Responses to reviewers, Ayres et al., October 23, 2015.

Please note the additional author comment submitted during the open discussion period on ACPD (posted on 27 July, 2015). In addition to responding to the reviewer comments, as noted below, we have made changes to the manuscript to include another CIMS dataset for the correlation analysis of organic nitrates. These additions are described thoroughly in those previous online comments, and updates are included in this document. In the course of this addition, changes were made to some of the figures. All the altered figures are included at the end of this document for easy reference. We have also added some supplemental material for clarification of the measured N_2O_5 vs the predicted N_2O_5 uncertainty. To facilitate the review process we have copied the reviewer comments *in italics*. Our responses are in non-italics. We have responded to all the referee comments and made alterations to our paper described below. Reviewer comments are numbered here for clear cross-referencing.

Responses to reviewer #1:

We thank this reviewer for pointing out several ways in which we could strengthen this paper and clarify the analysis.

R1.0. This manuscript reported the measurements of organic nitrates and the NOy budget during the SOAS campaign. The authors estimated the NO3 radical concentration and then calculated the cumulative losses of NO3 radical. Based on the correlation between the cumulative losses of NO_3 *radical to terpenes and the measured particle-phase organic nitrate (ON), the authors concluded that the molar yield of aerosol phase monoterpene nitrate ranges from 23 - 44%. While the writing is clear, the conclusions are not very novel and not well justified. I recommend accepting manuscript after major revisions.*

R1.1. Major comments:
Firstly, regarding the organic nitrates, Xu et al. (2015a) already demonstrated the importance of biogenic VOCs (especially monoterpenes) + NO_3 *in the SE US. Furthermore, Xu et al. (2015b) systematically evaluated the contribution of ON to ambient organic aerosol at multiple sites and in all seasons in the SE US. These two studies are clearly relevant and should be discussed.*

We thank the reviewer for pointing out this oversight, and we are glad to add the following text to the introduction (paragraph 7) summarizing the Xu et al. (2015) papers as they relate to the present work:

"Xu et al. (2015a) have reported that organic aerosol from nitrate radical oxidized monoterpenes are strongly influenced by anthropogenic pollutants and contribute to 19-34% of the total OA content (labeled less-oxidized oxygenated organic aerosols, LO-OOA). Monoterpene oxidation products show a large contribution to LO-OOA year-round (Xu et al., 2015b). Another AMS factor specific to reactive uptake of isoprene oxidation products (e.g. IEPOX), Isoprene-OA, is isolated in the warmer summer months in both urban as well as rural areas across the southeastern United States and contributes 18-36% of summertime OA (Hu et al., 2015; Xu et al., 2015a). LO-OOA is seen predominantly during nighttime hours, implying NO_3 oxidation of monoterpenes, and is strongly correlated specifically with the nitrate functionality in organic nitrates (Xu et al., 2015b). It is suggested that during the summer months, increasing nighttime LO-OOA balances with increasing daytime isoprene-OA to give the observed constant OA concentration over the diurnal cycle."

R1.2. Secondly, the authors used the organic nitrate measured by AMS extensively in the analysis. However, how the ON is measured by AMS is not discussed in the text. It is a little misleading to say that "HR-ToF-AMS was used to measure submicron organic and inorganic nitrate aerosol composition" (page 16241 line 15 – 17) without further justification. If the concentration of ON is calculated based on the NO+/NO2+ ratio method proposed by Farmer et al. (2010), more details should be definitely included in the text. Specifically, the NO+/NO2+ ratio for organic nitrates appear to be dependent on the specific systems (e.g., it is about 5 for isoprene ON, but about 10 for monoterpene ON). Even for ammonium nitrate, the NO+/NO2+ ratio can also vary. What NO+/NO2+ values did the authors use for organic nitrates and inorganic nitrates specifically in the equation proposed by Farmer et al.? Xu et al. (2015b) used NO+/NO2+ ratio of 5 and 10 for estimating organic nitrate contributions in the SE US and the uncertainties associated with this method were discussed. Regardless of the choice of the NO+/NO2+ ratio for organic nitrates, when using AMS data along to estimate organic nitrate concentrations, the authors should explain their methods clearly and justify their approaches.

We thank the reviewer for pointing out this omission and are glad to add the following clarification of the AMS ON analysis method to the experimental section discussing the AMS.

"Organic nitrates in the particle phase ($pRONO_2$) decompose prior to ionization on the AMS vaporizer to NO_2^+ organic fragments, hence $pRONO_2$ cannot be quantified directly from AMS data. The contribution of $pRONO_2$ to total particular nitrate was calculated using the method first discussed in Fry et al. (2013) and is briefly summarized here. This method relies on the different fragmentation patterns observed in the AMS for organic nitrates vs NH_4NO_3, specifically the ratio of the ions NO_2^+ to NO^+. Since this ratio depends on mass spectrometer tuning, vaporizer settings and history, Fry and coauthors proposed to interpret the field ratio of these ions in relation to the one recorded for NH_4NO_3 (which is done routinely during in-field calibrations of the instrument). Using such normalized ratios, most field and chamber observations of pure organic nitrates are consistent with $(NO_2^+/NO^+)/((NO_2^+/NO^+)_{ref}$ of 1/2.25 (Farmer et al., 2010) to 1/3 (Fry et al., 2009) of the calibration ratio. The data reported here was calculated using the 1/2.25 ratio derived from Farmer et al. (2010) and used in Fry et al. (2013), interpolating linearly between pure ammonium nitrate and organic nitrate. It should be noted that a) the relative ionization efficiency (RIE) for both types of nitrate is assumed to be the same (since similar neutrals are produced) and b) that the organic part of the molecule will be quantified as OA in the AMS. Therefore, while only equivalent NO_2 $pRONO_2$ can be reported from AMS measurements, this makes the technique well suited for comparison with the TD-LIF method"

We would like to add that while the authors are aware of some individual chamber measurements that are slightly outside the range of 1/2.25-1/3 ratio for $pRONO_2$, in the course of now 5 field campaigns over North and South America the authors have not observed ratios smaller than 1/3 for ambient aerosols (Day et al., 2015 in prep.), suggesting that the normalized ratio is a fairly robust quantity in ambient data.

R1.3. Thirdly, the authors estimated the molar yield of aerosol phase monoterpene nitrates by correlating the cumulative losses of NO3 radical to monoterpene to total aerosol ON. However, I have some concerns regarding the authors' interpretation.

R1.3.1. While the x-axis is the predicted losses of NO3 radical to monoterpene, the y-axis is total aerosol ON, which also includes isoprene ON. Thus, the slope cannot be interpreted as yield of monoterpene ON.

