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Secondary organic aerosol (SOA) yields from NO$_3$ radical + isoprene based on nighttime aircraft power plant plume transects

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Abstract. Nighttime reaction of nitrate radicals (NO$_3$) with biogenic volatile organic compounds (BVOC) has been proposed as a potentially important but also highly uncertain source of secondary organic aerosol (SOA). The southeastern United States has both high BVOC and nitrogen oxide (NO$_x$) emissions, resulting in a large model-predicted NO$_3$-BVOC source of SOA. Coal-fired power plants in this region constitute substantial NO$_x$ emissions point sources into a nighttime atmosphere characterized by high regionally widespread concentrations of isoprene. In this paper, we exploit nighttime aircraft observations of these power plant plumes, in which NO$_3$ radicals rapidly remove isoprene, to obtain field-based estimates of the secondary organic aerosol yield from NO$_3$ + isoprene. Observed in-plume increases in nitrate aerosol are consistent with organic nitrate aerosol production from NO$_3$ + isoprene, and these are used to determine molar SOA yields, for which the average over nine plumes is 9% ($\pm$5%). Corresponding mass yields depend on the assumed molecular formula for isoprene-NO$_3$-SOA, but the average over nine plumes is 27% ($\pm$14%), on average larger than those previously measured in chamber studies (12%–14% mass yield as $\Delta$OA / $\Delta$VOC after oxidation of both double bonds). Yields are larger for longer plume ages. This suggests that ambient aging processes lead more effectively to condensable material than typical chamber conditions allow. We discuss potential mechanistic explanations for this difference, including longer ambient peroxy radical lifetimes and heterogeneous reactions of NO$_3$-isoprene gas phase products. More in-depth studies are needed to better understand the aerosol yield and oxidation mechanism of NO$_3$ radical + isoprene, a coupled anthropogenic–biogenic source of SOA that may be regionally significant.

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1 Introduction

Organic aerosol (OA) is increasingly recognized as a globally important component of the fine particulate matter that exerts a large but uncertain negative radiative forcing on Earth’s climate (Myhre et al., 2013) and adversely affects human health around the world (Lelieveld et al., 2015). This global importance is complicated by large regional differences in OA concentrations relative to other sources of aerosol such as black carbon, sulfate, nitrate and sea salt. OA comprises 20%–50% of total fine aerosol mass at continental mid-latitudes, but more in urban environments and biomass burning plumes, and up to 90% over tropical forests (Kanakidou et al., 2005; Zhang et al., 2007). Outside of urban centers and fresh biomass burning plumes, the majority of this OA is secondary organic aerosol (SOA) (Jimenez et al., 2009), produced by oxidation of directly emitted volatile organic compounds followed by partitioning into the aerosol phase. Forests are strong biogenic VOC emitters, in the form of isoprene (C$_5$H$_8$), monoterpenes (C$_{10}$H$_{16}$), and sesquiterpenes (C$_{15}$H$_{24}$), all of which are readily oxidized by the three major atmospheric oxidants, OH, NO$_3$ and O$_3$. The total global source of biogenic SOA from such reactions remains highly uncertain, with a view estimating it at 90±90 TgC yr$^{-1}$ (Hallquist et al., 2009), a large fraction of which may be anthropogenically controlled (Spracklen et al., 2011; Goldstein et al., 2009; Carlton et al., 2010; Hoyle et al., 2011). As most NO$_3$ arises from anthropogenic emissions, OA production from NO$_3$ + isoprene is one mechanism that could allow for the anthropogenic control of biogenic SOA mass loading.

Isoprene constitutes nearly half of all global VOC emissions to the atmosphere, with a flux of $\sim$ 600 Tg yr$^{-1}$ (Guenther et al., 2006). As a result, accurate global biogenic SOA budgets depend strongly on yields from isoprene oxidation. Recent global modeling efforts find that isoprene SOA is produced at rates from 14 (Henne and Seinfeld, 2006; Hoyle et al., 2007) to 19 TgC yr$^{-1}$ (Heald et al., 2008), which implies that it could constitute 27% (Hoyle et al., 2007), 48% (Henne and Seinfeld, 2006) or up to 78% (Heald et al., 2008) of total SOA (based also on varying estimates of total SOA burden in each study). More recent observational constraints on SOA yield from isoprene find complex temperature-dependent mechanisms that could affect vertical distributions (Worton et al., 2013) and suggest that isoprene SOA constitutes from 17% (Hu et al., 2015) to 40% (Kim et al., 2015) and up to 48% (Marais et al., 2016) of total OA in the southeastern United States (SEUS). This large significance comes despite isoprene’s low SOA mass yields, two recent observational studies estimated the total isoprene SOA mass yield to be $\sim$ 3% (Marais et al., 2016; Kim et al., 2015), and modeling studies typically estimate isoprene SOA yields to be 4% to 10%, depending on the oxidant, in contrast to monoterpenes’ yields of 10% to 20% and sesquiterpenes’ yields of $>40$% (Pye et al., 2010). Furthermore, laboratory studies of SOA mass yields may have a tendency to underestimate these yields, if they cannot access the longer timescales of later-generation chemistry, or are otherwise run under conditions that limit oxidative aging of first-generation products (Carlton et al., 2009).

Laboratory chamber studies of SOA mass yield at OA loadings of $\sim$ 10 µg m$^{-3}$ from isoprene have typically found low yields from O$_3$ (1% Kleindienst et al., 2007) and OH (2% at low NO$_x$ to 5% at high NO$_x$ Kroll et al., 2006; Dommen et al., 2009; 1.3% at low NO$_x$ and neutral seed aerosol pH but rising to 29% in the presence of acidic sulfate seed aerosol due to reactive uptake of epoxydiols of isoprene IEPOX Surratt et al., 2010). One recent chamber study on OH-initiated isoprene SOA formation focused on the fate of second-generation RO$_2$ radical found significantly higher yields, up to 15% at low NO$_x$ (Liu et al., 2016), suggesting that omitting later-generation oxidation chemistry could be an important limitation of early chamber determinations of isoprene SOA yields. Another found an increase in SOA formed with increasing HO$_2$ to RO$_2$ ratios, suggesting that RO$_2$ fate could also play a role in the variability of previously reported SOA yields (D’Ambro et al., 2017).

For NO$_3$ oxidation of isoprene, early chamber experiments already pointed to higher yields (e.g., 12% Ng et al., 2008) than for OH oxidation. Ng et al. (2008) also observed chemical regime differences: SOA yields were approximately two times larger when chamber conditions were tuned such that first-generation peroxy radical fate was RO$_2$ + RO$_2$ dominated than when it was RO$_2$ + NO$_3$ dominated. In addition, Rollins et al. (2009) observed a significantly higher SOA yield (14%) from second-generation NO$_3$ oxidation than that when only one double bond was oxidized (0.7%). This points to the possibility that later-generation, RO$_2$ + RO$_2$ dominated isoprene + NO$_3$ chemistry may be an even more substantial source of SOA than what current chamber studies have captured. Schwantes et al. (2015) investigated the gas-phase products of NO$_3$ + isoprene in the RO$_2$ + HO$_2$ dominated regime and found the major product to be isoprene nitroxy hydroperoxide (INP, 75%–78% molar yield), which can photochemically convert to isoprene nitroxy hydroxyepoxide (INHE), a molecule that might contribute to SOA formation via heterogeneous uptake similar to IEPOX. Here again, multiple generations of chemistry are required to produce products that may contribute to SOA.

