Organic Nitrate Aerosol Formation via NO$_3$ + Biogenic Volatile Organic Compounds in the Southeastern United States

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Abstract.

Gas- and aerosol-phase measurements of oxidants, biogenic volatile organic compounds (BVOC) and organic nitrates made during the Southern Oxidant and Aerosol Study (SOAS campaign, Summer 2013) in central Alabama show that nitrate radical (NO₃⁻) reaction with monoterpenes leads to significant secondary aerosol formation. Cumulative losses of NO₃⁻ to terpenes are correlated with increase in gas- and aerosol-organic nitrate concentrations made during the campaign. Correlation of NO₃⁻ radical consumption to organic nitrate aerosol formation as measured by Aerosol Mass Spectrometry and Thermal Dissociation - Laser Induced Fluorescence suggests a molar yield of aerosol phase monoterpene nitrates of 23-44%. Compounds observed via chemical ionization mass spectrometry (CIMS) are correlated against predicted NO₃⁻ loss to BVOC, and show C₁₀H₁₅NO₅ and C₁₀H₁₇NO₅ as major NO₃⁻-oxidized terpene products being incorporated into aerosols. The comparable isoprene product C₅H₉NO₅ was observed to contribute less than 1% of the total organic nitrate in the aerosol phase and correlations show that it is principally a gas phase product from nitrate oxidation of isoprene. Organic nitrates comprise 30-45% of the NOₓ budget during SOAS.

Inorganic nitrates were also monitored and showed that during incidents of increased coarse-mode mineral dust, HNO₃ uptake produced nitrate aerosol at rates comparable to that of organic nitrate produced via NO₃⁻ + BVOC.
Secondary Organic Aerosol (SOA), formed from the oxidation of volatile organic compounds (VOCs) by ozone (O$_3$), hydroxyl radical (OH), or nitrate radical (NO$_3$), affects visibility as well as regional and global radiative climate forcing [Myhre et al., 2013; Bellouin et al., 2011; Feng and Penner, 2007; Goldstein et al., 2009]. Aerosol has been studied as a source for significant risk factors for pulmonary and cardiac disorders [Nel, 2005; Pope and Dockery, 2006]. Organic aerosol (OA) contributes a large fraction of the total tropospheric submicron particulate matter (PM) [De Gouw, 2005; Heald et al., 2005; Zhang et al., 2007]. Biogenic volatile organic compounds (BVOC) are dominant precursors in SOA formation [Goldstein and Galbally, 2007; Spracklen et al., 2011]. SOA is a significant fraction of total aerosol mass in the Southeastern United States (SEUS) (predicted to be 80-90% of the organic aerosol load, Ahmadov et al., 2012, Stocker et al., 2013). Understanding the interaction of anthropogenic pollutants with BVOC is vital to improving our understanding of the human impact on SOA formation [Carlton et al., 2010; Spracklen et al., 2011] and the associated radiative forcing of climate change [Stocker et al., 2013].

Nitrogen oxides (NO$_x$ = NO + NO$_2$), common byproducts of combustion, are linked to aerosol formation in the troposphere via daytime and nighttime oxidation mechanisms [Rollins et al., 2012]. Total reactive nitrogen, NO$_x$, consists of NO$_x$, as well as NO$_x$ reaction products, including NO$_3$, HNO$_3$, HONO, alkyl nitrates, peroxynitrates and other particulate nitrates. Alkyl nitrates produced from oxidation of VOC are related to tropospheric ozone generation [Chameides, 1978] and, via low-volatility products, can lead to formation of SOA [Hallquist et al., 2009]. Oxidation of NO$_x$ to nitric acid (HNO$_3$) can also produce inorganic nitrate aerosol via heterogeneous uptake of HNO$_3$ onto mineral or sea salt aerosols [Vlasenko et al., 2006] and via co-partitioning with ammonia to form semi-volatile NH$_4$NO$_3$ [Lee et al., 2008].

Nitrogen oxides are primarily emitted as NO [Nizich et al., 2000; Galloway et al., 2004; Wayne et al., 1991]. NO is oxidized to NO$_2$ and further to the highly reactive NO$_3$ radical. NO$_3$ is especially predominant at night when loss via photolysis and NO reaction are at a minimum [Horowitz et al., 2007; von Kuhlmann et al., 2004; Xie et al., 2013].

The formation of NO$_3$ and the associated N$_2$O$_5$ in the atmosphere have been studied in detail [Bertram and Thornton, 2009; Brown and Stutz, 2012; Brown et al., 2011; Wagner et al., 2013]. The hydrolysis of N$_2$O$_5$ to HNO$_3$ can be important in the prediction of the tropospheric oxidant burden with respect to the O$_3$ production, and therefore OH radical production [Dentener and Crutzen, 1993; Evans and Jacob, 2005]. However, previous studies in Eastern Texas have found N$_2$O$_5$ uptake into aerosols to be relatively low in the southern United States (TexAQS average $\gamma$ of 0.003) [Brown et al., 2009; Riemer et al., 2009].