The organic nitrate aerosol may contain some amount of isoprene ON, however, we believe this contribution to be small. The periods of observed aerosol ON buildup were always at night, when NO_3 radical reactions with MT are much more prevalent than NO_3 + isoprene. Consequently, when we create the same scatter plots with NO_3 + isoprene we see poor correlation. In general, due to its lower molecular weight, we expect first-generation oxidation products of isoprene to be more volatile than those from MTs. The FIGAERO CIMS data detects abundant C_{10} organic nitrates in the particle phase, including the slightly oxidized products that we expect first-generation products. However, the slightly-oxidized C_5 products that we would expect to be first-generation NO_3 + isoprene products occur exclusively in the gas phase, with the only particle-phase C_5 nitrates observed consisting of more highly oxidized formulae that may or may not be isoprene-derived. Furthermore, daytime first-generation isoprene nitrate produced via OH-initiated RO_2 + NO chemistry is expected to have a short lifetime to hydrolysis to nitric acid, because the nitrate groups will be primarily tertiary (Hu et al., 2011). Xu et al. (2015b) discuss isoprene + NO_3 products peaking at night and early morning and their likelihood of producing gas-phase water-soluble organic carbon (WSOC), but remaining in the gas phase. Because of these factors, we believe the contribution of isoprene ON to our analysis to be minimal, and any small contribution they do make will serve only to further render our molar yield estimates a lower limit.

We have added text in Section 3.1.2 Organic Nitrate Product Analysis, 4th paragraph:

" The median particulate fraction of $C_5H_9NO_5$ (particle phase/total) observed by the UW-CIMS was less than 1%, and $C_5H_9NO_{5(p)}$ comprised less than 1% of total particulate organic nitrate (Lee et al., 2015). Those C_5 species that are observed in the particle phase constitute less than 12% of total particulate organic nitrate mass (as measured by the UW-CIMS, Lee et al., 2015, Supplemental Information), and are more highly oxidized molecules, inconsistent with first-generation NO_3 + isoprene products. This suggests that most (especially first-generation) isoprene nitrate products remain in the gas phase. The correlation of gas phase first-generation isoprene nitrate concentrations with NO_3 loss again provides evidence about the oxidative sources of these molecules (Figure 8). $C_5H_9NO_5$ (panels a and c) shows the strongest correlation with $(NO_{3,loss})_{integ}$ to isoprene among all the individual molecules ($R^2 = 0.54$ for UW and 0.70 for CIT), suggesting that this compound is a product of NO_3 oxidation. The better correlations of these C_5 species than observed in Figure 7 may be due to slower gas phase losses of organic nitrates relative to the semi-volatile C_{10} species. Using the calibrated mixing ratios from CIT for $C_5H_9NO_5$, we calculate an approximate lower limit molar yield of 7%. The $C_5H_9NO_4$ and $C_4H_7NO_5$ isoprene products (panels b and d) show poorer correlation with $(NO_{3,loss})_{integ}$ to isoprene ($R^2 = 0.11$ and 0.35, respectively), suggesting that these products are not (exclusively) a NO_3 + isoprene product, and may instead be a photochemically or ozonolysis produced organic nitrate, via RO_2 +NO."

R1.3.2. In page 16247 line 26-28, the authors cited Lee et al. 2015 (not published) to argue that isoprene ON accounts for < 0.5% of total particle-phase ON. However, according to the abstract (page 16237 line 13-16), it seems like that 0.5% is only the fraction of C5H9NO5 in total aerosol ON, instead of the fraction of all isoprene ON in total aerosol ON. This discrepancy needs to be reconciled. In fact, how are isoprene ON identified from the CIMS measurements? Since Lee et al. 2015 is not published, the authors need to provide more justifications about Lee et al. to help readers understand.

See added manuscript text in response to comment R1.3.1 above, which clarifies that very little $C_5H_9NO_5$ is in the particle-phase and refers to forthcoming Lee et al paper.

R1.3.3. The calculated yields (both ON yield and SOA yield) should be compared to the values in the literature. For example, Boyd et al. (2015) reported the ON yield from b-pinene + NO3. Fry et al. (2011) reported the yields from limonene + NO3.

We have added the following summary of the organic nitrate (ON) yields reported for α-pinene, β-pinene and limonene to Section 3.1.1(paragraph 4): "Several chamber studies have measured organic nitrate yields from NO_3 oxidation of individual terpenes: Spittler et al. (2006) and Fry et al. (2014) both found 10-15% total organic nitrate (ON) yield for α-pinene; Fry et al. (2009) found 45% total ON yield for β-pinene under humid conditions, Fry et al. (2014) found 22% under dry conditions, and Boyd et al. (2015) found aerosol organic nitrate to comprise 45-74% of OA produced from NO_3 + β–pinene; and Fry et al. (2011) found 30% total ON yield while Fry et al. (2014) found 54% for limonene. A mix of these chamber organic nitrate yields are consistent with the observed molar yield range reported here, which uses only NO_3 losses to monoterpenes."
Note: these comparisons are a bit complex, because Boyd et al. (2015) measured only aerosol-phase ON, while the other yields here are for total (gas + aerosol) ON, but we hope to have made this clear by careful wording.

We have also added a rough calculation of the conversion from molar yield to SOA mass yield to Section 3.1.1: "To derive SOA mass yield from these correlations, we propose the following rough calculation. Conversion of the reported molar yield to an SOA mass yield requires assuming 1:1 reaction stoichiometry of NO_3 with monoterpenes (MW =

136 g mol^{-1}) and estimating the average molecular weight (250 g mol^{-1}) of the condensing organic nitrates. Using the range of molar yields determined here (23-44%), this conversion gives an SOA mass yield range from 42% to 81%. These apparent aggregated yields of SOA from NO_3 + monoterpene are higher than one might expect from laboratory-based yields from individual monoterpenes, particularly since NO_3 + α-pinene SOA yields are essentially zero (Fry et al., 2014; Hallquist et al., 1999; Spittler et al., 2006) and α-pinene is a dominant monoterpene in this region. For β-pinene, Fry et al. (2009), Fry et al. (2014) and Boyd et al. (2015) found SOA mass yields in the 30-50% range at relevant loading and relative humidity, and Fry et al. (2011) and Fry et al. (2014) found limonene SOA yield of 25-57%. Because the actual average molecular weight of the condensing species is unknown, this comparison is not straightforward, but it appears that the aggregate SOA yield suggests higher ultimate SOA mass yields than simple chamber experiments dictate, perhaps suggesting that post-first generation products create more condensable species."

R1.3.4. Fourthly, section 3.3 is highly speculative. The authors totally ignored the BVOC concentrations. Centreville site is located in a forest, where BVOC concentrations are much higher than other locations.

Geron et al. (2000) shows county-level monoterpene emissions across the United States, and we understand the map in Figure 3 of Geron's paper to show that BVOC emissions at CTR are, in fact, reasonably representative of the SEUS region. We also have compared the monoterpene molar emissions from the SEUS (Geron et al., 2000, Figure 4 shows 7-410 μg C m^{-2} hr^{-1}, which translates to 0.05 – 2.6 mol MT m^{-2} hr^{-1}) to the annual NOx emissions from the NEI database over the 8-state region of the SEUS considered in section 3.3 of our paper (2.3 Tg NOx yr^{-1} over the 900,000 km^2 area translates to an average emission rate of 0.04 mol NOx m^{-2} yr^{-1}). This comparison shows that on average, NOx is the limiting reagant throughout the region, supporting our use of NOx emissions rates to determine PM emissions from this chemistry. The consistency of measured MO-OOA and LO-OOA loadings across several monitoring stations in the SEUS (Xu et al., 2015a) provides additional evidence of the regional representativeness of the CTR site.