As the SOA yield appears to be highest for NO$_3$ radical oxidation, and isoprene is such an abundantly emitted BVOC, oxidation of isoprene by NO$_3$ may be an important source of OA in areas with regional NO$_x$ pollution. As the SOA yield with neutral aerosol seed appears to be an order of magnitude larger than that from other oxidants, even if only 10% of isoprene is oxidized by NO$_3$, it will produce comparable SOA to daytime photo-oxidation. For example, Brown et al. (2009) concluded that NO$_3$ contributed more SOA from isoprene than OH over New England, where $>20$% of isoprene emitted during the previous day was available at sunset to undergo dark oxidation by either NO$_3$ or O$_3$. The corre-
sponding contribution to total SOA mass loading was 1%–17% based on laboratory yields (Ng et al., 2017). Rollins et al. (2012) concluded that multi-generational NO$_3$ oxidation of biogenic precursors was responsible for one-third of nighttime organic aerosol increases during the CalNex-2010 experiment in Bakersfield, CA. In an aircraft study near Houston, TX, Brown et al. (2013) observed elevated organic aerosol in the nighttime boundary layer, and correlated vertical profiles of organic and nitrate aerosol in regions with rapid surface level NO$_3$ radical production and BVOC emissions. From these observations, the authors estimated an SOA source from NO$_3$ + BVOCs within the nocturnal boundary layer of 0.05–1 µg m$^{-3}$ h$^{-1}$. Carlton et al. (2009) note the large scatter in chamber-measured SOA yields from isoprene photooxidation and point throughout their review of SOA formation from isoprene to the likely importance of poorly understood later generations of chemistry in explaining field observations. We suggest that similar differences in multi-generational chemistry could explain the variation among the (sparse) chamber and field observations of NO$_3$ + isoprene yields described in the previous paragraph, and summarized in a recent review of NO$_3$ + BVOC oxidation mechanisms and SOA formation (Ng et al., 2017).

The initial products of NO$_3$ + isoprene include organic nitrates, some of which will partially partition to the aerosol phase. Organic nitrates in the particle phase (pRONO$_3$) are challenging to quantify with online methods, due to both interferences and their often overall low concentrations in ambient aerosol. Hence, field datasets to constrain modeled pRONO$_3$ are sparse (Ng et al., 2017; Fisher et al., 2016). One of the most used methods in recent studies, used also here, is quantification with the Aerodyne Aerosol Mass Spectrometer (AMS). Organic nitrates thermally decompose in the AMS vaporizer and different approaches have been used to apportion the organic fraction contributing to the total nitrate signal. Allan et al. (2004a) first proposed the use of nitrate peaks at $m/z$ 30 and 46 to distinguish various nitrate species with the AMS. Marcolli et al. (2006), in the first reported tentative assignment of aerosol organic nitrate using AMS data, used cluster analysis to analyze data from the 2002 New England Air Quality Study. In that study, cluster analysis identified two categories with high $m/z$ 30 contributions. One of these peaked in the morning when NO$_3$ was abundant and was more prevalent in plumes with the lowest photochemical ages, potentially from isoprene oxidation products. The second was observed throughout the diurnal cycle in both fresh and aged plumes, and contained substantial $m/z$ 44 contribution (highly oxidized OA). A subsequent AMS laboratory and field study discussed and further developed methods for separate quantification of organic nitrate (in contrast to inorganic nitrate) (Farmer et al., 2010). A refined version of one of these separation methods, based on the differing NO$_3^+$/NO$_2^+$ fragmentation ratio for organic vs. inorganic nitrate, was later employed to quantify organic nitrate aerosol at two forested rural field sites where strong biogenic VOC emissions and relatively low NO$_x$ combined to make substantial organic nitrate aerosol concentrations (Fry et al., 2013; Ayres et al., 2015). Most recently, Kiendler-Scharr et al. (2016) used a variant of this method to conclude that across Europe, organic nitrates comprise ~40% of submicron organic aerosol. Modeling analysis concluded that a substantial fraction of this organic nitrate aerosol is produced via NO$_3$ radical initiated chemistry. Chamber studies have employed this fragmentation ratio method to quantify organic nitrates (Boyd et al., 2015; Bruns et al., 2010; Fry et al., 2009, 2011; Rollins et al., 2009), providing the beginnings of a database of typical organonitrate fragmentation ratios from various BVOC precursors.

Measurements conducted at the SOAS ground site in Centreville, Alabama in 2013 found evidence of significant organonitrate contribution to SOA mass loading. Xu et al. (2015) reported that organic nitrates constituted 5% to 12% of total organic aerosol mass from AMS data applying a variant of the NO$_3^+$/NO$_2^+$ ratio method. They identify a nighttime-peak “LO-OOA” AMS factor, which they attribute to mostly NO$_3$ oxidation of BVOC (in addition to O$_3$ + BVOC). They estimated that the NO$_3$ radical oxidizes 17% of isoprene, 20% of $\alpha$-pinene, and 38% of $\beta$-pinene in the nocturnal boundary layer at this site. However, applying laboratory-based SOA yields to model the predicted increase in OA, Xu et al. (2015) predict only 0.7 µg m$^{-3}$ of SOA would be produced, substantially lower than the measured nighttime LO-OOA production of 1.7 µg m$^{-3}$. The more recent analysis of Zhang et al. (2018) found a strong correlation of monoterpene SOA with the fraction of monoterpene oxidation attributed to NO$_3$, even for non-nitrate containing aerosol, suggesting an influence of NO$_3$ even in pathways that ultimately eliminate the nitrate functionality from the SOA, such as hydrolysis or NO$_2$ regeneration. Ayres et al. (2015) used a correlation of overnight organonitrate aerosol buildup with calculated net NO$_3$ + monoterpene and isoprene reactions to estimate an overall NO$_3$ + monoterpene SOA mass yield of 40%–80%. The factor of two range in this analysis was based on two different measurements of aerosol-phase organic nitrates. These authors used similar correlations to identify specific CIMS-derived molecular formulae that are likely to be NO$_3$ radical chemistry products of isoprene and monoterpene, and found minimal contribution of identified first-generation NO$_3$ + isoprene products to the aerosol phase (as expected based on their volatility). Lee et al. (2016) detected abundant highly functionalized particle-phase organic nitrates at the same site, with apparent origin both from isoprene and monoterpene, and both daytime and nighttime oxidation, and estimated their average contribution to submicron organic aerosol mass to be between 3%–8%. For the same ground campaign, Romer et al. (2016) found evidence of rapid conversion from alkyl nitrates to HNO$_3$, with total alkyl nitrates having an average daytime lifetime of 1.7 h.
Xie et al. (2013) used a model constrained by observed alkyl nitrate correlations with O$_3$ from the INTEX-NA/ICARTT 2004 field campaign to determine a range of isoprene nitrate lifetimes between 4 and 6 h, with 40%–50% of isoprene nitrates formed by NO$_3$ + isoprene reactions. Laboratory studies show that not all organic nitrates hydrolyze to HNO$_3$ equally rapidly: primary and secondary organic nitrates were found to be less prone to aqueous hydrolysis than tertiary organic nitrates (Durer et al., 2011; Hu et al., 2011; Fisher et al., 2016; Boyd et al., 2015). This suggests that field-based estimates of the contribution of organic nitrates to SOA formation could be a lower limit, if they are based on measurement of those aerosol-phase nitrates. This is because if hydrolysis is rapid, releasing HNO$_3$ but leaving behind the organic fraction in the aerosol phase, then that organic mass would not be accurately accounted for as arising from nitrate chemistry. This was addressed in a recent modeling study of SOAS (Pye et al., 2015) in which modeled hydrolysis products of particulate organic nitrates of up to 0.8 µg m$^{-3}$ additional aerosol mass loading in the southeastern U.S. were included in the estimate of change in OA due to changes in NO$_x$. Another recent GEOS-Chem modeling study using gas- and particle-phase organic nitrates observed during the SEAC4RS and SOAS campaigns similarly found RONO$_2$ to be a major sink of NO$_3$ across the SEUS region (Fisher et al., 2016; Lee et al., 2016).

Complementing these SOAS ground site measurements, the NOAA-led SENEX (Southeast Nexus) aircraft campaign conducted 18 research flights focused in part on studying the interactions between biogenic and anthropogenic emissions that formed secondary pollutants between 3 June and 10 July 2013 (Warneke et al., 2016). Flight instrumentation focused on measurement of aerosol precursors and composition enable the present investigation of OA yields using this aircraft data set. Edwards et al. (2017) used data from the SENEX night flights to evaluate the nighttime oxidation of BVOC, observing high nighttime isoprene mixing ratios in the residual layer that can undergo rapid NO$_3$ oxidation when sufficient NO$_3$ is present. These authors suggest that past NO$_x$ reductions may have been uncoupled from OA trends due to NO$_3$ not having been the limiting chemical species for OA production, but that future reductions in NO$_x$ may decrease OA if NO$_3$ oxidation of BVOC is a substantial regional SOA source. As isoprene is ubiquitous in the nighttime residual layer over the southeastern United States and the NO$_3$ + isoprene reaction is rapid, NO$_3$ reaction will be dominant relative to O$_3$ in places with anthropogenic inputs of NO$_x$ (Edwards et al., 2017 conclude that when NO$_2$/ BVOC > 0.5, NO$_3$ oxidation will be dominant). Hence, a modest NO$_3$ + isoprene SOA yield may constitute a regionally important OA source.

