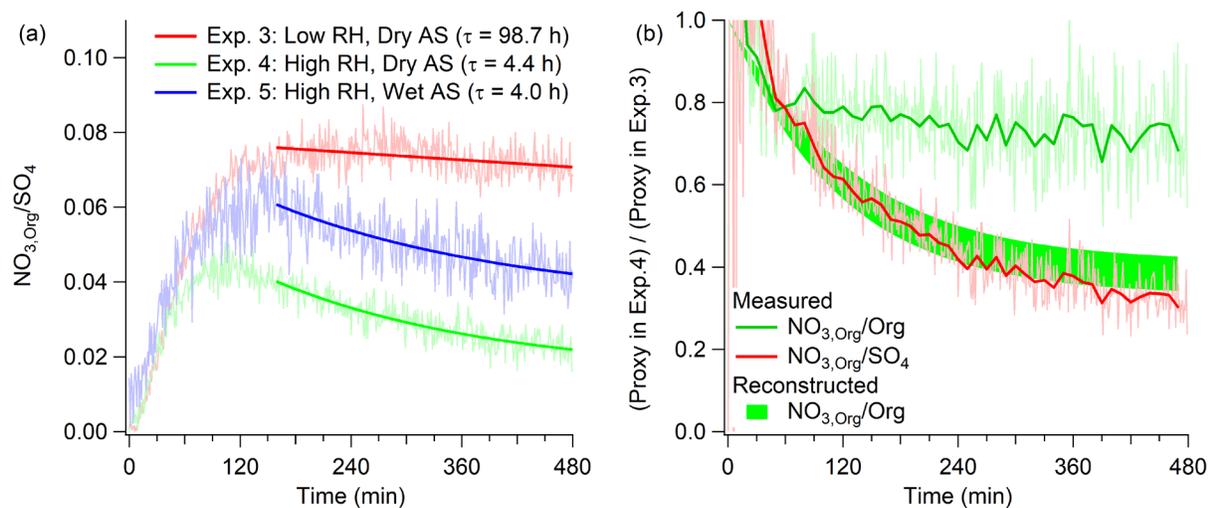
Figure 3. (a) Time-series data of $NO_{3,Org}/SO_4$ from Exp. 3-5 (α-pinene+OH·) and the exponential fits with corresponding characteristic times. (b) $NO_{3,Org}/Org$, $NO_{3,Org}/SO_4$, reconstructed $NO_{3,Org}/Org$ based on the decay rate of $NO_{3,Org}/SO_4$. Each proxy in Exp. 4 is divided by that in Exp. 3 to determine the relative decay between high and low RH experiments.

(a) α-pinene+OH

Low RH, Dry AS
High RH, Dry AS
High RH, Wet AS
High RH, Wet SA+MS

$_pON / OA$ (mass ratio)

Time (min)

(b) β-pinene+OH

$_pON / OA$ (mass ratio)

Time (min)

(c) α-pinene+NO$_3$

RO$_2$+NO$_3$
RO$_2$+HO$_2$

$_pON / OA$ (mass ratio)

Time (min)

(d) β-pinene+NO$_3$

$_pON / OA$ (mass ratio)

Time (min)

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Figure 4. Time-series data of $_pON$/OA in (a) α-pinene+OH· from Exp. 1-5, (b) β-pinene+OH· from Exp. 6-7, (c) α-pinene+NO$_3$· from Exp. 8-13, and (d) β-pinene+NO$_3$· from Exp. 14-15. Data points are colored by conditions concerning reactor RH and phase state of seed aerosol. For α-pinene+NO$_3$·, data points are also shaped differently depending on the expected dominant RO$_2$· fate.

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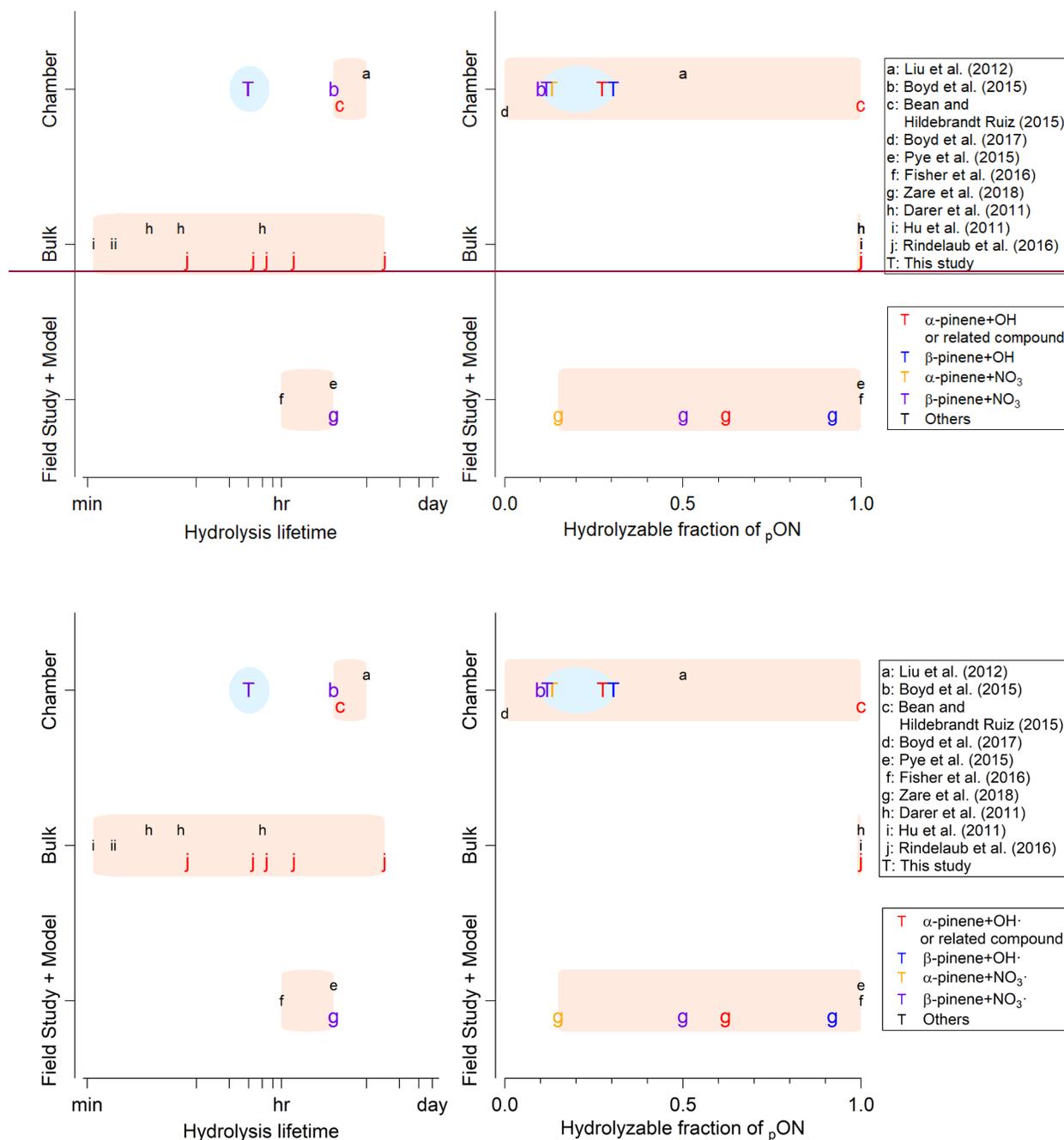
Figure 5. Comparison of hydrolysis lifetime of organic nitrate and hydrolyzable fraction of $_p$ON in literature. "Chamber" refers to laboratory studies of organic nitrate aerosol via chamber experiments, "Bulk" refers to laboratory studies of organic nitrate compounds using bulk solution measurements, and "Model" refers to modeling studies using ambient measurement data as constraints. Data points are colored by the system of VOC and oxidant condition explored in this study and are alphabetized based on the

