

NO_y fate at SOAS 2013: Organonitrate Formation via NO₃ + BVOC and Inorganic Nitrate Formation via Heterogeneous Uptake of HNO₃



Benjamin R. Ayres¹, Hannah M. Allen¹, Danielle C. Draper¹, Robert Wild², Steven S. Brown², Abigail Koss^{3,4}, Joost A. De Gouw^{3,4}, Douglas A. Day^{3,4}, Pedro Campuzano-Jost^{3,4}, Brett B. Palm^{3,4}, Weiwei Hu^{3,4}, Jose L. Jimenez^{3,4}, Kevin F. Olson⁵, Allen H. Goldstein⁵, Paul Romer⁵, Ronald C. Cohen⁵, Karsten Baumann⁶, Eric Edgerton⁶, Benjamin Lee⁷, Claudia Mohr⁸, Joel Thornton⁷, Juliane L. Fry¹

¹Reed College, Portland, OR; ²NOAA-ESRL, Boulder, CO; ³Cooperative Institute for Research in Environmental Sciences, Boulder, CO; ⁴University of Colorado Boulder, Boulder, CO; ⁵University of California Berkeley, Berkeley, CA; ⁶Atmospheric Research and Analysis, Inc.; ⁷University of Washington, Seattle, WA; ⁸Karlsruhe Institute of Technology, Karlsruhe, Germany



What we learned

- Sum of individual components of NO_y and measured NO_y match within 86%
- Steady state predicted N₂O₅ and measured N₂O₅ correlate well; steady state NO₃ was used in rate calculations due to ambient concentrations being below the detection limit of the instrument (Cavity Ring Down, RONALD)
- NO₃ + BVOC reactions account for almost 50% of NO₃ loss during the day
- Predicted NO₃ + BVOC loss rates correlated with aerosol mass spectrometry (AMS) peak data provide a molar yield of 23% NO₃ reaction to aerosol phase organic nitrate
- Chemical Ionization Mass Spectrometry (CIMS) coupled to a FIGAERO analyzes m/z of gas and aerosol phases:
 - Correlations against predicted NO₃ + isoprene show only gas phase C₃H₅NO₃ production; no aerosol phase isoprene nitrate product is measured
 - Correlations against NO₃ + monoterpene show that products with the formula C₁₀H₁₇NO₃ partition to the aerosol phase
 - Inorganic NO₃ analysis by ion chromatography shows dust events catalyze heterogeneous uptake of HNO₃

SOAS Site

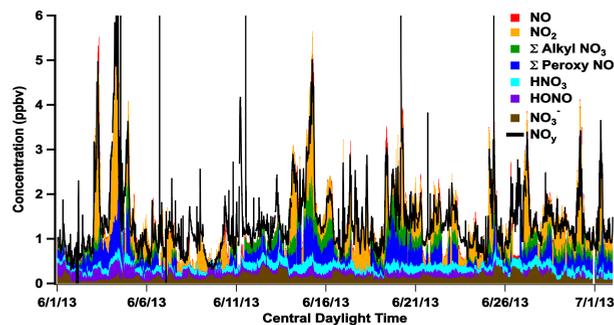
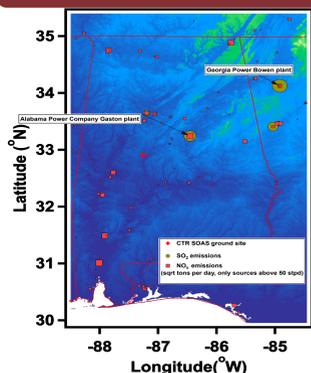


Figure 1 - Regional Map. SOAS site is denoted by +

Figure 2 - NO_y comparison. Stacked spectra shows that the sum of individual NO_y components match total NO_y measured

- Central Alabama is a humid subtropical environment with an average daily high temperature of 28.4 °C
- Emissions of SO₂ and NO_x come from regional power plants in Alabama and Georgia. The Gaston Plant emits 19.5 square tons of SO₂ and 6.5 square tons of NO_x per day (Figure 1)
- Σ Alkyl NO₃ & Σ Peroxy NO₃ measured by Thermal Dissociation - Laser Induced Fluorescence, NO_y by cavity ring down spectroscopy and HNO₃, HONO & NO₃ by Monitor of Aerosol and Gas Analyzer (MARGA)
- The individual NO_y components show that NO₂, sum alkyl nitrates and sum peroxyalkyl nitrates are the main contributors to NO_y (Figure 2)
- Organonitrates make a substantial contribution to the NO_y budget (Figure 2)
- Relatively constant contributions of NO_y come from HNO₃ and HONO

