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 (BVOCs) and organic nitrates made during the Southern Oxidant and Aerosol Study (SOAS campaign, Summer 2013) in central Alabama show that a nitrate radical (NO$_3$) reaction with monoterpenes leads to significant secondary aerosol formation. Cumulative losses of NO$_3$ to terpenes are correlated with increases in gas- and aerosol-organic nitrate concentrations made during the campaign. Correlation of NO$_3$ 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 to predicted nitrate loss to BVOCs and show C$_{10}$H$_{17}$NO$_5$, likely a hydroperoxy nitrate, as a major nitrate-oxidized terpene product being incorporated into aerosols. The comparable isoprene product C$_5$H$_9$NO$_5$ 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 between 30 and 45% of the NO$_3$ budget during SOAS. Inorganic nitrates were also monitored and showed that during incidents of increased coarse-mode mineral dust, HNO$_3$ uptake produced nitrate aerosol mass loading at a rate comparable to that of organic nitrate produced via NO$_3$ + BVOCs.

1 Introduction

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 (Bellouin et al., 2011; Feng and Penner, 2007; Goldstein et al., 2009; Myhre et al., 2013). 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 (BVOCs) 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 BVOCs 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 (NOx = NO + NO2), 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, NOy, consists of NOx as well as NO2 reaction products, including NO3, HNO3, HONO, alkyl nitrates, peroxynitrates and all particular organic nitrates. Alkyl nitrates produced from oxidation of VOCs 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 NOx to nitric acid (HNO3) can also produce inorganic nitrate aerosol via heterogeneous uptake of NO3 onto mineral or sea salt aerosols (Vlasenko et al., 2006) and via co-partitioning with ammonia to form semi-volatile NH4NO3 (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 NO2 and further to the highly reactive NO3 radical. NO3 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 NO3 and the associated N2O5 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 N2O5 to HNO3 can be important in the prediction of the tropospheric oxidant burden with respect to the O3 production, and therefore OH radical production (Dentener and Crutzen, 1993; Evans and Jacob, 2005). However, previous studies in eastern Texas have found N2O5 uptake into aerosols to be relatively low in the southern United States (TexAQS average γ of 0.003) (Brown et al., 2009; Riemer et al., 2009).

NO3 is an effective nocturnal oxidizer of VOCs (Atkinson and Arey, 2003, 1998; Calogirou et al., 1999; Winer et al., 1984). NO3 oxidation is especially reactive towards unsaturated, non-aromatic hydrocarbons of which BVOCs are major global constituents. NO3 is less reactive towards aromatic compounds and saturated hydrocarbons, which are major compounds of anthropogenic VOCs. Nitrate oxidation of some BVOCs, such as β-pinene and limonene, 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., 2009, 2011; Boyd et al., 2015). Analysis of previous field studies have characterized the loss of NO3 to its major daytime sinks, including reaction with NO and photolysis, as well as its loss to BVOCs during both daytime and nighttime (Aldener et al., 2006; Brown et al., 2005).

Nitrogen-containing oxidation products include alkyl nitrates (RONO2), peroxynitrates (RO2NO2) and nitric acid (HNO3) (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., HNO3) can be quantified using ion chromatography (IC; Makkonen et al., 2012; Trebs et al., 2004) as well as chemical ionization mass spectrometry (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 (NO3) 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 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 aerosol mass spectrometry 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 SEUS and contributes 18–36% of summertime OA (Hu et al., 2015; Xu et al., 2015a). LO-OOA is seen predominantly during nighttime hours, implying NO3 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. Xu et al. (2015b) estimated that the total particle-phase organic nitrates contribute 5–12% of total OA in the southeastern US in summer.

In this paper, we use the initial products (ex. C10H17NO5), as well as total aerosol-phase organic nitrates, to track NO3 radical contributions to SOA formation during Southern Oxidant and Aerosol Study (SOAS). We analyze the role of NO3 oxidation of BVOCs both at night and during the day. Nitrate sinks have been determined for measured BVOCs and correlations of observed alkyl nitrate products versus these calculated loss rates are discussed.
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Figure 1. Map of Alabama with SO\textsubscript{2} and NO\textsubscript{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 in square-root tons per day, and only sources above 50 square-root tons per day are shown. For reference, the Alabama Power Company Gaston Plant emits 19.52 kg h\textsuperscript{-1} SO\textsubscript{2} and 6.43 kg h\textsuperscript{-1} NO\textsubscript{x}.

