We thank the reviewers for their valuable comments. We have addressed each comment below in bold italic text, and indicate where necessary the corresponding changes we have made to the manuscript.

Anonymous Referee #1

## **General Comments**

In general, this is a very well written manuscript focused on experiments that investigated secondary organic aerosol formation from isoprene oxidation under low humidity scenarios in which nitrogen oxide levels were varied. It includes an assessment of the molecular formulas of the constituents, as well as their volatility. A comparison is made to volatility (vapor pressure) prediction methodologies, as well as to recent field results. It is certainly a topic of much current interest in the atmospheric chemistry community and is appropriate for ACP. Scientifically, there are no major faults with the paper, as it is standard methodologies (chamber at PNNL, for example – please do not misinterpret, as I recognize the difficulty of doing chamber measurements) along side those that are considered cutting edge (FIGAERO, for example) but evaluated and tested.

However, at times, I felt as if I were reading two papers that had been combined into one – that is, there could have been one manuscript that focused on these experiments with a comparison to field results; there are certainly sufficient data to do so. A second manuscript could have focused on the comparison of the volatility measurements to vapor pressure predictive capabilities. While the inability to predict vapor pressures of SOA constituents is not a new finding, the depth to which this area can be probed with the FIGAERO measurements is new and novel – perhaps warranting a second manuscript? This would certainly improve the readability of this manuscript. There were not significant issues with the writing, but the length and density of the manuscript made it slightly difficult to read.

Overall, I have no trouble recommending publication (following the authors addressing relatively minor specific comments below) based on its timeliness, topic, and high quality science. However, I would encourage both the editor and the authors to consider whether the manuscript could be split, simply to improve readability and perhaps to increase impact.

## We appreciate the referee's concern, and we have removed section 3.5 and figure 8 regarding the SOAS field data.

## **Specific Comments**

It might be helpful to include a short figure that shows the chemical structure of specific molecules that are included in the discussion (ISOPOOH, ISOP(OOH)2, IEPOX, etc.) for the individuals who might not think about this on a daily basis.

# We added a simple schematic showing isoprene and its major first and second generation oxidation products at both low and high-NO<sub>x</sub>. High NO<sub>x</sub> arrows are highlighted in blue.

Typo, p. 6, line 144, no need for the word "the"

## Fixed

Typo, p.7, line 168, "were" should be "was" (suite is singular)

## Fixed

Typo, p. 8, line 192, programmed has two m's

## Fixed

In Figure 1, it might be beneficial to show subsets that allow for seeing shorter periods of time. The length of time included/compressed on the x-axis makes seeing detail nearly impossible.

# We added a supplemental online document with enlarged versions of figure 1 to show more detail. We prefer to show all the data collected in this case given the continuous flow approach used.

On page 10, lines 227 and 231. What is the basis for the factor of 1.5 to correct for wall losses?

The correction is determined by comparing the size distributions of ammonium sulfate particles in the inlet and exit flows of the chamber, prior to any SOA deposition. The size dependent particle wall-loss rate is then calculated based on the known chamber residence time and the difference in the number size distributions. The methods to determine the particle wall loss corrections are explained in more detail elsewhere [Liu et al., 2016] for this set of experiments. We refer readers to that paper more clearly now when discussing particle wall loss corrections.

Typo, p. 16, line 365, data suggest, not suggests

## Fixed

P. 19, third sentence of paragraph beginning on line 435 could be re-written for clarity.

## Reworded to:

However, the disagreement for  $C_5H_{12}O_6$  (Fig. 5, bottom left, circles) cannot be explained solely by thermal decomposition of lower volatility material for two reasons: the thermogram shape is nearly Gaussian and therefore behaves like a single component, and the predicted  $F_p$  is much larger than measured (opposite to the above situation).

On page 20, with the discussion of use of the measured Tmax to predict the Fp for comparison to measured Fp: Perhaps I am missing something, but this seems like a circular argument. It should be the case that a measured parameter that is related to Fp should do a better job predicting Fp than something unrelated like the vapor pressure estimation technique. I don't think that this adds very much to the paper. I do find the information that allows an investigation of predicted Fp as a function of molecular formula to be quite interesting and useful though.

We have tried to improve this section as the reviewer is perhaps missing what we think is an important distinction. The measured  $F_p$  depends upon measured gas and particle phase concentrations of a compound the predicted  $F_p$  depends upon (among other parameters) the C<sup>\*</sup> and total OA. In comparing measured and modeled Fp, there is an initial assumption that gas-particle equilibrium is achieved, and that the C\* is known. With the FIGAERO, we can independently constrain the C\* from the thermogram to use in the predicted  $F_{p}$ . That is, the temperature where a compound's signal reaches a maximum ( $T_{max}$ ), is indicative of its C\* [Lopez-Hilfiker et al., 2014] but is largely independent of that compound's condensed-phase concentration. Thus using the FIGAERO measurement of C\* can improve the prediction of  $F_p$  so that issues related to the validity of gas-particle equilibration timescales or the role of thermal decomposition during measurement of particle composition can be the focus of assessing causes of disagreement between theory and measurement (see [Lopez-Hilfiker et al., 2014; Lopez-Hilfiker et al., 2016] ). The following sentences have been added in a short succeeding paragraph to clarify its importance:

There are a number of possible reasons why measured and predicted  $F_p$  do not agree, with one being that our methods to estimate C\* are flawed. This potential source of error can be addressed directly with the FIGAERO-CIMS thermogram, independently of the measured  $F_p$ , thereby allowing for a more robust assessment of whether (i) the assumption of gas-particle equilibrium is reasonable, (ii) there are possible biases in the measured  $F_p$  due to thermal decomposition, or (iii) the C\* estimation methods are valid. The above analysis demonstrates that all possibilities arise in this data set.

On page 21, lines 473-475. Please reword for clarity. Which models predicted higher C\*? And aren't group-contribution methods models? Perhaps word choice needs to be adjusted (or explain what the difference is).

Agreed, group-contribution methods are models, although we use "method" here to refer specifically to the group-contribution calculations, while "model" refers to a continuum solvent model [Kurten et al., 2016] and 0-D box model [Valorso et al., 2011] which are more computationally expensive than the group-contribution methods. We have changed the wording throughout the text to be consistent, as well as altering this sentence to include the specific models:

Our observations suggest this assumption is incorrect, at least to the extent employed in these methods, and is supported by previous work that found group-contribution methods predicted significantly lower C\* than two computational models, the conductor-like screening model for real solvents (COSMO-RS) [Kurten et al., 2016] and the generator for explicit chemistry and kinetics of organics in the atmosphere (GECKO-A) [Valorso et al., 2011], did for compounds with multiple functionalities.

Page 23, line 525. Does the change in viscosity imply a change in chemical composition? Do the measurements reflect that somehow?

We note that the  $T_{max}$  shift occurs for compounds with the same chemical composition and thus we assume that the compounds have the same structure. It is unclear why this  $T_{max}$  shift occurs, and we can therefore only suggest possible explanations. We do not have direct measurements of the viscosity of the particles.

On Figure 5, for predicted Fp (based on equation 1 and an estimated C\* from group contribution methods), a COA is needed. What value was used here?

We reworded the sentence starting on line 418 to specify where  $C_{OA}$  came from:

 $F_p$  were predicted using equation 1 with  $C_{OA}$  measured by the AMS and C\* calculated via the EVAPORATION group-contribution method [Compernolle et al., 2011], which generally gave similar estimates as the Capouet and Muller approach [2006].

## Anonymous Referee #2

## **General Comments**

In this manuscript the authors report results of a study of the formation of aerosol from the OH oxidation of isoprene. Experiments were conducted in an environmental chamber under high and low NOx conditions, and gas and aerosol composition and particle volatility were analyzed using a FIGAERO-CIMS instrument with iodide ionization. A major focus was an evaluation of the effects of NOx on organic nitrate and SOA formation, gas-particle partitioning, and particle volatility. Information was also obtained on the possible role of oligomer formation on SOA composition and yield. The lab results were used to help interpret measurements made with the same instrument at the 2013 SOAS campaign, providing additional insight into the role of isoprene in aerosol C1 chemistry. The study was well done, including measurements, data analysis, and interpretation. The manuscript is also well written. Overall the manuscript is of high quality and represents an important contribution to atmospheric chemistry. I recommend it be published after the following comments are addressed.

## **Specific Comments**

1. Line 160–162: Were the seed particles dried before entering the chamber. If not, might they not stay as deliquesced particles since the 50% RH is above the efflorescence point?

Yes, they passed through a diffusion drier before entering the chamber. The relative humidity of the drier output is routinely verified to be <30%, below the efflorescence point of ammonium sulfate particles [Cziczo and Abbatt, 2000]. We also verified that the seed particles were effloresced by comparing the size distribution of the particles exiting the 50% RH chamber.

2. Lines 212–215: If wall loss of NO is significant would you expect wall loss of organic vapors to also be significant?

This sentence was moved earlier in the paper into the "experimental overview" section from the "Gas-particle Partitioning: Saturation Vapor Concentrations and Oligomeric Content" section into the paragraph where particle wall loss is discussed:

Operating the chamber in continuous flow mode possibly reduces the net flux of organic compounds to the walls, at least for low volatility to semi volatile compounds, as some degree of equilibration can occur [Liu et al., 2016; Shilling et al., 2008]. Nonetheless, our vapor concentration data may be biased low due to some amount of loss to the walls.

Furthermore, we do not have evidence that a significant fraction of NO is lost to the walls, though it was not measured and Teflon is known to be somewhat permeable. We removed the last part of the sentence in question to prevent confusion that wall deposition is a main fate. NO is likely reacting fast enough with peroxy radicals that wall loss is not a significant fate.

3. Lines 226–227: It would be useful to explain how you get the factor of 1.5 used to correct AMS data for particle wall loss.

## See our response to reviewer #1's comment above.

4. I am aware of the mechanism for forming IEPOX under low NOx conditions, in which OH is lost from an –OOH group as the epoxide is formed. Is there an analogous mechanism for forming IEPOX under high NOx conditions in which NO2 is lost from a Â<sup>\*</sup>n–ONO2 group? If so it might be worth mentioning.

# Good point, IEPOX can be formed from the reaction of isoprene hydroxy nitrate with OH [Jacobs et al., 2014; Lee et al., 2014; St Clair et al., 2016], albeit at fairly low overall yields. See response to comment #6, we added a sentence mentioning this possibility.