618   reference. The relevant systems explored in this study are emphasized by enlarging the corresponding font

619   size. Pink shaded regions are ranges reported in literature, while blue shaded regions are ranges reported in

620   this study.

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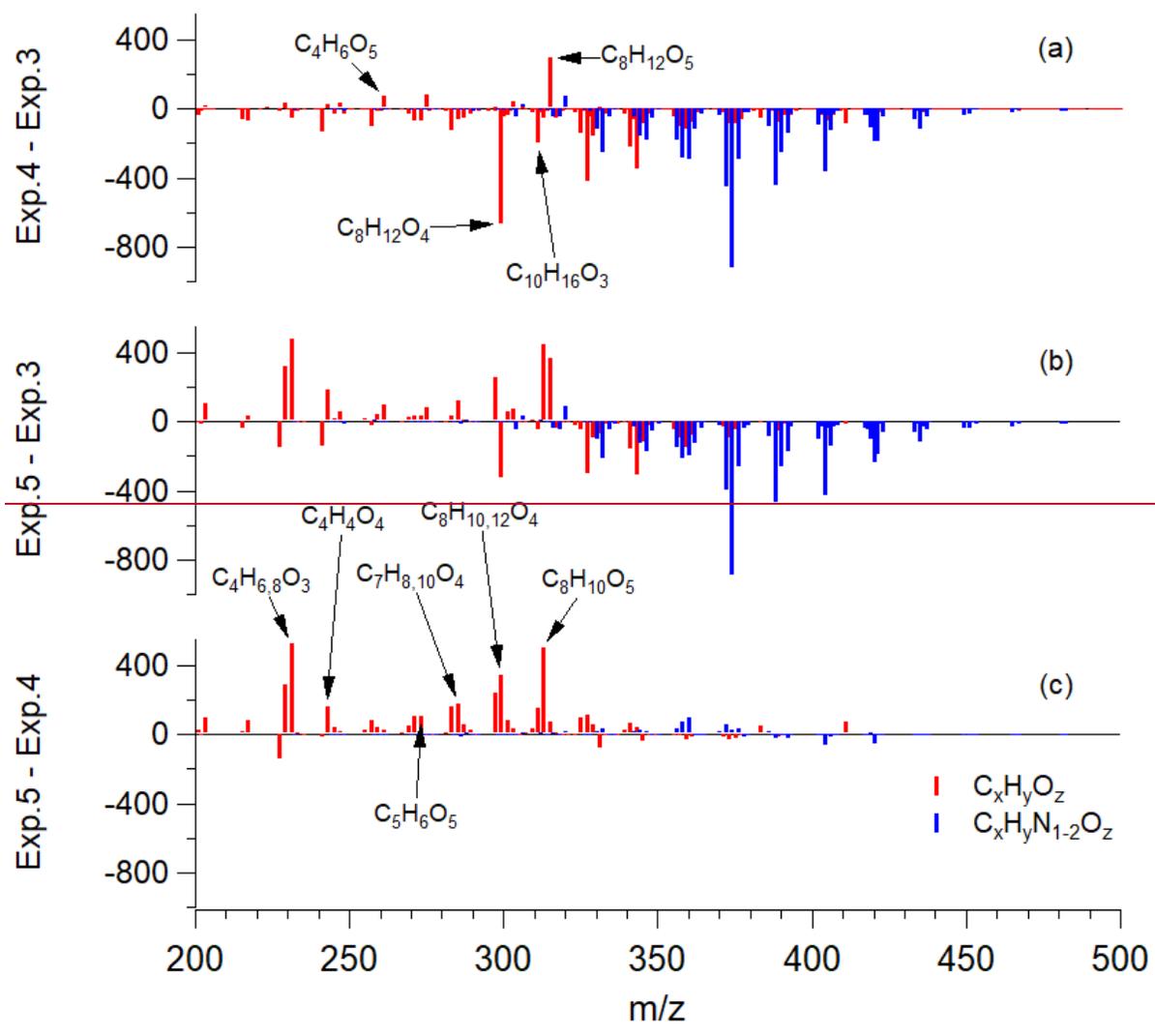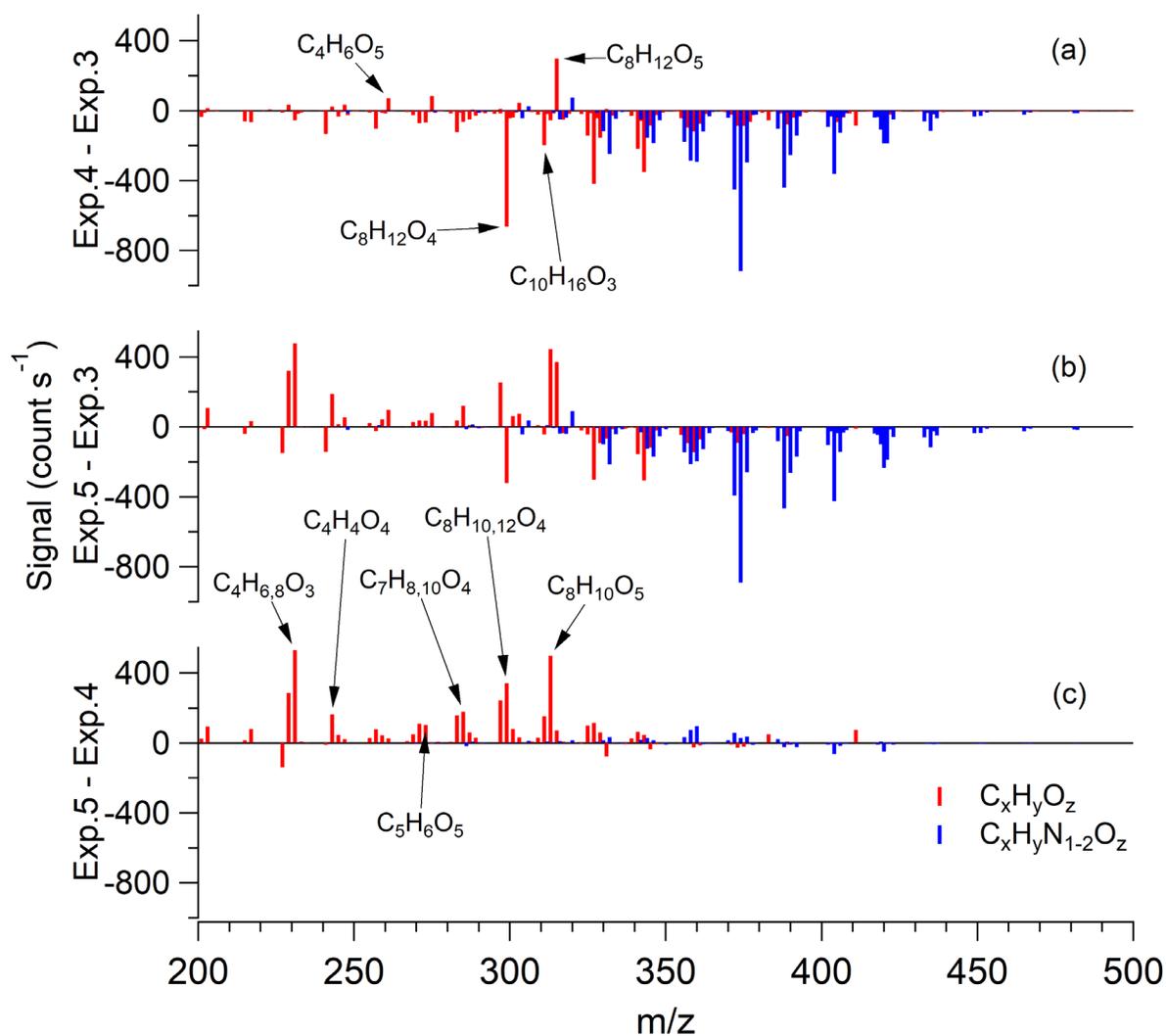
Figure 6. FIGAERO-HR-ToF-I-CIMS difference mass spectra of SOA in α-pinene+OH·. (a) Exp. 4 (high RH, dry AS) minus Exp. 3 (low RH, dry AS). (b) Exp. 5 (high RH, wet AS) minus Exp. 3 (low RH, dry AS). (c) Exp. 5 (high RH, wet AS) minus Exp. 4 (high RH, dry AS). Bars are colored by the difference in chemical composition (i.e., red for $C_xH_yO_z$ and blue for $C_xH_yN_{1-2}O_z$). Prominent masses are labeled with the corresponding chemical formulae without an iodide ion.