NO$_3$ is an effective nocturnal oxidizer of BVOC [Atkinson and Arey, 2003, 1998; Calogirou et al., 1999; Winer et al., 1984]. NO$_3$ oxidation is especially reactive towards unsaturated, non-aromatic hydrocarbons of which BVOC are major global constituents. NO$_3$ is less reactive towards aromatic...
compounds and saturated hydrocarbons, major compounds of anthropogenic VOCs. Nitrate oxidation of some BVOC compounds, such as \( \beta \)-pinene, lead to rapid production of SOA in laboratory experiments with high yields (Griffin et al., 1999; Jimenez et al., 2009; Zhang et al., 2007; Hallquist et al., 2009; Fry et al., 2011; 2009; Boyd et al., 2015). Analysis of previous field studies have characterized the loss of \( \text{NO}_3 \) to its major daytime sinks, including reaction with NO and photolysis, as well as its loss to BVOC during both daytime and nighttime (Aldener et al., 2006; Brown et al., 2005).

Nitrogen-containing oxidation products include alkyl nitrates (RONO\(_2\)), peroxynitrates (RO\(_2\)NO\(_2\)) and nitric acid (HNO\(_3\)) (Brown and Stutz, 2012; Perring et al., 2013), all of which may partition to the aerosol phase and contribute to SOA (via direct reaction or catalysis) (Kroll and Seinfeld, 2008).

Ambient concentrations of alkyl nitrates and peroxynitrates can be quantified using laser-induced fluorescence (Day et al., 2002; Rollins et al., 2010) and mass spectrometry methods (Bahreini et al., 2008; Farmer et al., 2010; Beaver et al., 2012; Fry et al., 2013). Ions and acids (i.e. HNO\(_3\)) can be quantified using ion chromatography (IC, Makkonen et al., 2012; Trebs et al., 2004) as well as CIMS (Beaver et al., 2012). The combination of these instruments, as well as others discussed below, allow for the determination of a total ambient oxidized nitrogen (\( \text{NO}_y \)) budget, which enables the interpretation of the importance of nitrogen oxides in SOA formation.

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 \( \text{NO}_3 \) 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.

The 2013 SOAS campaign was a comprehensive field intensive in central Alabama near Centre-ville (CTR), in which concentrations of oxidants, BVOC and aerosol were measured with a particular focus on understanding the effects of anthropogenic pollution on SOA formation. The site was chosen due to its high biogenic VOC emissions as well as its relatively large distance from anthropogenic pollution (Figure 1). 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 includ-
ing 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 + NO3 reactions throughout the region. 

Alabama is home to a number of power plant facilities that are large point sources of NOx capable of being carried long distances. Alabama’s non-interstate roadways also have large emissions of NOx, though a majority of the emissions come from urban areas. Although the NOx emissions have been steadily dropping since 1998, they are still substantial (2.70 million tons in reported for SEUS in 1999 to 1.75 million tons in 2008, [Blanchard et al., 2013]). Frequent controlled biomass burning events (crop burning, [Crutzen and Andreae, 1990]), as well as vehicular sources (Dallmann et al., 2012) also contribute to local NOx emissions and PM concentrations (a full analysis of contributions can be found at the EPA National Emissions Inventory, http://www.epa.gov/ttn/chief/net/2011inventory.html).

In the present study, we investigate the production of SOA species from NO3 reaction with monoterpenes. NO3 loss to BVOC is calculated and compared to AMS and TD-LIF measurements of aerosol organic nitrates, as well as individual product nitrates measured by CIMS. We compare this NO3 loss to BVOC to an alternate fate of NOx, heterogeneous HNO3 uptake to produce inorganic nitrate aerosol, which is considered in detail in a companion paper (Allen et al., 2015). These two pathways from NOx to nitrate aerosol shown in Scheme 1 alternated dominance during SOAS.

2 Experimental

Measurements for the SOAS campaign took place near the Talladega National Forest, 6 miles southwest of Brent, AL (32.9029 N, 87.2497 W), from June 1 - July 15, 2013. The forest covers 157,000 acres to the northwest and southeast of Centerville, AL. Figure 1 shows a map of the site location as well as nearby point sources of anthropogenic NOx and SO2. The site is in a rural area representative of the transitional nature between the lower coastal plain and Appalachian highlands (Das and Aneja, 2003). Wind direction varied during SOAS allowing for periods of urban influence from sources of anthropogenic emissions located near the sampling site, including the cities of Montgomery, Birmingham, Mobile and Tuscaloosa (Hidy et al., 2014). The closest large anthropogenic NOx emission point sources are the Alabama Power Company Gaston Plant located near Birmingham and the Green County Power Plant southwest of Tuscaloosa (EPA Air Markets Program 2013).

Two cavity ringdown spectrometers (CRDS) were used to determine ambient mixing ratios of NOx, O3, NOy, NO3 and N2O5 (Wild et al., 2014, Wagner et al., 2011). CRDS is a high sensitivity optical absorption method based on the decay time constant for light from an optical cavity composed of two high reflectivity mirrors. NO2 is measured using its optical absorption at 405 nm in one channel, and O3, NO and total NOx are quantitatively converted to NO2 and measured simultaneously by 405 nm absorption on three additional channels. NO3 is measured at its characteristic strong absorption band at 662 nm. N2O5 is quantitatively converted to NO3 by thermal dissociation.
and detected in a second 662 nm channel with a detection limit of 1 pptv (30 s, 2 \(\sigma\)) for NO\(_3\) and 1.2 pptv (30 s, 2 \(\sigma\)) for N\(_2\)O\(_5\) (Dubé et al., 2006; Wagner et al., 2011).

