**Transition from high to low NOx control of nighttime oxidation in the Southeast U.S.**

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**The influence of nitrogen oxides (NOx) on daytime atmospheric oxidation cycles is well known, with clearly defined high and low-NOx regimes that determine emission control strategies for regulated secondary pollutants such as ozone. Nighttime oxidation also influences secondary pollutants but lacks a similar clear definition of high and low-NOx regimes, even though such regimes exist. Decreases in anthropogenic NOx emissions in the U.S. and Europe coincided with increases in Asia over the last 10 to 20 years, and have altered both daytime and nocturnal oxidation cycles. Here we present measurements of chemical species in the lower atmosphere from day-and nighttime research flights over the southeast U.S., supplemented by atmospheric chemistry simulations. We find that nighttime oxidation of biogenic volatile organic compounds (BVOC) is NOx-limited when the ratio of NOx to BVOC is below approximately 0.5, and becomes independent of NOx at higher ratios. The nighttime ratio of NOx to BVOC in 2013 averaged 0.6 aloft. We suggest that nighttime oxidation in the southeast U.S. is in transition between NOx-dominated and ozone-dominated. These findings help explain observed trends in secondary pollutants and place the NOx dependence for nighttime processes on a quantitative footing.**

Biogenic Volatile Organic Compounds (BVOCs) are a major emission to Earth’s atmosphere, providing the starting material for surface ozone (O3) and secondary organic aerosols (SOA). The dominant BVOC emissions are isoprene and monoterpenes, with the former emitted exclusively during the daytime. Oxidation by OH radicals dominates daytime BVOC removal[1](#_ENREF_1). The interplay between BVOCs and NOx in the photochemical (sunlight driven) production of O3 is well known, with non-linear responses to NOx and VOC emissions critically determining mitigation strategies.

The dominant nighttime oxidants for BVOCs are O3 and the nitrate radical (NO3). Both react rapidly with BVOCs, although their rate coefficients and concentrations can differ by orders of magnitude[2](#_ENREF_2),[3](#_ENREF_3). Their relative importance depends on the ratio of NO3 production to BVOC oxidation by O3[4](#_ENREF_4). Reaction with NO3 greatly accelerates nighttime BVOC consumption and can limit nighttime BVOC lifetimes to seconds rather than hours[5](#_ENREF_5).

Interaction between NOx and BVOCs depends on the diel variation in boundary layer structure (Fig. 1). During late afternoon, regional emissions mix throughout the convective boundary layer, typically 1-2 km deep during summer[6](#_ENREF_6). During evening a residual layer forms, isolated from further surface emissions which accumulate within a shallower nocturnal boundary layer. Late afternoon mixing ratios of BVOCs, NOx and O3 govern overnight chemistry within the residual layer. Emissions from elevated point sources, such as power plants, provide highly localized additional sources of NOx to the residual layer[7](#_ENREF_7). Morning residual layer breakup mixes overnight reaction products through the developing convective boundary layer.

The fate of residual layer BVOC, NOx and O3 is important for predictive capability of air quality and climate. Reactions of NO3 with BVOC can be a significant source of SOA[8-20](#_ENREF_8). Laboratory SOA yields for NO3-isoprene oxidation are larger than for other oxidants[16](#_ENREF_16),[19](#_ENREF_19), and models suggest enhancement of 40-50% in isoprene-derived SOA due to NO3 oxidation in the southeast U.S.[17](#_ENREF_17),[18](#_ENREF_18). Reactions of NO3 with BVOC also produce high yields of gas and particulate phase organic nitrates[12](#_ENREF_12),[19](#_ENREF_19),[21-23](#_ENREF_21), accounting for a large fraction of organic nitrates on regional and global scales[24-26](#_ENREF_24), and representing a significant sensitivity in modeled O3[27](#_ENREF_27).