The 2013 SOAS campaign was a comprehensive field intensive study in central Alabama near Centreville (CTR), in which concentrations of oxidants, BVOCs 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 (Fig. 1). County-level monoterpane emissions across the US shows the CTR site gives a regional representation of monoterpane emissions in the SEUS (Geron et al., 2000). Furthermore, Xu et al. (2015b) showed 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 eight-state region including the CTR site) of BVOCs (estimated from Geron et al., 2000) to NO\textsubscript{x} emissions (from 2011 NEI database) suggests that NO\textsubscript{x} is the limiting reagent in NO\textsubscript{x}-driven BVOCs oxidation throughout the region and demonstrates that the CTR site is regionally representative.

Alabama is home to a number of power plant facilities that are a large point sources of NO\textsubscript{x} capable of being carried long distances. Alabama’s non-interstate roadways also have large emissions of NO\textsubscript{x}, though a majority of the emissions come from urban areas. Although the NO\textsubscript{x} 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 NO\textsubscript{x} emissions and PM concentrations (a full analysis of contributions can be found at the EPA National Emissions Inventory, http://www.epa.gov/tnn/chieft/net/2011inventory.html).

In the present study, we investigate the production of SOA species from NO\textsubscript{3} reaction with monoterpenes. NO\textsubscript{3} loss to BVOCs is calculated and compared to aerosol mass spectrometry (AMS), chemical ion mass spectrometry (CIMS), and thermal dissociation laser-induced fluorescence (TD-LIF) measurements of aerosol-organic nitrates. We compare this to an alternate fate of NO\textsubscript{x}, heterogeneous HNO\textsubscript{3} uptake to produce inorganic nitrate aerosol, which is considered in detail in a second paper (Allen et al., 2015). Both pathways from NO\textsubscript{x} to nitrate aerosol shown in Scheme 1 are produced at various times in the SEUS.

Scheme 1. Generalized reaction fate for NO\textsubscript{3} in the troposphere. Oxidation of NO\textsubscript{2} from atmospheric oxidants leads to two possible paths.

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 1 June–15 July 2013. The forest covers 157 000 acres to the northwest and southeast of Centreville, AL. Figure 1 shows a map of the site location as well as nearby point sources of anthropogenic NO\textsubscript{x} and SO\textsubscript{2}. 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 NO\textsubscript{x} emission point sources are the
Alabama Power Company Gaston Plant located near Birming-
ham and the Green County Power Plant southwest of
Tuscaloosa (EPA Air Markets Program 2013).

Two cavity ringdown spectrometers (CRDSs) were used to
determine ambient mixing ratios of NO\(_x\), O\(_3\), NO\(_y\), NO\(_3\) and
N\(_2\)O\(_3\) (Wild et al., 2014; Wagner et al., 2011). A CRDS is a
high sensitivity optical absorption method based on the de-
cay time constant for light from an optical cavity composed
of two high reflectivity mirrors. NO\(_2\) is measured using its
optical absorption at 405 nm in one channel, and O\(_3\), NO,
and total NO\(_x\) are quantitatively converted to NO\(_2\) and mea-
sured simultaneously by 405 nm absorption on three addi-
tional channels. NO\(_3\) is measured at its characteristic strong
absorption band at 662 nm. N\(_2\)O\(_3\) 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, 2\(\sigma\))
for NO\(_3\) and 1.2 pptv (30 s, 2\(\sigma\)) for N\(_2\)O\(_3\) (Dubé et al., 2006;
Wagner et al., 2011).