5. Lines 336–338: This sentence is confusing to me. Are you saying that HO2 reacts with an alkene C=C double bond? I don't think this happens.

## Agreed. This sentence was changed to this:

Two possible sources of this compound are the reaction of the ISOPOOH derived peroxy radical ( $C_5H_{11}O_6$ ) with  $RO_2$ , or a dihydroxy alkene undergoing reaction with OH and  $O_2$  to form a dihydroxy peroxy radical, followed by reaction with  $HO_2$ .

6. Lines 344–348 and elsewhere: What about the possibility that HNO3 serves as an acid catalyst under high NOx conditions?

This is an interesting suggestion. Our two major tracers of IEPOX multiphase chemistry,  $C_5H_{12}O_4$  and  $C_5H_{10}O_3$ , both decrease in concentration in the particle phase with increasing NO<sub>x</sub>, arguing against HNO<sub>3</sub> acidifying the aerosol sufficiently to enhance "traditional" IEPOX SOA formation, but it may be driving some formation of oligomers from IEPOX. This idea would require more detailed experiments to assess. We have added the following sentences:

These two tracers are also observed in the  $NO_x$  addition experiments performed in continuous-flow mode, though at lower concentrations. In these experiments there was not enough NO to completely suppress ISOPOOH formation and therefore IEPOX formation from ISOPOOH + OH. Moreover, IEPOX can also form, albeit at lower yields, from OH reactions with the first-generation isoprene hydroxy nitrate [Jacobs et al., 2014; Lee et al., 2014; St Clair et al., 2016]. However, the formation of IEPOX SOA tracers is more puzzling given the very low reactive uptake of IEPOX expected on solid inorganic seed coated with isoprene SOA [Gaston et al., 2014; Riedel et al., 2015]. Perhaps nitric acid catalyzed IEPOX multiphase chemistry is contributing to the formation of these tracers at high  $NO_x$ . That said, observation of these tracers, also in the absence of  $NO_x$  addition, indicates that this explanation not sufficient.

7. Lines 394–395: I'm not sure what "included" means here. Do you mean the estimates have been corrected for these effects? Could make this clearer.

## See 8. below. This paragraph was slightly rearranged and sentences reworded to make the error corrections more clear.

8. Lines 393–394. What are the estimated uncertainties in the measured values of Fp?

The measured  $F_p$  values contain errors primarily from losses of gaseous vapors to the chamber walls as well as losses in the sampling inlet. Because the sampling inlet was short (1 m) and the flow volume was high (12 lpm) for the data presented in this plot, we expect inlet losses to be at most 25-44% assuming a diffusivity of 0.05-0.1 cm<sup>2</sup> s<sup>-1</sup> and irreversible loss at the wall. We made this more explicit in the text:

The largest source of error in the measured  $F_p$ , beyond thermal decomposition during desorption, is diffusion-controlled vapor losses in the inlet which were corrected for by assuming a diffusivity of 0.05-0.1 cm<sup>2</sup> s<sup>-1</sup>, although the variability is not discernable on the log scale. Inlet losses are 25-44% for the range of diffusivities, a small effect on the comparison of measured and predicted  $F_p$  as we show below.

9. Lines 481–502: With regards to the possible presence of accretion reaction products: Do you observe any masses with identical profiles to C5H12O6 or C5H10O6 that would be indicative of co-products of the thermal decomposition reactions?

On lines 445-460 we discuss the reasons these specific compounds do not show evidence of being thermal decomposition products. We added "as opposed to thermal decomposition" to the end of the sentence on line 459-460to make it clearer. We also added a paragraph to the end of section 3.3 and a corresponding figure (now Fig. 6) indicating evidence of accretion products measured by the FIGAERO-CIMS, as well as adding the sum of signal from compounds having 6 or more carbons to the bottom left panel of Figure 7 (previously Fig. 6).

10. Lines 521–525: Is it likely that SOA can have high viscosity at the temperatures used for thermal desorption?

How isoprene SOA viscosity varies as a function of temperature remains poorly studied, though our expectation is that viscosity lowers significantly as the aerosol is heated to 200 °C. It would be interesting to examine the

**Responses to Referees** 

thermal desorption behavior of SOA as a function of known viscosity but this has not been done. It is possible that there are two phases present, one with low viscosity that persists to temperature higher than 100 <sup>0</sup>C. However, we have no evidence for two organic phases.

**Technical Comments** 

1. Line 477: Should be "predicted".

## Fixed

2. Line 490: Should be FIGAERO-CIMS

## Fixed

3. Throughout the paper it seems like you switch arbitrarily from FIGAERO to FIGAERO-CIMS. I suggest you choose one and stick with it.

## We changed all "FIGAERO" references to "FIGAERO-CIMS" except where specifically talking about the unit itself.

4. Line 618: Is the volatility of IEPOX really known to 5 significant figures?

Good catch. We have reduced the number of significant figures to 1, more in line with previously stated c\*'s throughout the text, and reduced all other group-contribution method obtained c\*'s to 1 significant figure as well.

*Note: there was an error in the pie chart (figure 4) where we were previously not accounting for collection volume for the "other" portion of the pie. The updated figure does not change our conclusions.* 

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# Molecular composition and volatility of isoprene photochemical oxidation secondary organic aerosol under low and high NO<sub>x</sub> conditions

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36 Abstract. We present measurements of secondary organic aerosol (SOA) formation from isoprene photochemical oxidation in an environmental simulation chamber at a variety of oxidant 37 conditions and using dry neutral seed particles to suppress acid catalyzed multiphase chemistry. 38 39 A high-resolution time-of-flight chemical ionization mass spectrometer (HRToF-CIMS) utilizing iodide-adduct ionization coupled to the Filter Inlet for Gases and AEROsols (FIGAERO) 40 41 allowed for simultaneous online sampling of the gas and particle composition. Under high  $HO_2$ and low NO conditions, highly oxygenated ( $O:C \ge 1$ ) C<sub>5</sub> compounds were major components 42  $(\sim 50\%)$  of the SOA. The SOA composition and effective volatility evolved both as a function of 43 44 time and as a function of input NO concentrations. Organic nitrates increased in both the gas-45 and particle-phases as input NO increased, but the dominant non-nitrate particle-phase components monotonically decreased. We use comparisons of measured and predicted gas-46 47 particle partitioning of individual components to assess the validity of literature-based groupcontribution methods for estimating saturation vapor concentrations. While there is evidence for 48 equilibrium partitioning being achieved on the chamber residence time scale (5.2 hours) for some 49 50 individual components, significant errors in group-contribution methods are revealed. In 51 addition, >30% of the SOA mass, detected as low-molecular weight semi-volatile compounds, cannot be reconciled with equilibrium partitioning. These compounds desorb from the 52 FIGAERO at unexpectedly high temperatures given their molecular composition, indicative of 53 thermal decomposition of effectively lower volatility components such as larger molecular 54 55 weight oligomers.

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57 **1** Introduction

58 Atmospheric aerosol particles reduce visibility, adversely affect human health, and have uncertain overall effects on global climate [*Poschl*, 2005], with particles smaller than 1  $\mu$ m in 59 diameter playing important roles. Submicron particles typically contain a significant fraction of 60 61 organic material, on the order of 20-90% [Jimenez et al., 2009; Zhang et al., 2007]. Particulate organic material can be emitted directly to the atmosphere, known as primary organic aerosol, or 62 formed from the gas-to-particle conversion of volatile organic compound (VOC) oxidation 63 products which can partition [Donahue et al., 2011; Riipinen et al., 2011] or react 64 heterogeneously [Docherty et al., 2005; Gaston et al., 2014; Jang et al., 2002; Surratt et al., 65 66 2007; Surratt et al., 2006] on existing particles, or homogeneously nucleate to form new particles [Kirkby et al., 2016]. This condensed phase organic material arising from gas to particle 67 conversion is known as secondary organic aerosol (SOA). 68

69 Biogenic VOC (BVOC) contribute significantly to SOA. Emitted at rates of 500 TgC year<sup>-1</sup> [Guenther et al., 2012] and with a high reactivity, isoprene (C<sub>5</sub>H<sub>8</sub>) has the potential to 70 71 contribute substantially to SOA, even if the overall conversion is inefficient. Initially, the 72 observed products of isoprene oxidation were of high volatility, which led to the hypothesis that isoprene did not generate SOA [Pandis et al., 1991]. However, subsequent chamber experiments 73 showed that the yield of SOA from isoprene photochemical oxidation can range from <1-29% 74 with the highest yields achieved either with acidic aqueous seed particles [Surratt et al., 2010] or 75 as a transient during successive oxidative aging [Kroll et al., 2006]. Chemically speciated 76 77 measurements of atmospheric aerosol components in an isoprene-rich environment identified polyol compounds likely formed from isoprene oxidation [Claeys et al., 2004; Paulot et al., 78 2009b]. Subsequent chamber studies have shown that, under low NO conditions, isoprene reacts 79 80 with OH followed by HO<sub>2</sub> to form a hydroxy hydroperoxide, ISOPOOH, which further reacts

81 with OH to form the isoprene epoxy diol, IEPOX (see Scheme 1) [Paulot et al., 2009a; Paulot et al., 2009b]. Both laboratory and field studies suggest that IEPOX plays an important role in the 82 formation of isoprene SOA (iSOA) via acid catalyzed heterogeneous reactions on deliquesced 83 84 particles [Gaston et al., 2014; Lin et al., 2013a; Lin et al., 2014; Lin et al., 2012; Lin et al., 2013b; Liu et al., 2014; Paulot et al., 2009b; Surratt et al., 2010; Surratt et al., 2006]. In the 85 absence of acidic seed particles, iSOA yields have generally been low, but functional group 86 analyses suggested a significant contribution of peroxide moieties and a complex dependence 87 upon NO<sub>x</sub> [Dommen et al., 2006; King et al., 2010; Kroll et al., 2005; 2006; Sato et al., 2011; Xu 88 et al., 2014; Zhang et al., 2011]. Despite these advances, a comprehensive molecular 89 characterization of photochemical iSOA has been lacking. 90

Much attention has been focused on the formation of SOA derived from IEPOX 91 chemistry; however, understanding the formation of SOA from pathways other than IEPOX is 92 important for quantifying SOA in environments where the SOA is likely formed via other 93 mechanisms due to the lack of acidic seed. Three recent studies have performed photochemical 94 oxidation on either ISOPOOH [Krechmer et al., 2015; Riva et al., 2016] or both isoprene and 95 ISOPOOH [Liu et al., 2016] in the absence of wet acidic seed in order to study the mechanism of 96 97 iSOA formation when the IEPOX pathway is suppressed. These studies identified several  $C_5H_{8-}$ <sub>12</sub>O<sub>4-8</sub> compounds in both the gas- [Krechmer et al., 2015] and particle- [Liu et al., 2016; Riva et 98 al., 2016] phases. Liu et al. [2016] found that under the photochemical conditions of their 99 100 chamber, the most abundant compound in the particle-phase was  $C_5H_{12}O_6$ , ISOP(OOH)<sub>2</sub>, 101 presumed to be a dihydroxy dihydroperoxide formed from the reaction of an organic peroxy radical  $(RO_2)$  derived from ISOPOOH + OH followed by further reaction with hydroperoxy 102 103 radicals (HO<sub>2</sub>) (see Scheme 1) [Liu et al., 2016]. However, the iSOA yields starting from

isoprene reported by Liu et al. [2016] were substantially higher than those starting from
ISOPOOH alone as reported by Krechmer et al. [2015], and generally higher than most previous
iSOA studies in the absence of deliquesced acidic seed particles [*Dommen et al.*, 2006; *King et al.*, 2010; *Xu et al.*, 2014].