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 (\(\Sigma\)ANs), total peroxy nitrates (\(\Sigma\)PNs) and aerosol phase \(\Sigma\)ANs (Rollins et al., 2012). High-resolution time-of-flight aerosol mass spectrometry (HR-ToF-AMS, hereafter AMS, DeCarlo et al., 2006; Canagaratna et al., 2004 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). 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 particulate 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\(_4\)NO\(_3\), specifically the ratio of the ions NO\(_2^+\)/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\(_4\)NO\(_3\) (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\(^+\))\text{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. These measurements correlate well to one another, but the magnitudes differ by a factor of approximately 2-4 for unknown reasons, with TD-LIF being larger than AMS (see Supplemental Information).

Two chemical ionization mass spectrometers (Caltech’s cTOF-CIMS and University of Washington’s HR-ToF-CIMS, hereafter both referred to as CIT-CIMS and UW-CIMS respectively, Bertram et al., 2011; Yatavelli et al., 2012; Lee et al., 2014; Nguyen et al., 2015) were used to identify specific organic nitrate product ions, specifically monoterpene (Eddingsaas et al., 2012) and isoprene products (Crounse et al., 2013, 2006; Beaver et al., 2012). The CIT-CIMS measured only gas phase products (Beaver et al., 2012; Nguyen et al., 2015) while the UW-CIMS employed a Filter Inlet for Gas and Aerosol (FIGAERO) to separate aerosol and gas species (Lopez-Hilfiker et al., 2014; Lee et al., 2014, 2015). Both spectrometers are capable of resolving ions with different elemental formulae at common nominal m/z.

On-line cryostat-Gas Chromatography-Mass Spectrometer (GC-MS) was used to measure mixing ratios of gas phase BVOC species (Goldan et al., 2004; Gilman et al., 2010). BVOC emissions at
the CTR site are dominated by isoprene, α-pinene, β-pinene, and limonene (Supplemental Figure S4, Stroud et al., 2002; Goldan et al., 1995). Surface area concentration was calculated from number distribution measurements of a hygroscopicity scanning mobility particle sizer (SMPS) and optical particle sizer (OPS) similar to a Dry-Ambient Aerosol Size Spectrometer (Stanier et al., 2004). Boundary layer height was measured using a CHM 15k-Nimbus and method employs photon counting of back-scattered pulse of near-IR light (1064 nm) via LIDAR principle. A Metrohm Monitor for Aerosols and Gases in Ambient Air (MARGA, Makkonen et al., 2012; Trebs et al., 2004; Allen et al., 2015, PM2.5 size-cut), which combines a wet-rotating denuder and steam jet aerosol collector inlet with positive and negative ion chromatography, measured inorganic ion concentrations at 1-hour time resolution in both the aerosol- and gas-phases.

Site infrastructure consisted of a 65-foot tower, with the top platform set above the canopy height for sampling to prevent bias between measurements, and seven trailers located in a field 90 m south of the tower. The tower instruments used for this analysis consisted of the two CRDS, CIT-CIMS, TD-LIF and a cryostat GC-MS. The field trailers contained the AMS, SMPS, APS, UW-CIMS and MARGA.

3 Results

3.1 Organic NOx sink: NO3 + BVOC production of organic nitrate SOA

During the SOAS campaign, we monitored reactant and product species indicative of NO3 + BVOC, which may partition into the aerosol phase and consequently serve as a source of first generation SOA. NO3 reaction with biogenic alkenes forms organic nitrates (R1).

\[
\text{NO}_3 + \text{BVOC} \rightarrow \text{RONO}_2 + \text{other products} \quad \text{(R1)}
\]

\[
\text{NO}_3 \quad \text{and} \quad \text{N}_2\text{O}_5 \quad \text{(which exists in equilibrium with NO}_2 + \text{NO}_3) \quad \text{in the region were consistently low during the campaign. The resulting NO}_3 \text{ mixing ratio was below the detection limit of the cavity ringdown instrument (1 pptv) for the entire campaign. Calculated steady-state N}_2\text{O}_5 \text{ was validated against observed measurements (see below) and NO}_3 \text{ predicted from the steady-state approximation was used for all calculations involving NO}_3 \text{ radical mixing ratios. Using the rate constant for NO}_2 + \text{O}_3 \text{ (Table 1), the production rate of the nitrate radical (P(NO}_3)) \text{ is given by:}
\]

\[
P(\text{NO}_3) = k_{O_3+NO_2}[O_3][NO_2] \quad \text{(1)}
\]

The calculated loss rate of NO3, \(\tau(\text{NO}_3)\), to reactions with individual BVOC, NO and photolysis, \(j_{\text{NO}_3}^*\), modeled for clear sky from MCM, (Saunders et al., 2003) is

\[
\tau(\text{NO}_3) = \frac{1}{(\sum i k_{\text{NO}_3+BVOC_i}[BVOC_i] + k_{\text{NO}_3+NO}[NO] + j_{\text{NO}_3}^*)} \quad \text{(2)}
\]
$j_{\text{NO}_3}$ 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 $j_{\text{NO}_3}$ values were 0.175 s$^{-1}$ for clear sky at the daily solar maximum. After normalizing, typical values of $j_{\text{NO}_3}$ were 0.110 s$^{-1}$ during daytime.