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 (ΣEPNs) and aerosol-
phase ΣANs (Rollins et al., 2012). A high-resolution time-
of-flight aerosol mass spectrometry (HR-ToF-AMS, here-
after 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 sepa-
ration method described in Fry et al. (2013). Organic ni-
trates in the particle phase (\(p\)RONO\(_2\)) decompose prior to
ionization on the AMS vaporizer to NO\(_3\)\(^+\) organic fragments;
hence, \(p\)RONO\(_2\) cannot be quantified directly from AMS
data. The contribution of \(p\)RONO\(_2\) to total particulate ni-
trate was calculated using the method first discussed in Fry
et al. (2013) and briefly summarized here. This method re-
does on the different fragmentation patterns observed in the
AMS for organic nitrates vs. NH\(_4\)NO\(_3\), specifically the ra-
tio of the ions NO\(_3\)\(^+\) to NO\(^+\). Since this ratio depends on
mass spectrometer tuning, vaporizer settings, and history, Fry
et al. (2013) 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 infield calibrations of the instru-
ment). Using such normalized ratios, most field and cham-
ber observations of pure organic nitrates are consistent with
(NO\(_3\)\(^+\)/NO\(^+\))/(NO\(_3\)\(^+\)/NO\(^+\))\(_{ref}\) of 1/2.25 (Farmer et al.,
2010) to 1/3 (Fry et al., 2009) of the calibration ratio. Xu
et al. (2015b) also used this method for the SEUS and dis-
cussed the estimated uncertainties. The data reported here
were calculated using the 1/2.25 ratio derived from Farmer
et al. (2010) and used in Fry et al. (2013), interpolating lin-
early 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\(_2\) \(p\)RONO\(_2\) can be re-
ported 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 magni-
tudes differ by a factor of approximately 2–4 for unknown
reasons, with TD-LIF being larger than AMS (see Supple-
ment).

Two chemical ionization mass spectrometers (Caltech’s
cTOF-CIMS and University’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
monoterpenes (Eddingsaas et al., 2012) and isoprene prod-
tections (Crounse et al., 2013, 2006; Beavere 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 sepa-
rate 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 nomi-
nal \(m/z\).

An online cryostat-Gas Chromatography-Mass Spectrom-
eter (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, \(\alpha\)-pinene, \(\beta\)-pinene, and limonene (Fig. S1 in the
Supplement; Stroud et al., 2002; Goldan et al., 1995). Surface
area concentration was calculated from number distri-
bution measurements of a hygroscopicity scanning mobil-
ity 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 the method employs a photon count-
ing of back-scattered pulse of near-IR light (1064 nm) via li-
dar principle. 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 com-
bines a wet-rotating denuder/steam jet aerosol collector in-
let with positive and negative ion chromatograph, measured in-
organic ion concentrations at a 1 h 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 lo-
cated in a field ~90 m south of the tower. The tower in-
struments used for this analysis consisted of the two CRDSs,
CIT-CIMS, TD-LIF, and a cryostat GC-MS. The field trail-
ers contained the AMS, SMPS, APS (aerodynamic particle
sizer), UW-CIMS, and MARGA.
the entire campaign. Calculated steady-state N\(_2\)O reaction with biogenic alkenes forms organic nitrates (Reaction R1).

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

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

\[
P(\text{NO}_3) = k_{\text{O}_3 + \text{NO}_2}[\text{O}_3][\text{NO}_2]. \tag{1}
\]

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

\[
\tau(\text{NO}_3) = \frac{1}{\sum_i k_{\text{NO}_3 + \text{BVOC}}[\text{BVOC}]_i + k_{\text{NO}_3 + \text{NO}}[\text{NO}] + j_{\text{NO}_3}}.
\tag{2}
\]

\(j_{\text{NO}_3}\) values were calculated from solar zenith angles and \(\text{NO}_3\) 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 Eqs. (1) and (2), a steady-state predicted \(\text{NO}_3\) mixing ratio \([\text{NO}_3]\) can be calculated:

\[
[\text{NO}_3]_{\text{SS}} = \frac{P(\text{NO}_3)}{\tau(\text{NO}_3)}. \tag{3}
\]

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

\[
[\text{N}_2\text{O}_5]_{\text{SS}} = K_{\text{eq}}[\text{NO}_2][\text{NO}_3]_{\text{SS}}. \tag{4}
\]