108 Furthermore, there is significant interest in understanding how anthropogenic pollutants 109 affect SOA yields [Shilling et al., 2013; Weber et al., 2007; Xu et al., 2015], and there have been several chamber studies to understand the role of NO<sub>x</sub> specifically on iSOA yields [Dommen et 110 al., 2006; King et al., 2010; Kroll et al., 2005; 2006; Xu et al., 2014; Zhang et al., 2011]. The 111 112 general effect of NO<sub>x</sub> on the newly discovered non-IEPOX SOA system has been described 113 previously [Liu et al., 2016]. The total SOA mass concentration was shown to be stable for input NO concentrations from 0-20 ppb, with a sharp decrease in SOA mass concentration at the 114 115 highest input NO concentration (50 ppb). While these studies have advanced our knowledge of the possible mechanisms of iSOA formation, in order to more accurately assess the environments 116 in which this pathway will operate, it remains important to further quantify (a) the branching 117 118 between the formation of the  $C_5H_{11}O_6$  peroxy radical versus the formation of IEPOX from the 119 reaction between ISOPOOH and OH, (b) the fate of the  $C_5H_{11}O_6$  peroxy radical under various 120 environmental conditions, as well as (c) the volatility of the SOA formed under various environmental conditions and (d) the role of the broader suite of oxidation products in the 121 formation of this non-IEPOX SOA. 122

We present laboratory chamber studies of the gas- and particle-phase composition resulting from both the low- and high-NO<sub>x</sub> photochemical oxidation of isoprene with the goal of better understanding the chemical mechanisms of iSOA formation and the evolution of its volatility and composition over time, specifically points (c) and (d) above. We compare the

observed gas-particle partitioning of several oxidation products to an assumption of equilibrium 127 128 partitioning theory. In this analysis, we use the measured thermograms of particle-phase components to assess commonly used group-contribution methods for estimating saturation 129 130 vapor concentrations, C\*. Moreover, we use a combined composition-volatility framework [Lopez-Hilfiker et al., 2015] to quantify the presence of more refractory oligomer-like 131 components of the SOA. From these analyses we find (*i*) the direct effect of higher  $NO_x$  (i.e. all 132 else being constant) is a suppression of iSOA yields at very high input NO concentrations (50 133 ppb); (ii) a large shift to more refractory components and N-containing products with increasing 134 135 NO<sub>x</sub>; (*iii*) a generally important role for oligomerization reactions and other multiphase chemistry irrespective of NO<sub>x</sub> concentrations, even at relatively low precursor concentrations, 136 likely involving a broad suite of isoprene oxidation products. 137

138

139 2 Experimental methods

## 140 2.1 Chamber Operation

141 Experiments were performed in Pacific Northwest National Laboratory's (PNNL) 10.6 m<sup>3</sup> polytetrafluoroethylene (PTFE) environmental chamber. The chamber has been described in 142 143 detail elsewhere [Liu et al., 2012], and a portion of the data discussed herein were obtained from the same experiments described in Liu et al. [2016]. Additional experiments with identical 144 chamber operation were conducted to examine a wider range of oxidant conditions. The chamber 145 146 was primarily operated in continuous-flow mode where reactants were continuously delivered at a constant rate to allow reaction precursors and products to reach steady state concentrations 147 [Shilling et al., 2008]. The extent of reaction is controlled by oxidant concentrations and the 148 149 residence time of air within the chamber, typically 5.2 hours. We also discuss a time-dependent 150 "batch mode" experiment also performed during 2015 for comparison purposes where the 151 chamber is filled with a fixed amount of isoprene and oxidant precursors in the dark and then the 152 chemistry is followed for ~6 hours after turning on the UV-VIS lights.

153 Isoprene was delivered into the chamber via a calibrated cylinder (Matheson, 20 ppm in nitrogen) and mass flow controller. OH radicals were generated by the photolysis of H<sub>2</sub>O<sub>2</sub>. An 154 155 aqueous solution of  $H_2O_2$  was introduced into the chamber via an automated syringe operated at various flow rates to achieve a range of H<sub>2</sub>O<sub>2</sub>, and therefore OH and HO<sub>2</sub>, concentrations. Quasi-156 monodisperse, effloresced 50 nm diameter solid ammonium sulfate seed particles were 157 continually added to facilitate the partitioning of oxidized VOC onto particle surfaces as opposed 158 to chamber walls [Zhang et al., 2014] for the formation of SOA. When desired, NO was added 159 via a calibrated cylinder (Matheson, 500 ppm in nitrogen) and mass flow controller. During the 160 161 continuous-flow experiments RH was controlled to ~50 %, while the batch mode experiment was performed under dry conditions (~10% RH). 162

163

#### 164 2.2 Instrumentation

A suite of online instruments was utilized to monitor gas- and particle-phase composition. Ozone and NO/NO<sub>2</sub>/NO<sub>x</sub> concentrations were measured using commercial instruments (Thermo Environmental Instruments models 49C and 42C, respectively). Aerosol number and volume concentrations were measured with a scanning mobility particle sizer (SMPS, TSI model 3936). An Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HRToF-AMS) monitored bulk submicron organic and inorganic aerosol composition. The evolution of isoprene was monitored with an Ionicon proton-transfer-reaction mass spectrometer (PTR-MS). 172 A high-resolution time-of-flight chemical ionization mass spectrometer (HRToF-CIMS) 173 using iodide-adduct ionization as described previously [B H Lee et al., 2014] was coupled to a Filter Inlet for Gases and AEROsols (FIGAERO) [Lopez-Hilfiker et al., 2014] for measuring a 174 175 suite of oxygenated products in the gas- and particle-phase. The HRToF-CIMS provides measurements of molecular composition, although cannot provide structural information and 176 therefore cannot differentiate between isobaric compounds. Briefly, the FIGAERO is an inlet 177 manifold that allowed for measurement of both gas- and particle-phase molecular composition 178 with approximately hourly time resolution. To collect particles, chamber air was drawn through a 179 180 1.27 cm OD (2014) or 0.635 cm OD (2015) stainless steel tube at 2.5 slpm across a Teflon filter (Zefluor® 24 mm diameter, 2.0 µm pore size, Pall Corp.) for 31 (2014), 42 (2015), or 25 (batch) 181 182 minutes. Through a separate inlet chamber air was simultaneously sampled at 22 slpm (2014) or 183 12 slpm (2015) through a 1.9 cm OD, 2 m long (2014) or 1.1 m long (2015) PTFE tube for gasphase analysis. The gas-phase analysis required sub-sampling a portion of the flow after dilution 184 185 to maintain linearity of response in the chemical ionization. After a particle collection period, 186 gas-phase analysis ends and the filter containing collected particles is actuated to a location downstream of an ultra-high purity (UHP) N<sub>2</sub> source and immediately upstream of an orifice into 187 the HRToF-CIMS. UHP N<sub>2</sub>, continually passed across the filter at 2.5 slpm, was heated at a rate 188 of 10 or 15 °C min<sup>-1</sup> to 200 °C for a temperature-programmed thermal desorption and then kept 189 at 200 °C for the remainder of the desorption time (60 min total 2014, 70 min 2015, 40 min 190 191 batch). The coupled FIGAERO HRToF-CIMS will be referred to herein as the FIGAERO-CIMS. The temperature axis of the FIGAERO thermograms is calibrated with compounds having 192 193 known enthalpies of sublimation [Lopez-Hilfiker et al., 2014]. Lopez-Hilfiker et al. [2014] have 194 shown that pure compounds, or mixtures of non-interacting compounds, have consistent thermogram shapes throughout time and reach a maximum signal at characteristic temperature ( $T_{max}$ ) which can be related to their enthalpies of sublimation and therefore sub-cooled pure component vapor pressures. In this way, the  $T_{max}$  of detected compounds can be used to estimate their C\* at ambient conditions even if the structure is unknown.