Several modeling studies have investigated the effects of changing NO$_x$ on global and SEUS OA. Hoyle et al. (2007) found an increase in global SOA production from 35 to 53 Tg yr$^{-1}$ since preindustrial times, resulting in an increase in global annual mean SOA mass loading of 51%, attributable in part to changing NO$_x$ emissions. Zheng et al. (2015) found only moderate SOA reductions from a 50% reduction in NO emissions: 0.9%–5.6% for global NO$_x$ or 6.4%–12.0% for southeastern US NO$_x$, which they attributed to buffering by alternate chemical pathways and offsetting tendencies in the biogenic vs. anthropogenic SOA components. In contrast, Pye et al. (2015) find a 9% reduction in total organic aerosol in Centreville, AL for only 25% reduction in NO$_x$ emissions. A simple limiting-reagent analysis of NO$_3$ + monoterpane SOA from power plant plumes across the United States found that between 2008 and 2011, based on EPA-reported NO$_x$ emissions inventories, some American power plants shifted to the NO$_3$-limited regime (from 3.5% to 11% of the power plants), and showed that these newly NO$_3$-limited power plants were primarily in the southeastern United States (Fry et al., 2015). The effect of changing NO$_x$ on SOA burden is clearly still in need of further study.

Here, we present aircraft transects of spatially discrete NO$_x$ plumes from electric generating units (EGU), or power plants (PP), as a method to specifically isolate the influence of NO$_3$ oxidation. These plumes are concentrated and highly enriched in NO$_3$ over a scale of only a few km (Brown et al., 2012), and have nitrate radical production rates ($P$(NO$_3$)) 10–100 times greater than those of background air. The rapid shift in $P$(NO$_3$) allows direct comparison of air masses with slow and rapid oxidation rates attributable to the nitrate radical, effectively isolating the influence of this single chemical pathway in producing SOA and other oxidation products. Changes in organic nitrate aerosol (pRONO$_2$) concentration and accompanying isoprene titration enable a direct field determination of the SOA yield from NO$_3$ + isoprene.

2 Field campaign and experimental and modeling methods

The Southeast Nexus (SENEX: http://esrl.noaa.gov/csd/ projects/SENEX/; last access: 8 August 2018) campaign took place 3 June through 10 July 2013 as the NOAA WP-3D aircraft contribution to the larger Southeast Atmospheric Study (SAS: http://www.eol.ucar.edu/field_projects/sas/; last access: 8 August 2018), a large, coordinated research effort focused on understanding natural and anthropogenic emissions, oxidation chemistry and production of aerosol in the summertime atmosphere in the southeastern United States. The NOAA WP-3D aircraft operated 18 research flights out of Smyrna, Tennessee, carrying an instrument payload oriented towards elucidating emissions inventories and reactions of atmospheric trace gases, and aerosol composition and optical properties (Warneke et al., 2016). One of the major goals of the larger SAS study is to quantify the fraction of organic aerosol that is anthropogenically controlled, with
a particular focus on understanding how OA may change in the future in response to changing anthropogenic emissions.

The subset of aircraft instrumentation employed for the present analysis of nighttime NO$_3$ + isoprene initiated SOA production includes measurements used to determine NO$_3$ radical production rate ($P$(NO$_3$) = $k_{NO_3}$+$O_3$(T) [NO$_2$] [O$_3$]), isoprene and monoterpene concentrations, other trace gases for plume screening and identification, aerosol size distributions and aerosol composition. The details on the individual measurements and the overall aircraft deployment goals and strategy are described in Warneke et al. (2016). Briefly, NO$_2$ was measured by UV photolysis and gas-phase chemiluminescence (P-CL) and by cavity ringdown spectroscopy (CRDS), which agreed within 6%. O$_3$ was also measured by both gas-phase chemiluminescence and CRDS and agreed within 8%, within the combined measurement uncertainties of the instruments. Various volatile organic compounds were measured with several techniques, including for the isoprene and monoterpene of interest here, proton reaction transfer mass spectrometry (PTR-MS) and canister whole air samples and post-flight GC-MS analysis (iWAS/GCMS). A comparison of PTR-MS and iWAS/GCMS measurements of isoprene during SENEX has high scatter due to imperfect time alignment and isoprene’s high variability in the boundary layer, but the slope of the intercomparison is 1.04 (Warneke et al., 2016); for more details on the VOC intercomparisons; see also Lerner et al. (2017). Acetonitrile from the PTRMS was used to screen for the influence of biomass burning. Sulfur dioxide (SO$_2$) was used to identify emissions from coal-fired power plants. All gas-phase instruments used dedicated inlets, described in detail in the supplemental information for Warneke et al. (2016).

Aerosol particles were sampled downstream of a low turbulence inlet (Wilson et al., 2004), after which they were dried by ram heating, size-selected by an impactor with 1 µm aerodynamic diameter size cut-off, and measured by various aerosol instruments (Warneke et al., 2016). An ultra-high-sensitivity aerosol sizing spectrometer (UHSAS, Particle Metrics, Inc., Boulder, CO Brock et al., 2011; Cai et al., 2008) was used to measure the dry submicron aerosol size distribution down to about 70 nm. Data for the UHSAS are reported at 1 Hz whereas AMS data were recorded roughly every 10 s. The ambient (wet) surface areas were calculated according to the procedures described in Brock et al. (2016).

A pressure-controlled inlet (Bahreini et al., 2008) was employed to ensure that a constant mass flow rate was sampled by a compact time-of-flight aerosol mass spectrometer (C-ToF-AMS), which measured the non-refractory aerosol composition (Drewnick et al., 2005). The aerosol volume transmitted into the AMS was calculated by applying the measured AMS lens transmission curve (Bahreini et al., 2008) to the measured particle volume distributions from the UHSAS. For the entire SENEX study, the mean, calculated fraction of aerosol volume behind the 1 micron impactor that was transmitted through the lens into the AMS instrument was 97% (with ±4% standard deviation), indicating that most of the submicron aerosol volume measured by the sizing instrument was sampled by the AMS.

After applying calibrations and the composition-dependent collection efficiency following Middlebrook et al. (2012), the limits of detection for the flight analyzed here were 0.05 µg m$^{-3}$ for nitrate, 0.26 µg m$^{-3}$ for organic mass, 0.21 µg m$^{-3}$ for ammonium, and 0.05 µg m$^{-3}$ for sulfate, determined as three times the standard deviation of 10 s filtered air measurements obtained for 10 min during preflight and 10 min during postflight (110 datapoints). Note that the relative ionization efficiency for ammonium was 3.91 and 3.87 for the two bracketing calibrations and an average value of 3.9 was used for the flight analyzed here. An orthogonal distance regression (ODR-2) of the volume from composition data (AMS mass plus refractory black carbon) using a mass weighted density as described by Bahreini et al. (2009) vs. the volume based on the sizing instruments (after correcting for AMS lens transmission as above) had a slope of 1.06 for the entire SENEX study and 72% of the data points were within the measurements’ combined uncertainties of ±45% (Bahreini et al., 2008). However, for the flight analyzed here, the same regression slope was 1.58, which is slightly higher than the combined uncertainties. It is unclear why the two types of volume measurements disagree more for this flight. This does not change the conclusions of this work because this has been incorporated into the error in aerosol organic nitrate, which still show positive enhancements in pRONO$_3$ overall, and post-flight GC-MS analysis (iWAS/GCMS). A comparison of PTR-MS and iWAS/GCMS measurements of isoprene during SENEX has high scatter due to imperfect time alignment and isoprene’s high variability in the boundary layer, but the slope of the intercomparison is 1.04 (Warneke et al., 2016); for more details on the VOC intercomparisons; see also Lerner et al. (2017). Acetonitrile from the PTRMS was used to screen for the influence of biomass burning. Sulfur dioxide (SO$_2$) was used to identify emissions from coal-fired power plants. All gas-phase instruments used dedicated inlets, described in detail in the supplemental information for Warneke et al. (2016).

