



Supplement of

Organic nitrate aerosol formation via NO_3 + biogenic volatile organic compounds in the southeastern United States

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As discussed in the main paper, there exists an unresolved discrepancy between organic nitrate measurements from the various instruments at SOAS. While AMS total nitrate concentrations agree well between the CU AMS and the Georgia Tech AMS (apportioned most of the time as 100% organic nitrate), TD-LIF reports organic nitrate concentrations 2-4 times higher (resulting in a difference of about a factor of two when these different datasets are used in the "buildup" analysis of section 3.1.1). Because of the dominance of organic nitrate at this site, the difference in pRONO_2 between the instruments is not due to misclassification of AMS total nitrate as inorganic nitrate (details below), but stems from both AMS instruments (and the UW-CIMS) disagreeing with the TD-LIF on the total amount of organically-bound NO_2 present in the particle phase. One possible explanation is the difference in size-cuts of the instruments (PM_{10} for AMS, $\text{PM}_{2.5}$ for TD-LIF), however, organic nitrate SOA would be unlikely to dominate in this size range. Another possibility is that the TD-LIF detects some organic nitrates that are not detected as nitrate by the AMS; again, this explanation seems unlikely given that the AMS vaporizer temperature (600°C) would likely dissociate any molecules that would thermally dissociate in the 350°C oven. In the absence of other explanations, however, we treat TD-LIF as providing an upper limit, and AMS a lower limit, to the contribution of organic nitrates to the particle phase.

AMS Collection Efficiency (CE) was estimated according to Middlebrook et al. (2012). The sum of AMS + BC submicron volume estimated using the measured mass and the density of each component (Salcedo et al., 2006; Kuwata et al., 2012) agreed within 10% with the volume recorded by two colocated scanning mobility particle sizer (SMPS) instruments. Each species, including nitrate was compared with a second HR-AMS on site run by the Georgia Tech Group (Xu et al., 2015a), and was also found to be within 10%. Lastly, as described in Attwood et al. (2014), the calculated extinction based on the AMS mass agreed very well with colocated in-situ measurements of aerosol extinction during SOAS.

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

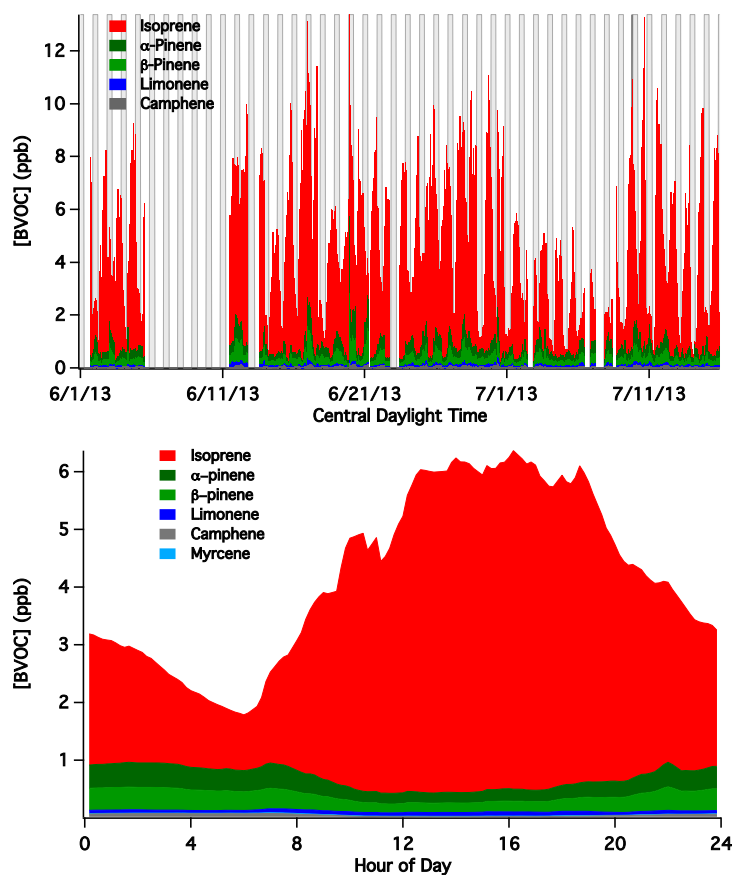


Figure S1. Biogenic alkene concentrations measured using GC-MS (Goldan et al., 2004). The instrument shows isoprene is the dominant BVOC with α - & β - pinene showing the next highest concentrations. Shading delineates day (white) and night (gray). Both the full spectra and diurnally averaged spectra are shown for clarity.