- 199
- 200 2.3 Experimental Overview

Figure 1 presents a time series of all steady-state experiments. The left and right columns contain 201 experiments conducted in May of 2014 and 2015, respectively. The top panels show the input 202 concentrations of isoprene, hydrogen peroxide, and NO, as well as the isoprene and  $C_5H_{10}O_3$ 203 (ISOPOOH + IEPOX) concentrations measured at the chamber output. The phrases "input NO", 204 "input H<sub>2</sub>O<sub>2</sub>", and "input isoprene", refer to the concentration of precursor that would be in the 205 206 chamber if there were no loss mechanisms except for dilution. For example, in Figure 1, top, the input isoprene (dashed green line) is flat, while the amount of isoprene remaining in the 207 chamber, i.e. what is measured with the PTR-MS (solid green line), varies depending on the 208 209 chamber chemical environment. Thus, while we state that we input 0-50 ppb NO in the chamber, 210 in reality steady-state NO concentrations in the chamber are much lower for the majority of the 211 chamber residence time, in fact, usually below the detection limit of the NO analyzer due to loss mechanisms such as photochemical conversion to NO<sub>2</sub> and nitrate formation. 212

In Figure 1 (top row) we show the time series of gas-phase species: input concentrations of isoprene which were generally similar across both years (26 ppbv 2014, 20 ppbv 2015), NO, and  $H_2O_2$ , as well as gas-phase measurements of the isoprene remaining in the chamber and  $C_5H_{10}O_3$ . As discussed above, the HRToF-CIMS cannot differentiate isobaric compounds and thus  $C_5H_{10}O_3$  represents the sum of ISOPOOH and IEPOX. It is important to note that while we 218 are suppressing the uptake of IEPOX into the particle-phase, it is still produced at a yield of 219 about 70-80% [St Clair et al., 2016] from the reaction of ISOPOOH + OH. The middle row shows the organic aerosol (OA) as measured by the AMS with the AMS blanks highlighted in 220 221 black squares. Steady-state periods for analysis were determined by an unchanging OA concentration over a period of 2 or more hours typically at least 24 hours after an intentional 222 change in experimental conditions. The bottom panels show the time series of a few dominant 223 224 particle-phase components as measured by the FIGAERO-CIMS: C<sub>5</sub>H<sub>12</sub>O<sub>6</sub>, C<sub>5</sub>H<sub>12</sub>O<sub>5</sub>, and C<sub>5</sub>H<sub>11</sub>NO<sub>7</sub>. The organic nitrate is scaled by a factor of 20 to show its time series on the same 225 226 scale, although it is near zero when NO is not added to the chamber. The grey shaded areas in the 227 left column indicate when there was a chamber cleaning followed by a dark  $NO_3$  + isoprene experiment that is not discussed here. By systematically scanning H<sub>2</sub>O<sub>2</sub> and NO concentrations 228 229 independently, we were able to test the response and composition of the SOA across a range of oxidant conditions, ranging from more pristine to polluted in terms of NO<sub>x</sub> concentrations. 230

All AMS and particle-phase FIGAERO-CIMS data have been multiplied by a factor of 231 232 1.5 to correct for particle wall losses as described in Liu et al. [2016], and where we also 233 describe the effect of seed particle surface area concentrations on SOA mass yields from this system in order to assess indirectly the role of vapor wall loss. The effect of added seed was 234 minimal and as such data shown here have not been corrected for vapor wall losses. Operating 235 the chamber in continuous flow mode possibly reduces the net flux of organic compounds to the 236 237 walls, at least for low volatility to semi volatile compounds, as some degree of equilibration can occur [Liu et al., 2016; Shilling et al., 2008]. Nonetheless, our vapor concentration data may be 238 239 biased low due to some amount of loss to the walls.

### 241 **3 Results & Discussion**

## 242 3.1 Effect of NO<sub>x</sub> on Major Gas- and Particle-Phase Species

The gas- [Krechmer et al., 2015] and particle-phase [Liu et al., 2016; Riva et al., 2016] species 243 244 detected from isoprene photochemical oxidation when examining the non-IEPOX SOA pathway 245 have been discussed previously. These studies identified several  $C_5H_{8-12}O_{4-8}$  compounds, among 246 many others, and the findings presented here are broadly consistent. Figure 2 summarizes all compounds measured as an iodide-adduct in both the gas- (top) and particle- (bottom) phases at 247 both low (left) and high (right) input NO (20 ppb) for average spectra at steady state. The square 248 249 root of the background subtracted signals were taken to show the dynamic range and then 250 normalized to the maximum signal within each individual plot. Green bars represent organic compounds with formula  $C_xH_vO_zI$ , while blue are organic nitrates (OrgN) with formula 251 252  $C_xH_yNO_zI$ -. It is possible that dinitrates were measured, but due to their occurrence at masses where non-nitrates would be observed, they are difficult to conclusively identify and thus are not 253 presented here. Major peaks are labeled with letters corresponding to compounds in Table 1. It is 254 255 important to note that while the same molecular composition may be present in both the gas- and 256 particle-phase, we do not suggest that they all exist as the same structure in each phase, although 257 some likely do. We will discuss this further in later sections.

From Figure 2, the two largest signals detected by the FIGAERO-CIMS in the gas-phase at both low and high input NO are  $CH_2O_2$  (presumably formic acid) and  $C_5H_{10}O_3$  (presumably the sum of IEPOX and ISOPOOH). With the addition of NO, the  $CH_2O_2$  signal becomes noticeably larger than that of  $C_5H_{10}O_3$ , likely due to increased fragmentation. Even without adding NO to the chamber there is still a small amount of NO<sub>x</sub> present, likely from photolysis of inorganic nitrate on the chamber walls, as we measure non-negligible OrgN concentrations, 264 although the signal is very small relative to organics. The amount of OrgN in the gas-phase increases with increased NO addition as expected. The majority of the OrgN compounds have 5 265 or fewer carbons and no one component dominates the OrgN. Notable signals include for 266 example C<sub>4</sub>H<sub>7</sub>NO<sub>5</sub> and C<sub>5</sub>H<sub>9</sub>NO<sub>5-6</sub>. The two largest signals detected by the FIGAERO-CIMS in 267 268 the particle-phase at both low and high input NO are  $C_5H_{12}O_6$  and  $C_5H_{12}O_5$ . Other compounds 269 with the isoprene  $C_5$  backbone but one degree of unsaturation also represent some of the largest signals at low-NO<sub>x</sub>, such as  $C_5H_{10}O_{4-7}$ . As in the gas-phase, no one component dominates the 270 particle-phase OrgN, although one of the strongest signals is  $C_5H_{11}NO_7$ , the nitrate analogue to 271 272  $C_5H_{12}O_6$ , formed from the same  $C_5H_{11}O_6$  peroxy radical (see Scheme 1). Compounds with the formula C<sub>5</sub>H<sub>7,9,11</sub>NO<sub>4-8</sub> are all observed in the particle-phase, consistent with field observations 273 274 from an isoprene-emitting forest during the Southern Oxidant and Aerosol Study campaign [Lee et al., 2016]. For compounds that are detected in the particle-phase, their T<sub>max</sub> and thermogram 275 shape are also listed in Table 1 and lends information on the nature of these compounds which 276 will be discussed in further detail later on. 277

The general effect of  $NO_x$  on the SOA in this system has been described previously [Liu 278 et al., 2016]. Here we highlight the effect of input NO concentrations on individual compounds 279 280 by focusing on three of the most prominent particle-phase species (Fig. 3, top). As the input NO concentration increases, C<sub>5</sub>H<sub>12</sub>O<sub>6</sub> and C<sub>5</sub>H<sub>12</sub>O<sub>5</sub> decrease nonlinearly. C<sub>5</sub>H<sub>11</sub>NO<sub>7</sub>, presumably 281 produced from the ISOPOOH + OH  $C_5H_{11}O_6$  peroxy radical increases initially with increasing 282 283 NO addition. Above moderate NO input (>10 ppb),  $C_5H_{11}NO_7$ , a nitrate, begins to decrease with further increases in NO addition, likely a result of ISOPOOH also decreasing as the C<sub>5</sub>H<sub>9</sub>O<sub>3</sub> 284 peroxy radical reacts more with NO as opposed to HO<sub>2</sub>. This behavior supports previous 285 286 observations of low isoprene SOA yields at high NO<sub>x</sub> [Kroll et al., 2005; 2006; Lane et al., 2008;

287 Xu et al., 2014; Zhang et al., 2011], though we note a monotonic NO<sub>x</sub> dependence of SOA yield 288 in our experiments [Liu et al., 2016]. The bottom panel of Figure 3 depicts the mass fraction of OrgN as a function of input NO. The mass fraction of OrgN increases rapidly between 0 and 10 289 290 ppb NO input and more modestly above that. At the highest input NO concentration, OrgN make up ~40% of the organic aerosol mass detected by the FIGAERO-CIMS. This estimate carries 291 292 uncertainty due to the inability to calibrate to every OrgN compound, as well as a lack of a single 293 dominant OrgN. At the highest input NO, the AMS measurements also indicate that OrgN make up ~40% of the SOA mass, assuming a molecular weight of the typical OrgN of 148 g/mol based 294 295 on the measured FIGAERO-CIMS particle-phase OrgN distribution, which is consistent with our 296 findings. Though considerable uncertainties exist with respect to quantification of OrgN using both the AMS and the FIGAERO-CIMS, the agreement between these independent 297 298 measurements suggests the calibration factors applied to the FIGAERO-CIMS OrgN signals are 299 reasonable. We draw two main conclusions from this analysis: (1) the complementary increase in 300 OrgN and decrease in non-nitrates likely accounts for the stable SOA mass yields at lower input 301 NO concentrations as reported previously [Liu et al., 2016], with the highest input NO concentrations resulting in a decrease in both OrgN and non-nitrates, corresponding to the sharp 302 303 decrease in SOA mass yield at the highest input NO concentration (50 ppb), and (2) while there is no one OrgN that is most prominent in the gas or particle phase, the total OrgN can comprise 304 up to 40% of the SOA mass at high input NO concentrations (50 ppb). 305

306

## **307 3.2 Time Evolution of Low NO<sub>x</sub> Isoprene SOA Composition**

To examine how isoprene photochemical SOA evolves over time, a time-dependent experiment
was conducted (Fig. 4) similar to a previous batch mode study [*Kroll et al.*, 2006]. In this "batch

mode" experiment, isoprene, H<sub>2</sub>O<sub>2</sub>, and solid ammonium sulfate seed were injected into the 310 311 chamber, and then the lights were turned on. The chemistry of the closed system was allowed to evolve in time without further input of reactants. Each pie chart represents a FIGAERO-CIMS 312 313 particle-phase desorption measurement over the course of the experiment. The data are converted to mass concentration as discussed previously [Lee et al., 2016; Liu et al., 2016], the overall size 314 of each pie chart is proportional to the amount of AMS measured OA (5.6, 10.8, 10.6, 10.4 µg m<sup>-</sup> 315 <sup>3</sup> from left to right, corrected for particle wall loss), and the time is the mid-point of the particle 316 collection period (which lasted 25 minutes) relative to the initiation of the chemistry. The 317 318 desorption just prior to the isoprene injection is used as the baseline, and the corresponding mass 319 spectra are subtracted from the succeeding desorptions. Unlike the work of Kroll et al. [2006] who saw SOA volume maximize after ~3-4 hours of oxidation followed by a large decrease in 320 321 total volume attributed to photochemical processing, the measurements presented here did not follow the reaction progress long after the maximum OA concentration was achieved (<1 hour) 322 and thus we did not observe a significant decrease in mass. 323