630   Table 1. Summary of experimental conditions considered in this study.

Exp.	Precursor VOC	Oxidant precursor	Reactor RH	Seed
1	α-pinene (25 ppb)	H_2O_2 (2 ppm), NO (6 ppb min^{-1})	~~~5~~1-3 %	Effloresced AS[b]
2	α-pinene (25 ppb)	H_2O_2 (2 ppm), NO (6 ppb min^{-1})	~~~50-70~~48-65 %[a]	Deliquesced SA+MS[c]
3	α-pinene (25 ppb)	H_2O_2 (2 ppm), NO (2 ppb min^{-1})	~~~5~~2-6 %	Effloresced AS
4	α-pinene (25 ppb)	H_2O_2 (2 ppm), NO (2 ppb min^{-1})	~~~50-70~~53-66 %[a]	Effloresced AS
5	α-pinene (25 ppb)	H_2O_2 (2 ppm), NO (2 ppb min^{-1})	~~~50-70~~57-72 %[a]	Deliquesced AS
6	β-pinene (25 ppb)	H_2O_2 (2 ppm), NO (6 ppb min^{-1})	~~~5~~1-3 %	Effloresced AS
7	β-pinene (25 ppb)	H_2O_2 (2 ppm), NO (6 ppb min^{-1})	~~~50-70~~53-70 %[a]	Deliquesced SA+MS
8	α-pinene (12 ppb)	N_2O_5 (80 ppb)	~~~5~~2-3 %	Effloresced AS
9	α-pinene (12 ppb)	N_2O_5 (80 ppb)	~~~60-70~~67-71 %	Deliquesced SA+MS
10	α-pinene (12 ppb)	N_2O_5 (80 ppb)	~~~5~~1-6 %	Effloresced AS
11	α-pinene (12 ppb)	N_2O_5 (80 ppb)	~~~60-70~~69-74 %	Deliquesced AS
12	α-pinene (12 ppb)	N_2O_5 (80 ppb), HCHO (25 ppm)	~~~5~~3-8 %	Effloresced AS
13	α-pinene (12 ppb)	N_2O_5 (80 ppb), HCHO (25 ppm)	~~~60-70~~67-71 %	Deliquesced AS
14	β-pinene (12 ppb)	N_2O_5 (80 ppb)	~~~5~~2-5 %	Effloresced AS
15	β-pinene (12 ppb)	N_2O_5 (80 ppb)	~~~60-70~~56-72 %	Deliquesced SA+MS

631   [a]The target for the initial reactor RH is ~70 %. However, the irradiation of UV light increases the reactor

632   temperature by several degree Celsius and hence decreases RH.

633   [b]Ammonium sulfate

634   [c]Sulfuric acid and magnesium sulfate

635

636   Table 2. Hydrolysis lifetime and corresponding fraction of hydrolyzable $_p$ON.

System	Hydrolysis lifetime	Hydrolyzable fraction (F_H)[a]
α-pinene+OH·	<30 min	23–32 %
β-pinene+OH·	<30 min	27–34 %
α-pinene+NO$_3$·	<30 min	9–17 %
β-pinene+NO$_3$·	<30 min	9–15 %

637   [a]Lower or higher limit of hydrolyzable $_p$ON fraction is based on the assumptions that organic moiety of

638   hydrolysis products remains in aerosol or partitions back to the gas phase.