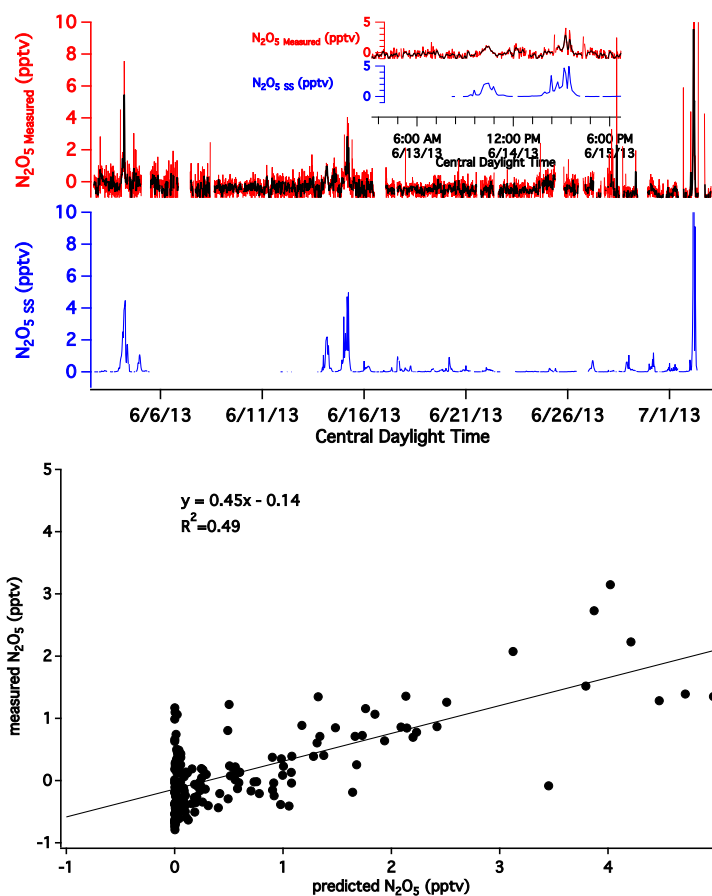


Figure S2. Steady state predicted (blue) and measured (red, binomial smoothed in black) N_2O_5 mixing ratio during the campaign. The inset provides a closer look at the N_2O_5 peaks that occur 13-June to 16-June, demonstrating the congruence of the timing and magnitude of predicted mixing ratios. The scatter plot shows the correlation of the the measured N_2O_5 versus predicted N_2O_5 , using binomial smoothed measured data during the periods 2-June to 6-June and 14-June to 16-June only, to avoid incorporating excess zero noise on the measured variable. We conclude that in general our steady-state prediction tracks measured N_2O_5 reasonably well, though it overestimates measured $[\text{N}_2\text{O}_5]$ by approximately a factor of two.