324 The absolute and relative concentration of  $C_5H_{12}O_6$  in the particle-phase decreases from 40% of the particle-phase SOA to 17% over the four hours of oxidation. The absolute mass of 325 SOA also changes, primarily increasing, during the experiment, reaching a peak of 11.6  $\mu$ g m<sup>-3</sup> at 326 t = 4.3 hours. This suggests  $C_5H_{12}O_6$  is transforming either within the particle-phase via 327 hydrolysis or other mechanisms, or in the gas-phase, with efficient gas-particle equilibration, due 328 329 to reaction with OH or photolysis [Baasandorj et al., 2010; Hsieh et al., 2014; Roehl et al., 2007], with a particle-phase half-life of ~4 hours. Gas-phase oxidation seems unlikely given that 330 typically greater than 95% of the  $C_5H_{12}O_6$  is found in the particle-phase (Fig. 5) when OA >2 µg 331 m<sup>-3</sup>. While many of the detected compounds are present at constant mass fractions throughout 332

333 time,  $C_5H_{12}O_5$ ,  $C_5H_{12}O_4$ , and  $C_5H_{10}O_3$  increase.  $C_5H_{12}O_5$  has been observed previously in the 334 gas-phase from ISOPOOH oxidation [Krechmer et al., 2015], and was also shown to be a large fraction of the particle-phase from isoprene oxidation [Liu et al., 2016], but its production 335 336 mechanism is uncertain. Krechmer et al. [2015] suggest it could be formed from the oxidation of an impurity in the ISOPOOH, although the experiments presented here use isoprene as the 337 BVOC precursor, ruling out this explanation. In these experiments,  $C_5H_{12}O_5$  is observed within 338 the first hour of isoprene oxidation and increases to ~18% of the OA mass within 1.5 hours, 339 becoming relatively stable thereafter. Two possible sources of this compound are the reaction of 340 341 the ISOPOOH-derived peroxy radical  $(C_5H_{11}O_6)$  with RO<sub>2</sub>, or a dihydroxy alkene undergoing reaction with OH and  $O_2$  to form a dihydroxy peroxy radical, followed by reaction with HO<sub>2</sub>. It 342 is also possible that  $C_5H_{12}O_5$  could be formed in the condensed phase from hydrolysis reactions. 343 Further work is required to understand the source of this compound. 344

The other two compounds that increase with time,  $C_5H_{12}O_4$  and  $C_5H_{10}O_3$ , likely isomers 345 of 2-methyl tetrols and alkene triols respectively, are traditional markers of IEPOX derived SOA 346 347 [Claeys et al., 2004; Ding et al., 2008; Edney et al., 2005; Kourtchev et al., 2005; Surratt et al., 2010; Xia and Hopke, 2006]. This result is unexpected given that using effloresced (solid) 348 349 ammonium sulfate seed at a RH below the deliquescence point (RH ~50%) together with an SOA coating should strongly suppress the known acid catalyzed IEPOX multiphase chemistry 350 [Gaston et al., 2014; Lin et al., 2013a; Lin et al., 2014; Lin et al., 2012; Lin et al., 2013b; Liu et 351 352 al., 2014; Nguyen et al., 2014; Paulot et al., 2009b; Surratt et al., 2010; Surratt et al., 2006]. We tested the uptake of an authentic IEPOX standard onto dry, crystalline ammonium sulfate seed 353 354 under conditions similar to these, though during continuous-flow mode, and found no 355 measurable uptake and SOA formation [Liu et al., 2016]. However, it is consistent with previous

356	work that found both of these tracers in the SOA when isoprene was oxidized in the absence of
357	deliquesced acidic seed [ <i>Edney et al.</i> , 2005; <i>Kleindienst et al.</i> , 2009]. C <sub>5</sub> H <sub>12</sub> O <sub>4</sub> and C <sub>5</sub> H <sub>10</sub> O <sub>3</sub> are
358	less than 1% of the SOA for the first 2 hours and then gradually increase to 10% and 6% of the
359	SOA, respectively, after 4 hours. Interestingly, the FIGAERO-CIMS thermograms for these
360	tracers have broad maxima at much higher $T_{max}$ than would be consistent with their elemental
361	composition. Lopez-Hilfiker et al. [2016b] noted two modes in the thermogram of $C_5H_{12}O_4$ , one
362	with a $T_{max}$ as expected based on its structure and another with a higher $T_{max}$ indicating an
363	effectively lower volatility component thermally decomposing. These two tracers are also
364	observed in the NO <sub>x</sub> addition experiments performed in continuous-flow mode, though at lower
365	concentrations. In these experiments there was not enough NO to completely suppress
366	ISOPOOH formation and therefore IEPOX formation from ISOPOOH + OH. Moreover, IEPOX
367	can also form, albeit at lower yields, from OH reactions with the first-generation isoprene
368	hydroxy nitrate [Jacobs et al., 2014; L Lee et al., 2014; St Clair et al., 2016]. However, the
369	formation of IEPOX SOA tracers is more puzzling given the very low reactive uptake of IEPOX
370	expected on solid inorganic seed coated with isoprene SOA [Gaston et al., 2014; Riedel et al.,
371	2015]. Perhaps nitric acid catalyzed IEPOX multiphase chemistry is contributing to the
372	formation of these tracers at high NO <sub>x</sub> . That said, observation of these tracers, also in the absence
373	of $NO_x$ addition, indicates that this explanation not sufficient.

The chemical mechanism leading to the measurement of these tracers in the particle phase is unknown, but given that the experimental conditions strongly suppressed the traditional acid catalyzed aqueous IEPOX chemistry, perhaps these tracers are not solely derived from aqueous IEPOX chemistry but isoprene photochemical oxidation more generally. In conclusion,  $C_5H_{12}O_6$  condenses rapidly and initially makes up a majority of the SOA mass, but over time its contribution decreases as other compounds such as  $C_5H_{12}O_5$ ,  $C_5H_{12}O_4$ , and  $C_5H_{10}O_3$  increase. Our data suggest these compounds may be formed in the particle phase from heterogeneous reactions and/or during the thermal desorption analysis, but more work is required to determine their sources.

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## 384 3.3 Gas-particle Partitioning: Saturation Vapor Concentrations and Oligomeric 385 Content

The volatility of the products generated from the non-IEPOX C<sub>5</sub>H<sub>12</sub>O<sub>6</sub> pathway [Krechmer et al., 386 387 2015; Liu et al., 2016; Riva et al., 2016] will be a crucial aspect of its contribution to SOA formation and the lifetime of the resulting SOA against dilution, gas-phase oxidation, and 388 depositional losses. The capability of the FIGAERO-CIMS to measure the concentration of 389 390 individual species in both the gas- and particle-phase allows for a direct measurement of the particle-phase fraction  $(F_p)$ , which is the particle-phase concentration relative to the gas- and 391 particle-phase concentrations per volume of air. The F<sub>p</sub> can also be calculated from an 392 393 assumption of equilibrium absorptive partitioning theory first described by Pankow [1994] using equation 1 as first reported by Donahue et al. [2006], where C\* is the saturation vapor 394 concentration ( $\mu g m^{-3}$ ) of the pure substance and C<sub>OA</sub> is the concentration of organic aerosol ( $\mu g$ 395 m<sup>-3</sup>). 396

397 
$$F_p = \left(1 + \frac{C^*}{C_{OA}}\right)^{-1}$$
 (1)

Equation 1 neglects the activity coefficient and molecular weight differences for simplicity, though any C\* derived from a comparison to equation 1 would implicitly include these factors. Calibration standards do not exist for a vast majority of compounds in SOA and therefore the C\* are largely unknown, mitigating somewhat the impact of such simplifications. Group-

402 contribution methods exist to estimate C\*, where each functional group represents a discrete, 403 empirically determined contribution to the equilibrium vapor pressure of a compound [Capouet and Muller, 2006; Compernolle et al., 2011; Nannoolal et al., 2008; Pankow and Asher, 2008]. 404 405 These approaches carry substantial uncertainty for atmospheric SOA systems, in large part due to the lack of enough standards to develop a robust parameterization. In addition, these approaches 406 do not directly address the potential of functional group interactions, such as intramolecular 407 hydrogen bonding, which when not included can lead to C\* estimates that are significantly 408 biased low [Kurten et al., 2016]. 409

Measured F<sub>p</sub> were determined using the FIGAERO-CIMS for a subset of major particle-410 411 phase components from 2015 (Fig. 5). A short (1-2 m) laminar flow Teflon inlet line with a short residence time (<1 s) was coupled to the chamber for the detection of gases by the FIGAERO-412 CIMS. The largest source of error in the measured  $F_p$ , beyond thermal decomposition during 413 desorption, is diffusion-controlled vapor losses in the inlet which were corrected for by assuming 414 a diffusivity of 0.05-0.1 cm<sup>2</sup> s<sup>-1</sup>, although the variability is not discernable on the log scale. Inlet 415 416 losses are 25-44% for the range of diffusivities, a small effect on the comparison of measured and predicted  $F_p$  as we show below. 417

F<sub>p</sub> were predicted using equation 1 with  $C_{OA}$  measured by the AMS and C\* calculated via the EVAPORATION group-contribution method [*Compernolle et al.*, 2011], which generally gave similar estimates as the Capouet and Muller approach [2006]. The Nannoolal method [2008] was also explored, but it gave C\* estimates that varied by several orders of magnitude for structurally similar compounds, as well as estimates that were unexpectedly low based on FIGAERO-CIMS measurements and what one would expect based on molecular structure, consistent with previous findings [*Kurten et al.*, 2016]. The SIMPOL method of Pankow and Asher [2008] was also applied to select compounds and is discussed below. A major limitation of this analysis is that we do not know the structure of the molecules detected, only the elemental composition, and so we make assumptions based on the most likely functional groups expected from the chemical conditions of the chamber and from the elemental composition (e.g., degrees of unsaturation, oxygen to carbon ratio). In many cases these assumptions have little impact on our conclusions as the inferred errors are far larger than expected from possible isomers.