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1006

1   **Supporting Information for**

2

3   **Chemical Composition and Hydrolysis of Organic Nitrate Aerosol formed from Hydroxyl and**

4   **Nitrate Radical Oxidation of α-pinene and β-pinene**

5

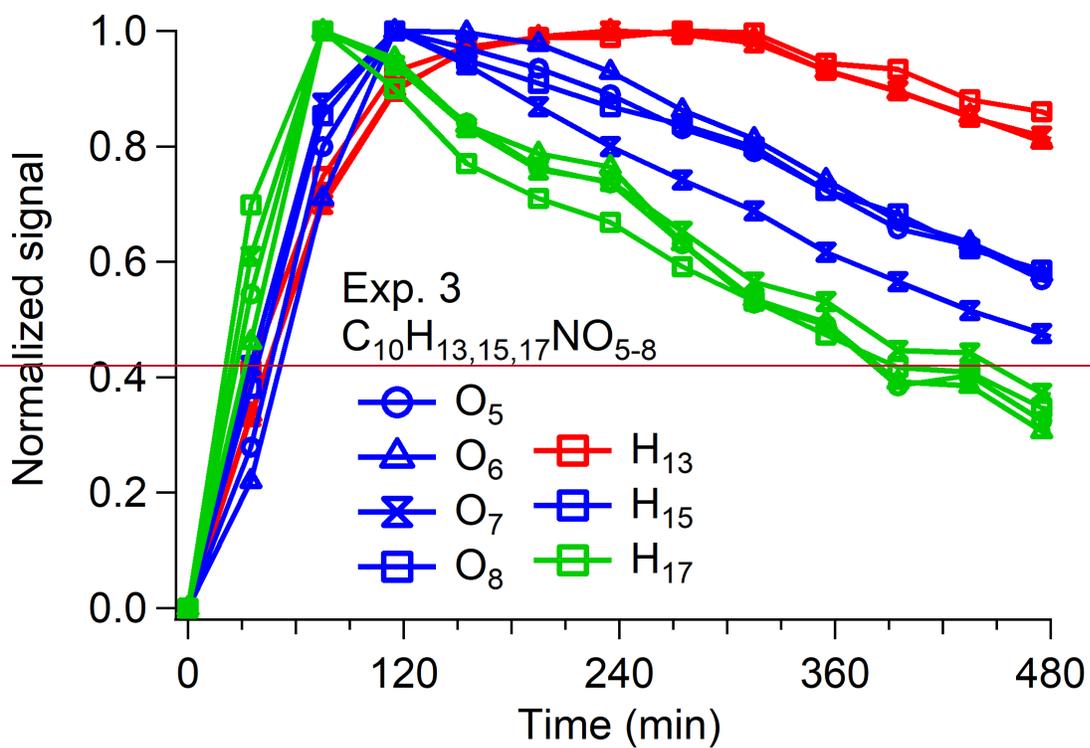6   Masayuki Takeuchi[1] and Nga L. Ng[2,3*]

7

8   [1]School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, Georgia, 30332,

9   USA

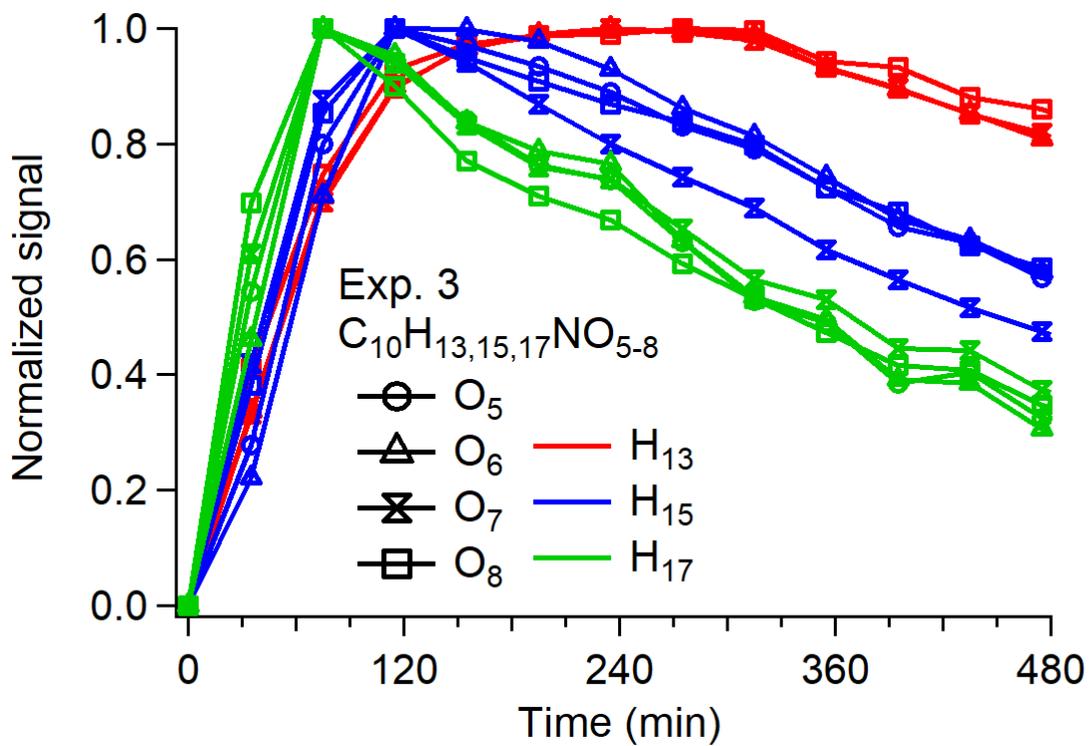10   [2]School of Chemical and Bimolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia,

11   30332, USA

12   [3]School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, 30332,

13   USA

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15

Exp. 3
$C_{10}H_{13,15,17}NO_{5-8}$

O₅ legend:
- O_5 (blue circle)
- O_6 (blue triangle)
- O_7 (blue x)
- O_8 (blue square)
- H_{13} (red square)
- H_{15} (blue square)
- H_{17} (green square)

16

Exp. 3
$C_{10}H_{13,15,17}NO_{5-8}$

- O_5 (black circle)
- O_6 (black triangle)
- O_7 (black x)
- O_8 (black square)
- H_{13} (red line)
- H_{15} (blue line)
- H_{17} (green line)