There are few direct observations of residual layer composition. Zaveri *et al*.[28](#_ENREF_28) presented evidence for accumulation of particle phase organic nitrate in a residual layer influenced by power plant NOx in coastal New England. Another study found rapid reactions of NO3 with alkenes and aldehydes during overnight transport of an urban plume from Houston, TX[29](#_ENREF_29). Stone *et al*.[30](#_ENREF_30) established NO3 loss to be dominated by heterogeneous reactions of N2O5 during summer and winter from nighttime flights over the UK in 2010. Brown *et al.*[31](#_ENREF_31),[32](#_ENREF_32) identified a distinct anticorrelation between NO3 and isoprene as a defining characteristic of the summertime, polluted residual layer from measurements in New England in 2004. Here, nighttime reaction with NO3 was responsible for approximately 20% of regional isoprene oxidation, 1-17% of total residual layer SOA, and 60% of isoprene derived SOA[31](#_ENREF_31). Finally, a study[33](#_ENREF_33) in Houston in 2006 provided evidence of an SOA source from NO3-monoterpene oxidation in the nocturnal boundary layer.

Here, we present measurements from nighttime flights during the SENEX (Research at the nexus between air quality and climate in the Southeast U.S.) campaign. Summertime BVOC emission rates in the Southeast U.S. rival those of tropical regions[34](#_ENREF_34),[35](#_ENREF_35). The upper panels in Fig. 2 show observed NO2 and isoprene mixing ratios along the flight tracks. Residual layer isoprene was widespread, while NO2 was localized in regions downwind of major urban areas and power plants. The aircraft instrumention is described in the SI and further in Warneke *et al*. [36](#_ENREF_36).

**Nocturnal competition between NO3 and O3 oxidation**

During the onset of nocturnal stratification, mean isoprene and monoterpene mixing ratios were 710 and 37 pptv respectively (Fig. S1), while O3 was 40-55 ppbv. Observed NOx varied from approximately 0.1 ppbv in background air to tens of ppbv within power plant plumes. Corresponding NO3 production rates (*P*NO3), defined from the reaction of NO2 with O3 (Eqn. S3), varied between 0.01 and 1.2 ppbv hr‑1 with a mean of 0.1 ppb hr-1, and are comparable with previous studies where significant NO3 (10-100’s pptv) and N2O5 (100-1000’s pptv) mixing ratios were observed[31](#_ENREF_31). However, NO3 during SENEX was generally below the ~3 pptv instrument limit of detection, and N2O5 mixing ratios were commonly below ~10 pptv outside of NOx rich plumes. Rapid NO3 reactivity with BVOCs accounted for >90 % of residual layer NO3 loss on both flights (Fig. S4).

BVOC loss rates to NO3 and O3 provides a direct metric for the degree to which NOx competes for BVOC oxidation in the residual layer[4](#_ENREF_4),[31](#_ENREF_31),[37](#_ENREF_37). Due to the low observed NO3 concentrations, the NO3 contribution has been calculated assuming steady-state between production and loss. Figure 2(c) and (d) show observed BVOC oxidation rates *via* NO3 and O3, time averaged to the discrete whole air sampler (WAS) speciated VOC data. During both flights, NO3 oxidation of residual layer BVOCs was on average slightly higher than that by O3 (Fig. 2(e) and (f)).

The SENEX night flights sampled through 3.5 and 5.5 hours after sunset on June 19th and July 2nd respectively but did not sample residual layer oxidation over an entire night (~9.5–11 hours in June-August at 33.7° N). The lack of emissions, deposition, and significant mixing[7](#_ENREF_7) within the residual layer means each measurement point can be considered to be spatially independent, and makes an observationally constrained box model a valid tool to investigate evolution of BVOC oxidation. Individual model calculations were performed for each of the 99 WAS samples from both flights using the DSMACC model[38](#_ENREF_38), containing the full MCM v3.3.1 chemistry scheme[39](#_ENREF_39), and constrained to all available observations (see SI).