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The ratio of the corrected NO$_3$ / NO$^+$ signals was then used to calculate the fraction of aerosol nitrate that was organic (pRONO$_2$) or inorganic (ammonium nitrate) based on the method described first in Fry et al. (2013). Here we used an organic NO$_3$ / NO$^+$ ratio that was equal to the ammonium nitrate NO$_3$ / NO$^+$ ratio from our calibrations divided by 2.8. This factor was determined from multiple datasets (see discussion in the Supplement). The ammonium nitrate NO$_3$ / NO$^+$ ratio was obtained from the two calibrations on 30 June and 7 July that bracketed the flight on 2 July, which is analyzed here. It was 0.514 and 0.488, respectively, and for all of the data from both calibrations it averaged 0.490. Hence, the organic nitrate NO$_3$ / NO$^+$ ratio was estimated to be 0.175. This is the first time, to our knowledge, that UMR measurements of aerosol nitrate have been corrected with HR correlations and used to apportion the corrected nitrate into inorganic or organic nitrate species.

The time since emission of intercepted power plant plumes was estimated from the slope of a plot of O$_3$ against NO$_2$. For nighttime emitted NO$_3$ plumes that consist primarily of NO (Peischl et al., 2010), O$_3$ is negatively correlated with NO$_2$ due to the rapid reaction of NO with O$_3$ that produces NO$_2$ in a 1:1 ratio:

$$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2. \quad (R1)$$

Reaction (R1) goes rapidly (NO pseudo first order loss rate coefficient of 0.03 s$^{-1}$ at 60 ppb O$_3$) to completion, so that all NO is present as NO$_2$, as long as the plume NO does not exceed background O$_3$ after initial mixing of the plume into background air. Subsequent oxidation of NO$_2$ via Reaction (R2) leads to an increasingly negative slope of O$_3$ vs. NO$_2$:

$$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2. \quad (R2)$$

Equation (1) then gives plume age subsequent to the completion of (R1) in terms of the observed slope, $m$, of O$_3$ vs. NO$_2$ (Brown et al., 2006).

$$t_{\text{plume}} = \frac{\ln[1 - S(m + 1)]}{Sk_1\text{O}_3} \quad (1)$$

Here $S$ is a stoichiometric factor that is chosen for this analysis to be 1 based on agreement of plume age with elapsed time in a box model run initialized with SENEX flight conditions (see below); $k_1$ is the temperature dependent bimolecular rate constant for NO$_2$ + O$_3$ (Reaction R2) and $\text{O}_3$ is the average O$_3$ within the plume.

We calculate plume ages using both a stoichiometric factor of 1 (loss of NO$_3$ and N$_2$O$_5$ dominated by NO$_2$ reactions) and 2 (loss dominated by N$_2$O$_5$ reactions), although we note that the chemical regime for NO$_3$ + N$_2$O$_5$ loss may change over the lifetime of the plume, progressing from 1 to 2 as the BVOC is consumed. We use $S=1$ values in the analysis that follows. As the more aged plumes are more likely to have $S$ approach 2, this means that some of the older plumes may have overestimated ages. Figure S3 shows the plume age calculated by Eq. (1) using modeled NO$_3$, NO$_2$, and O$_3$ concentrations for $S=1$ and $S=2$, from nighttime simulations of plume evolution using an observationally constrained box model. This confirms that for nighttime plumes, $S=1$ plume ages match modeled elapsed time well. The model used for this calculation, and those used to assess peroxy radical lifetimes and fates in Sect. 4.3, was the Dynamically Simple Model of Atmospheric Chemical Complexity (DSMACC Emmerson and Evans, 2009) containing the Master Chemical Mechanism v3.3.1 chemistry scheme (Jenkin et al., 2015). More details on the model approach are provided in the Supplement.

### 3 Nighttime flight selection

There were three nighttime flights (takeoffs on the evenings of 19 June, 2 and 3 July 2013, Central Daylight Time) conducted during SENEX, of which one (2 July) surveyed regions surrounding Birmingham, Alabama, including multiple urban and power plant plume transects. As described in the introduction, these plume transects are the focus of the current analysis as they correspond to injections of concentrated NO (and subsequently high $P$NO$_3$) into the regionally widespread residual layer isoprene. The nighttime flight on 3 July, over Missouri, Tennessee and Arkansas sampled air more heavily influenced by biomass burning than biogenic emissions. The 19 June night flight sampled earlier in the evening, in the few hours immediately after sunset, and sampled more diffuse urban plume transects that had less contrast with background air. Therefore, this paper uses data exclusively from the 2 July flight, in which nine transects of well-defined NO$_3$ plumes from power plants emitted during darkness can be analyzed to obtain independent yields measurements.

A map of the 2 July flight track is shown in Fig. 1a. After takeoff at 8:08 pm local Central Daylight Time on 2 July, 2013 (01:08 a.m. UTC 3 July 2016), the flight proceeded towards the southwest until due west of Montgomery, AL, after which it conducted a series of east-west running tracks while working successively north toward Birmingham, AL. Toward the east of Birmingham, the aircraft executed overlapping north-south tracks at six elevations to sample the E. C. Gaston power plant. During the course of the flight, concentrated NO$_3$ plumes from the Gaston, Gorgas, Miller and Greene City power plants were sampled. Around 01:30 and 02:30 a.m. Central Daylight Time (05:30 and 06:30 a.m. UTC), two transects of the Birmingham, AL urban plume were measured prior to returning to the Smyrna, TN airport base.
The flight track is shown colored by the nitrate radical production rate, \( P(\text{NO}_3) \), to show the points of urban and/or power plant plume influence:

\[
P(\text{NO}_3) = k_2(T)\left[\text{NO}_2\right][\text{O}_3].
\]

Here, \( k_2 \) is again the temperature-dependent rate coefficient for reaction of \( \text{NO}_2 + \text{O}_3 \) (Atkinson et al., 2004), and the square brackets indicate concentrations. Figure 1b further illustrates the selection of power plants plumes: sharp peaks in \( P(\text{NO}_3) \) are indicative of power plant plume transects, during which isoprene mixing ratios also are observed to drop from the typical regional residual layer background values of \( \sim 1 \) ppb, indicative of loss by \( \text{NO}_3 \) oxidation (an individual transect is shown in more detail below in Fig. 2). Also shown in Fig. 1b are measured concentrations of isoprene and monoterpene throughout the flight, showing substantial residual layer isoprene and supporting the assumption that effectively all \( \text{NO}_3 \) reactivity is via isoprene (see calculation in next section). Residual layer concentrations of other VOCs that could produce SOA (e.g., aromatics) are always below 100 pptv, and their reaction rates with \( \text{NO}_3 \) are slow. Edwards et al. (2017) have shown that \( \text{NO}_3 \) and isoprene mixing ratios for this and other SENEX night flights exhibit a strong and characteristic anticorrelation that is consistent with nighttime residual layer oxidation chemistry.

4 Results

4.1 Selection of plumes

Figure 2 shows a subset of the 2 July flight time series data, illustrating three \( \text{NO}_3 \) plumes used for analysis. The large \( \text{NO}_3 \) source and isoprene loss was accompanied by an increase in organic nitrate aerosol mass, which we attribute to the \( \text{NO}_3 + \text{isoprene} \) reaction based on prior arguments. We observed each plume as a rapid and brief perturbation to background conditions, in the order of \( 10-50 \) s, or \( 1-5 \) km in spatial scale. Each plume’s perturbed conditions can correspond to different plume ages, depending on how far downwind of the power plant the plume transect occurred.