Text was added to the introduction section (paragraph 7) to summarize these comparisons:

"County-level monoterpene emissions across the US shows the CTR site gives a regional representation of monoterpene emissions in the SEUS (Geron et al., 2000). Furthermore, Xu et al. (2015b) show that the CTR site is representative of more-oxidized and less-oxidized oxygenated organic aerosols (MO-OOA and LO-OOA, respectively) loadings across several monitoring stations in the SEUS. Comparison of annual molar emissions in the SEUS (an 8-state region including the CTR site) of BVOC (estimated from Geron et al. 2000) to NOx emissions (from 2011 NEI database) suggest that NOx is the limiting reagent in BVOC + NOx reactions throughout the region and demonstrates that the CTR site is regionally representative."

Specific Comments:

R1.5. Page 16241, line 1-2. Some discussions need to be better organized. For example, it is better to move this sentence after introducing GC-MS (page 16241 line 26-29). Another example is page 16243 line 7-9. The heterogeneous uptake of N2O5 is better discussed together with page 16245 line 1-10.

We have moved the BVOC sentence after GC-MS and N_2O_5 loss statement to uptake section.

R1.6. Page 16242 line 1-9. It would be helpful to include the size cuts of all instruments.

We have added size cuts to the experimental section:

"Thermal Dissociation Laser-Induced Fluorescence (TD-LIF, $PM_{2.5}$ size-cut) (Day et al., 2002; Farmer et al., 2010; Rollins et al., 2010) was used to measure total alkyl nitrates (ΣANs), total peroxy nitrates (ΣPNs) and aerosol phase ΣANs (Rollins et al., 2012). High-resolution time-of-flight aerosol mass spectrometry (HR-ToF-AMS, hereafter AMS, DeCarlo et al., 2006, Canagaratna et al., 2007, PM_1 size-cut) was used to measure submicron organic and inorganic nitrate aerosol composition using the nitrate separation method described in Fry et al. (2013)." and "A Metrohm Monitor for Aerosols and Gases in Ambient Air (MARGA, Makkonen et al., 2012; Trebs et al., 2004; Allen et al., 2015, $PM_{2.5}$ size-cut), which combines a wet-rotating denuder/steam jet aerosol collector inlet with positive and negative ion chromatograph, measured inorganic ion concentrations at 1-hour time resolution in both the aerosol- and gas-phases."

R1.7. Page 16242 line 23-24. It would be helpful to show the detection limit of cavity ringdown instrument.

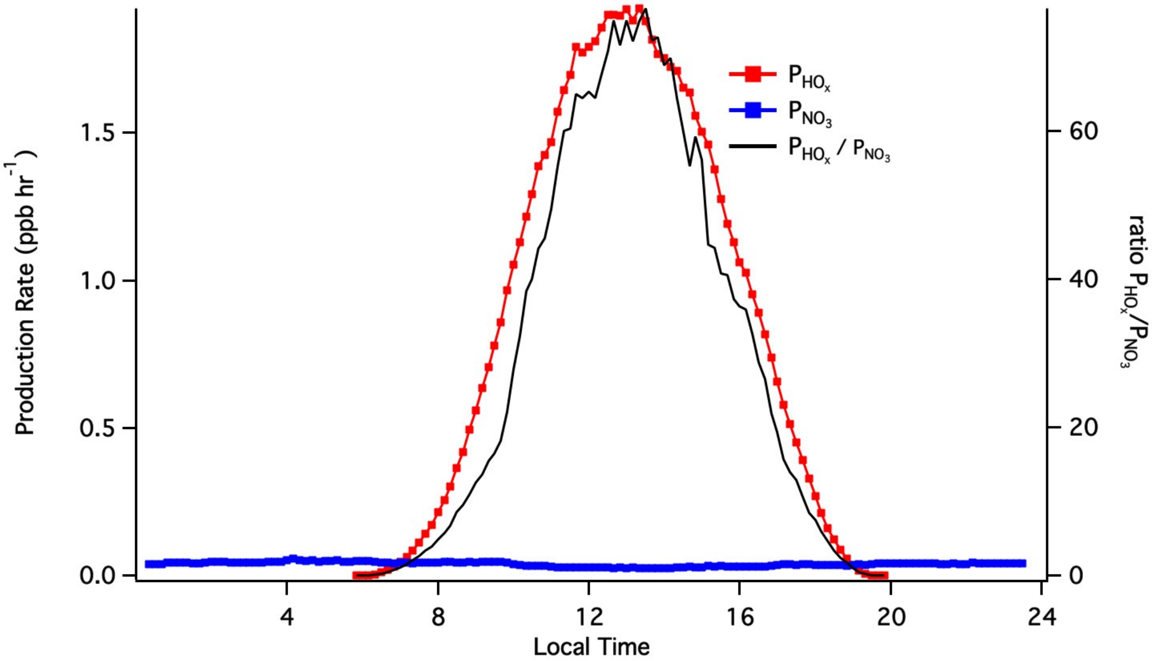
We have added the detection limit (1 pptv) to the experimental section: "N_2O_5 is quantitatively converted to NO_3 by thermal dissociation and detected in a second 662 nm channel with a detection limit of 1 pptv (30 s, 2σ) for NO_3 and 1.2 pptv (30 s, 2σ) for N_2O_5 (Dubé et al., 2006; Wagner et al., 2011)."

R1.8. Page 16244 line 23-25. The authors concluded that half of the daytime NO3 losses are due to reaction with BVOCs. However, this conclusion is highly dependent on the jNO3 value. The description of jNO3 calculation is not clear. What's the uncertainty of this value? How sensitive is the fate of NO3 to jNO3? In addition, this conclusion is a little misleading. Even if half of NO3 radical reacts with BVOC in the day, what's the concentration of NO3 concentration in the day? Is BVOCs+ NO3 an important pathway for SOA formation during daytime?

Yes, OH oxidation dominates BVOC oxidation during the day, so NO_3 should hence be a minor contributor compared to OH oxidation. Our point here is primarily that the conventional wisdom that the only daytime fate of NO_3 is to photolyze or react with NO is not true in a region with high [BVOC].

To assess daytime NO_3/OH competition, we calculated the production rate of HO_x (P_{HOx}) from formaldehyde and ozone photolysis (using photolysis rate constants from Saunders et al. 2003, [HCHO] from Fiber-LIF measurements (University of Wisconsin-Madison) and $[H_2O]$ calculated from realtive humidity and barometric pressure (Atmospheric Research & Analysis)) and compared this to the $P(NO_3)$ calculation presented in the paper $P(HO_x)$ ranges from 10-70 times larger than $P(NO_3)$ from 9 am to 7 pm local time. This suggests a smaller reaction rate of BVOC + NO_3 when compared to BVOC + OH, given their comparable reaction rate constants. However, near a large NO_x source (such as downwind of a power plant), NO_3 could be a competitive oxidant in BVOC oxidation.

$$P_{HO_x} = 2J_{O_3 \rightarrow O^1D}[O_3]\frac{k_1[H_2O]}{k_1[H_2O]+k_2[N_2+O_2]} + 2J_{H_2CO}[H_2CO]$$



We have adjusted the text in section 3.1 to reflect this: "Approximately half the daytime NO_3 losses are due to reaction with BVOC. (Note, this does not necessarily imply that NO_3 reaction is a substantial loss process *from the perspective of BVOC*; during the day, P(HOx) exceeds $P(NO_3)$ by a factor of 10-70 at SOAS, so OH will typically dominate.) However, from the standpoint of NO_3 lifetime, previous forest campaigns …"

We also changed the text in the section 3.1 (paragraph 3) to be more descriptive as to the calculation of $j(NO_3)$ as follows: "$j(NO_3)$ values were calculated from solar zenith angles and NO_3 photolysis rates (Saunders et al. 2003). The values were then adjusted for cloud cover by taking measured solar radiation values (Atmospheric Research and Analysis, Inc., W/m^2) and normalizing their peak values to those of the modeled photolysis data. Peak modeled $j(NO_3)$ values were 0.175 s^{-1} for clear sky at the daily solar maximum. After normalizing, typical values of $j(NO_3)$ were 0.110 s^{-1}."