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 \(\text{N}_2\text{O}_5\) to the measured \(\text{N}_2\text{O}_5\) mixing ratios for the campaign demonstrates that both timing and magnitude of predicted \(\text{N}_2\text{O}_5\) peaks match observations (Fig. S2). Predicted steady-state \(\text{N}_2\text{O}_5\) tracked observations when the latter were available, and propagation of the error of calculated \(\text{N}_2\text{O}_5\) shows peak measured values fall within uncertainty bounds of the predicted (Fig. S3a); therefore, \(\text{NO}_3\) is hereafter used as the best estimate of \(\text{NO}_3\) to calculate production rates of BVOC nitrate products. \(\text{NO}_3\) peaks at 1.4 ppt ± 0.4 ppt. Propagation of errors in rate constants in the \(\text{NO}_3\) calculation (Fig. S3a) shows that the error spans or is close to a mixing ratio of 0 for \(\text{NO}_3\) during the entire campaign when data were available. Correlation of measured \(\text{N}_2\text{O}_5\) vs. predicted \(\text{N}_2\text{O}_5\) shows that during periods of high \(\text{N}_2\text{O}_5\), we overestimate the concentration by a factor of 2 (Fig. S2). Furthermore, propagation of error in the \(\text{NO}_3\) calculation (Fig. S3b) shows that the error encompasses the measured \(\text{NO}_3\) during the entire campaign when data were available, showing that predicted \(\text{NO}_3\) is consistent with the lack of detection of \(\text{NO}_3\) by CRDSs.

### Table 1. \(\text{NO}_3\) kinetic rate constants and equilibrium constants used to determine losses.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A</th>
<th>E/R(^a)</th>
<th>B(^b)</th>
<th>(k(298 \text{ K}))</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{O}_3 + \text{NO}_2 \rightarrow \text{O}_2 + \text{NO}_3)</td>
<td>(1.2 \times 10^{-13})</td>
<td>2450</td>
<td></td>
<td></td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>(\text{NO}_3 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_3)</td>
<td>(2.7 \times 10^{-27})</td>
<td>11 000</td>
<td></td>
<td></td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>(\text{NO} + \text{NO}_3 \rightarrow 2\text{NO}_2)</td>
<td>(1.5 \times 10^{-11})</td>
<td></td>
<td>-170</td>
<td></td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>Isoprene + (\text{NO}_3) → Products</td>
<td>(3.03 \times 10^{-12})</td>
<td>446</td>
<td></td>
<td></td>
<td>Calvert et al. (2000)</td>
</tr>
<tr>
<td>(\alpha)-pinene + (\text{NO}_3) → Products</td>
<td>(1.19 \times 10^{-12})</td>
<td></td>
<td>-490</td>
<td></td>
<td>Calvert et al. (2000)</td>
</tr>
<tr>
<td>(\beta)-pinene + (\text{NO}_3) → Products</td>
<td>(2.51 \times 10^{-12})</td>
<td></td>
<td></td>
<td></td>
<td>Calvert et al. (2000)</td>
</tr>
<tr>
<td>Camphene + (\text{NO}_3) → Products</td>
<td>(6.6 \times 10^{-13})</td>
<td></td>
<td></td>
<td></td>
<td>Calvert et al. (2000)</td>
</tr>
<tr>
<td>Myrcene + (\text{NO}_3) → Products</td>
<td>(1.1 \times 10^{-11})</td>
<td></td>
<td></td>
<td></td>
<td>Calvert et al. (2000)</td>
</tr>
<tr>
<td>Limonene + (\text{NO}_3) → Products</td>
<td>(1.22 \times 10^{-11})</td>
<td></td>
<td></td>
<td></td>
<td>Calvert et al. (2000)</td>
</tr>
</tbody>
</table>

\(^a\) Reaction rate constants are reported as \(k(T) = Ae^{-(E_a/R)/T}\), in units of (cm\(^3\) molecule\(^{-1}\) s\(^{-1}\))