Candidate plumes were initially identified by scanning the time series flight data for any period where the production rate of nitrate radical (\( P(\text{NO}_3) \)) rose above 0.5 ppbv h\(^{-1}\). This threshold was chosen to be above background noise and large enough to isolate only true plumes (see Fig. 1a). The value is thus subjectively chosen, but was consistently applied across the dataset. For each such period, a first screening removed any of these candidate plumes that occurred during missed approaches or other periods where radar altitude above ground level (a.g.l.) was changing, because in the stratified nighttime boundary layer structure, variations in altitude may result in sampling different air-masses, rendering the adjacent out of plume background not necessarily comparable to in-plume conditions. A second criterion for rejection of a plume was missing isoprene or AMS data during brief plume intercepts. No selected plumes on 2 July showed enhanced acetonitrile or refractory black carbon, in-
Figure 2. Three representative plume transect observations from the 2 July 2013 flight (plumes are identified by the peaks in \( P(\text{NO}_3) \), listed in Table 1 at times 02:18, 02:20, and 02:21 UTC). Note the difference in sulfate enhancement in the three plumes, which is largest in the third plume, and is accompanied by increases in ammonium. In all three cases, the isoprene concentration drops in the plumes, accompanied by a clear increase in organic nitrate, no changes in the inorganic nitrate, and modest changes in organic aerosol mass concentrations.

indicating no significant biomass burning influence. Finally, two plumes downwind of the Gaston power plant (at 03:10 and 03:14) were removed from the present analysis, because (03:10) the background isoprene was changing rapidly, preventing a good baseline measurement, and (03:14) there was no observed decrease in isoprene concentration in-plume (as well as no increase in nitrate aerosol). The 03:14 plume was apparently too recently emitted to have undergone significant nighttime reaction; its \( O_3 / \text{NO}_2 \) slope was unity, within the combined measurement error of \( O_3 \) and \( \text{NO}_2 \) (Eq. 1). After this filtering, there are 9 individual plume observations for determination of \( \text{NO}_3 + \text{isoprene} \) SOA yields (see Table 1). The rapid increases in \( P(\text{NO}_3) \) appeared simultaneously with significant decreases in isoprene and increases in aerosol nitrate. The aerosol and isoprene measurements (taken at data acquisition rates < 1 Hz) were not exactly coincident in time, which leads to some uncertainty in the yield analysis below.

Derivation of SOA yields from observed changes in isoprene and aerosol mass in plumes depends on two conditions, and has several caveats that will be discussed in the text that follows (see Table 3 below for a summary of these caveats). The two conditions are (1) that the majority of VOC mass consumed by \( \text{NO}_3 \) in plumes is isoprene (rather than monoterpenes or other VOC), and then that (2a) the change in aerosol organic mass concentration during these plumes is due to \( \text{NO}_3 + \) isoprene reactions, and/or (2b) the change in aerosol nitrate mass concentration is due to \( \text{NO}_3 + \) isoprene reactions. There are separate considerations for each of these conditions.

For the first condition, we note that the isoprene to monoterpenes ratio just outside each plume transect was always high (a factor of 10 to 70, on average 26). With the 298 K \( \text{NO}_3 \) rate constants of \( \sim 5 \times 10^{-12} \text{ cm}^2 \text{ molecule}^{-1} \text{s}^{-1} \) for monoterpenes and \( 6.5 \times 10^{-13} \text{ cm}^2 \text{ molecule}^{-1} \text{s}^{-1} \) for isoprene (Calvert et al., 2000), isoprene (\( \sim 2 \) ppb) will always react faster with nitrate than monoterpenes (\( \sim 0.04 \) ppbv).

At these relative concentrations, even if all of the monoterpene is oxidized, the production rate of oxidation products will be much larger for isoprene. Contribution to aerosol by \( \text{N}_2\text{O}_5 \) uptake is also not important in these plumes. Edwards et al. (2017) calculated the sum of \( \text{NO}_3 \) and \( \text{N}_2\text{O}_5 \) loss throughout this flight and showed that it is consistently \( \text{NO}_3 + \text{BVOC} \) dominated (Fig. S4 of that paper). As isoprene depletes, \( \text{N}_2\text{O}_5 \) uptake will increasingly contribute to \( \text{NO}_3 \) loss, but as shown below, we are able to rule out a substantial source of inorganic nitrate for most plumes. We also know that despite increased OH production in-plume, the isoprene loss is still overwhelming dominated by \( \text{NO}_3 \) (Fig. S5 in Edwards, et al., 2017).

The second condition requires that we can find an aerosol signal that is attributable exclusively to \( \text{NO}_3 + \) isoprene reaction products, whether it be organic aerosol (OA) or organic nitrate aerosol (pRONO\(_3\)) mass loading, or both. We note that the ratio of in-plume aerosol organic mass increase to pRONO\(_3\) mass increase is noisy (see discussion below at Fig. 6), but indicates an average in-plume \( \Delta \text{OA} \) to \( \Delta\text{pRONO}_3 \) ratio of about 5. The large variability is primarily due to the fact that the variability in organic aerosol mass between successive 10 s data points for the entire flight is quite large (of order 0.75 \( \mu \text{g m}^{-3} \)) and comparable to many of the individual plume \( \Delta \text{OA} \) increases, far exceeding the expected organonitrate driven increases in OA, which are roughly twice the pRONO\(_3\) mass increases. It is also possible that in these plumes, where total aerosol mass is elevated, semivolatile organic compounds may repartition to the aerosol phase, contributing a non-pRONO\(_3\) driven variability in \( \Delta \text{OA} \). For example, if some gas phase IEPOX is present in the residual layer, it may be taken up into the highly acidic aerosol from the power plants. Alternatively, very polar gas-phase compounds could partition further into the higher liquid water associated with the sulfate in the plume. Therefore, in-plume organic aerosol increases cannot be attributed clearly to \( \text{NO}_3 + \) isoprene SOA production, so we do not use them in the SOA yield calculations.

This leaves consideration 2b, whether all increase in nitrate mass is due to \( \text{NO}_3 + \) isoprene reactions. Here we must evaluate the possibility of inorganic nitrate aerosol production in these high-\( \text{NO}_3 \) plumes. Fine-mode aerosol inorganic nitrate can be formed by the (reversible) dissolution of HNO\(_3\)\(_{(g)}\) into aqueous aerosol. In dry aerosol samples, in-
organic nitrate is typically in the form of ammonium nitrate (NH₄NO₃), when excess ammonium is available after neutralization of sulfate as (NH₄)₂SO₄ and NH₄(HSO₄). Due to the greater stability of ammonium sulfate salt relative to nitric acid, in high-sulfate plumes with limited ammonium, inorganic nitrate aerosol will typically evaporate as HNO₃(g) (Guo et al., 2015) (Reaction R3):

\[ 2\text{NH₄NO}_3(aq) + \text{H}_2\text{SO}_4(aq)(\text{NH₄})_2\text{SO}_4(aq) + 2\text{HNO}_3(g). \]  

(R3)

Inorganic nitrate can also form when crustal dust (e.g., CaCO₃) or sea salt (NaCl) are available. Uptake of HNO₃ is rendered favorable by the higher stability of nitrate mineral salts, evaporating CO₂ or HCl. Inorganic nitrate can also be produced by the heterogeneous uptake of N₂O₅ onto aqueous aerosol; Edwards et al. (2017) demonstrated that this process is negligible relative to NO₃+ BVOC for the 2 July SENEX night flight considered here.

There are several lines of evidence that the observed nitrate aerosol is organic and not inorganic. First, examination of the NO₃⁻ / NO⁺ (interference-corrected m/z 46 : m/z 30) ratio measured by the aircraft AMS (Fig. 3) shows a ratio throughout the 2 July flight, including the selected plumes, that is substantially lower than that from the bracketing ammonium nitrate calibrations. This lower AMS measured NO₃⁻ / NO⁺ ratio has been observed for organic nitrates (Farmer et al., 2010), and some mineral nitrates (e.g., Ca(NO₃)₂ and NaNO₃; Hayes et al., 2013), which are not important in this case because aerosol was dominantly submicron. As described above, we can separate the observed AMS nitrate signal into pRONO₂ and inorganic nitrate contributions. These mass loadings are also shown in Fig. 3, indicating dominance of pRONO₂ throughout the flight.