The main uncertainty in jNO3 comes from the solar radiation measurement, which has a report error of +/- 20%. The following was also added to the Figure 4 caption to describe uncertainties: "Uncertainties in rate constants of BVOC + NO_3 range from +/- 30% for α-pinene to up to a factor of two for isoprene (Calvert et al., 2000); NO measurements had +/- 35% uncertainty, BVOC measurements +/- 20%, and photolysis +/- 20% based on solar radiation measurement uncertainty."

R1.9. Page 16246 line 12 - 25. This part needs to be better organized, since the authors jump from figure 6 to figure 7 and back to figure 6 again.

We have fixed the figure ordering.

R1.10. Page 16246 line 17 - 19. It is not clear how the conclusion is drawn. Do the authors have any evidence that the compounds shown in figure 7 are first-generation products?

We have removed this paragraph.

R1.11.Page 16247 line 7. Delete Lee et al.

We have corrected the Lee et al. references as seen in the bibliography at the end of this document.

R1.12. Page 16247 line 26 - 28. How the isoprene oxidation products are differentiated from monoterpene oxidation products from the CIMS measurements? In addition, one cannot reach the conclusion that most of the isoprene ON remains in the gas phase just based on that observation that isoprene ON accounts for <0.5 of total aerosol ON. Both gas and particle phase isoprene ON data are required to investigate the partitioning.

Isoprene and monoterpene oxidation products are discerned based on C_5 or C_{10} structures, assuming that these CIMS instruments have minimal fragmentation.

$C_5H_9NO_5$ gas/particle partitioning is now directly referenced in the "Organic Nitrate Product Analysis" section (paragraph 4), see response R1.3.1 above. The combined facts that (1) essentially all $C_5H_9NO_5$ is in the gas phase, and (2) only the gas-phase $C_5H_9NO_5$ product correlates well with the cumulative NO_3 + isoprene losses are consistent with first generation NO_3 + isoprene remaining in the gas-phase, while further oxidized later-generation products may condense.

R1.13. Figure 5. How are the start and stop points selected?

The start and stop are the beginning and end of the ON buildup periods for each instrument (estimated trough and peak) as seen in Figure 5, with typically one "buildup" observed each night when data is available.. We have added text to elucidate this to the "Calculation of NO_3 loss to BVOC" section (paragraph 1): "The beginning and end of the buildup periods were chosen as the approximate trough and peak values for the individual analyses (CIMS, AMS and TD-LIF). This buildup of aerosol $RONO_2$ was only observed after sunset, with one buildup event per night."

R1.14. Figure 8. Why do the authors use maxima in this plot?

We have changed the labels to match previous figures.

R1.15. Figure S2 is not optimal. Firstly, both y-axes should have the same scale to facilitate comparison. Secondly, a scatter plot would be helpful.

The scales were changed to put all analysis on the same scale.

We have added the scatter plot requested to the supplemental with an explanation of the correlation. We also added a short sentence about the comparison to Section 3.1 (paragraph 5) "Correlation of measured N_2O_5 vs predicted N_2O_5 shows during periods of high N_2O_5, we overestimate the concentration by a factor of two (Figure S1)."

Responses to reviewer #2:

We thank the reviewer for excellent suggestions, particularly the recommendations on how to quantify uncertainties in NO_3 mixing ratio, which have helped us to substantially strengthen this analysis.

R2.0. In this manuscript the authors analyze data taken during the SOAS campaign to estimate the molar yield of particle-phase organic nitrates from nitrate radical (NO3) oxidation of BVOCs. Briefly, they calculate NO3 loss due to oxidation of BVOCs using measured concentrations of BVOCs, estimated concentrations of NO3 and literature values of the BVOC + NO3 rate constants, and compare that to the total amount of particle-phase organic nitrates measured using two instruments (AMS and TD-LIF). The subject of the manuscript is of general interest to the ACP community. However, important details on the data analysis are missing, some uncertainties are glanced over, and some results may be overstated considering those uncertainties. In summary, I recommend publication after major revisions and consideration of my specific comments below.

Specific comments

R.2.1. Measurements of particle-phase organic nitrates
The authors use measurements of organic nitrates from an AMS and a TD-LIF instrument but provide close to no information on the data analysis from those instruments. For example, for the AMS:
R2.1.1. How were organic nitrates separated from inorganic nitrates (e.g. what NO/NO2 ratios were assumed or measured for organic and inorganic nitrates) and what uncertainty is associated with that separation (and the associated molar yield estimate)?

We have added the description of the technique used for AMS particle phase organic nitrate apportionment as already discussed in the response to the first reviewer (R1.2.). The uncertainties, as well as the impact on the agreement with the other instruments, are discussed in the next section.

R2.1.2. How was the collection efficiency estimated (which influences the total mass concentration), and what is the uncertainty in that estimate? How do total concentrations from the AMS compare to concentrations of those species measured using other instruments?

To address this comment and the estimation of the $pRONO_2$ uncertainty from AMS measurements, we have added the following text the supplemental information discussion of the comparison among organic nitrate instruments:

"AMS Collection Efficiency (CE) was estimated according to Middlebrook et al., (2012). The sum of AMS + BC submicron volume estimated using the measured mass and the density of each component (Salcedo et al., 2006, Kuwata et al., 2011) agreed within 10% with the volume recorded by two collocated scanning mobility particle sizer (SMPS) instruments. Each species, including nitrate was compared with a second HR-AMS on site run by the Georgia Tech Group (Xu et al., 2015a, Xu et al., 2015b), and was also found to be within 10%. Lastly, as described in Attwood et al., (2015), the calculated extinction based on the AMS mass agreed very well with collocated in-situ measurements of aerosol extinction during SOAS."

R2.1.1. The authors further state that particle-phase ON concentrations measured by the TD- LIF instrument were twice as high as concentrations measured by the AMS "for unknown reasons". This should be discussed further and at least potential explanations should be provided. Is the uncertainty in measurements from these two instruments potentially high enough to explain the differences?