Using equations 1 & 2 a steady-state predicted NO$_3$ mixing ratio ($\text{NO}_3,\text{SS}$) can be calculated:

$$[\text{NO}_3]_{\text{SS}} = \frac{P(\text{NO}_3)}{\tau(\text{NO}_3)}$$

(NO$_3$$_{\text{SS}}$ can then be used to calculate steady-state predicted N$_2$O$_5$ from the N$_2$O$_5$ equilibrium (Table 1) and measured NO$_2$:

$$[\text{N}_2\text{O}_5]_{\text{SS}} = K_{\text{eq}}[\text{NO}_2][\text{NO}_3]_{\text{SS}}$$

where $K_{\text{eq}}$ is $2.7 \times 10^{-27} \exp(11000/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Sander et al., 2011 see Table 1). Comparison of the predicted N$_2$O$_5$ to the measured N$_2$O$_5$ mixing ratios for the campaign demonstrates that both timing and magnitude of predicted N$_2$O$_5$ peaks match observations (Figure S1). Predicted steady-state N$_2$O$_5$ tracked observations when the latter were available and propagation of the error of calculated N$_2$O$_5$ 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. Correlation of measured N$_2$O$_5$ vs predicted N$_2$O$_5$ shows that during periods of high N$_2$O$_5$, we overestimate the concentration by a factor of two (Figure S1). Furthermore, propagation of error in the NO$_3$,SS calculation (Figure S2b) shows that the error encompasses the measured NO$_3$ during the entire campaign when data was available, showing that predicted NO$_3$,SS is consistent with the lack of detection of NO$_3$ by CRDS.

A substantial fraction (30-45%) of the NO$_x$ budget is comprised of organic nitrates ($\Sigma$ANs $+$ $\Sigma$PNs, Figure S3). Measurements of gas phase and aerosol phase alkyl nitrates show that a substantial fraction of the organic nitrates are in the aerosol phase (30% when aerosol phase AMS is compared to TD-LIF total $\Sigma$ANs vs 80% when comparing aerosol phase $\Sigma$ANs to TD-LIF total $\Sigma$ANs at 5 am CDT) when total $\Sigma$ANs concentration builds up (Figures 2 & 3). The average diurnal cycle shown in Figure 3 also shows that TD-LIF measured $\Sigma$ANs are almost completely in the aerosol phase at night, but only about 50% in the aerosol phase during the day. During peaks in NO$_3$,SS, we see corresponding spikes in the $\Sigma$ANs concentrations as well as organic nitrate concentration from AMS, all of which occur during nighttime periods (Figure 2). This is consistent with organic nitrates formed by NO$_3$ + BVOC rapidly partitioning into the aerosol phase.

BVOC measurements show large mixing ratios of isoprene throughout the entire campaign (daytime peaks above 8 ppb), followed by $\alpha$- and $\beta$-pinene (peak nighttime mixing ratios of 0.5-1 ppb,
Using the measured mixing ratios of VOC, and their reaction rates with NO₃, predicted NO₃ losses are calculated and compared to organic nitrate aerosol. Figure 4 shows the diurnally averaged NO₃ losses for the entire campaign period (June 1 - July 15, 2013). Daytime losses include photolysis and reaction with NO. Approximately half the daytime losses are due to reaction of NO₃ with BVOC (Note, this does not necessarily imply that NO₃ reaction is a substantial loss process from the perspective of BVOC; during the day, P(\text{HO}_x) exceeds P(\text{NO}_3) by a factor of 10-70 at SOAS, so OH will typically dominate.) However, from the standpoint of NO₃ lifetime, previous forest campaigns have assumed NO₃ + monoterpenes reactions to be important only during the night and that photolysis and NO losses were the dominant NO₃ sinks during the day (Geyer et al., 2001; Warneke et al., 2004). In this study, we predict significant losses of NO₃ to isoprene and monoterpenes during daylight hours.

To assess heterogeneous losses of N₂O₅ to particles, an uptake rate coefficient of N₂O₅ into deliquesced aerosols is estimated using PM surface area (S_A, nm²/cm³), the molecular speed of N₂O₅ (\bar{c}, m/s) and the uptake coefficient (\gamma_{N₂O₅}).

\[
k_{\text{het}} = \frac{1}{4} \times \gamma_{N₂O₅} \times \bar{c}_{N₂O₅} \times S_A \tag{5}
\]

Conditions of high relative humidity in the SEUS necessitated a higher \gamma of 0.02 as the uptake coefficient (Bertram and Thornton, 2009; Crowley et al., 2011) which represents an upper limit from previous field studies (Brown et al., 2009, Brown et al., 2006). We predict heterogeneous N₂O₅ uptake to be very small over the campaign despite high relative humidity. When PM$_{2.5}$ concentration was at its highest in mid-July, the calculated uptake rate coefficient was calculated at 1.6 \times 10^{-3} s⁻¹ in mid July, representing less than 1% of the loss of NO₃.

### 3.1.1 Calculation of NO₃ loss to BVOC

Using literature NO₃ + BVOC rate coefficients and calculated NO₃,SS, we calculate instantaneous NO₃ loss rates ((NO₃,loss)$_{\text{inst}}$) for the campaign.

\[
(NO₃,\text{loss})_{\text{inst}} = \sum_i k_{\text{NO₃}+\text{VOC}_i} [\text{VOC}_i][NO₃]_{\text{SS}} \tag{6}
\]

BVOC mixing ratios from GC-MS and rate constants shown in Table 1 were used to calculate the time-integrated nitrate loss to reactions with BVOC.

\[
(NO₃,\text{loss})_{\text{integ}} = \sum_{i,t} (NO₃,\text{loss})_{\text{inst},i} \times \Delta t \tag{7}
\]

Specifically, time loss of NO₃ radical to reaction with BVOC ((NO₃,loss)$_{\text{integ}}$) were calculated during periods of increasing RONO$_2$ concentrations as monitored by CIMS or aerosol phase RONO$_2$ monitored by AMS or TD-LIF during SOAS. 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. The boundary layer during night hours is relatively stable, such that NO\textsubscript{x} and BVOC measurements can be considered an area-wide average and this simple box model can be used to calculate \((\text{NO}_3, \text{loss})_{\text{integ}}\)\textsuperscript{5,7,8}.