The range of conditions (Fig. 2) means multiple simulations of residual layer oxidation have been performed for low, medium and high NOx environments (Fig. S5). This analysis supports the conclusion that residual layer BVOC oxidation during SENEX occurred predominantly through NO3 (58 %) and O3 (28 %), with a lesser contribution from OH (14%). Nocturnal oxidation was responsible for removal of >65 % of sunset BVOCs in all simulations over the 9.5 hour night, with 32 of the 99 simulations showing oxidation of >95 % of sunset BVOC. Thus, 1.9 and 2.9 μg m-3 of BVOC mass was oxidized in the residual layer over a 9.5-hour night for the June 19th and July 2nd flights respectively (Fig. S7).

**NOx control of the nocturnal fate of BVOCs**

Average nocturnal BVOC oxidation during SENEX occurred through NO3, but competition with O3 was variable, especially in low-NOx air masses. Neglecting the smaller contribution from OH, the rate of nighttime BVOC oxidation is as follows.

 (1)

Here *k*O3 and *k­*NO3 are bimolecular rate constants for the reaction of the BVOC with either oxidant. When [BVOC] is large enough that NO3 can be considered to be in approximate steady state between production from NO2 + O3 and loss to NO3 + BVOC, [NO3] is given by:

 (2)

Substitution of equation (2) into (1) shows that the relative concentrations of NO2 and BVOC determine whether nitration or ozonolysis is the dominant nocturnal oxidant.

 (3)

For rate coefficients at 298 K[3](#_ENREF_3), the ratio of NO2 to isoprene at which NO3 and O3 reactions with isoprene are equal is approximately 0.4[4](#_ENREF_4),[31](#_ENREF_31). Figure 3(a) compares the observed instantaneous BVOC oxidation *via* NO3 and O3 (as per Fig. 2c-d) against NOx/BVOC with that calculated from a series of representative model calculations to illustrate the control of NOx on nighttime oxidation. To enable comparison, the role of nocturnal OH in the observed data was estimated using the modeled OH-BVOC loss fraction (see SI). The agreement between observed and modeled BVOC loss fractions illustrates the importance of the NOx/BVOC ratio in controlling nighttime oxidation, and provides confidence in the model skill in reproducing nocturnal oxidation during SENEX.

The BVOC loss fraction attributable to NO3 increases with NOx/BVOC ratio. The change from O3 to NO3 domination occurs at NOx/BVOC of approximately 0.5, similar to the ratio derived from the simplified kinetic argument in equation (3). The response of nocturnal oxidation to NOx is non-linear, but distinct from the well-known, non-linear NOx response of photochemical processes. Photochemical oxidation is proportional to NOx at low levels due to the recycling of OH through peroxy radical reactions with NO, and inversely proportional to NOx at high levels due to NOx-radical removal reactions[40](#_ENREF_40). These NOx-sensitive and NOx-saturated regimes define the response of photochemical O3 production and are central to emission reduction strategies. We have shown that a similar transition exists for residual layer BVOC oxidation. At night, BVOC oxidation is proportional to NOx at low levels due to the increased contribution from NO3, and becomes independent of NOx at high levels when rapid oxidation consumes BVOCs within a few hours of sunset. Model outputs in Fig. 3b and 3c illustrate these nocturnal high and low NOx BVOC oxidation regimes. Figure 3b shows that the fraction of BVOC oxidized overnight is slightly less than 50% at zero NOx but exceeds 90% at a sunset NOx/BVOC ratio of 1 and 99% at a sunset NOx/BVOC ratio of 1.4. As the sunset NOx/BVOC ratio increases, overnight NOx oxidation shifts from organic to inorganic dominated, producing mainly organic nitrate from the NO3 isoprene reaction up to a sunset NOx/BVOC ratio of 3, and mainly inorganic nitrate (HNO3 + ClNO2 + 2×N2O5) above that ratio (Fig. 3c), where HNO3 and ClNO2 are derived from heterogeneous reaction of N2O5 on aerosol particles.

**Implications of changes in the NOx to BVOC ratio**

The U.S. has experienced large recent reductions in NOx emissions. The U.S. EPA National Emissions Inventory suggests a >40% reduction from 2000 – 2013, with a steeper rate, 32% between 2005 – 2011, inferred from satellite observations[41](#_ENREF_41). These reductions, combined with the near equivalence of O3 and NO3 nighttime BVOC oxidation during SENEX, suggest that 2013 represents a transition for nocturnal chemistry from a NOx dominated recent past to an O3 dominated future.