If the SOA formed according to equilibrium partitioning theory as first described by 431 Pankow [1994], the F<sub>p</sub> measured by the FIGAERO-CIMS and the C\* calculated using group-432 433 contribution methods should be in agreement over a range of organic aerosol mass 434 concentrations. Figure 5 indicates two immediate challenges to testing partitioning theory. First, a large number of mostly small carbon number compounds have a much higher measured F<sub>p</sub> 435 relative to the predicted F<sub>p</sub> based on their group-contribution determined C\*. The C\* estimates 436 would have to be in error by five or more orders of magnitude, which is likely not the case as 437 438 there are many measurements of vapor pressures for similar compounds. Furthermore, the 439 thermograms of these compounds appear broad, not Gaussian as expected for individual noninteracting compounds [Lopez-Hilfiker et al., 2014], and do not peak until ~85 °C or higher, see 440 441 Table 1, which is also inconsistent with the calibrated composition-enthalpy of sublimation relationship scaled for the FIGAERO used here [Lopez-Hilfiker et al., 2014]. We attribute this 442 behavior to thermal decomposition of lower volatility components during the desorption process 443 444 giving rise to smaller molecular weight, more volatile components as in previous studies of IEPOX SOA tracers in the southeast U.S. [Lopez-Hilfiker et al., 2016b], α-pinene derived 445 chamber SOA [Lopez-Hilfiker et al., 2015], and biomass burning organic aerosol in the 446 447 northwest U.S. [Gaston et al., 2016]. That is, the disagreement between measured and predicted

F<sub>p</sub> for these compounds is not necessarily a failure of equilibrium partitioning theory, nor evidence that equilibrium had not been achieved, but rather that the compounds desorbing were actually part of another larger molecular weight oligomerization product, the C\* and gas-phase concentrations of which are unknown.

The second challenge to testing gas-particle partitioning is illustrated in the F<sub>p</sub> for two 452 representative compounds,  $C_5H_{12}O_6$  and  $C_5H_{10}O_6$  (Fig. 5, bottom panels). That there is 453 reasonable agreement between measured and predicted F<sub>p</sub> (Fig. 5, bottom right, circles) for 454  $C_5H_{10}O_6$  suggests that equilibrium partitioning is potentially achieved in the chamber. However, 455 456 the disagreement for  $C_5H_{12}O_6$  (Fig. 5, bottom left, circles) cannot be explained solely by thermal decomposition of lower volatility material for two reasons: the thermogram shape is nearly 457 Gaussian and therefore behaves like a single component, and the predicted F<sub>p</sub> is much larger than 458 459 measured (opposite to the above situation). This behavior implies inaccurate C\* derived from the 460 group-contribution methods as opposed to thermal decomposition.

The EVAPORATION group-contribution method [Compernolle et al., 2011] used in 461 Figure 5 and that of Capouet and Muller [2006] both produce a C\* of 0.03  $\mu$ g m<sup>-3</sup> for C<sub>5</sub>H<sub>12</sub>O<sub>6</sub> 462 when assuming it is a dihydroxy dihydroperoxide, while the SIMPOL method predicts  $2 \mu g m^{-3}$ 463 [*Pankow and Asher*, 2008]. For  $C_5H_{10}O_6$ , assumed to be a hydroxy dihydroperoxy aldehyde, 464 EVAPORATION [*Compernolle et al.*, 2011] predicts 4 µg m<sup>-3</sup>, the Capouet and Muller [2006] 465 method predicts 2 µg m<sup>-3</sup>, and SIMPOL [*Pankow and Asher*, 2008] suggests 20 µg m<sup>-3</sup>. That the 466  $C_5H_{12}O_6$  values vary by 2 orders of magnitude while the  $C_5H_{10}O_6$  values vary by a factor of 10 467 suggests the need for better experimental constraints. Using the measured  $T_{max}$  from the 468 FIGAERO-CIMS thermograms, the C\* of C<sub>5</sub>H<sub>12</sub>O<sub>6</sub> and C<sub>5</sub>H<sub>10</sub>O<sub>6</sub> were determined to be 0.7 and 469 7  $\mu$ g m<sup>-3</sup>, respectively. These values were then used to re-calculate the predicted F<sub>p</sub> using 470

equation 1. The original group-contribution calculated  $F_p$  is shown alongside the adjusted points in the bottom panels of Figure 5 as navy crosses. The root mean square error of both  $C_5H_{12}O_6$ and  $C_5H_{10}O_6$  is minimized when comparing the measurements with the adjusted  $F_p$ , indicating

474 that the calibrated FIGAERO-CIMS temperature axis can more accurately determine the C\*.

There are a number of possible reasons why measured and predicted  $F_p$  do not agree, with one being that our methods to estimate C\* are flawed. This potential source of error can be addressed directly with the FIGAERO-CIMS thermograms, independently of the measured  $F_p$ , thereby allowing for a more robust assessment of whether (*i*) the assumption of gas-particle equilibrium is reasonable, (*ii*) there are possible biases in the measured  $F_p$  due to thermal decomposition, or (*iii*) the C\* estimation methods are valid. The above analysis demonstrates

481 that all possibilities arise in this data set.

In the case of  $C_5H_{12}O_6$  the FIGAERO-CIMS determined C\* is much closer to the 482 SIMPOL estimation, and significantly higher than that estimated by the other group-contribution 483 484 methods. We suspect the large differences between measured and group-contribution method estimates of C\* in this case are due to the lack of vapor pressure data on compounds with 485 hydroperoxide groups, specifically multifunctional hydroperoxides: there is only data on four 486 487 hydroperoxide containing compounds on which these methods are based [*Capouet and Muller*, 2006; Compernolle et al., 2011]. It can be argued that -OH and -OOH groups will lower the C\* 488 489 relative to the precursor by a comparable amount, with the possibility that a -OOH group could lower it slightly more due to the additional oxygen. For example, the C\* of 2-methyl-1,2,3,4-490 butanol ( $C_5H_{12}O_4$ ) was calculated to be 9 to 34 µg m<sup>-3</sup>, depending on the method used [*Capouet* 491 and Muller, 2006; Compernolle et al., 2011], roughly 250-1000 times greater than the C\* 492 493 estimates for  $C_5H_{12}O_6$ . That is, a molecule with the same number of distinct –OH containing 494 functional groups is predicted to have a very different C\* because the vapor pressure lowering of -OOH groups assumed by these group-contribution methods is larger than that for an -OH 495 group. Our observations suggest this assumption is incorrect, at least to the extent employed in 496 497 these methods, and is supported by previous work that found group-contribution methods predicted significantly lower C\* than two computational models, the conductor-like screening 498 model for real solvents (COSMO-RS) [Kurten et al., 2016] and the generator for explicit 499 500 chemistry and kinetics of organics in the atmosphere (GECKO-A) [Valorso et al., 2011], did for compounds with multiple functionalities. Conversely, we assume  $C_5H_{10}O_6$  is a hydroxy 501 502 dihydroperoxy aldehyde, also with two -OOH groups, but the group contribution methods accurately predicted a C\* consistent with that inferred from the FIGAERO-CIMS T<sub>max</sub>. This 503 agreement may be a coincidence or indicative of the fact that multifunctional compounds with 504 505 slightly different functional groups can have significantly different intramolecular interactions, leading to significantly different saturation vapor concentrations [Compernolle et al., 2011]. 506

Figure 5 leads to two main conclusions. The first is that testing equilibrium partitioning 507 theory is a challenge without a direct constraint on the C\* like the FIGAERO-CIMS desorption 508 T<sub>max</sub> due to possibly large systematic errors in the C\* predicted from group-contribution 509 510 methods. Moreover, thermal decomposition of higher molecular weight compounds, such as oligomers, into smaller molecular weight compounds generates uncertainty in the measured F<sub>p</sub> in 511 that the FIGAERO-CIMS T<sub>max</sub> derived C\* does not correspond in such cases to the observed 512 513 molecule. This result leads to our second conclusion: a surprisingly large fraction of the iSOA is resistant to evaporation, indicating it will have a longer lifetime against dilution [Kroll et al., 514 2006]. Approximately 30-45% of the SOA mass detected by the FIGAERO-CIMS desorbs at 515 516 temperatures greater than 80 °C, much of that above 100 °C, which corresponds to effective

enthalpies of sublimation >150 kJ mol<sup>-1</sup> in our FIGAERO-CIMS assuming no diffusion 517 limitations to evaporation from the particles that exist at these temperatures (for example, due to 518 highly viscous phases). We note that Kroll et al. [2006] also found evidence for a significant 519 520 mass fraction of large molecular weight compounds when applying the AMS to low-NO<sub>x</sub>, non-IEPOX iSOA. We conclude that oligomerization products are the cause of this more refractory 521 SOA component, but, we cannot determine from the thermograms alone whether the 522 oligomerization process is reversible at ambient temperatures on longer timescales than the  $\sim 1$ 523 hour desorptions. That the SOA yield from isoprene is significantly higher for similar organic 524 525 mass loadings than that reported from ISOPOOH only, suggests an important role for the broader distribution of oxidation products formed in addition to those from ISOPOOH. One possible 526 reason is that these mostly semi volatile products can contribute to lower volatility products via 527 528 oligomerization chemistry [Jathar et al., 2016; Sato et al., 2011; Tsai et al., 2015].

The sum of thermogram signals across all ions with formula  $C_xH_yO_zN_{0-1}I$ - is presented in 529 Figure 6, with the value of x specified for each thermogram. We measured non-negligible signal 530 531 for compounds with 6 or more carbons, consistent with the possibility of oligomerization products. Such compounds account for ~5-15% of detected mass. Compounds with 6-7 carbons 532 make up a majority of the signal for compounds with greater than 5 carbons, though we also 533 detected significant signal in C<sub>8</sub>-C<sub>10</sub> compounds, themselves making up 3-8% of detected mass. 534 We measure a monoterpene impurity at 0.3% of the isoprene concentration in our gas cylinder 535 which could result in ~0.05-0.1  $\mu$ g m<sup>-3</sup> of monoterpene SOA, i.e. 0.3-2.8% of the SOA mass, 536 significantly lower than the sum of all compounds with 6 or more carbons as well as the sum of 537 just  $C_{8-10}$  compounds. Furthermore, the ratio of  $C_{6-7}$  to  $C_{10}$  compounds is 5-10 times higher than 538 539 we detect in monoterpene + OH experiments performed in the same chamber with the same

FIGAERO-CIMS. We also note that a previous study similar to the ones presented here detected  $C_{10}H_{20-22}O_{6-9}$  compounds, as well as a fragment ion in the AMS at m/z 91 corresponding to  $C_{7}H_{7}$ + which was tentatively attributed to thermal decomposition of dimers and oligomers on the vaporizer, among other possibilities [*Riva et al.*, 2016]. The mass concentration of these compounds with 6 or more carbons was found to increase with isoprene reacted (Fig. 6, bottom). At the highest isoprene reacted, these contribute on order 25% to the total OA mass detected.