Under the assumption of a constant nighttime boundary layer height and an approximately uniform, area wide source that limits the time rate of change due to horizontal advection (i.e., a nighttime box), the time integrals of RONO\textsubscript{2} produced provide estimates of the evolution of RONO\textsubscript{2} concentrations at night (this assumption was verified using CO to minimize first order effects of dilution from changes in the boundary layer \cite{Blanchard11}). Time periods of CIMS RONO\textsubscript{2} or aerosol buildup were chosen to determine time intervals for calculation of \((\text{NO}_3, \text{loss})_{\text{integ}}\) when data was available.

\((\text{NO}_3, \text{loss})_{\text{integ}}\) is the calculated time integral of the reaction products of NO\textsubscript{3} with individual or combined mixing ratios of BVOC and \(\Delta t\) is the time step between each calculated value of \((\text{NO}_3, \text{loss})_{\text{inst},i}\). Data are averaged to 30 minute increments, a time step sufficient to resolve the observed rate of change. Figure 5 shows an example of the resulting calculated integrated NO\textsubscript{3} losses from \cite{7} to both isoprene and summed monoterpenes. These nightly loss values are correlated with organic nitrate gas- and aerosol-phase measurements and linear fits and correlation coefficients were calculated to aid in the interpretation of gas- and aerosol-phase organic nitrate formation. Note that these peak times occur during nighttime hours when the boundary layer is shallow (Figure S5).

### 3.1.2 Implied organic nitrate and SOA yields

The correlation slopes in Figure 6 are in ppb\textsubscript{aerosol}/ppb\textsubscript{\((\text{NO}_3, \text{loss})_{\text{integ}}\)} and indicate the average molar organic nitrate aerosol yield. The AMS and TD-LIF measurements of aerosol phase organic nitrates suggest a molar yield of 23 and 44%, respectively (Figure 6). This calculation uses all available data from each instrument and assumes no other processes are taking place. We note that without knowledge of the average molecular weight of the aerosol organic nitrate, only molar yield estimates are possible. Several chamber studies have measured organic nitrate yields from NO\textsubscript{3} oxidation of individual terpenes: Spittler et al. \cite{2006} and Fry et al. \cite{2014} both found 10-15% total organic nitrate (ON) yield for \(\alpha\)-pinene (entirely in the gas phase); Fry et al. \cite{2009} found 45% total ON yield for \(\beta\)-pinene under humid conditions, Fry et al. \cite{2014} found 22% under dry conditions, and Boyd et al. \cite{2015} found aerosol organic nitrate to comprise 45-74% of OA produced from NO\textsubscript{3} + \(\beta\)-pinene; and Fry et al. \cite{2011} found 30% total ON yield while Fry et al. \cite{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\textsubscript{3} losses to monoterpenes.

To derive an estimated 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\textsubscript{3} with monoterpenes (MW = 136 g mol\textsuperscript{-1}) and estimating the average molecular weight (250 g mol\textsuperscript{-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 a limonene SOA yield of 25-57%. Because the actual average molecular weight of the condensing species is unknown (we do not include sesquiterpene oxidation products and higher molecular weight BVOC products as reported by Lee et al. (2015), with which we would calculate larger SOA mass yields), 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.

Since nitrate product buildup occurs over multiple hours (Figure 5), the rapid particulate organic nitrate losses (timescale of 2-4 hours) found by researchers at the University of Washington are a lower limit. 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). Because understanding of these nitrate loss processes is poor, a quantitative estimate of how this would affect derived molar yields would be premature.

Finally, because this yield is based on total ambient monoterpene concentrations, it incorporates nitrate radical loss to α-pinene, which is known to produce very modest yields of SOA (0-10%) from NO$_3$ reaction (Fry et al., 2014; Spittler et al., 2006). This suggests effective overall SOA yields from other BVOC must be large.

### 3.1.3 Organic Nitrate Product Analysis

Observations of NO$_3$,SS compared to TD-LIF and AMS (Figure 2) suggest aerosol organic nitrates are dominated by nighttime NO$_3$ + BVOC, rather than other known nitrate-producing reactions (e.g. RO$_2$ + NO), which would dominate during the daytime and would not coincide with peaks in [NO$_3$].

Researchers at University of Washington describe the observation of particle phase C$_{10}$ organic nitrate concentrations peaking at night during SOAS (Lee et al. 2015), consistent with high SOA yield from NO$_3$ + monoterpenes. Observed C$_{10}$ organic nitrates include many highly oxidized molecules, suggesting that substantial additional oxidation beyond the first-generation hydroxynitrates occurs (Lee et al. 2015). Specific first generation monoterpene organic nitrate compounds were identified and measured in the gas- and aerosol-phases (Lopez-Hilfiker et al., 2014; Beaver et al., 2017). Using the (NO$_3$,loss)$_{integ}$ calculations, another correlation analysis is conducted to identify key gas- and aerosol-phase products of NO$_3$ oxidation. Observed buildups in gas- and aerosol-phase organic
nitrate concentrations from each CIMS are scattered against predicted \((\text{NO}_3,\text{loss})_{\text{integ}}\) to monoterpenes (Figure 7). The generally good correlations suggest that all of the molecular formulae shown here have contributions from NO3 oxidation. Comparisons of observed \(R^2\) values and slopes for each of these correlation plots may then provide some mechanistic insight. For example, the species with larger \(R^2\) (\(C_{10}H_{17}NO_5\)) may indicate a greater contribution to these species from NO3 radical chemistry. If we assume the same sensitivity across phases in the cases where the same species is observed (Figure 7a/b and d/e), we can estimate the relative amount in each phase by the ratio of the slopes. This would suggest that \(C_{10}H_{15}NO_5\) partitions more to the particle phase than \(C_{10}H_{17}NO_5\).