Research flights during the 1999 Southern Oxidant Studies, prior to the rapid NOx reductions, provide a comparison to the 2013 study. Figure 4 compares NOx, isoprene and the NOx/isoprene ratio (further comparisons in Fig. S10). Only daytime data are available from 1999, but comparison of daytime flights is appropriate as late afternoon convective boundary layer composition determines residual layer chemistry. Median and mean NOx decreased by factors of 3.1 and 4, respectively, between the 1999 and 2013. Median and mean isoprene was larger by a factor of 2.3 and 1.8, respectively. The 2013 median NOx/isoprene ratio of 0.6 was slightly above the NOx regime transition value of 0.5, in accord with the above analysis. The mean ratio was larger at 1.3. The 1999 data has median and mean NOx/isoprene of 10 and 26 respectively. Although several factors can contribute to variability in the NOx/isoprene on any given day, the comparison indicates that available NOx prior to 2000 was easily sufficient to maintain a NOx dominated nocturnal regime.

The 2013 southeast U.S. residual layer exhibits variable NOx/BVOC with a median (~0.6) near the center of the falloff of overnight BVOC oxidation for an isoprene dominated system (Fig. 3b), but firmly in the regime where organic nitrate production dominates over inorganic nitrate (Fig. 3c). The SENEX dataset thus provides unique insight into NOx control of nocturnal BVOC oxidation. Further NOx reductions will lead to proportional reductions in nighttime organic nitrate production. Recent studies suggests that next day O3 is sensitive to the fraction of isoprene oxidized overnight[42](#_ENREF_42) and the fate of organic nitrogen from NO3-isoprene reactions[27](#_ENREF_27). Levels of NOx characteristic of the recent past lead to greater overnight residual layer organic nitrate production, but potentially not in direct proportion to the amount of NOx. A twofold increase in sunset NOx/BVOC, characteristic of changes suggested by emissions inventories, would saturate nighttime BVOC oxidation and organic nitrate production without significant inorganic nitrate production, while larger changes in NOx/BVOC, characteristic of the 1999 data (Fig. 4), would result in a large increase in overnight production of inorganic nitrate, but only a small increase in organic nitrates.

Recent trends in nocturnal organic nitrate production should represent trends in nighttime SOA production from NO3-isoprene oxidation[17](#_ENREF_17),[18](#_ENREF_18). If so, the response of this SOA source to NOx would be insensitive to past NOx reductions in a NOx saturated residual layer, but sensitive to current and future NOx reductions. Trend analysis of SOA in the southeast U.S. indicates that it has not fallen as rapidly as anthropogenic emissions of SO2 and NOx[43](#_ENREF_43) despite strong evidence that these pollutants play a role in SOA production[44-47](#_ENREF_44). The dependence of NO3-BVOC SOA on NOx will contribute to the complex non-linear sensitivity of biogenic SOA to anthropogenic emissions, and needs to be represented in models evaluating SOA air quality and climate impacts[17](#_ENREF_17),[18](#_ENREF_18).

Unlike the U.S., many regions of the world with large BVOC emissions, such as China and India, have experienced increasing NOx emissions in the recent past, with implications for nighttime processing, next day O3 production and aerosol composition. Currently however, there is insufficient data to assess the impacts of these trends outside of the U.S. and Europe.

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**Author contributions**

The analysis presented in this paper was performed by PME and SSB. Model simulations were performed by PME. All other co-authors were instrumental in the collection of the data used in this analysis. The manuscript was written by PME and SSB. All authors discussed the results and commented on the manuscript.

**Figure 1 |** **Schematic of nighttime BVOC oxidation*.***Showing BVOC oxidation by O3 and NO3, emission sources for NOx and BVOC, and diurnal variation in boundary layer structure. Although the vertical axis is not to scale, the residual layer constitutes the majority of the air mass beneath the inversion.