17

18   Figure S1. FIGAERO-HR-ToF-I-CIMS time-series data of select organic nitrate aerosol~~s (i.e.,~~

19   ~~C$_{10}$H$_{13,15,17}$NO$_{5-8}$)~~. All combinations of C$_{10}$H$_{13,15,17}$NO$_{5-8}$ with different oxygen and nitrogen numbers are

20   shown here. Different symbols correspond to compounds with different oxygen numbers, while different

21   colors correspond to compounds with different nitrogen numbers. Shown are the data from Exp. 3 (α-

22   pinene+OH·), though very similar trends are observed for β-pinene+OH· from Exp. 6.
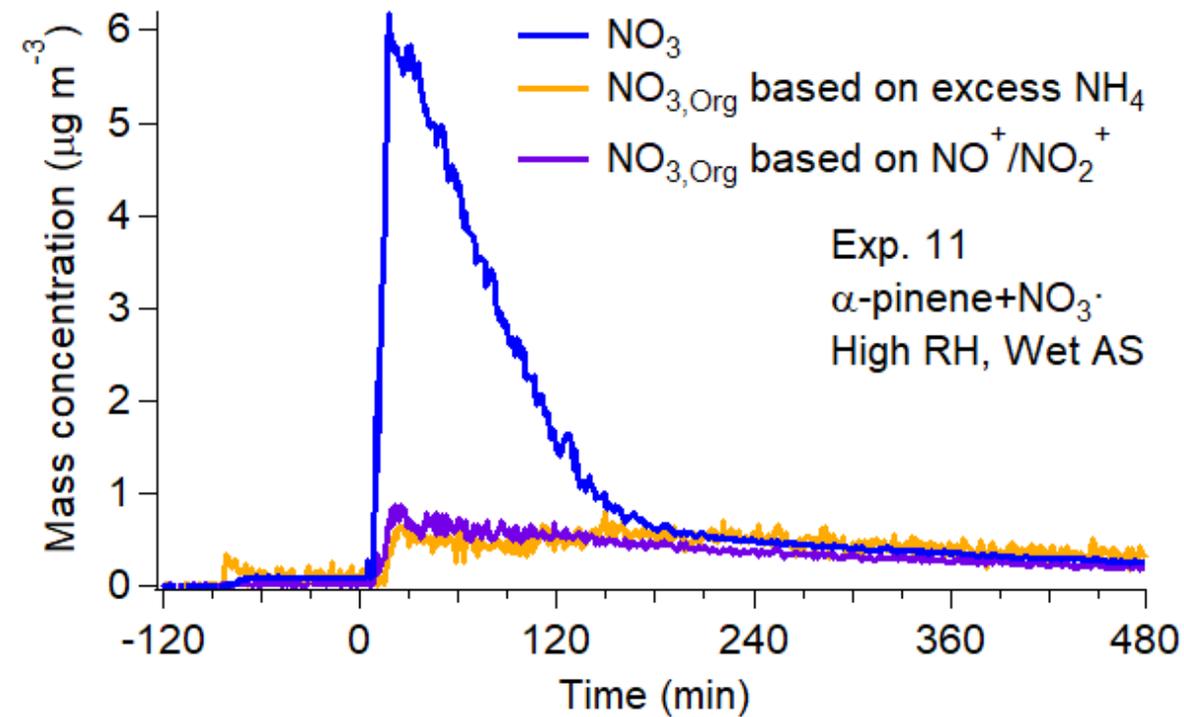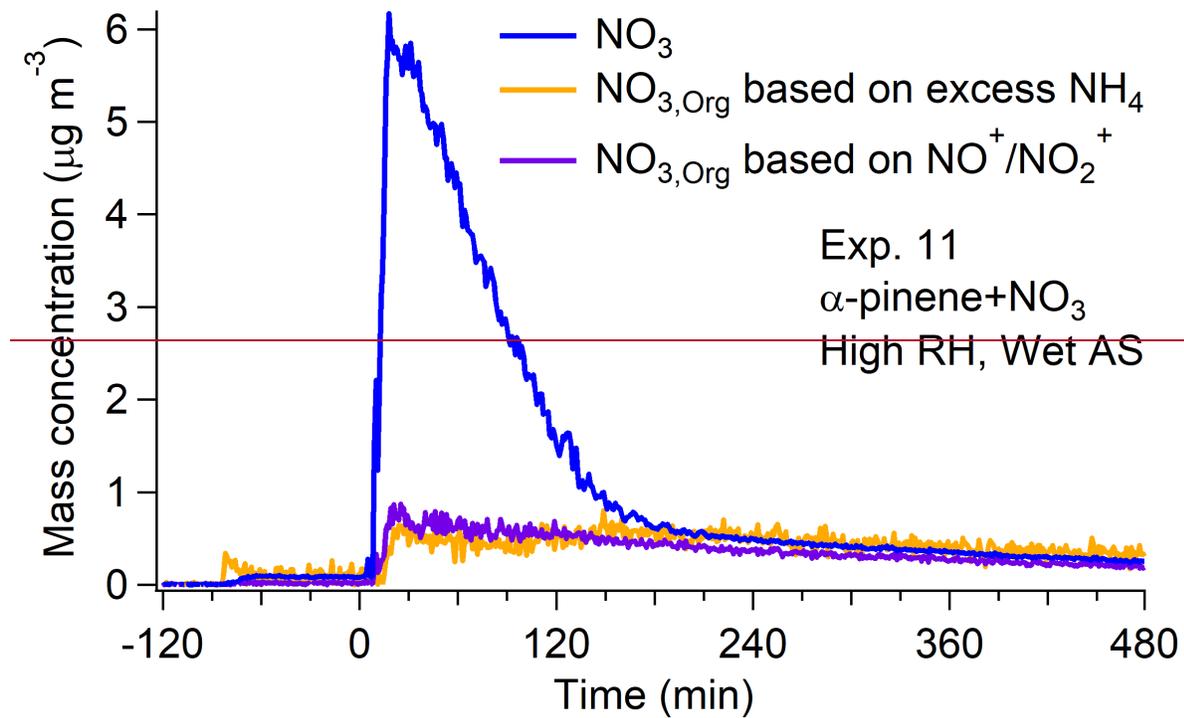
23
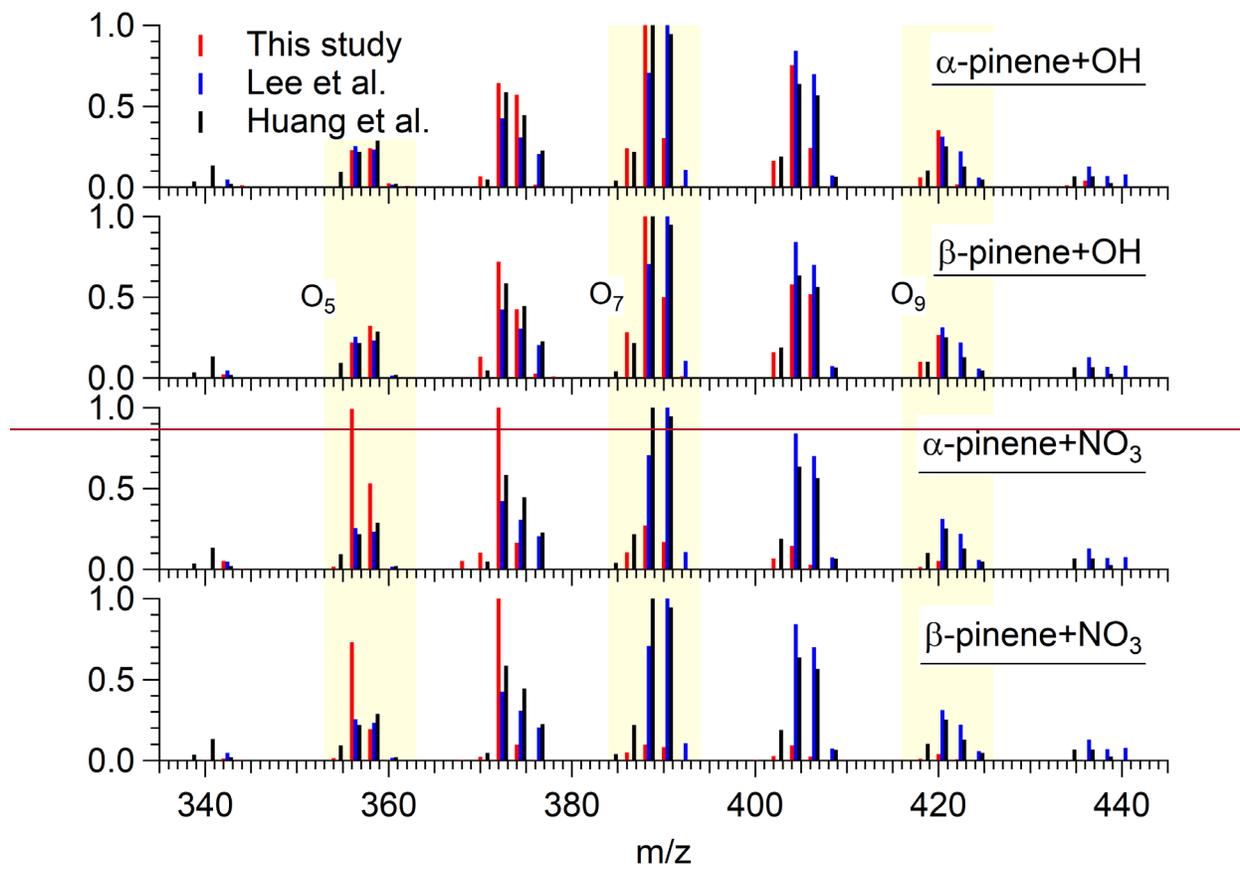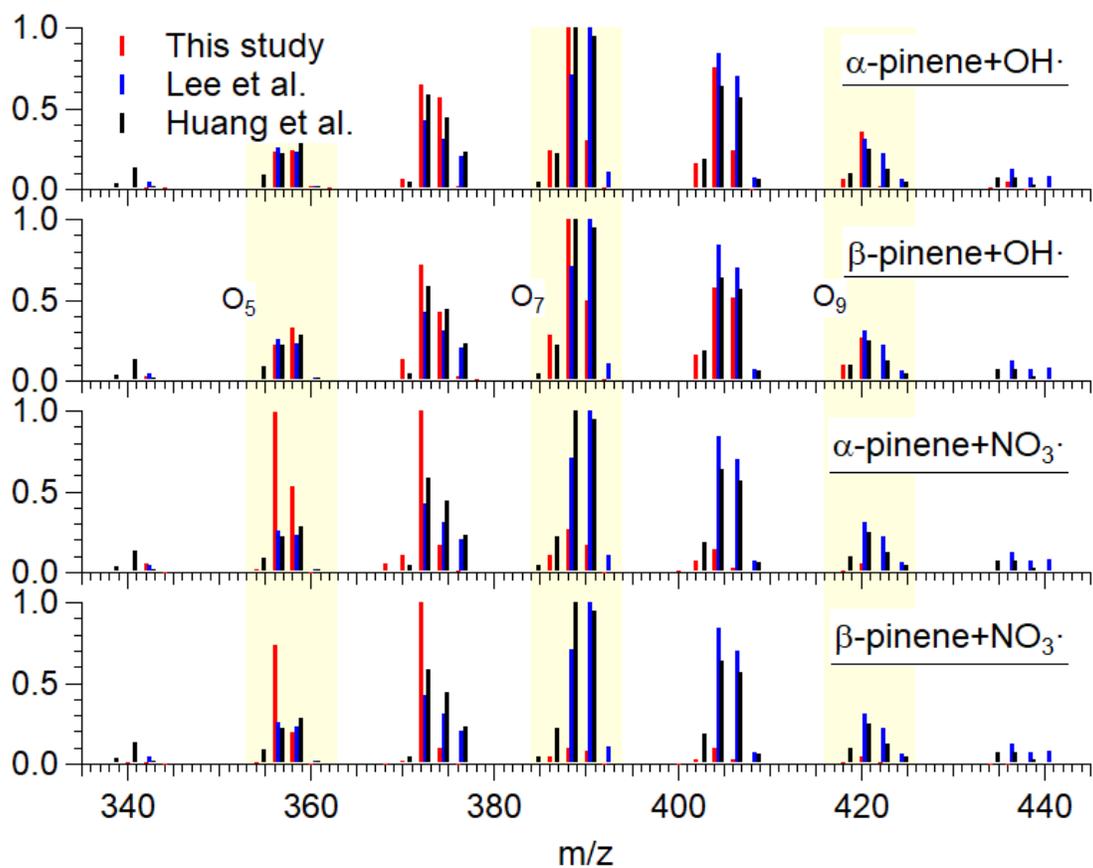
Figure S2. Comparison of FIGAERO-HR-ToF-I-CIMS mass spectra of organic nitrate aerosols (i.e., $C_{10}H_{11,13,15,17,19,21}NO_{4-11}$) with ambient measurement data (Lee et al., 2016; Huang et al., 2019). All mass spectra are normalized to the maximum signal.