Although the gas phase monoterpenes nitrate product correlations display substantial scatter, likely due to their multiple possible sources and rapid partitioning to the aerosol phase, we can use the calibrated mixing ratios measured by the CIT-CIMS to calculate approximate lower limit molar yields for \(C_{10}H_{15}NO_5\) (0.4%), \(C_{10}H_{17}NO_5\) (3%), and \(C_{10}H_{17}NO_4\) (3%) from NO3, based on the slope of correlations shown in panels c, f and h. We estimate these to be lower limits, because no losses of these species during the period of buildup is taken into account in this correlation analysis. The median particulate fraction of \(C_5H_9NO_5\) (particle phase/total) observed by the UW-CIMS was less than 1%, and \(C_5H_9NO_4(p)\) 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 NO3 + 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 NO3 loss again provides evidence about the oxidative sources of these molecules (Figure 8). \(C_5H_9NO_5\) (panels a and b) shows the strongest correlation with \((\text{NO}_3,\text{loss})_{\text{integ}}\) 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 NO3 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 \(C_4H_9NO_5\) isoprene products (panels c and d) show poorer correlation with \((\text{NO}_3,\text{loss})_{\text{integ}}\) to isoprene (\(R^2 = 0.11\) and 0.35, respectively), suggesting that these products are not (exclusively) a NO3 + isoprene product, and may instead be a photochemically or ozonolysis produced organic nitrate, via \(\text{RO}_2 + \text{NO}\).

We note that the two CIMS for which data is shown in Figures 7 and 8 were located at different heights: the CIT-CIMS was atop the 20 meter tower, collocated with the measurements used to determine \([\text{NO}_3]_{\text{integ}}\), while the UW-CIMS measured at ground level. Particularly at nighttime, it is possible that this lower 20 meters of the nocturnal surface layer can become stratified, so some scatter and differences in correlations between instruments arising from this occasional stratification are not unexpected.
3.2 Comparison to Inorganic \(\text{NO}_x\) sink: \(\text{NO}_3^-\) aerosol production from heterogeneous uptake of \(\text{HNO}_3\)

Partitioning of semivolatile ammonium nitrate into aerosol represented a small fraction of aerosol contribution throughout the campaign based on AMS and MARGA data \(\text{Allen et al.} [2015]\). A more important route of \(\text{NO}_x\) conversion to nitrate aerosol occurred via \(\text{HNO}_3\) heterogeneous reaction on the surface of dust or sea salt particles (Scheme 1). This process, which was observed to be especially important during periods of high mineral or sea salt supermicron aerosol concentrations, is described in detail in a companion paper \(\text{Allen et al.} [2015]\). Briefly, we observe that while concentrations of organic and inorganic nitrate aerosol are generally comparable (Figure S3 and Figure 3), the inorganic nitrate is more episodic in nature. Periods of highest \(\text{NO}_3^-\) concentration as measured by the MARGA were observed during two multi-day coarse-mode dust events, from June 9 to 15 and June 23 to 30, while organic nitrates have a more regular diurnal pattern indicative of production from locally-available reactants, with most of the organic nitrate present in the condensed phase (Figure 3).

In order to estimate the fluxes of \(\text{NO}_x\) loss to aerosol via the two pathways shown in Scheme 1, we calculate the reactive losses of \(\text{NO}_2\) to organic nitrate (limiting rate is taken to be \(\sum k_i [\text{NO}_3^-][\text{BVOC}]_i\), with the included terpenes \(\alpha\)-pinene, \(\beta\)-pinene, limonene and camphene) and to inorganic nitrate via heterogeneous \(\text{HNO}_3\) uptake \(\text{Allen et al.} [2015]\). A substantial fraction of the surface area is in the transition regime, so \(\text{HNO}_3\) uptake is reduced due to diffusion limitations. To account for this, a Fuchs-Sutugin correction is applied \(\text{Seinfeld and Pandis} [2006]\):

\[
\text{Rate} = \frac{\sum R_p S_a}{R_p} D_g \left( \frac{0.75\alpha(1 + Kn)}{Kn^2 + Kn + 0.283Kn\alpha + 0.75\alpha} \right) [\text{HNO}_3] \tag{8}
\]

with \(S_a\) is surface area, \(R_p\) is the radius, \(D_g\) is the diffusivity of \(\text{HNO}_3\) in air \((0.118 \text{ cm}^2 \text{ s}^{-1})\) and \(\alpha\) is estimated at 0.1 for an upper limit.