\(^b\) Equilibrium constants are reported as \(K_{\text{eq}} = Ae^{B/T}\), in units of (cm\(^3\) molecule\(^{-1}\))
A substantial fraction (30–45 %) of the NO3 budget is comprised of organic nitrates (ΣAN + ΣPN; Fig. S4). 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 ΣANs vs. 80 % when comparing aerosol-phase ΣANs to TD-LIF total ΣANs at 17:00 CDT – Central Daylight Time) when total ΣAN concentration builds up (Figs. 2 and 3). The average diurnal cycle shown in Fig. 3 also shows that TD-LIF measured ΣANs are almost completely in the aerosol phase at night, but only about 50 % in the aerosol phase during the day. During peaks in NO3, we see corresponding spikes in the ΣAN concentrations as well as organic nitrates formed by NO3 + BVOCs rapidly partitioning into the aerosol phase.

Figure 2. Nitrate radical concentration estimated by the steady-state approximation (red trace) shows several instances where peaks in NO3 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 are 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 PM1 size cut, while MARGA and TD-LIF had a PM2.5 size cut. See text and Supplement for more details on this comparison.

Figure 4. Average diurnal profile of NO3/N2O5 losses 1 June–15 July 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 and N2O5 data are from CRDSs, and photolysis losses are calculated as described in Sect. 3.1. Uncertainties in rate constants of BVOCs + NO3 range from 2 % for myrcene to ~40 % for β-pinene (Calvert et al., 2000). Uncertainties in rate constants of BVOCs + NO3 range from ±30 % for α-pinene to up to a factor of 2 for isoprene (Calvert et al., 2000); NO measurements had ±35 % uncertainty, BVOC measurements ±20 %, and photolysis ±20 % based on solar radiation measurement uncertainty.
speed of N$_2$O$_5$ ($\bar{c}$, m s$^{-1}$), and the uptake coefficient ($\gamma N_2O_5$).

\[ k_{\text{het}} = \frac{1}{4} \times \gamma N_2O_5 \times \bar{c}N_2O_5 \times S_A \]  

(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, 2006). We predict heterogeneous N$_2$O$_5$ 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 NO$_3$.

### 3.1.1 Calculation of NO$_3$ loss to BVOCs

Using literature NO$_3$ + BVOC rate coefficients and calculated NO$_3$,SS, we calculate instantaneous NO$_3$ loss rates (($\text{NO}_3\text{,loss})_{\text{inst}}$) for the campaign.

\[ (\text{NO}_3\text{,loss})_{\text{inst}} = \sum_i k_{\text{NO}_3 + \text{VOC}}([\text{VOC}] [\text{NO}_3]\text{,SS} \]  

(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 BVOCs.

\[ (\text{NO}_3\text{,loss})_{\text{integ}} = \sum_{i=1}^{n} (\text{NO}_3\text{,loss})_{\text{inst},i} \times \Delta t \]  

(7)

Specifically, time loss of NO$_3$ radical to reaction with BVOCs (($\text{NO}_3\text{,loss})_{\text{integ}}$) 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$_3$ and BVOC measurements can be considered an area-wide average and this simple box model can be used to calculate ($\text{NO}_3\text{,loss})_{\text{integ}}$ (Eqs. 6, 7).

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$_2$ produced provide estimates of the evolution of RONO$_2$ concentrations at night (this assumption was verified using CO to minimize first-order effects of dilution from changes in the boundary layer (Blanchard et al., 2011)). Time periods of CIMS RONO$_2$ or aerosol buildup were chosen to determine time intervals for calculation of ($\text{NO}_3\text{,loss})_{\text{integ}}$ when data were available.

($\text{NO}_3\text{,loss})_{\text{integ}}$ is the calculated time integral of the reaction products of NO$_3$ with individual or combined mixing ratios of BVOCs, and $\Delta t$ is the time step between each calculated value of ($\text{NO}_3\text{,loss})_{\text{integ}}$. Data are averaged to 30 min increments, a time step sufficient to resolve the observed rate of change. Figure 5 shows an example of the resulting calculated integrated NO$_3$ losses from Eq. (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 (Fig. S5).
3.1.2 Implied organic nitrate and SOA yields

The correlation slopes in Fig. 6 are in \( \text{ppb}_{\text{aerosol}}/\text{ppb}_{\text{NO}_3}\text{ loss}_{\text{mon}} \) 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 (Fig. 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\(_3\) oxidation of individual terpenes: Spittler et al. (2006) and Fry et al. (2014) both found 10–15 % total organic nitrate (ON) yield for \( \alpha \)-pinene; Fry et al. (2009) found 45 % total ON yield for \( \beta \)-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\(_3\) + \( \beta \)-pinene; 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.