30

31

32

33   Figure S3. Concentrations of NO_3 and $NO_{3,Org}$ derived from two independent methods. "Excess NH_4"

34   refers to a method to apportion the inorganic nitrate contribution to NO_3 based on the increase in NH_4 and

35   "NO^+/NO_2^+" refers to the method based on its ratio (Farmer et al., 2010).
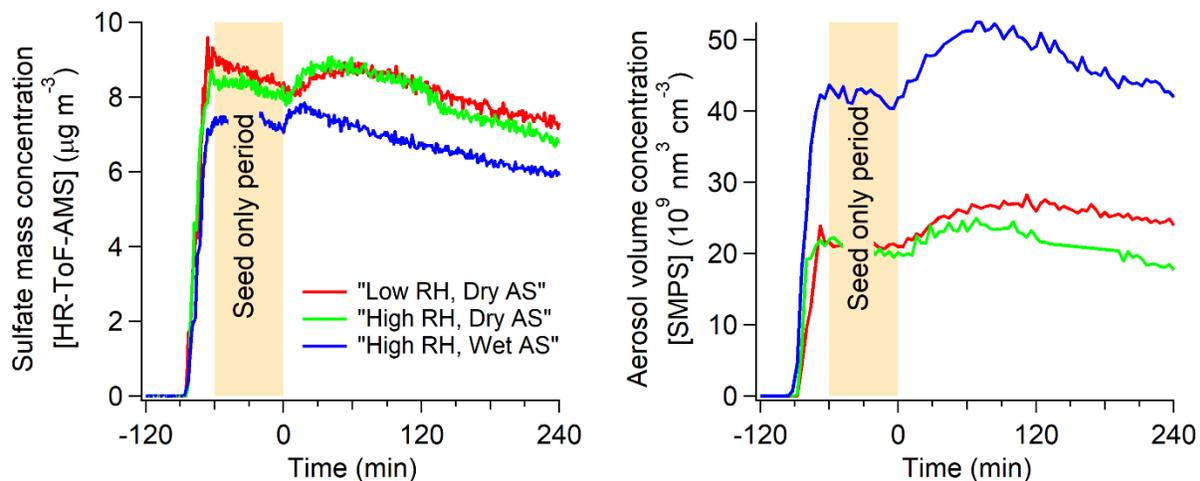
36

37 Figure S4. HR-ToF-AMS time-series data of SO$_4$ and SMPS aerosol volume concentration in Exp. 3 (low

38 RH, dry AS), Exp. 4 (high RH, dry AS), and Exp. 5 (high RH, wet AS). A significant difference in the

39 volume concentration among the experiments indicates the deliquesced nature in Exp. 5 (high RH, wet AS)

40 and the effloresced nature of seed particles in Exp. 4 (high RH, dry AS).
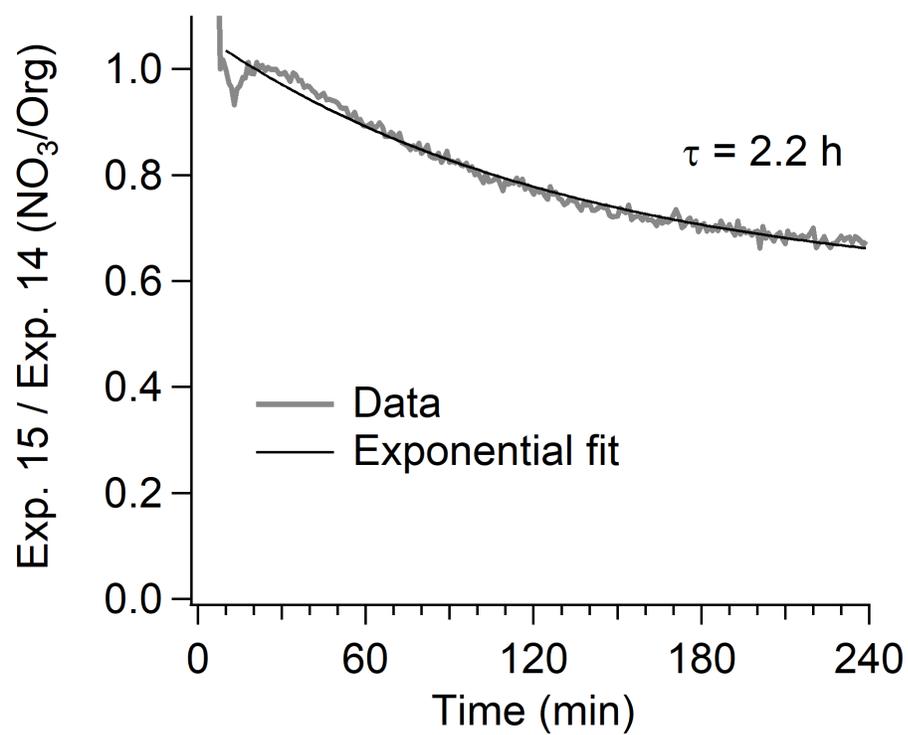
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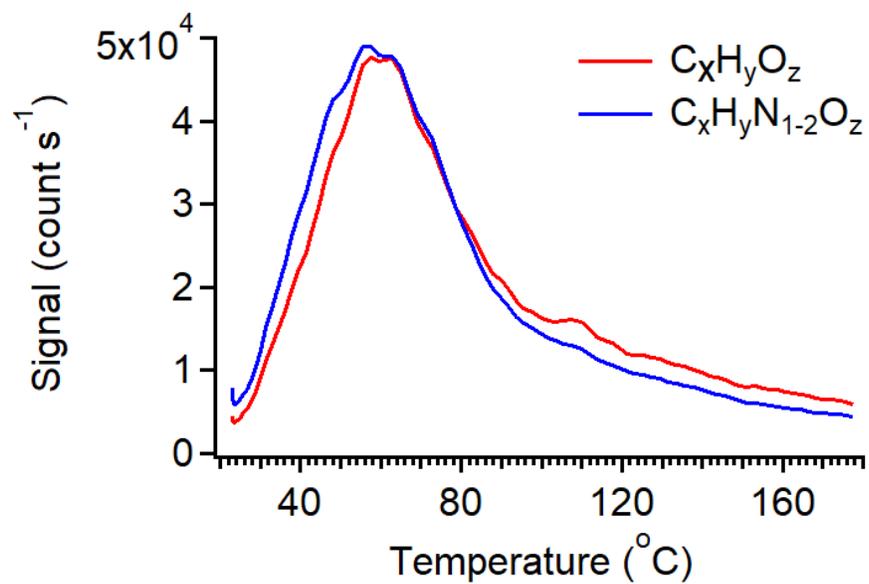
Figure S5. Thermal desorption profiles of $C_xH_yO_z$ and $C_xH_yN_{1-2}O_z$ in FIGAERO-HR-ToF-I-CIMS from