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## 7 **3.4** Role of NO<sub>x</sub> in iSOA volatility

548 Previous studies using thermal denuders and either an AMS or a tandem differential mobility measurement of particle size distributions have found that iSOA formed in the presence of NO<sub>x</sub> 549 is less volatile relative to that formed in HO<sub>2</sub>-dominant regimes [Kleindienst et al., 2009; Xu et 550 551 al., 2014]. We compare the iSOA volatility under different regimes by looking at the sum thermograms for compounds with formulae  $C_x H_v O_z N_{0-1} \Gamma$ . These sum thermograms are plotted as 552 a function of temperature for both low- and high-NO<sub>x</sub> conditions in Figure 7, bottom left and 553 554 right, respectively. Since  $C_5H_{12}O_6$  is a large portion of the SOA mass concentration in these 555 experiments (e.g. Fig. 4), it is shown separately in dark green with the remainder of the summed 556 signal shown in light green.  $C_5H_{12}O_6$  is clearly a large contribution to the sum signal in both the low- and high-NO<sub>x</sub> cases, although more so in the low NO<sub>x</sub> regime, with the remaining 557 thermogram signal primarily located in the lower volatility (higher temperature) "tail" of the 558 559 desorption. We have also showed in the bottom left low NO<sub>x</sub> figure a sum of the thermograms 560 for all compounds with 6 or more carbons, i.e. the sum of all thermograms in Figure 6. We note that the sum of these compounds makes up ~6% of the total signal. At high NO<sub>x</sub>, there are two 561 562 clear modes in the thermogram remaining after removing the  $C_5H_{12}O_6$  contribution (light green),

563 one mode at roughly the same  $T_{max}$ , and therefore volatility, of  $C_5H_{12}O_6$ , and the other mode at a higher T<sub>max</sub>, ~110 °C, suggesting a larger fraction of detected iSOA mass at high NO<sub>x</sub> is resistant 564 to evaporation compared to the low  $NO_x$  case. We also note that the  $T_{max}$  of individual 565 566 compounds shifts to higher values with the addition of NO<sub>x</sub> except for the highest mass 567 compounds (see Table 1). Although the thermograms for many of these compounds do not have 568 a distinct Gaussian shape, making determination of the T<sub>max</sub> uncertain or undefined, the shift to higher T<sub>max</sub> for the same compounds could indicate not just lower volatility products in the form 569 of oligomers, but also potentially a change in the overall particle viscosity causing the iSOA to 570 571 be more resistant to evaporation with the addition of NO<sub>x</sub>.

572 A sum thermogram of  $\alpha$ -pinene ozonolysis that has been previously reported [Lopez-Hilfiker et al., 2015] is displayed alongside those of the low- and high-NO<sub>x</sub> experiments (Fig. 7, 573 574 top) for comparison. The  $\alpha$ -pinene SOA has a bimodal sum thermogram, similar to that of the high-NO<sub>x</sub> iSOA with the second lower volatility modes in the same temperature range. The 575 higher volatility mode of the a-pinene SOA corresponds in temperature space to that of the 576 577 higher volatility mode of the low-NO<sub>x</sub> iSOA. The multiple modes of the  $\alpha$ -pinene sum thermogram have the same relative maxima in signal space, unlike the isoprene sum 578 579 thermograms.  $\alpha$ -Pinene ozonlysis apparently generates a larger fraction of lower volatility SOA relative to isoprene photochemical oxidation, although isoprene photochemical SOA has 580 components in the same volatility ranges of  $\alpha$ -pinene ozonlysis SOA, and the relative size of the 581 582 various modes and location in temperature space is dependent on the amount of  $NO_x$ .

The contribution of the effectively lower volatility components inferred from thermograms in Figure 7 is likely underestimated in both the low- and high-  $NO_x$  cases because the thermograms are presented as ion signal, not mass concentration. If we converted into mass 586 concentration units prior to calculating the summed thermogram, the contribution of  $C_5H_{12}O_6$ 587 would be significantly less than implied in Figure 7. The integrated contribution of  $C_5H_{12}O_6$ would instead be more similar to that shown in Figure 4 for which we applied calibration 588 589 estimates based on ISOPOOH and a range of other oxygenated compounds, together with the 590 ion-molecule collision limited sensitivity discussed previously [Liu et al., 2016; Lopez-Hilfiker et 591 *al.*, 2016a]. In conclusion, the low-NO<sub>x</sub> SOA has an overall higher volatility and the addition of 592 NO<sub>x</sub> results in lower volatility material making up a larger fraction of the SOA, although the total SOA yield is lower [Liu et al., 2016], in general agreement with previous studies showing 593 594 that increasing NO<sub>x</sub> leads to lower volatility SOA [Kleindienst et al., 2009], likely by enhancing 595 oligomerization [Dommen et al., 2006; Xu et al., 2014]. However, many of these previous studies were carried out in very different concentration regimes with different detection techniques, so 596 597 that the data we present offers an additional contribution to the general importance of oligomerization. 598

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#### 600 4 Conclusions

We have explored the composition and volatility of isoprene SOA at low and high NO<sub>x</sub> 601 602 concentrations utilizing effloresced ammonium sulfate seed to prevent IEPOX uptake and thus suppress IEPOX multiphase chemistry. We measured compositions of products reported in 603 previous works of similar experiments [Krechmer et al., 2015; Liu et al., 2016; Riva et al., 604 605 2016], in particular  $C_5H_{12}O_6$  and related highly oxidized compounds. We note that these compounds have also been observed in the atmosphere in isoprene rich regions [*Riva et al.*, 606 2016]. We examined the saturation vapor concentrations of several of the most dominant 607 608 particle-phase signals and tested the accuracy of various group-contribution methods to

determine the C\*. Of the three group-contribution methods assessed, the SIMPOL approach [*Pankow and Asher*, 2008] gave the closest estimates of C\* compared to those determined from the thermograms. The vapor pressure lowering effect of –OOH groups, assumed to be abundantly present in this system, appears to be greatly overestimated in two commonly used methods [*Capouet and Muller*, 2006; *Compernolle et al.*, 2011]. Through these analyses we found that a significant fraction of SOA components we measure are likely thermal decomposition fragments, characterized by broad thermograms and higher than expected  $T_{max}$ .

That such a large fraction (30-45%) of the non-IEPOX iSOA is of low volatility implies 616 617 the lifetime of non-IEPOX iSOA is longer than would previously be expected. Together with the thermal decomposition fragments, we also observe compounds with 6 or greater carbons, 618 supporting an important role for oligomerization chemistry. These findings suggest that 619 620 experiments which assess the SOA formation potential of isoprene or one of its oxidation products alone likely underestimate the overall potential due to the participation of a broad suite 621 of products in oligomerization chemistry. Further work on the role of oligomerization chemistry 622 623 in this system is needed to verify that the higher iSOA yield observed by Liu et al. [2016] from isoprene is indeed caused by semi volatile products participating in oligomerization reactions. 624 625 Furthermore, we have shown here that the addition of NO has a strong effect on the amount of  $C_5H_{12}O_6$  produced, and while the overall volatility of the OA decreases with NO<sub>x</sub>, the total 626 amount of OA also decreases [Liu et al., 2016], indicating that in polluted regions the amount of 627 628 SOA formed from this pathway will be diminished, but the SOA will be longer lived against dilution. In conclusion, due to the high yield of IEPOX from ISOPOOH + OH it has been 629 630 assumed to be the most important pathway for the formation of iSOA, however, its relatively high volatility ( $\sim 2 \times 10^4 \ \mu g \ m^{-3}$  [*Compernolle et al.*, 2011]) and the fact that it requires such 631

specific conditions to form SOA efficiently implies that the formation of SOA from the nonIEPOX pathway discussed herein can also play an important role in many environments
regardless of sulfate aerosol concentrations.

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950 Figure and Table Captions
951 Scheme 1. A simplified schematic of isoprene and its major oxidation products. Products formed in the presence of NO<sub>x</sub> are identified with blue arrows.
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954 Table 1. Gas- and particle-phase compounds detailed in the mass spectra in Figure 2 (top). Many molecular compositions are observed in both the gas- and particle-phase. If the composition is charmed in the matricle phase of Table 1. Gas- and particle phase of the mass spectra in Figure 2 (top). Many molecular compositions are observed in both the gas- and particle-phase. If the composition is

observed in the particle phase, a  $T_{max}$  is listed at both low (0 ppb input NO) and high (20 ppb input NO) NO<sub>x</sub>. The desorption shape is also listed and is consistent across NO<sub>x</sub> conditions. The significance of the  $T_{max}$  and desorption shape are discussed in detail in the text. If the compound is only detected in the gas phase, "NA" is listed in the  $T_{max}$  and thermogram columns, indicating that those values are not applicable.

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962 Figure 1. Overview of the 2014 and 2015 measurements taken at PNNL. The left column is data from the 2014 campaign, the right column is 2015. The top row shows gas-phase compounds 963 964 measured by the PTR-MS and FIGAERO-CIMS, as well as input concentrations of H<sub>2</sub>O<sub>2</sub>, NO, and isoprene. Middle row shows the OA as measured by the AMS. Steady state periods are 965 966 shown within magenta circles, AMS blanks as black squares. Select particle phase species measured by the FIGAERO-CIMS are in the bottom row. Grey shaded areas in each column 967 968 indicate when chamber lights were off for chamber cleaning and a dark NO<sub>3</sub> experiment (in 2014) which is not discussed here. Note that the axis limits are not the same due to a wide range 969 970 in concentrations across years, while C<sub>5</sub>H<sub>12</sub>O<sub>5</sub> has been enhanced 5x and C<sub>5</sub>H<sub>11</sub>NO<sub>7</sub> has been 971 enhanced 20x in the bottom rows to clearly show the behavior of each species on the same axis.