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\(_3\) 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\(_3\) + \( \alpha \)-pinene SOA yields are essentially zero (Fry et al., 2014; Hallquist et al., 1999; Spittler et al., 2006) and \( \alpha \)-pinene is the dominant monoterpene in this region. For \( \beta \)-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...
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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) and (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) and (b), suggesting it is not exclusively a product of NO₃ oxidation, or has rapid losses.

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 (Fig. 5), the rapid particulate organic nitrate losses (timescale of 2–4 h) 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 NO₃ reaction (Fry et al., 2014; Spittler et al., 2006). This suggests effective overall SOA yields from other BVOCs must be large.

3.1.3 Organic nitrate product analysis

Observations of NO₃,SS compared to TD-LIF and AMS (Fig. 2) suggest aerosol-organic nitrates are dominated by nighttime NO₃ + BVOCs, rather than other known nitrate-producing reactions (e.g., RO₂ + NO), which would dominate during the daytime and would not coincide with peaks in [NO₃].

Researchers at University of Washington described the observation of particle phase C₁₀ organic nitrate concentrations peaking at night during SOAS (Lee et al., 2015), consistent with high SOA yield from NO₃ + monoterpenes. Observed C₁₀ 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 monoterpenic organic nitrate compounds were identified and measured in the gas and aerosol phases (Lopez-Hilfiker et al., 2014; Beaver et al., 2012). Using the (NO₃,loss)integ calculations, another correlation analysis is conducted to identify key gas- and aerosol-phase products of NO₃ oxidation. Observed buildups in gas- and aerosol-phase organic nitrate concentrations from each CIMS are scattered against predicted (NO₃,loss)integ to monoterpenes (Fig. 7). The generally good correlations suggest that all of the molecular formulae shown here have contributions from NO₃ chemistry. 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 $R^2$ (C₁₀H₁₇NO₅) may indicate a greater
Contributions to these species from nitrate radical chemistry. If we assume the same sensitivity across phases in the cases where the same species is observed (Fig. 7a/b and d/e), we can estimate the relative amount in each phase by the ratio of the slopes. This would suggest that C10H15NO3 partitions preferentially to the particle phase, while C10H17NO3 partitions preferentially to the gas phase.

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 yield of 7%. The C5 lower 20 m 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.

In the period of buildup is taken into account in this correlation analysis.

The median particulate fraction of C3H7NO3 (particle phase) observed by the UW-CIMS was less than 1%, and C5H3NO5 was comprised less than 1% of total particulate organic nitrate (Lee et al., 2015). Those C5 species that are observed in the particle phase constitute less than 12% of total particulate organic mass as measured by the UW-CIMS; Lee et al., 2015, Supplement), 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 (Fig. 8).

C5H9NO3 (panels a and b) shows the strongest correlation with (NO3, lost) to isoprene among all the individual molecules (R2 = 0.54 for UW and 0.70 for CIT), suggesting that this compound is a product of NO3 oxidation. The better correlations of these C5 species than those observed in Fig. 7 may be due to slower gas-phase losses of organic nitrates relative to the semi-volatile C10 species. Using the calibrated mixing ratios from CIT for C3H7NO3, we calculate an approximate lower limit molar yield of 7%. The C5H9NO3 and C4H9NO3 isoprene products (panels c and d) show poorer correlation with (NO3, lost) to isoprene (R2 = 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 RO2 + NO.