We want to reemphasize that all the instrumental groups involved have been unable to find an explanation for this disagreement, especially since all instruments were properly calibrated and operated, and good agreement has been found in previous campaigns among the same instruments (Fry et al., 2013). We have added the following to the supplemental section:

"As discussed in the main paper, there exists an unresolved discrepancy between organic nitrate measurements from the various instruments at SOAS. While AMS total nitrate concentrations agree well between the CU AMS and the Georgia Tech AMS (apportioned most of the time as 100% organic nitrate), TD-LIF reports organic nitrate concentrations 2 to 4 times higher (resulting in a difference of about a factor of two when these different datasets are used in the "buildup" analysis of section 3.1.1). Because of the dominance of organic nitrate at this site, the difference in $pRONO_2$ between the instruments is not due to misclassification of AMS total nitrate as inorganic nitrate (details below), but stems from both AMSs (and the UW CIMS) disagreeing with the TD-LIF on the total amount of organically-bound NO_2 present in the particle phase. One possible explanation is the difference in size-cuts of the instruments (PM_1 for AMS, $PM_{2.5}$ for TD-LIF), however, organic nitrate SOA would be unlikely to dominate in this size range. Another possibility is that the TD-LIF detects some organic nitrates that are not detected as nitrate by the AMS; again, this explanation seems unlikely given that the AMS vaporizer temperature (600 °C) would likely dissociate any molecules that would thermally dissociate in the 350 °C oven. In the absence of other explanations, however, we treat TD-LIF as providing an upper limit, and AMS a lower limit, to the contribution of organic nitrates to the particle phase.

We estimate the precision of the $pRONO_2$ apportionment to be around 20% (based on the stability of the calibration ratio and combined precision of the ion concentrations at typical SOAS ambient concentrations), although the assumption of a universal ratio for all organic nitrates might not hold in all cases (especially for smaller and/or branched nitrates). However, outside of a few inorganic nitrate episodes, during most of the SOAS deployment >90% of AMS nitrate was apportioned as organic. Hence the discrepancy between TD-LIF and AMS cannot be attributed to uncertainties in the organic/inorganic apportionment for the AMS."

R2.2. Calculation of NO3ss

The concentrations of NO3 were calculated assuming steady state since NO3 concentrations were below the detection limit of the cavity ringdown spectrometer throughout the campaign. Concentrations of NO3 are essential for the analysis and conclusions presented in the manuscript. Therefore, the uncertainty associated with these estimated NO3 concentrations should be quantified in the text. Also, what is the detection limit of NO3 in the cavity ringdown spectrometer? Are the calculated/estimated concentrations always below the detection limit? If not this could indicate a problem in either the measurement or the estimation method.

We respectfully disagree that the NO_3 concentrations are essential for the analysis and conclusions presented in this manuscript. While these concentrations are useful, the more important quantity in the analysis is the nitrate radical production rate. So long as the majority of the NO_3 production goes to reaction with BVOC (as shown in this manuscript), the NO_3 concentration itself does not need to be known exactly.

Nevertheless, we have added text to discuss the limits and uncertainty with the CRDS (1 pptv). We have also added another supplemental figure (now S2) that shows propagated error bars for the predicted N_2O_5 compared to the measured values. This shows that measured values fall within the error of the predicted values. This is also discussed in the caption: “Propagated error analysis from raw data allows us to compare our calculated values of N_2O_5 to the measured values. Measured values of N_2O_5 fall within uncertainty bounds of predicted N_2O_5 giving us confidence that $NO_{3,SS}$ used in the calculation of predicted N_2O_5 can be substituted for all further rate calculations. b) We also used this method to show that $NO_{3,SS}$ error always encompass the detection limit of the instrument (1 pptv, 30 s, 2_). The predicted NO_3 levels from the steady state analysis fall within the range of uncertainty in the NO_3 measurements. However, the lack of any systematic deviation from the baseline during periods when NO_3 is predicted to be present at small levels may indicate unquantified inlet loss for measurement of this reactive species in this environment. The more robust N_2O_5 comparison provides confidence in the NO_3 steady state calculation.”

We’ve added a statement in section 3.1 concerning $NO_{3,SS}$ uncertainty: “Predicted steady-state N_2O_5 tracked observations when the latter were available and propagation of the error of calculated N_2O_5 shows peak measured values fall within uncertainty bounds of the predicted (Figure S2a); therefore, $NO_{3,SS}$ is hereafter used as the best estimate of NO_3 to calculate production rates of BVOC-nitrate products. $NO_{3,SS}$ peaks at 1.4 ppt ± 0.4 ppt. Propagation of errors in rate constants in the $NO_{3,SS}$ calculation (Figure S2b) shows that the error spans or is close to a mixing ratio of 0 for NO_3 during the entire campaign when data was available.”

R2.3. Figure S2: the information in this figure (measured and calculated/predicted N2O5) is important to evaluate the calculated NO3 concentrations; however it is difficult *to obtain that information from the figure. A scatter plot of measured vs. calculated concentrations with correlation coefficient would seem more appropriate. Also, can the imperfect agreement between measured and modeled N2O5 be used to quantify uncertainties in the calculated NO3ss? What NO3 concentrations would be consistent with the measured N2O5 concentrations and how do those NO3 concentrations compare to the calculated concentrations currently used?*

We have added the scatter plot requested to the supplemental with an explanation of the correlation. We also added a short sentence about the comparison to Section 3.1 (paragraph 5) "Correlation of measured N_2O_5 vs predicted N_2O_5 shows during periods of high N_2O_5, we overestimate the concentration by a factor of two (Figure S1)." Please note the 662 nm laser for NO_3 detection malfunctioned shortly after the large peak on 7/2/13 in the prediction. It is possible that its wavelength control and thus its spectral overlap with the NO_3 transition was compromised during this period. Considering that its response to this event differed from its response to the others, we have omitted this period from the comparison.

R2.4. Pg. 16244, line 10: does it make sense to compare AMS PM nitrate to total nitrate measured by the TD-LIF when we know that the PM nitrate measurements of these two instruments differ by a factor of 2?

We edited the text to clarify that the comparison was TD-LIF, not AMS: "… 80% when comparing aerosol phase ΣANs to TD-LIF total ΣANs from at 5am…"

R2.5. Pg. 16246, lines 21-24: These lines seem to imply that a molar yield can be determined from plots such as Fig 6. This seems a bit optimistic considering uncertainties and other processes which may be taking place. It seems more appropriate to state that the slopes are consistent with these molar yields assuming that no other processes are taking place.

We added a clarification statement: "… assumes no other processes are taking place."

R2.6. Pg 16247, lines 5-8: The results of Lee et al., 2015 are important to this study. If the paper is still not available additional information should be provided in the supplement of this study. In this case, the rapid loss of PM nitrates observed by Lee et al. should be discussed further. What are potential reasons for this loss (PM hydrolysis of ONs?) Also, what would be the molar yields of organic nitrates after accounting for this rapid loss? In other words, rather than simply state that the molar yields are a lower bound estimate, could the authors also provide an updated estimate accounting for the effects of that observed loss of PM nitrate?

We added text to section 3.1.2 (paragraph 3), "This also does not take into account heterogeneous hydrolysis (Boyd et al., 2015; Cole-Filipiak et al., 2010; Liu et al., 2012), photolysis (Epstein et al., 2014; Müller et al., 2014), or reaction with the hydroxyl radical (OH) (Lee et al., 2011)."

R2.7. Pg. 16247, lines 26-28: The authors state "Less than 0.5% of total particle-phase or- ganic nitrates observed with the CIMS (Lee et al., 2015) were isoprene oxidation products, suggesting that most of the isoprene nitrate products remain in the gas phase." This statement seems to assume that 1) We know the identity of all isoprene nitrate products and 2) The CIMS can accurately measure and quantify all of these products. It is not clear whether these assumptions are justified. More information needs to be provided (again, this information may be in Lee et al., which is not yet available) or the statement needs to be modified.