**Figure 2 | Flight data from the SENEX night flights**. Color and size coded by NO2 (a) and isoprene (b) mixing ratios and instantaneous BVOC loss rates to NO3 (c) and O3 (d). Maps indicate location of major urban and power plant NOx sources, sized by their 2013 emissions. Pie charts show after sunset and below 2 km altitude average BVOC loss fractions attributable to NO3 (blue) and O3 (red) for 19th June (e) and 2nd July (f) flights.

**Figure 3 | NOx/BVOC control of nocturnal BVOC oxidation*.*** a)Fraction of observed instantaneous BVOC loss to NO3 and O3 against observed NOx/BVOC ratio (points). Model calculated fraction of BVOC loss to NO3, O3 and OH against model NOx/BVOC ratio (lines). Observed points that deviate significantly from model prediction arise from other NO3 loss processes not represented in the model (e.g., N2O5 uptake, Fig. S3). (b) Model-simulated variation of fraction of BVOC oxidized via each oxidant, and (c) amount of organic and inorganic nitrate produced overnight in the residual layer against sunset NOx/BVOC (using average SENEX sunset BVOC mixing ratio).

**Figure 4 | Comparison of observed 1999 and 2013 southeast U.S. composition*.*** Distributions of A. NOx, B. Isoprene and C. NOx / isoprene ratio for daytime flights in July, 1999 and June 2013 over Atlanta, GA. Bars, boxes and whiskers represent median, 25th and 75th percentiles, and 10th and 90th percentiles, respectively, while open circles and bars represent mean averages and standard deviations.

**Methods**

**Residual layer 2013 observations.** The P-3 instrument payload, as well as the performance of individual instruments, is described in Warneke *et al*. [36](#_ENREF_36). The remainder of this paragraph identifies the instruments relevant to the analysis of nighttime atmospheric chemistry presented in this work. Reactive nitrogen and ozone were measured by a custom-built chemiluminescence instrument[48](#_ENREF_48),[49](#_ENREF_49). Nighttime nitrogen oxides, NO3 and N2O5, were measured by 662-nm cavity ring-down spectroscopy[50](#_ENREF_50),[51](#_ENREF_51). Biogenic VOCs were measured by both proton transfer reaction mass spectrometry (PTR-MS) that continuously measured isoprene, total summed monoterpenes and summed methyl vinyl ketone and methacrolein[52](#_ENREF_52). A whole air sampler (WAS) with Gas-Chromatography Mass-Spectrometry (GC-MS) analysis measured isoprene, speciated monoterpenes and speciated oxygenates in discrete samples (~72 per flight) [53](#_ENREF_53). Formaldehyde was measured at high time resolution using an instrument based on laser induced fluorescence[54](#_ENREF_54).

**Model simulations**. The lack of emissions, deposition, and significant mixing[7](#_ENREF_7) within the residual layer makes an observationally constrained box model a valid tool to elucidate the chemical processes there. This approach enables the investigation of BVOC oxidation as it evolves throughout the night, and evaluation of the potential role of unmeasured species such as BVOC oxidation products (OVOCs) and nocturnal OH.

The model calculations were performed using the 0-dimensional Dynamically Simple Model of Atmospheric Chemical Complexity (DSMACC[38](#_ENREF_38)). Model simulations were constrained using observed NO2, O3, isoprene, α-pinene, β-pinene, methacrolein (MACR) and methyl-vinyl ketone (MVK) at the observed sample time after sunset, with the concentrations of these species before and after this time point determined by the chemistry scheme. The concentrations of all other constraining species were fixed throughout the 11.5-hour simulations at their observed value. For each WAS observation made all other observations were averaged to the WAS sample time. Table S2 shows the species constrained in the model, and the mean observed value over all WAS samples modeled.

**Data availability.** All field and modeling data used in this analysis are available from the corresponding author upon request. Observations from both the 2013 and 1999 studies are also publicly available at https://www.esrl.noaa.gov/csd/groups/csd7/measurements/.

**Methods references**

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