Exp. 3. Data points are averages of three desorption cycles around the peak SOA growth.
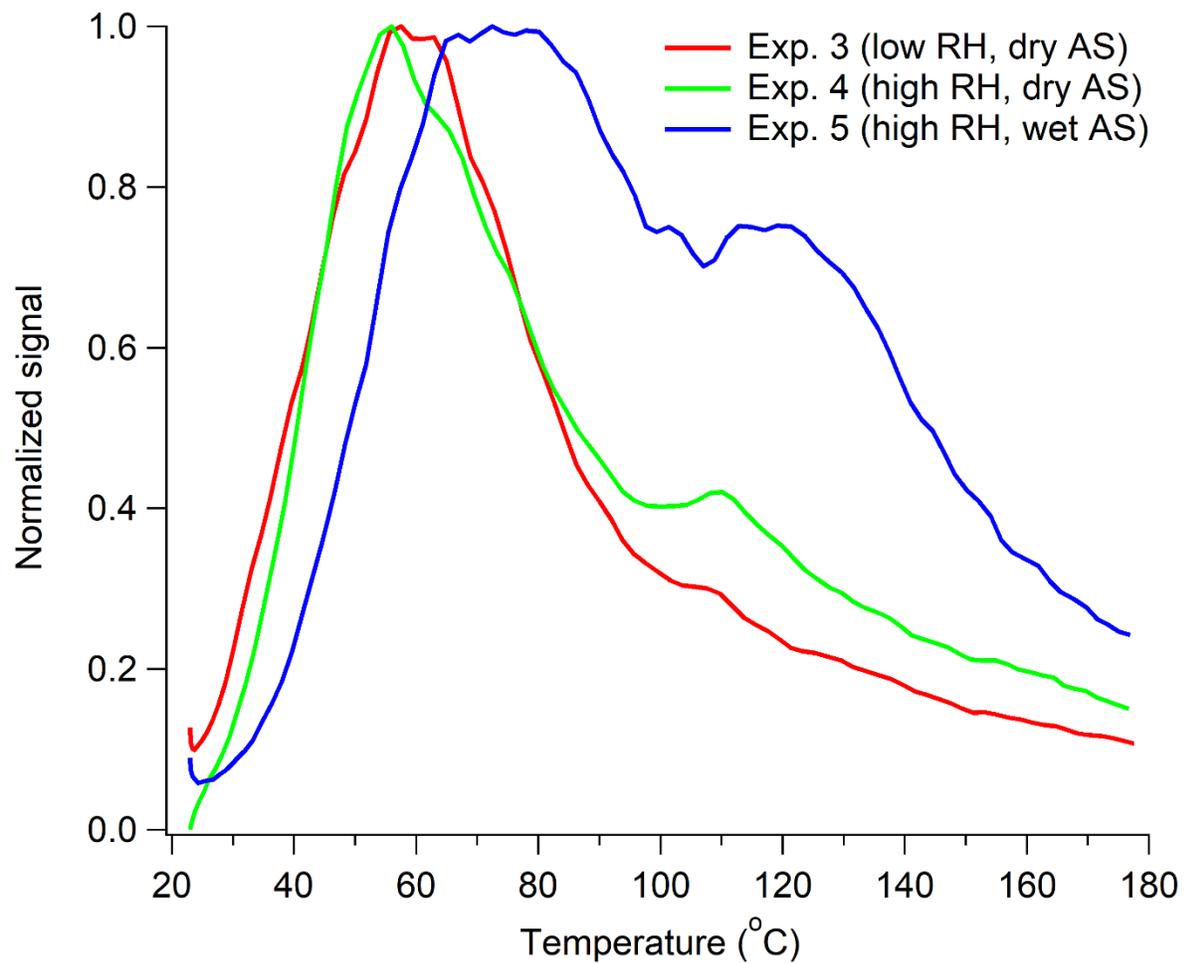
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$\tau = 2.2$ h

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Figure S56. Time-series data of NO_3/Org in Exp. 15 normalized to that in Exp. 14 based on the method

present in prior study (Boyd et al., 2015).

51

52   Figure S67. Average thermogram of organic aerosol (i.e., organic nitrate and non-nitrated organic

53   aerosol) at the peak of SOA growth in Exp. 3-5. Signals are normalized to the maximum signal for each

54   experiment.

55   Table S1. Summary of R_{AN} and R_{ON} applied to derive the concentration of $NO_{3,Org}$. R_{AN} from 300 nm

56   ammonium nitrate particle at the nearest date is used unless noted otherwise. R_{ON}/R_{AN} used for high RH

57   experiments are taken from the same experiment but under low RH experiments.

ID	R_{AN}	R_{ON}	R_{ON}/R_{AN}
1	2.87	6.25	2.18
2	2.87	6.25	2.18
3	2.80	5.75	2.05
4	2.80	5.75	2.05
5	2.88	5.91	2.05
6	3.06	5.02	1.64
7	3.06	5.02	1.64
8	3.24	8.64	2.67
9	2.87	7.66	2.67
10	2.70	8.24	3.05
11	2.80	8.55	3.05
12	2.80	8.60	3.07
13	2.88	8.85	3.07
14	2.87	7.13	2.48
15	2.56[a]	6.36	2.48

58   [a]R_{AN} is taken from 30-min average of NO^+/NO_2^+ during seed only period as the R_{AN} from the calibration at

59   the nearest date is slightly higher.

60

61

62   Table S2. Fraction of $_p$ON based on the number of carbon in each system.

System	$C_{\leq 9}$ $_p$ON	C_{10} $_p$ON	C_{11-19} $_p$ON	C_{20} $_p$ON
α-pinene+OH·	47 %	52 %	1 %	0 %
β-pinene+OH·	58 %	41 %	1 %	0 %
α-pinene+NO₃·	11 %	26 %	8 %	54 %
β-pinene+NO₃·	10 %	58 %	4 %	28 %

63

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