See response to comments 1.3.1. above

R2.8. Pg. 16248, line 1: It is not clear to me that these scatter plots can reveal the oxidative source as stated here. It seems more appropriate to state that the scatter plots are consistent with one product being more likely associated with NO3 oxidation than the other.

We have added a statement to clarify this in section 3.1.3 (paragraph 4): "The correlation of gas-phase first-generation isoprene nitrate concentrations with NO_3 loss again provides evidence about the oxidative sources of these molecules (Figure 8). "

R2.9. Figure 1. This figure could be made clearer by increasing font sizes and the size of the marker indicating the location of the field site.

We have increased sizes as requested

R2.10. Figure 2. It is a bit difficult to see if and when NO3ss and AN concentrations cor- relate. Please consider overlaying these traces or otherwise making the figure clearer (e.g. providing a scatter plot). Are the PM nitrate measurements (black trace) from the TD-LIF, AMS or CIMS instrument?

The caption was edited for clarification: "Figure 2. Nitrate radical concentration estimated by the steady-state approximation (red trace) shows several instances where peaks in NO_3 concentration correspond to times of ΣAN (gaseous+aerosol) buildup (light blue trace) from TD-LIF and particle phase organic nitrate from AMS (dark blue). The black overlay in TD-LIF ΣANs is the aerosol phase measurement of ΣANs and qualitatively shows that, when data is available, a large portion of the organic nitrates appear to be in the aerosol phase."

R2.11. Figure 4. What are the uncertainties associated with these NO3/N2O5 losses?

We have added a brief discussion of uncertainty to the Figure 4; please see response to R1.8. above.

Figures that were discussed above are included here for ease of reference.

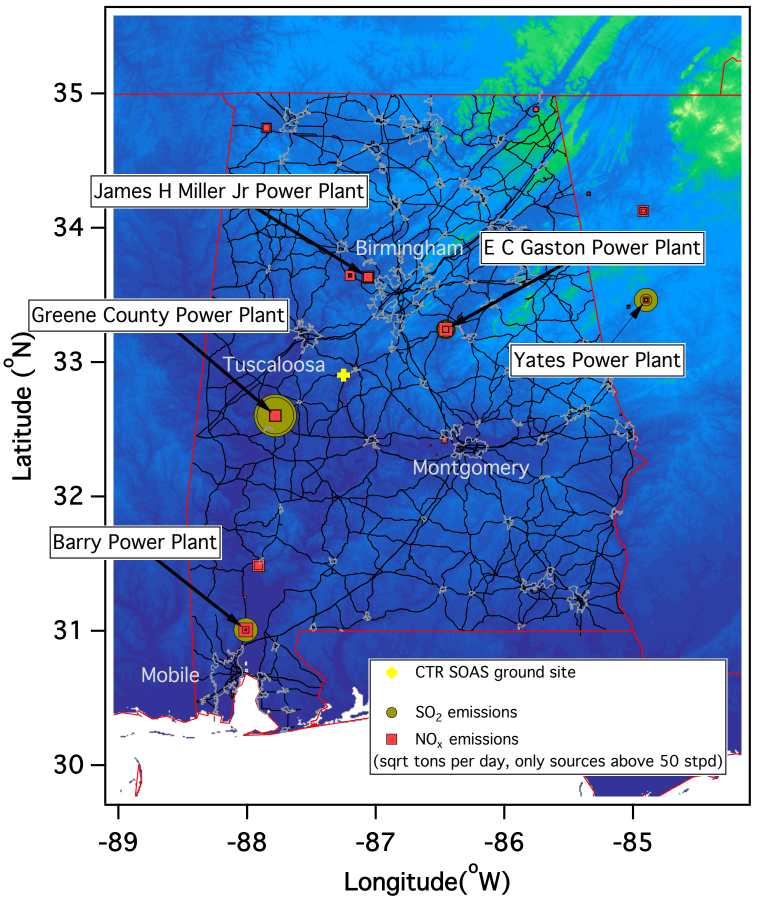


Figure 1. Map of Alabama with SO_2 and NO_x emissions point sources shown, as well as major roadways (black) . Centreville is located in Central Alabama about 55 miles SSW of Birmingham, AL. Major highways, city limits and major contributors to emissions are referenced for Alabama. The size of the emission markers depicts the relative concentrations of the pollutants according to the 2013 EPA Air Markets Program. For reference, the Alabama Power Company Gaston Plant emits 19.52 kg hr^{-1} SO_2 and 6.43 kg hr^{-1} NO_x.

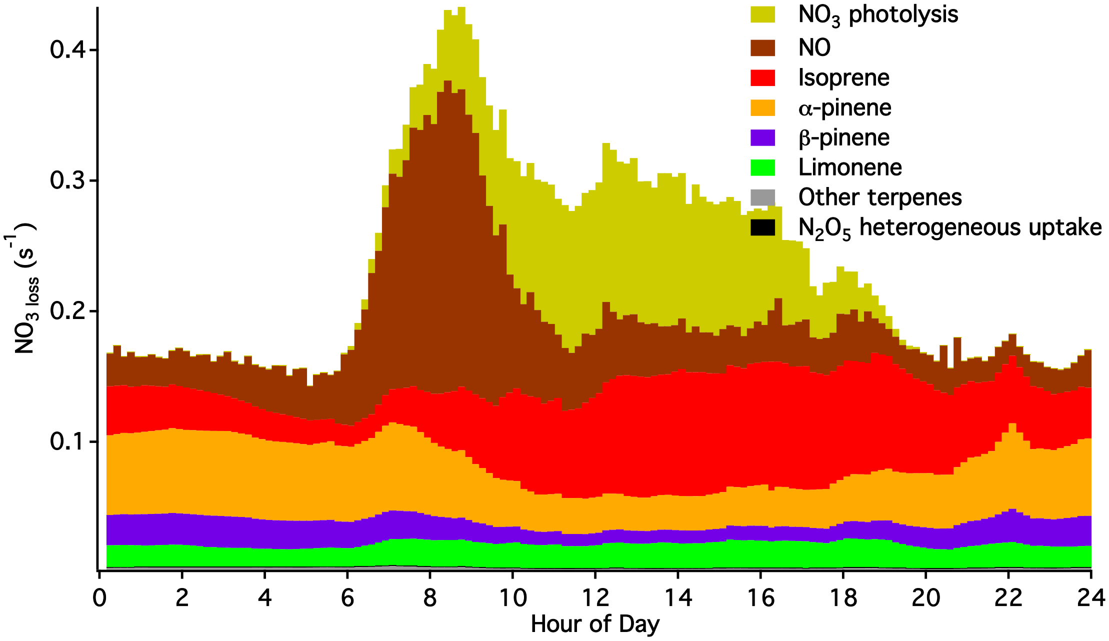


Figure 4. Average diurnal profile of NO$_3$/N$_2$O$_5$ losses June 1 - July 15, 2013. NO and photolysis losses peak during the daytime (in fact, nighttime NO$_3$ + NO loss is likely zero, and even [NO] below the instrument detection limits would cause the non-zero rates shown here), however losses to alkenes are significant during both night and day. Terpene losses are calculated from GC-MS data, NO & N$_2$O$_5$ data are from CRD, and photolysis losses are calculated as described in Section 3.1. Uncertainties in rate constants of BVOC + NO$_3$ range from +/- 30% for α-pinene to up to a factor of two for isoprene (Calvert et al., 2000); NO measurements had +/- 35% uncertainty, BVOC measurements +/- 20%, and photolysis +/- 20% based on solar radiation measurement uncertainty.