We can also employ the comparison of other AMS-measured aerosol components during the individual plumes to assess the possibility of an inorganic nitrate contribution to total measured nitrate. Figure S5a shows that the in-plume increases in sulfate are correlated with increases in ammonium with an \( R^2 \) of 0.4. The observed slope of 5.4 is characteristic of primarily (NH₄)HSO₄, which indicates that the sulfate mass is not fully neutralized by ammonium. However, we note that if the largest observed aerosol nitrate increase is due solely to ammonium nitrate, the ammonium increase would be only 0.11 µg m⁻³, which would be difficult to discern from the NH₄ variability of order 0.11 µg m⁻³. However, the slope is consistent with incomplete neutralization of the sulfate by ammonium, which would make HNO₃(g) the more thermodynamically favorable form of inorganic nitrate. The ion balance for the ammonium nitrate calibration particles and the plume enhancements are shown in Fig. S5b. Complete neutralization of the calibration aerosols is nearly always within the gray 10 % uncertainty band for the relative ionization efficiency of ammonium (Bahreini et al., 2009). In contrast, many of the plume enhancements are near the 1 : 2 line (as primarily ammonium bisulfate) within the combined 10 % ammonium and 15 % sulfate uncertainty error bars or without ammonium (sulfuric acid). Thus, NH₄NO₃ is unlikely to be stable in the aerosol phase under the conditions of these plumes, consistent with the AMS observations.

A plot of the calculated plume enhancements from the derived apportionment into organic (pRONO₂) and inorganic (ammonium) nitrate is shown in Fig. 4. The increases in aerosol nitrate for nearly all of the plumes appear to be mostly due to enhancements in pRONO₂. Based on these considerations, we conclude that in-plume pRONO₂ mass increases are a consequence (and thus a robust measure) of organic nitrate aerosol produced from NO₃ + isoprene. As each isoprene molecule condensing will have one nitrate group, the ratio of these increases to isoprene loss is a direct measure of the molar organic aerosol yield from NO₃-isoprene oxidation.

Table 1 shows the selected plumes to be used for yield analysis. Wherever possible, multiple points have been averaged for in-plume and background isoprene and nitrate aerosol concentrations; in each case the number of points used is indicated and the corresponding standard deviations are reported. In two cases (02:20 and 03:03 plumes), the plumes were so narrow that only a single point was measured in-plume at the 10 s time resolution of the PTR-MS and AMS; for these “single-point” plumes it is not possible to calculate error bars. Error bars were determined using the standard deviations calculated for in-plume and background isoprene and nitrate aerosol concentrations, accounting also
4.2 SOA yield analysis

A molar SOA yield refers to the number of molecules of aerosol organic nitrate produced per molecule of isoprene consumed. In order to determine molar SOA yields from the data presented in Table 1, we convert the aerosol organic nitrate mass loading differences to mixing ratio differences (ppt) using the NO$_3$ molecular weight of 62 g mol$^{-1}$ (the AMS organic nitrate mass is the mass only of the $-\text{ONO}_2$ portion of the organonitrate aerosol). At standard conditions of 273 K and 1 atm (all aerosol data are reported with this STP definition), 1000 ppt NO$_3$ = 2.77 µg m$^{-3}$, so each $\Delta M_{\text{pRONO}}$ is multiplied by 361 ppt (µg m$^{-3}$)$^{-1}$ to determine this molar yield:

$$Y_{\text{SOA, molar}} = \frac{(\text{pRONO}_{2\text{plume}} \pm SD_{\text{pRONO}_{2\text{plume}}}) - (\text{pRONO}_{2\text{bkg}} \pm SD_{\text{pRONO}_{2\text{bkg}}})}{361 \text{ ppt NO}_3 \pm SD_{\text{isopNO}_3}}$$

The SOA molar yields resulting from this calculation are shown in Table 2, spanning a range of 5%–28%, with uncertainties indicated based on the SDs in measured AMS and isoprene concentrations. In addition to this uncertainty based on measurement precision and ambient variability, there is an uncertainty of 50% in the AMS-derived organic nitrate mass loadings (see Supplement) and 25% in the PTR-MS isoprene concentrations (Warneke et al., 2016). The average molar pRONO$_2$ yield across all plumes, with each point weighed by the inverse of its standard deviation, is 9%. (As noted below, the yield appears to increase with plume age, so this average obscures that trend.) An alternate graphical analysis of molar SOA yield from all nine plumes plus one “null” plume (03:14, in which no isoprene had yet reacted and is thus not included in Tables 1 and 2) obtains the same average molar yield of 9% (Fig. 5). Here, the molar yield is the slope of a plot of plume change in pRONO$_2$ vs. plume change in isoprene. The slope is determined by a linear fit with points weighted by the square root of the number of AMS data points used to determine in-plume pRONO$_2$ in each case. This slope error gives a rather narrow uncertainty range for the slope (0.0930 ± 0.0011); to obtain an upper limit in the uncertainty of this molar yield we apply the combined instrumental uncertainties, based on adding in quadrature the PTR-MS uncertainty of 5% and the AMS uncertainty of 50%. This gives an overall uncertainty of 50.2%, resulting in upper and lower limit slopes of 0.140 and 0.046, respectively; we use this maximum uncertainty estimate to report the average molar yield as 9% (+5%). We have not corrected the calculated yields for the possibility of NO$_3$ heterogeneous uptake, which could add a nitrate functionality to existing aerosol. Such a process could be rapid if the uptake coefficient for NO$_3$ were 0.1, a value characteristics of unsaturated substrates (Ng et al., 2017), but would not contribute measurably at more conventional NO$_3$ uptake coefficients of 0.001 (Brown and Stutz, 2012).

To estimate SOA mass yields, we need to make some assumption about the mass of the organic molecules containing the nitrate groups that lead to the observed nitrate aerosol mass increase. The observed changes in organic aerosol are too variable to be simply interpreted as the organic portion of the aerosol organic nitrate molecules. We conservatively assume the organic mass to be approximately double the nitrate mass (62 g mol$^{-1}$), based on an “average” molecular structure of an isoprene nitrate with three additional oxygens: e.g., a tri-hydroxynitrate (with organic portion of formula C$_3$H$_{11}$O$_3$, 119 g mol$^{-1}$), consistent with 2nd-generation oxidation product structures suggested in Schwantes et al. (2015). Based on this assumed organic to nitrate ratio, all plumes’ expected organic mass increases would be less than the typical variability in organic of 0.75 µg m$^{-3}$. This assumed structure is consistent with oxidation of both double bonds, which appears to be necessary for substantial condensation of isoprene products, and which structures would have calculated vapor pressures sufficiently low to partition to the aerosol phase (Rollins et al., 2009). Another possible route to low vapor pressure products is intramolecular H rearrangement reactions, discussed below in Sect. 4.3, which would not require oxidant reactions at both double bonds. In the case of oxidant reactions at both double bonds, it is difficult to understand how the second double bond would be oxidized unless by another nitrate radical,
Table 1. List of plumes used in this NO$_3$ + isoprene SOA yield analysis. For each plume, the delta values listed indicate the difference between in-plume and outside-plume background in average observed concentration, and the standard deviations (SD) are the propagated error from this subtraction. (For $\Delta$NO$_3$ from pRONO$_2$, the standard deviations also include error propagated as described in the caption for Fig. 4) After each plume number, the numbers of points averaged for isoprene (10 s resolution) and AMS (10 s resolution) are listed, respectively. As the isoprene data were reported at a lower frequency, these numbers are typically lower to cover the same period of time. Plume numbers annotated with * indicate brief plumes for which only single-point measurements of in-plume aerosol composition were possible. Additional AMS and auxiliary data from each plume is included in the Supplement, Table S3.

<table>
<thead>
<tr>
<th>Plume number</th>
<th>7/2/13 plume time (UTC)</th>
<th>$P$(NO$_3$) (ppbv h$^{-1}$)</th>
<th>$\Delta$ISO(ppt)</th>
<th>$\Delta$NO$_3$ (µg m$^{-3}$)</th>
<th>$\Delta$NO$_3$ from pRONO$_2$ (µg m$^{-3}$)</th>
<th>$\Delta$NO$_3$ from NH$_4$NO$_3$ (µg m$^{-3}$)</th>
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<td>−335</td>
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<td>[0.047]</td>
<td>[0.012]</td>
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$^a$ Plume 5 has the smallest $\Delta$NO$_3$$_{aero}$ and may be affected by background pRONO$_2$ variability. $^b$ Plume 8 has a measurable increase in inorganic nitrate as well as organic.