NO₃/N₂O₅ and BVOC Concentrations at SOAS

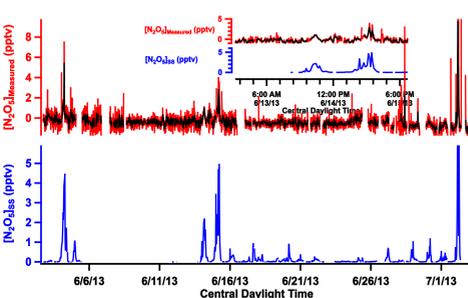


Figure 3 - Comparison of steady state and measured N₂O₅ correlate well

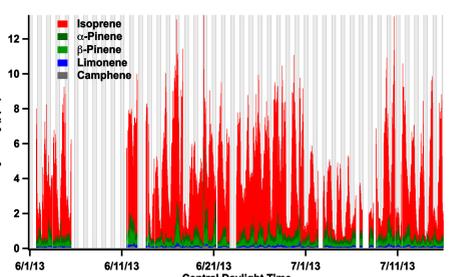


Figure 4 - VOC concentrations over the SOAS campaign

- N₂O₅ and NO₃ were measured using a cavity ring down spectrometer for nitrate radical (RONALD, NOAA ESRL)
- Steady state [NO₃]_{ss} was calculated using NO₃ production rates and loss rates of NO₃ to BVOC, NO and photolysis
- Steady state loss rates of [N₂O₅]_{ss} was calculated using [NO₃]_{ss}, [NO₂]_{ss} and K_{eq} NO₂ + NO₂
- Measured [N₂O₅]_{ss} correlates well with [NO₃]_{ss} values for the campaign (Figure 3)
- [NO₃] was consistently below detection limits during SOAS so values of [NO₃]_{ss} are used for all following calculations
- BVOC analysis from cryostat gas chromatography (TACOH, CIRES) shows high concentrations of isoprene followed by α-pinene and β-pinene (Figure 4)
- [NO₃]_{ss} loss to BVOC can be calculated from this data
- [NO₃]_{ss} tracks ΣANs, most of which is in the aerosol phase as seen in TD-LIF (Figure 5)

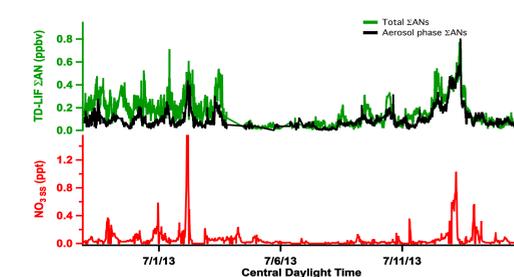


Figure 5 - ΣAN spectra show that almost all alkyl nitrates are in aerosol phase and steady state nitrate tracks well with alkyl nitrate production

Predicted NO₃ + BVOC

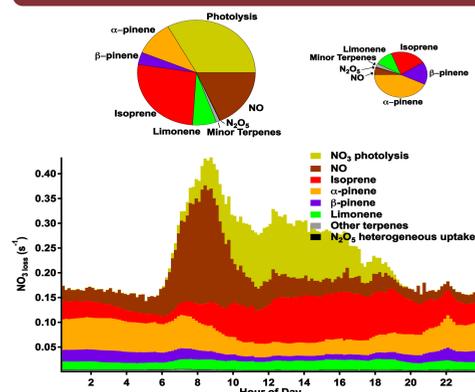


Figure 6 - Diurnal averaged NO₃ loss for June 1 - July 15. Pie graphs depict amount of loss and are sized by loading

Reaction	A-Factor	E/R	k(298 K) (molecules cm ⁻³ s ⁻¹)
O ₃ + NO ₂ → O ₂ + NO ₃	1.2 × 10 ¹¹	2450	2.51 × 10 ¹¹
NO ₂ + NO ₂ → N ₂ O ₄	2.7 × 10 ²⁷	11000	6.6 × 10 ¹¹
NO + NO ₂ → 2NO ₃	1.5 × 10 ¹¹	-170	1.1 × 10 ¹¹
Isoprene + NO ₃ → Product	3.03 × 10 ¹¹	446	1.19 × 10 ¹²
α-pinene + NO ₃ → Product	1.19 × 10 ¹²	-490	1.22 × 10 ¹¹
β-pinene + NO ₃ → Product			2.51 × 10 ¹¹
Camphene + NO ₃ → Product			6.6 × 10 ¹¹
Myrcene + NO ₃ → Product			1.1 × 10 ¹¹
Limonene + NO ₃ → Product			1.22 × 10 ¹¹