Since we have seen that the organic nitrates are present predominantly in the condensed phase, we take this comparison to be the relative rate of production of organic nitrate aerosol vs. inorganic nitrate aerosol (Figure 9), and we see that over the summer campaign, the rates are comparable in magnitude, but peak at different times. This analysis suggests that substantial nitrate aerosol (peak values of 1 \(\mu\text{g m}^{-3}\text{hr}^{-1}\), with average rates 0.1 \(\mu\text{g m}^{-3}\text{hr}^{-1}\) for both inorganic and organic nitrate rates) is produced in the SEUS by both inorganic and organic routes (depicted in Scheme 1), converting local \(\text{NO}_x\) pollution to particulate matter. We note that this calculation accounts only for the production rates of these two types of nitrate aerosol and does not account for subsequent chemistry that may deplete one faster than the other; hence, relative mass concentrations are not necessarily expected to correlate directly to these relative production rates.
3.3 Implications of NO$_3$ oxidation on SOA formation in the SEUS

The importance of the NO$_3$ + BVOC reaction SOA has only recently been recognized (Beaver et al., 2012; Fry et al., 2013; Rollins et al., 2012; Pye et al., 2010) showed that including NO$_3$ radical oxidation increased predicted SOA yields from terpenes by 100% and total aerosol concentrations by 30% (Pye et al., 2010). The results of this study underscore the importance of NO$_3$ in SOA formation. Measured aerosol organic nitrate concentrations are correlated with the reaction of NO$_3$ with BVOC. This pathway is especially important before sunrise when competing oxidants (O$_3$ and OH) are at a minimum.

We can estimate the contribution of this NO$_3$ + BVOC mechanism to total particulate matter using the 2011 NEI data for the states included in the 2004 Southern Appalachian Mountain Initiative study (SAMI, Odman et al., 2004): Kentucky, Virginia, West Virginia, North Carolina, South Carolina, Tennessee, Alabama and Georgia (http://www.epa.gov/ttn/chief/net/2011inventory.html). In this 8-state region, the NEI reported emissions of 2.3 Tg yr$^{-1}$ ($2.5 \times 10^6$ tons yr$^{-1}$) of nitrogen oxides and 0.8 Tg yr$^{-1}$ ($9 \times 10^5$ tons yr$^{-1}$) of PM$_{2.5}$ in 2011. We can estimate the fraction of the NO$_x$ emitted that is converted to PM using several assumptions. NO$_2$ is estimated to contribute 50% of the NO$_x$ budget (Figure S3), so we multiply the NO$_x$ emission by 0.5 to account for half of the instantaneous NO$_x$ residing in the atmosphere as other NO$_x$ species at any given time. An average lifetime of 16 hours for O$_3$ + NO$_2$ reaction was calculated ($1/k(O_3)$) and, with an average nighttime length of 9 hours, we estimate about 55% of NO$_2$ is converted to NO$_3$ overnight. Using the average molar organic nitrate aerosol yield of 30% determined in this study and an estimated molecular weight of 250 g mol$^{-1}$ for oxidized product (terpene hydoxynitrate with two additional oxygen functional groups, Draper et al., 2015), we convert from molar yield to mass yield of organic nitrate aerosol. This assumes that NO$_x$ is the limiting reagent for SOA production from this chemistry; as noted in the introduction, comparison of regional NO$_x$ and BVOC emissions rates supports this assumption. Finally, using the summed NEI NO$_x$ emissions data for the SAMI states, we calculate a source estimate of 0.6 Tg yr$^{-1}$ of NO$_3$-oxidized aerosol. Adding this to the NEI primary PM$_{2.5}$ emissions estimate of 0.8 Tg yr$^{-1}$ gives a total 1.4 Tg yr$^{-1}$, showing that NO$_3$ initiated SOA formation would contribute a substantial additional source of PM$_{2.5}$ regionally, nearly doubling primary emissions. Model calculations by Odman et al. (2004) for the SAMI states estimated 1 Tg yr$^{-1}$ of total PM$_{2.5}$ in 2010, including primary and secondary sources. Their modeled PM$_{2.5}$ emissions are lower than our rough estimate here, despite the fact that actual 2010 NO$_x$ emissions were 2.3 Tg yr$^{-1}$ rather than the 3 Tg yr$^{-1}$ projected at that time. Hence, despite successful reduction of regional NO$_x$ emissions (Blanchard et al., 2013), this work suggests that secondary PM$_{2.5}$ production from NO$_3$ oxidation of regionally abundant BVOCs remains a substantial anthropogenic source of pollution in the SEUS.
4 Conclusions

The contribution of NO₃ + BVOC to SOA formation is found to be substantial in the terpene-rich SEUS. An estimated 23-44% of nitrate radical lost to reaction with monoterpenes becomes aerosol phase organic nitrate. Predicted nitrate losses to isoprene and to monoterpenes are calculated from the steady-state nitrate and BVOC mixing ratios and then time integrated during evenings and nights as RONO₂ aerosol builds up. Correlation plots of AMS, TD-LIF, and CIMS measurements of gas- and aerosol-phase organic nitrates against predicted nitrate losses to monoterpenes indicate that NO₃ + monoterpenes contribute substantially to observed nitrate aerosol. Two specific C₁₀ structures measured by CIMS are shown to be NO₃ radical products by their good correlation with cumulative (NO₃,loss)_{integ}; their semi-volatile nature leads to their variable partitioning between gas- and aerosol-phase. Calibrated gas phase mixing ratios of selected organic nitrates allow estimation of lower limit molar yields of C₅H₉NO₅, C₁₀H₁₇NO₄, C₁₀H₁₇NO₅ from NO₃ reactions (7%, 3%, and 3% respectively). The fact that these molar yields of monoterpane nitrates are substantially lower that the aggregated aerosol phase organic nitrate yield may suggest that further chemical evolution is responsible for the large SOA yields from these reactions, consistent with Lee et al. [2015]. The NO₃ + BVOC source of nitrate aerosol is comparable in magnitude to inorganic nitrate aerosol formation, and is observed to be a substantial contribution to regional PM₂·₅.