Table 2. SOA Yields for each plume observation, estimated plume age, and likely origin. See text for description of uncertainty estimates. For the mass yields, the calculated SOA mass increase includes both the organic and (organo)nitrate aerosol mass; the measurements for OA increases shown in Fig. 6 do not include the nitrate mass.

<table>
<thead>
<tr>
<th>Plume number</th>
<th>Plume time (UTC)</th>
<th>SOA molar yield (fraction)</th>
<th>SOA mass yield (µg m$^{-3}$)</th>
<th>Plume age from O$_3$/NO$_2$ clock assuming $S = 1$ (h)</th>
<th>Likely NO$_3$ origin &amp; altitude (m)</th>
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<td>0.09</td>
<td>0.25</td>
<td>2.5 Greene County @ 540 m</td>
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<td>0.21</td>
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<td>6.3 Gaston @ 1280 m</td>
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</tbody>
</table>
Error bars on pRONO2 differences, for plumes in which multi-point averages were possible. The propagated standard deviations of the (in plume–out plume) difference isoprene’s molecular weight of 68.12 g mol$^{-1}$. Observed decrease in isoprene, converted to µg m$^{-3}$.

$\Delta_1$M$_{pRONO_2}$, $\Delta_1$M$_{isoprene}$

**Figure 5.** SOA molar yield can be determined as the slope of $\Delta pRONO_2$ vs. $\Delta$ isoprene, both in mixing ratio units. The linear fit is weighted by square root of number of points used to determine each in-plume pRONO2, with intercept held at zero. The slope coefficient ± one standard deviation is 0.0930 ± 0.0011. Larger “outside” high and low limits of the slope (shown as dashed red and blue lines) are obtained by adding and subtracting from this slope the combined instrumental uncertainties, based on adding in quadrature the PTR-MS uncertainty of 5 % and the AMS uncertainty of 50 %. Note that the SOA mass yield reported here is based on the (assumed) mass of organic aerosol plus the (organono)nitrate aerosol formed in each plume. If instead the yield were calculated using only the assumed increase in organic mass (i.e., $2 \times \Delta M_{pRONO_2}$ instead of $3 \times \Delta M_{pRONO_2}$), which would be consistent with the method used in Rollins, et al. (2009) and Brown et al. (2009), the mass yields would be two-thirds of the values reported here. However, as SOA mass yield is typically defined based on the total increase in aerosol mass, we use the definition with the sum of the organic and nitrate mass here. This results in an average SOA mass yield of 27 %, with propagated instrumental errors (see caption to Fig. 5) giving a range of 27 % ± 14 %.

We note also that correlation of in-plume increases in OA with pRONO2 (Fig. 6) point to a substantially larger 5 : 1 organic-to-nitrate ratio; if this were interpreted as indicating that the average molecular formula of the condensing organic nitrate has 5 times the organic mass as nitrate, this would increase the SOA mass yields reported here. However, due to the aforementioned possibility of additional sources of co-condensing organic aerosol, which led us to avoid using OA in determining SOA yields, we do not consider this to be a direct indication of the molecular formula of the condensing organic nitrate. Including OA in the SOA yield determination, based on this 5 : 1 slope rather than the assumed 2 : 1 OA : pRONO2, would give 2.5 times larger SOA mass yields than reported here.

Finally, the large range in observed yields can be interpreted by examining the relationship to estimated plume age. Using the slope of $O_3$ to NO$_2$ (Eq. 1) to estimate plume age as described above, a weak positive correlation is observed.

\[ Y_{SOA, mass} = \frac{\left( pRONO_{2,plume} \pm SD_{pRONO_{2,plume}} \right) - \left( pRONO_{2,bkg} \pm SD_{pRONO_{2,bkg}} \right)}{\left( isoprene_{plume} \pm SD_{isoprene_{plume}} \right) - \left( isoprene_{bkg} \pm SD_{isoprene_{bkg}} \right)} \times \frac{329 \text{ ppt}}{\mu g m^{-3}} \times 3 \]
Table 3. Several caveats to the present SOA yields analysis are listed below, alongside the expected direction each would adjust the estimated yields. As we do not know whether or how much each process may have occurred in the studied plumes, we cannot quantitatively assess the resulting uncertainties, so we simply list them here. See text above for more detailed discussion.

<table>
<thead>
<tr>
<th>Process</th>
<th>Effect on determined SOA yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic nitrate aerosol loses NO₃ functional group</td>
<td>Larger, because the non-nitrate OA would not be counted in this analysis</td>
</tr>
<tr>
<td>Both double bonds in isoprene are oxidized by NO₃: two nitrates per condensing molecule</td>
<td>Smaller, because the assumed organic to nitrate mass ratio assumes one nitrate per molecule</td>
</tr>
<tr>
<td>NO₃ oxidizes daytime isoprene oxidation products (e.g., ISOPOOH) to make new aerosol</td>
<td>Smaller, because this would produce organic nitrate aerosol without corresponding decrease in isoprene, so that some of existing SOA production is misattributed to isoprene + NO₃</td>
</tr>
<tr>
<td>Assumed organic to nitrate mass ratio is incorrect</td>
<td>Unknown direction of effect, depends on whether assumed ratio is high or low</td>
</tr>
<tr>
<td>Daytime-produced IEPOX uptake onto acidic particles</td>
<td>No effect (only changes ΔOA, not nitrate)</td>
</tr>
<tr>
<td>Suppression of O₃ + monoterpene or O₃ + isoprene SOA in plumes</td>
<td>No effect (only changes ΔOA, not nitrate)</td>
</tr>
</tbody>
</table>

(Table 2, Fig. S4), suggesting that as the plume ages, later-generation chemistry results in greater partitioning to the condensed phase of NO₃ + isoprene organonitrate aerosol products. This is consistent with the observation by Rollins et al. (2009) that second-generation oxidation produced substantially higher SOA yields than the oxidation of the first double bond alone, but we note that these mass yields (averaging 27%, would be 18% using the organic mass only) are higher than even the largest yield found in that chamber study (14%, used organic mass only).

We observe increasing SOA yield, from a molar yield of around 10% at 1.5 h up to 30% at 6 h of aging. The lowest yields observed are found in the most recently emitted plumes, suggesting the interpretation of the higher yields as a consequence of longer aging timescales in the atmosphere.

4.3 Mechanistic considerations

These larger SOA mass yields from field determinations (average 27%) relative to chamber work (12%–14%; see introduction) may arise for several reasons. We first assess the volatility of assumed first- and second-generation products using group contribution theory in order to predict partitioning. After a single oxidation step, with a representative product assumed to be a C₅ hydroperoxynitrate, the saturation vapor pressure estimated by group contribution theory (Pankow and Asher, 2008) at 283 K would be 2.10 × 10⁻³ Torr (saturation mass concentration C* = 1.7 × 10⁴ µg m⁻³ for MW = 147 g mol⁻¹), while a double-oxidized isoprene molecule (assuming a C₅ dihydroxy dinitrate) has an estimated vapor pressure of 7.95 × 10⁻⁸ Torr (C* = 1.01 µg m⁻³ for MW = 226 g mol⁻¹). This supports the conclusion that while the first oxidation step produces compounds too volatile to contribute appreciably to aerosol formation, oxidizing both double bonds of the isoprene molecule is sufficient to produce substantial partitioning, consistent with Rollins et al. (2009). This is also true if the second double bond is not oxidized by nitrate (group contribution estimate P_vap for a C₅ tri-hydroxy nitrate is 7.7 × 10⁻⁸ Torr, C* = 0.79 µg m⁻³ for MW = 181 g mol⁻¹). These C* saturation concentration values suggest that no dimer formation or oligomerization is required to produce low-enough volatility products to condense to the aerosol phase; however, such oligomerization would result in more efficient condensation. The fact that Rollins et al. (Rollins et al., 2009) did not observe larger mass yields may indicate that it takes longer than a typical chamber experiment timescale to reach equilibrium, or that this absorptive partitioning model did not accurately capture those experiments, or that substantial loss of semivolatiles to the chamber walls (e.g., Krechmer et al., 2016) suppressed apparent yields.