We note that the two CIMS for which data are shown in Figs. 7 and 8 were located at different heights: the CIT-CIMS was atop the 20 m tower, collocated with the measurements used to determine [NO3]ss, while the UW-CIMS measured at ground level. Particularly at nighttime, it is possible that this lower 20 m 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 NOx sink: NO3 aerosol production from heterogeneous uptake of HONO

Partitioning of semi-volatile ammonium nitrate into aerosol represented a small fraction of aerosol contribution throughout the campaign based on AMS and MARGA data (Allen et al., 2015). A more important route of NOx conversion to nitrate aerosol occurred via HONO 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 (Allen et al., 2015). Briefly, we observe that while concentrations of organic and inorganic nitrate aerosol are generally comparable (Fig. 3), the inorganic nitrate is more episodic in nature. Periods of highest NO3− concentration as measured by the MARGA were observed during two multi-day coarse-mode dust events, from 9 to 15 and 23 to 30 June, 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 (Fig. 3).

In order to estimate the fluxes of NOx loss to aerosol via the two pathways shown in Scheme 1, we calculate the reactive losses of NO2 to organic nitrate (limiting rate is taken to be ∑i([NO3][BVOC]), with the included terpenes α-pinene, β-pinene, limonene, and camphene) and to inorganic nitrate via heterogeneous HONO uptake (Allen et al., 2015). A substantial fraction of the surface area is in the transition regime, so NO3− uptake is reduced due to diffusion limitations. To account for this, a Fuchs–Sutugin correction is applied (Seinfeld and Pandis, 2006):

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

where \(S_a\) is surface area, \(R_p\) is the radius, \(D_g\) is the diffusivity of HNO3 in air (0.118 cm2 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 (Fig. 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 μg m−3 h−1, with average rates 0.1 μg m−3 h−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 NOx 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 the 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 NO3 oxidation on SOA formation in the SEUS

The importance of the NO3 + 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 NO3 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 NO3 in SOA formation. Measured aerosol-organic nitrate concentrations are correlated with the reaction of NO3 with BVOCs. This pathway is especially important before sunrise when competing oxidants (O3 and OH) are at a minimum.

We can estimate the contribution of this NO3 + 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 eight-state region, the NEI reported emissions of 2.3 Tg yr\(^{-1}\) (2.5 \times 10^6 \text{ yr}^{-1}) of nitrogen oxides and 0.8 Tg yr\(^{-1}\) (9 \times 10^5 \text{ yr}^{-1}) of PM\(_{2.5}\) in 2011. We can estimate the fraction of the NO3 emitted that is converted to PM using several assumptions. NO2 is estimated to contribute 50% of the NOx budget (Fig. S4), so we multiply the NO2 emission by 0.5 to account for half of the instantaneous NO3 residing in the atmosphere as other NOx species at any given time. An average lifetime of 16 h for O3 + NO2 reaction was calculated (1/\([k(O3)]\)) and, with an average nighttime length of 9 h, we estimate about 55% of NO2 is converted to NO3 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 hydroxynitrate 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 NO3 is the limiting reagent for SOA production from this chemistry; as noted in the introduction, comparison of regional NOx and BVOC emissions rates supports this assumption. Finally, using the summed NEI NO3 emissions data for the SAMI states, we calculate a source estimate of 0.6 Tg yr\(^{-1}\) of NO3-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 NO3 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 NOx emissions were 2.3 Tg yr\(^{-1}\) rather than the 3 Tg yr\(^{-1}\) projected at that time. Hence, despite successful reduction of regional NOx emissions (Blanchard et al., 2013), this work suggests that secondary PM\(_{2.5}\) production from NO3 oxidation of regionally abundant BVOCs remains a substantial anthropogenic source of pollution in the SEUS.

4 Conclusions

The contribution of NO3 + BVOCs 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 RONO\(_2\) 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)\(_\text{integ}\) : their semi-volatile nature leads to their variable partitioning between gas and aerosol phase. Calibrated gas-phase mixing ratios of selected organic nitrates allow for estimation of lower limit molar yields of C\(_5\)H\(_9\)NO\(_3\), C\(_{10}\)H\(_{17}\)NO\(_4\), C\(_{10}\)H\(_{17}\)NO\(_5\) from NO3 reactions (7, 3, and 3 % respectively). The fact that these molar yields of monoterpane nitrates are substantially lower than 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 PM\(_{2.5}\).
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