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Table 1. NO$_3$ kinetic rate constants and equilibrium constants used to determine losses.

| Reaction                          | A          | E$_a$/R* | B** | k(298 K) | Source                  |
|----------------------------------|------------|----------|------|----------|-------------------------|
| O$_3$ + NO$_2$ → O$_2$ + NO$_3$  | $1.2 \times 10^{-13}$ | 2450     |      |          | Sander et al. (2011)    |
| NO$_3$ + NO$_2$ ⇌ N$_2$O$_5$      | $2.7 \times 10^{-27}$ | 11000    |      |          | Sander et al. (2011)    |
| NO + NO$_3$ → 2NO$_2$             | $1.5 \times 10^{-11}$ | -170     |      |          | Sander et al. (2011)    |
| Isoprene + NO$_3$ → Products      | $3.03 \times 10^{-12}$ | 446      |      |          | Calvert et al. (2000)   |
| α-pinene + NO$_3$ → Products      | $1.19 \times 10^{-12}$ | -490     |      |          | Calvert et al. (2000)   |
| β-pinene + NO$_3$ → Products      | $2.51 \times 10^{-12}$ |          |      |          | Calvert et al. (2000)   |
| Camphene + NO$_3$ → Products      | $6.6 \times 10^{-13}$ |          |      |          | Calvert et al. (2000)   |
| Myrcene + NO$_3$ → Products       | $1.1 \times 10^{-11}$ |          |      |          | Calvert et al. (2000)   |
| Limonene + NO$_3$ → Products      | $1.22 \times 10^{-11}$ |          |      |          | Calvert et al. (2000)   |

* Reaction rate constants are reported as: k(T) = A $e^{-(E_a/R)/T}$, in units of (cm$^3$ molecule$^{-1}$ s$^{-1}$)

** Equilibrium constants are reported as: K$_{eq}$ = A $e^{B/T}$, in units of (cm$^3$ molecule$^{-1}$)
Scheme 1 Generalized reaction fate for NO₂ in the troposphere. Oxidation of NO₂ from atmospheric oxidants leads to two possible paths.
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 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.

Figure 3. Diurnally averaged organic and inorganic nitrates show organic nitrates peaking in the early morning and inorganic nitrates peaking midday. Note the AMS had a PM$_{1}$ size-cut, while MARGA and TD-LIF had a PM$_{2.5}$ size-cut. See text and supplemental information for more details on this comparison.
Figure 4. Average diurnal profile of NO₃/N₂O₅ losses June 1 - July 15, 2013. NO and photolysis losses peak during the daytime (in fact, nighttime NO₃ + 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 & N₂O₅ data are from CRD, and photolysis losses are calculated as described in Section 3.1. Uncertainties in rate constants of BVOC + NO₃ range from 2% for myrcene to - 40% for β-pinene (Calvert et al., 2000). Uncertainties in rate constants of BVOC + NO₃ 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 5. Sample calculation of \( \langle \text{NO}_3, \text{loss} \rangle \text{integ} \) overlaid against aerosol RONO₂ measured by AMS (red). The monoterpenes maxima correlate well with the AMS maxima (black dots). Minima and maxima (black dots) were chosen for the beginning and end of AMS buildup periods, respectively. The time period shown is arbitrarily chosen.
Figure 6. Scatter plots of aerosol RONO$_2$ (AMS & TD-LIF) compared to (NO$_3$,loss)$_{cum}$. The magnitudes of the two particle phase organic nitrate measurements differ by a factor of ≈ 2-4 for unknown reasons, however the slope can be used as a relative molar yield of NO$_3$ loss to monoterpenes. Time period for AMS comparison is June 9 - July 15, 2013 and for TD-LIF is June 27 - July 15, 2013.
Figure 7. Scatter plots of selected molecules’ concentration buildups against time-integrated monoterpane losses to NO₃ radical, during periods of observed organic nitrate buildup measured by CIMS. Panels a & d show particle phase C₁₀H₁₅NO₅ and C₁₀H₁₇NO₅ measured by the UW FIGAERO; b & e show gas phase C₁₀H₁₅NO₅ and C₁₀H₁₇NO₅ 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 C₁₀H₁₇NO₄ 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: C₁₀H₁₅NO₅, 0.4%; C₁₀H₁₇NO₅, 3%; and C₁₀H₁₇NO₄, 3%.
Figure 8. Gas phase CIMS data correlated to predicted isoprene + NO₃, during periods of buildup of these C₅ and C₄ nitrates as measured by each CIMS. Panels a & b show C₅H₉NO₅, which is well correlated to predicted isoprene + NO₃ suggesting this is a NO₃ 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 C₅H₉NO₄ is poorly correlated to isoprene + NO₃ suggesting that this product comes (at least in part) from another oxidative source (e.g. RO₂+NO). Panel d, C₄H₇NO₅, also shows a poorer correlation than panels a & b, suggesting it is not exclusively a product of NO₃ oxidation, or has rapid losses.

Figure 9. Over the campaign, similar magnitudes of the rate of formation of organic and inorganic nitrate aerosol (according to the pathways shown in Scheme 1) are observed, though peaks occur at different times.
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