Determination of yields from ambient atmospheric data differs from chamber determinations in several additional respects. First, ambient measurements do not suffer from wall loss effects, such that no corrections are necessary for loss of aerosol or semi-volatile gases (Matsunaga and Ziemann, 2010; Krechmer et al., 2016). Second, ambient measurements take place on the aging time scale of the atmosphere rather than a time scale imposed by the characteristics of the chamber or the choice of oxidant addition. Third, the typical lifetime of the initially produced nitrooxy-isoprene-RO₂ radical is more representative of the ambient atmosphere rather than a chamber. The unique conditions of a high NOₓ power plant plume affect lifetime and fates of peroxy radicals, as described below.
Figure 7. Simulated peroxy radical concentration (a, d), loss rates (b, e), and lifetime (c, f), using the MCM v3.3.1 chemical mechanism, for conditions typical of a nighttime intercepted power plant plume (a–c) and the same plume initial conditions run for daytime simulation (d–f, local noon occurs at 5 h). Included are total peroxy radical concentration and losses, as well as the highlighted subclasses HO$_2$, CH$_3$O$_2$, total nitrooxy-isoprene-RO$_2$ and the total hydroxy-isoprene-RO$_2$ produced from OH oxidation. The righthand panels show HO$_2$, CH$_3$O$_2$ and the dominant hydroxy-isoprene-RO$_2$ ISOPBO$_2$ and ISOPDO$_2$ ($\beta$-hydroxy-peroxy radicals from OH attack at carbons 1 and 4, respectively) lifetime on the left axis and nitrooxy-isoprene-RO$_2$ on the right axis, showing nighttime lifetimes an order of magnitude longer than daytime for this NO$_3$ + isoprene derived RO$_2$ radical (NISOPO$_2$).

To help interpret these in-plume peroxy radical lifetimes, a box model calculation using the MCM v3.3.1 chemistry scheme was run (see details in the Supplement). This box model shows substantially longer peroxy radical lifetimes during nighttime than daytime, initializing with identical plume-observed conditions. These long peroxy radical lifetimes may have consequences for comparison to chamber experiments: for example, in Schwantes et al.’s (2015) chamber experiment on the NO$_3$ + isoprene reaction mechanism, the HO$_2$-limited nitrooxy-RO$_2$ lifetime was at maximum 30 s. In the plumes investigated in this study, peroxy radical lifetimes are predicted to be substantially longer (>200 s early in the night; see Fig. 7), allowing for the possibility of different bimolecular fates, or of unimolecular transformations of the peroxy radicals that may result in lower-volatility products (e.g., auto-oxidation to form highly oxidized molecules Ehn et al., 2014).

The typically assumed major fate of nighttime RO$_2$ in the atmosphere is reaction with HO$_2$ to yield a hydroperoxide, NO$_3$-ROOH. This is shown in the model output above as the green reaction, and is responsible for half of early RO$_2$ losses in the MCM modeled plume. Schwantes et al. (2015) proposed reaction of these nighttime derived hydroperoxides with OH during the following day as a route to epoxides, which in turn can form SOA via reaction with acidic aerosol. Reaction of hydroperoxides with nighttime generated OH may similarly provide a route to SOA through epoxides, albeit more slowly than that due to photochemically generated OH.

The predicted longer nighttime peroxy radical lifetimes may enable unique chemistry. For example, if nitrooxy-isoprene-RO$_2$ self-reactions are substantially faster than assumed in the MCM, as suggested by Schwantes et al. (2015), RO$_2$ + RO$_2$ reactions may compete with the HO$_2$ reaction even more than shown in Fig. 7, and dimer formation may be favored at night, yielding lower volatility products. The 5 : 1 AMS organic to nitrate ratio observed in the SOA formed in Rollins et al. (2009), and consistent with aggregated observations reported here, may suggest that in some isoprene units the nitrate is rereleased as NO$_2$ in such oligomerization reactions. We note that this larger organic to nitrate ratio would mean higher SOA mass yields than estimated in Table 2.

Alternatively, longer nighttime peroxy radical lifetimes may allow sufficient time for intramolecular reactions to produce condensable products. This unimolecular isomerization (auto-oxidation) of initially formed peroxy radicals is a potentially efficient route to low-volatility, highly functionalized products that could result in high aerosol yields. For OH-initiated oxidation of isoprene, laboratory relative rate experiments found the fastest 1,6-H-shift isomerization reaction to occur for the hydroxy-isoprene-RO$_2$ radical at a rate of 0.002 s$^{-1}$ (Crounse et al., 2011), meaning that peroxy rad-
ics must have an ambient lifetime of > 500 s for this process to be dominant. As shown in Fig. 7, the simulated power plant plume peroxy radical lifetimes are long (>200 s), so an isomerization reaction at this rate may play a significant role. However, a recent study has demonstrated that OH-initiated and NO₃-initiated RO₂ radicals from the same precursor VOC can have very different unimolecular reactive fates due to highly structurally sensitive varying rates of reactions of different product channels (Kurtén et al., 2017). A similar theoretical study on the rate of unimolecular autooxidation reactions of nitrooxy-isoprene-RO₂ radicals would be valuable to help determine under what conditions such reactions might occur, and this knowledge could be applied to comparing chamber and field SOA yields.

4.4 Atmospheric implications and needs for future work

As this paper proposes higher SOA yield for the NO₃ + isoprene reaction than measured in chamber studies, we conclude with some discussion of the implications for regional aerosol burdens, and further needs for investigation in the NO₃ + isoprene system.

Using an isoprene + NO₃ yield parameterization that gave a 12 % SOA mass yield at 10 µg m⁻³, Pye et al. (2010) found that adding the NO₃ + isoprene oxidation pathway increased isoprene SOA mass concentrations in the southeastern United States by about 30 %, increases of 0.4 to 0.6 µg m⁻³. The larger NO₃ + isoprene SOA mass yields suggested in this paper, with average value of 30 %, could double this expected NO₃ radical enhancement of SOA production. Edwards et al. (2017) concluded that the southeastern US is currently in transition between NOₓ-independent and NOₓ-controlled nighttime BVOC oxidation regime. If NOₓ-isoprene oxidation is a larger aerosol source than currently understood, and if future NOₓ reductions lead to a stronger sensitivity in nighttime BVOC oxidation rates, regional SOA loadings could decrease by a substantial fraction from the typical regional summertime OA loadings of 5 ± 3 µg m⁻³ (Saha et al., 2017).

Analysis of the degree of oxidation and chemical composition of NOₓ + isoprene SOA would help to elucidate mechanistic reasons for the different field and lab SOA yields. For example, the potential contribution of the uptake of morning-after OH + NISOPOOH produced epoxides, discussed above in Sect. 4.3, onto existing (acridic) aerosol could be quantified by measurement of these intermediates or their products in the aerosol phase. Assessment of degree of oxidation could help determine whether auto-oxidation mechanisms are active. Future similar field studies would benefit from the co-deployment of the complementary tool of a Chemical Ionization Mass Spectrometer (CIMS) to detect NOₓ + isoprene products such as organic nitrates (Slade et al., 2017; Lee et al., 2016). Due to the potentially large effect on predicted SOA loading in regions of high isoprene emissions, a better mechanistic understanding of these observed yields is crucial.

Data availability. All data is available at: https://esrl.noaa.gov/csd/groups/csd7/measurements/2013senex/P3/DataDownload/ (National Oceanic and Atmospheric Administration, 2018).

The Supplement related to this article is available online at https://doi.org/10.5194/acp-18-11663-2018-supplement.

Author contributions. JLF, SSB, and AMM conducted data analysis and wrote the paper. PME contributed modeling and writing. DAD, PCJ, and JLJ contributed data analysis and writing. Other co-authors contributed data.

Competing interests. The authors declare that they have no conflict of interest.

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