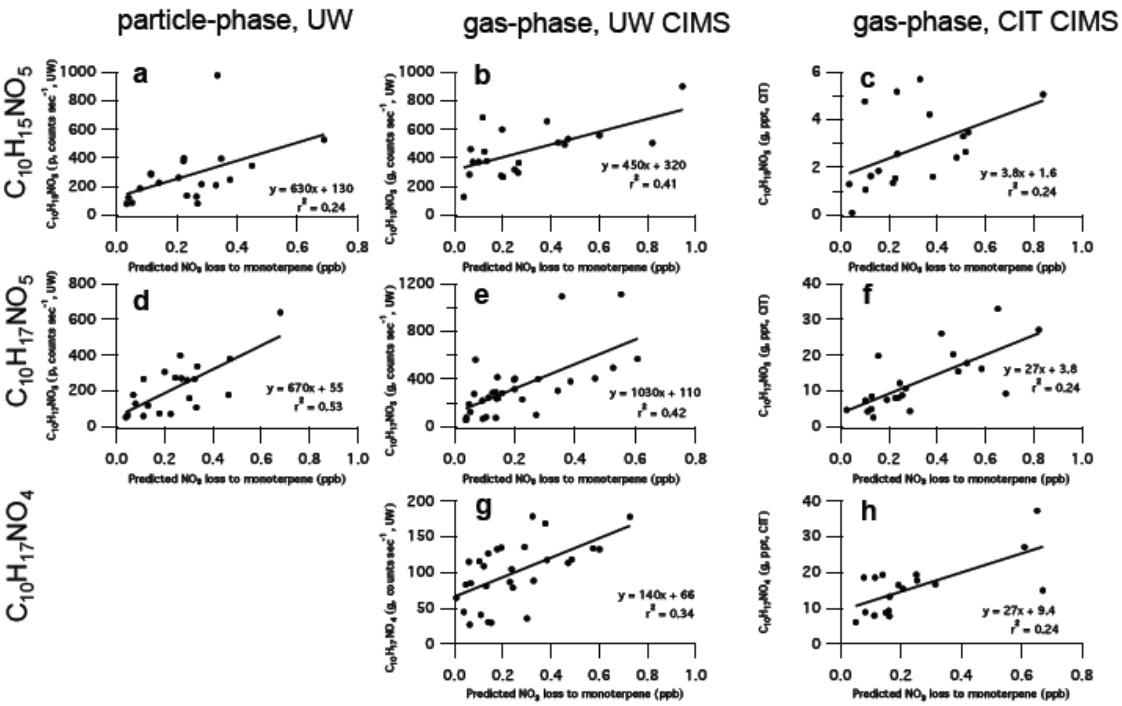


Figure 7. Scatter plots of selected molecules' concentration buildups against time integrated monoterpene losses to NO$_3$ radical, during periods of observed organic nitrate buildup measured by CIMS. Panels a & d show particle phase $C_{10}H_{15}NO_5$ and $C_{10}H_{17}NO_5$ measured by the UW FIGAERO; b & e show gas phase $C_{10}H_{15}NO_5$ and $C_{10}H_{17}NO_5$ also measured by UW; c & f show the same gas phase species measured by the CIT CIMS, with calibrated concentrations. Panels g & h show gas phase $C_{10}H_{17}NO_4$ measured by both CIMS. The gas phase correlations with calibrated mixing ratios measured by the CIT-CIMS (panels c, f, & h) allow for a rough estimation of the lower limit molar yields via the slopes: $C_{10}H_{15}NO_5$, 0.4%; $C_{10}H_{17}NO_5$, 3%; and $C_{10}H_{17}NO_4$, 3%.

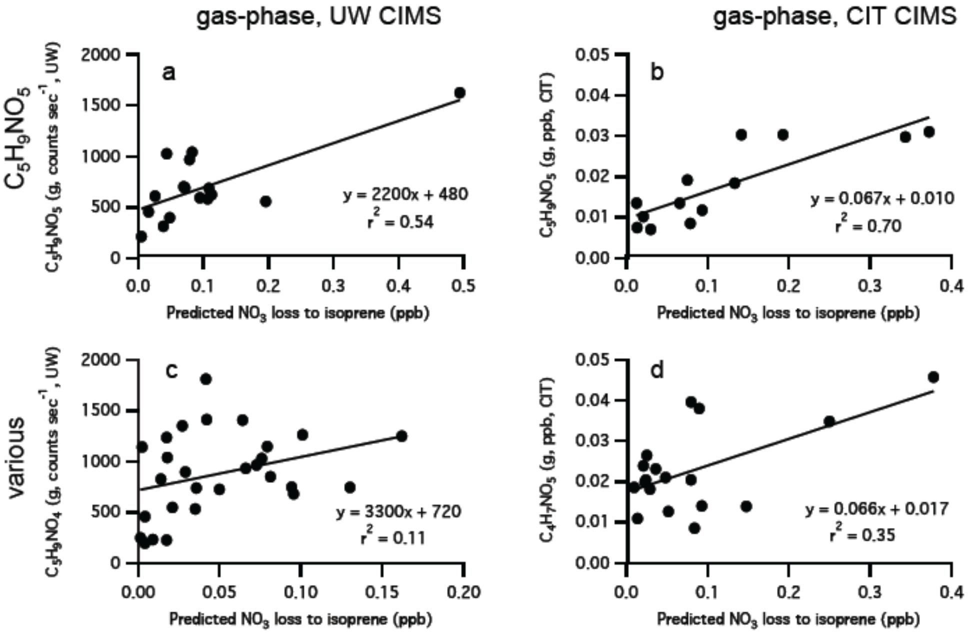


Figure 8. Gas phase CIMS data correlated to predicted isoprene + NO_3, during periods of buildup of these C_5 and C_4 nitrates as measured by each CIMS. Panels a & b show $C_5H_9NO_5$, which is well correlated to predicted isoprene + NO_3 suggesting this is a NO_3 gas phase product, with the calibrated mixing ratios measured by CIT enabling estimation of an approximate lower limit molar yield of 7%. Panel c shows that $C_5H_9NO_4$ is poorly correlated to isoprene + NO_3 suggesting that this product comes (at least in part) from another oxidative source (ex. RO_2+NO). Panel d, $C_4H_7NO_5$, also shows a poorer correlation than panels a & b, suggesting it is not exclusively a product of NO_3 oxidation, or has rapid losses.