- NO₃ loss during the day is due to photolysis, reaction with NO and reaction with BVOCs
- Almost 25% of daytime NO₃ loss is from C₁₀ terpenes (Figure 6)
- Almost 15% of nighttime NO₃ loss is from Isoprene
- Close to half of nighttime NO₃ loss comes from α-pinene
- Modeled photolysis is normalized to solar radiation values (W m⁻²) to account for cloud cover
- Predicted NO₃ loss is calculated using published NO₃ + BVOC values

$$(\text{NO}_3, \text{loss})_{\text{pred}} = k_{\text{NO}_3 + \text{VOC}} [\text{VOC}] [\text{NO}_3]_{\text{ss}}$$

$$\text{RONO}_{2, \text{Cumulative}} = \sum (\text{NO}_3, \text{loss})_{\text{pred}} \times \Delta t$$

- RONO_{2, Cumulative} is correlated to measured mass spectrometry data (Figure 7)

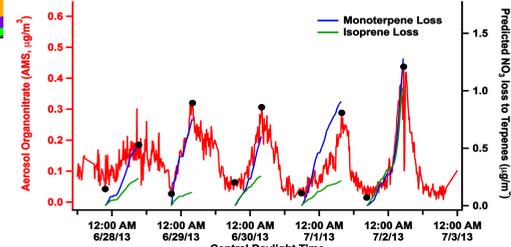


Figure 7 - AMS data overlaid with predicted cumulative NO₃ loss. Black dots denote start and stop of predicted buildup of NO₃ loss

Correlations of MS Products with RONO_{2, Cumulative}

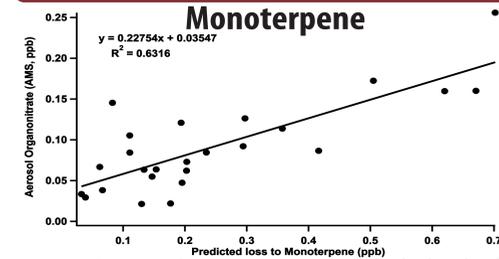


Figure 8 - AMS organonitrate is strongly correlated with predicted NO₃ loss to monoterpenes

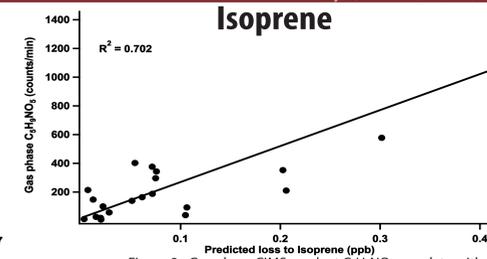


Figure 9 - Gas phase CIMS product C₁₀H₁₇NO₃ correlate with predicted NO₃ loss to isoprene

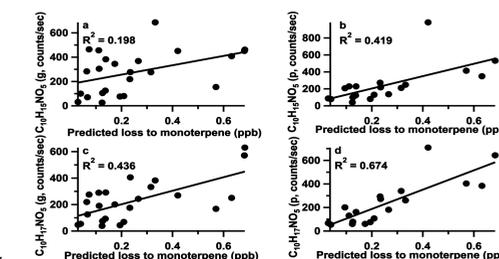


Figure 10 - Individual CIMS m/z peak correlations show C₁₀H₁₇NO₃ is the only well correlated product to NO₃ loss to monoterpenes

- AMS NO₃ mass loading in organonitrates is correlated with RONO_{2, Cumulative} to monoterpenes with a slope of 0.23 giving a 23% molar yield of organonitrate from NO₃ (Figure 8)
- Gas phase C₁₀H₁₇NO₃ correlates well with NO₃ loss to isoprene (Figure 9)
- Aerosol phase C₃H₅NO₃ & C₃H₇NO₃ were not detected during SOAS
- Individual CIMS products correlated against predicted NO₃ show which products are from NO₃ radical reaction and which are not (ex. RO₂ + NO) using the best fit analysis
- Gas phase is not well correlated suggesting another type of reaction is taking place
- Aerosol phase shows C₁₀H₁₇NO₃ appears to be a product of NO₃ reaction with an R² value of 0.674

Comparison of Oxidants

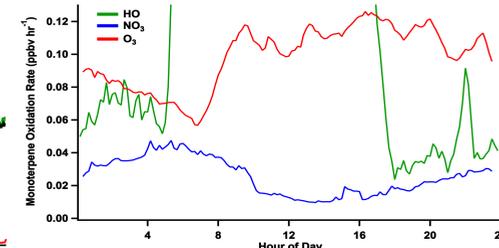


Figure 11 - Oxidant reaction rates with monoterpenes.