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**Figure 2.** Mass spectra for compounds with composition  $C_xH_yO_zI$ - (green) and  $C_xH_yNO_zI$ - (blue) at low (left) and high (right) NO input in both the gas- (top) and particle- (bottom) phases. Bars are sized by the square root of signal (counts s<sup>-1</sup> for the gas-phase, counts for the particle-phase) to show the dynamic range. Major components are labeled with letters corresponding to those found in Table 1.

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**Figure 3.** Top: Normalized signals of  $C_5H_{12}O_6$  and  $C_5H_{11}NO_7$ , believed to originate in the gas phase from the same  $C_5H_{11}O_6$  peroxy radical, as well as  $C_5H_{12}O_5$ , as a function of input NO. Signal is normalized to maximum signal for each compound to show the relative behaviors. Bottom: The mass fraction of organic nitrates as a function of NO. Mass fraction refers to the mass concentration of FIGAERO-CIMS measured OrgN relative to the total mass concentration of organics (non-nitrogen containing + OrgN) measured by the FIGAERO-CIMS.

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**Figure 4.** Time evolution of particle-phase concentrations in a batch mode isoprene photochemical oxidation experiment at low-NO<sub>x</sub>. Time increases from left to right and the size of the pies is proportional to the amount of OA present which is: 5.6, 10.8, 10.6, 10.4  $\mu$ g m<sup>-3</sup> from left to right.

**Figure 5.** Top: Predicted versus measured fraction in the particle-phase ( $F_p$ ). Predicted  $F_p$  is obtained from equation 1 where C\*s were calculated with the EVAPORATION groupcontribution method [*Compernolle et al.*, 2011] labeled as "Group-Cont. C\*" in the bottom panels. Measured  $F_p$  is the direct measurement from the FIGAERO. Bottom: The  $F_p$  can also be predicted based on the calibrated FIGAERO temperature axis as discussed in the methods and is shown as the predicted  $F_p$  here. Agreement can be reached for two representative compounds where the  $F_p$  is over and correctly predicted (left, right respectively).

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**Figure 6.** Top: Sum of the thermogram signal for compounds with formula  $C_xH_yO_zI$ -, where x is varied across each thermogram and represents compounds with 6 or more carbons. Bottom: The sum off the mass concentration of all compounds with 6 or more carbons relative to the mass concentration of organic aerosol as a function of isoprene reacted.

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**Figure 7.** Top: Sum thermograms of  $\alpha$ -pinene + O<sub>3</sub> compared to isoprene (C<sub>5</sub>H<sub>8</sub>) photooxidation 1004 with and without  $NO_x$ . The  $\alpha$ -pinene sum thermogram has been reported previously (Lopez-1005 1006 Hilfiker et al. [2015], Fig 5). Bottom: The sum thermograms at low (left) and high (right) input 1007 NO. The thermogram of  $C_5H_{12}O_6$ , the largest signal in both cases, is separated out (dark green) and the sum of the remaining signal minus  $C_5H_{12}O_6$  is displayed as the remaining signal (light 1008 green). At Low NO input, the sum of compounds with 6 or more carbons is specified (pink 1009 triangle/line), while at high NO input the sum of OrgN and the sum of non-nitrate organics are 1010 plotted (dashed lines, independent of solid lines) to show the relative thermogram features. 1011

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1024 Scheme 1. A simplified schematic of isoprene and its major oxidation products. Products formed 1025 in the presence of  $NO_x$  are identified with blue arrows.

Letter	Mass	Molecular Composition	Particle-phase T <sub>max</sub> , Low NO <sub>x</sub>	Particle-phase T <sub>max</sub> , High NO <sub>x</sub>	thermogram shape
a	172.9105	CH <sub>2</sub> O <sub>2</sub> I-	87	94	broad
b	202.9211	C <sub>2</sub> H <sub>4</sub> O <sub>3</sub> I-	113	115	broad
с	216.9367	C <sub>3</sub> H <sub>6</sub> O <sub>3</sub> I-	76	100	broad
d	230.9524	C <sub>4</sub> H <sub>8</sub> O <sub>3</sub> I-	87	115	broad
e	244.968	$C_5H_{10}O_3I$ -	NA	NA	NA
f	258.9473	C <sub>5</sub> H <sub>8</sub> O <sub>4</sub> I-	76, 111	70, 115	double
g	275.9374	C <sub>4</sub> H <sub>7</sub> NO <sub>5</sub> I-	88	115	broad
h	289.9531	C <sub>5</sub> H <sub>9</sub> NO <sub>5</sub> I-	NA	NA	NA
i	305.948	C <sub>5</sub> H <sub>9</sub> NO <sub>6</sub> I-	NA	NA	NA
j	246.9473	C <sub>4</sub> H <sub>8</sub> O <sub>4</sub> I-	95	110	broad
k	278.9735	$C_5H_{12}O_5I$ -	60	48	Gaussian
1	294.9684	$C_5H_{12}O_6I$ -	63	56	Gaussian
m	323.9586	C <sub>5</sub> H <sub>11</sub> NO <sub>7</sub> I-	72	50	Gaussian
n	339.9535	C <sub>5</sub> H <sub>11</sub> NO <sub>8</sub> I-	53	45	Gaussian

**Table 1.** Gas- and particle-phase compounds detailed in the mass spectra in Figure 2 (top). Many molecular compositions are observed in both the gas- and particle-phase. If the composition is observed in the particle phase, a  $T_{max}$  is listed at both low (0 ppb input NO) and high (20 ppb input NO) NO<sub>x</sub>. The desorption shape is also listed and is consistent across NO<sub>x</sub> conditions. The significance of the  $T_{max}$  and desorption shape are discussed in detail in the text. If the compound is only detected in the gas phase, "NA" is listed in the  $T_{max}$  and thermogram columns, indicating that those values are not applicable.





Figure 1. Overview of the 2014 and 2015 measurements taken at PNNL. The left column is data 1056 1057 from the 2014 campaign, the right column is 2015. The top row shows gas-phase compounds measured by the PTR-MS and FIGAERO-CIMS, as well as input concentrations of H<sub>2</sub>O<sub>2</sub>, NO, 1058 and isoprene. Middle row shows the OA as measured by the AMS. Steady state periods are 1059 shown within magenta circles, AMS blanks as black squares. Select particle phase species 1060 measured by the FIGAERO-CIMS are in the bottom row. Grey shaded areas in each column 1061 indicate when chamber lights were off for chamber cleaning and a dark NO<sub>3</sub> experiment (in 1062 1063 2014) which is not discussed here. Note that the axis limits are not the same due to a wide range in concentrations across years, while  $C_5H_{12}O_5$  has been enhanced 5x and  $C_5H_{11}NO_7$  has been 1064 enhanced 20x in the bottom rows to clearly show the behavior of each species on the same axis. 1065 1066

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**Figure 2.** Mass spectra for compounds with composition  $C_xH_yO_zI$ - (green) and  $C_xH_yNO_zI$ - (blue) at low (left) and high (right) NO input in both the gas- (top) and particle- (bottom) phases. Bars are sized by the square root of signal (counts s<sup>-1</sup> for the gas-phase, counts for the particle-phase) to show the dynamic range. Major components are labeled with letters corresponding to those found in Table 1.



**Figure 3.** Top: Normalized signals of  $C_5H_{12}O_6$  and  $C_5H_{11}NO_7$ , believed to originate in the gas phase from the same  $C_5H_{11}O_6$  peroxy radical, as well as  $C_5H_{12}O_5$ , as a function of input NO. Signal is normalized to maximum signal for each compound to show the relative behaviors. Bottom: The mass fraction of organic nitrates as a function of NO. Mass fraction refers to the mass concentration of FIGAERO-CIMS measured OrgN relative to the total mass concentration of organics (non-nitrogen containing + OrgN) measured by the FIGAERO-CIMS.

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**Figure 4.** Time evolution of particle-phase concentrations in a batch mode isoprene photochemical oxidation experiment at low-NO<sub>x</sub>. Time increases from left to right and the size of the pies is proportional to the amount of OA present which is: 5.6, 10.8, 10.6, 10.4  $\mu$ g m<sup>-3</sup> from left to right.





**Figure 5.** Top: Predicted versus measured fraction in the particle-phase ( $F_p$ ). Predicted  $F_p$  is obtained from equation 1 where C\*s were calculated with the EVAPORATION groupcontribution method [*Compernolle et al.*, 2011] labeled as "Group-Cont. C\*" in the bottom panels. Measured  $F_p$  is the direct measurement from the FIGAERO. Bottom: The  $F_p$  can also be predicted based on the calibrated FIGAERO temperature axis as discussed in the methods and is shown as the predicted  $F_p$  here. Agreement can be reached for two representative compounds where the  $F_p$  is over and correctly predicted (left, right respectively).



**Figure 6.** Top: Sum of the thermogram signal for compounds with formula  $C_xH_yO_zI$ -, where x is varied across each thermogram and represents compounds with 6 or more carbons. Bottom: The sum off the mass concentration of all compounds with 6 or more carbons in arbitrary units as a function of isoprene reacted.





**Figure 7.** Top: Sum thermograms of  $\alpha$ -pinene + O<sub>3</sub> compared to isoprene (C<sub>5</sub>H<sub>8</sub>) photooxidation 1113 with and without  $NO_x$ . The  $\alpha$ -pinene sum thermogram has been reported previously (Lopez-1114 Hilfiker et al. [2015], Fig 5). Bottom: The sum thermograms at low (left) and high (right) input 1115 NO. The thermogram of  $C_5H_{12}O_6$ , the largest signal in both cases, is separated out (dark green) 1116 and the sum of the remaining signal minus  $C_5H_{12}O_6$  is displayed as the remaining signal (light 1117 green). At Low NO input, the sum of compounds with 6 or more carbons is specified (pink 1118 triangle/line), while at high NO input the sum of OrgN and the sum of non-nitrate organics are 1119 plotted (dashed lines, independent of solid lines) to show the relative thermogram features. 1120