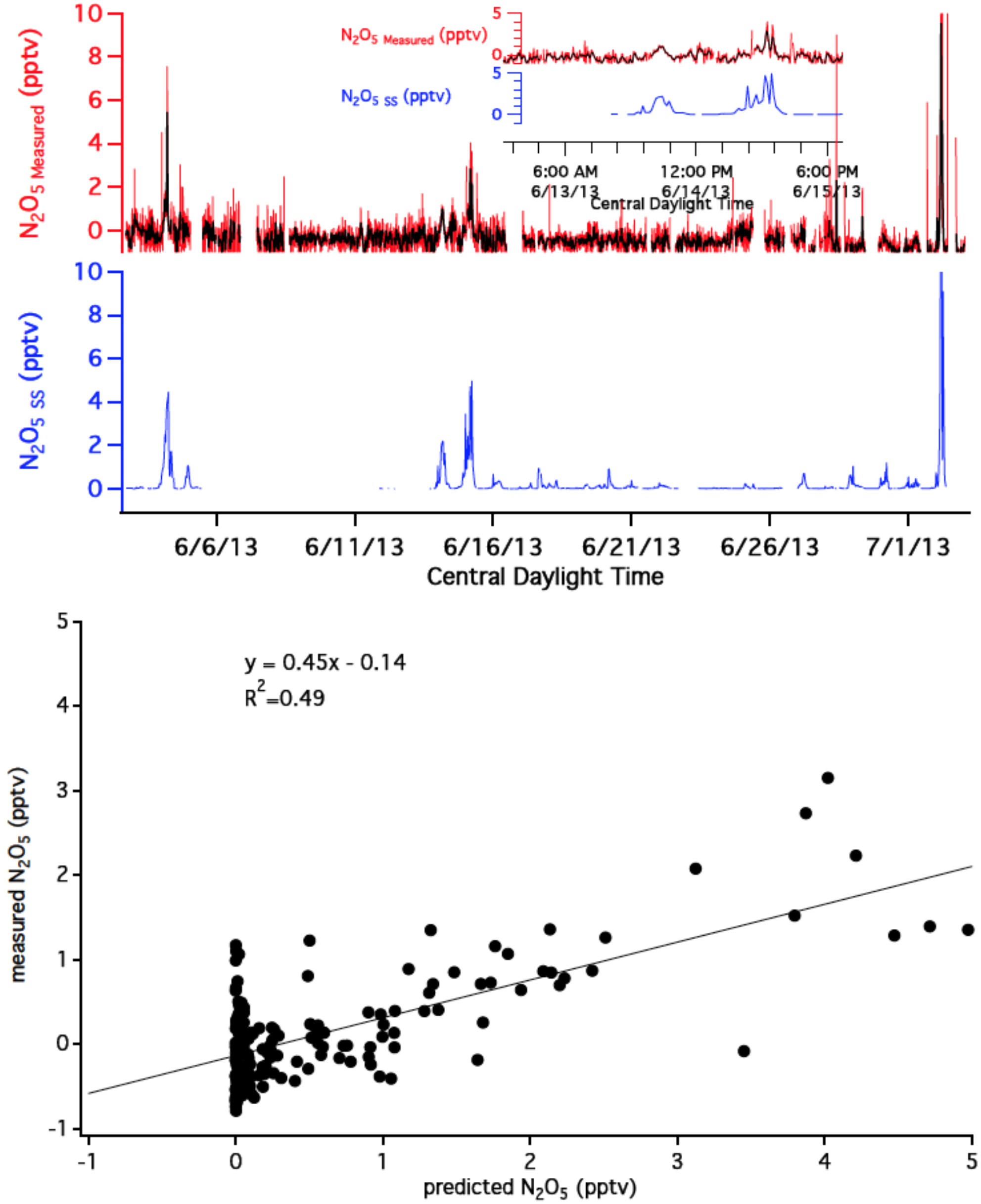


Figure S1. Steady state predicted (blue) and measured (red, binomial smoothed in black) N_2O_5 mixing ratio during the campaign. The inset provides a closer look at the N_2O_5 peaks that occur 13-June to 16-June, demonstrating the congruence of the timing and magnitude of predicted mixing ratios. The scatter plot shows the correlation of the measured N_2O_5 versus predicted N_2O_5, using binomial smoothed measured data during the periods 2-June to 6-June and 14-June to 16-June only, to avoid incorporating lots of zero noise on the measured variable. We conclude that in general our steady-state prediction tracks measured N_2O_5 reasonably well, though it overestimates measured $[N_2O_5]$ by approximately a factor of two.

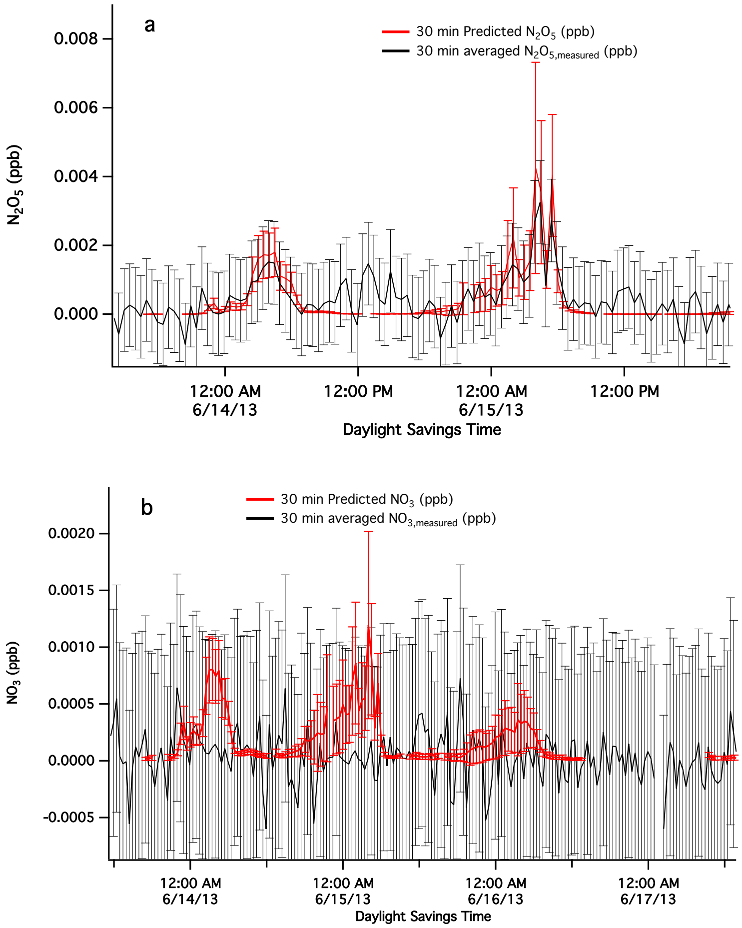


Figure S2. a) Propagated error analysis from raw data allows us to compare our calculated values of N_2O_5 to the measured values. Measured values of N_2O_5 fall within uncertainty bounds of predicted N_2O_5 giving us confidence that $NO_{3,SS}$ used in the calculation of predicted N_2O_5 can be substituted for all further rate calculations. b) We also used this method to show that $NO_{3,SS}$ error always encompass the detection limit of the instrument (1 pptv, 30 s, 2σ). The predicted NO_3 levels from the steady state analysis fall within the range of uncertainty in the NO_3 measurements. However, the lack of any systematic deviation from the baseline during periods when NO_3 is predicted to be present at small levels may indicate unquantified inlet loss for measurement of this reactive species in this environment. The more robust N_2O_5 comparison provides confidence in the NO_3 steady state calculation.

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