- OH dominates daytime oxidation rates with a peak of 0.6 ppbv/hr
- NO₃ rates are most dominant in the early morning hours when O₃ concentrations are at their lowest (blue and red trace respectively)
- Nighttime oxidation of total monoterpenes proceed at approximately equal rates from NO₃ and O₃ (blue and red traces respectively)
- Monoterpenes used in calculations are α-pinene, β-pinene, camphene, myrcene and limonene

Heterogeneous uptake of HNO₃ on Dust

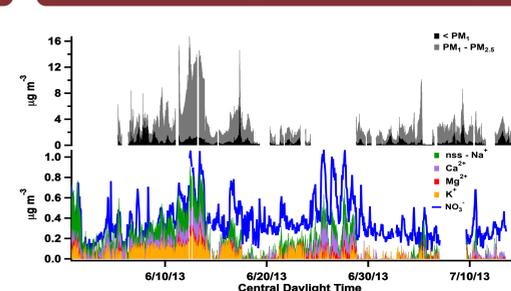


Figure 12 - PM and Ion Chromatography spectra of the SOAS campaign

Element	Dust Event I		Dust Event II	
	Composition (%)	Si Ratio	Composition (%)	Si Ratio
Al	26.8	0.64	26.2	0.59
Si	41.8	1	45.2	1
K	5.1	0.12	5.5	0.11
Ca	2.4	0.06	3.3	0.07
Ti	1.1	0.03	1.1	0.02
Mn	0.2	<0.01	0.1	<0.01
Fe	9.3	0.22	9.4	0.21
Na	12.0	0.31	7.5	0.18
Mg	1.4	0.02	1.8	0.04

- Two observed periods of high NO₃⁻ are correlated with high PM_{2.5} aerosol mass loading
- High NO₃⁻ is also correlated with high sea salt and non sea salt minerals
- Elemental analysis of the high sea salt events shows higher Na⁺ content and contains Cl⁻ (not shown)
- The second dust event shows no Cl⁻ as well as higher Ca²⁺ and Si loading
- Wind trajectory modelling shows wind coming from the Gulf of Mexico during the first event could explain the high Cl⁻ content

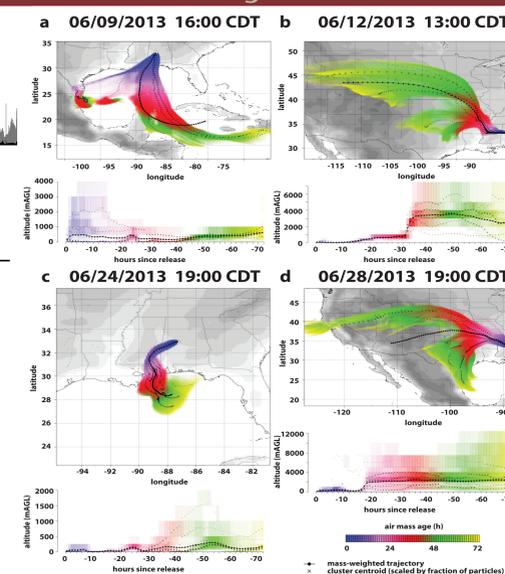


Figure 13 - Back trajectories of wind over the SOAS campaign

- Modelling also shows continental United States sources of mineral origin during the two events
- High Si and Ca²⁺ loading during the second event leads us to believe the source is terrestrial in origin

Inorganic and Organic NO₃ fate

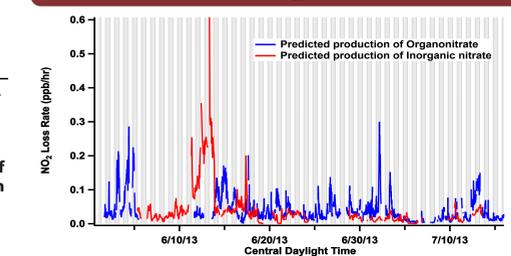


Figure 14 - Loss rates of inorganic nitrate to dust via HNO₃ and nitrate radical to BVOC

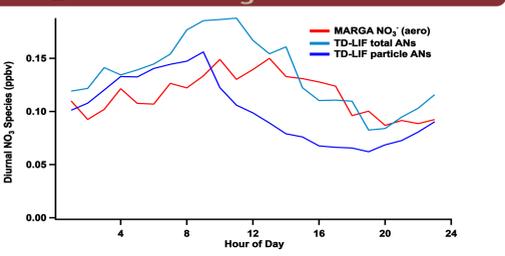


Figure 15 - Diurnally averaged inorganic nitrate concentration (IC) compared to alkyl nitrate concentrations (TD-LIF) show similar average magnitudes



- Rate of NO₃⁻ uptake is driven by PM_{2.5} via heterogeneous uptake of HNO₃ onto the surface of mineral aerosols
- An average value of 10% uptake (γ_{HNO₃}) for HNO₃ was used to calculate the rate of uptake
- Rate = 1/4 γ_{HNO₃} S_A V_{HNO₃} [HNO₃]
- Organic and Inorganic rates are comparable in magnitude with different peak times over the SOAS campaign (Figure 14)
- Inorganic NO₃ magnitudes are also comparable to alkyl nitrate magnitudes over the SOAS campaign (Figure 15)
- Organic rates calculated using (NO₃, loss)_{pred} and time (see Predicted NO₃ + BVOC)

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