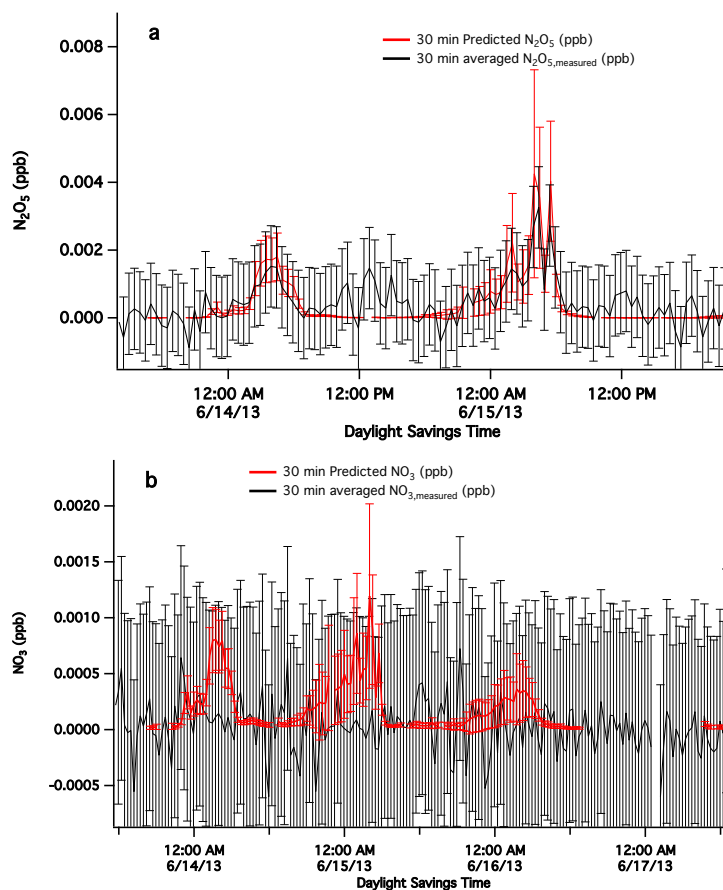


Figure S3. a) Propagated error analysis from raw data allows us to compare our calculated values of N_2O_5 to the measured values. Measured values of N_2O_5 fall within uncertainty bounds of predicted N_2O_5 giving us confidence that $\text{NO}_{3,\text{SS}}$ used in the calculation of predicted N_2O_5 can be substituted for all further rate calculations. b) We also used this method to show that $\text{NO}_{3,\text{SS}}$ error always encompass the detection limit of the instrument (1 pptv, 30 s, 2σ). The predicted NO_3 levels from the steady state analysis fall within the range of uncertainty in the NO_3 measurements. However, the lack of any systematic deviation from the baseline during periods when NO_3 is predicted to be present at small levels may indicate unquantified inlet loss for measurement of this reactive species in this environment. The more robust N_2O_5 comparison provides confidence in the NO_3 steady state calculation.

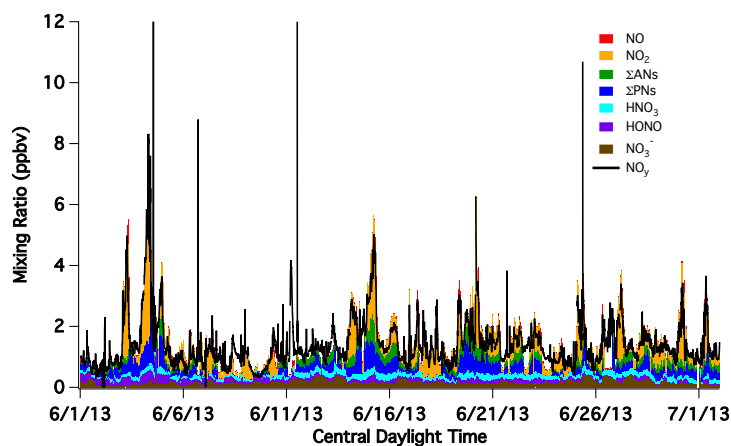


Figure S4. Measured NO_y comparison to individual oxidized nitrogen compounds ($\text{NO}_x + \text{NO}_z$). The calculated sums of $\text{NO}_x + \text{NO}_z$ overestimates NO_y measurements by 10%, but correlates to the measured NO_y with a R^2 of 0.87. Organic nitrates ($\Sigma\text{ANs} + \Sigma\text{PNs}$) comprise on average 30% of nighttime and 45% of daytime NO_y , while NO_2 comprises 30% of daytime and 50% of nighttime NO_y .

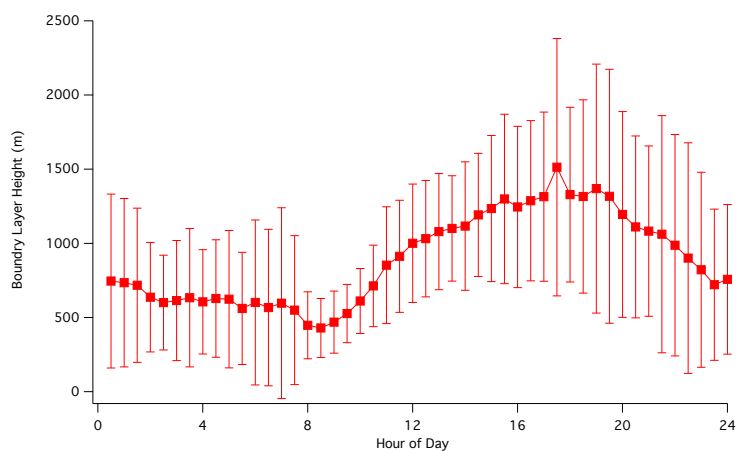


Figure S5. Diurnally averaged Planetary Boundary Layer height shows stability of the boundary layer at night. PBL was taken with a CHM 15k-Nimbus using LIDAR principle.

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